THE ELECTROSYNTHESIS OF DIARYLIODONIUM SALTS

by

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ABSTRACT

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The objective of this study was to investigate the electrosynthesis of diaryliodonium salts from the anodic oxidation of aryl iodides and arenes in an acid medium. The voltammogram of the solvent was recorded using a carbon rotating disc electrode. There was evidence of oxidation of the carbon electrode and/or intercalation of anions into the carbon.

The voltammograms of a series of aryl iodides and arenes were recorded at a carbon rotating disc electrode. It was seen that their oxidation potential's were dependent on the ring substituents. The aryl iodides had lower oxidation potential than the corresponding arene. The voltammogram of a diaryliodonium bisulfate was recorded at a vitreous carbon disc electrode and there was no evidence for the oxidation or reduction of the iodonium salt.

The cell conditions necessary for selective and efficient coupling of a aryl iodide and arene to give dimethyldiphenyliodonium salt were investigated. 4-Iodotoluene and toluene was adopted as the 'model' system. The isolated iodonium salts were seen to contain two isomers. A number of organic side products of the electrolysis were also identified.

A small series of symmetric, asymmetric and cyclic iodonium salts were successfully electrochemically synthesised, under constant current control, in order to demonstrate the generality of the electrolysis. The iodonium salts were isolated and characterised by NMR and mass spectroscopy.

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CHAPTER 1

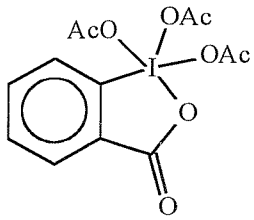
Introduction

1.1 Hypervalent Iodoarene Compounds.

Iodine was first isolated from the ash of seaweed by B. Courtois in 1811, and was named by J. L. Gay Lussac in 1813. Its name derived from the Greek term to mean 'violet coloured', which describes the characteristic lustrous purple colour of re-sublimed crystalline iodine.[1] Iodine is a component of many organic compounds; the most familiar are the alkyl iodides and aryl iodides where the formal oxidation state of iodine is -1.

Iodine is however the largest of the common halogens, the least electronegative and most polarisable; it can bear a positive charge and is able to form stable polycoordinated, multivalent compounds. Willgerodt first reported the preparation of an organoiodine compound, $PhICl_2$, in 1886 and by the time he published a review of polyvalent iodine in 1914 nearly 500 compounds were known[1].

There has been a renaissance in the interest hypervalent compounds with several reviews[1, 4, 22] and two books[3,57] on the topic. There is a bewildering array of iodine compounds; having a valency from 1 to 5 and being coordinated with widely different electronegative ligands, from elements to complex organic moieties. Varvoglis[3] catagorised the more common hypervalent iodine compounds into two broad areas: individual compounds and classes; see Table 1.1.1.

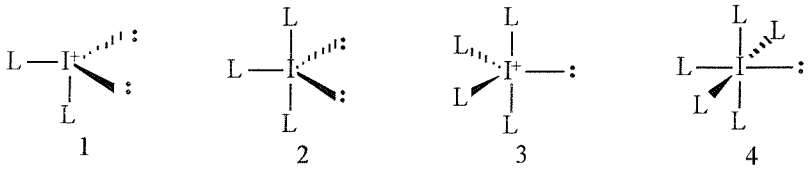
a) Individual Compound	Formula
(dichloroiodo)benzene	$PhICl_2$
(diacetoxyiodo)benzene	$PhI(OAc)_2$
[bis(trifluoroacetoxy)iodo]benzene	$PhI(O_2CCF_3)_2$
iodosylbenzene	PhIO
[(hydroxy)(tosyloxy)iodo]benzene	PhI(OH)OTs
iodylbenzene	$PhIO_2$
Dess-Martin reagent	

b) Classes	
diaryliodonium salts	$Ar_2I^+ X^-$
vinyl phenyl iodonium salts	$PhI^+(CH{=}CHR) X^-$
alkynyl phenyl iodonium salts	$PhI^+(C{\equiv}CR) X^-$
perfluoroalkyl phenyl iodonium salts	$PhI^+Rf X^-$
iodonium ylides and dipoles	diverse formulas

Table 1.1.1

1.2 Structure of Hypervalent Iodoarene Compounds.

There is a broad variety of structural classes known for polyvalent iodine species, they differ in the number of valence electrons (N) surrounding the central atom, the number of ligands (L) directly attached to the central iodine atom and their chemical nature. In terms of the Martin-Arduengo N-X-L designation[27] (X = I in the case of hypervalent iodine compounds), four types of structures are important when considering organic polyvalent iodine compounds, see Scheme 1.2.1.[1]



Scheme 1.2.1

Species 1and 2, designated 8-I-2 and 10-I-3, are called iodanes and are considered derivatives of trivalent iodine. Structural species 3 and 4, 10-I-4 and 12-I-5 periodanes, represent the most common structural type of pentavalent iodine[1].

The traditional classification of organic polyvalent iodine is based on the number of carbon ligands attached to the iodine centre. Some specific examples are shown in Table 1.2.1.[4]

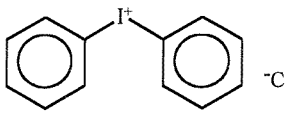
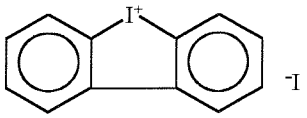
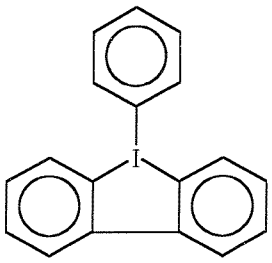
Class	Description	Specific Examples
1	Iodine(III) compounds with one carbon-iodine bond.	a) (diacetoxyiodo)toluene, $CH_3C_6H_5I(OCOCH_3)_2$ (dichloroiodo)benzene, $C_6H_5ICl_2$ b) PhIO, iodosylbenzene
2	Iodine(III) compounds with two carbon-iodine bonds on the same iodine atom.	diphenyliodonium chloride  dibenziodolium iodide, (biphenyleneiodonium iodide) 
3	Iodine(III) compounds with three carbon-iodine bonds on the same iodine atom.	5-phenyl-5H-dibenziodole 
4	Iodine(V) compounds with one carbon-iodine bond.	iodylbenzene $C_6H_5IO_2$
5	Iodine(V) compounds with two carbon-iodine bond.	diphenyliodyl acetate, $(C_6H_5)_2IO(OCOCH_3)$

Table 1.2.1

The structural geometry classification and classification by the number of carbon bonds of hypervalent iodine are not mutually exclusive and can be combined into a single table.

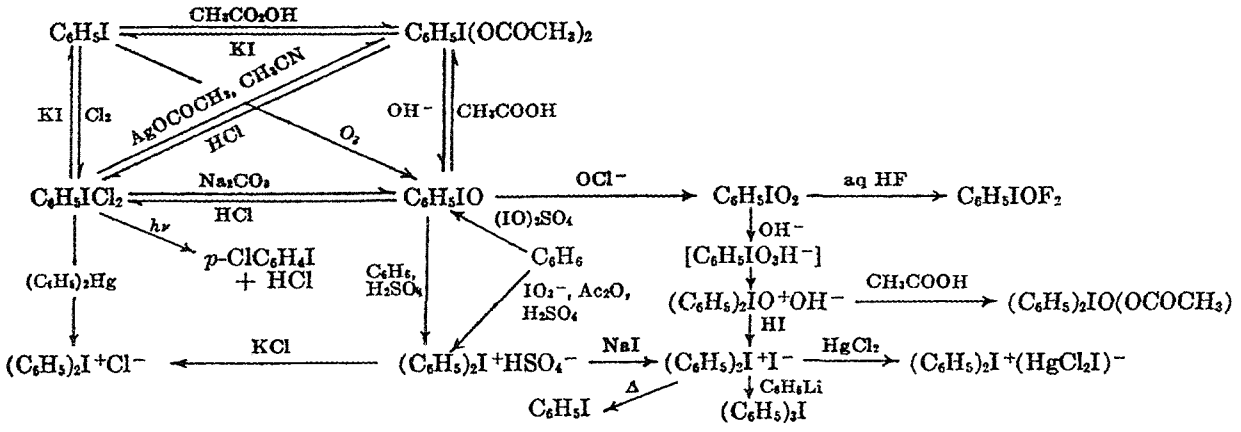
According to this revised form of classification there are three general 'Types' for trivalent iodines and two for the pentavalent iodines, see Table 1.2.2.

Type	Description
1	Structure class 1 or 2 with one carbon iodine bond. There are many examples of organic iodosyl compounds (ArIO) and their derivatives (RIX_2, where X is any non-carbon ligand).
2	Structure class 1 and 2 with two carbon iodine bonds. This type includes the iodonium salts ($R_2I^+ X^-$).
3	Structure class 3 with three carbon iodine bonds. This class is the least investigated because of the poor thermal stability of the compounds.
4	Structure class 3 with 1 carbon bond (RIO_2) and various derivatives (RIX_4 or RIX_2O)
5	Structure class 4 with 2 carbon iodine bonds. This type includes the iodylsalts (R_2IO^+X)

Table 1.2.2.

1.3 Preparation of Hypervalent Iodoarene Compounds

Banks summarised the possible interconversions of the hypervalent iodide compounds[4], see Scheme 1.3.1.

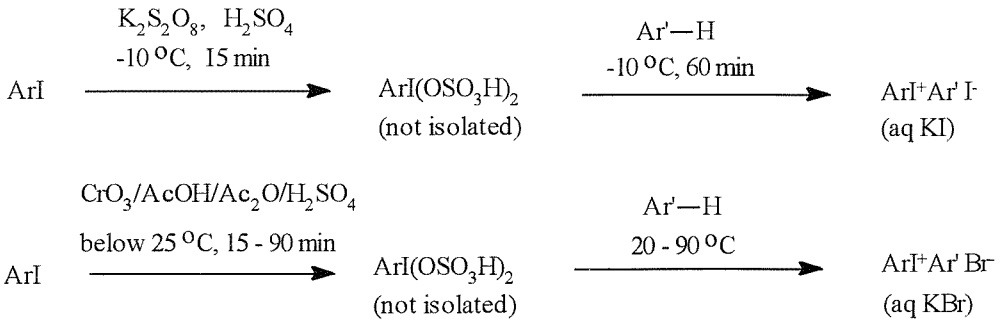


Scheme 1.3.1.

The scheme shows the possible precursors to a hypervalent iodine compounds and the action of acid or base on these hypervalent iodine compounds.

1.3.1 Organic Preparation of Diaryliodonium Salts.

The most common two step procedure for the preparation of diarylidonium salts depends on the prior synthesis of iodyl ($ArIO_2$) or iodosyl arenes (ArIO) {or their diacetates [$ArI(OAc)_2$]} from the starting iodoarene, followed by acid coupling with an arene or activated arene, e.g. silylated[1]. A more efficient system would is to oxidise the aryl iodide *in situ* and couple to the arene in the same reaction vessel. Beringer *et al*[5] developed a true one pot synthesis by oxidising aryl iodides to their I(III) bisulfate analogue *in situ* using potassium persulfate, where temperature was vigorously controlled. Similarly Kazimierczalk *et al*[6] carried out *in situ* oxidation of aryl iodides with a CrO_3/ AcOH/ Ac_2O/ H_2SO_4 followed by addition of the arene. Both these methods rely on the aryl iodide being available, see Scheme 1.3.1.1.



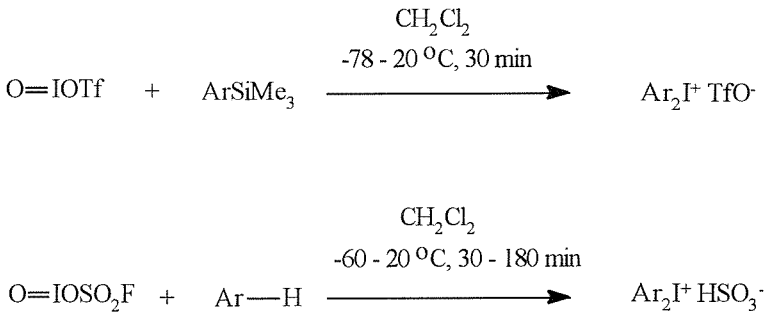
Scheme 1.3.1.1.

The bis(bisulfate)iodoarene [$ArI(OSO_3H)_2$] is in equilibrium with an ion-pair and it is this cation which undergoes electrophilic reaction[22], see Scheme 1.3.1.2.

Scheme 1.3.1.2.

Synthesis of the diaryliodonium salt can be achieved without the aryl iodide being available. When an inorganic iodosyl derivative is used, it is possible to form the two carbon iodine bonds *in-situ* and not have a pre-formed aryl iodide; iodosyl trifluoromethanesulfonate reacts with trimethyl silylarene to give diaryliodonium triflate and iodosylfluorosulfate reacts with arenes to give diaryliodonium bisulfate[7,8]. Iodosyl fluorosulfate (O=IO SO_2F) is prepared from fluorosulfonic acid, iodine and iodine(V)

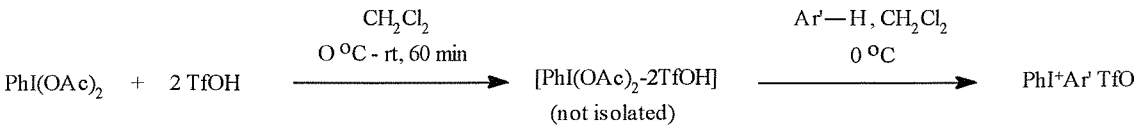
iodine(V) oxide under anhydrous conditions. This use of an inorganic iodosyl derivative narrows the scope of the synthesis to symmetric diaryliodonium salts, see Scheme 1.3.1.3[7,8].



Scheme 1.3.1.3.

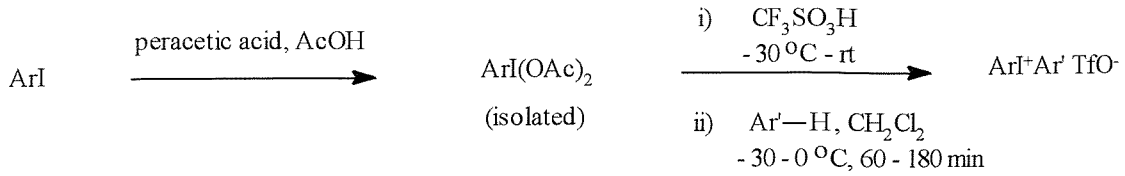
When using metallated species, such as silyl arenes, the bond strength is in the order C_{aryl} — Hg< C_{aryl} — Sn< C_{aryl} — Si, so the hypervalent iodine reagent will react more readily with the species with the weakest bond.[10]

Kitamura developed a preparation of 4-substituted diphenyliodonium trifluoromethanesulfonate by reacting iodosylbenzene or [(diacetoxy)iodo]benzene with an arene in the presence of trifluoromethane sulfonic acid, see Scheme 1.3.1.4. This technique allows the synthesis of asymmetric diaryliodonium salts, but where one of the aryl groups is a simple phenyl[9, 26].



Scheme 1.3.1.4.

The applicability of the Kitamura coupling is broadened by the preparation of generalised [(diacetoxy)iodo]benzenes, which couple to arenes to give diaryliodonium salts where both rings are substituted. Though the preparation of generalised [(diacetoxy)iodo]arenes introduces a further synthesis step[11], see Scheme 1.3.1.5.

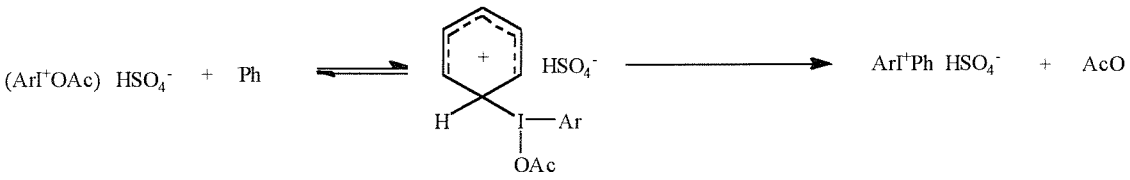


Scheme 1.3.1.5.

The reaction of [(diacetoxy)iodo]arene proceeds by the formation of an ion pair species[22], see Scheme 1.3.1.6..

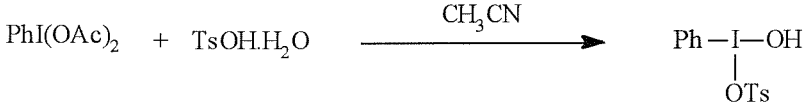
Scheme 1.3.1.6.

The iodine (III)-oxygen bonds in [(diacetoxy)iodo]benzene are hypercovalent and so the structure is 10-I-3. On reaction with a molecule of sulfuric acid, the subsequent bisulfate group was not ligating the iodine centre .Therefore the iodine (III) structure is 8-I-2. The cation undergoes typical electrophilic substitution process[22], see Scheme 1.3.1.7.



Scheme 1.3.1.7.

The action of $TsOH.H_2O$ on a suspension of (diacetoxyiodo)benzene in acetonitrile forms [hydroxy(tosyloxy)iodo]benzene, commonly known as Koser's reagent[3], see Scheme 1.3.1.8.



Scheme 1.3.1.8.

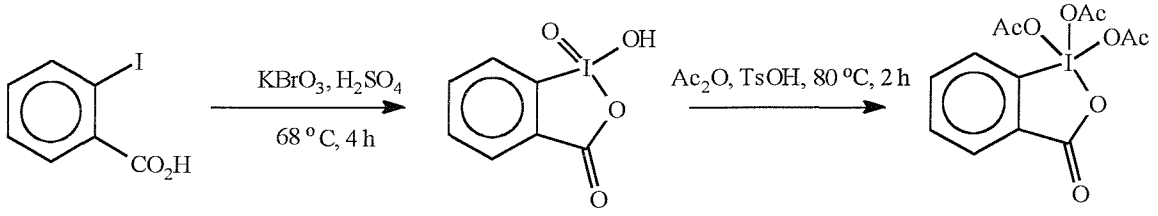
Koser's reagent is commercially available which simplifies its use in synthesis. Analysis of the structure of Koser's reagent shows that the I—OTs bond is some what elongated, so that the salt is viewed as a convenient source of $PhI^{+}OH$, this active electrophile is postulated to exist in $PhIO/H_2SO_4$ and $(IO)_2SO_4/H_2SO_4$[22]. The *in-situ* formation of iodylsulfate $(IO)_2SO_4$ can only be used to form symmetric diaryliodonium salts.

In summary the organic synthesis of diaryliodonium salts is a two stage procedure involving the initial oxidation of an aryl iodide followed by acid catalysed coupling with an arene or activated arene (silylated or stannated). In some cases the first step may be avoided by using a commercial iodosyl or [(diacetoxy)iodo] compound with an arene, but the availability of such compounds is limited and generally limits one of the aryl substituents to a phenyl ring. The use of an inorganic iodosyl was described, *ibid*, but leads only to symmetric iodonium salts and the solvent used was dichloromethane. The closest procedure to a one-pot synthesis of diaryliodonium salts was Kazimierczalk[6] and Beringer[5] but both methods involved stoichiometric amounts of oxidising agent. It was also apparent that the presence of oxidisers in organic solvents was hazardous.

1.3.2 Organic Preparation of Cyclic Hypervalent Iodine Reagents.

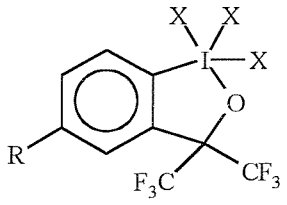
1.3.2.1 Cyclic Iodine (V): One Carbon Iodine Bond.

A common group of hypervalent iodine (V) are the cyclic analogues of iodylarene ($ArIO_2$). The incorporation of the pentavalent iodine into a five membered ring imparts an increase in stability. The parent compound of this series, iodylbenzoic acid is formed by the oxidation of 2-iodobenzoic acid, which is in turn a precursor for the triacetate derivative , commonly refereed to as the Dess-Martin reagent[3], see Scheme 1.3.2.1.1

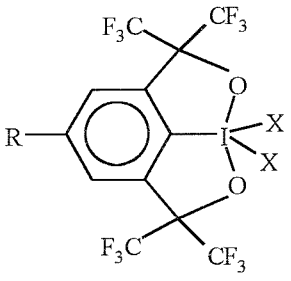


Scheme 1.3.2.1.1

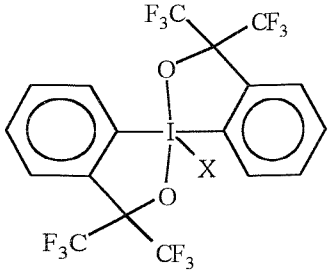
A number of analogues were subsequently prepared by Martin[1], see Scheme 1.3.2.2..



R = H, Me
X = F, OAc, $OCOCF_3$



R = H, t-Bu
2X = O or X = F, OTf, $OCOCF_3$

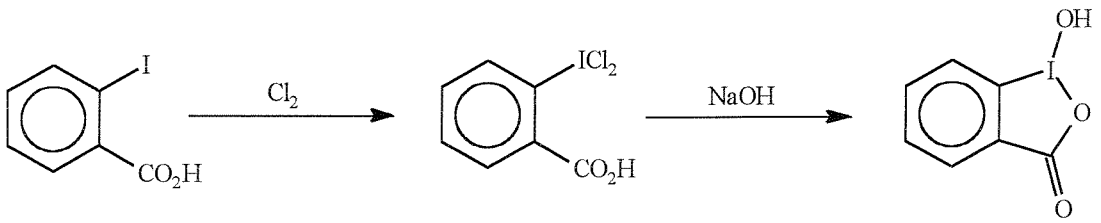


X = F,Cl, Br, O^- OTf, $OCOCF_3$, $NHCMe_3$

Scheme 1.3.2.1.2

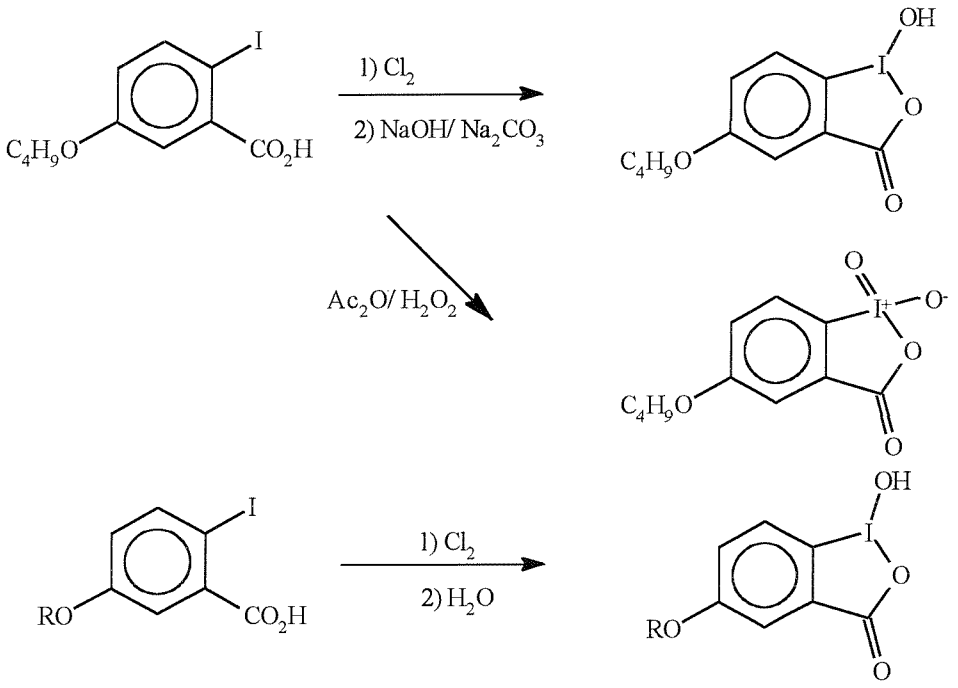
1.3.2.2 Cyclic Iodine (III): One Carbon Iodine Bond.

The parent compound of this series may be considered to be 2-iodosylbenzoic acid , which has been formed by the oxidation of 2-iodobenzoic acid, via the dichloride intermediate[3], see Scheme 1.3.2.2.1.



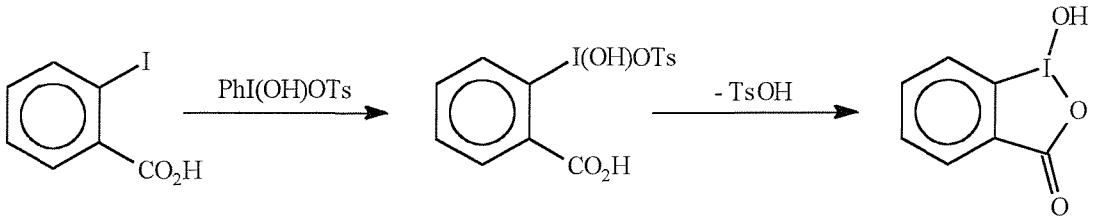
Scheme 1.3.2.2.1.

The use of chlorine, to initially form the iodo dihalide with eventual hydrolysis, has been used to prepare a number of derivatives of 2-iodosylbenzoic acid[14,15,17], see Scheme 1.3.2.2.2.



Scheme 1.3.2.2.2

A more convenient method of preparation, of 2-iodosylbenzoic acid, is to use Koser's reagent. The ligands in Koser's reagent are transferred to the 2-iodobenzoic acid, to give 2-[(hydroxy)tosyloxy)iodo]benzoic acid, which is not isolated as there is rapid cyclisation to give 2-iodosylbenzoic acid[13], see Scheme1.3.2..2.3.



Scheme 1.3.2.2.3

Synthesis of 2-iodosylbenzoic acid is now redundant for the synthetic chemist, as the reagent is commercially available. A small survey of the literature for the synthesis of iodosylbenzoic acid derivatives, show that a range of oxidisers have been used[14, 15, 16, 17, 18]. The pertinent results are shown in Scheme 1.3.2.2.4.

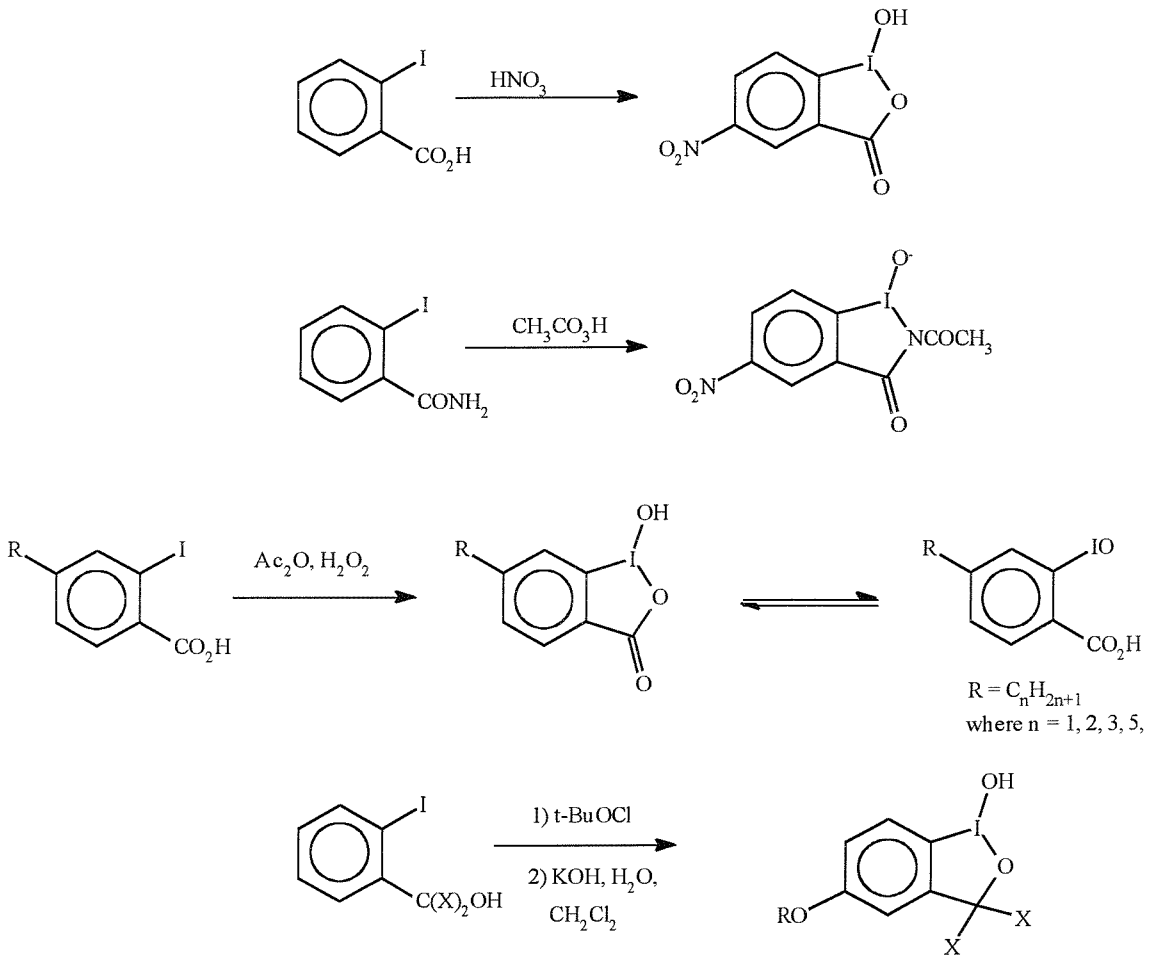
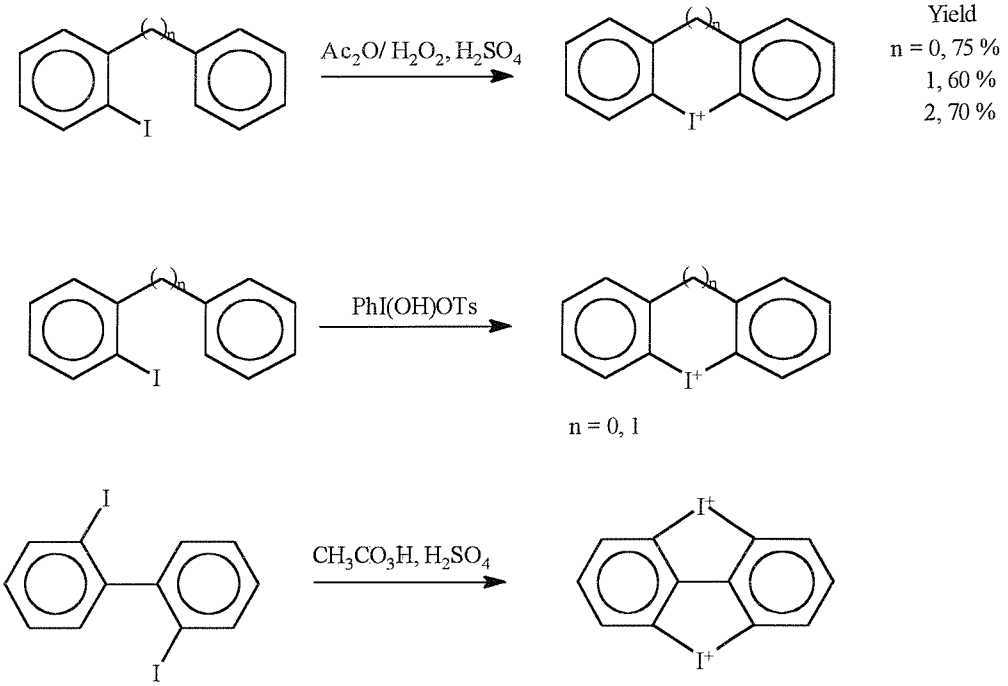


Figure 1.3.2.2.4

A point to note is that the oxidation system of acetic anhydride and hydrogen peroxide is cited twice in the oxidation of aryl iodides, see Scheme 1.3.2.2.2. and Scheme 1.3.2.2.4. In one case it gave the iodosyl derivative of the parent molecule, where in the other it is the iodyl derivative of its parent compound. So it was clearly seen that the oxidation state achieved by an iodo substrate was dependent on both the oxidation conditions and on the substrate itself It was apparent that a mixture of hydrogen peroxide and acetic anhydride was a hazardous solution and so would be unsuitable for a commercial process.

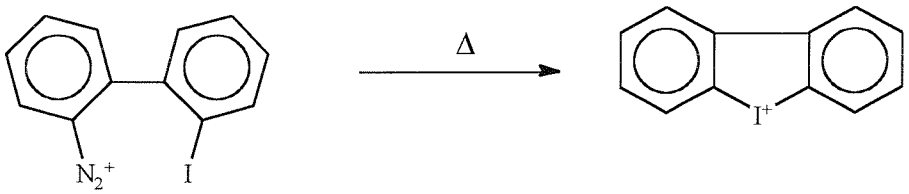
1.3.2.3 Cyclic Iodine (III): Two Carbon Iodine Bonds

The synthetic preparations of cyclic iodonium salts are similar to those for acyclic diaryliodonium salts. A common feature is that the iodine (III) species, be it an iodosyl group or a [(hydroxy)(tosyloxy)iodo]arene, is formed *in-situ*, as they readily cyclise and so cannot be isolated[12,19, 20], see Scheme 1.3.2.3.1.



Scheme 1.3.2.3.1

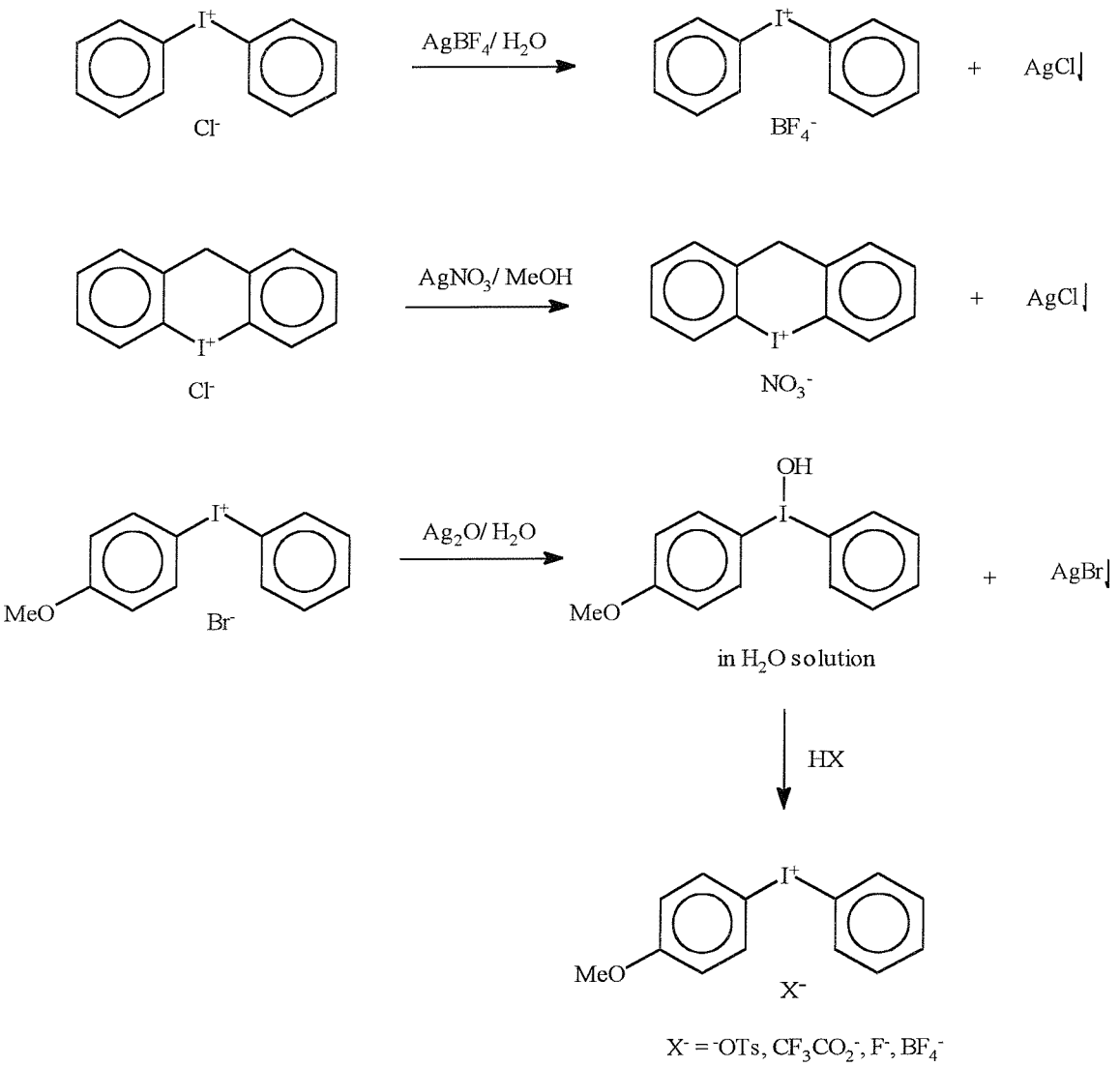
A technique which is unique to the synthesis of cyclic iodonium salts is the pyrolysis of iododiazonium salts[21], see Scheme 1.3.2.3.2.



Scheme 1.3.2.3.2

1.3.3 Anion Metathesis of Diaryliodonium Salts.

The diaryliodonium cation has been isolated with a variety of counter ions: these include F^-, Cl^-, Br^-, I^-, HSO_4^-, SO_4^{2-}, RCO_2^-, $CF_3CO_2^-$, picrate, IO_3^-, ClO_4^-, BF_4^-, $ArSO_3^-$, PF_6^-, SbF_6^-, AsF_6^-, HO^-, $HgCl_3^-$ and NO_3^-. There are many examples of metathesis of diaryliodonium salts, but the experimental technique is equally variable. One method is to dissolve the iodonium salt in a solvent, then to precipitate the cation using an appropriate inorganic salt. Aqueous solutions of diaryliodonium bisulfate when treated with sodium or potassium halide can yield the diaryliodonium halide. It is not necessarily a pre-requisite to isolate the bisulfate first. The solubility of the diaryliodonium halide decreases with increasing atomic weight of the halide ion. This means they are relatively easy to isolate, but difficult to dissolve for further reaction. Diaryliodonium fluoroborates can be prepared by reaction of the salt with silver nitrate or silver fluoroborate on a suspension or solution of the halide. The diaryliodonium hydroxides can be treated with a number of acids, HX, to give the corresponding salt, $ArI^+Ar^{'}X^-$, see Scheme 1.3.2.9.[22]



Scheme 1.3.2.9.

1.4 Applications of Diaryliodonium Salts

1.4.1 Synthetic Application

The application of diaryliodonium salts in synthesis has been reviewed[2,56,60] in the literature. There principle use has been as arylating reagents.

Varvoglis[56] reviewed the arylation of heteroatomic nucleophiles using a diaryliodonium salt and a summary of such reactions is shown in Table 1.4.1.1.

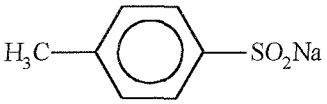
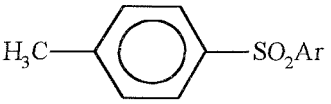
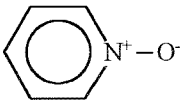
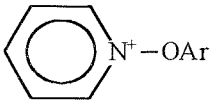
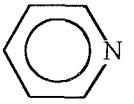
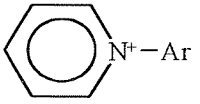
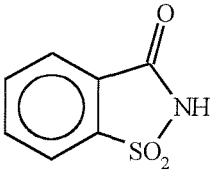
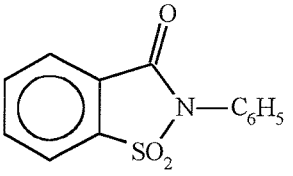
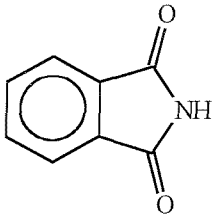
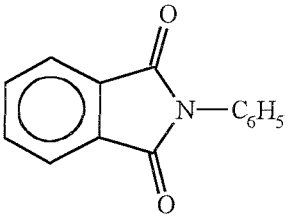
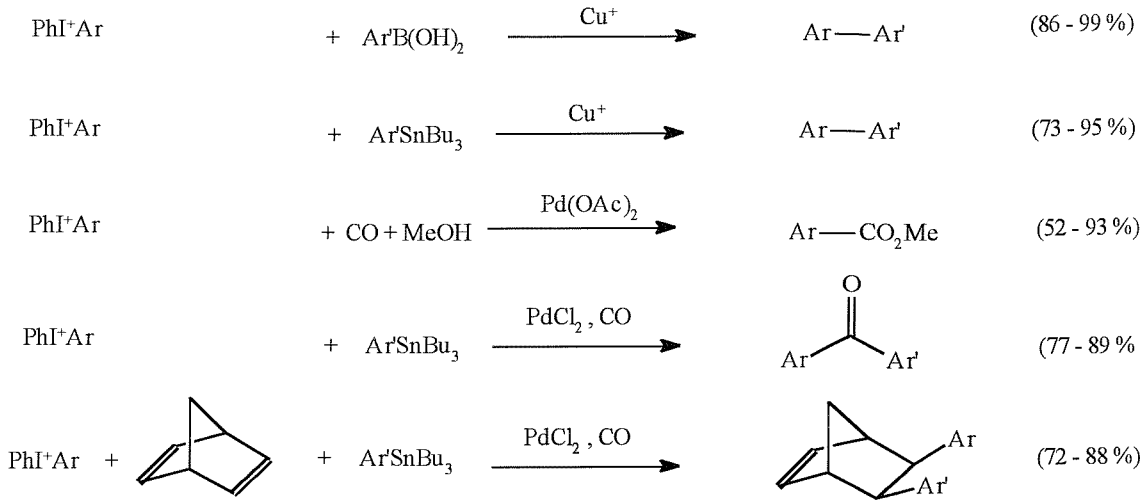
Substrate	Product
RONa	ROAr
Ar'ONa	ArOAr'
C_6H_5—CO_2Na	C_6H_5—$CO_2C_6H_5$
	
	
	
	
	
$(C_6H_5)_3P$	$(C_6H_5)_4P^+$

Table 1.4.1.1

As well as being used to form carbon heteroatom bonds, diaryliodonium salts have been used to form carbon-carbon bonds. Iodonium salts are frequently used for the functionalisation of carbonyl compounds in the α-position[2]. Also the diaryliodonium salts have been shown to have a role in well known organic reactions, such as the Stille, Suzuki and the Heck cross coupling reactions. Scheme 1.4.1.1 provides a summary of these relatively efficient cross coupling reactions involving carbon-carbon bond formation.



Scheme 1.4.1.1

1.4.2 Biological Applications

There has been considerable interest in the antimicrobial properties of hypervalent iodine compounds; this interest has focused on diaryliodonium salts and their heteroaromatic analogues. Stang[1] and Koser[22] reviewed the patent literature . The anti-microbial activity of iodonium compounds has been reported to be effective against Gram negative bacteria, Gram positive bacteria, fungi, yeast's, molds, mildews and slimes, etc.

Table 1.4.2.1 is a summary of the reviews by Stang and Koser of some general iodonium salt structures and their associated biological activity claims.

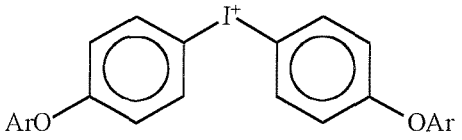
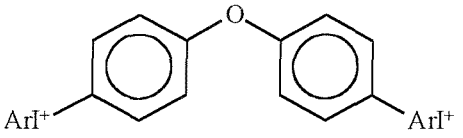
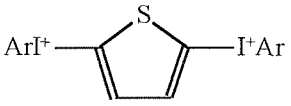
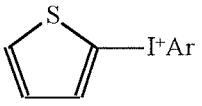
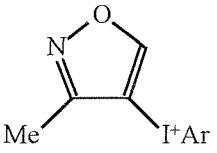
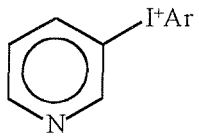
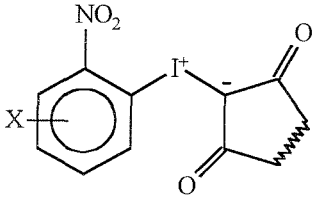
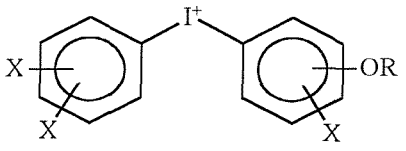
Structure	Biological Activity
	Antimicrobial activity against bacteria, fungi, and protects the ground portion of terrestrial plants, seeds and roots against microbial activity.
	Antimicrobial activity against bacteria, fungi, and protects the ground portion of terrestrial plants, seeds and roots against microbial activity.
	Antimicrobials for the inhibitions of the growth of bacteria and fungal organisms that attack the ground portion of terrestrial plants, seeds and roots. Control, several bacteria, molds, mildews, fungi and slimes.
	
	Control against bacteria, fungi, yeasts and protects the ground portion of terrestrial plants, seeds and roots. Attacks organisms responsible for mould, mildew, rot and decay.
	Toxic to bacteria, fungi, and protect the ground portion of terrestrial plants, seeds and roots. Antimicrobial to organisms responsible for mold, mildew, rot, and decay.
	Active against a range of bacteria, fungi, algae, and yeasts.
	Anti-microbial to bacteria; anthelminitic agents i.e. a substance which expels or destroys intestinal worms.

Table 1.4.2.1.

To have application *in vivo* the anti-microbial agent must have a low LD_{50} value, which is the concentration level of the substrate which is required to kill 50 % of the test mammals employed after oral administration. For mice the LD_{50} of diphenyliodonium chloride and p-chlorophenyl(2-thienyl)iodonium chloride was 56.2 mg/ kg and > 4000 mg/ kg respectively. As future antibiotics the (thienyl)iodonium salts would appear to be the better candidates.

The structure also has a significant influence on the potency of the iodonium salts, i.e. p-chlorophenyl(2-thienyl)iodonium chloride caused 100 % kills of *Salmonella typhosal* at levels in the range 1 to 5 ppm, whilst the diphenyliodonium chloride was completely in active at 10 ppm, and was not active until levels of 500 ppm were reached.

As well as being antimicrobial they have possible direct medical application, i.e. diphenyliodonium salts, have been shown to be effective in the treatment of hypertension[1].

1.4.3 Photo Applications

Koser[22] reported that diaryliodonium salts are photoactive and are useful initiators for cationic and free radical polymersation . The activity of a specific diaryliodonium salts is dependent on the counter ion. Koser[22] reports an experiment where a 3 mil film of 3-vinylcyclohexene dioxide containing by weight 3 % diphenyliodonium salt was applied to a glass slide The slide was then exposed to an ultra violet source. The minimum time required to form a film which was tack-free was dependent on the counter ion to the diphenyliodonium cation; the results are summarised in Table 1.4.3.1.

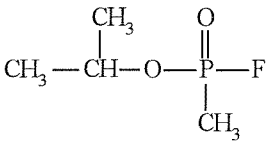
Counter ion to diphenyliodonium cation	Curing time / Seconds
BF_4^-	30
PF_6^-	20
SbF_6^-	3-5

Table 1.4.3.1

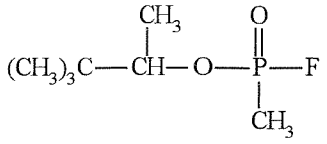
1.4.4 Decontamination of Chemical Warfare Agents

Hypervalent iodine compounds may have a role in decontamination, aimed at eliminating the hazard of chemical warfare agents. This is required on the battlefield, laboratories, pilot plants, storage and destruction sites[36].

Two of these 'nerve agents', the G agents are; 2-propyl methylphosphonofluoridate (GB or Sarin) and 3,3'-dimethyl-2-butylmethylphosphonofluoridate (GD or Soman), see Scheme 1.4.4.1.



GB



GD

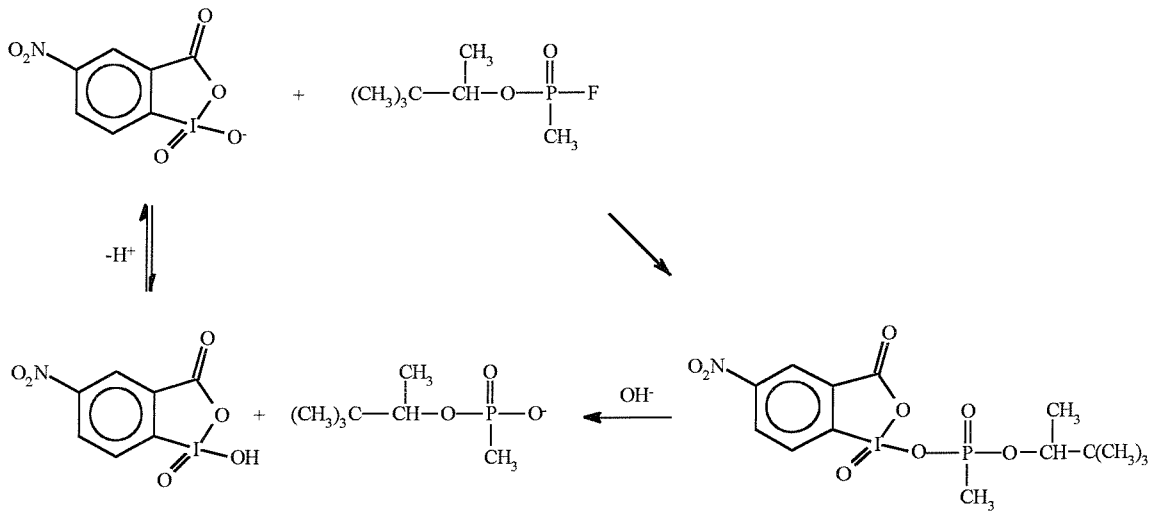
Scheme 1.4.4.1

These G agents act on acetylcholinesterrase. Their toxic expression is to interfere with respiration and nervous functions and can kill in minutes.

Detoxification of these agents is achieved by the simple strategy of hydrolysis of the phosphorus fluorine bond resulting in conversion to the corresponding phosphonic acid, which is non-toxic.

Moss pioneered the use of hypervalent iodine reagents as possible catalysts for the hydrolysis of the G agents; his investigation used a G agent mimic, p-nitrophenyl diphenylphosphate. He showed that analogues of 2-iodosylbenzoic[37] acid and 2-iodoxylbenzoic [15, 37]acid were efficient catalyst for the hydrolysis of phosphorus fluorine bond.

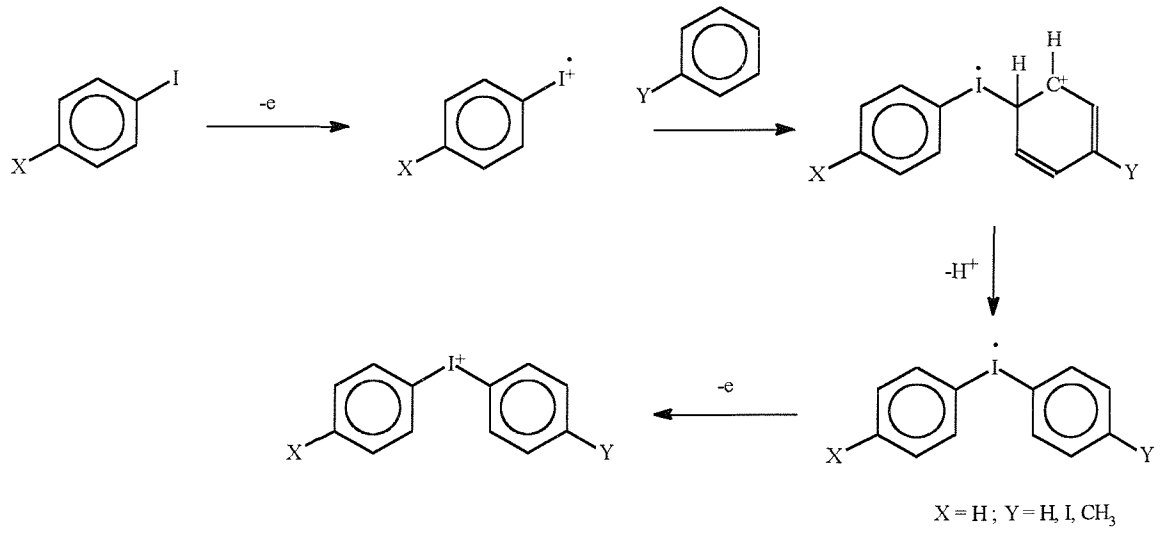
It was realised that 2-iodosylbenzoic acid and 2-iodylbenzoic acid analogues could be potent oxygen nucleophiles, and so can cleave reactive phosphates, see Scheme 1.4.4.2.



Scheme 1.4.4.2

1.5 Electrochemical Synthesis of Diaryliodonium Salts

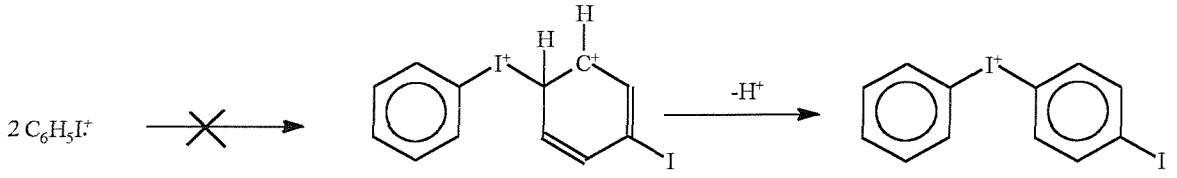
The first electrochemical synthesis of diaryliodonium salts was reported by Miller and Hoffmann[23]. They reported that the major product of iodobenzene oxidation was 4-iododiphenyliodonium perchlorate. The potentiostatic electrolysis were carried out at 1.6 V vs. Ag. The cell current was directly proportional to the iodobenzene concentration and was interpreted as indicating that the rate limiting step was first order with respect to iodobenzene. It was suggested that the salt was formed via an ECE mechanism; the initially formed iodobenzene cation radical was attacked by a neutral molecule of iodobenzene, which was converted to the product by the loss of a proton and a further electron, as shown in Scheme 1.5.1.



Scheme 1.5.1.

Attempts to measure the life time of the cation radical indicated that it was less than 0.02 seconds. An alternative mechanism would be EEC, where a two electron transfer was the initial step. The formation of a free iodobenzene dication was less attractive than a cation on electrostatic grounds. Hoffmann did consider a dication intermediate, such as iodobenzene diperchlorate, but such a species has not been identified in the literature.

The cross coupling of iodobenzene and benzene, to give diphenyliodonium perchlorate, at potentials where the benzene was electroinactive, provides evidence of the reactivity of the iodyl cation radical towards aromatic molecules and supports the postulation that 4-iododiphenyliodonium perchlorate does not arise from the dimerisation of cation radicals, see Scheme 1.5.2.



Scheme 1.5.2.

Hoffmann argued that the production of iodosylbenzene, by reaction of the iodobenzene cation radical with traces of water in the cell was not a route to the diaryliodonium salt, under the specific reaction conditions, see Scheme 1.5.3.

$$ArI + H_2O \xrightarrow{-2e,\ -H^+} ArI^+O$$

Scheme 1.5.3

Hoffmann made this assertion because iodosylbenzene did not couple with iodobenzene when dissolved in acetonitrile acidified with perchloric acid. The electrolysis of iodobenzene in aqueous acetonitrile (8 %) did not give the iodonium product. Water was seen to depress the yield of diaryliodonium salt.

Wendt *et al*[24] further investigated the formation of diaryliodonium salts[24]. They reported the voltammogram of iodobenzene in acetonitrile/ 0.1 M $NaClO_4$ contained a two electron wave with a constant slope, $\partial E/\partial \log \{(i_{lim} - i)/ i\} = 120$ mV, where the formal charge transfer coefficient was ca. 0.5. The addition of benzene to the solution did not change the half wave potential nor the appearance of the wave..

Wendt investigated the kinetics of homogenous coupling of [(diacetoxy)iodo]benzene with benzene and iodobenzene, see Scheme 1.5.4.

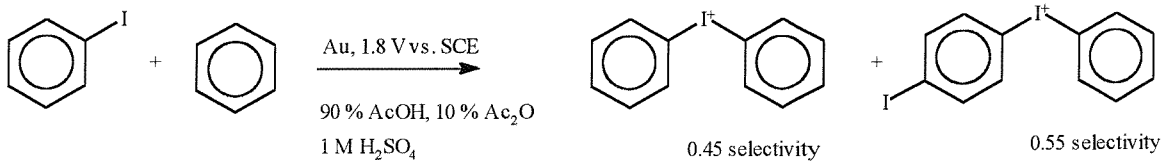
$$PhI(AcO)_2 + PhH \xrightarrow{H_2SO_4,\ AcOH} (PhI^+Ph)\,AcO^- + AcOH \quad 1.$$

$$PhI(AcO)_2 + PhI \xrightarrow{H_2SO_4,\ AcOH} (IPhI^+Ph)\,AcO^- + AcOH \quad 2$$

(rate of reaction 1/ rate of reaction 2) = 30/1

Scheme 1.5.4

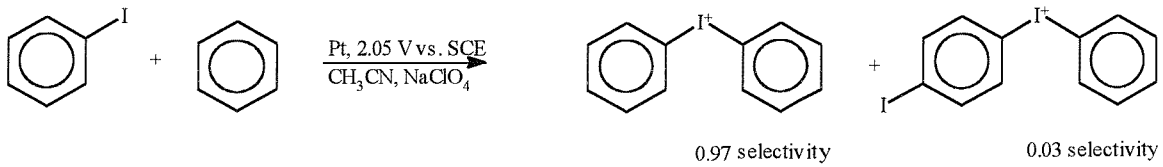
Wendt's work showed that [(diacetoxy)iodo]benzene preferentially coupled to benzene rather than iodobenzene. Wendt contrasted this with the electrolysis of an equimolar solution of iodobenzene and benzene carried out at a gold working electrode. The diphenyliodonium cation and 4-iodophenylphenyliodonium cation were formed in equal yield. Wendt argued that if the chemical coupling of the iodobenzene cation radical with the neutral aromatic was happening in the solvent, then it should have similar kinetics to the homogeneous coupling of [(diacetoxy)iodo]benzene and so should give the diphenyliodonium salt as the major product. The electrolysis of iodobenzene and benzene is summarised in Scheme 1.5.5.



Scheme 1.5.5

The distribution of electrolysis products was interpreted by Wendt as meaning that the reaction between the iodobenzene cation radical and the neutral aromatic was not happening in the solution phase, but took place between adsorbed species on the surface of the electrode.

Wendt repeated the electrolysis of iodobenzene and benzene, but changed the working anode to platinum. The major product was now the diphenyliodonium cation, see Scheme 1.5.6.

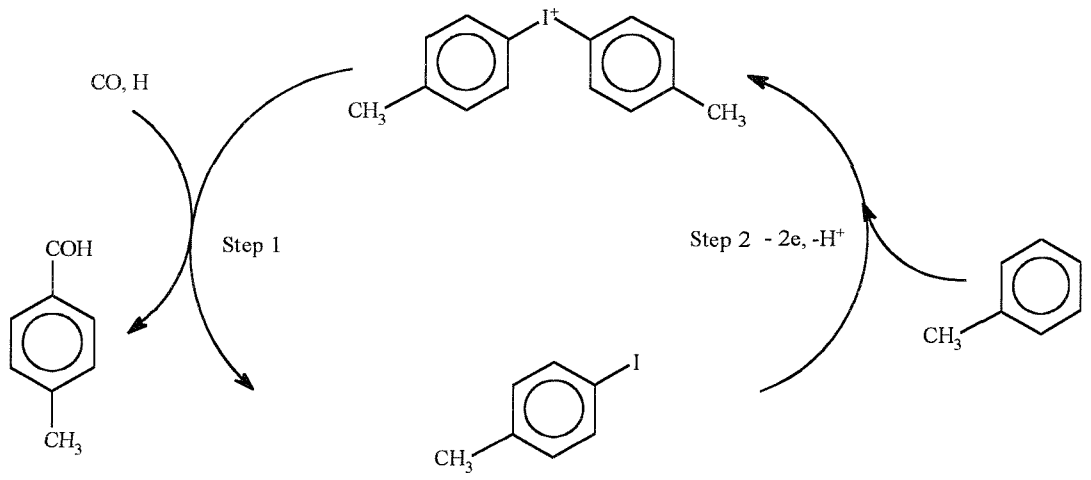


Scheme 1.5.6

There was an improvement in the selectivity of the electrolysis of iodobenzene and benzene when the electrode was changed from platinum to gold. It was this dependence of the reaction product on the electrode material used, that persuaded Wendt that the reaction involved adsorbed species.

It may also be argued that too many experimental parameters had changed between the electrolysis at the gold and platinum electrode to make a logical comparison about the relative selectivities, towards 4-iodophenylphenyliodonium salts. So Wendt's assertion of specific adsorption of iodobenzene and iodobenzene cation radical in the mechanistic sequence was not convincing.

The electrosynthesis of diaryliodonium salts was then not pursued for two decades until Weinberg[25] re-investigated the synthesis. His interest was a commercial one; terephthalic acid is an important feed stock for the synthesis of polyethyleneterephthalate (PET), and so it was envisaged that a route to terephthalic acid from toluene would be commercially viable. A system was proposed where toluene was electrochemically coupled with 4-iodotoluene to give the 4,4'-dimethyldiphenyliodonium cation. The 4,4'-dimethyldiphenyliodonium cation was then to be reacted with carbon monoxide, in the presence of a platinum catalyst, to give 4-tolualdehyde and 4-iodotoluene, effectively re-cycling the 4-iodotoluene. This is summarised in Scheme 1.5.7.



Scheme 1.5.7

Weinberg developed an economic solvent and supporting electrolyte, acetic acid/ 5 % sulfuric acid/ 2% acetic anhydride, with a graphite anode and cathode for the coupling of 4-iodotoluene and toluene, to give the 4, 4'-dimethyldiphenyliodonium salt with excellent current efficiencies and chemical selectivities. No investigation of the generality of the substrates which could be coupled was considered.[25]

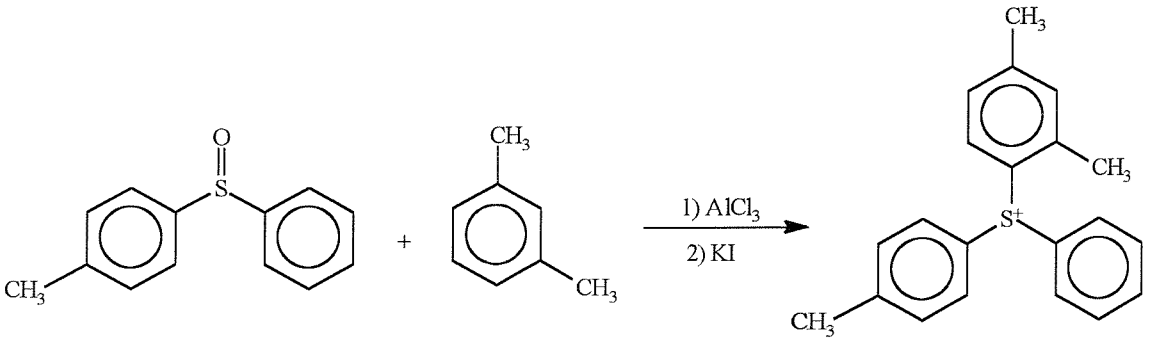
Weinberg considered the possibility that oxidation was achieved indirectly through an inorganic intermediate. The first hypothesis was that electrogenerated persulfate mediated the oxidation. An electrosynthesis, in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride, was carried out with no aromatic present. Then, the aromatics were added. No iodonium salt product was formed. Therefore it was concluded that persulfate did not appear to be an intermediate. This was a reasonable conclusion as persulfates do have a proven record in iodonium salt formation, under acidic conditions.

A second series of experiments were concerned with the possibility that anodically generated iodine, iodate or periodate was involved. An electrolysis was conducted with potassium iodide dissolved in the solvent supporting electrolyte suspension, acetic acid/ 5 % sulfuric/ 2 % acetic anhydride, then the aromatics were added. There was a low conversion to iodonium salts, with good selectivity. Potassium iodate was added to the electrolyte solution with 4-iodotoluene and toluene, but no charge passed. There was no

iodonium product. Potassium periodate was added to the electrolyte solution with 4-iodotoluene and toluene, but no charge passed, there was a slow coupling to give the dimethyldiphenyliodonium salt. The slow kinetics associated with the inorganic oxidisers persuaded Weinberg that the oxidation of 4-iodotoluene was a direct process at the electrode and not mediated.

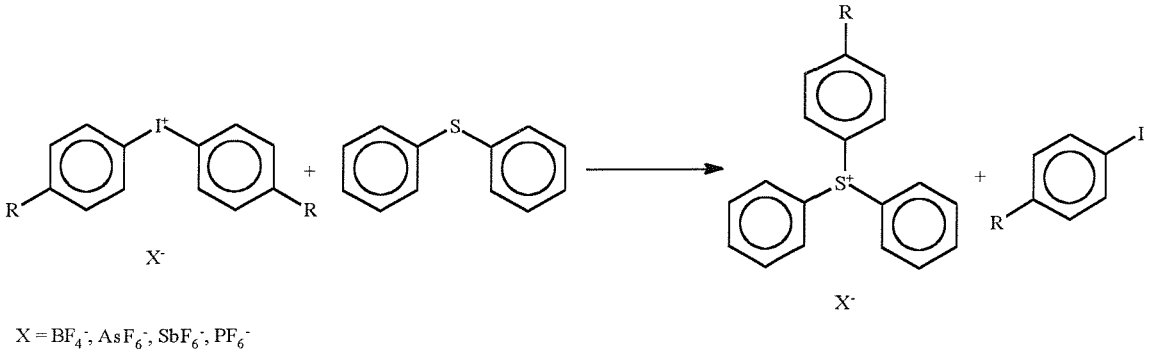
1.6 Organic Preparation of Triarylsulfonium Salts.

A effort was made during the course of this research to synthesize triaryl sulfonium salts, as these 8-S-3 species were analogous to the 8-I-2 diaryliodonium salts. McEwen[39] reports the synthesis of the triarylsulfonium salts from sulfur precursors in the IV oxidation state. Sulfoxides were condensed with arenes in the presence of a Lewis acid, see Scheme 1.5.1.



Scheme 1.6.1

An alternative synthesis of triarylsulfonium salts was the arylation of diarylsulfides with diaryliodonium salts[40]. The transfer of the aryl group, from the diaryliodonium salts to the diaryl sulfide, was catalyzed by either copper (I) or copper (II) reagents. It was essential for the success of these reactions that the counter ion to the diaryliodonium salt was non-nucleophilic in nature, thus avoiding competition between the anion and the weakly nucleophilic diarylsulfide, see Scheme 1.6.2.

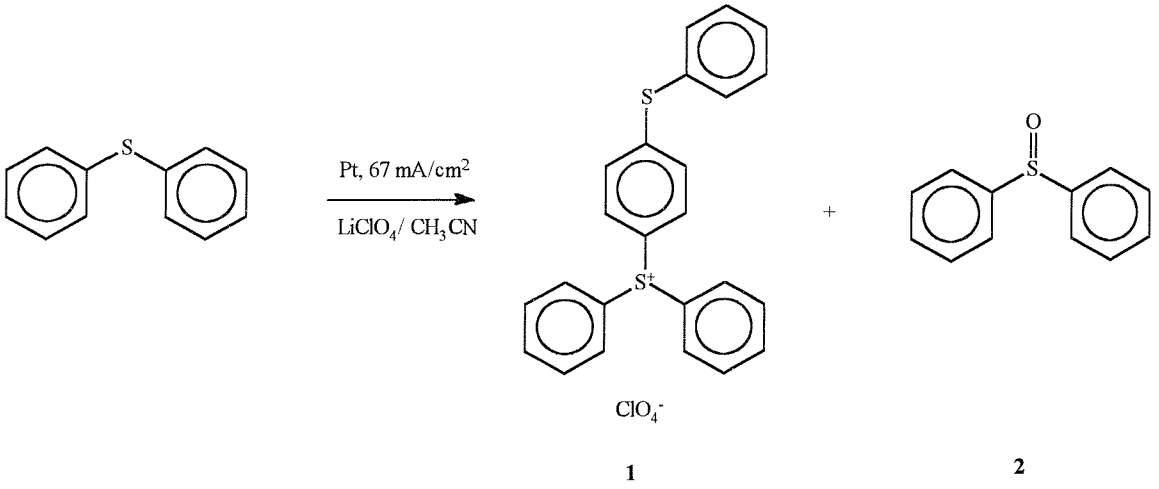


$X = BF_4^-, AsF_6^-, SbF_6^-, PF_6^-$

Scheme 1.6.2

1.7 Electrochemical Synthesis of Triarylsulfonium Salts.

The first report of the electrochemical preparation of a triarylsulfonium salt was made by Torii[41]; a galvanostatic electrolysis of a phenyl sulfide solution was carried out until one equivalent of charge had passed. Two products were identified, at the end of the electrolysis; phenyl sulfoxide and a sulfonium salt, see Scheme 1.7.1.



Scheme 1.7.1

The product distribution, between 1 and 2 was reported to be dependent on the water content of the solvent, see Table 1.7.1.

$[H_2O]^a$	1[b]	2[b]
0	71	1
0.1	63	4
1.0	46	25

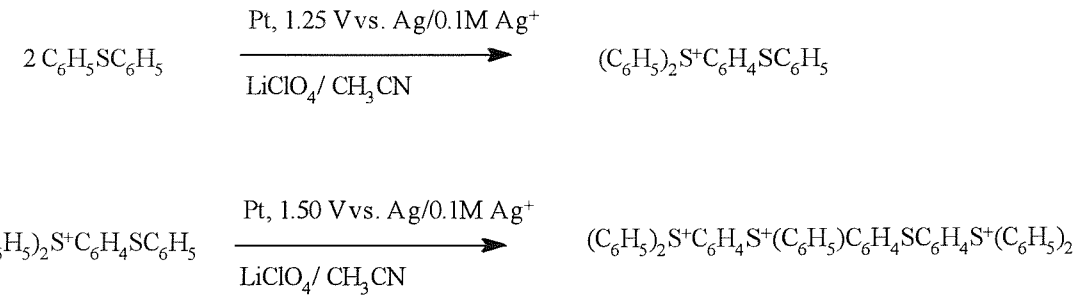
a) milliliters of water in 10 ml of acetonitrile solution

b) yield based on recovered phenyl sulfide

Table 1.7.1.

It was clear that sulfonium salt formation was the major product in the absence of water, whilst sulfoxide increased as the water content was raised.

Magno and Bontempelli[55] similarly investigated the electrolysis of phenyl sulfide in acetonitrile, but were fastidious in their drying of the acetonitrile solvent. They recorded the cyclic voltammogram of phenyl sulfide at a platinum sphere electrode. And reported that the voltammogram consisted of three peaks. The potentials at which these peaks occurred was used to determine the potential at which three consecutive potentiostatic electrolysis of a solution of phenyl sulfide were carried out. After each electrolysis a cyclic voltammogram was recorded. The number of peaks in the voltammogram were seen to diminish by one after each electrolysis. The first and second electrolysis were carried out at 1.25 and 1.50 V vs. Ag/0.1 M Ag^+, respectively, see Scheme 1.7.2 for the assigned structures of the products.



Scheme 1.7.2

It can be seen that the products of each electrolysis were considered to be an oxidative dimerisation of the starting material.

A third electrolysis was carried out at a potential of 1.80 V vs. Ag/0.1 M Ag^{+}, but the compound was unstable, so only a speculative structure was assigned.

Chapter 2

Experimental

2.1 Chemicals and Reagents

Each of the following organic compounds were used as received;

Substrate	Supplier	Purity %
iodobenzene	Aldrich	98
3-iodotoluene	Aldrich	99
2-iodobenzoic acid	Aldrich	98
4-methoxyacetophenone	Aldrich	99
tert-butylbenzene	Aldrich	99
ethylbenzene	Aldrich	99
iodobenzene diacetate	Aldrich	98
1-iodonaphthalene	Aldrich	98
1-iodo-4-nitrobenzene	Aldrich	98
fluorobenzene	Aldrich	99
9-iodophenanthracene	Aldrich	97
1,4-benzoquinone	Aldrich	98
cumene	Aldrich	99
naphthalene	Aldrich	98
4-iodotoluene	Aldrich	99
4-iodoanisole	Aldrich	99
2-iodotoluene	Aldrich	98
toluene	Fisher	—
phenyl sulfide	Fluka	97
benzene	Fisons	99
2-iodobiphenyl	Lancaster	98
anisole	Lancaster	99
2-bromobiphenyl	Lancaster	98

2-iodosylbenzoic acid	Sigma	96

Each of the following solvents was used as received;

Solvent	**Supplier**	**Purity %**
acetonitrile	Aldrich	99.93
acetic anhydride	Aldrich	99
(methyl sulfoxide)-d_6	Aldrich	99.9
acetic acid	BDH	100
diethyl ether	GPR	98
dichloromethane	GPR	99

Each of the following inorganic reagents were used as received;

Reagent	**Supplier**	**Purity**
fluoroboric acid	Aldrich	48 wt. % solution in water
methanesulfonic acid	Aldrich	99
trifluoromethanesulfonic acid	Aldrich	99
potassium iodate	Aldrich	98
ammonium hydroxide	Aldrich	NH_3 28-30 % in water
potassium iodide	BDH	99.8
ammonium chloride	M & B	98
sulfuric acid	Fisher	98

2.2 Electrodes, Cells and Procedures

2.2.1. Voltammetry Recorded at a Stationary/Rotating Disc Electrode

A working electrode of vitreous carbon (diameter, 3.0 mm) was used for the electroanalytical studies. This was constructed by sealing a short rod of vitreous carbon in a PTFE sleeve. The disc was initially abraded on a series of decreasing roughness grades of emery paper and then polished with alumina powder (1.0 and 0.3 μm,

Beuhler), on moistened polishing cloth (Buehler). The electrode was rinsed between the various polishing stages with de-ionised water. Before the polished electrode was introduced into the cell it was rinsed and dried. The drying was achieved by lightly touching the surface with a paper towel. The effect was to draw the water away from the surface, rather than wiping it clear. Between scans, the electrode was polished only if there was considerable hysteresis between the forward and backward scan. If there was hysteresis then the electrode was re-polished with alumina powder (1.0 and 0.3 μm). All electroanalytical experiments were conducted at ambient temperature in a three electrode cell with three compartments, see Figure 2.2.1.1.

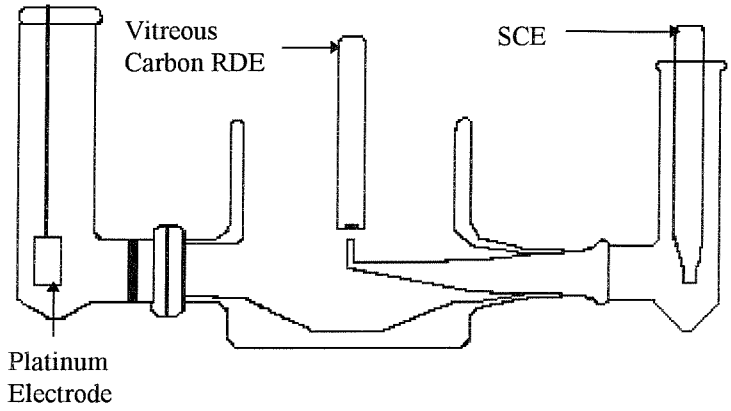


Figure 2.2.1.1 *Three compartment cell used for the voltammery recorded using a disc electrode.*

A platinum mesh was used as the counter electrode (surface area 5 cm^2). The potential at the working electrode was measured versus a saturated calomel electrode (SCE), which was housed within the Luggin capillary compartment.
Typically, a solution of 1 mM of electroactive species was used in the solvent supporting electrolyte system. It was deemed unnecessary to degas the solvents, as there was not a significant back ground current due to dissolved gases, see Figure 2.2.1.2.

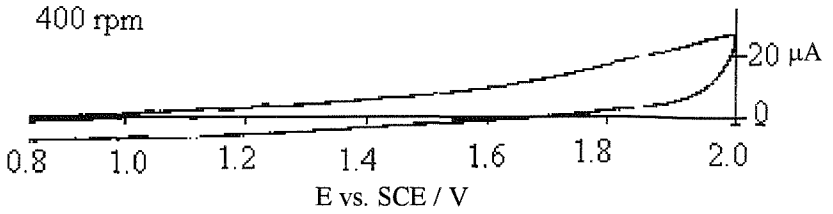


Figure 2.2.1.2 *Voltammogram of AcOH/ 5 % H_2SO_4/ 2 % Ac_2O using a vitreous carbon rotating disc electrode (diameter 3 mm), platinum counter electrode, scan rate 0.02 V/s. Rotation rate 400 rpm.*

2.2.2 Galvanostatic Electrolysis in an Undivided Cell

The undivided cell, in which the majority of galvanostatic electrolysis were carried out, is illustrated in Figure 2.2.2.1. The simple batch cell consisted of a 250 cm^3 beaker where a sheet of carbon felt (dimensions; 20 cm x 4 cm, thickness 1.5 cm) was formed into a cylindrical anode around the perimeter of the beaker and a graphite cathode (dimensions; 13.8 cm × diameter 2.5 cm) was placed at the centre of the beaker. There was a uniform gap, of 0.75 cm, between the two electrodes. To prevent short circuiting the electrodes were separated by a PVC mesh. During the electrolysis, the solution was stirred with a magnetic stirrer bar

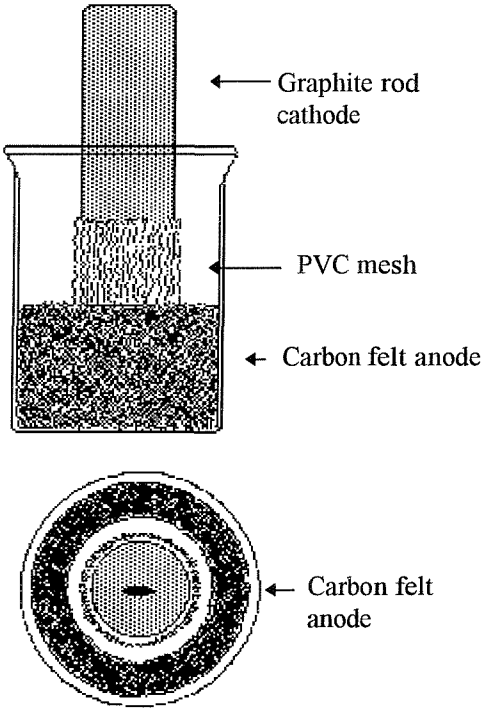


Figure 2.2.2.1 *Beaker cell used for galvanostatic electrolysis.*

A smaller cell was necessary for a series of experiments where the constant current was varied in a series of electrolyses. The cell was similar to that shown in Figure 2.2.2.1 but a smaller beaker was used, of volume 80 cm^3. The carbon felt anode was also of smaller dimensions (0.6 cm × 4 cm × 13 cm). The same graphite cathode was used. The cell was charged with a reduced volume of electrolysis solution, 50 cm^3.

The electrolyses were carried out in accordance with the following procedure; to the cell was added a 100cm^3 solution of iodoarene (0.2M) and arene (0.3M) in the supporting solvent electrolyte system. A constant current, usually 400 mA (5 mA cm^{-2}), was passed until a charge of 1.6 F (80 % theoretical charge for the complete 2 electron conversion of iodoarene) had been applied to the system. A water bath was used to maintain the solution at a temperature of 298 K. The anodic current density was calculated assuming only the face of the felt parallel to the cathode was active. The consumption of the starting material and the formation of product was followed by hplc analysis. The sampling protocol, for the hplc analysis, of the reaction mixture was strictly adhered to; 25 μl of the reaction solution was removed with a pipette (Autoclavable BCL 5000 DG), this sample was then diluted with 975 μl of acetonitrile (hplc grade) in a mass spec vial before being loaded on the auto sampler carousel. The sample concentration was ca. 22 mg/ cm^3.

At the end of the electrolysis the reaction mixture was often studied by electrospray mass spectroscopy; an aliquot was removed from the reaction solution using a capillary. The contents, of the capillary, were tapped into the mass spec vial and diluted with acetonitrile. The sample concentration was ca. 0.4 mg/cm^3.

After the electrolysis had been concluded, the electrodes were washed with hot methanol and the washings were combined with the reaction mixture. The solvents were removed *in vacuo* and the resulting oil was partitioned between an aqueous phase and an organic phase, of diethyl ether. The aqueous layer was then treated with 3 g of potassium iodide, dissolved in a minimum amount of water. If the reaction had been successful then an immediate precipitation of material was seen when the potassium

iodide was added. This material was separated and dried on the filter paper The isolated product, was typically characterised by H-NMR, ^{13}C-NMR and DEPT-135 spectroscopic analysis. The molecular weight of the cation was recorded by electrospray mass spectroscopy. It was also possible to isolate iodonium compound, as the bisulfate, by the addition of diethyl ether to the electrolyte. Four volumes of diethyl ether for every volume of reaction mixture. A precipitate was formed which was collected by filtration This recovery was incomplete and additional material was isolated as the iodide salt, *ibid.*

The diethyl ether phase contained the lipophylic starting materials and products. The diethyl ether was removed *in vacuo*; the subsequent oil was diluted with dichloromethane. An aliquot of the dichloromethane solution was removed (10 μl) and diluted with additional dichloromethane (990 μl)and analysed by a gas chromatography electron impact mass spectroscopy system (GC-MS). Sample concentration was ca. 0.09 mg/cm^3.

The success of the electrolysis, of aryl iodide and arene, was determined by whether the iodonium salt had been formed or not. This success was measured by two parameters chemical selectivity and current efficiency.

The chemical selectivity of the electrolysis was the moles of iodonium salt isolated, divided by the amount of moles of aryl iodide consumed. The moles of aryl iodide consumed was calculated by considering the reduction in the peak height in the hplc chromatogram recorded at the end of the electrolysis relative to the peak height at before any charge was passed. The formulae of chemical selectivity is shown in Figure 2.2.2.2.

$$\text{Chemical Selectivity} = \frac{\text{Moles of Iodonium Salt isolated}}{\text{Moles of Aryl Iodide consumed}}$$

Figure 2.2.2.2. *Chemical Selectivity was the ratio of the isolated moles of iodonium salt and the moles of aryl iodide consumed. The amount of aryl iodide was calculated by considering the reduction in peak height during the electrolysis*

The current efficiency was determined by the success of the electrolysis to form the iodonium salt. Faradays Law was used to calculate the amount of charge required to form the amount of iodonium salt isolated and this value was divided by the amount of charge actually passed. The formulae for current efficiency is shown in Figure 2.2.2.3.

$$\text{Current Efficiency} = \frac{\text{Charge required to form isolated Iodonium Salt}}{\text{Charge passed during electrolysis}}$$

Figure 2.2.2.3 *The Current Efficiency was the ratio of charge required to form the amount of isolated iodonium salt, relative to the actual charge passed.*

2.2.3 Potentiostatic Electrolysis in an Undivided Cell

The undivided cell in which all constant potential electrolysis was carried out is shown in Figure 2.2.3.1. The cell is a two compartment 'pipe shaped' glass vessel . Anodic oxidation was carried out at a graphite disc (diameter 2.5 cm, area 4.9 cm^2). The disc was sealed into a PTFE sleeve. Parallel to the graphite anode was a platinum mesh cathode (area 4cm^2). A Luggin capillary faced the graphite electrode and a saturated calomel electrode (SCE) was housed within the Luggin compartment.

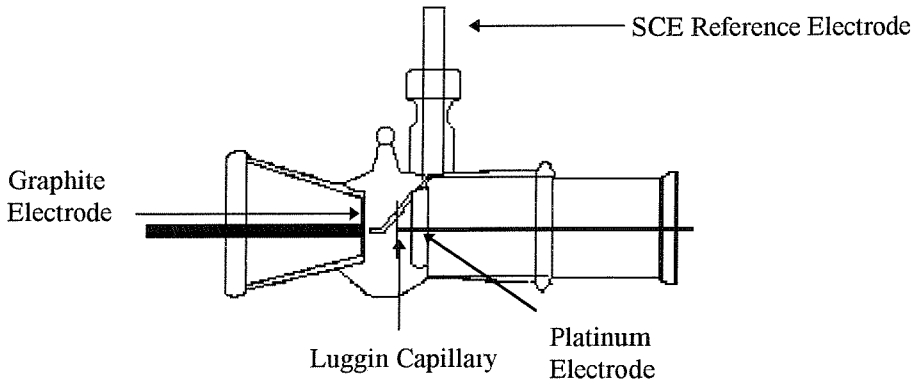


Figure 2.2.3.1 *Undivided two compartment cell used for potentiostatic electrolysis.*

The cell described, *ibid,* was charged with the relevant solution; 25 cm^3 of the electrolysis solution was poured into the Luggin compartment and entered into the

working compartment via the Luggin capillary. The reaction solution was stirred in the working compartment by a stirrer bar, which fitted into a specially made well in the bottom of the cell. The potential applied at the working electrode was determined by considering the voltammogram of the electroactive species in the relevant solvent supporting electrolyte system, measured using the vitreous carbon disc electrode. The potential was always set below the mass transport limited region determined from the voltammogram.

The consumption of the starting material and the formation of product was followed by hplc analysis. The sampling protocol of the reaction mixture was strictly adhered to; 25 μl of the reaction solution was removed with a pipette (Autoclavable BCL 5000 DG), this sample was then diluted with 975 μl of acetonitrile (hplc grade) in a mass spec vial before being loaded on the auto sampler carousel. The sample concentration was ca. 22 mg/ cm^3.

At the end of the electrolysis the reaction mixture was often analysed by electrospray mass spectroscopy; an aliquot was removed from the reaction solution using a capillary, the contents were tapped into the mass spec vial and diluted with acetonitrile. The sample concentration was ca. 0.4 mg/cm^3. The reaction mixture was worked up in accordance with the following procedure; the reaction mixture was reduced in volume under vacuum, the subsequent oil was separated between an aqueous phase and an organic phase, of diethyl ether. The aqueous phase was treated with potassium iodide, 0.75 g dissolved in a minimum amount of water. With a successful reaction there was generally a precipitation of material at this point. The material was isolated by filtration and dried. It was analysed by ^{1}H-NMR, ^{13}C-NMR and DEPT-135.

The diethyl ether phase was reduced down to a dark oil, under vacuum. This was then diluted with dichloromethane. An aliquot of the dichloromethane solution was removed (10 μl) and diluted with additional dichloromethane (990 μl)and analysed by a gas chromatography electron impact mass spectroscopy system (GC-MS). Sample concentration was ca. 0.09 mg/cm^3. This was used to determine the non-ionic organic side products of the reaction.

2.3 Instrumentation

For voltammetry investigations, a Hi-Tek PPRI waveform generator was used to generate the potential profile; this was applied to the cell via a Hi-Tek DT2101 potentiostat. The working electrode was mounted on an EG & G PARC Model 616 rotating disc control unit. The resultant current-potential curves were recorded on a Bryans Instruments x-y chart recorder.

The potential in the potentiostatic electrolysis was applied using a Hi-Tek DT2101 potentiostat. The current was integrated using the digital integrator; this was built by the Electronics Workshop.

To obtain a constant current source for the galvanostatic electrolysis, a Hi-Tek DT2101 potentiostat was modified by connecting the terminals of the working electrode and reference electrode with a resistor (24 W, 2 Ω). The anode was attached to the working electrode terminal whilst the cathode was attached to the secondary electrode terminal. The current was integrated using a digital integrator. The reaction temperature was maintained by having the cell sit within a water jacket through which water circulated. This water was maintained at a temperature of 289 K by a Camlab W14 water bath.

The hplc analysis was carried out using a Hewlett Packard Series 1100 system with a ultra violet detector. The column was a Phenomenex column, (150 mm × 30 mm, 5 μm). Two gradient elution program were used. The first and more commonly used was to ramp the solvent form 100 % water (0.12 % trifluoroacetic acid) to 100 % acetonitrile (0.12 % trifluroacetic acid) over ten minutes, then to hold the eluent at 100 % acetonitrile (0.12 % trifluoroacetic acid) for 15 minutes. The second solvent program was to ramp the solvent from 100 % water (0.12 % trifluoroacetic acid) to 100 % acetonitrile (0.12 % trifluoroacetic acid over 20 minutes then to hold the eluent at 100 % acetonitrile (0.12 % trifluoroacetic acid) for 5 minutes.

The samples for NMR investigation were nearly always dissolved in deuterated methyl sulfoxide and the spectra was recorded on a Bruker 300MHz machine, using tetra-methylsilane (0.03 % v/v) as internal standard.

The positive and negative electrospray mass spectra were recorded using a Hewlett Packard 1050 system

The gas chromatography with a mass spec detector was a two module system. The gas chromatography was carried out using a Thermo Quest CE Instruments, where the column was an Rtx®-5MS, (15 m × 0.25 mm/ D, 0.25 μm). Helium was used as the carrier gas. The detector was a GC 2000 Series Finnigan Trace MS;

2.4 Organic Preparation

All organic preparations were carried out in accordance with the methods taken from the literature.

2.4.1. Preparation of 4,4′-Dimethyldiphenyliodonium cation[5]

To a suspension of potassium iodate (5 g) in toluene (7.5 cm^3), acetic acid (22.5 cm^3) and acetic anhydride (10 cm^3) was added a mixture of sulfuric acid (5 cm^3) and acetic acid (7.5 cm^3). Through out the addition the reaction was maintained below 3°C using an acetone/ice bath. The addition of acid caused the suspension to turn yellow in colour. The reaction was stirred overnight, at ambient temperature, then split into two equal portions.

Portion 1: Isolation as the bisulfate[5].

The inorganic compounds were removed by filtration. To the clear filtrate was added diethyl ether (14 cm^3). This caused an immediate clouding. The solution was cooled in an acetone/ice bath and a white powder precipitated. The precipitate was collected and by filtration (1.7 g) and dried on the paper. The ^{1}H-NMR spectrum, of the isolated material, was recorded in methyl sulfoxide-d_6, see Figure 2.4.1.1.

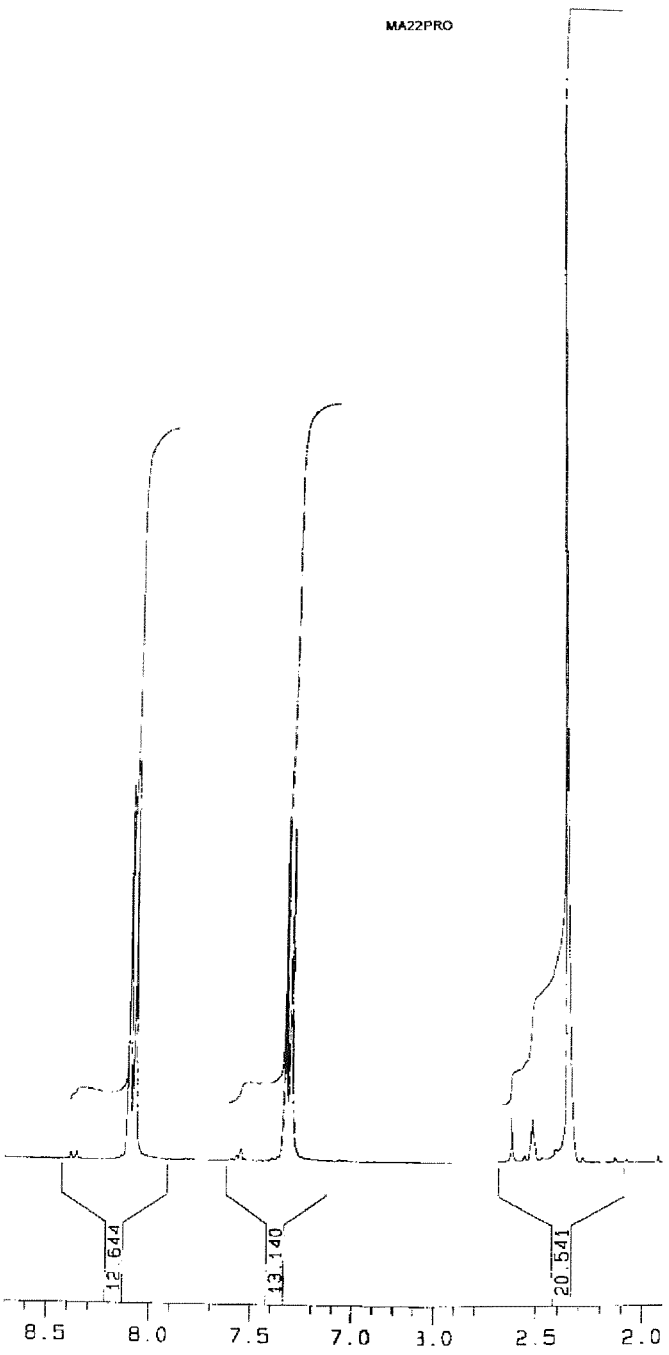


Figure 2.4.1.1. *^{1}H-NMR spectrum of the material isolated from the reaction of potassium iodate and toluene, using the method of Beringer[5] and precipitated by the addition of diethyl ether.*

Consideration of the ^{1}H-NMR showed that were three peaks, at 8.1, 7.3 and 2.3 ppm. The aromatic protons, 8.1 and 7.3 ppm, showed a doublet splitting pattern which was

expected for an aromatic ring that was *para* substituted. In addition there was a singlet at 2.3 ppm, which was assigned to a methyl group. The three peaks at; 8.1, 7.3 and 2.3 ppm, had integration values of 2:2:3 receptively. This was as expected for the 4,4-dimethyldiphenyliodonium cation. In addition the ^{13}C-NMR spectrum, of the isolated material, was recorded, see Figure 2.4.1.2.

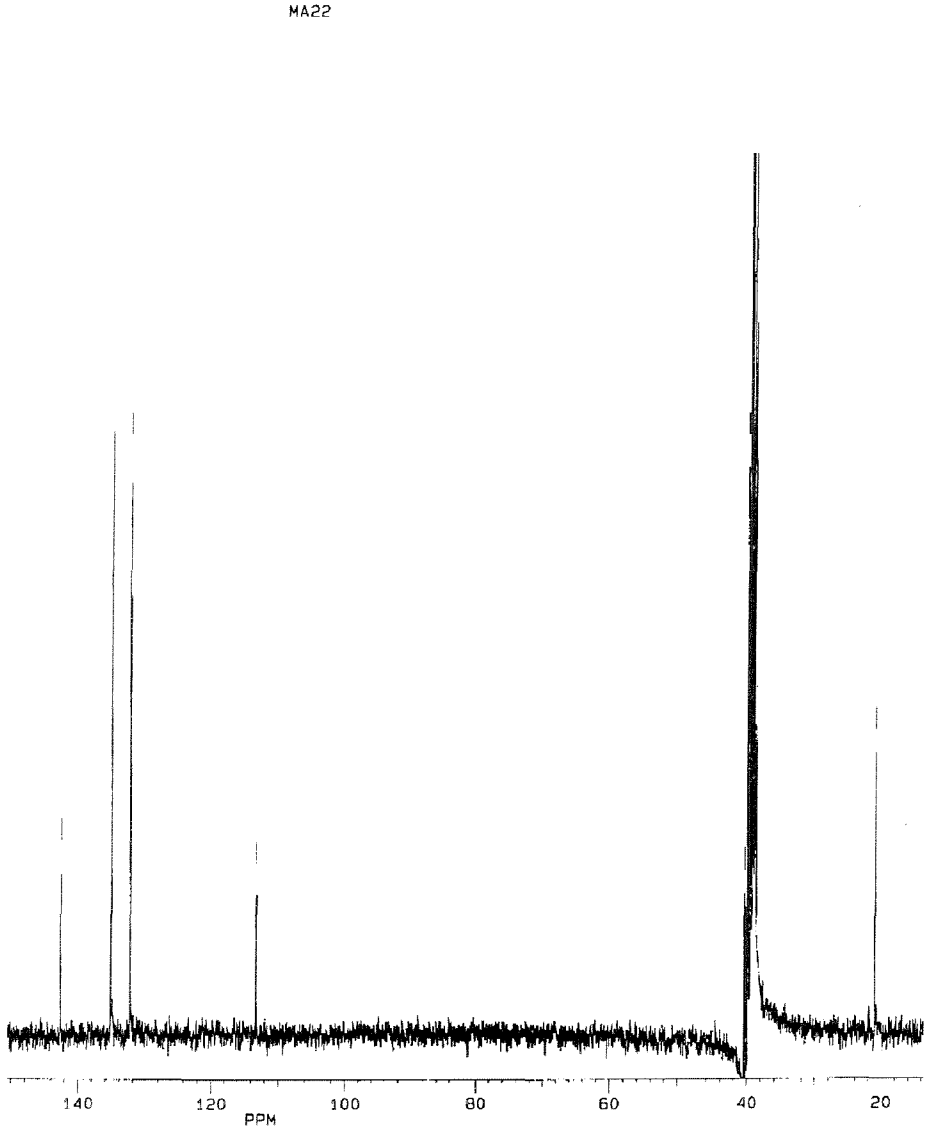
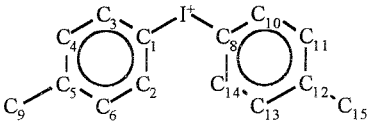
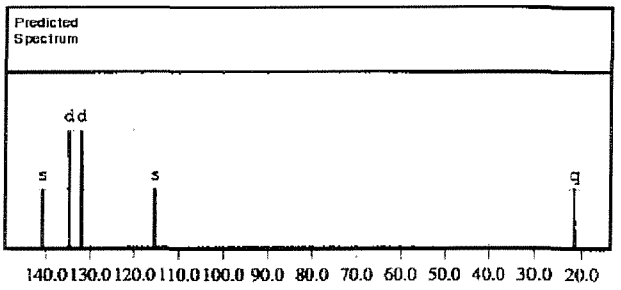


Figure 2.4.1.2. *^{13}C-NMR spectrum of the material isolated from the reaction of potassium iodate and toluene, using the method of Beringer[5] and precipitated by the addition of diethyl ether..*

In the ^{13}C-NMR spectrum there were four signals in the aromatic region[35]. The two very much more intense signals, 135.1 and 132.4 ppm were interpreted as being methine carbon signals and the weaker signals, 142.5 and 113.2 ppm, due to quaternary carbon atoms. There was one signal in the alkyl region[35], at 20.9 ppm. The presence of four aromatic signals would suggest a *para* substituted aromatic ring. The SpecInfo program[47] was used to calculate the chemical shift values for the 4,4'-dimethyldiphenyliodonium cation, see Figure 2.4.3 for the report.





atom	calculated chemical shift value (ppm)	multiplicity
1	115.40	s
2	134.80	d
3	134.80	d
4	131.96	d
5	140.71	s
6	131.96	d
8	115.40	s
9	21.75	q
10	134.80	d
11	131.96	d
12	140.71	s
13	131.96	d
14	134.80	d
15	21.75	q

Figure 2.4.1.3 *^{13}C-NMR spectrum of 4,4'-dimethyldiphenyliodonim cation calculated using the SpecInfo program[47].*

The calculated chemical shift value for the ^{13}C-NMR spectrum of 4,4'-diemthyldiphenyliodonium cation were in excellent agreement with the spectrum of the isolated material. To complete the characterisation of the isolated material a DEPT-135 spectrum was recorded, three signals were seen, two in the aromatic region, at 135.1 and 132.4 ppm and one in the alkyl region at 20.9 ppm.
Consideration of the DEPT-135, showed that the intense aromatic signals at 135.1 and 132.4 ppm were methine carbons, because of their positive phase[35]. The alkyl signal at 20.9 also has a positive phase, and was due either to a methine carbon or a methyl carbon. The fact that the starting material, toluene, had a methyl group meant it was it was sensible to assign the signal, at 20.9 ppm, to a methyl group. Comparison of the DEPT-135 spectrum to the ^{13}C-NMR spectrum of the isolated material, showed that two aromatic signals seen in the ^{13}C-NMR spectrum, at 142.5 and 132.4, were missing from the corresponding DEPT-135 spectrum. This was interpreted as these signals being due to quaternary carbon atoms[35].

A few crystals of the isolated sample were dissolved in acetonitrile and the sample was submitted for positive ion electrospray mass spectroscopy. A single ion , 309 Da, was seen. This was what was expected for the dimethyldiphenyliodonium cation.
In conclusion the electrospray and ^{1}H-NMR, ^{13}C-NMR, DEPT-135 spectra showed that we were successful in isolating 4,4'-dimethyldiphenyliodonium bisulfate. The NMR spectra provided the reference against which the spectra of material synthesised electrochemically could be compared. A yield of 35 % for this reaction was calculated; based on the moles of isolated material, 4,4'-dimethyldiphenyliodonium bisulfate divided by the number of the moles of potassium iodate in the reaction mixture at the beginning of the reaction

Portion 2. Isolation as the Chloride[45]
The yellow suspension was poured onto ice (10 g), which caused the inorganic compounds to dissolve. The solution was extracted with diethyl ether (2×10 cm^3). The aqueous phase was treated with activated carbon (0.18 g). On removal of the carbon by

filtration, the filtrate was treated with ammonium chloride (2.5 g in 7.5 cm^3 of water) and cooled by standing the vessel in an acetone/ice bath. A precipitate was collected (1.8 g) by filtration. The filtrate was cooled (acetone/ice bath), then treated with ammonium chloride (2 g dissolved in a minimum amount of water). A further crop material was collected (1.3 g) by filtration. The filtrate was treated with ammonia (0.88 g/cm^3, $5cm^3$) and the subsequent precipitate was collected. The precipitates from each stage were combined. The crude material was re-crystallised from methanol, and white crystals (2.9 g) were collected. The ^{1}H-NMR and ^{13}C-NMR and DEPT-135 spectra were recorded and were compared to the spectra of the material identified as 4,4'-dimethyldiphenyliodonium bisulfate A yield of 70 % was recorded.

The difference in yield, of isolated dimethyldiphenyliodnium cation, between the material isolated as the bisulfate, ca. 35 %, and the material isolated as the chloride, ca. 70 %, was in retrospect due to the fact that the iodonium halides were generally less soluble in water than the iodonium bisulfate.

2.4.2 Preparation of 4,4'-Dimethyldiphenyliodonium Iodide

The preparation of 4,4'-dimethyldiphenyliodonium iodide was based on the work of Beringer[5, 45] *et al.* To a vigorously stirred suspension of potassium iodate (20 g) in toluene (30 cm^3), acetic acid (90 cm^3) and acetic anhydride (40 cm^3), was added a solution of sulfuric acid (20 cm^3) and acetic acid (30 cm^3). Throughout the addition the reaction temperature was maintained below 3 °C in an acetone/ice bath. The reaction was stirred for 26 hours at room temperature.

The inorganic compounds were removed by filtration and washed with acetic acid. The washings and reaction mixture were combined (210 cm^3). The solution was diluted with water (210 cm^3) and extracted with diethyl ether (3 × 100 cm^3). The aqueous phase was treated with a few milligrams of sodium sulfite and them with potassium iodide (9 g dissolved in a minimum amount of water). A white precipitate was seen to form immediately and was collected by filtration (36 g). Some of the material was dissolved in methyl sulfoxide-d_6 and the H^1-NMR spectrum was recorded., see Figure 2.4.2.1.

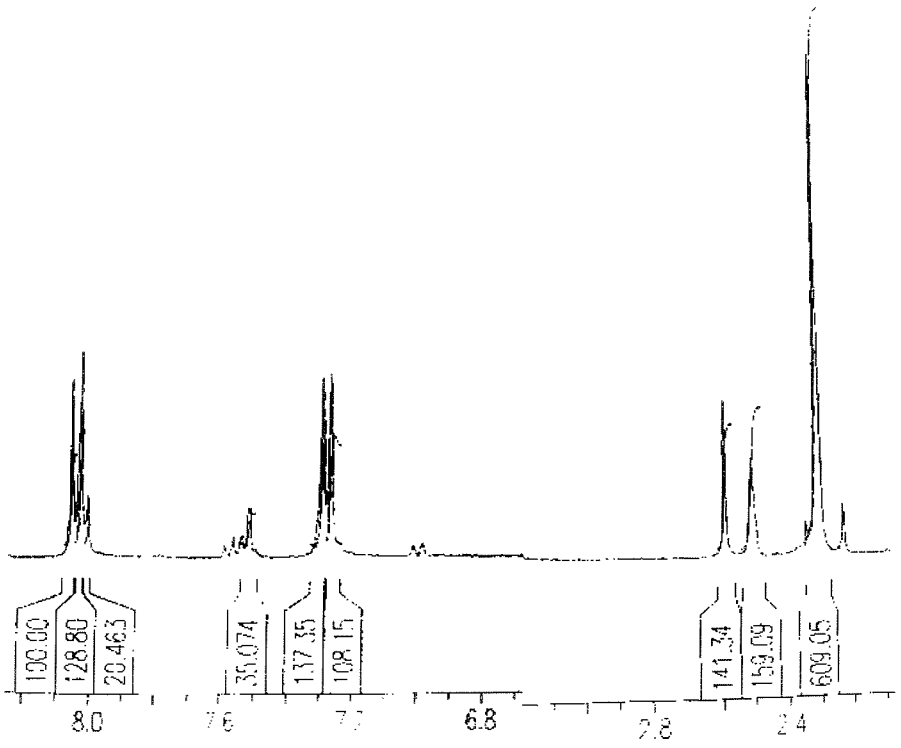


Figure 2.4.2.1. *^{1}H-NMR spectrum of the material isolated from the reaction of potassium iodate and toluene, using the method of Beringer[5] and precipitated by the addition of potassium iodide.*

The ^{1}H-NMR spectrum was compared to that of 4,4'-dmethyldiphenyliodonium bisulfate, see Section 4.2.1. The two spectra were very similar, it was noted that both spectra contained additional peaks which were not due to the 4,4'-dimethyldiphenyliodonium cation. The peaks were assigned to a small amount of the 2,4'-dimethyldiphenyliodonium cation also isolated, see Figure 4.5.1.1.1. The dual production of the minor product 2,4'-dimethyldiphenyliodonium cation and the major product 4,4'-dimethyldiphenylidonium cation in the organic synthesis was not recognised by the original workers[5]. Similarly the ^{1}H-NMR spectra for the 4,4'-dimethyldiphenyliodonium bisulfate and the 4,4'-dimethyldiphenyliodonium chloride, prepared by the method of Beringer, similarly showed peaks whose magnitude and

position was consistent with the 2,4'-dimethyldiphenyliodonium bisulfate and chloride respectively being present in the isolated material.

In addition the ^{13}C-NMR spectrum was recorded, see Figure 2.4.2.2.

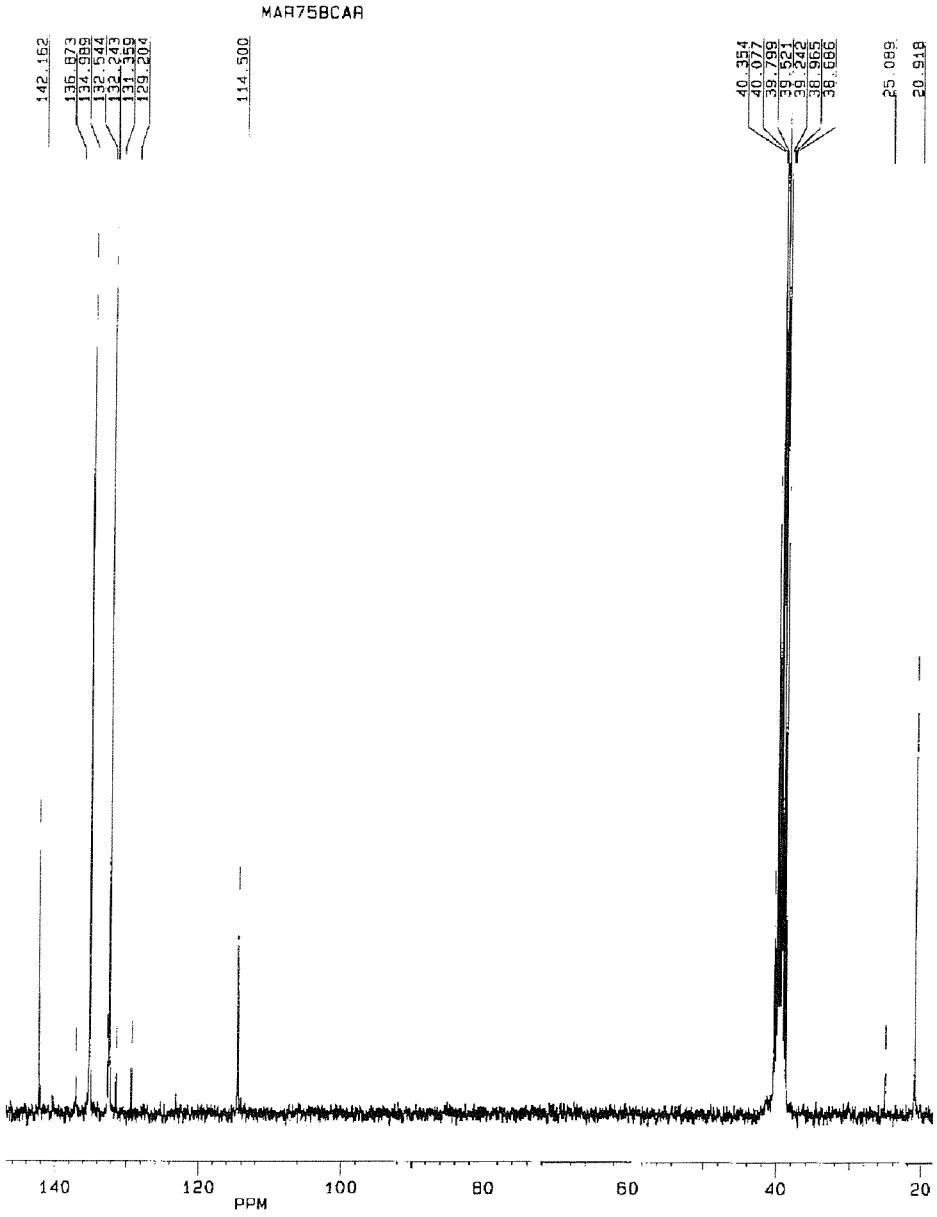


Figure 2.4.2.2. *^{13}C-NMR spectrum of the material isolated from the reaction of potassium iodate and toluene, using the method of Beringer[5] and precipitated by the addition of potassium iodide.*

The ^{13}C-NMR spectrum was compared to that of 4,4'-dimethyldiphenyliodonium bisulfate. There were additional minor peaks present, which were assigned to the 2,4'-dimethyldiphenyliodonium cation.

The DEPT-135 spectrum of the isolated material was also recorded, see Figure 2.4.2.3, and was again similar to that of 4,4'-dimethyldiphenyliodonium bisulfate

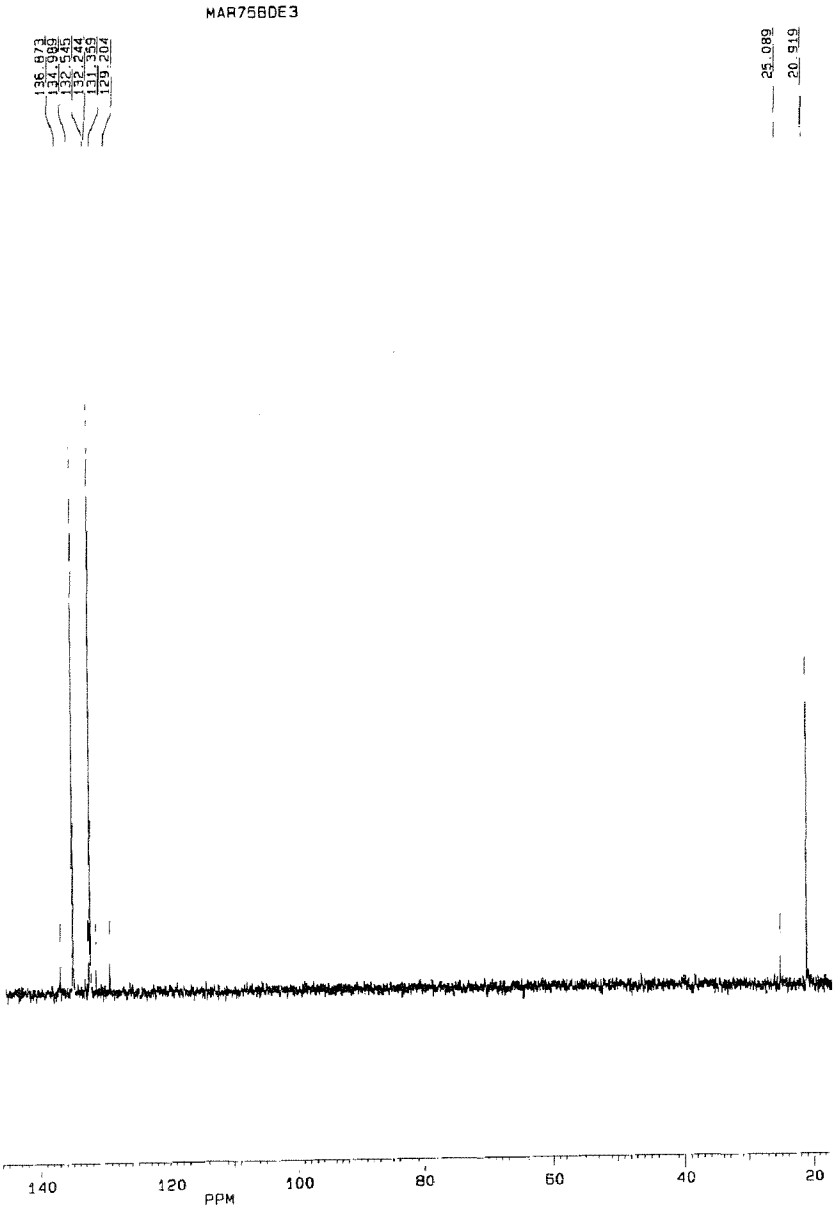


Figure 2.4.2.3. *DEPT-135 spectrum of the material isolated from the reaction of potassium iodate and toluene, using the method of Beringer[5] and precipitated by the addition of potassium iodide.*

As before, a sample of the precipitate was dissolved in acetonitrile was submitted for positive ion electrospray mass spectroscopy, a single ion of 309 Da was seen. This ion is what was expected for the dimethyldiphenyliodonium cation. A yield of 90 % was calculated.

2.4.3 Preparation of 4-Methoxydiphenyliodonium Triflate[9]

To a suspension of [(diacetoxy)iodo]benzene (0.66 g) in dichloromethane (10 cm^3) at 0 °C was added trifluoromethanesulfonic acid (0.4 cm^3). The addition of trifluoromethanesulfonic acid turned the solution yellow in colour. The reaction was stirred for one hour at room temperature. After which, anisole (0.24 cm^3) was added. The reaction was stirred for an additional one hour, after which diethyl ether was added to the reaction mixture. This was left standing overnight. Grey crystals separated from the brown oil and were collected by filtration. These crystals were separated on a filter paper and re-crystallised from petroleum ether (60-80), to give a white powder (0.78 g). The ^{1}H-NMR was recorded, see Figure 2.4.3.1

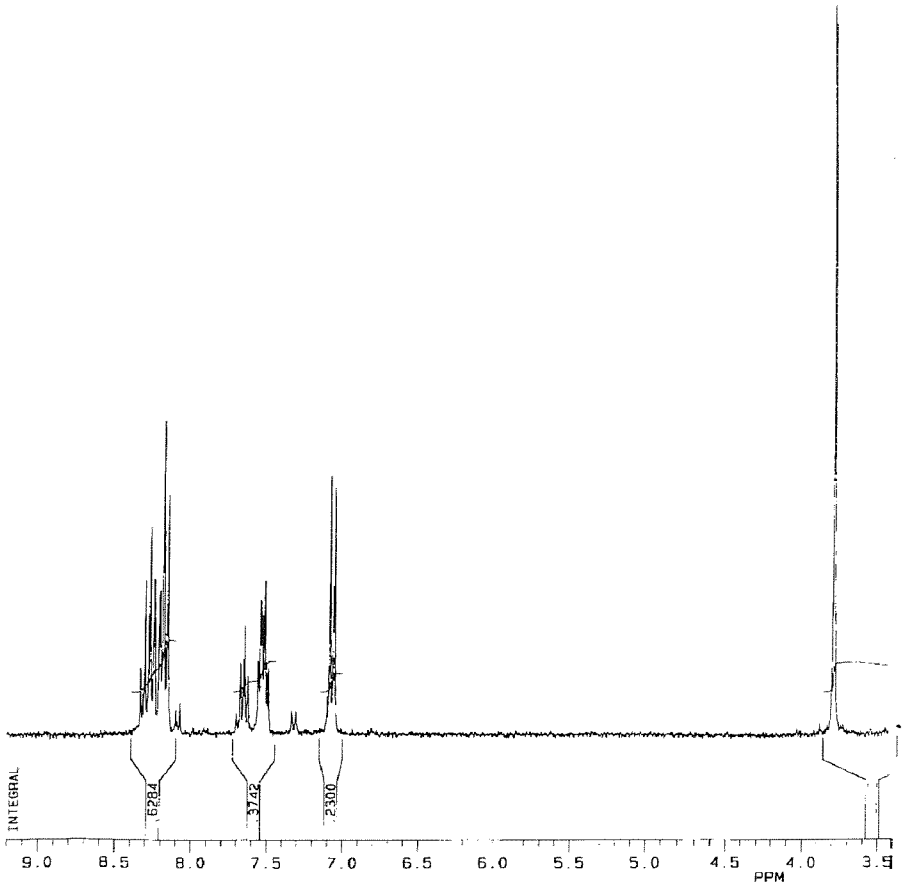


Figure 2.4.3.1. *^{1}H-NMR spectrum of the material isolated from the reaction of [(diacetoxy)iodo)]benzene and anisole, using the method of Kitamurar[9] and precipitated by the addition of diethyl ether.*

The ^{1}H-NMR spectrum was more complex than that recorded for the symmetric 4,4'-dimethyldiphenyliodonium cation. There was a singlet peak a 3.8 ppm which can be assigned to a methoxy proton, also a doublet can be seen at 7.1 ppm and another doublet is mixed in with the multiplet at ca. 8.2. This spectrum was compared to the spectrum of 4,4'-dimethoxydiphenyliodonium iodide, see Figure 4.6.2. The spectrum of the symmetric 4,4'-dimethoxyldiphenyliodonium iodide contained a doublet peak at 8.1 and 7.1 ppm and a singlet at 3.8 ppm. We can therefore assign the protons on the *para* substituted ring in 4-methoxyphenylphenyl iodonium triflate by comparison to the symmetric 4,4'-dimethoxydiphenyliodonium iodide. Note also that the ratio of the integration of the peaks at 7.1 and 3.8 ppm for the 4-methoxyphenylphenyliodnium cation as expected was ca. 3:2.

A dilute solution of the isolated material in acetonitrile was prepared and analysed by positive ion mass spectroscopy. A single ion at 311 Da was seen, which is what was expected for the 4-methoxyphenylphenyliodonium cation.

2.4.4 Preparation of 4-Methyldiphenyliodonium Triflate[9]

To a suspension of [(diacetoxy)iodo]benzene (0.66 g) in dichloromethane (10 cm^3) at 0°C was added triflic acid (0.4 cm^3). The addition of triflic acid turned the solution yellow in colour. The reaction was stirred for one hour, at room temperature. After which toluene (0.2 cm^3) was added drop wise. The solution was stirred for a further hour. Diethyl ether was added to the reaction mixture and the solution was left to stand overnight. White crystals (0.71 g) separated from the brown oil and were collected by filtration. The H^1-NMR spectrum, of the isolated material dissolved in methyl sulfoxide-d_6, was recorded, see Figure 2.4.4.1.

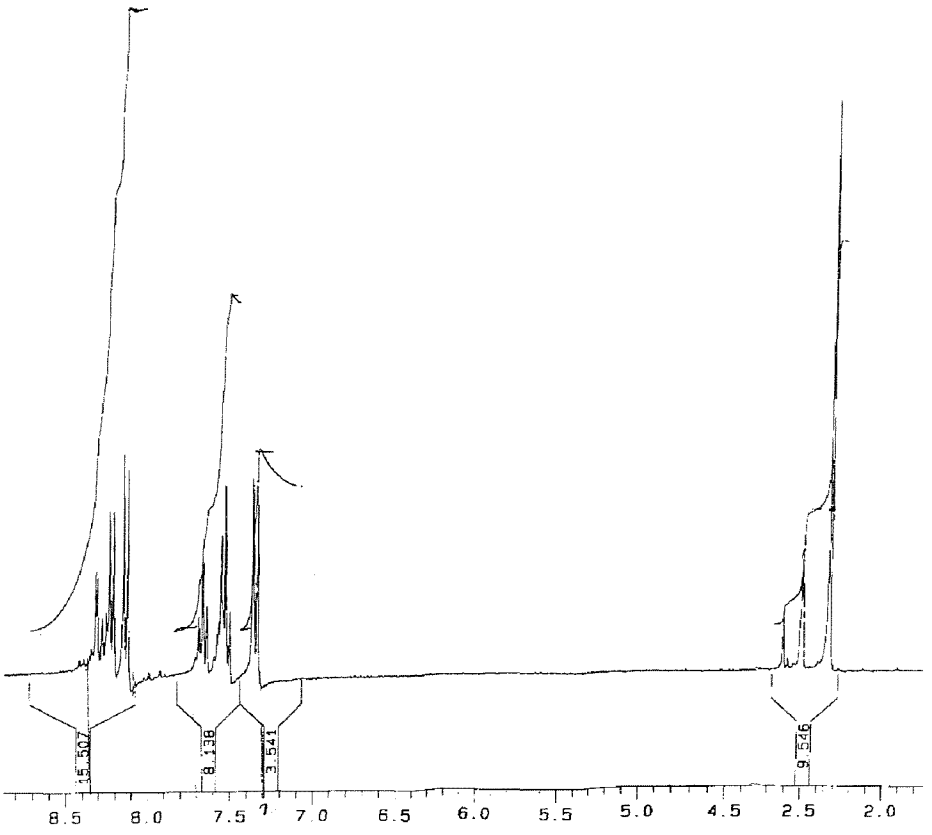


Figure 2.4.4.1. *^{1}H-NMR spectrum of the material isolated from the reaction of [(diacetoxy)iodo)]benzene and toluene, using the method of Kitamurar[9] and precipitated by the addition of diethyl ether.*

The ^{1}H-NMR was compared to the spectrum of 4-methoxyphenylphenyliodonium triflate, see Figure 2.4.3.1., the peak splitting was very similar, but there was a difference in the chemical shift values, due to the replacement of the methoxy group by a methyl group. The methyl peak had a chemical shift value of 2.3 ppm, where as the methoxy group had a chemical shift value of 3.8 ppm . The ^{1}H-NMR spectrum of 4,4'-dimethyldiphenyliodonium bisulfate had the same value for its methyl protons as the spectrum of our isolated material. A doublet was seen at 7.3 ppm, which again was seen in the spectrum of 4,4'-dimethyldiphenyliodonium bisulfate.

A small sample of the material was dissolved in acetonitrile and submitted for positive ion electrospray mass spectroscopy. A single ion of 295 Da was seen. The methylphenylphenyliodonium cation was expected to have a molecular ion of 295 Da The yield of the reaction was calculated to be 80 %.

2.4.5 Preparation of 2-Iodophenylphenylmethane[58]

2-Benzylaniline (5 g) was dissolved in a solution of water (11.6 cm^3) and hydrochloric acid (11.6 cm^3). The solution was cooled to below 5 °C, using an acetone/ ice bath. A solution of sodium nitrite (3.34 g) in water (16.7 cm^3) was added slowly, maintaining the temperature below 5 °C. After all the sodium nitrite was added, the solution was allowed to stir at room temperature for one hour. Then a solution of potassium iodide was slowly added to the reaction mixture (7.7 g dissolved in 8.35 cm^3 of water). The addition of potassium iodide caused a tar to be formed in the reaction mixture. The solution was left stirring for a further hour. Subsequently the reaction mixture was separated between a 3 M aqueous solution of sodium hydroxide and an organic phase of diethyl ether. The diethyl ether phase was separated and mixed with silica. The solvent was then removed *in vacuo* and the remaining silica was loaded on to a column of silica. The organic compound was eluted with hexane. A clear oil was obtained which was analysed by ^{1}H-NMR spectroscopy, see Figure 2.4.5.1.

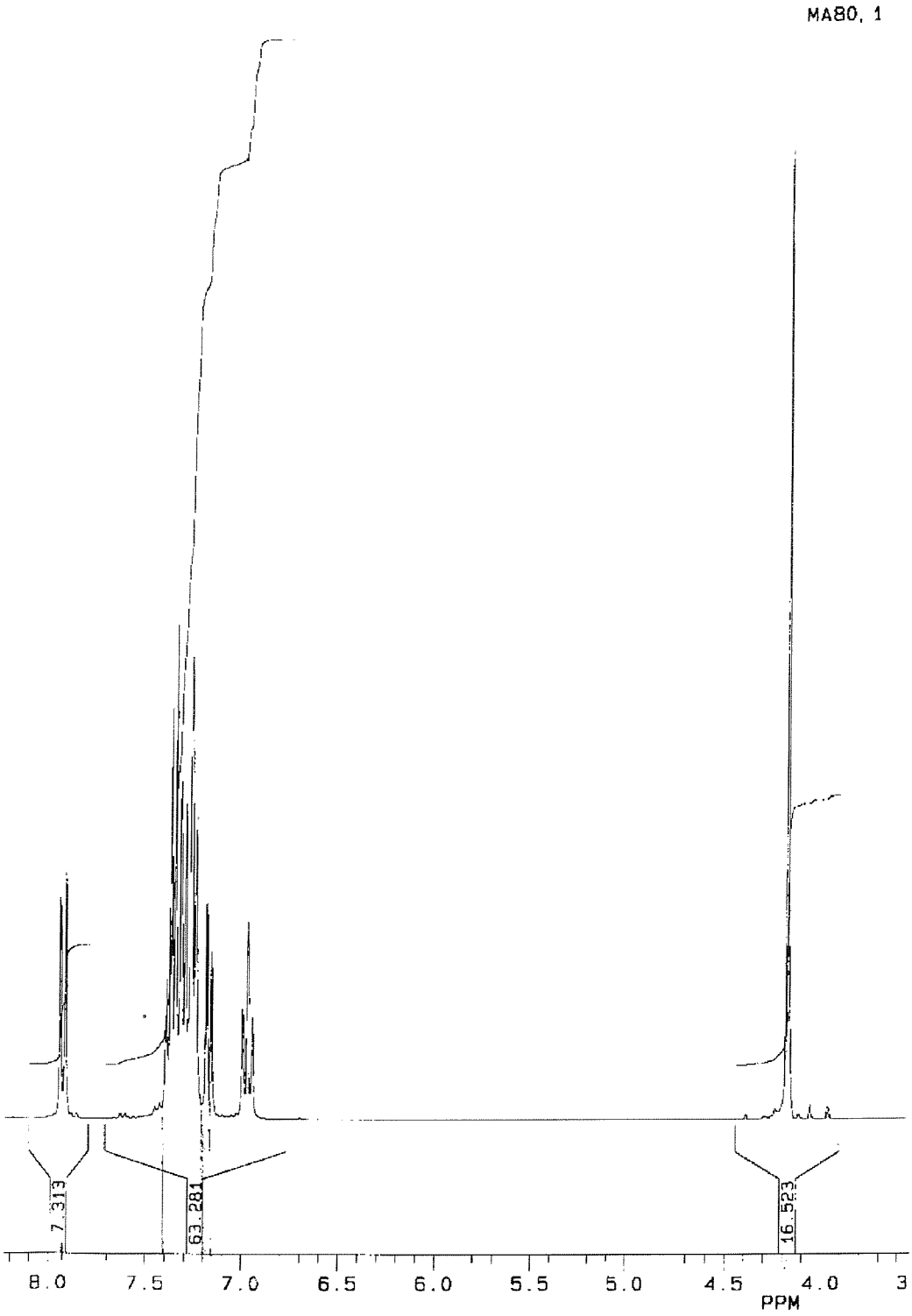
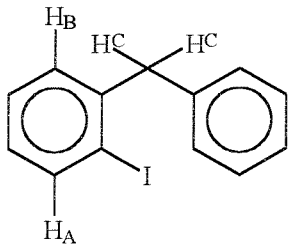


Figure 2.4.5.1 *^{1}H-NMR spectrum of the material isolated after the diazotisation of 2-benzyl aniline and its subsequent reaction with potassium iodide.*

There were five signals in the ^{1}H-NMR spectrum of the isolated material; a doublet at 7.92 ppm, a multiplet between 7.40 and 7.20 ppm, a doublet of 7.15 ppm and a singlet at 4.15 ppm. The signals were in the ration 1:6:1:1. A ^{1}H-NMR spectrum of the starting material was similarly recorded and compared to that in Figure 2.5.1. It was apparent that the splitting pattern was similar between the starting material and the isolated material, but there had been a general down field shift in the chemical shift values. The doublet and singlet signals were assigned in accordance with Table 2.4.5.1.



δ ppm	Proton
7.92	H_A
7.15	H_B
4.20	H_C

Table 2.4.5.1

There are seven protons left which can be accounted for; the triplet at 6.98 ppm corresponds to one proton whilst the multiplet between 7.20 and 7.40 ppm contains the remaining six protons.

CHAPTER 3

Voltammetric Studies

3.1 Introduction

This thesis reports the electrosynthesis of diaryliodonium salts by the oxidation of aryl iodides in a media relatively little used for electrochemistry. Hence, this chapter reports voltammetric studies designed to provide background information about the electrochemistry of the media and the anodic oxidation of both aryl iodides and arenes. Solutions and electrode preparation were as described in Section 2.2.1. The cell used to record the voltammograms at a rotating disc electrode, RDE, was that described in Section 2.2.1. In all experiments the voltage was measured with respect to an aqueous saturated calomel electrode (SCE).

3.2 Voltammetry of Solvent Media

3.2.1 Vitreous Carbon RDE

The voltammogram of acetic acid / 5 % sulfuric acid/ 2 % acetic anhydride was recorded, at a series of rotation rates. The potential was scanned between -0.4 and 2.4 V vs. SCE at a rate of 20 mV/s. The initial potential at the vitreous carbon RDE was 0.4 V vs. SCE. Figure 3.2.1.1 shows the voltammogram recorded with a rotation rate of 900 rpm.

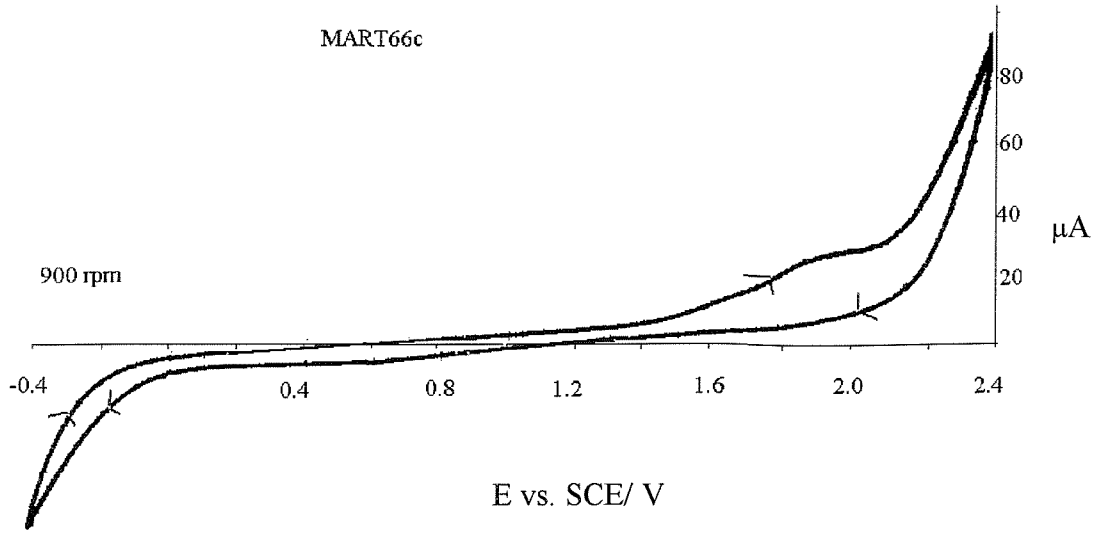


Figure 3.2.1.1 *Voltammogram of AcOH/ 5 % H_2SO_4/ 2 % Ac_2O recorded at a vitreous carbon RDE (diameter 3 mm), at a scan rate of 20 mV/ s.*

Oxidation was seen to be initiated at ca. 0.8 V and to increase more rapidly after 1.4 V. The current was seen to reach a plateau at ca. 2.0 V. The current increased again beyond 2.05 V vs. SCE. There was seen only a slight dependence of the limiting current on rotation rate. There was a reduction wave on the back scan between 1.0 V and 0.2 V vs. SCE. The current was seen to then increase rapidly in magnitude negative to 0.0 V vs. SCE, due to hydrogen evolution.

Into the working electrode compartment was then added 12 cm^3 volume of acetic anhydride. This raised the acetic anhydride content from 2 % to ca. 25 % in the working electrode compartment. The voltammogram of the solution was then recorded without dismantling the cell and re-polishing the electrode. The potential scanning regime was the same as that described for the acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride solution, see Figure 3.2.1.2..

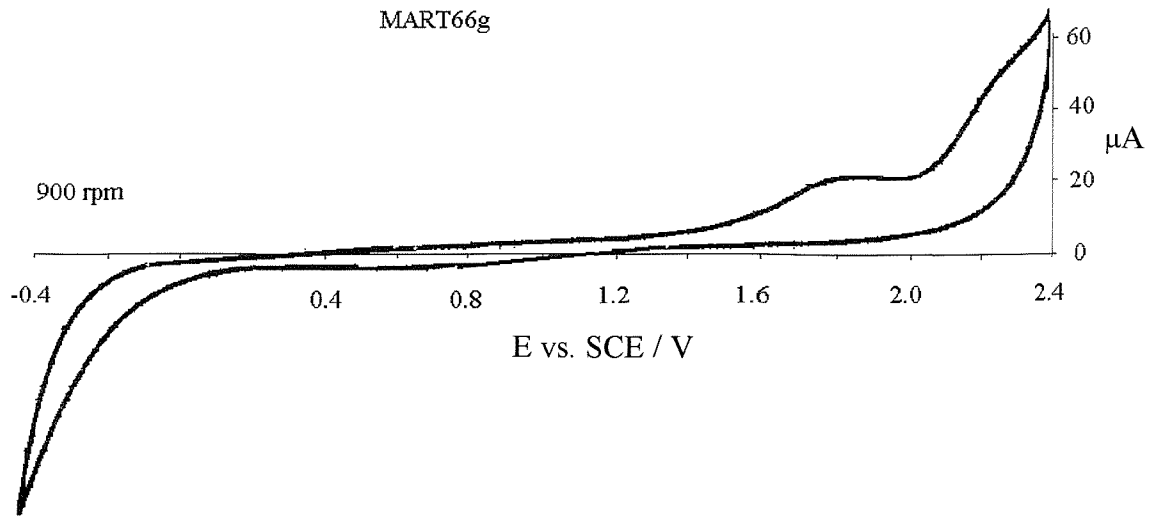


Figure 3.2.1.2 *Voltammogram of AcOH/ 5 % H_2SO_4/ ca.25 % Ac_2O recorded at a vitreous carbon RDE (diameter 3 mm), at a scan rate of 20 mV/ s.*

The response was essentially similar. It was seen that there was a significant current associated with the acetic acid/ 5 % sulfuric acid/ 2 or 25 % acetic anhydride above a potential of 1.6 V vs. SCE. It was therefore important to recognise that the voltammetry of aryl iodides and arenes would be distorted if their waves occurred in this region.

3.2.2 Graphite RDE

The voltammogram of acetic acid / 5 % sulfuric acid/ 2 % acetic anhydride was recorded, at a graphite rotating disc electrode (RDE), between 0 and 2.2 V vs. SCE at a scan rate of 20 mV/ s, see Figure 3.2.2.1.

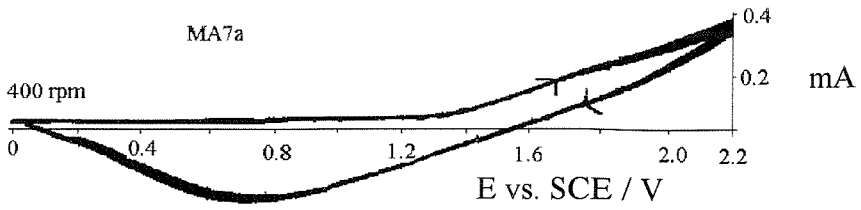


Figure 3.2.2.1 *Voltammogram of AcOH/ 5 % H_2SO_4/ 2 % Ac_2O recorded at a graphite carbon RDE (diameter 5 mm), at a scan rate of 20 mV/ s. Rotation rate 400 rpm*

In the voltammogram, *ibid*, there was an oxidation wave which started at 1.3 V vs. SCE on the forward scan and a broad reduction peak on the back scan which started at ca. 1.6 V vs. SCE. The total anodic and cathodic charges are similar indicating a surface oxidation or intercalation process. The currents measured during the recording of the voltammogram was an order of magnitude greater than those measured at a vitreous carbon electrode, even though the graphite discs geometric area was only ca. 3 times the area of the vitreous disc. The difference in current densities probably arises from differences in surface area or bulk structure. The features on the voltammogram appeared drawn out and this may have been due to the increased IR drop associated with the increase in cell current. The fact that the graphite disc had redox behaviour complicates the interpretation of the voltammetry of the aryl iodides and arenes. We also have to consider that possibility of whether the carbon felt was similarly oxidised in the electrolysis cell.

The effect of 4-iodotoluene had on the voltammogram of acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride recorded at the graphite rotating disc electrode was investigated; into the working electrode compartment was added increasing amounts of 4-iodotoluene and the voltammogram was recorded each time. Figure 3.2.2.2 shows the voltammogram recorded at a graphite electrode in the presence of a 0.4 M concentration of 4-iodotoluene.

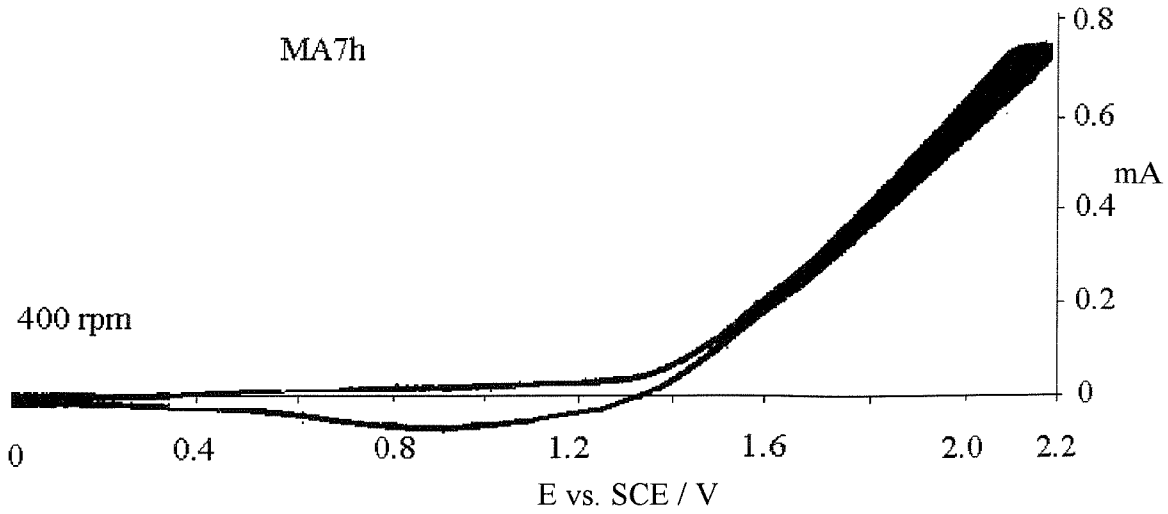


Figure 3.2.2.2 *Voltammogram of a 0.4 M concentration of 4-iodotoluene in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O recorded at a graphite RDE (diameter 5 mm), at a scan rate of 20 mV/ s. Rotation rate 400 rpm*

It was apparent from the voltammogram, *ibid*, that the addition of 4-iodotoluene caused an increase in the anodic current and a decrease in the cathodic current. Table 3.2.2.1 is a summary of the results from a series of voltammograms where the concentration of 4-iodotoluene in the working electrode compartment was increased.

Concentration of 4-iodotoluene (M)	**oxidation charge (mC) Q_{ch}**	**reduction charge (mC) Q_d**	**Current Efficiency α**
0	16.0	16.0	1
0.002	16.0	16.0	1
0.005	22.5	6.0	0.38
0.08	27.0	3.0	0.11
0.1	31.5	2.8	0.09
0.2	40.0	1.2	0.03
0.4	40.0	0.4	0.01

Table 3.2.2.1.

It was apparent that the oxidation charge increased, whilst the reduction charge decreased with the increasing concentration of 4-iodotoluene. This effected the 'charge recovery efficiency', which was defined according to the equation in Figure 3.2.2.3.

$$\text{Charge Recovery Efficiency} = \frac{\text{Reduction charge } Q_d}{\text{Oxidation charge } Q_{ch}}$$

Figure 3.2.2.3 *Charge Recovery Efficiency was the ratio of the charge under the oxidation wave relative to the charge under the reduction peak.*

Into the working compartment of the electroanalytical cell containing acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride was added a 12 cm^3 volume of acetic anhydride. This effectively raised the acetic anhydride content of the solvent to ca. 25 %. The voltammogram of the solution was then recorded at the graphite electrode under identical conditions to those described, *ibid.* The voltammogram is shown in Figure 3.2.2.4.

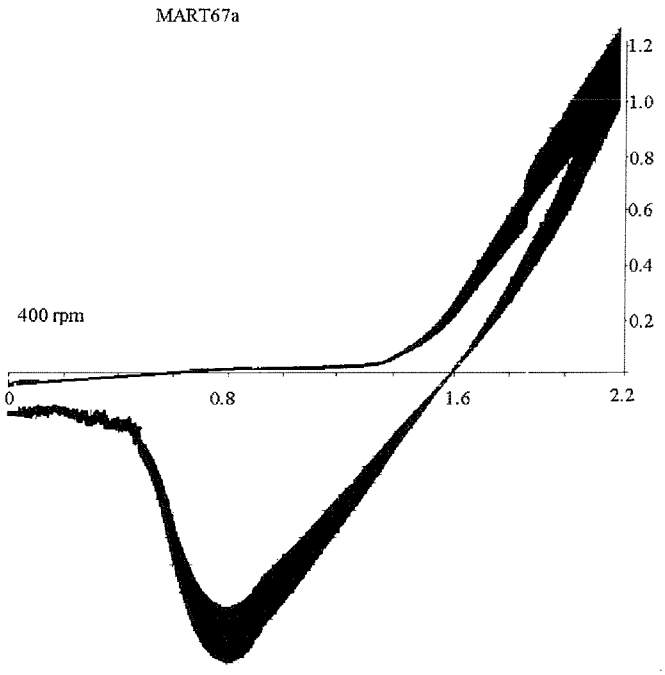
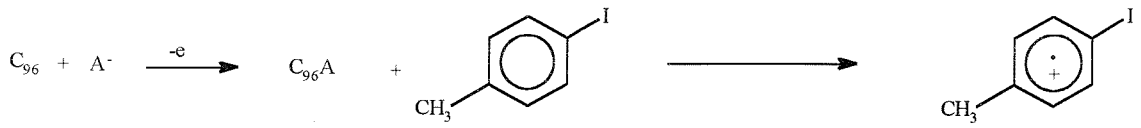


Figure 3.2.2.4 *Voltammogram of AcOH/ 5 % H_2SO_4/ ca. 25 % Ac_2O recorded at a graphite RDE (diameter 5 mm), at a scan rate of 20 mV/ s.*

Increasing the acetic anhydride content of the cell lead to an increase in both the anodic wave and the cathodic peak.

It is well known that graphite can be oxidised by chemical and electrochemical means to form macrocations, and that the positive charge can be compensated by the insertion of certain anions between the planes of the graphite lattice[48]. Beck *et al* recorded the cyclic voltammetric curves of 4 M sulfuric acid at a graphite composite electrode, CPP (80 % graphite, 20 % polypropylene)[48]. There were seen to be three peaks on the positive scan with corresponding peaks on the reverse scan. These local maxima were assigned to the surface of the graphite having disscrete configurations ($C_{96}A$, $C_{72}A$, etc.) at specific potentials, so that the surface became saturated and the current only rose again when the potential has moved sufficiently positive enough to allow the graphite to adopt the next oxidation state.

A mechanism which accounts for the increase in anodic current on the forward scan and the near elimination on the cathodic current on the back scan, seen in Scheme 3.2.2.1, is where the charge at the anode is irreversibly transferred to the 4-iodotoluene so reducing the graphite and the graphite is immediately re-oxidised.



Scheme 3.2.2.1.

3.3 Voltammetry of Ferrocene

3.3.1 Vitreous Carbon RDE

Ferrocene was selected as the model system since it is stable in most media and generally undergoes a reversible one electron oxidation to the ferrocinium cation. Figure 3.3.1.1 shows the voltammograms recorded at a scan rate of 20 mV s^{-1} for a freshly prepared solution of 1 mM ferrocene in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride at a vitreous carbon RDE, diameter 3 mm.

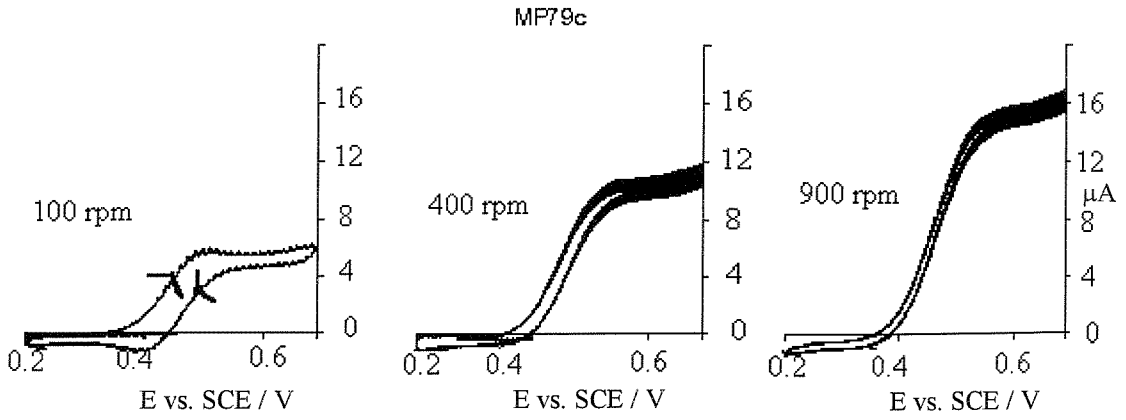


Figure 3.3.1.1 *Voltammogram of freshly prepared solution of ferrocene (1mM) concentration in AcOH/ 5% H_2SO_4/ 2% Ac_2O recorded at a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s.*

The voltammogram of ferrocene exhibited well formed oxidation wave with a half wave potential of 0.45 V vs. SCE. There was little hysteresis between the forward and the back scan, showing that the surface was not passivated. The limiting current of the oxidation wave was seen to occur positive of 0.48 V vs. SCE. According to Figure 3.3.1.2a the limiting current, I_L was proportional to the square root of rotation rate, $\omega^{1/2}$. This result was in accordance with the Levich equation, for the limiting current for an electrode reaction under mass transport control[42]. The wave in the voltammogram of ferrocene, recorded at a rotation rate of 400 rpm, was analysed using the Tomes analysis, see Figure 3.3.1.2b. The gradient of the line in Figure 3.3.1.2b was ca. 68 mV. The gradient was within experimental error of 60 mV, and so the wave can be interpreted as being the result of a reversible one electron transfer[43].

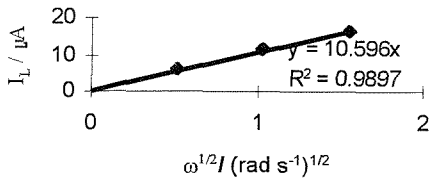


Figure 3.3.1.2a *Levich analysis of I_L vs. $\omega^{1/2}$ for a freshly prepared solution of ferrocene at 1mM concentration in AcOH/5 % H_2SO_4/2 % Ac_2O using a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s. Data was taken from the voltammograms shown in Figure 3.3.1.1*

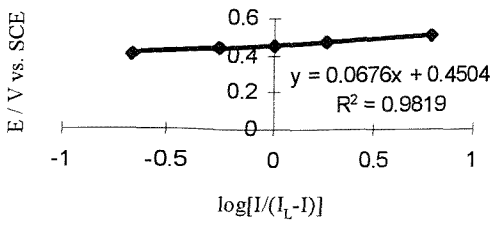


Figure 3.3.1.2b *Tomes analysis of the E vs. the log[(I_L- I)/I] for a freshly prepared solution of ferrocene at 1mM concentration in AcOH/5 % H_2SO_4/2 % Ac_2O using a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s. Data was taken from the voltammogram recorded at 400 rpm shown in Figure 3.3.1.1*

3.3.2 Carbon Fibre Micro Disc Electrode

Figure 3.3.2.1 shows the voltammogram recorded at a scan rate of 20 mV s^{-1} for a freshly prepared solution of 20.4 mM ferrocene in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride at a carbon fibre disc electrode, diameter 7 μm.

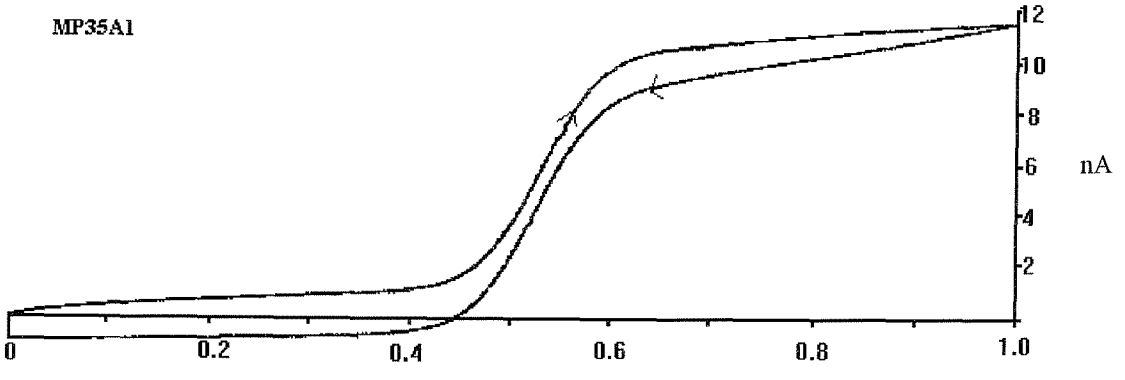


Figure 3.3.2.1 *Voltammogram of freshly prepared solution of ferrocene (1mM) concentration in AcOH/ 5% H_2SO_4/ 2% Ac_2O recorded at a carbon fibre disc electrode (diameter 7 μm), platinum counter electrode, scan rate 0.02V/s.*

The wave in the voltammogram of ferrocene, was analysed using the Tomes equation[43], see Figure 3.3.2.2. The gradient of the line was ca. 70 mV. The gradient was within experimental error of 60 mV, and so the wave can be interpreted as being the result of a reversible one electron transfer.

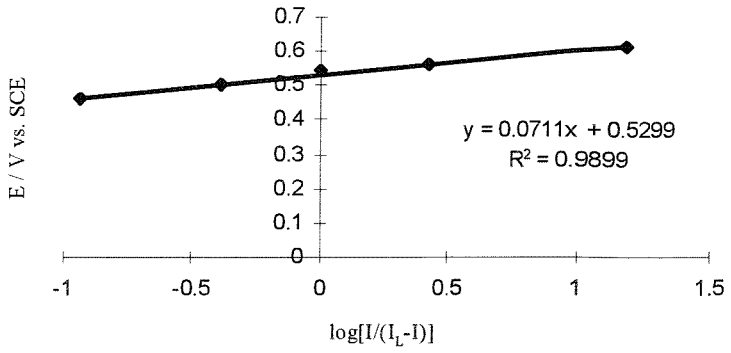


Figure 3.3.2.2 *Tomes analysis of the E vs. the log[(I$_L$- I)/I] for a freshly prepared solution of ferrocene at 20.4 mM concentration in AcOH/5 % H_2SO_4/2 % Ac_2O using a carbon fibre disc electrode (diameter 7 μm), platinum counter electrode, scan rate 0.02V/s. Data was taken from the voltammogram in Figure 3.3.2.1.*

The fresh solution of ferrocene was orange in colour , but on standing for a couple of hours the solution turned dark green in colour.

A series of voltammograms of the ferrocene in the acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride were then recorded over a period of time, a second wave was seen to develop, while the initial wave decreased in height. The voltammogram recorded after 4 hours is shown in Figure 3.3.2.3.

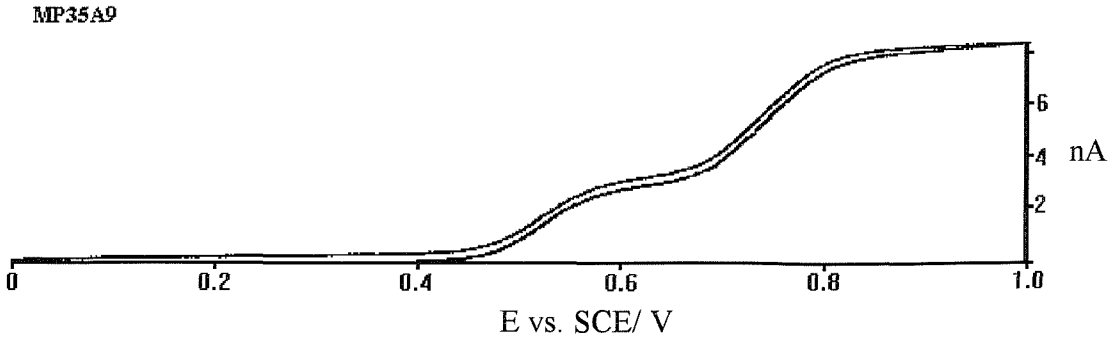


Figure 3.3.2.3 *Voltammogram of a solution of ferrocene (1mM) concentration in AcOH/ 5% H_2SO_4/ 2% Ac_2O recorded at a carbon fibre disc electrode(diameter 7 μm), platinum counter electrode, scan rate 0.02V/s. After 4 hours.*

The second wave had a half wave potential of 0.73 V vs. SCE and applying Tomes criteria, $E_{3/4}$-$E_{1/4}$, a value of 70 mV was recorded. This value was close to that for a reversible one electron oxidation implying that it is due to a substituted ferrocene.

It was suggested that ferrocene was reacting with the solvent to give an acetyl derivative, therefore the voltammogram of mono-acetyl ferrocene was recorded. A solution of 1 mM mono-acetyl ferrocene in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride was prepared. The solution was dark purple in colour. The voltammogram was recorded at a carbon fibre electrode, see Figure 3.3.2.4.

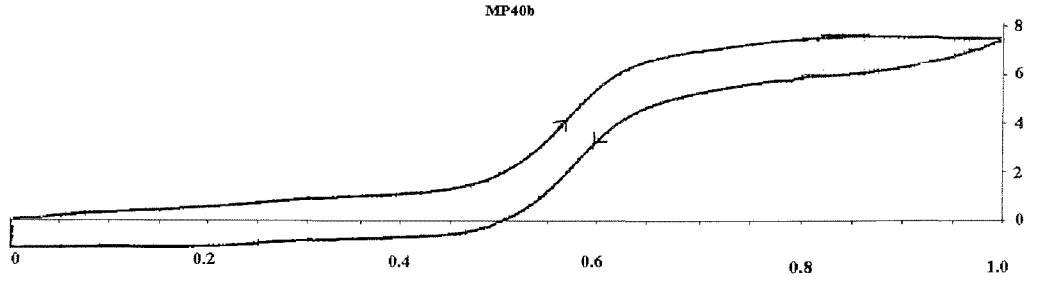


Figure 3.3.2.4 *Voltammogram of a fresh solution of mono-acetyl ferrocene (1mM) concentration in AcOH/ 5% H_2SO_4/ 2% Ac_2O recorded at a carbon fibre disc electrode(diameter 7 μm), platinum counter electrode, scan rate 0.02V/s*

A well formed wave was recorded, with a half wave potential of 0.56 V vs. SCE. Since the solution of mono-acetyl ferrocene was purple in colour and that the half wave potential was not the same as that recorded for the second curve recorded in the ferrocene solution it was concluded that ferrocene did not react to give mono-acetyl ferrocene when left standing in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride. The electrolysis studies, see Section 4.6 revealed that a 0.3 M concentration of anisole was sulfonated to 4-methoxybenzenesulfonic acid when similarly left standing in a solution of acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride and to a lesser extent in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride. It was then concluded that ferrocene was possibly undergoing sulfonation in the solvent media.

3.4 Voltammetry of p-Quinone

Having recorded the voltammograms of a one electron transfer process at a vitreous carbon electrode, see Section 3.3.1, we were similarly keen to record the voltammogram of a 2 electron transfer process. This would enable us to estimate the number of electrons associated with the oxidation of a range of aromatic compounds by comparing the wave heights to those obtained using these reference compounds. Therefore the voltammogram of *p*-quinone was recorded as this was expected to show a two electron reduction wave under the conditions in the cell.

Figure 3.4.1 shows the voltammograms recorded at a scan rate of 20 mV s^{-1} for a freshly prepared solution of 1 mM p-quinone in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride at a vitreous carbon RDE, diameter 3 mm.

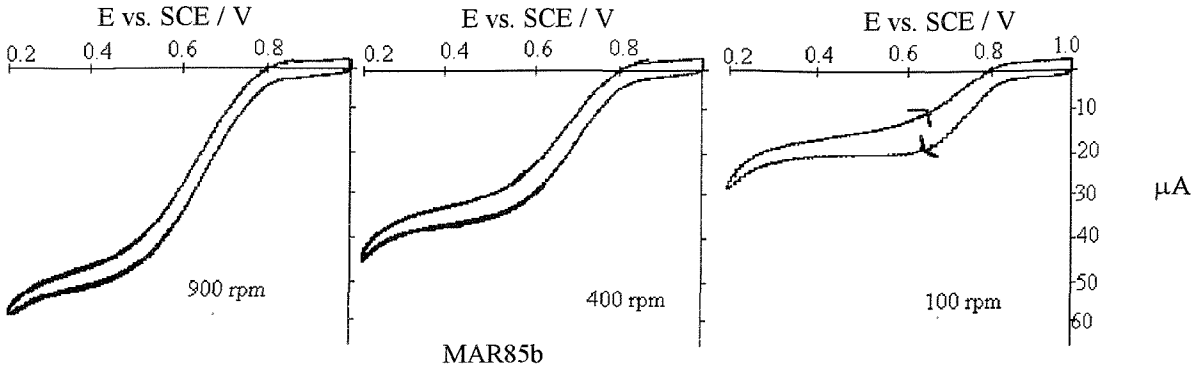
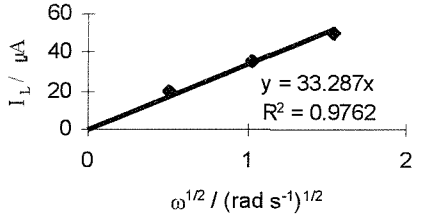


Figure 3.4.1 *Voltammogram of freshly prepared p-quinone at 1mM concentration in AcOH/ 5% H_2SO_4/25 % Ac_2O using a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s.*

A well formed reduction wave was observed at $E_{1/2}$ = 0.69 V vs. SCE. There was only a small amount of hysteresis between the forward and the back scans of the voltammogram. According to the data analysis using the Levich equation, see Figure 3.3.2a, the limiting current, I_L, was proportional to the square root of rotation rate, $\omega^{1/2}$. This means that the limiting current was mass transport controlled. The voltammogram of *p*-quinone, recorded at a rotation rate of 400 rpm, was analysed using Tomes equation[42]. The result is shown in Figure 3.4.2b.



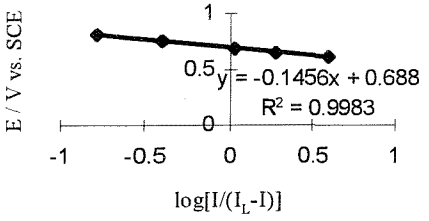


Figure 3.4.2a Levich analysis of I_L vs. $\omega^{1/2}$ for a *freshly prepared solution of p-quinone at 1mM concentration in AcOH/5 % H_2SO_4/ 25 % Ac_2O using a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s. Data was taken from the voltammograms shown in Figure 3.4.1*

Figure 3.4.2b *Tomes analysis of the E vs. the log[(I_L- I)/I] for a freshly prepared p-qunione solution of 1mM concentration in AcOH/5 % H_2SO_4/ 25 % Ac_2O using a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s. Data was taken from the voltammogram recorded at 400 rpm in Figure 3.4.1*

The gradient of the line in Figure 3.4.2b was ca. -150 mV. The gradient for a reversible two electron transfer would be ca. 29.5 mV, therefore the reduction of *p*-quinone was irreversible, under the conditions used to record the voltammogram.

For a simple electron transfer process at an electrode, the wave height for the limiting current, measured at a RDE, is proportional to the number of electrons transferred[42]. Therefore the wave height for the two electron reduction of *p*-quinone to hydroquinone, would be expected to be twice the height of the wave for the one electron oxidation of ferrocene to the ferrocinium cation. The wave height of ferrocene, at a rotation rate of 400 rpm, was 11 μA and that for *p*-quinone measured under similar conditions was 36 μA. It was therefore apparent that the wave height of *p*-quinone was ca. 3 times the height of that measured for ferrocene. The ferrocene oxidation wave may be too small, because of its homogenous chemistry and the limiting current density for the *p*-quinone may be a more reliable guide of the limiting current for a two electron process.

3.5 Voltammetry of Aryl Iodides

3.5.1 Voltammetry of 4-Iodotoluene

Weinberg *et al*[25] reported the oxidation of 4-iodotoluene and its subsequent coupling to toluene. A series of voltammograms were recorded so as to increase our understanding of the mechanism of the reaction.

3.5.1.1 Voltammograms of 4-Iodotoluene in Acetic acid/5 % Sulfuric acid/ 25 % Acetic Anhydride

Figure 3.5.1.1.1 shows the voltammogram of a 1 mM solution of 4-iodotoluene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride, recorded at a vitreous carbon RDE, with a scan rate of 20 mV s^{-1}.

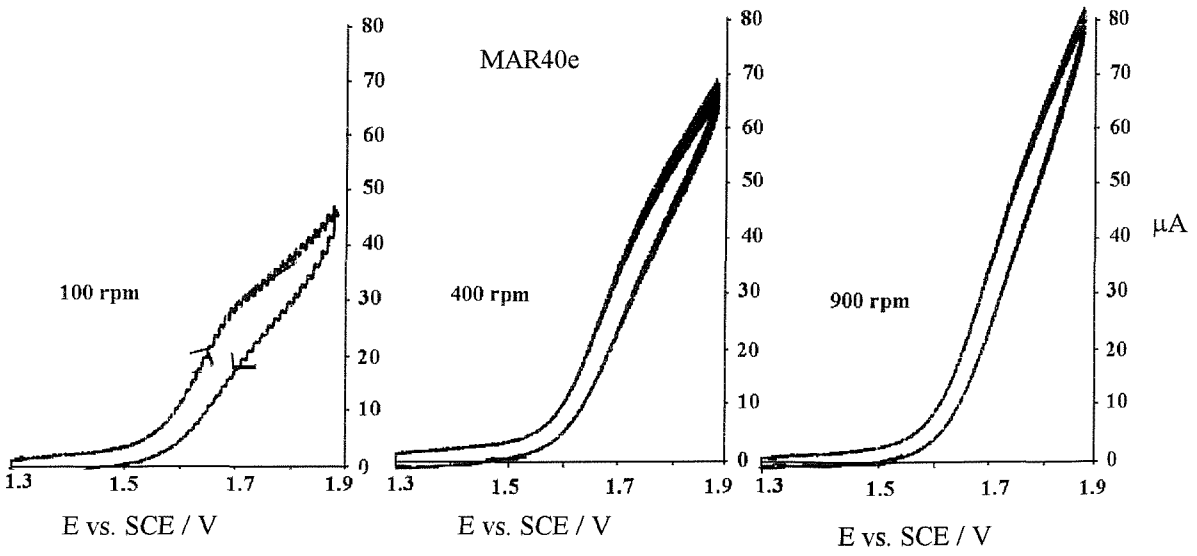


Figure 3.5.1.1.1 *Voltammogram of freshly prepared solution of 4-iodotoluene at 1mM concentration in AcOH/ 5% H_2SO_4/ 25 % Ac_2O recorded at a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s.*

The oxidation wave of 4-iodotoluene had a half wave potential of 1.69 V vs. SCE. There was little hysteresis between the forward and back scans reflecting that there was no rapid passivation of the electrode surface on the back scan. The shape of the wave, became less clear as the rotation rate was increased. This was due in part to a possible distortion of the curve by IR drop which became more significant as the current increased with increasing rotation rate. It was previously noted that there was significant back ground current measured in the absence of aryl iodide above 1.6 V vs. SCE. It was not possible to be certain how much of the observed limiting current of 4-iodotoluene was associated with the back ground current, see Figure 3.2.1.

The cyclic voltammogram of 4-iodotoluene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride was recorded; 10 mg of 4-iodotoluene was added to the electrolyte in the working electrode compartment, which had ca. 50 cm^3 of a solution of acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride. The solution was stirred, then allowed to settle. The working electrode was stationary through out. The potential was swept between -0.4 V and 1.9 V vs. SCE at a scan rate of 20 mV/ s, the initial potential was 0.4 V vs. SCE, see Figure 3.5.1.1.2

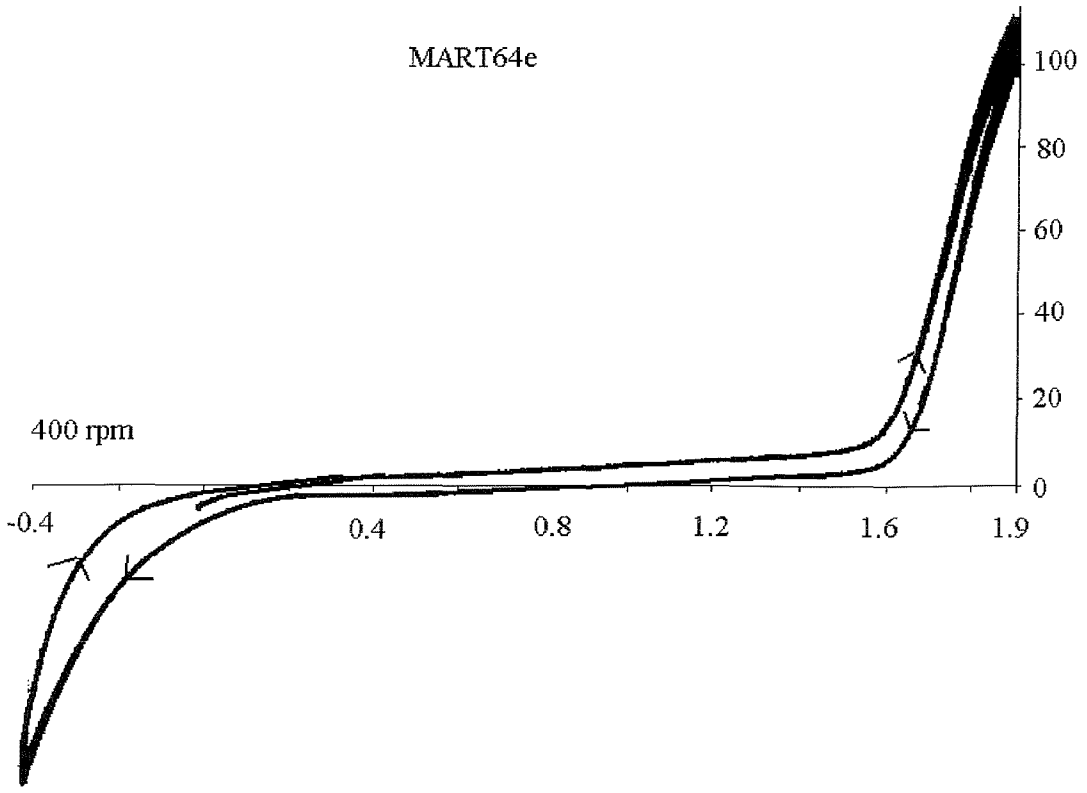


Figure 3.5.1.1.2 *Cyclic voltammogram of freshly prepared solution of 10 mg of 4-iodotoluene in ca. 50 cm^3 solution of AcOH/ 5% H_2SO_4/ 25 % Ac_2O recorded at a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s.*

The oxidation of 4-iodotoluene was clearly seen to be initiated at a potential of ca.1.5 V vs. SCE. On the reverse scan there were no obvious reduction peaks for the oxidation product of 4-iodotoluene.

3.5.1.2 Voltammograms of 4-Iodotoluene in Acetic acid/5 % Sulfuric acid/ 2 % Acetic Anhydride

Figure 3.5.1.2.1 shows the voltammogram of a 1 mM solution of 4-iodotoluene in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride, measured at a vitreous carbon RDE, with a scan rate of 20 mV s^{-1}.

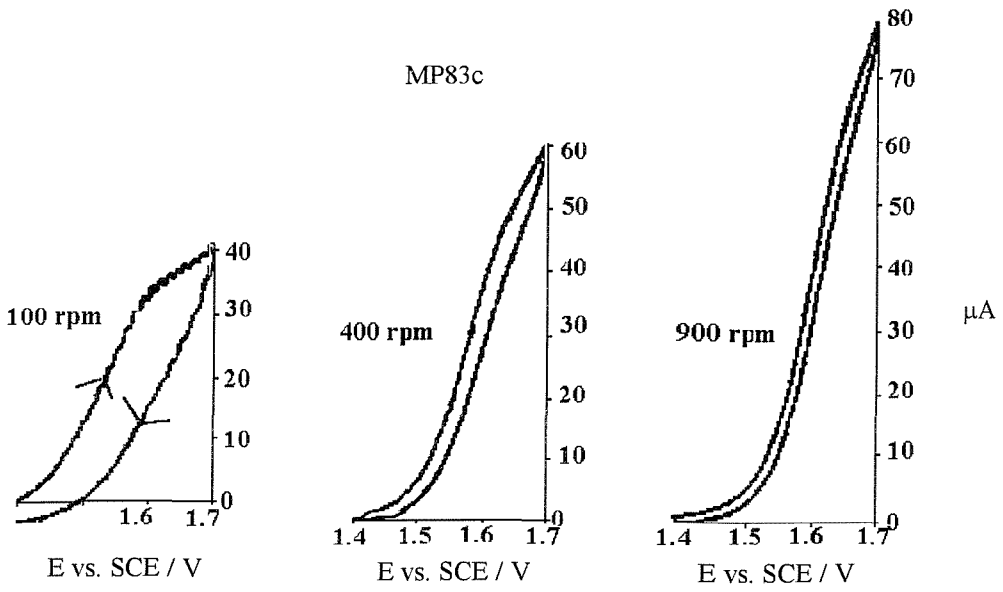


Figure 3.5.1.2.1 *Voltammogram of freshly prepared solution of 4-iodotoluene at 1mM concentration in AcOH/ 5% H_2SO_4/ 2 % Ac_2O recorded at a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s.*

The responses were very similar to those recorded for 4-iodotoluene recorded in 25 % acetic anhydride with an oxidation wave at a half wave potential of 1.58 V vs. SCE. At the slowest rotation rate, some hysteresis was apparent.

3.5.1.3 Comments on the Voltammetry of 4-Iodotoluene

For a 1mM concentration of 4-iodotoluene the voltammograms recorded in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride and acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride were very similar. This was reflected in the Tomes analysis, at a rotation rate of 400 rpm, where the gradient of the Tomes line were 52.4 mV and 51.6 mV for the 25 % and 2 % acetic anhydride solution respectively. From the Tomes analysis the half wave potential for the oxidation of 4-iodotoluene in the 25 % and 2 % solution were 1.69 and 1.58 V vs. SCE respectively.

3.5.2 Voltammetry of 4-Iodoanisole

The voltammogram of 1mM concentration of 4-iodoanisole was recorded between the limits 1.0 V to 1.7 V vs. SCE, see Figure 3.5.2.1.

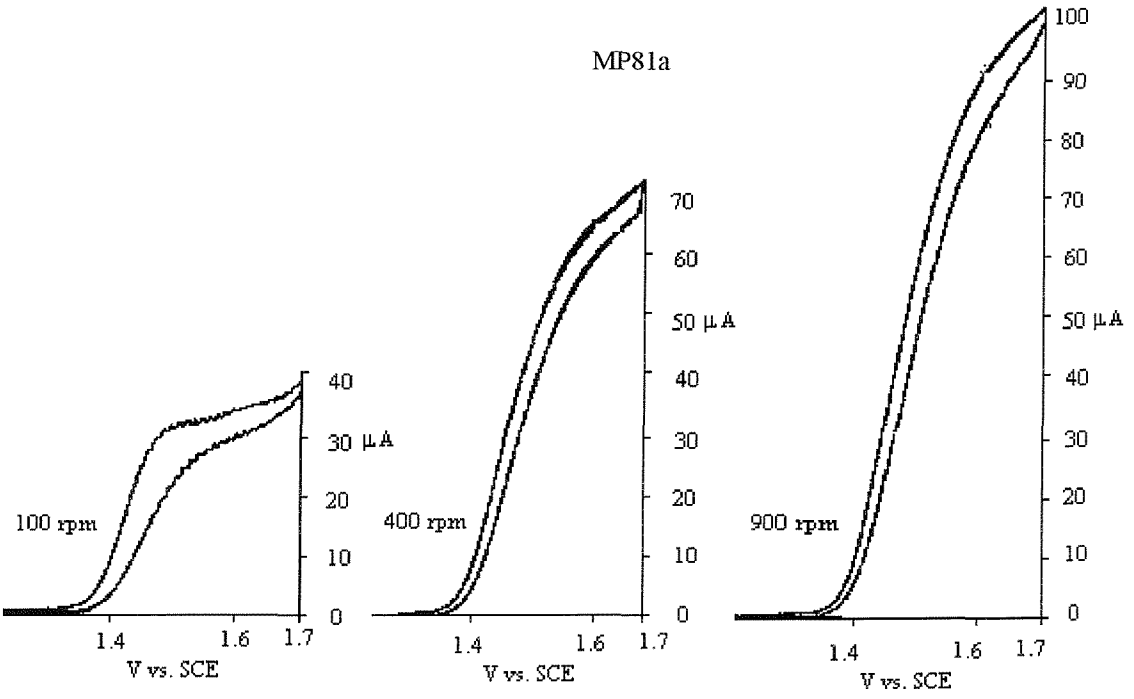
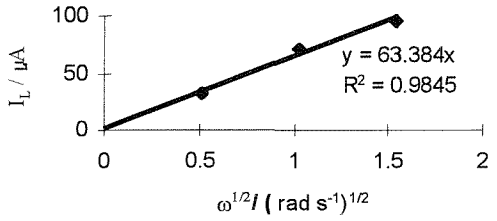


Figure 3.5.2.1 *Voltammogram of 4-iodoanisole at 1mM concentration in AcOH/5% H_2SO_4/2% Ac_2O using a vitreous carbon rotating disc electrode (diameter 3mm), scan rate 0.02 V/s.*

The voltammograms of 4-iodoanisole showed an oxidative wave at a half wave potential of 1.46 V vs. SCE. There was little hysteresis between the forward and back scan. The limiting current was proportional to the square root of rotation rate, see Figure 3.5.2.2a. The wave recorded at 400 rpm was analysed using the Tomes equation to see if the oxidation was reversible, see Figure 3.5.2.2b The gradient was 94 mV, therefore the oxidation of 4-iodoanisole was irreversible[43].



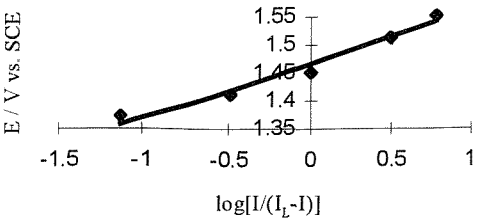


Figure 3.5.2.2a Levich analysis of I_L vs. $\omega^{1/2}$ for a *freshly prepared solution of 4-iodoanisole at a 1mM concentration in AcOH/5 % H_2SO_4/2 % Ac_2O using a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s. Data was taken from the voltammograms shown in Figure 3.4.2.1*

Figure 3.5.2.2b *Tomes analysis of the E vs. the log[(I_L- I)/I] for a freshly prepared solution of 4-iodoanisole at a 1mM concentration in AcOH/5 % H_2SO_4/2 % Ac_2O using a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s. Data was taken from the voltammogram recorded at 400 rpm in Figure 3.4.2.1*

The voltammogram of 4-iodoanisole was then recorded, but the upper potential limit was increased to 2.0 V vs. SCE, see Figure 3.5.2.3.

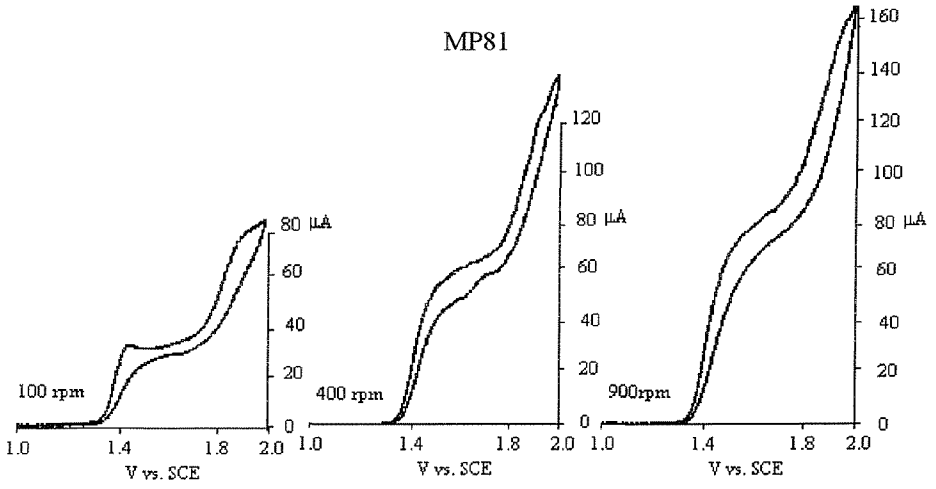


Figure 3.5.2.3 *Voltammogram of 4-iodoanisole at a 1mM concentration in AcOH/5% H_2SO_4/2% Ac_2O using a vitreous carbon rotating disc electrode (diameter 3mm), scan rate 0.02 V/s*

A second wave was clearly seen to occur after the original wave. The second wave was interpreted as being the further oxidation of material formed in the first wave and involved the same number of electrons as the first wave.

A final series of voltammograms were recorded, where the upper voltage limit was raised to 2.3 V vs. SCE, see Figure 3.5.2.4.

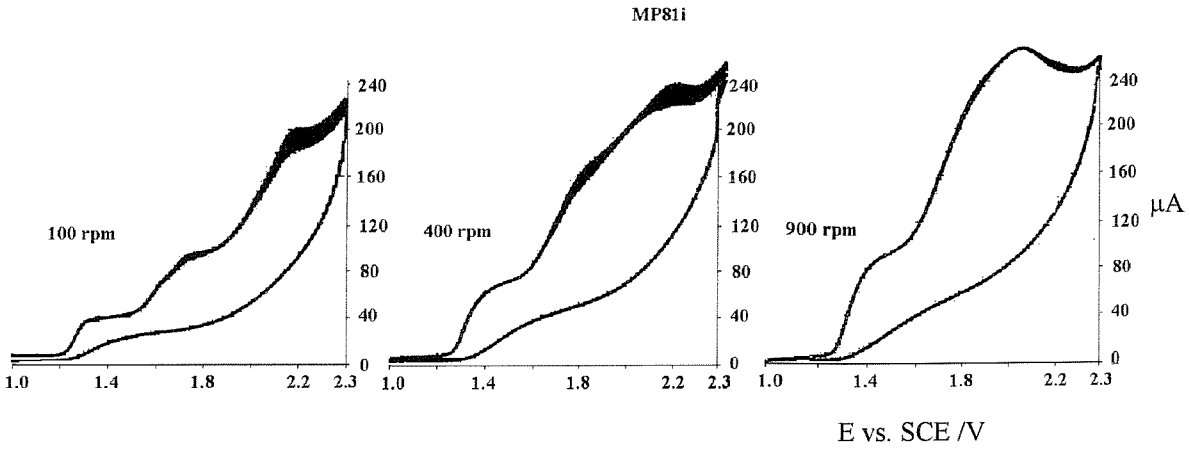


Figure 3.5.2.4 *Voltammogram of 4-iodoanisole at 1mM concentration in AcOH/5% H_2SO_4/2% Ac_2O using a vitreous carbon rotating disc electrode (diameter 3mm), scan rate 0.02 V/s*

At a rotation rate of 100 rpm, three waves in the voltammogram of 4-iodoanisole were recorded, but at higher rotation rates it was more difficult to distinguish between the second and third wave. The extension of the upper limit meant that there was strong hysteresis between the forward and back scan with more current recorded for the forward scan relative to the back scan. It was apparent that the oxidation event taking place in the third wave was leading to rapid passivation of the electrode.

3.5.3 Voltammetry of Iodobenzene

The voltammogram of iodobenzene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride was recorded at a vitreous carbon rotating disc electrode, see Figure 3.5.3.1.

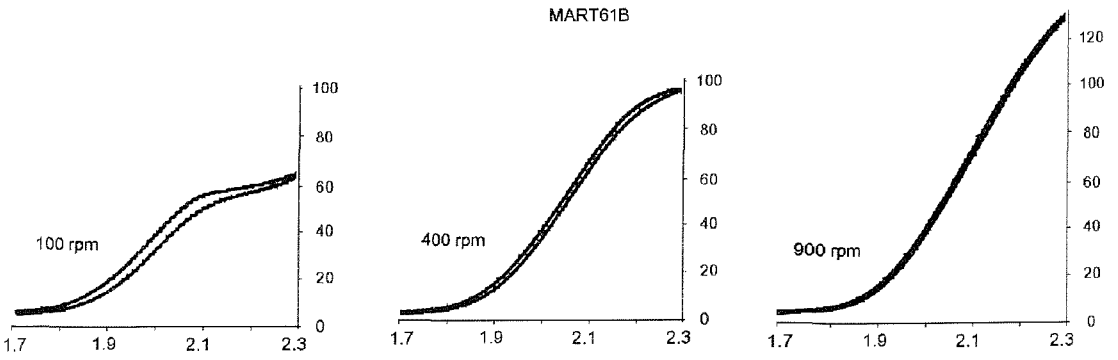


Figure 3.5.3.1 *Voltammogram of iodobenzene at a 1mM concentration in AcOH/5% H_2SO_4/25% Ac_2O using a vitreous carbon rotating disc electrode (diameter 3mm), scan rate 0.02 V/s*

The oxidation waves are very drawn out and the potential for the oxidation of iodobenzene are very much more positive from those of 4-iodotoluene. The plateau was seen to increase with rotation rate, but interference form IR drop and solvent oxidation distorts the curves.

3.5.4 Voltammetry of 1-tert-Butyl-4-iodobenzene

The voltammogram of 1-*tert*-butylbenzene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride was recorded at a vitreous carbon rotating disc electrode, see Figure 3.5.4.1 The voltammograms of 1-*tert*-butyl-4-iodobenzene are of similar height and shape of those recorded for 4-iodotoluene under similar conditions. The half wave potential for the wave recorded at a rotation rate of 400 rpm was estimated to be 1.85 V vs. SCE. The value of $E_{3/4}$ - $E_{1/4}$ for the wave recorded at 400 rpm was 100 mV, so the application Tomes criteria it was seen that the oxidation was irreversible.

The half wave potential recorded for 4-iodotoluene under 'identical' conditions to that used for 1-*tert*-butyl-4-iodobenzene was 1.69 V vs. SCE. Therefore there was an increase in oxidation potential of 160 mV on replacing a methyl group by a *tert*-butyl

group. Into the 1 mM concentration of 1-*tert*-butlyl-4-iodobenzene in the working electrode compartment of the RDE analytical cell was added 10 mg of 4-iodotoluene. A voltammogram was recorded. The voltammograms now showed a wave prior to the wave for 1-*tert*-butly-4-iodobenzene which was the oxidation of 4-iodotoluene, so this observation was real.

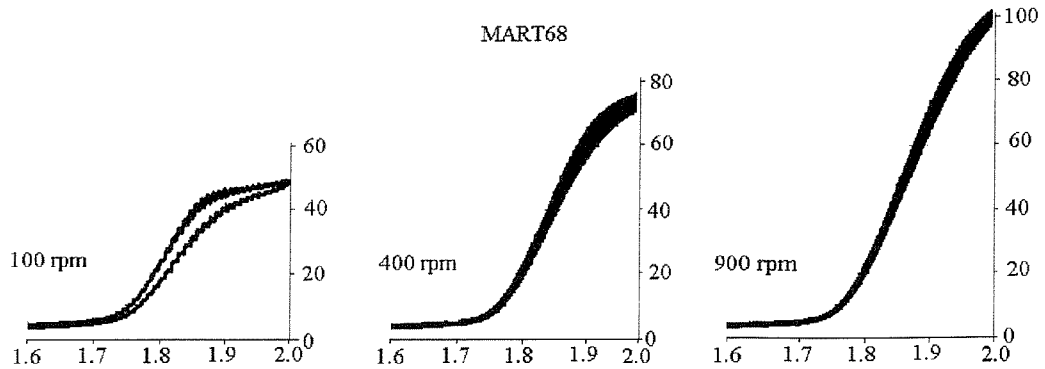


Figure 3.5.4.1 *Voltammogram of 1-tert-Butyl-4-iodobenzene at a 1mM concentration in AcOH/5% H_2SO_4/25 % Ac_2O using a vitreous carbon rotating disc electrode (diameter 3mm), scan rate 0.02 V/s*

The ease of oxidation of 4-iodotoluene relative to 1-*tert*-butlyl-4-iodobenzene would seem anomalous, as the *tert*-butyl group is recognised as being a stronger electron donor than the methyl group. Therefore there should be a higher electron density in the iodobenzene substituted with the *tert*-butyl group than that substituted with a methyl group. The fact that 1-*tert*-butly-4-iodobenzenewas oxidised at a higher potential relative to 4-iodotoluene would suggest that the two compounds were not being oxidised to analogous products. There was evidence for this hypothesis from the electrolysis of 4-iodotoluene in the absence of an arene ; a major product of this electrolysis was 4-iodobenzyl acetate. It can be seen that as the cation radical of 1-*tert*-butly-4-iodobenzene does not have a hydrogen atom in the benzyl position therefore it cannot be substituted with a acetoxy group at the benzyl carbon. It is this lack of a benzyl proton in the *tert*-butyl group which was therefore responsible for the higher oxidation potential of 1-*tert*-butyl-4-iodobenzene relative to 4-iodotoluene.

3.6 Voltammetry of Arenes

3.6.1 Voltammetry of Toluene

Figure 3.6.1.1 shows the voltammogram of a 1 mM solution of toluene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride, recorded at a vitreous carbon RDE, with a scan rate of 20 mV s^{-1}. The electrode was polished between each scan in accordance with the procedure described in Section 2.2.1

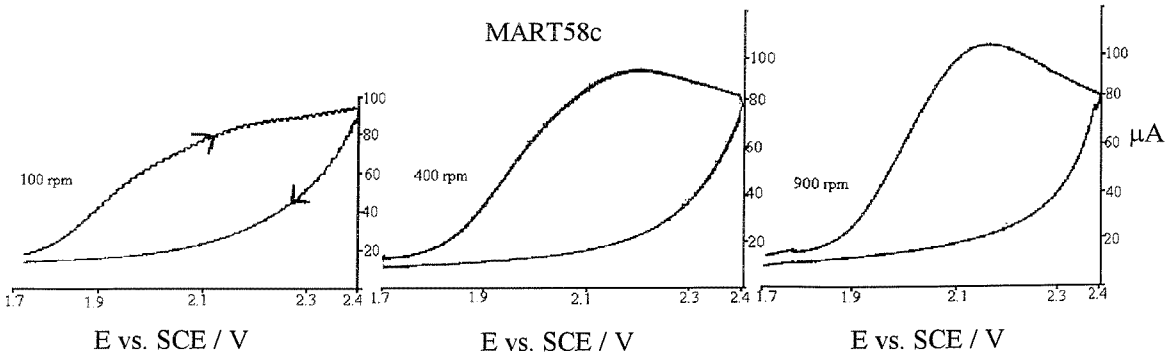


Figure 3.6.1.1 *Voltammogram of freshly prepared solution of toluene at 1mM concentration in AcOH/ 5% H_2SO_4/ 25 % Ac_2O recorded at a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s.*

There were several pertinent points to consider about the voltammogram of toluene; the oxidation waves were 'poorly shaped' and there was strong hysteresis between the forward and back scan with very much more current associated with the forward scan than with the back scan, indicating tarring of the electrode. Figure 3.6.1.2a was the voltammogram of toluene, recorded at a rotation rate of 400 rpm, with a polished electrode. A second voltammogram was then recorded without polishing the electrode after the first scan, see Figure 3.6.1.2b.

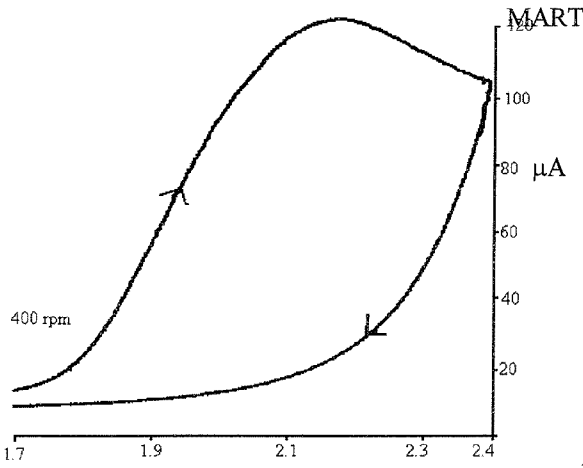


Figure 3.6.1.2a *Voltammogram of freshly prepared solution of toluene at 1mM concentration in AcOH/ 5% H_2SO_4/ 25 % Ac_2O recorded at a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s. Electrode was polished before voltammogram was recorded*

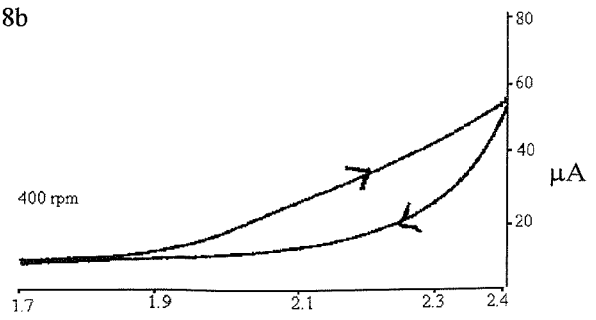


Figure 3.6.1.2b *Voltammogram of freshly prepared solution of toluene at 1mM concentration in AcOH/ 5% H_2SO_4/ 25 % Ac_2O recorded at a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s. Electrode was polished before voltammogram was recorded. Electrode was not polished since recording the voltammogram in Figure 3.6.1.2a*

It was clear from the comparison of Figures in 3.6.1.2a and 3.6.1.2b that the electrode was passivated when oxidising toluene at its surface, probably by an insulating polymer. An important feature to note was that the oxidation of toluene was initiated at a potential of ca. 1.8 V vs. SCE. If we consider the voltammogram of 4-iodotoluene, see Figure 3.5.1.1, the oxidation starts at a potential of ca. 1.5 V vs. SCE and the limiting current is reached before a potential of ca. 1.8 V vs. SCE. It is clear that the presence of an iodine atom *para* to the methyl group in 4-iodotoluene has reduced it oxidation potential relative to toluene.

3.6.2 Voltammetry of Anisole

The voltammogram of acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride was recorded using a vitreous carbon RDE, between the limits of 0 V and 2.0 V vs. SCE, at a scan rate of 20 mV /s and a rotation rate of 400 rpm. The recorded voltammogram was

similar in appearance to that recorded previously. Into the working electrode compartment was then added 5.4 μl of anisole, the solution was vigorously stirred, to give an anisole concentration in the working electrode compartment of ca. 1 mM. The voltammogram was then recorded again an oxidation of anisole was seen to be initiated at ca. 1.4 V, see Figure 3.5.6.1a. There was considerable hysteresis between the forward and back scan. This was reminiscent of toluene, see Section 3.6.1. A second voltammogram was recorded immediately after the first scan, see Figure 3.6.2.1b. The current measured throughout the scan was lower and again there was hysteresis between the forward and back scan. This result emphasised the fact that anisole was oxidised on the vitreous carbon and that the product lead to tarring of the surface, although not as rapidly as toluene.

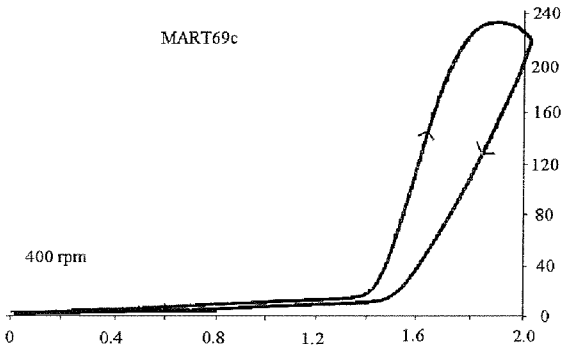


Figure 3.6.2.1a *Voltammogram of freshly prepared solution of anisole at ca. 1mM concentration in AcOH/ 5% H_2SO_4/ 25 % Ac_2O recorded at a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s. Electrode was polished before voltammogram was recorded*

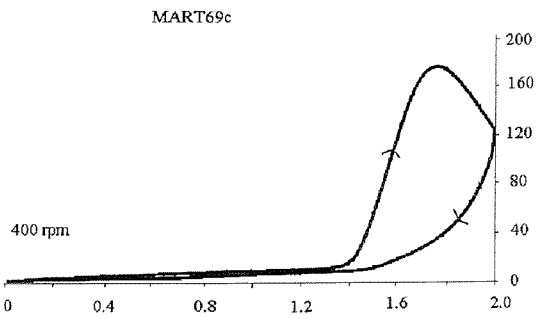


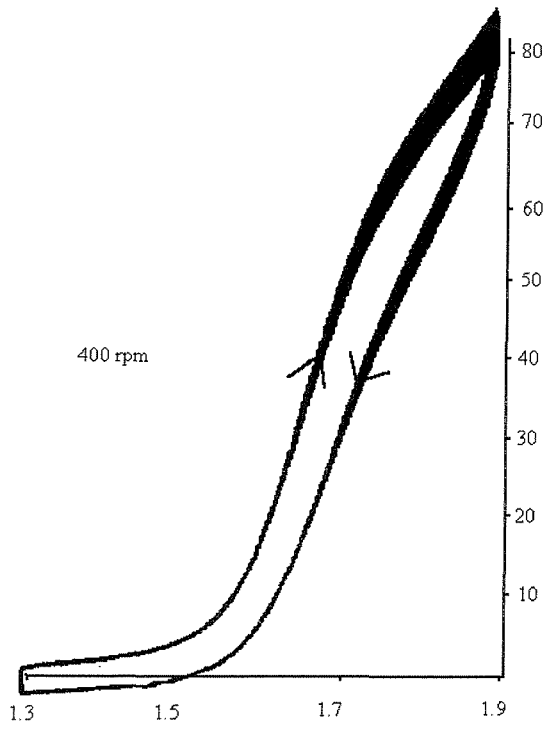
Figure 3.6.2.1b *Voltammogram of freshly prepared solution of anisole at ca. 1mM concentration in AcOH/ 5% H_2SO_4/ 25 % Ac_2O recorded at a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s. Electrode was not polished since recording the voltammogram in Figure 3.6.2.1a*

It was noted that the oxidation peak of anisole occurred at a similar potential to that of 4-iodoanisole. To the working electrode compartment was added 11 mg of 4-iodoanisole and the solution was stirred vigorously. The voltammogram, for a solution containing both anisole and 4-iodoanisole was then recorded. It was seen that the

oxidation peak had moved to a slightly lower potential. It was therefore concluded that 4-iodoanisole had a lower oxidation potential than anisole, but that the difference was not as great as that between 4-iodotoluene and toluene.

3.7 Voltammetry of 4-Iodotoluene and Toluene

The voltammogram of a 1m M concentration of 4-iodotoluene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride was recorded between the limits of 1.3 and 1.9 V vs. SCE at a scan rate of 20 mV/s and a rotation rate of 400 rpm, see Figure 3.7.1a. Then into the cell was added a series of 5.4 μl aliquots of toluene. The solution was stirred vigorously after each addition. Then the voltammogram of the solution was recorded. The toluene concentrations measured were ca. 0.5, ca. 1.0 and ca. 2 mM, see Figure 3.7.1b. It was apparent that the addition of toluene distorted the end of the wave, but did not change the overall appearance or position of the 4-iodotoluene wave.



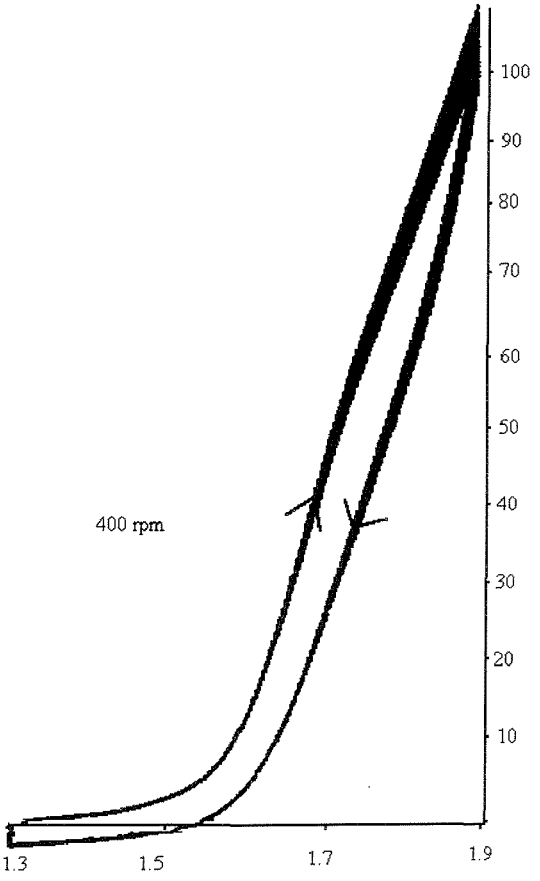
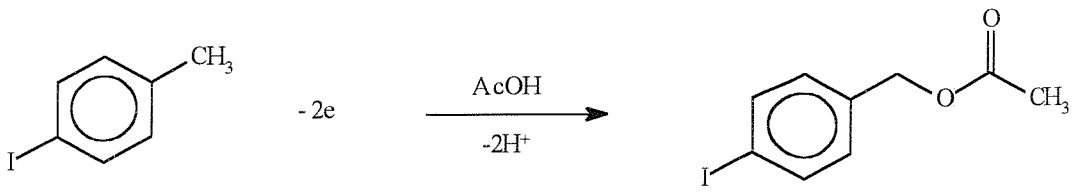


Figure 3.7.1a *Voltammogram of freshly prepared solution of 4-iodotoluene at 1mM concentration in AcOH/ 5% H_2SO_4/ 25 % Ac_2O recorded at a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s.*

Figure 3.7.1b *Voltammogram of a solution of 4-iodotoluene at 1mM concentration and toluene at ca. 2 mM concentration in AcOH/ 5% H_2SO_4/ 25 % Ac_2O recorded at a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s.*

It was seen from the voltammetry of 4-iodotoluene that its oxidation waves were independent of the solvent, see Section 3.5.1.

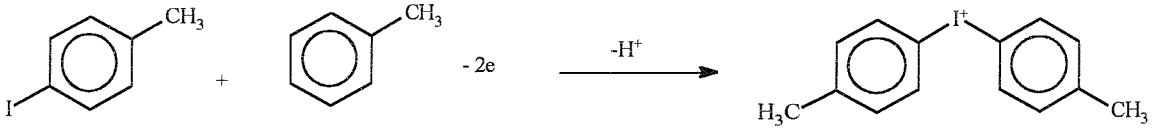
The electrolysis of 4-iodotoluene in acetic acid 5 % sulfuric acid/ 2 or 25 % acetic anhydride, Section 4.2 gave 4-iodobenzylacetate as the major product, see Scheme 3.7.1.



Scheme 3.7.1

The electrosynthesis of 4-iodobenzyl acetate was a two electron process, therefore the wave height in the voltammogram of 4-iodobenzene would reflect this.

The electrolysis of 4-iodotoluene and toluene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride formed the dimethyldiphenyliodonium salt in good yield. The mechanism of this reaction similarly involved a two electron transfer, see Scheme 3.7.2.



Scheme 3.7.2

Again the wave height recorded at the vitreous carbon RDE should reflect the number of electrons transferred. If there was a transition in the mechanism from that which led to 4-iodobenzyl acetate to that which led to the dimethyldiphenyliodonium cation after the addition of toluene, then we expect some change in the voltammogram, but only if the coupling reactions differed markedly in the rates of reaction.

The voltammetry would appear to preclude any self coupling of 4-iodotoluene as this would be a one electron transfer process, see Scheme 3.7.3 and so would be expected to be half as high as those waves recorded for solutions containing equimolar amounts of 4-iodotoluene and toluene. This was also in line with the electrolysis data, see Section 4.1, where there was no evidence for the self coupling product of 4-iodotoluene.

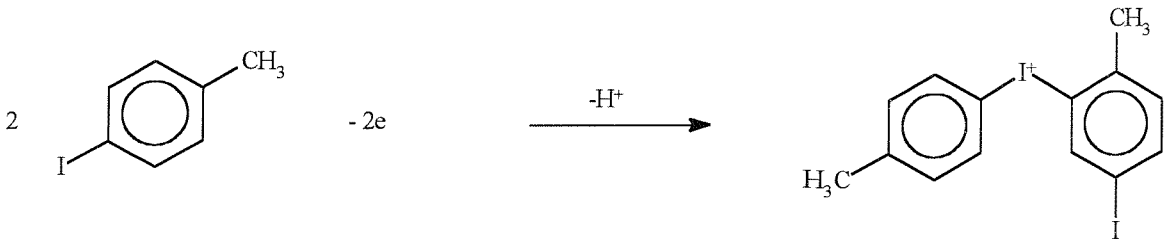


Figure 3.7.3

3.8 Voltammetry of Dimethyldiphenyliodonium Bisulfate

The voltammogram of the solvent acetic acid was recorded at between the limits of -0.4 V and 2.4 V vs. SCE at a scan rate of 20 mV/ s. The initial potential was 0.4 V vs. SCE. Into the cell was added 20 mg of dimethyldiphenyliodonium bisulfate. The solution was stirred vigorously and then a second voltammogram was recorded at a rotation rate of 400 rpm, see Figure 3.8.1.

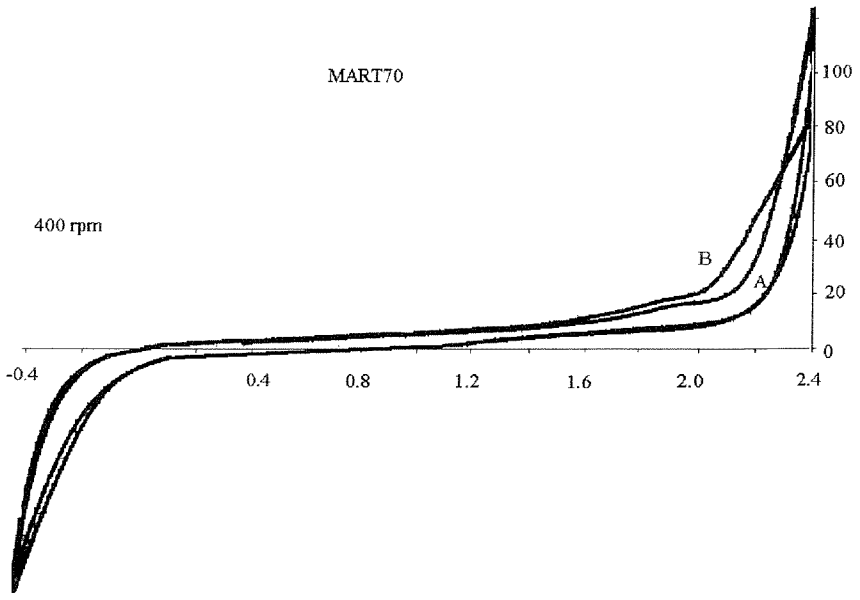


Figure 3.8.1 *A) Voltammogram of AcOH/5% H_2SO_4/25 % Ac_2O. Recorded using a vitreous carbon rotating disc electrode (diameter 3mm), scan rate 0.02 V/s*
B)Voltammogram of AcOH/5% H_2SO_4/25 % Ac_2O after 20 mg of dimethyldiphenyliodonium bisulfate was added. Recorded using a vitreous carbon rotating disc electrode (diameter 3mm), scan rate 0.02 V/s.

It was apparent from Curve B, in Figure 3.8.1, that there was an apparent increase in anodic current above 1.6 V vs. SCE on the forward scan after the addition of dimethyldiphenyliodonium bisulfate. The increase was so marginal that it was of no real significance. There a slight difference in the cathodic current on adding dimethyldiphenyliodonium bisulfate to the solution, but again the difference was not significant. The fact that iodonium salts could be prepared in good yield, see Section 4.1, in an undivided cell with a graphite cathode would lend evidence to the argument that iodonium salts were not reduced at a carbon based electrode. This was, in addition supported by a literature search which showed that iodonium salts were reduced at mercury cathodes[49,50, 51,52, 53, 54.]. Several of these papers showed a mechanism for reduction of the diaryliodonium salt which involved organo mercury intermediates.

CHAPTER 4

Results and Discussions: Diaryliodonium Salts

4.1 Electrolysis of 4-Iodotoluene and Toluene

As previously described , see Section 2.2.2, the electrolysis cell with a graphite cathode, surrounded by a carbon felt anode (approximate surface area of 80 cm^2) was charged with a solution of 0.2 M 4-iodotoluene and 0.3 M toluene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride. Constant current electrolysis was performed at a temperature of 298 K, by maintaining a current of 400 mA (current density at the anode was ca. 5 mA cm^{-2}) between the two electrodes until the charge passed corresponded to 1.6 F. During the electrolysis the solution was constantly stirred and aliquots of reaction mixture were removed for hplc analysis in order to monitor the consumption of starting material and the formation of the product. The initially high concentration of 4-iodotoluene and toluene, meant that the aliquots were diluted prior to injection onto the hplc column, the chromatograms are shown in Figure 4.4.1.

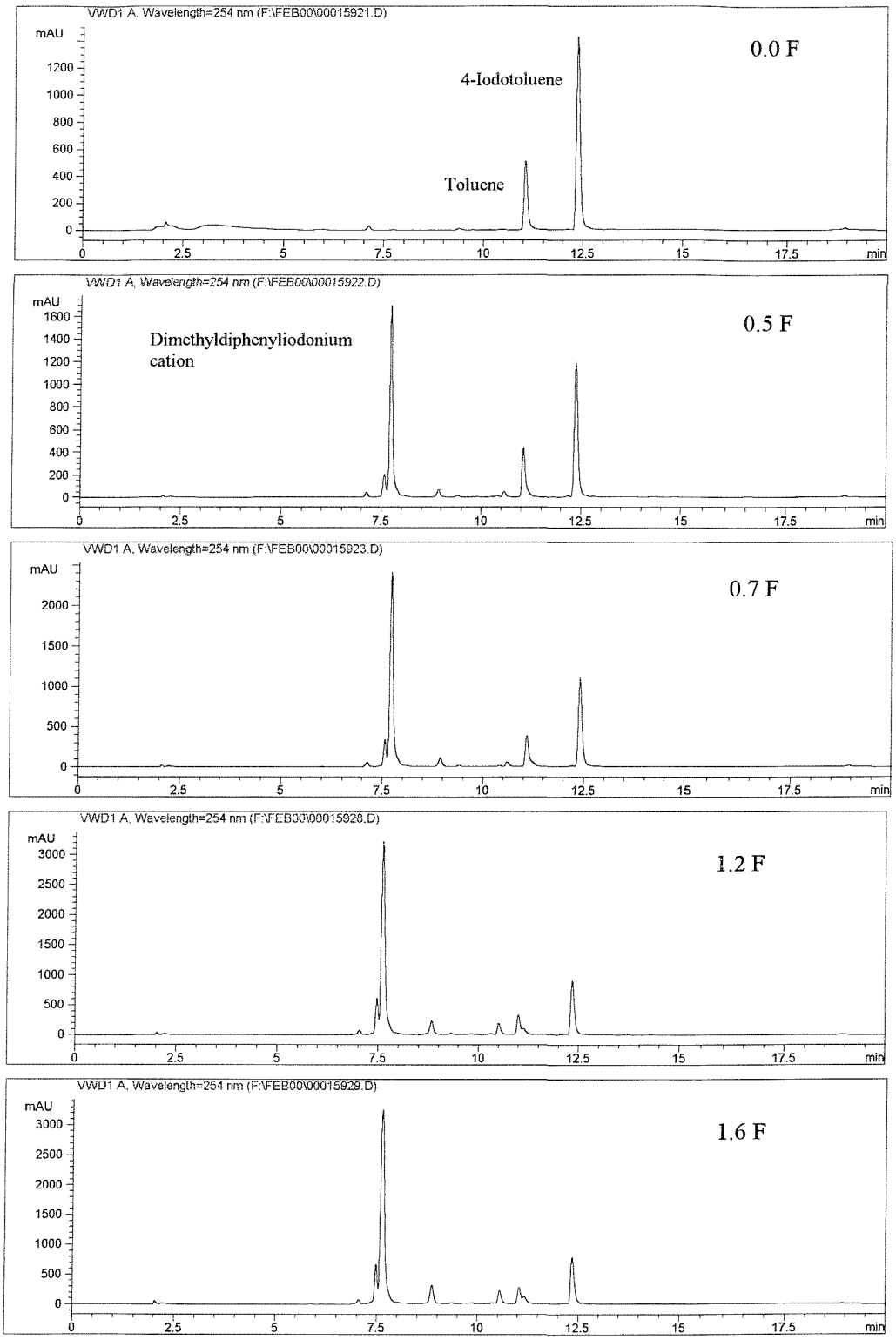


Figure 4.1.1 *The chromatograms recorded after a specified charge had been passed. The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O Note the change of scale on the y axis through the electrolysis.*

Before commencing the electrolysis the solution was clear, but during the course of the electrolysis, the solution darkened in colour. Consideration of the hplc chromatograms shown in Figure 4.1.1 show that there was consumption of the starting material and the production of a single major peak at ca. 7.6 minutes. An aliquot of the electrolysis was removed and diluted with acetonitrile for electrospray mass spectroscopy. The electrospray mass spectrum showed a single ion of m/z 309 Da, which was what was expected for the dimethyldiphenyliodonium cation. The reaction mixture was worked up in accordance with the following procedure. The electrodes were washed with hot methanol and the washings were combined with the reaction mixture. The solvents were removed *in vacuo* and the resulting oil was partitioned between an aqueous phase and an organic phase of diethyl ether. The aqueous phase was separated and treated with potassium iodide, 3 g dissolved in a minimum amount of water. The addition of the potassium iodide solution, caused an immediate precipitation of white powder. This material was separated on the filter paper, and dried. 2.90 g of this solid was formed. The ^{1}H-NMR spectrum was recorded, see Figure 4.1.2. The H-NMR spectrum was compared to that of 4,4'-dimethyldiphenyliodonium iodide, prepared in accordance with the methodology of Beringer[5], see Section 2.4.2. The spectrum of the material isolated by precipitation with potassium iodide from the 'worked up' electrolysis solution cell was identical to the reference spectrum of 4,4'-dimethyldiphenyliodonium iodide.

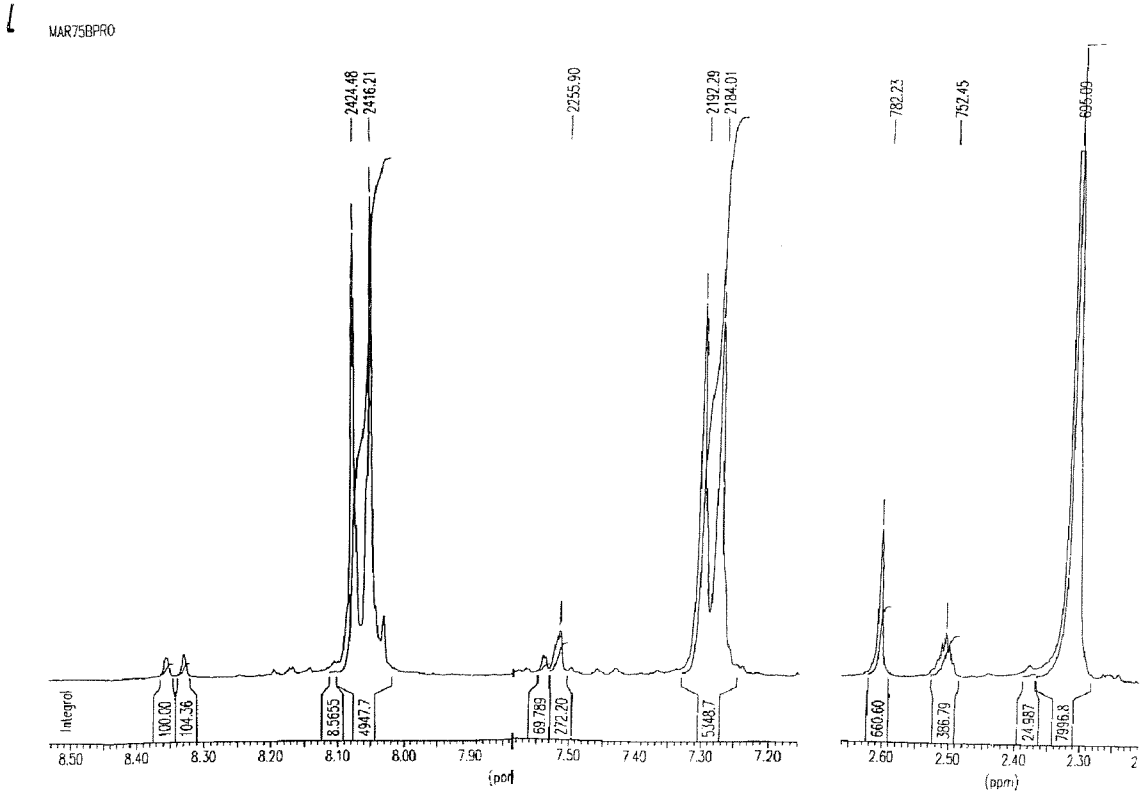


Figure 4.1.2. *The ^{1}H-NMR spectrum of material isolated from the electrolysis of 4-iodotoluene and toluene; isolated by precipitation after the addition of potassium iodide to the reaction mixture.*

An alternative work up was developed, where the electrolysis solution was first treated with diethyl ether; four volumes of diethyl ether were added to one volume of the electrolysis solution. White crystals were formed and were collected on the filter paper. The ^{1}H-NMR, ^{13}C-NMR and DEPT-135 NMR spectra were recorded. Figure 4.1.3 shows the ^{1}H-NMR spectrum of the material isolated from the electrolysis medium by precipitation with diethyl ether.

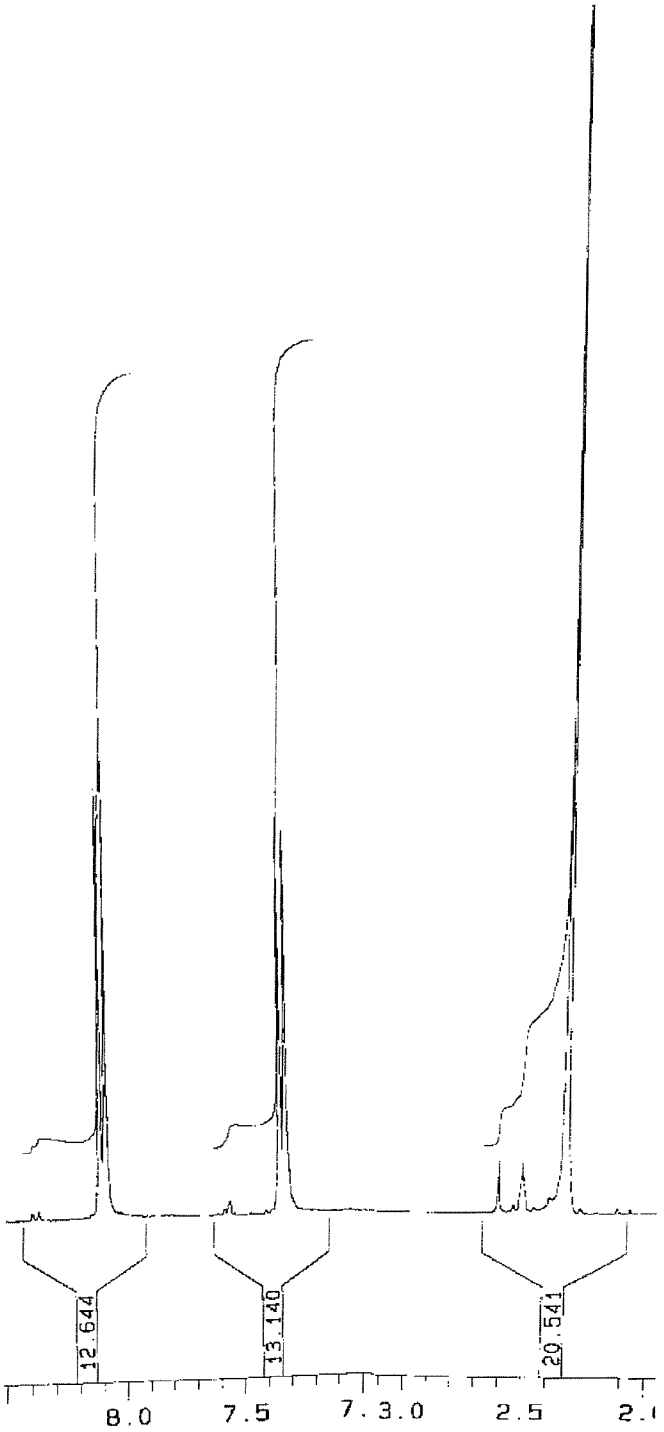


Figure 4.1.3. *The ^{1}H-NMR spectrum of material isolated from the electrolysis of 4-iodotoluene and toluene; isolated by precipitation after the addition of diethyl ether.*

The ^{1}H-NMR spectrum shows three major peaks; two of which were in the aromatic region, at 8.1 and 7.3 ppm, and showed the doublet splitting. The third peak, at 2.3 ppm, was in the alkyl region and was a singlet. This spectrum was compared to that of 4,4'-dimethyldiphenyliodonium bisulfate, see Figure 2.4.1.1. A comparison of the spectra, in Figure 2.4.1.1 and Figure 4.1.3, showed that they were very similar.

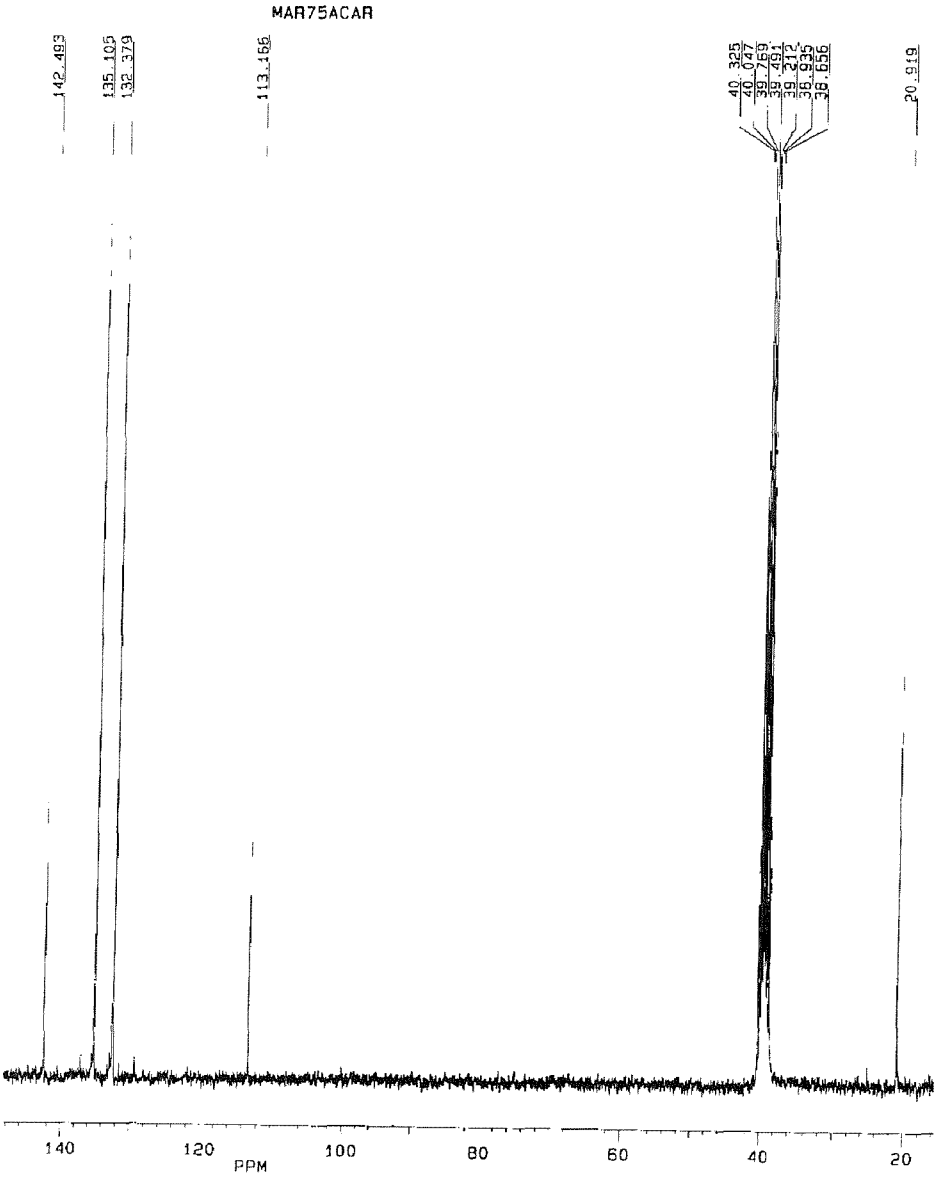


Figure 4.1.4. *The ^{13}C-NMR spectrum of material isolated from the electrolysis of 4-iodotoluene and toluene; isolated by precipitation after the addition of diethyl ether.*

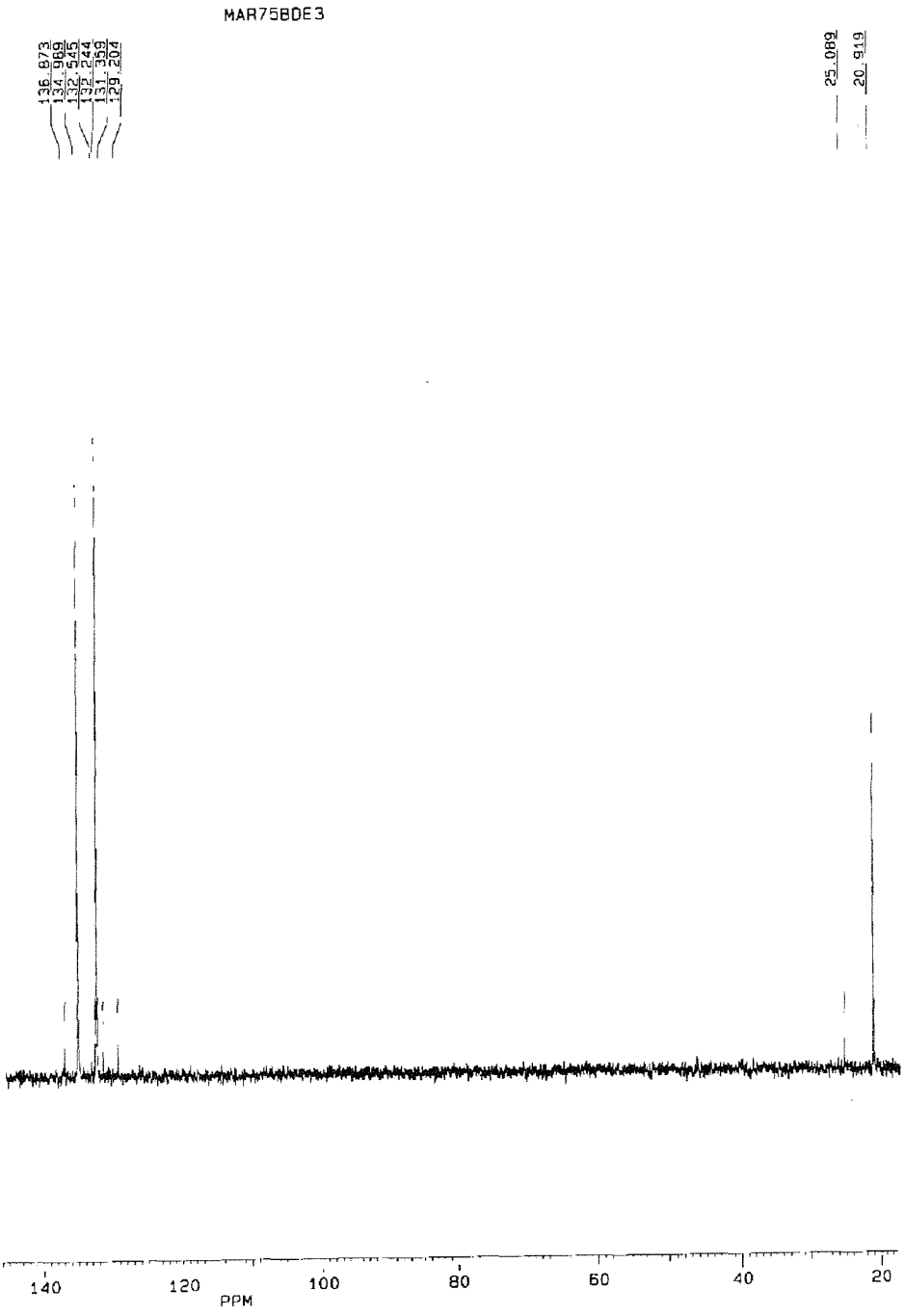


Figure 4.1.5. *The DEPT-135 spectrum of material isolated from the electrolysis of 4-iodotoluene and toluene; isolated by precipitation with diethyl ether.*

The ^{13}C-NMR and DEPT-135 were similarly recorded and compared to the spectra for 4,4'-dimethyldiphenyliodonium bisulfate, see Section 2.4.1. A comparison of the spectra

proved that the material isolated from the electrolysis reaction solution by the addition of diethyl ether was 4,4'-dimethyldiphenyliodonium bisulfate.

An hplc chromatogram of the electrochemically prepared dimethyldiphenyliodonium bisulfate is shown in Figure 4.1.6.

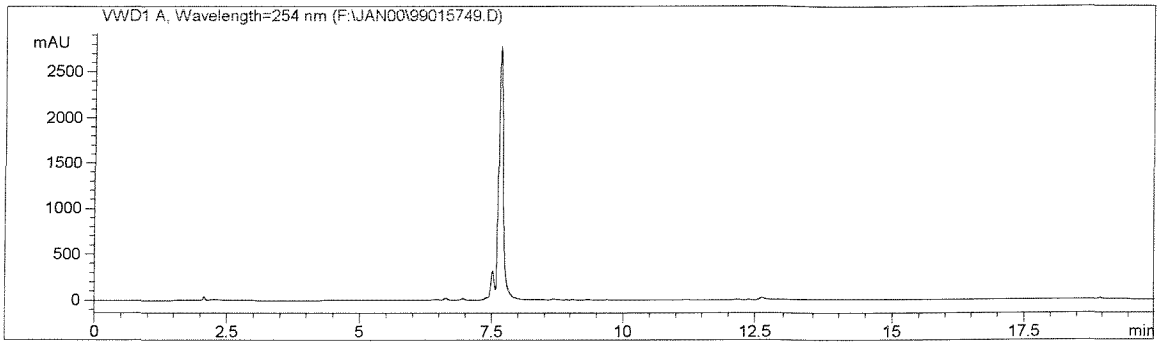


Figure 4.1.6. *Chromatogram of dimethyldiphenylidonium bisulfate separated from the electrolysis solution by the addition of diethyl ether and re-dissolved in a solvent of AcOH/ 5 % H_2SO_4/ 25 % Ac_2O.*

It was clear from the similar retention time of the major product peak seen in the chromatograms of the reaction mixture and the retention time of dimethyldiphenyliodonium bisulfate, see Figure 4.1.1 and Figure 4.1.4 respectively, that the peak which developed, with an elution time of ca. 7.6 minutes, during the electrolysis of 4-iodotoluene and toluene was due to the dimethyldiphenyliodonium cation. The isolation of the dimethyldiphenyliodonium cation by precipitation of the bisulfate, with diethyl ether, lead to incomplete recovery of the dimethyldiphenyliodonium cation. Therefore the mother liquor were reduced in volume, *in vacuo*. The resulting oil was treated in a manner similar to that described above; the oil was separated between an organic phase, of diethyl ether, and an aqueous phase. The addition of potassium iodide to the aqueous phase (3 g of potassium iodide, dissolved in a minimum amount of water), caused a precipitation of crystals, which were collected by filtration. The ^{1}H-NMR, ^{13}C-NMR and DEPT-135 NMR spectra of these crystals were recorded and compared to reference spectra of

4,4'-dimethyldiphenyliodonium iodide. The spectra were identical and so it was concluded that the material isolated was 4,4'-dimethyldiphenyliodonium iodide. Consideration of the ^{1}H-NMR of the electrochemically prepared dimethyldiphenyliodonium iodide and dimethyldiphenyliodonium bisulfate showed that the major fraction of the isolated dimethyldiphenyliodonium salt was the isomer 4,4'-dimethyldiphenyliodonium salt. The ^{1}H-NMR spectrum also showed several minor peaks, not attributable to the 4,4'-dimethyldiphenyliodonium salt. Consideration of the spectra of 2,4'-dimethyldiphenyliodonium iodide, see Section 4.5.1.1, showed that the unassigned peaks in Figure 4.1.3, were due to the presence of the 2,4-dimethyldiphenyliodonium isomer. Therefore the coupling of 4-iodotoluene and toluene led to a mixture of 4,4′-dimethyldiphenyliodonium and 2,4′-dimethyldiphenyliodonium cation. By comparing the relative peak heights in the ^{1}H-NMR spectrum of the isolated material, it was concluded that the isolated dimethyldiphenyliodonium cation contains two isomers, 4,4'-dimethyldiphenyliodonium and 2,4'-dimethyldiphenyliodonium cation in the ratio 9:1. This distribution of product between the two isomers has been previously reported[6, 25]. It is interesting to note that the hplc chromatograms show that the peak eluted at ca. 7.6 minutes, and assigned to the dimethyldiphenyliodonium cation, often has a shoulder, which can be assigned to the minor product 2,4-dimethyldiphenyliodonium cation.

We were interested in seeing how the concentration of reactants and product changed during the course of an electrolysis of 4-iodotoluene and toluene. Therefore the chromatograms shown in Figure 4.1.1 were analysed in order to determine the concentration of reactants and products as a function of charge passed, see Figure 4.1.7.

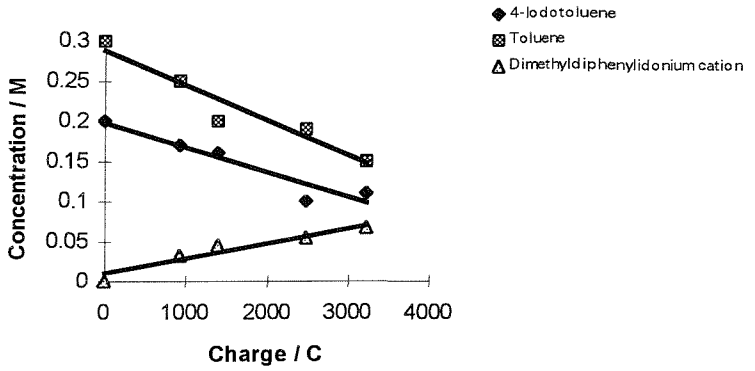


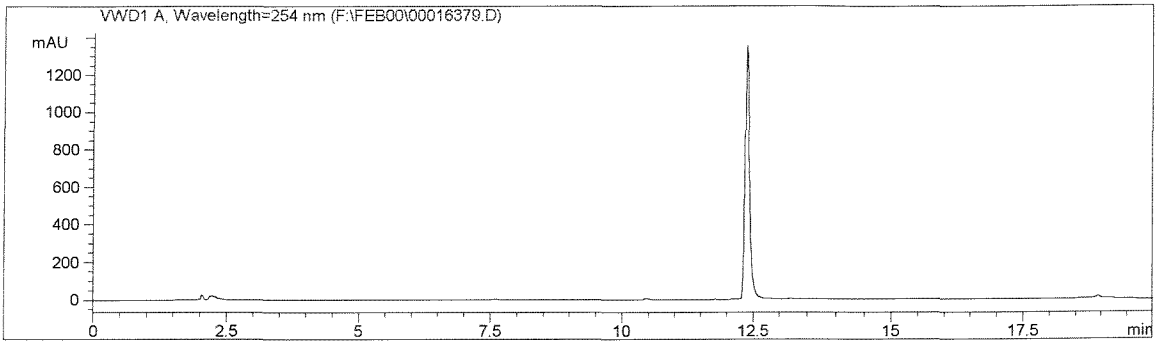
Figure 4.1.7. *The change in concentration of 4-iodotoluene, toluene and dimethyldiphenyliodonium cation, as a function of charge passed, during the galvanostatic electrolysis of a 100 cm^3 solution of 0.2 M 4-iodotoluene and 0.3 M toluene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride. The working electrode was carbon felt and the current density was 5 mA/cm^2.*

The pertinent point to note was that the consumption of reactants, 4-iodotoluene and toluene, were linear with charge passed. The production of dimethyldiphenyliodonium cation was also linear with charge passed. The chemical selectivity of the electrolysis was determined by measuring the ratio of moles of dimethyldiphenyliodonium cation isolated versus the moles of 4-iodotoluene consumed during the electrolysis. The moles of 4-iodotoluene consumed during an electrolysis was calculated by considering the depletion in peak height of 4-iodotoluene in the hplc chromatogram. The concentration of dimethyldiphenyliodonium cation was estimated from the hplc and the peak height was calibrated using a standard solution prepared from crystalline dimethyldiphenyliodonium bisulfate. The current efficiency for the reaction was calculated from amount of charge required to form the moles of isolated iodonium salt divided by the amount of charge that was actually passed during the electrolysis.

The chemical selectivity was 71 % and the current efficiency was 42 %, for the production of the dimethyldiphenyliodonium cation, in the experiment shown in Figure 4.1.7.

4.2 Electrolysis of 4-Iodotoluene

The beaker cell was filled with a solution of only 0.5 M 4-iodotoluene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride. Constant current electrolysis was performed at 298 K by maintaining a current of 400 mA (current density at the anode was ca. 5 mA cm^{-2}) between the two electrodes until the charge passed corresponded to 1.6 F. The electrolysis was again monitored by hplc analysis. The hplc traces corresponding to the solution at the beginning and the end of the electrolysis is shown in Figure 4.2.1.



Chromatogram recorded of a solution of 0.5 M 4-iodotoluene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O.

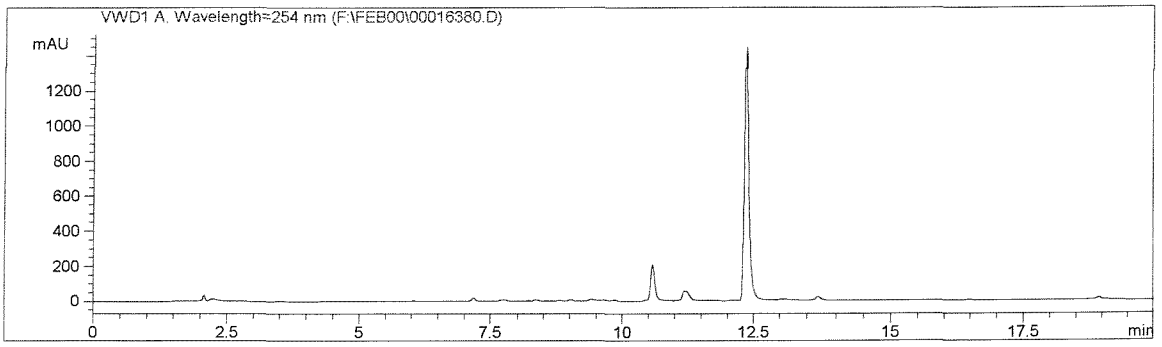


Figure 4.2.1 *Chromatogram of a solution of original composition 0.5 M 4-iodotoluene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O, after a charge of 1.6 F was passed, via a carbon felt anode at constant current of 5 mA/cm^2.*

The key features observed by comparing the hplc trace recorded at the beginning and the end of the electrolysis was that there was hardly any consumption of the 4-iodotoluene although two small additional peaks are seen to develop. The reaction mixture was worked up; the solution was partitioned between an aqueous phase and dichloromethane. An aliquot, of the dichloromethane solution, was removed and diluted

with acetonitrile before being injected onto the hplc column. The hplc trace of the dichloromethane phase showed that it contained the 4-iodotoluene and the two additional product peaks. A further aliquot of the dichloromethane phase was removed and diluted with dichloromethane. This sample was then injected into the GC-MS system, Figure 4.2.2 shows the GC- MS chromatogram.

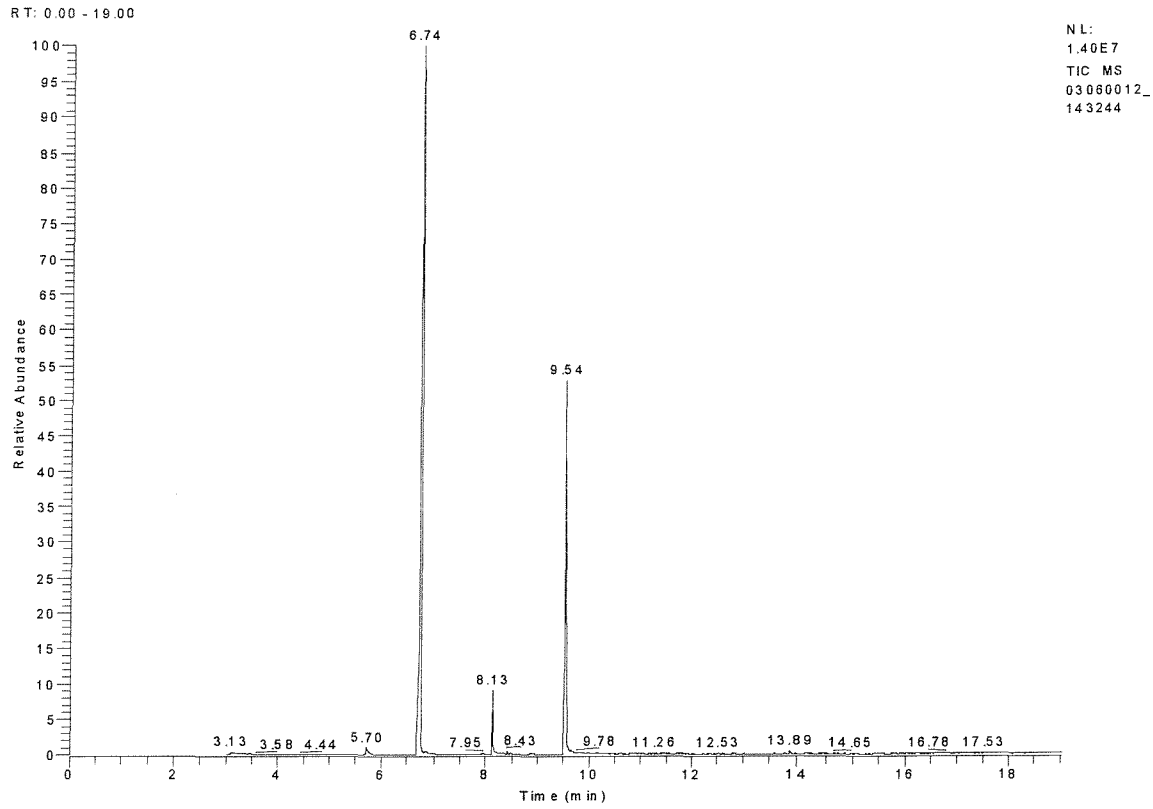


Figure 4.2.2 *Chromatogram of a solution of dichloromethane containing the starting material and non-ionic products of the electrolysis of a solution with an original composition of 0.5 M 4-iodotoluene in AcOH/ 5 % / H_2SO_4/ 25 % Ac_2O.*

The gas chromatogram clearly shows three peaks, with retention times of 6.74, 8.13, and 9.54 minutes. The mass spectra corresponding to the peaks in the gas chromatogram, *ibid,* are reported in Table 4.2.1.

Retention Time	**6.72**		**8.15**		**9.52**	
	m/z	Relative Intensity / %	m/z	Relative Intensity / %	m/z	Relative Intensity / %
	39	24	50	57	43	73
	63	36	51	29	89	100
	65	42	76	36	90	38
	89	23	77	30	217	48
	91	98	231	64	234	75
	218	100	232	100	276	50

Table 4.2.1.

According to Table 4.2.1, the mass spectra for the compound with the shortest elution time in the gas chromatogram, at 6.72 minutes, had a molecular ion of 218 Da. This was what would be expected for 4-iodotoluene, so the first peak in the gas chromatogram, see Figure 4.2.2 was assigned to the elution of 4-iodotoluene. The second peak in the gas chromatogram had an elution time of 8.15 minutes, the mass spectrum of this unknown compound had a molecular ion of 232 Da and there were two daughter ions of m/z 231 and 203 Da, whose relative intensities were 64 and 23 % respectively. The daughter ions were characteristic of an aromatic aldehyde[44], where the more abundant daughter ion resulted from the loss of a hydrogen atom,(232-H), and the lesser from the loss of an aldehyde functionality (232-CHO). Therefore the molecular ion was assigned to 4-iodobenzaldehyde. The last compound to elute from the gas chromatogram with an elution time of 9.52 minutes, had a mass spectrum which contained intense ions whose m/z value were 276, 217 and 43 Da. The ion at 276 Da was assigned to 4-iodobenzylacetate, which could cleave in one of two ways; the heavier ion, 217 Da can result by a charge-site initiated cleavage of 4-iodobenzylacetate, whilst the lighter is the result of radical site initiated cleavage of 4-iodobenzylacetate. The two fragmentation pathways of 4-iodobenzylacetate is summarised in Figure 4.2.3.

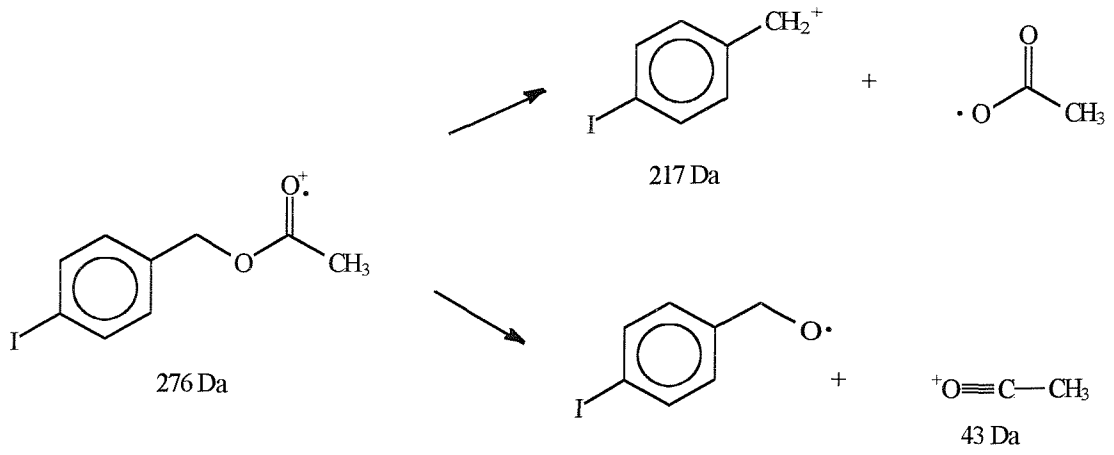
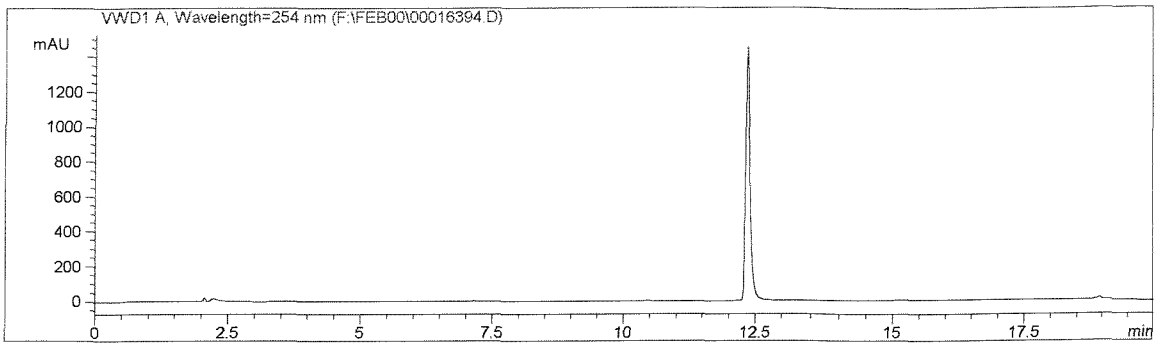


Figure 4.2.3 *Fragmentation pathway of 4-iodobenzyl acetate in the electron impact mass spectrometer.*

A second electrolysis of 4-iodotoluene was carried out in strict accordance with the electrolysis described above. The only parameter changed was to lower the acetic anhydride content in the solution to 2 %, the electrolysis solution contained 4-iodotoluene at a 0.5 M concentration in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride. A charge of 1.6 F was passed at a current density of 5 mA/cm^2 at the carbon felt anode. The hplc traces corresponding to the solution at the beginning and the end of the electrolysis are shown in Figure 4.2.4.



Chromatogram of a solution of original composition; 0.5 M 4-iodotoluene in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O

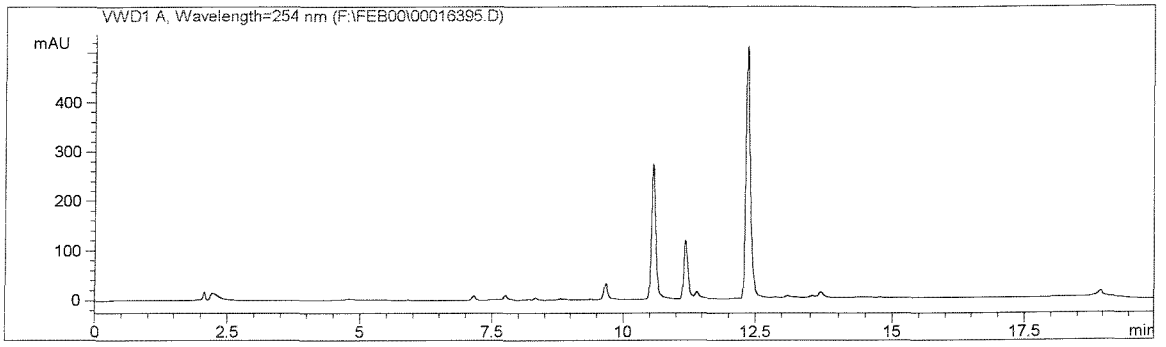


Figure 4.2.4 *Chromatogram of a solution of original composition 0.5 M 4-iodotoluene in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O, after a charge of 1.6 F was passed, via a carbon felt anode at constant current of 5 mA/cm^2.*

The hplc, *ibid*, showed that there was a decrease in the concentration of 4-iodotoluene and two main products were seen to develop. The reaction mixture was worked up in accordance with the procedure described above. Again the dichloromethane phase was analysed by GC-MS in the same way as described above. The GC-MS chromatogram was similar to that to that in Figure 4.2.2, so 4-iodobenzyl acetate and 4-iodobenzaldehyde were identified as reaction products.

In a separate, but relevant electrolysis of 4-iodotoluene; a solution of 0.2 M 4-iodotoluene and 0.3 M toluene in a 100 cm^3 volume of acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride was added to the galvanostatic cell described, see Section 2.2.2 . A charge of 1.5 F was passed, at a constant current of ca. 5 mA/cm^2. The reaction mixture was then partitioned between equal volumes of diethyl ether and water. The aqueous

phase was treated with potassium iodide, 3g dissolved in a minimum amount of water. The subsequent precipitate was isolated and its ^{1}H-NMR was recorded and the material was identified as dimethyldiphenyliodonium iodide. A thin layer chromatogram, TLC, of the diethyl ether phase was carried out where the mobile phase was cyclohexane/ethyl acetate, ratio 1:1. A single mobile spot was seen, under a 254 nm UV lamp. The diethyl ether phase was mixed with a minimum amount of silica. The solvent was then removed under vacuum, leaving the organic compounds loaded on the silica. The silica was then put on to a column of silica and the organic material was eluted with cyclohexane/ethyl acetate, ratio 1:1. The fractions which were seen to contain the UV active spot were collected and the solvent was removed under vacuum . A sample of the clear oil was diluted with chloroform-d_3 and the ^{1}H-NMR spectrum was recorded, see Figure 4.2.5.

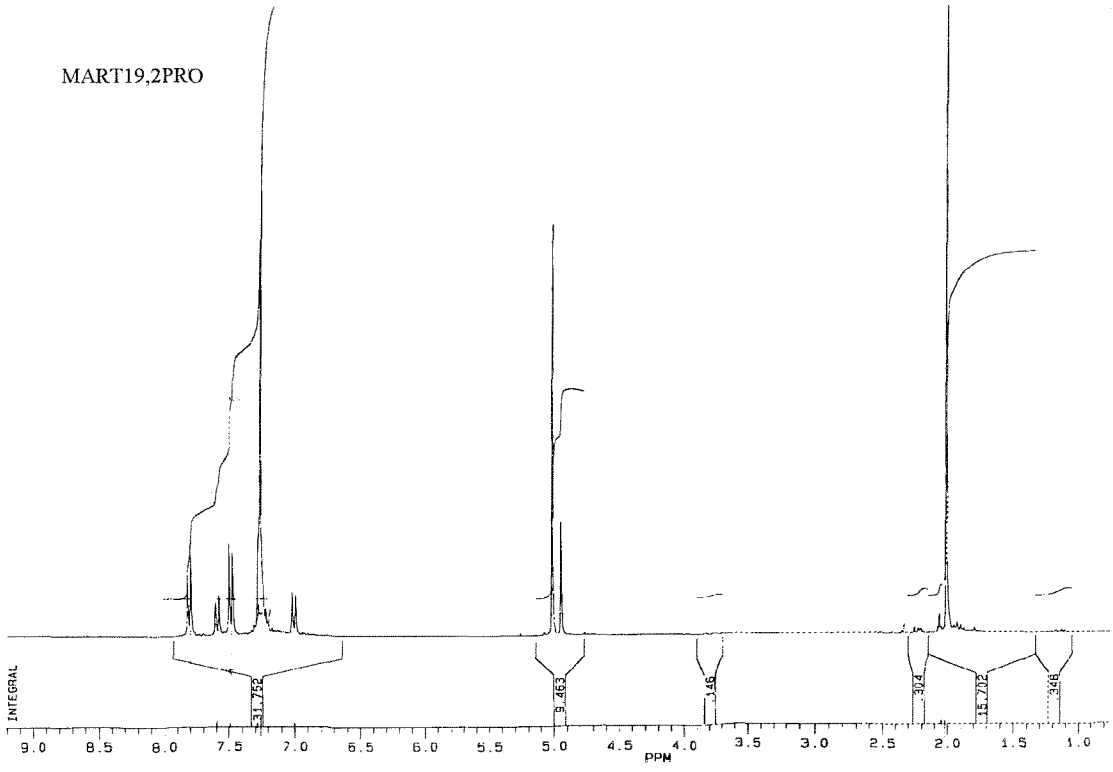


Figure 4.2.5 *^{1}H-NMR of the clear oil separated from the electrolysis reaction of 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/5 % H_2SO_4/ 2 % Ac_2O.*

The key features were that there were two set of doublet signals in the aromatic region. The splitting pattern suggested that both sets of signals were due to *para* substituted phenyl rings.

In addition the ^{13}C-NMR and DEPT-135 spectra of the sample were recorded, see Figure 4.2.6 and Figure 4.2.7 respectively,

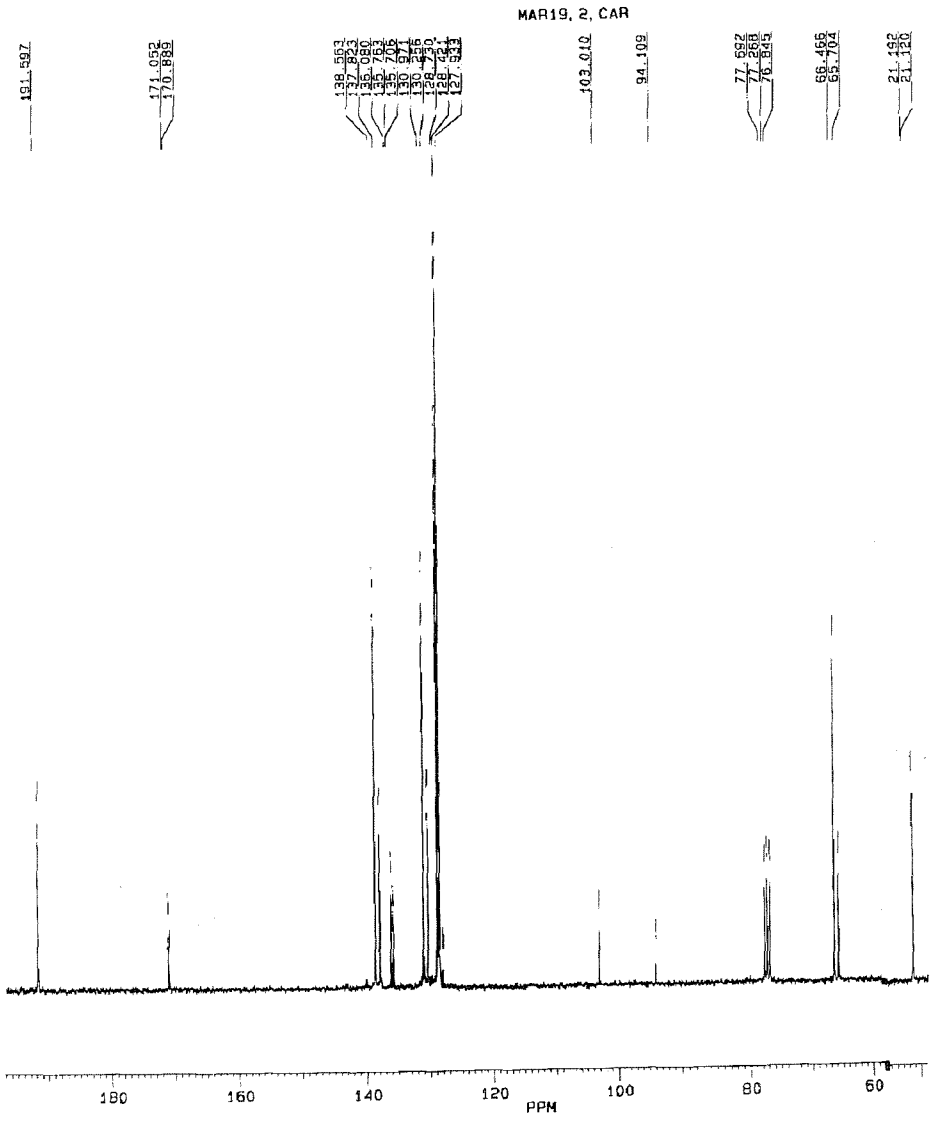


Figure 4.2.6 *^{13}C-NMR of the clear oil separated from the electrolysis reaction of 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O.*

Figure 4.2.7 *DEPT-135 spectrum of the clear oil separated from the electrolysis reaction of 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O.*

A comparison of the ^{13}C-NMR and DEPT-135 spectra was made; a signal in the ^{13}C-NMR spectrum at 171 ppm was not seen in the DEPT-135 spectrum. The down field position of the peak was indicative of a carbonyl group and the fact that it was that was not seen in the DEPT-135 spectrum, suggests that an ester functional group was

present in the sample. A signal at 191.6 ppm was seen in the ^{13}C-NMR and the DEPT-135 spectra, again the position of the signal would suggest a carbonyl group and the fact that the signal was present in the DEPT-135 signal infers an aldehyde group was present[35]. There were two signals, at 66.5 and 65.7 ppm, in the ^{13}C-NMR, both of which showed a negative phase in the DEPT-135 spectrum, which meant they were methylene carbon atoms. These signals had a relatively down field chemical shift value. It was therefore concluded they were benzyl carbon atoms. There were two signals, at 103.0 and 94.1 ppm, present in the ^{13}C-NMR, but which were not present in the DEPT-135 spectrum. It was concluded that these were quaternary carbon atoms.

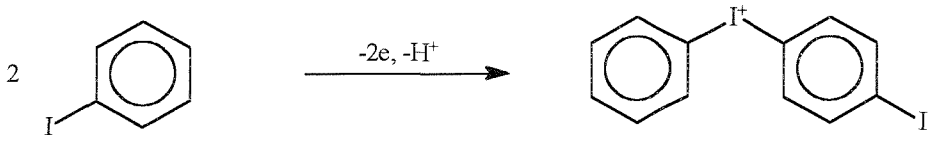
The structure of the products, 4-iodobenzylacetate and 4-iodobenzaldehyde, was confirmed by consideration of the ^{1}H-NMR spectrum, see Figure 4.2.5. The peaks in the ^{1}H-NMR were assigned to the functionalities of 4-iodobenzylacetate and 4 iodobenzaldehyde, see Table 4.2.2

Functionality in 4-Iodobenzyl acetate	**δ ppm**	**Functionality in 4-Iodobenzaldehyde**	**δ ppm**
Ar-H	7.80	Ar-CHO	9.85
Ar-H	7.50	Ar-H	7.60
Ar-CH_2	5.00	Ar-H	7.00
CH_3	2.00	Ar-CH_2	4.95

Table 4.2.2

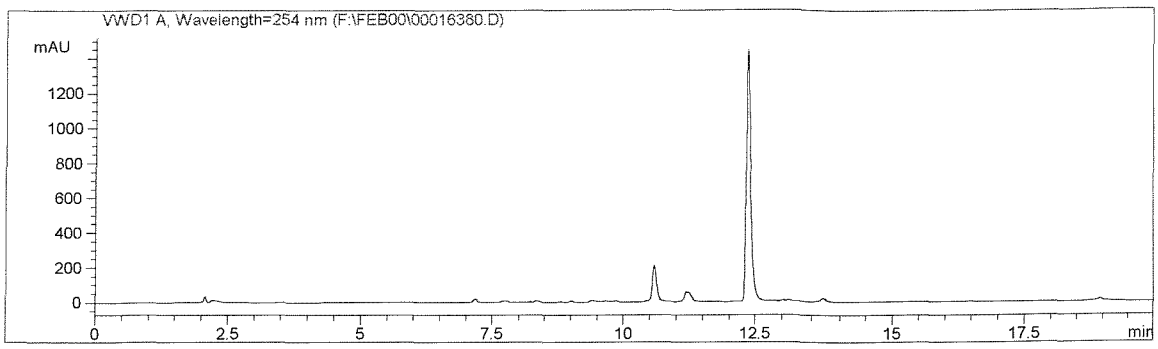
There were no unassigned peaks left, in the ^{1}H-NMR spectrum, after this assignment procedure. The intensity of the peaks in the ^{1}H-NMR indicated that in the isolated material the 4-iodobenzylacetate and 4-iodobenzaldehde were in the ratio 2:1.
In addition the ^{13}C-NMR and DEPT-135 spectra provided additional evidence to confirm that 4-iodobenzylacetate and 4-iodobenzaldehyde were in the isolated material..
In conclusion the products identified from the electrolysis of 4-iodotoluene with no toluene present were 4-iodobenzyl acetate and 4-iodobenaldehyde.

There was no evidence for the self coupling of 4-iodotoluene, to give an iodonium salt. Which was consistent with the observation made by Weinberg[25], who similarly reported that in his electrolysis system there was no self coupling product of 4-iodotoluene. This lack of self coupling of 4-iodotoluene is an interesting observation, when contrasted with that made by Hoffmann[23] and Wendt[24], who both reported that the major product of iodobenzene electrolysis in acetonitrile/perchlorate was 4-iododiphenyliodonium salt, see Scheme 4.2.1.



Scheme 4.2.1

A comparison of the hplc of 4-iodotoluene after 1.6 F was passed, in the solvent containing 25 % and 2 % acetic anhydride made in Figure 4.2.8. It is clear that both solution gave 4-iodobenzyl acetate and 4-iodobenzaldehyde as the products of electrolysis. It was apparent that there was a much higher yield of the 4-iodobenzyl acetate and 4-iodobenzaldehyde for the electrolysis in 2 % acetic anhydride compared to the 25 % acetic anhydride solution.



Chromatogram of a solution of original composition 0.5 M 4-iodotoluene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O, after a charge of 1.6 F was passed, via a carbon felt anode at constant current of 5 mA/cm^2.

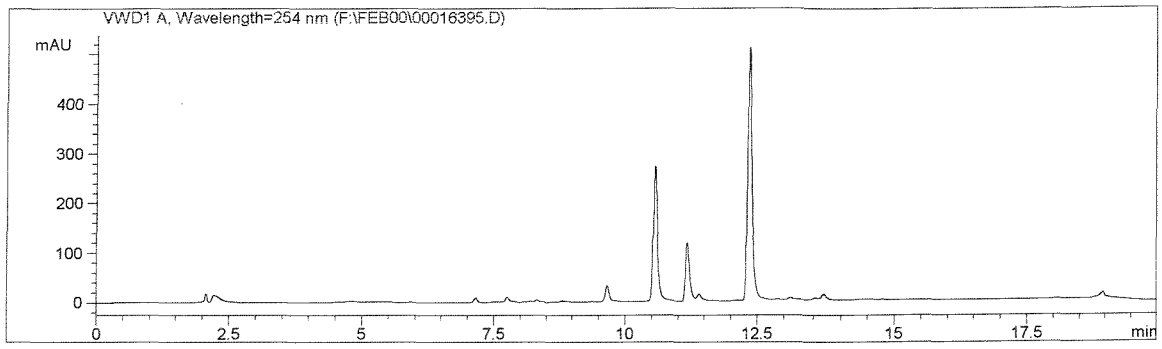
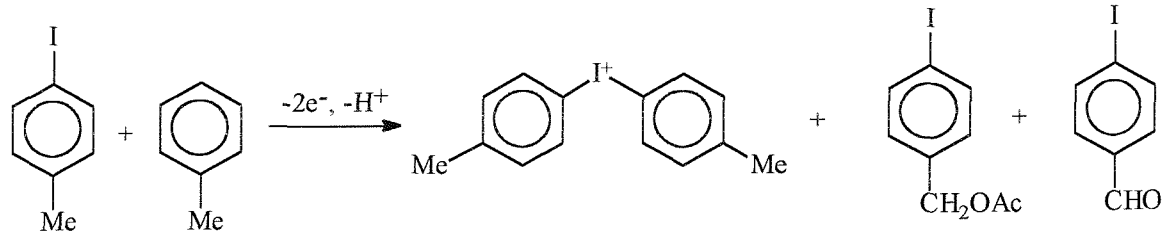


Figure 4.2.8 *Chromatogram of a solution of original composition 0.5 M 4-iodotoluene in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O, after a charge of 1.6 F was passed, via a carbon felt anode at constant current of 5 mA/cm^2.*

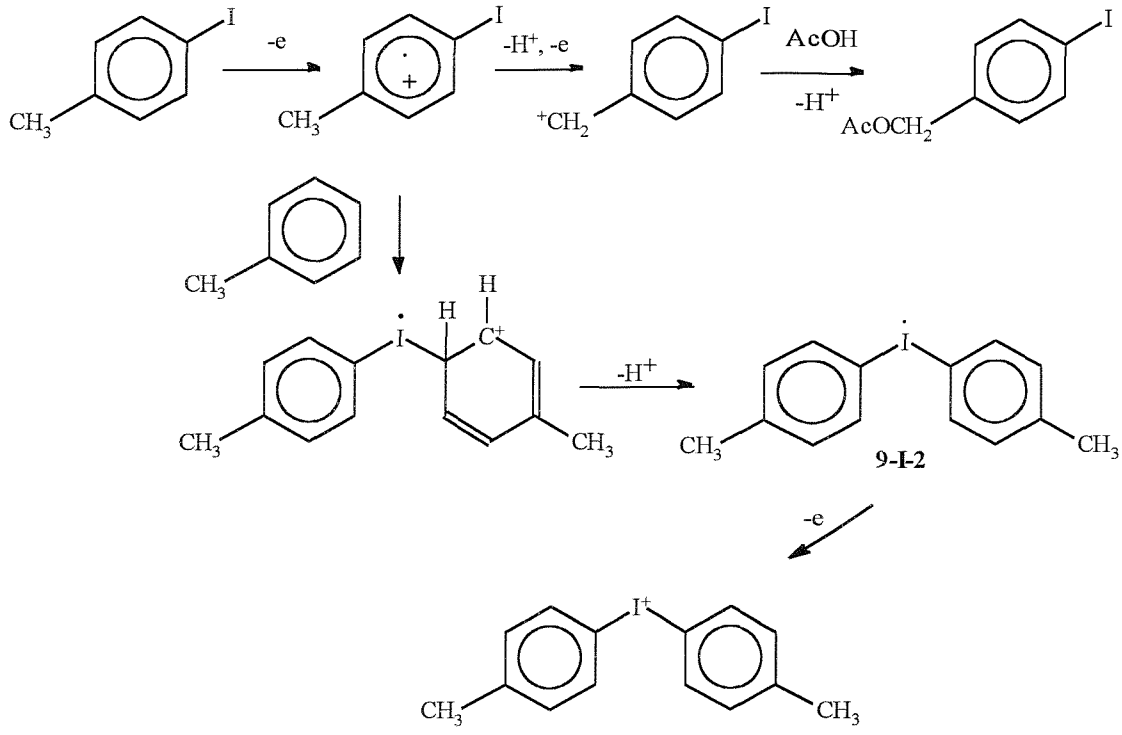
4.3 Consideration of the Mechanism: Oxidative Coupling of 4-Iodotoluene and Toluene

Three products were identified in the solution at the end of the electrolysis of 4-iodotoluene and toluene; dimethyldiphenyliodonium cation, 4-iodobenzyl acetate and 4-iodobenzaldehyde, the latter was very much the minor product, see Scheme 4.3.1.



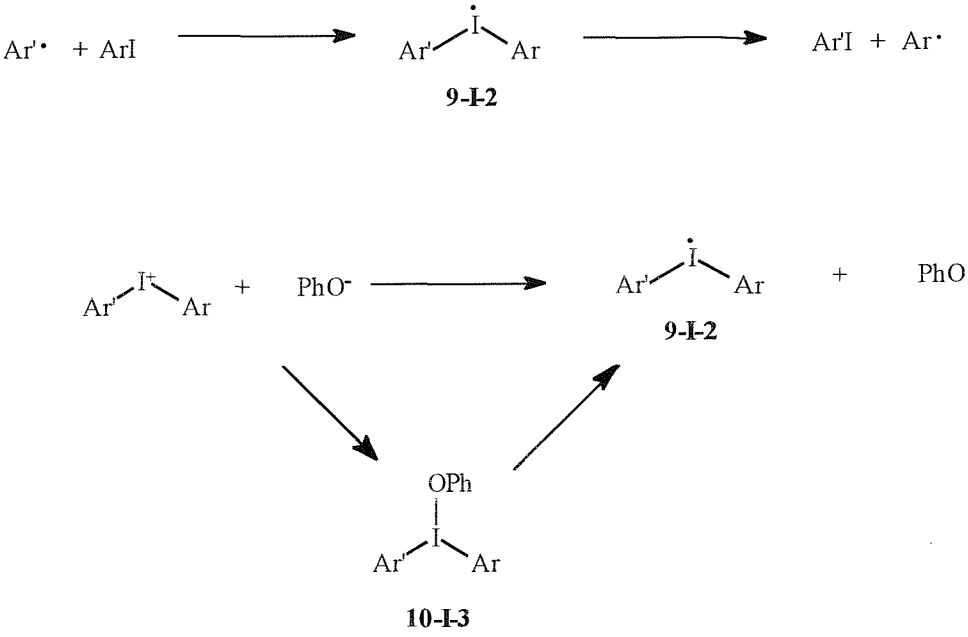
Scheme 4.3.1.

Acetoxylation of the alkyl moiety in a acetic acid media at a carbon electrode is a well documented reaction[30] and its production can be seen to occur through a possible common intermediate with that of the dimethyldiphenyliodonium cation. This is shown in Scheme 4.3.2.



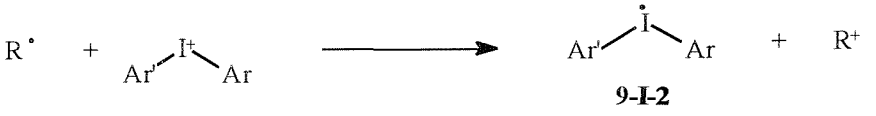
Scheme 4.3.2.

It can be seen above that the 4-iodotoluene cation radical undergoes competing reactions, loss of a proton and attack on toluene. The reaction with the toluene is shown to give a neutral radical intermediate, which according to Martin-Arduengo classification[27] is 9-I-2. The hypervalent iodanyl radical, 9-I-2, has been sited in the literature in the nucleophilic substitution[33] of diaryliodonium salts and in the mechanism for iodine transfer, between a radical and an aryl iodide[29,33], see Scheme 4.3.3.



Scheme 4.3.3

The same intermediate is postulated to explain the role of diaryliodonium salts play in photoinitiated polymerisation, where the diaryliodonium salt is reduced by a radical. The subsequent cation then initiates polymerisation[34], see Scheme 4.3.4.



Scheme4.3.4.

The electrochemical oxidation of perfluoroalkyl iodides and their subsequent reaction with solvent or electrolyte molecules is also believed to through a 9-I-2 intermediate[28]. It was therefore not unreasonable to conclude that such a 9-I-2 species was involved in our mechanism.

The benzaldehyde was formed by the further oxidation of the 4-iodobenzyl acetate. Acetic acid then nucleophilically adds to the exo-cyclic carbon resulting in the diacetate. The hydrolysis of the diacetate to the geminal diol and the de-condensation of this intermediate forms the aldehyde.

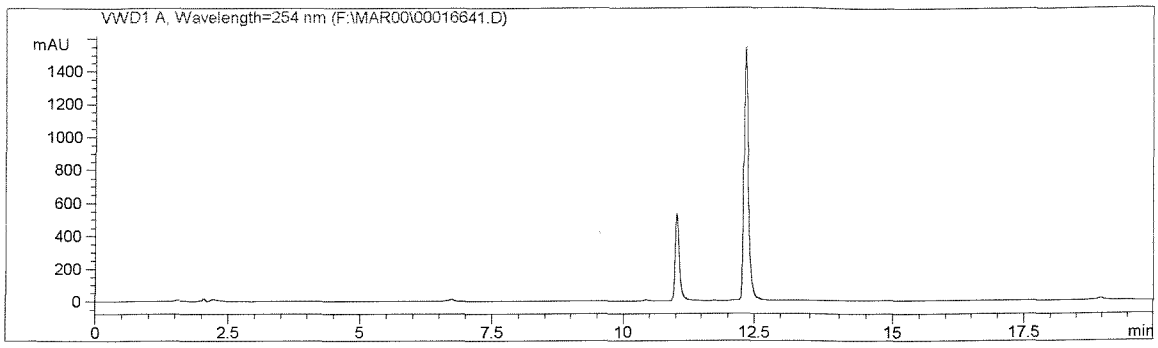
4.4 Development of Optimum Electrolysis Conditions: Electrolysis of 4-Iodotoluene and Toluene

It was important to establish how the electrolysis conditions effected the chemical selectivity and current efficiencies in respect to the electrosynthesis of diaryliodonium salts from the coupling of aryl iodide and arenes. A number of experiments were run where one parameter at a time was changed. The coupling of 4-iodotoluene and toluene was chosen as the model system. The parameters that were investigated were; the acetic anhydride content of the solvent system, the supporting electrolyte and the current density.

The coupling of 4-iodotoluene and toluene was used because of the previously reported success of the reaction shown above and reported earlier[25].

4.4.1.Acetic Anhydride Content

The effect that the acetic anhydride content of the solvent system had on the electrolysis of 4-iodotolunene and toluene was investigated. As previously described, see Section 2.2.2, the electrolysis cell was filled with a solution of 0.2 M 4-iodotoluene and 0.3 M toluene in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride. Constant current electrolysis was performed at 298 K, by maintaining a current of 400 mA (current density at the anode was ca. 5 mA cm^{-2}), between the two electrodes until the charge passed corresponded to 1.6 F had passed. The hplc chromatograms corresponding to the solution at the beginning and the end of the electrolysis are shown in Figure 4.4.1.1. At the end of the electrolysis an aliquot was removed and the electrospray mass spectrum of the solution was recorded. The electrospray mass spectrum showed an ion of m/z 309 Da of 100 % relative intensity, that was expected for the dimethyldiphenyliodonium cation



Chromatogram of a solution of original composition 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O

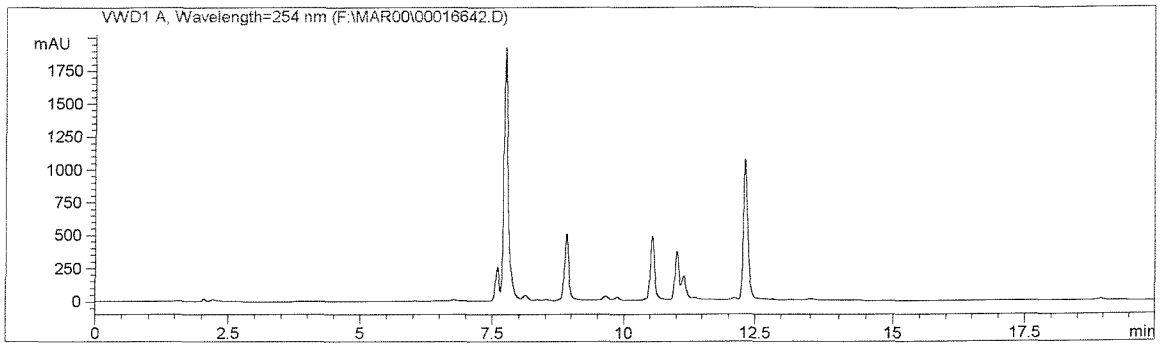


Figure 4.4.1.1 *Chromatogram of a solution of original composition 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O after a charge of 1.6 F had been passed.*

The key features observed by comparing the hplc trace recorded at the beginning and the end of the electrolysis was; there was a decrease in the concentration of 4-iodotoluene and toluene, three minor peak were seen to develop, with retention times of 11.0 10.5 and 8.9 minutes, and a major peak developed, with a retention time of 7.6 minutes

The reaction mixture was worked up in accordance with the standard procedure. The addition of the potassium iodide solution caused an immediate precipitation of white powder. This material was separated on the filter paper, and dried. A yield of 1.02 g was recorded. The ^{1}H-NMR, ^{13}C-NMR, and DEPT-135 analysis of the isolated material was carried out and the spectrum compared to that of 4,4'-dimethyldiphenylioodonium iodide, the material was similarly identified as the dimethyldiphenyliodonium iodide.. The chemical selectivity and current efficiency was 38 % and 16 % respectively.

The ether layer was reduced in volume under vacuum to a dark oil. This oil was diluted with dichloromethane, an aliquot was removed and further diluted with acetonitrile for hplc analysis, see Figure 4.4.1.2.

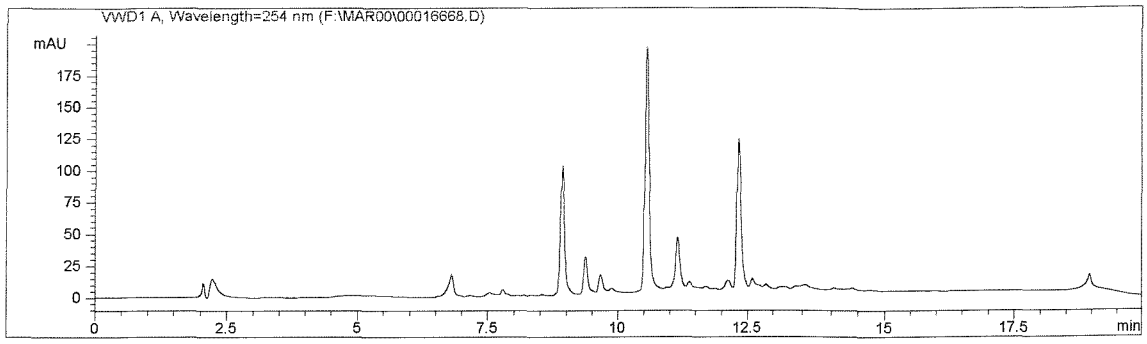


Figure 4.4.1.2 *Chromatogram of a dichloromethane solution containing the lipophilic products of the electrolysis of 4-iodotoluene and toluene in AcOH/ 5 % H_2SO_4/ 2 Ac_2O*

It was seen from the chromatogram, *ibid,* that the three minor product peaks identified, with retention times of 11.0, 10.5 and 8.9 minutes, were present in the dichloromethane solution. A further aliquot of the dichloromethane solution was removed and diluted with dichloromethane and submitted for GC-MS analysis, see Figure 4.4.1.3.

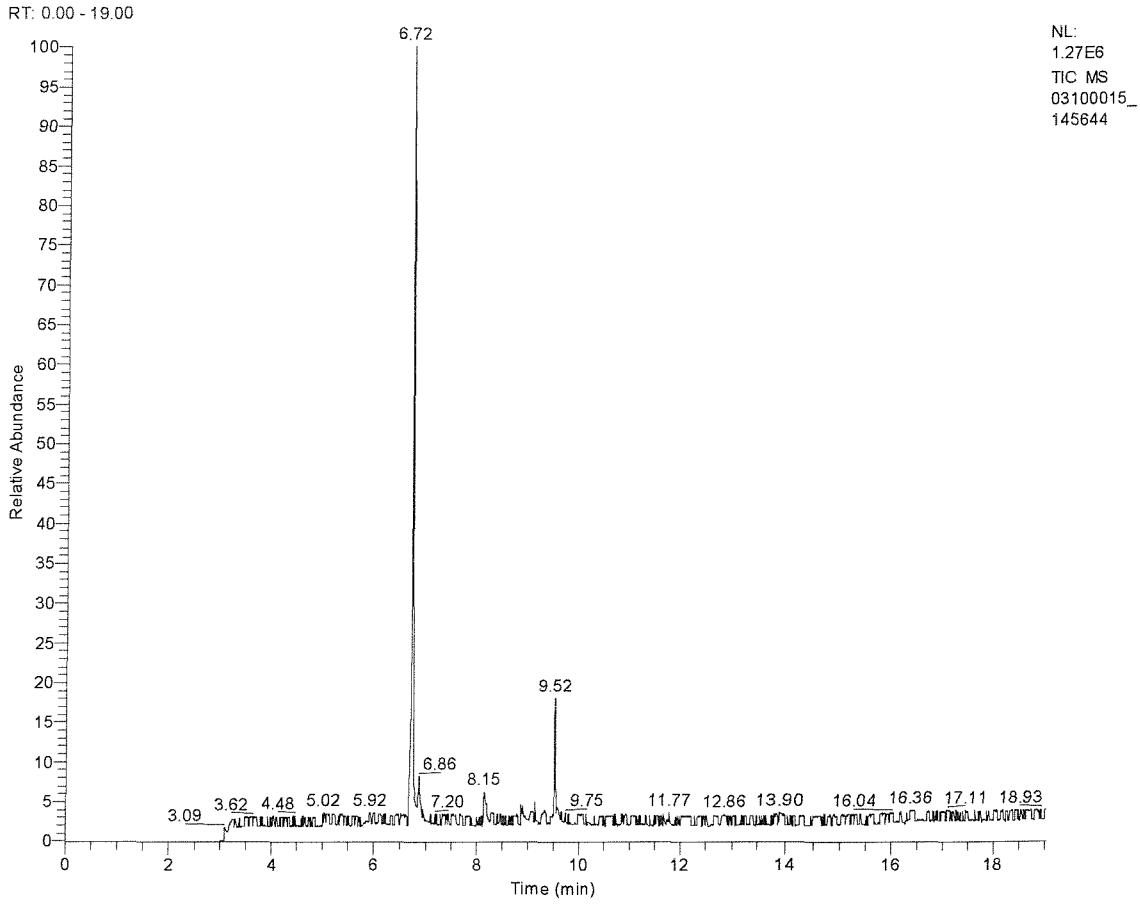


Figure 4.4.1.3 *Gas chromatogram of a dichloromethane solution containing the lipophilic products of the electrolysis of 4-iodotoluene and toluene in AcOH/ 5 % H_2SO_4/ 2 Ac_2O.*

There peaks were seen in the gas chromatogram; at 6.7, 8.2 and 9.5 minutes. Comparison of the retention times to those in Figure 4.2.2, showed that the peaks belonged to 4-iodotoluene, 4-iodobenzylacetate and 4-iodobenzaldehyde. The peak seen at 8.90 in the hplc chromatogram, see Figure 4.4.1.2, did not have a corresponding peak in the gas chromatogram.

The electrolysis of 4-iodotoluene and toluene was repeated, but where the acetic anhydride content was raised to 10 %. The electrolysis of a solution of 0.2 M 4-iodotoluene and 0.3 M toluene in acetic acid/ 5 % sulfuric acid/ 10 % acetic anhydride was carried out in the cell described above. Again a charge of 1.6 F was passed . The reaction was worked up in accordance with the procedures detailed above and a yield of

1.73 g of isolated material was recorded. The ^{1}H-NMR, ^{13}C-NMR, and DEPT-135 spectra were recorded and the material was again in the main 4,4'-dimethyldiphenyliodonium iodide with ca. 10 % of the isolated material being due to the 2,4'-dimethyldiphenyliodonium iodide.

The electrolysis of 4-iodotoluene and toluene was repeated for a third time, but where the acetic anhydride content was raised to 25 %. The electrolysis of a solution of 0.2 M 4-iodotoluene and 0.3 M toluene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride was carried out in the cell described above. Again a charge of 1.6 F was passed . The reaction was worked up in accordance with the procedures detailed above and a yield of 3.07 g of isolated material was recorded. The ^{1}H-NMR, ^{13}C-NMR, and DEPT-135 spectrum were recorded and 4,4'-dimethyldiphenyliodonium iodide was the main product, with ca. 10 % of the other isomer.
The chemical selectivity and current efficiency as a function of acetic anhydride content is summarised in Table 4.4.1.1

% Ac_2O	Chemical selectivity %	Current efficiency %
2	46	7.8
10	66	25
25	92	46

Table 4.4.1.1

It was seen that the acetic anhydride content of the reaction medium had a strong influence on the yield of the diaryliodonium salt. As the acetic anhydride content was raised, it was apparent that the reaction was more selective with respect to the diaryliodonium cation. Indeed, this is obvious as a qualitative conclusion from the hplc response. These also show that the yield of 4-iodobenzyl acetate and 4-iodobenzaldehyde increase with decreasing acetic anhydride content.

It was noted that the efficient coupling of 4-iodotoluene with toluene occurred in the solvent system, acetic acid/5 % sulfuricacid/25 % sulfuric acid, in contrast Weinberg[25] reported the efficient coupling of 4-iodotoluene and toluene in acetic acid/5 %sulfuric acid/ 2 % acetic anhydride. This difference may arise from the difference in the water content of the acids used, where the role of excess acetic anhydride is to 'mop up' water in the system.

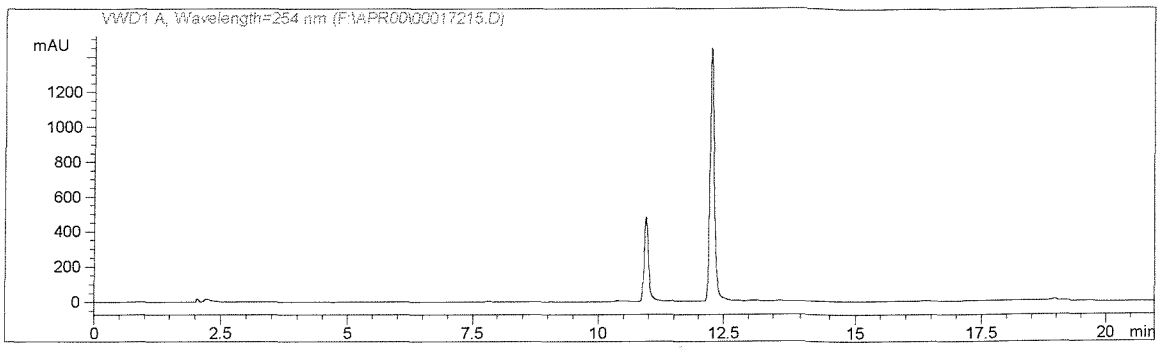
Hoffmann[23], see Section 1.5, similarly notes that the presence of water in the electrolysis solvent precludes the formation on an iodonium salt. In Section 2.4.2 we carried out the reaction between toluene and potassium iodate, in an acid medium in accordance with the procedure developed by Beringer[45]. If we consider the solvent composition in terms of the mass of the sulfuric acid and acetic anhydride relative to the mass of acetic acid, then the solvent composition used by Beringer was; acetic acid/ 29 % sulfuric acid/ 35 % acetic anhydride. Similarly Kazmierzak[6], see Section 1.3.1, carried out the oxidative coupling of aryl iodide and arene in a solvent medium whose composition was calculated to be; acetic acid/ 58 % sulfuric acid/ 48 % acetic anhydride.

It was noted that both these organic reactions were carried out in a solvent medium containing acetic acid, sulfuric acid and acetic anhydride. The use of a relatively high percentage of acetic anhydride, in both synthetic procedures, may suggest a solvent effect for the acetic anhydride, other than simply 'mopping up' excess water when it was raised from 2 to 25 % in our electrolysis medium.

4.4.2 Supporting Electrolyte

Another parameter was the strong acid.

The cell described in Section 2.2.2 was again used and the identical procedure was employed. The solution in the first electrolysis was 0.2 M 4-iodotoluene and 0.3 M toluene in acetic acid/ 5 % trifluoromethanesulfonic acid/ 2 % acetic anhydride. The hplc traces corresponding to the solution at the beginning and the end of the electrolysis are shown in Figure 4.4.2.1



The chromatograms recorded after a charge of 0 F had been passed. The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % CF_3SO_3H/ 2 % Ac_2O

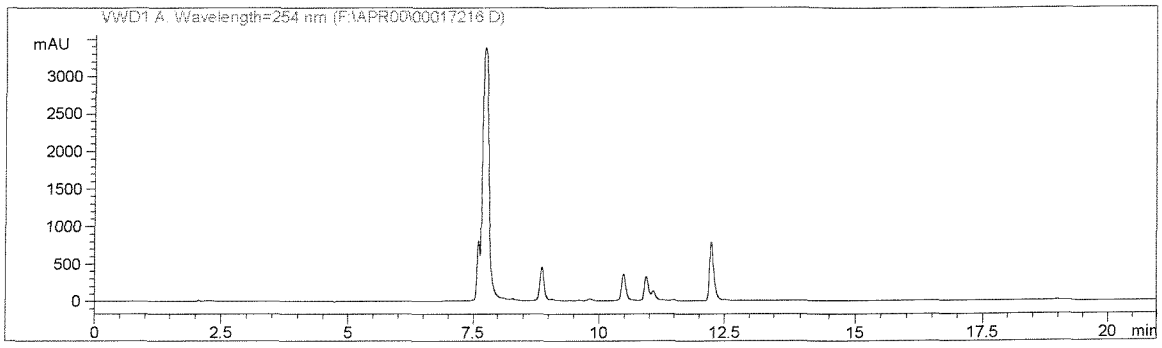
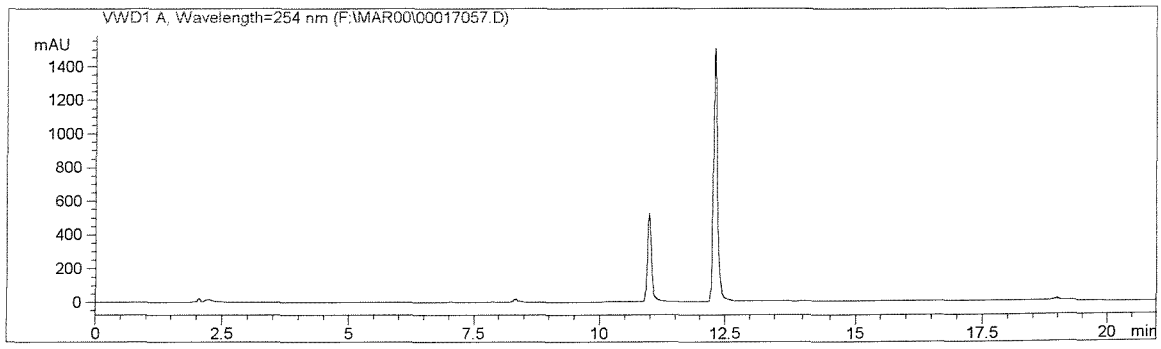


Figure 4.4.2.1 *The chromatograms recorded after a charge of 1.5 F had been passed. The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % CF_3SO_3H/ 2 % Ac_2O*

Consideration of the hplc chromatograms shown in Figure 4.4.2.1 show that there was consumption of the starting material and there was the production of a major peak at ca. 7.6 minutes. Aliquots was removed and diluted with acetonitrile for electrospray mass spectroscopy. The electrospray mass spectrum showed a single ion of m/z 309 Da, which was what was expected for the dimethyldiphenyliodonium cation. The electrolysis solution was worked up in accordance with the procedure described in Section 2.2.2. A 2.34 g yield of crystals was found. The ^{1}H-NMR, ^{13}C-NMR, and DEPT-135 analysis was carried out. The NMR spectra were compared to those of dimethyldiphenyliodonium iodide, prepared in accordance with the methodology of Beringer[45], see Section 2.4.2. The spectra of the material isolated by precipitation with potassium iodide from the 'worked up' electrolysis solution cell was identical to the reference spectra of 4,4'-dimethyldiphenyliodonium iodide, see Figure 2.4.2.1. Again it

was determined from the NMR spectra that ca. 10 % of the isolated material was the 2,4'-dimethyldiphenyliodonium iodide isomer. The chemical selectivity and current efficiency of the reaction with respect to the dimethyldiphenyliodonium cation was 57 % and 37 % respectively.

In a similar procedure to that described above, see Section 2.2.2, the electrolysis cell as charged with a solution of 0.2 M 4-iodotoluene and 0.3 M toluene in acetic acid/ 8 % fluoroboric acid/ 2 % acetic anhydride. The hplc traces corresponding to the solution at the beginning and the end of the electrolysis is shown in Figure 4.4.2.2.



The chromatograms recorded after a charge of 0 F had been passed. The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 8 % HBF_4/ 2 % Ac_2O

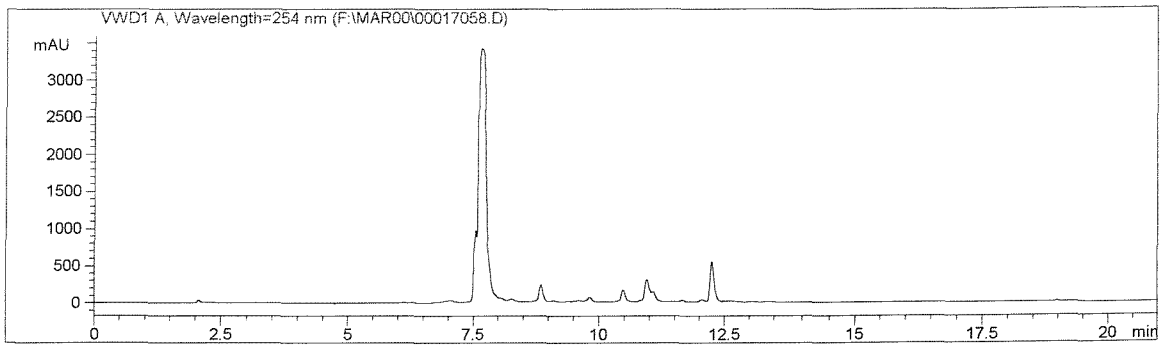
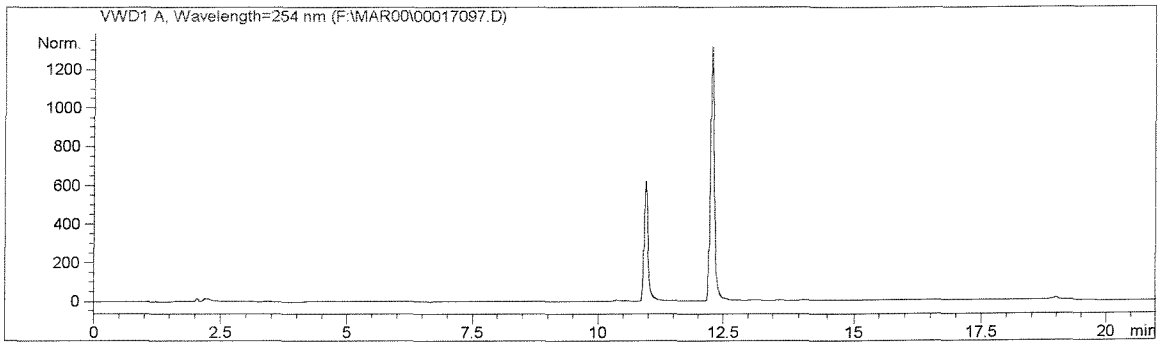


Figure 4.4.2.2 *The chromatograms recorded after a charge of 1.7 F had been passed. The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 8 % HBF_4/ 2 % Ac_2O.*

The reaction was worked up in accordance with the procedure described previously. The product was isolated by precipitation with potassium iodide and a yield of 7 g was recorded. The ^{1}H-NMR, ^{13}C-NMR, and DEPT-135 analysis was carried out and the

spectra was consistent with the dimethyldiphenyliodonium iodide. The chemical selectivity and current efficiency was 100 % and 96 % respectively.

Again in accordance with the procedure so far described, the electrolysis cell was charged with a solution of 0.2 M 4-iodotoluene and 0.3 M toluene in acetic acid/ 5 % methanesulfonic acid / 2 % acetic anhydride. Constant current electrolysis was performed at 298 K by maintaining a current of ca. 200 mA (current density at the anode was ca. 2.5 mA cm^{-2}), between the two electrodes until the charge passed corresponded to 1.6 F. It was necessary to use a lower current because the potentiostat was not able to give high enough voltage for a current of 400 mA. The hplc traces corresponding to the solution at the beginning and the end of the electrolysis is shown in Figure 4.4.2.3.



The chromatograms recorded after a charge of 0 F had been passed. The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % CH_3SO_3H/ 2 % Ac_2O

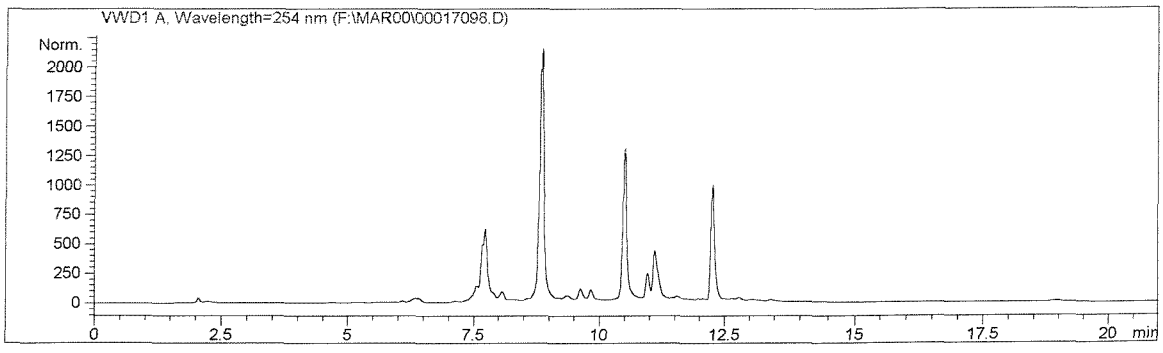


Figure 4.4.2.3 *The chromatograms recorded after a charge of 1.6 F had been passed. The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % CH_3SO_3H/ 2 % Ac_2O.*

Consideration of the hplc showed that there was a small peak at 7.6 minutes which was assigned to the dimethyldiphenyliodonium cation as well as peaks at 11.0 and 10.5 minutes, that were previously assigned to 4-iodobenzylacetate and 4-iodobenzaldehyde. There was also a substantial peak at 8 minutes, which was not identified.
The reaction mixture was worked up in accordance with the standard procedure. The aqueous phase was separated and treated with potassium iodide,3 g dissolved in a minimum amount of water. The addition of the potassium iodide solution, caused a cloudy appearance to the solution. It was decided to reduce the volume of solvent to 'encourage' precipitation, which was done under vacuum. Subsequent filtration of the aqueous phase failed to give enough material to be quantifiable. The hplc chromatogram, see Figure 4.4.2.3, shows a peak at 7.6 minutes, which has consistently proven to be for the dimethyldiphenyliodonium cation.

The effect of changing the supporting electrolyte on the chemical selectivity and current efficiency with respect to the formation of dimethyldiphenyliodonium salt is summarised in Table 4.4.2.1.

Solvent System; AcOH/ 2 % Ac_2O	**Chemical Selectivity %**	**Current Efficiency %**
5% H_2SO_4/	46	11
5% $MeSO_3H$/	10 <	10 <
5% CF_3SO_3H/	57	37
8% HBF_4	100	96

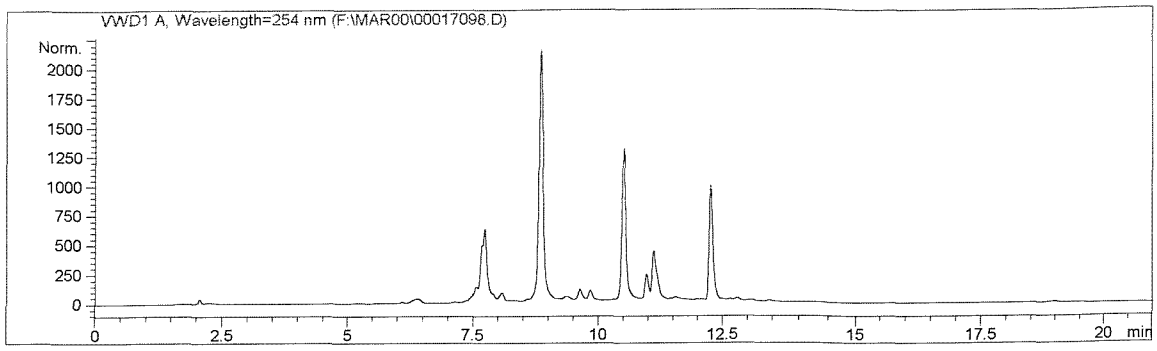
Table 4.4.2.1.

It was seen that by changing the strong acid parameter in the system there was a considerable effect on the chemical selectivity and current efficiency with respect to the formation of dimethyldiphenyliodonium cation. This was probably due to the relative resistance of the anion to anodic oxidation; fluoroborate was more resistant than methanesulfonate to oxidation at the anode and so gave the better yield of the

dimethyldiphenyliodonium cation. Similarly Fleischmann and Pletcher[38] showed that an increase in the 'useful' potential range of acetonitrile was possible by changing the anion in solution. They found that the potentials for which acetonitrile may be used as a supporting solvent was dependent on the anion and were in the order, PF_6^-> BF_4^-> ClO_4^-.

It was noted that a graphite rotating disc electrode, See Section 3.2.2, has shown "oxidation of the electrode". It was possible that this oxidation was influenced by the anion in solution, by modification of functional groups on the surface or through intercalation.

It was also possible that the acid influenced the speciation in the reaction mixture. Figure 4.4.2.4 shows the chromatogram recorded at the end of the electrolysis. The starting materials, 4-iodotoluene and toluene, had retention times of 12.3 and 10.9 minutes respectively. There were four product peaks seen in the chromatograms with retention times of 11.1, 10.5, 8.8 and 7.7 minutes. The peak at 7.7 minutes was indicative of the iodonium salt. The peaks at 10.5 and 8.8 minutes had previously been seen in the electrolysis of 4-iodotoluene when no toluene was present, see Section 4.2, and were assigned to 4-iodobenzyl acetate and 4-iodobenzaldehyde. In the chromatogram of the solution of 4-iodotoluene with no toluene present after electrolysis, there was no sign a peak at ca. 8.8 minutes. It was therefore apparent that the peak at 8.8 minutes was associated with toluene and its production was promoted by changing the acid from sulfuric acid to methanesulfonic acid, see Figure 4.4.2.4 The peak was not identified, but the chromatogram of an authentic sample of benzyl acetate was recorded under identical elution conditions. The retention time of benzyl acetate was 9.7 minutes, which eliminated it from being the unknown peak.



The chromatograms recorded after a charge of 1.6 F had been passed. The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % CH_3SO_3H/ 2 % Ac_2O

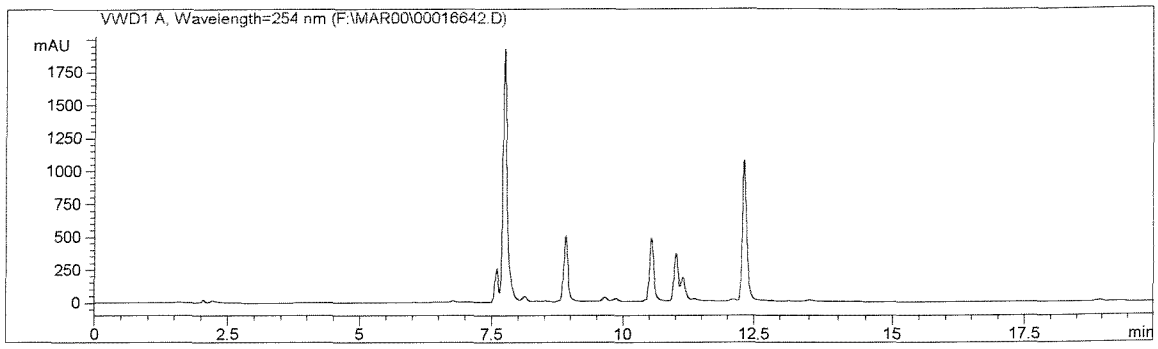


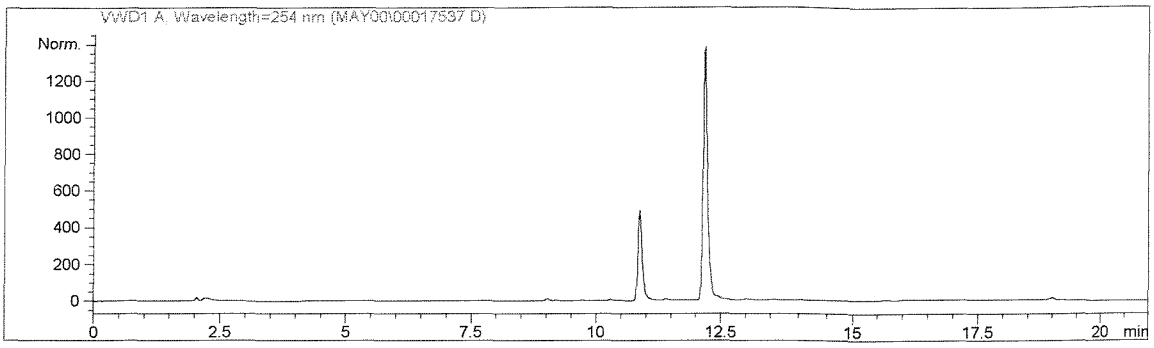
Figure 4.4.2.4 *Chromatogram of a solution of original composition 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O after a charge of 1.6 F had been passed.*

In Section 4.6, it will be shown that the chemistry of anisole is influenced strongly by the medium.

4.4.3 Current Density

The current density was changed in a series of electrolysis of 0.2 M 4-iodotoluene and 0.3 M toluene in acetic acid/5 % sulfuric acid/ 25 % acetic anhydride, to investigate its effect on the production of iodonium salts.

The electrolysis cell with a graphite cathode, surrounded by a carbon felt anode (approximate surface area of 52 cm^2) was charged with a 50 cm^3 solution of 0.2 M 4-iodotoluene and 0.3 M toluene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride. Constant current electrolysis was performed at 298 K, by maintaining a current of 104 mA (current density at the anode was ca. 2 mA cm^{-2}), between the two electrodes until the charge passed corresponded to 1.4 F. The hplc traces corresponding to the solution at the beginning and the end of the electrolysis is shown in Figure 4.4.3.1.



The chromatograms recorded after a charge of 0 F had been passed. The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O.

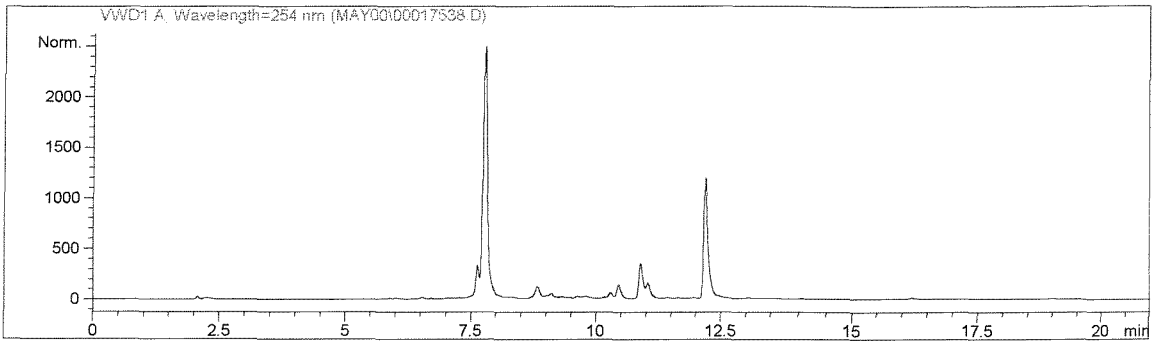
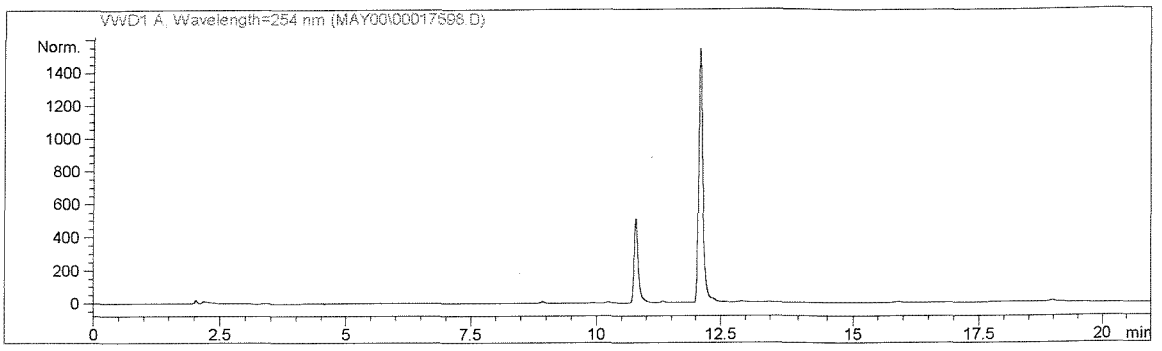


Figure 4.4.3.1 *The chromatograms recorded after a charge of 1.4 F had been passed, at a current density of 2 mA/cm^2. The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O.*

The reaction mixture was worked up in accordance with the following procedure; the electrodes were washed with hot methanol and the washings were combined with the reaction mixture. The solvents were removed *in vacuo* and the resulting oil was partitioned between an aqueous phase and diethyl ether. The aqueous phase was separated and treated with potassium iodide, 1.66g dissolved in a minimum amount of water. The addition of the potassium iodide solution caused an immediate precipitation of white powder. This material was separated on the filter paper, and dried. A yield of 0.62 g was recorded The ^{1}H-NMR, ^{13}C-NMR, and DEPT-135 analysis of the isolated material was carried out and the spectra compared to the reference spectra of 4,4'-dimethyldiphenylioodonium iodide. It was determined that ca 10 % of the yield was the 2,4'-dimethtyldiphenyliodonium iodide isomer. The chemical selectivity and current efficiency was 35 % and 19 % respectively.

A second electrolysis was performed on a fresh solution at a current of 208 mA (current density at the anode was ca. 4 mA cm^{-2}). The hplc traces at the beginning and the end of the electrolysis are shown in Figure 4.4.3.2.



The chromatograms recorded after a charge of 0 F had been passed. The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O

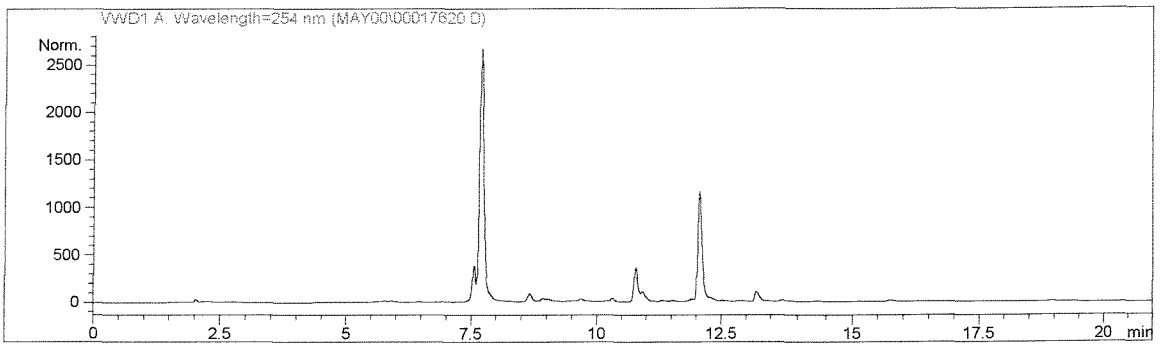
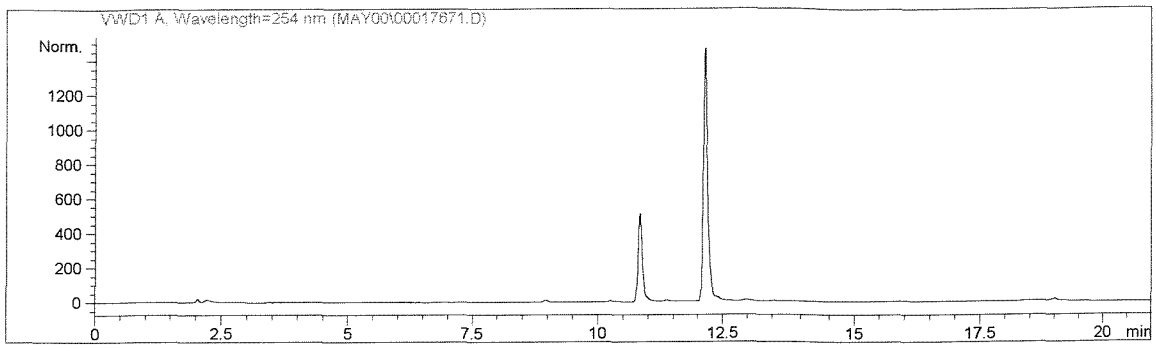


Figure 4.4.3.2 *The chromatograms recorded after a charge of 1.5 F had been passed, at a current density of 4 mA/cm^2. The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O*

The reaction mixture was worked up in accordance with the procedure described, *ibid.* A yield of 0.745 g was found. The material was identified as the dimethyldiphenyliodonium iodide. The chemical selectivity and current efficiency was 81 % and 22 % respectively.

An electrolysis of 4-iodotoluene and toluene was carried out by maintaining a current of 416 mA (current density at the anode was ca. 8 mA cm^{-2}), between the two electrodes until the charge passed corresponded to 1.8 F had passed. The hplc traces corresponding to the solution at the beginning and the end of the electrolysis is shown in Figure 4.4.3.3.



The chromatograms recorded after a charge of 0 F had been passed, The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O.

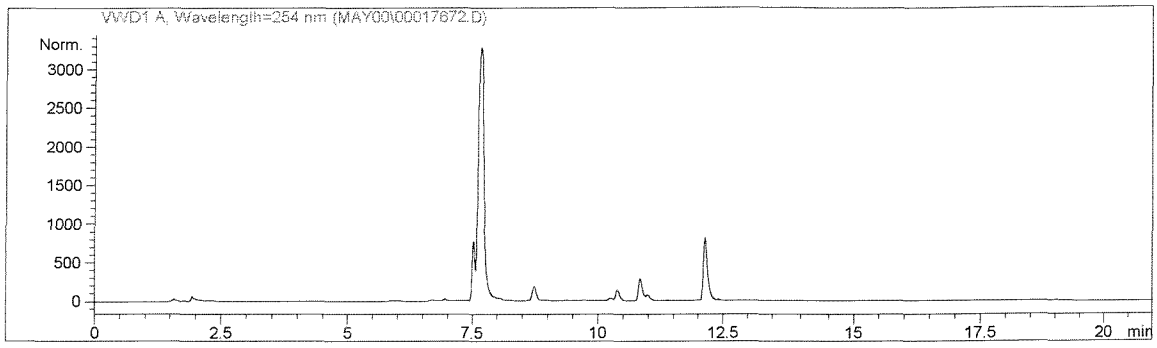
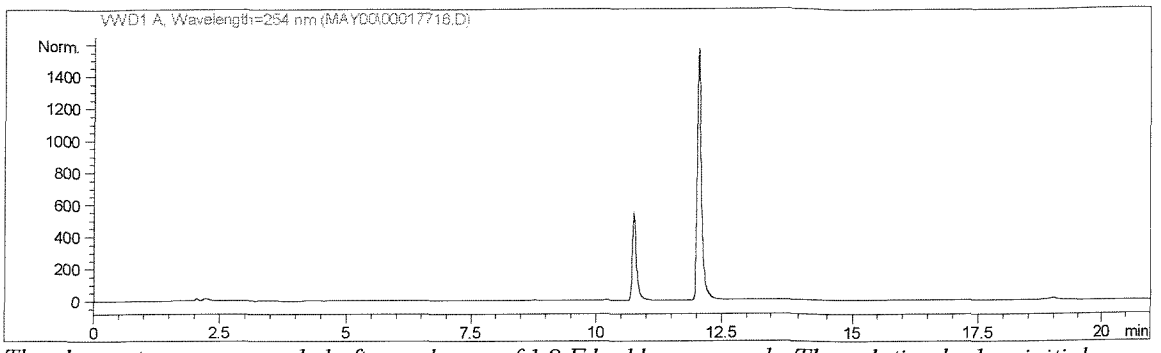


Figure 4.4.3.3 *The chromatograms recorded after a charge of 1.8 F had been passed, at a current density of 8 mA/cm^2. The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O.*

The reaction mixture was worked up in accordance with the procedure described previously, *ibid.*. A yield of 1.46 g was isolated. The chemical selectivity and current efficiency was 76 % and 37 % respectively.

A final electrolysis was carried out by maintaining a current of 832 mA (current density at the anode was ca. 16 mA cm^{-2}), between the two electrodes until the charge passed corresponded to 1.6 F had passed. The hplc traces corresponding to the solution at the beginning and the end of the electrolysis is shown in Figure 4.4.3.4.



The chromatograms recorded after a charge of 1.8 F had been passed.. The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O

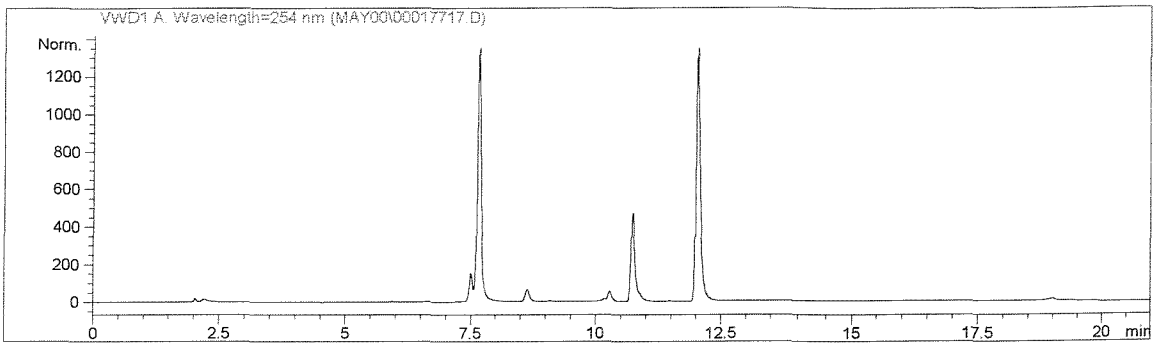


Figure 4.4.3.4 *The chromatograms recorded after a charge of 1.8 F had been passed, at a current density of 16 mA/cm^2. The solution had an initial composition of; 0.2 M 4-iodotoluene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O.*

The reaction was worked up in accordance with the procedure described, *ibid.* A 0.32 g yield of material was isolated after precipitation with potassium iodide. The ^{1}H-NMR spectrum was recorded and the material was identified as dimethyldiphenyliodonium iodide.

The selectivities and current efficiencies for all four electrolyses are summarised in Table 4.4.3.1.

Current Density mA/ cm^2	**Chemical Selectivity %**	**Current Efficiency %**
2	58	35
4	81	22
8	76	37
16	52	9

Table 4.4.3.1.

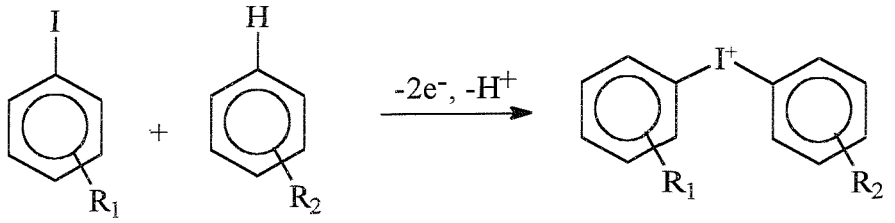
The current efficiency and selectivity of the electrolysis decreases on going from 8 to 16mA/ cm^2, whilst the selectivity of the reaction was poor when running the cell at 2 mA/cm^2. An optimum current density for the electrolysis of aromatic iodides and arenes was identified as being 5 mA/ cm^2 at the anode. At higher current densities, it was suspected that the mass transport of the aromatic material was a limiting factor and so solvent degradation also took place. The mass transport conditions in the beaker cell are only moderate.

4.5 Electrosynthesis of Alkyl Substituted Diaryliodonium Salts

It was important to define the scope of this electrolysis reaction and so a series of electrolyses were carried out in an effort to define which functional groups were acceptable to the electrolysis conditions.

4.5.1 Electrosynthesis of Di-Alkyl Substituted Diaryliodonium Salts

The generality of the procedure was examined by the electrolysis of other alkyl substituted iodobenzenes and alkylbenzenes in the preferred reaction conditions; As previously described , see Section 2.2.2, the electrolysis cell with a graphite cathode, surrounded by a carbon felt anode (approximate surface area of 80 cm^2) was charged with a solution of 0.2 M alkyl-iodobenzene and 0.3 M alkylbenzene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride. Constant current electrolysis was performed at a temperature of 298 K, by maintaining a current of 400 mA (current density at the anode was ca. 5 mA cm^{-2}) between the two electrodes. The products were isolated as the iodide and in some cases also as the bisulfate in accordance with the procedure described in Section 2.2.2. The successful electrolysis are summarised in Table 4.5.1.1.



R_1	R_2	Chemical Selectivity %	Current Efficiency %
4-Me	4-Me	92	46
3-Me	4-Me	83	27
2-Me	4-Me	77	37
4-Me	4-Et	71	22
4-Me	4-*i*-Pr	78	22
4-Me	4-*t*-Bu	92	44
4-*t*-Bu	4-Me	48	14
4-*t*-Bu	4-*t*-Bu	52	31

Table 4.5.1.1

It can be seen that the reaction is quite general for alkyl substituted arenes and aryl iodides. In all reactions where R_1 or R_2 was larger than the methyl group, only a single isomer was isolated.

The H^1-NMR, C^{13}-NMR, DEPT 135 and electro spray mass spectrum was recorded for each compound.

4,4′-Dimethyldiphenyliodonium bisulfate. ^{1}H NMR (300 MHz, d^6-DMSO); δ 8.09 (d, J = 8.3, 4H), 7.32 (d, J = 8.3, 4H), 2.34 (s, 6H): ^{13}C NMR (300 MHz, d^6-DMSO): δ 142.49,135.10, 132.37, 113.16, 20.91: MS (ES) calcd. for $C_{14}H_{14}I^+$ 309, found 309.

4,4′-Dimethyldiphenyliodonium iodide. ^{1}H NMR (300 MHz, d^6-DMSO); δ 8.04 (d, J = 8.3, 4H), 7.27 (d, J = 8.3, 4H), 2.30 (s, 6H): ^{13}C NMR (300 MHz, d^6-DMSO): δ 142.29,134.96, 132.26, 114.43, 20.88: MS (ES) calcd. for $C_{14}H_{14}I^+$ 309, found 309.

4-*iso*-Propyl-4′-methyldiphenyliodonium iodide. ^{1}H NMR (300 MHz, d^6-DMSO); δ 8.01 (d, J = 8.1, 4H), 7.35 (d, J = 7.7, 2H), 7.30 (d, J = 7.5, 2H) 2.9 (sept, J = 6.8, 1H), 2.30 (s, 3H), 1.15 (d, J = 6.8, 6H): ^{13}C NMR (300 MHz, d^6-DMSO): δ 152.75, 142.39, 135.15, 135.11, 132.33, 129.81, 114.12, 113.82, 33.35, 23.33, 20.92: MS (ES) calcd. for $C_{16}H_{18}I^+$ 337, found 337.

4-*tert*-Butyl-4′-methyldiphenyliodonium iodide. ^{1}H NMR (300 MHz, d^6-DMSO); δ 8.11 (d, J = 8.3, 2H), 8.06 (d, J = 8.6, 2H), 7.50 (d, J = 8.8, 2H), 7.30 (d, J = 8.3, 2H), 2.30 (s, 3H), 1.21 (s, 9H): ^{13}C NMR (300 MHz, d^6-DMSO): δ 154.86, 142.30, 135.18, 134.76, 132.31, 128.78, 114.22, 114.11, 34.95, 30.81, 20.93: MS (ES) calcd. for $C_{17}H_{20}I^+$ 351, found 351.

4-Ethyl-4′-methyldiphenyliodonium iodide. ^{1}H NMR (300 MHz, d^6-DMSO); δ 8.84 (d, J = 8.5, 2H), 8.80 (d, J = 8.3,2H), 7.32 (app t, J = 8.6, 4H) 2.61 (q, J = 7.5,2H), 2.31,(s, 3H) 1.13 (t, J = 7.5): ^{13}C NMR (300 MHz, d^6-DMSO): δ 148.14, 142.20, 135.07, 134.82, 132.20, 131.13, 114.59, 114.37, 27.93, 20.92, 15.28: MS (ES) calcd. for $C_{15}H_{16}I^+$ 323, found 323.

2-Methyl-4′-methyldiphenyliodonium iodide. ^{1}H NMR (300 MHz, d^6-DMSO);δ 8.34 (d, J = 7.7, 1H), 8.04 (d, J = 8.3, 2H), 7.52 (m, 3H), 7.26 (m, 2H), 2.61 (s, 3H), 2.30 (s, 3H): ^{13}C NMR (300 MHz, d^6-DMSO): δ 142.14, 140.27, 136.87, 134.93, 132.54, 132.32, 131.35, 129.19, 123.04, 114.10, 25.08, 20.89: MS (ES) calcd. for $C_{14}H_{14}I^+$ 309, found 309.

3-Methyl-4′-methyldiphenyliodonium iodide. ^{1}H NMR (300 MHz, d^6-DMSO);δ 8.08 (d, J = 8.5, 2H), 8.06 (s, 1H), 7.97 (d, J = 7.7, 1H), 7.44 (d, J = 7.5, 1H), 7.36 (app t, J = 7.7, 1H), 7.30 (d, J = 8.5, 2H), 2.31 (s, 6H): ^{13}C NMR (300 MHz, d^6-DMSO): δ 144.33, 141.66, 139.96, 135.12, 132.50, 136.32, 132.09, 131.36, 114.00, 118.00, 20.92, 20.83: MS (ES) calcd. for $C_{14}H_{14}I^+$ 309, found 309.

4,4′-*tert*-Dibutlyldiphenyliodonium iodide. ^{1}H NMR (300 MHz, d^6-DMSO); δ 8.13 (d, J = 8.6, 4H), 7.52 (d, J = 8.8, 4H), 1.25 (s, 18H): ^{13}C NMR (300 MHz, d^6-DMSO): δ155.06, 134.98, 128.98, 113.84, 34.96, 30.81: MS (ES) calcd. for $C_{20}H_{26}I^+$ 393, found 393.

4.5.1.1 Comments on the NMR Spectra of Di-Alkyl Substituted Diaryliodonium Salts

The ^{1}H-NMR of the material isolated from the electrolysis of 2-iodotoluene and toluene was used as a reference spectrum in the rest of the thesis to explain the anomalous peaks which occur in the spectra of 4,4′-dimethyldiphenyliodonium cations. Figure

4.5.1.1.1 shows the ^{1}H-NMR spectrum of the isolated material, from the electrolysis of 2-iodotoluene and toluene.

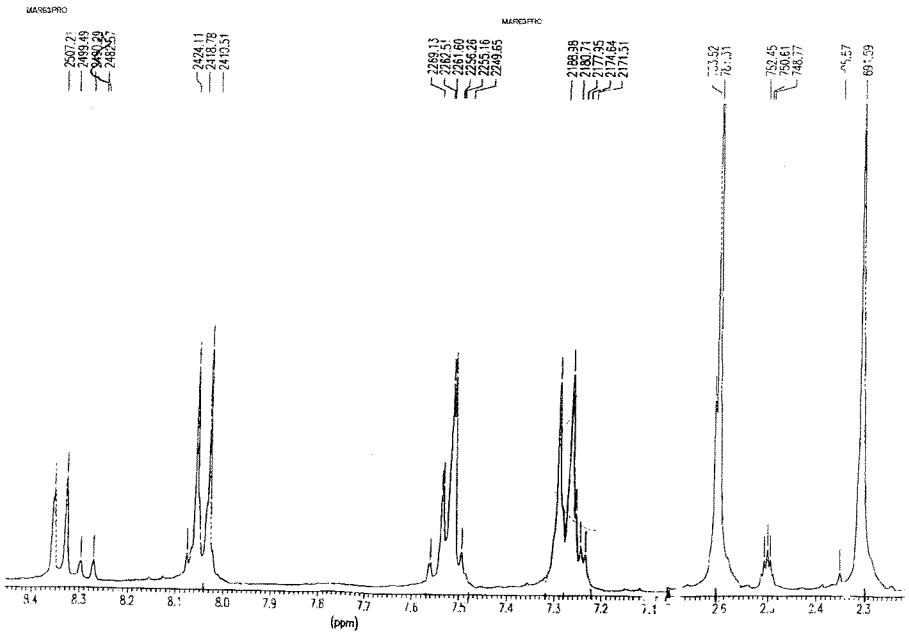


Figure 4.5.1.1.1 *The ^{1}H-NMR spectrum of the material isolated after the electrolysis of 2-iodotoluene and toluene*

There were six signals in the ^{1}H-NMR spectrum; 8.34, 8.04, 7.52, 7.26, 2.61, and 2.30 ppm, whose integral ratio was 1:2:3:2:3:3 respectively. The sum of the integrals was 14, which suggested the compound contained 14 protons. The dimethyldiphenyliodonium cation was expected to contain 14 protons. The two signals in the alkyl region, 2.61 and 2.30 ppm, whose integrals were 3 and 3 were assigned to two methyl groups. When this spectrum was compared to that of 4,4'-dimethyldiphenyliodonium cation, it was seen that this similarly had a signal at ca. 2.3 ppm which was assigned to the methyl protons. In the spectrum of 4,4'-dimethyldiphenyliodonium cation there were two doublet signals, both of which had a coupling constant of 8.3 Hz, at chemical shift values of 8.04 ppm and 7.27 ppm. The spectrum in Figure 4.5.1.1.1, similarly has a doublet at 8.04 ppm whose splitting constant was 8.3 Hz. A multiplet signal at ca . 7.26 ppm in the spectrum was dominated by a doublet whose splitting constant was 8.3 Hz. It was concluded that the material isolated, from the electrolysis of 2-iodotoluene and toluene, contained a phenyl ring which was *para* substituted with a methyl group and an

iodonium group. It was apparent that the second ring must have been *ortho* substituted, because of the fixed position of the methyl group and iodine atom in the starting material 2-iodotoluene. It was the multiplet at 7.52 ppm which was the most distinctive marker in a ^{1}H-NMR spectrum if 2,4'-dimethyldiphenyliodonium cation was present in the sample.

The ^{13}C-NMR and DEPT-135 spectra were recorded, see Figure 4.5.1.1.2 and Figure 4.5.1.1.3 respectively

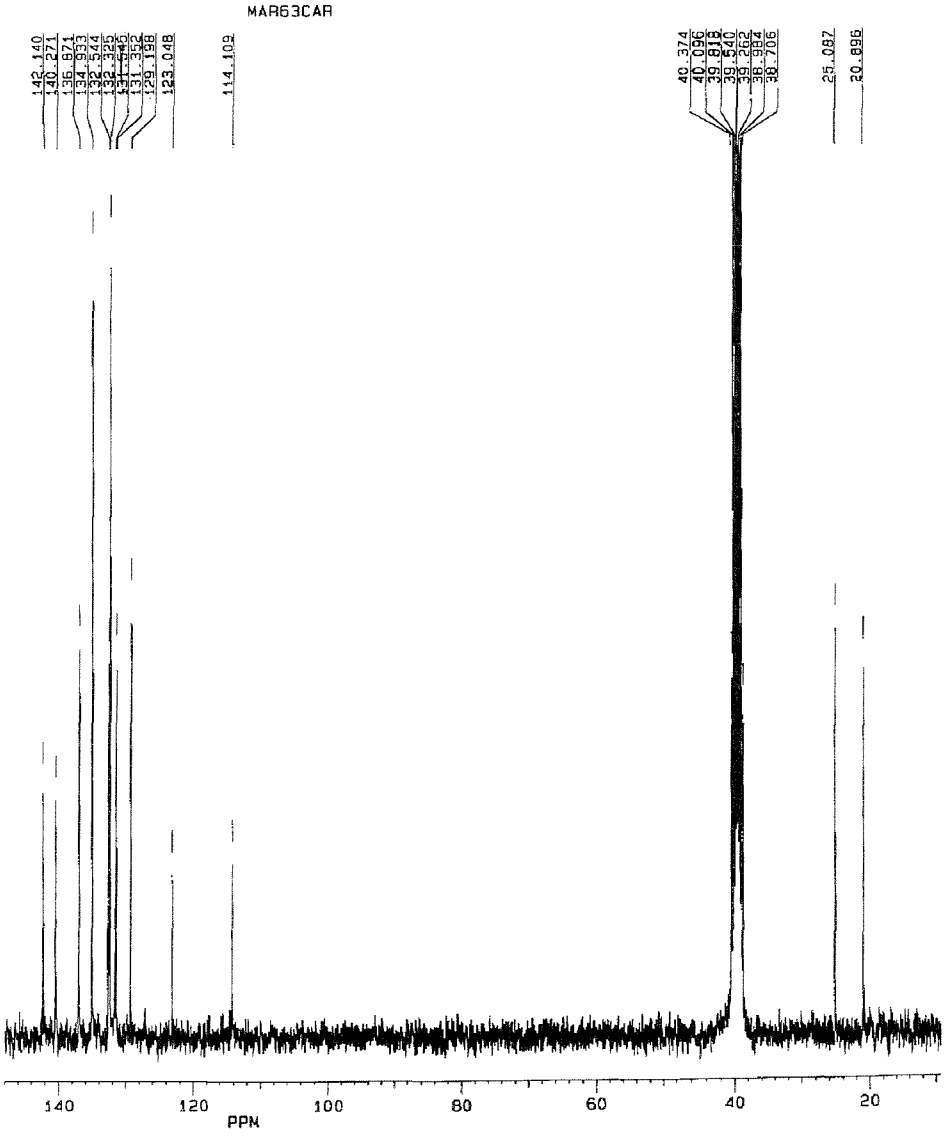


Figure 4.5.1.1.2 *The ^{13}C-NMR spectrum of the material isolated after the electrolysis of 2-iodotoluene and toluene*

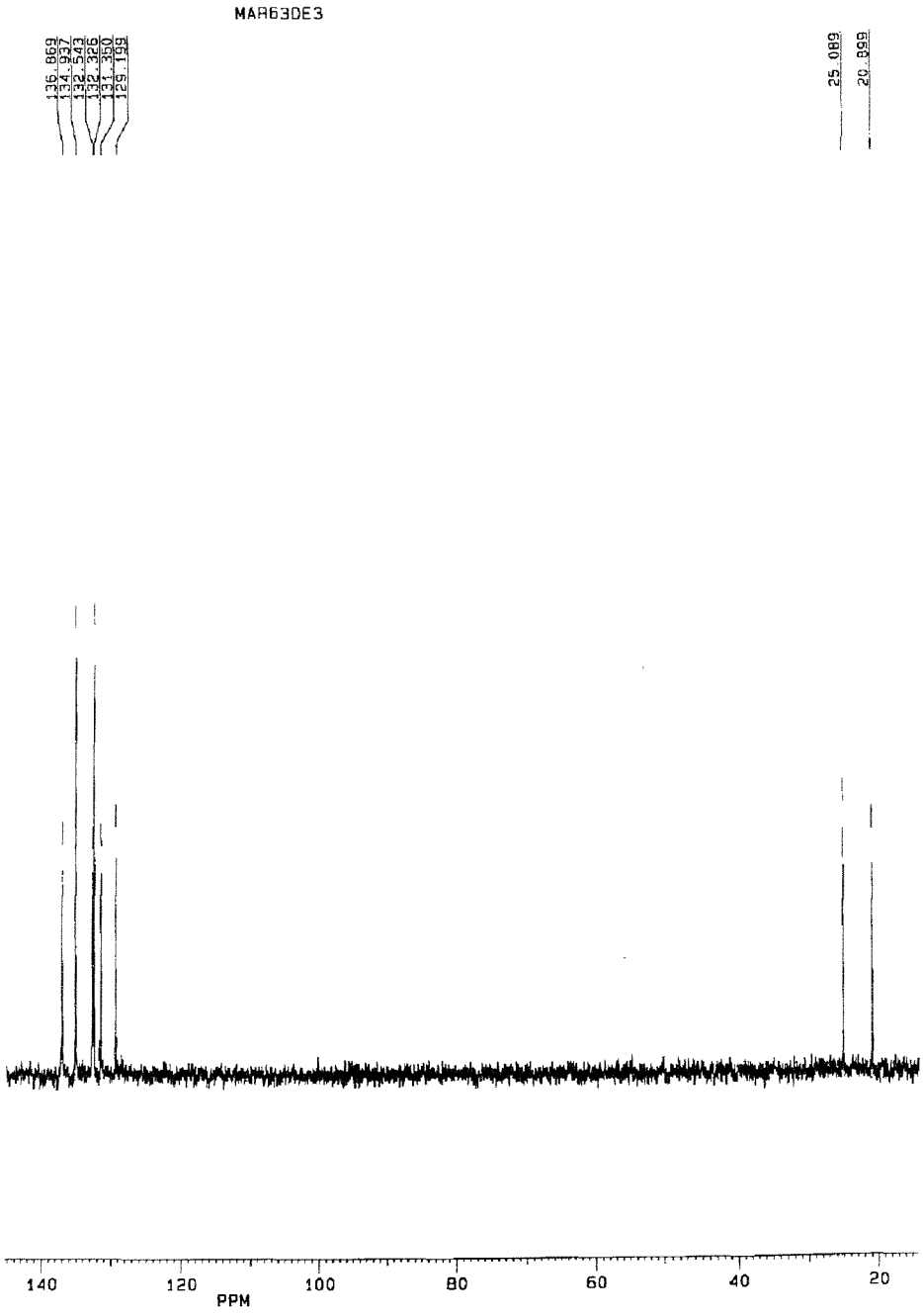


Figure 4.5.1.1.3 *The DEPT-135 spectrum of the material isolated after the electrolysis of 2-iodotoluene and toluene*

A comparison the ^{13}C-NMR AND DEPT-135 spectra showed that there were two signals at 25.1 and 20.9 ppm which were present in the ^{13}C-NMR and the DEPT-135 spectra. It was concluded that these were the two methyl carbon atoms in the

asymmetric molecule. Similarly there were two carbon atoms present at 123.0 and 114.0 ppm in the ^{13}C-NMR spectrum, but were not present in the DEPT-135, these peaks were assigned to the quaternary carbon atoms *ipso* to the iodonium group.

The ^{1}H-NMR spectrum of the material, isolated after the electrolysis of 3-iodotoluene and toluene is shown in Figure 4.5.1.1.4..

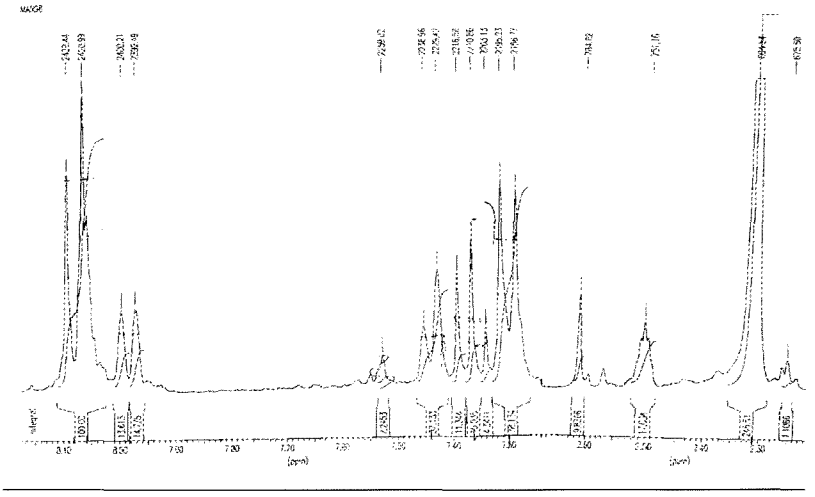


Figure 4.5.1.1.4 *The ^{1}H-NMR spectrum of the material isolated after the electrolysis of 3-iodotoluene and toluene.*

There were six main sets of peaks in the spectrum; 8.08, 7.97, 7.44, 7.36, 7.30 and 2.30 ppm. There were minor peaks at 2.60 and 7.52 ppm whose position and splitting was reminiscent of signals seen in the ^{1}H-NMR spectrum of 2,4'-dimethyldiphenyliodonium salt. The signal at 8.08 ppm has a doublet splitting pattern and appears to overlap on the highfield signal side with a singlet. The splitting constant of the doublet was 8.5 Hz, a doublet at 7.30 ppm similarly has a doublet spitting patterns with a constant of 8.5 Hz. These two signals were similar to those seen in the aromatic region of the ^{1}H-NMR spectra of 4,4'-dimethyldiphenyliodonium salts. This would indicate that the material isolated, from the electrolysis of 3-iodotoluene and toluene , contained a *para* substituted phenyl ring. A singlet, at 2.30 ppm, integrates to these two signals, at 8.30 and 8.08, in the ratio 6:2:2. The value of the integral, 6, for the signal at 2.30 ppm would suggest that this represented two methyl groups, i.e. six protons.

In addition the ^{13}C-NMR and the DEPT-135 spectra were recorded, see Figure 4.5.1.1.5and Figure 4.5.1.1.6 respectively.

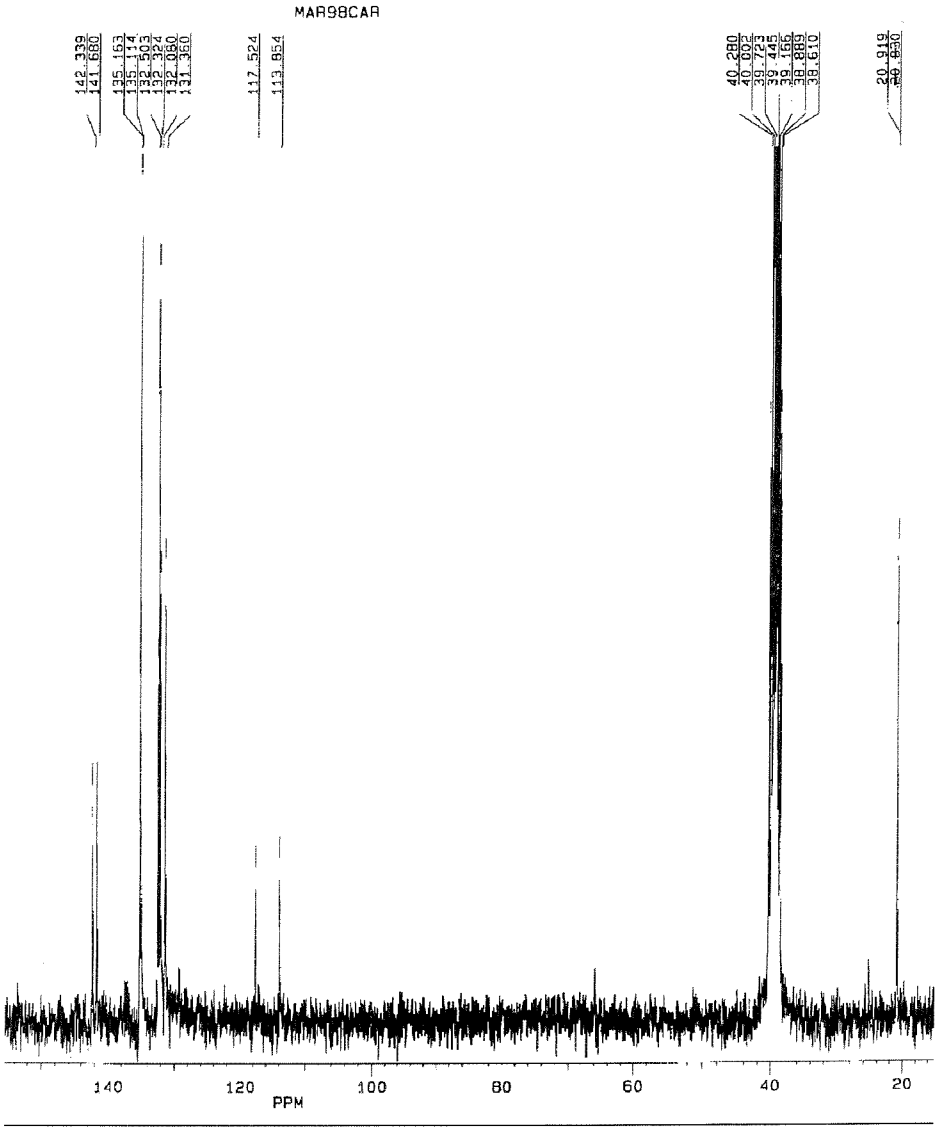


Figure 4.5.1.1.5 *The ^{13}C-NMR spectrum of the material isolated after the electrolysis of 3-iodotoluene and toluene.*

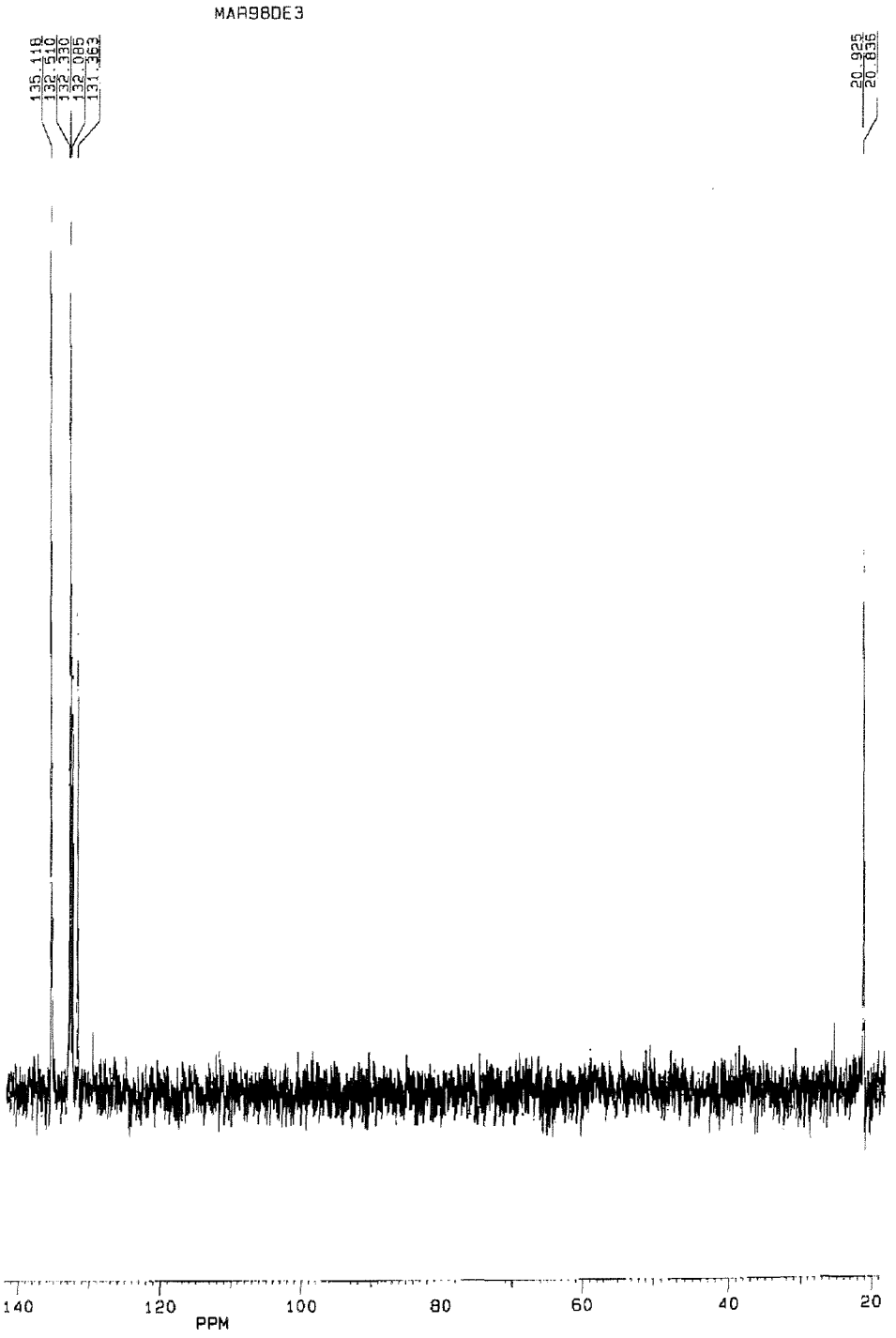
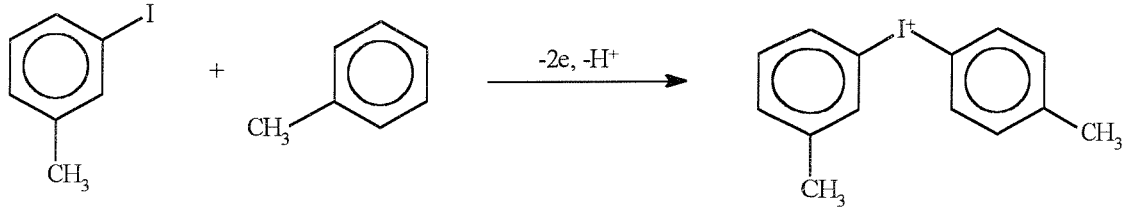


Figure 4.5.1.1.6 *The DEPT-135 spectrum of the material isolated after the electrolysis of 3-iodotoluene and toluene*

Comparison of the ^{13}C-NMR and the DEPT-135 spectra, of the material isolated from the electrolysis of 3-iodotoluene and toluene, showed the following pertinent points;

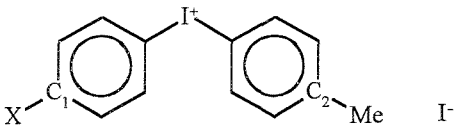
two signals were present at 20.9 and 20.8 ppm in both the ^{13}C-NMR and the DEPT-135 spectra, which indicated that two methyl groups were present in slightly different chemical environments. Two signals were seen at 117.5 and 113.8 ppm in the ^{13}C-NMR spectrum, but not the DEPT-135. These signals were probably the two quaternary carbons *ipso* to the iodonium group. The product shown in Scheme 4.5.1.1.1 accounts for the spectroscopic data.



Scheme 4.5.1.1.1

From the C^{13}-NMR for the 4-alkyl-4'-methyldiphenyliodonium series of salts, both the quaternary carbons, C—I$^+$, have a conserved chemical shift values in the range 113-115 ppm. This is a downfield shift form the parent aryl iodide, e.g. the quaternary carbon, C—I, in 4-iodotoluene has a value of 90.71 ppm. The cause of the downfield shift is the positive charge on the iodine atom, which reduces the electron density at the adjacent quaternary carbon atoms.

Similarly the quaternary carbon, C_2—Me, adjacent to the methyl group has a conserved chemical shift value of ca. 142 ppm, see Table 4.5.1.1.1. The quaternary carbon on the second ring adjacent to the alkyl substituent, C_1—X, has a chemical shift whose value is dependent on the size of the alkyl substituent, as the alkyl substituent increases the chemical shift value moves downfield.

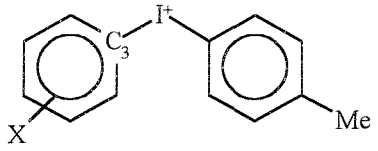


X	δ/ ppm, C_1—X	δ/ ppm, C_2—Me
CH_3	142.29	142.29
CH_3CH_2	148.14	142.20
$(CH_3)_2CH$	152.75	142.39
$(CH_3)_3C$	154.86	142.30

Table 4.5.1.1.1.

The downfield shift of the quaternary carbon, C_1—X, with the increasing size of the alkyl substituent, X, is mirrored by that calculated for the 4-substituted iodobenzene[35] parent molecule.

The three isomers of dimethyldiphenyliodonium iodide; 4, 4'-dimethyldiphenyliodonium, 3,4'-dimethyldiphenyliodonium, 2,4'-dimethyldiphenyliodonium, have a similar value for the quaternary carbon atom, C—I^+, for the ring where the methyl group is in the 4 position. In contrast the chemical shift for the quaternary carbon, C_3—I^+, increases as the methyl group changes position, in the order, *ortho>meta>para*. This is summarised in Table 4.5.1.1.2.



X	C_3 δ/ ppm,
ortho	123.05
meta	117.52
para	114.43

Table 4.5.1.1.2.

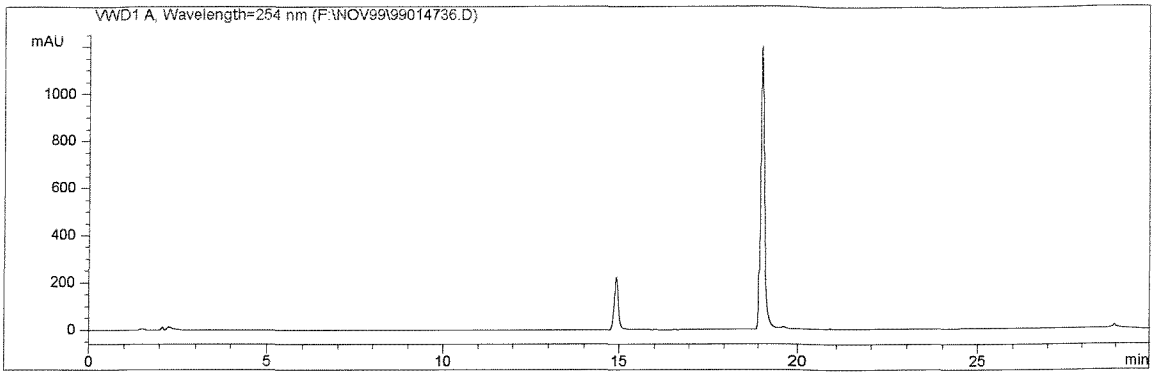
It can be seen that the reaction conditions favour the coupling of alkyl substituted iodobenzene and alkylbenzenes, forming both symmetric and asymmetric iodonium salts in good yields.

4.5.2 Electrosynthesis of Mono-Alkyl Substituted Diaryliodonium Salts

The organic literature contains many examples of diaryliodonium salts, where one of the aromatic rings is a simple phenyl group, see Section 1.3.1. It was therefore natural to attempt the electrosynthesis of 4-methyldiphenyliodonium salt. There were two potential strategies; to couple 4-iodotoluene with benzene or to couple iodobenzene with toluene.

4.5.2.1 Electrolysis of 4-Iodotoluene and Benzene

The beaker cell was filled with a solution of 0.2 M 4-iodotoluene and 0.3 M benzene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride. Galvanostatic electrolysis was performed at a current density of 5 mA cm^{-2}, until a charge of 3.0 F of charge was passed. Figure 4.5.2.1.1 shows that hplc recorded during the course of the electrolysis. Note the elution times are longer than those previously seen due to the use of a different solvent program (see Section 2.3).



Chromatogram of a solution of 0.2 M 4-iodotoluene and 0.3 M benzene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride.

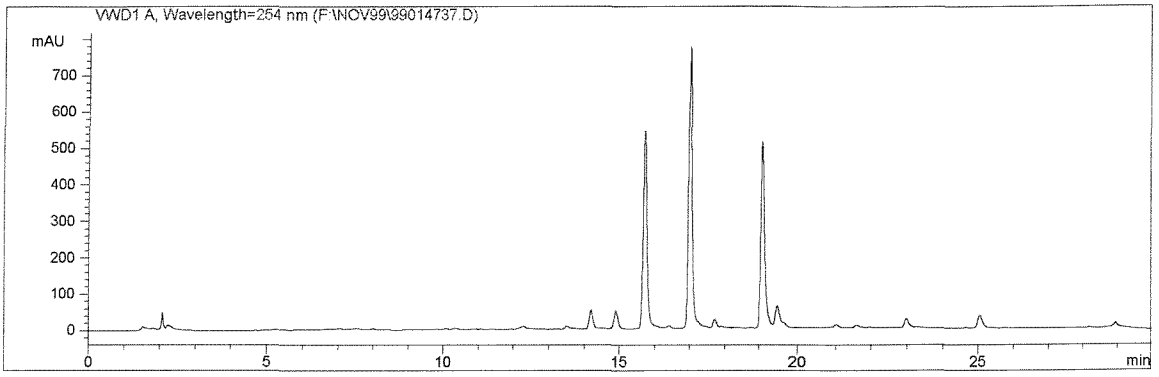


Figure 4.5.2.1.1 *Chromatogram of a solution of original composition of 0.2 M 4-iodotolunene and 0.3 M benzene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride, after 3.0 F of charge had been passed at a constant current of 5 mA/cm^2.*

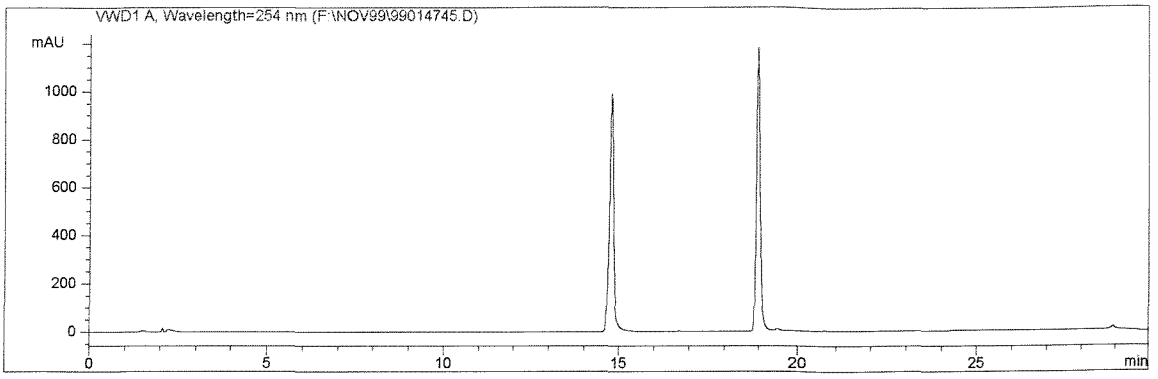
Consideration of the hplc chromatograms shown in Figure 4.5.2.1.1 show that there was consumption of the starting materials. The hplc chromatogram showed two major peaks had developed during the course of the electrolysis, with retention times at 15.7 and 17.0 minutes An aliquots was removed and diluted with acetonitrile for electrospray mass spectroscopy. The electrospray mass spectrum showed three ions with relative intensities greater than 10 %, see Table 4.5.2.1.1.

Relative Intensity %	**m/z**
15	296.1
23	309
100	295

Table 4.5.2.1.1

The ion with m/z of 295 Da was expected for methylphenylphenyliodonium cation. The reaction mixture was worked up in accordance with the following procedure; the electrodes were washed with hot methanol and the washings were combined with the reaction mixture. The solvents were removed *in vacuo* and the resulting oil was separated between an aqueous phase and an organic phase, of diethyl ether. The aqueous phase was separated and treated with potassium iodide,3 g dissolved in a minimum amount of water. No precipitate was seen. The hplc clearly shows no large peak which is due to the 4-methylphenylphenyliodonium cation. There are two major product peaks in the hplc and these are probably due to 4-iodobenzylacetate and 4-iodobenzaldehyde.

Benzene however is a poorer nucleophile than its alkyl substituted derivatives, so one strategy was to raise the benzene concentration in solution, to compensates for its possibly slow rate of coupling to the 4-iodotoluene cation radical. The electrolysis of 4-iodotoluene and benzene was therefore repeated under identical conditions except that the benzene concentration was raised to 1.5 M. Figure 4.5.2.1.2 shows that the hplc chromatograms recorded during the course of the electrolysis.



Chromatogram of a solution of 0.2 M 4-iodotoluene and 1.5 M benzene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride. Note a different elution program was used from that reported in the rest of this thesis

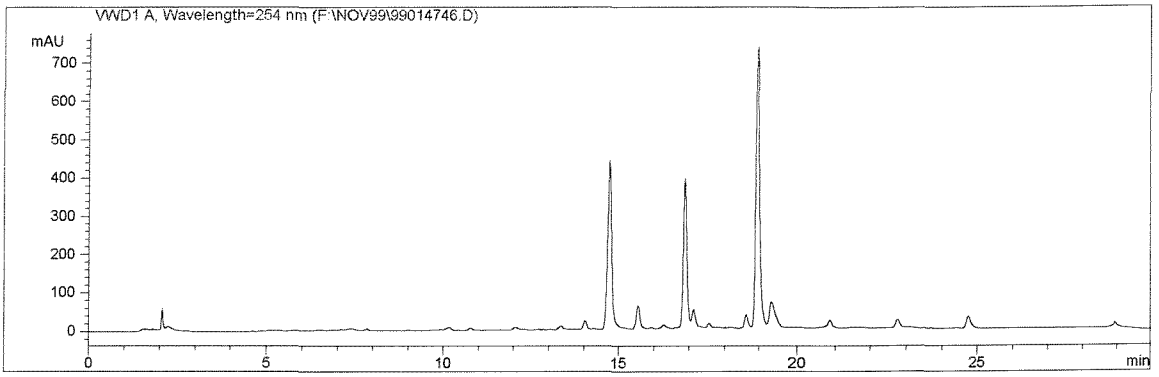


Figure 4.5.2.1.2 *Chromatogram of a solution of 0.2 M 4-iodotoluene and 1.5 M benzene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride, after 1.9 F was passed at a constant current of 5 mA/cm^2. Note a different elution program was used from that reported in the rest of this thesis*

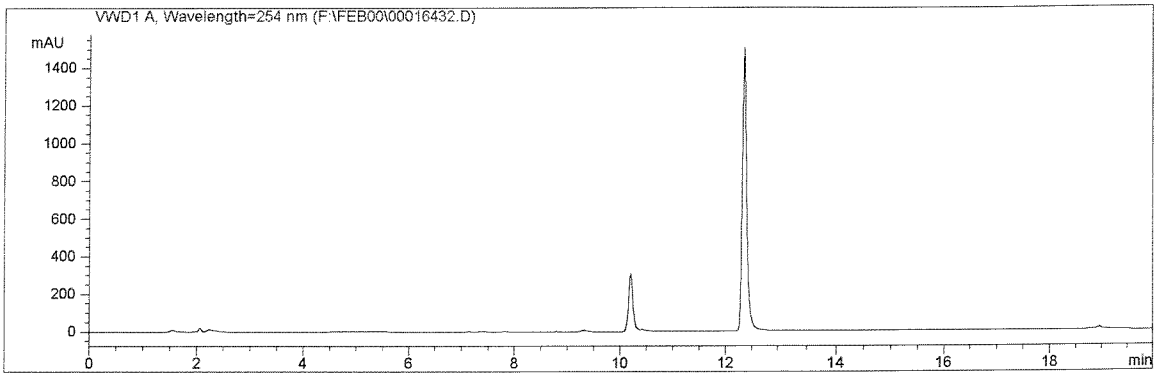
The benzene peak , elution time ca.15 minutes, had decreased in height by ca. 55 %, whilst the 4-idotoluene peak, elution time of ca. 19 minutes, had decreased in height by ca. 37 %. An additional intense peak was seen at the end of the electrolysis, elution time ca. 16.9. An aliquots was removed from the reaction mixture and diluted with acetonitrile for positive ion electrospray mass spectroscopy. The electrospray mass spectrum showed three peaks with relative intensities greater than 10 %, see Table 4.5.2.1.2.

Relative Intensity %	m/z
15	153.0
17	145.4
100	144.0

Table 4.5.2.1.2

There was no indication of an iodonium product even from the positive ion electrospray.

A further electrolysis was carried out on a solution of 0.2 M 4-iodotoluene and 0.3 M benzene in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride. The current density at the anode was ca. 5 mA cm^{-2}. Figure 4.5.2.1.3 shows that the hplc chromatograms recorded during the course of the electrolysis.



Chromatogram of a solution of 0.2 M 4-iodotoluene and 1.5 M benzene in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride

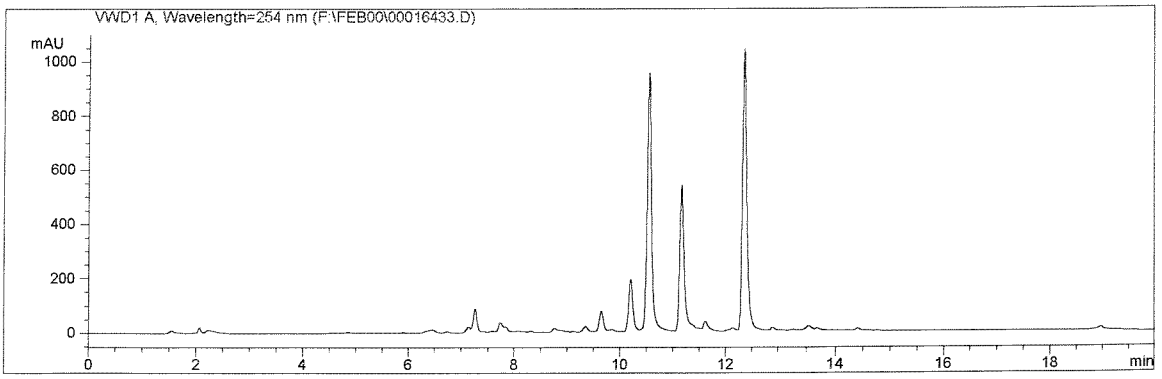


Figure 4.5.2.1.3 *Chromatogram of a solution of 0.2 M 4-iodotoluene and 1.5 M benzene in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride, after 1.9 F was passed at a constant current of 5 mA/cm^2*

The hplc chromatogram showed two new peaks at the end of the electrolysis, with retention times of 10.5 and 11.2 minutes. The reaction mixture was partitioned between dichloromethane and an aqueous phase. An aliquot was removed from the dichloromethane phase and was diluted with additional dichloromethane for GC-MS analysis, see Figure 4.5.2.1.4.

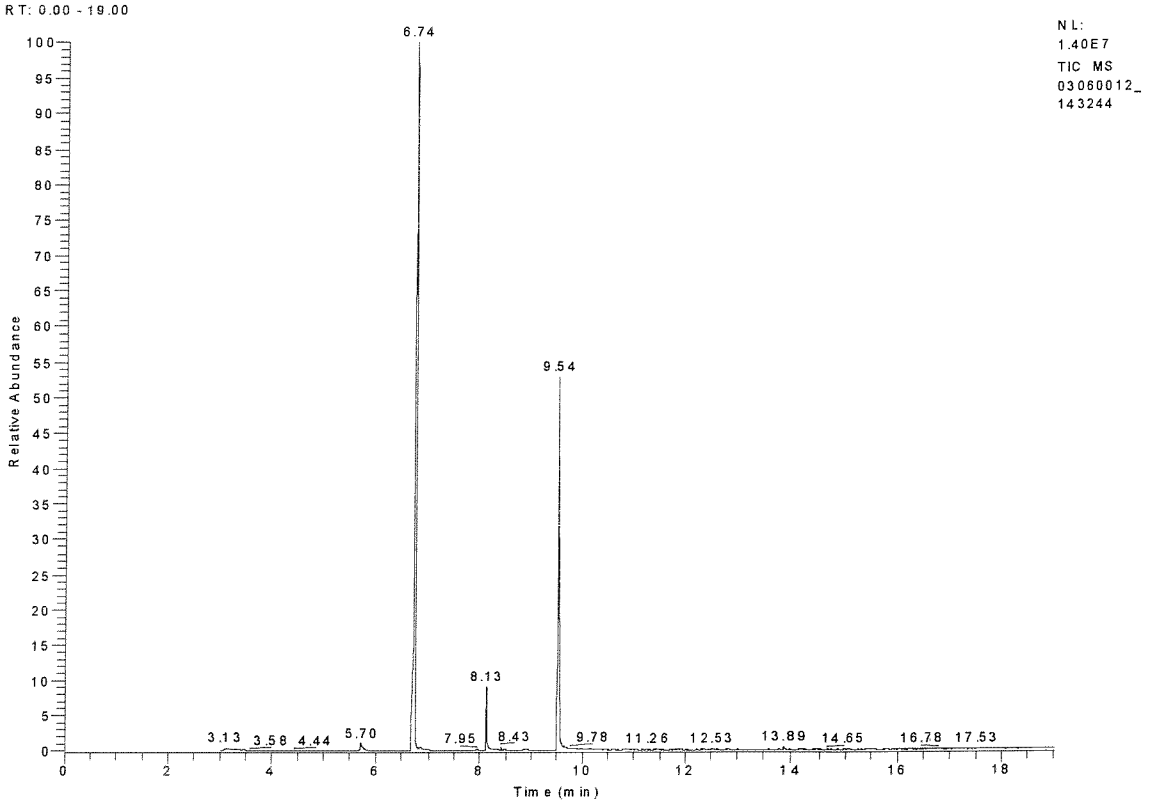


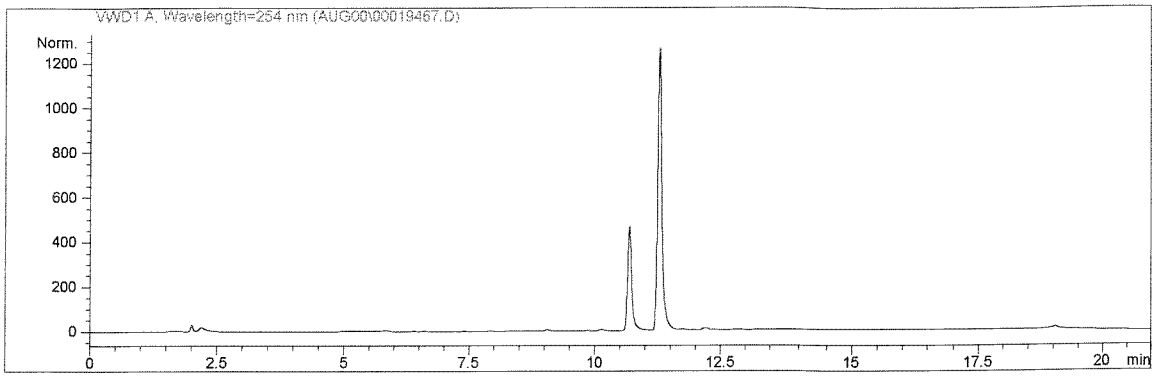
Figure 4.5.2.1.4

The chromatogram contained three peaks, and was compared to the chromatogram in Figure 4.2.2. It was determined that 4-iodobenzylacetate and 4-iodobenzaldehyde were the identifiable products from the electrolysis of 4-iodotoluene and benzene.

4.5.2.2 Electrolysis of Iodobenzene and Toluene

A solution of 0.2 M iodobenzene and 0.3 M toluene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride was electrolysed with a current density at the anode of ca. 5 mA cm^2

until a charge of 1.5 F had passed. Figure 4.5.2.2.1 shows that the hplc chromatograms recorded at the beginning and at the end of the electrolysis.



Chromatogram of 0.2 M 4-iodobenzene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O

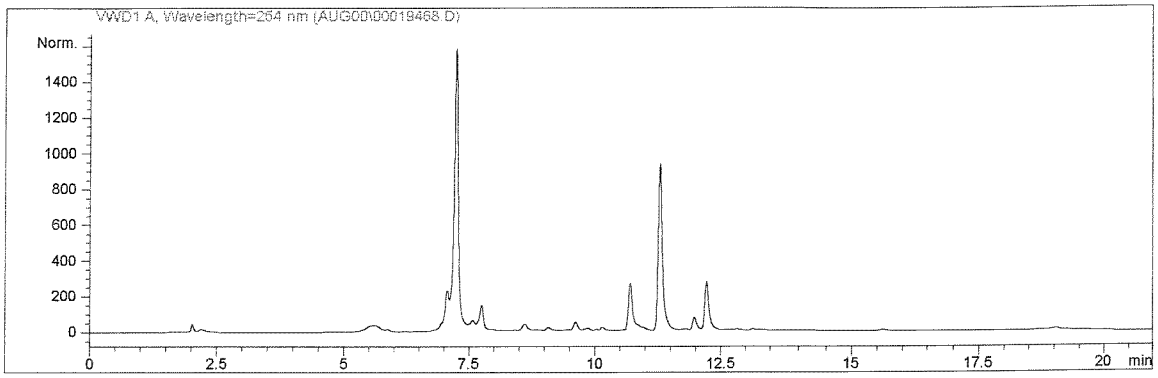


Figure 4.5.2.2.1 *Chromatogram of a solution of original composition 0.2 M iodobenzene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O, after a charge of 1.5 F was passed at a constant current of 5 mA/cm^2.*

A comparison of the hplc before and after a charge had passed showed that 2 minor peaks and 1 major peak had developed. The major electrolysis peak, with a retention time of 7.3 minutes, had a shoulder.

The major peak had a shape and elution time reminiscent of the dimethyldiphenyliodonium cation. An aliquot of reaction mixture was diluted with acetonitrile for electrospray mass spectroscopy analysis. One ion was seen with a m/z value of 295 Da was seen. This was the ion expected for the methylphenylphenyliodonium cation. The reaction mixture was worked up in accordance with the following procedure; the electrodes were washed with hot methanol and the washings were combined with the reaction mixture. The solvents were

removed *in vacuo* and the resulting oil was partitioned between an aqueous phase and diethyl ether. The aqueous phase was separated and treated with potassium iodide, 3 g dissolved in a minimum amount of water. The addition of the potassium iodide solution, caused an immediate precipitation of white powder. This material was separated on the filter paper, and dried. A 1.31 g yield of product was recorded. The ^{1}H-NMR spectrum was recorded, see Figure 4.5.2.2.2.

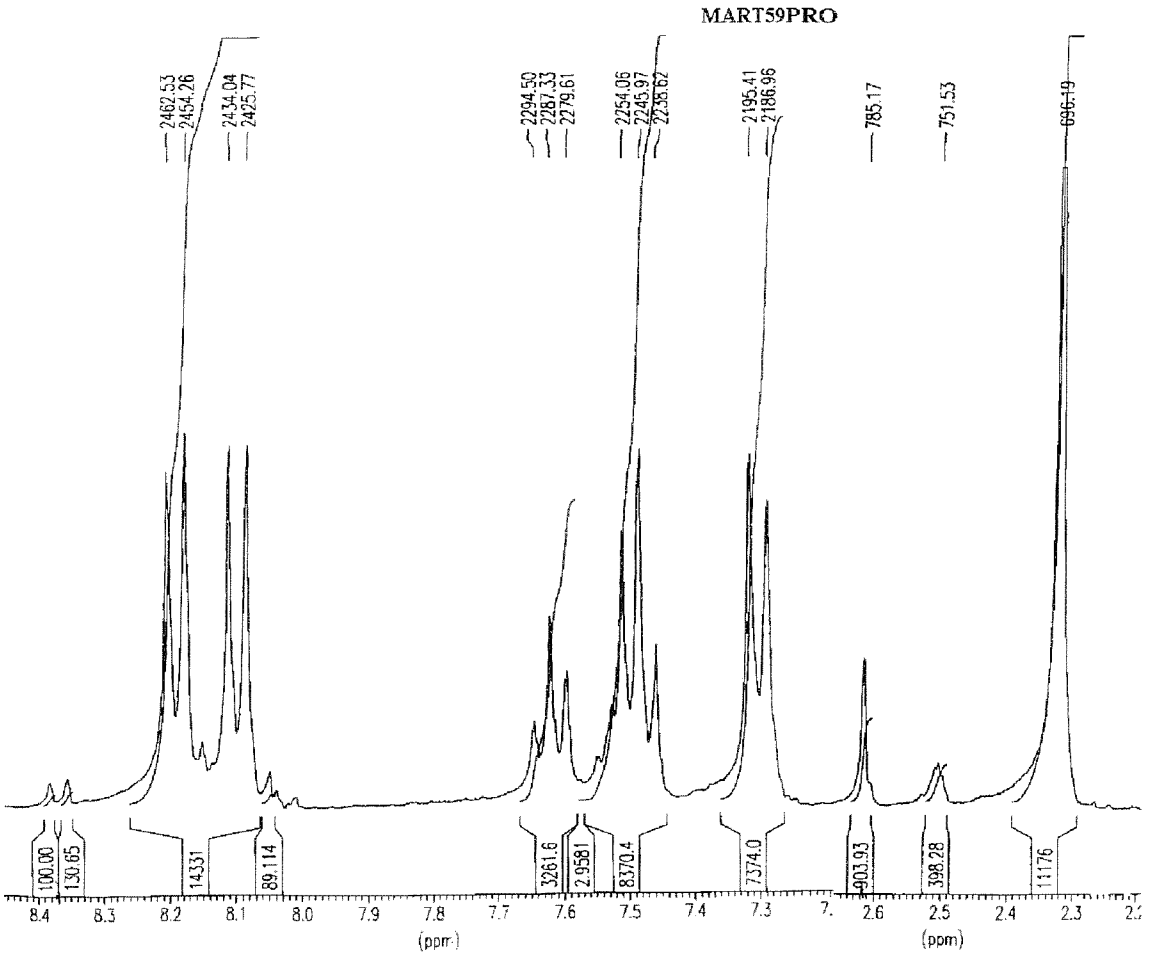
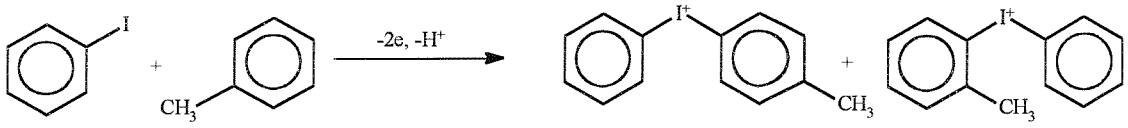


Figure 4.5.2.2.2 *^{1}H-NMR spectrum of material isolated after the electrolysis of iodobenzene and toluene*

The ^{1}H-NMR spectrum were compared to that of 4-methylphenylphenyliodonium triflate, see Section 2.4.4, prepared in accordance with the methodology of Kitamura[9].

The comparison clearly shows that the precipitate was 4-methylphenylphenylidonium cation.

There were two additional peaks seen in the ^{1}H-NMR spectrum of the material isolated from the electrolysis of iodobenzene and toluene , at 2.61 and 8.37 ppm. These peak were seen in the ^{1}H-NMR spectrum of 2,4'-dimethyldiphenylioodnium iodide and therefore were assigned to a compound containing an aromatic ring that substituted with a methyl group *ortho* to an iodonium group.. It was therefore concluded that the isolated material contained also the isomer 2-methylphenylphenyliodonium cation. The ratio of the integral of the signal at 2.61 and 2.30 was ca 1:12; therefore it was estimated that the 2-methylphenylphenyliodonium cation made up ca. 9 % of the isolated electrolysis product. The reaction is summarised in Scheme 4.5.2.1.1.



Scheme 4.5.2.1.1

Kitamura[9] similarly prepared 4-methylphenylphenyliodonium triflate from [(diacetoxy)iodo]benzene and toluene and similarly found that 8 % of the isolated material was the *ortho* isomer 2-methylphenylphenyliodonium triflate.

The ^{13}C-NMR and the DEPT-135 spectra, of the material isolated from the electrolysis of iodobenzene and toluene were recorded, see Figure 4.5.2.2.3 and Figure 4.5.2.2.4 respectively.

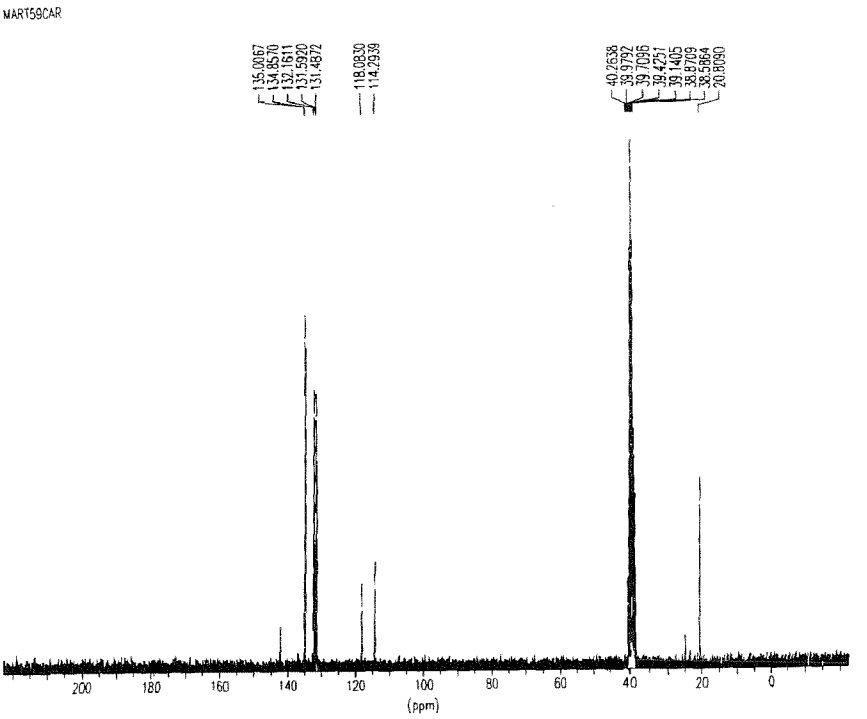


Figure 4.5.2.2.3 *^{13}C-NMR spectrum of material isolated from the electrolysis of iodobenzene and toluene*

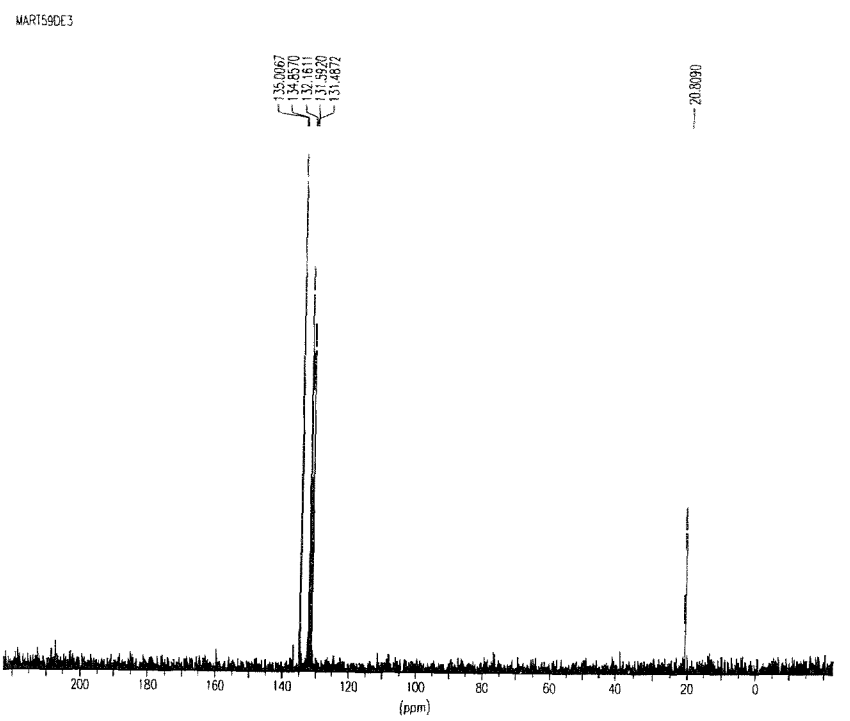


Figure 4.5.2.2.4 *DEPT-135 spectrum of material isolated from the electrolysis of iodobenzene and toluene*

A comparison of the ^{13}C-NMR and the DEPT-135 spectra was made; the two peaks seen in the ^{13}C-NMR spectrum, at 118.0 and 114.3 ppm, were not seen in the DEPT-135 spectrum. Therefore these signals were assigned to the aromatic carbon atoms *ipso* to the iodonium group. A peak was seen in the alkyl region , at 20.8 ppm, in both the ^{13}C-NMR and DEPT-135 spectra. Its value was exactly that see for the methyl carbon in 4,4'-dimethyldiphenyliodonium cation and so was similarly assigned to the methyl carbon in 4-methylphenylphenyliodonium cation. A very minor peak was seen in the ^{13}C-NMR spectrum with a chemical shift value of ca. 25 ppm, which was similar chemical shift value to the *ortho* methyl group in 2,4-dimethyldiphenyliodonium cation and so confirms that there was a small amount of the 2-methylphenylphenyliodonium cation present in the sample isolated from the electrolysis of iodobenzene and toluene.

4-Methylphenylphenyliodonium iodide. ^{1}H-NMR (300 MHz, d_6 - DMSO); δ 8.20 (D, J = 8.3, 2H), 8.10 (d, J = 8.3, 2H), 7.62 (app t 1H), 7.50 (m, 2H), 7.30 (d, J = 8.5, 2H), 2.30 (s, 3H): ^{13}C-NMR (300 MHz, d_6 - DMSO) δ 143.00, 135.01, 134.86, 132.16, 131.59, 131.49, 118.08, 114.29, 20.91: MS (ES) calcd. for $C_{13}H_{12}I^{+}$ 295, found 295.

The diethyl ether phase was reduced in volume under vacuum. The subsequent oil was diluted with dichloromethane, an aliquot of this was further diluted for GC-MS analysis, see Figure 4.5.2.2.5.

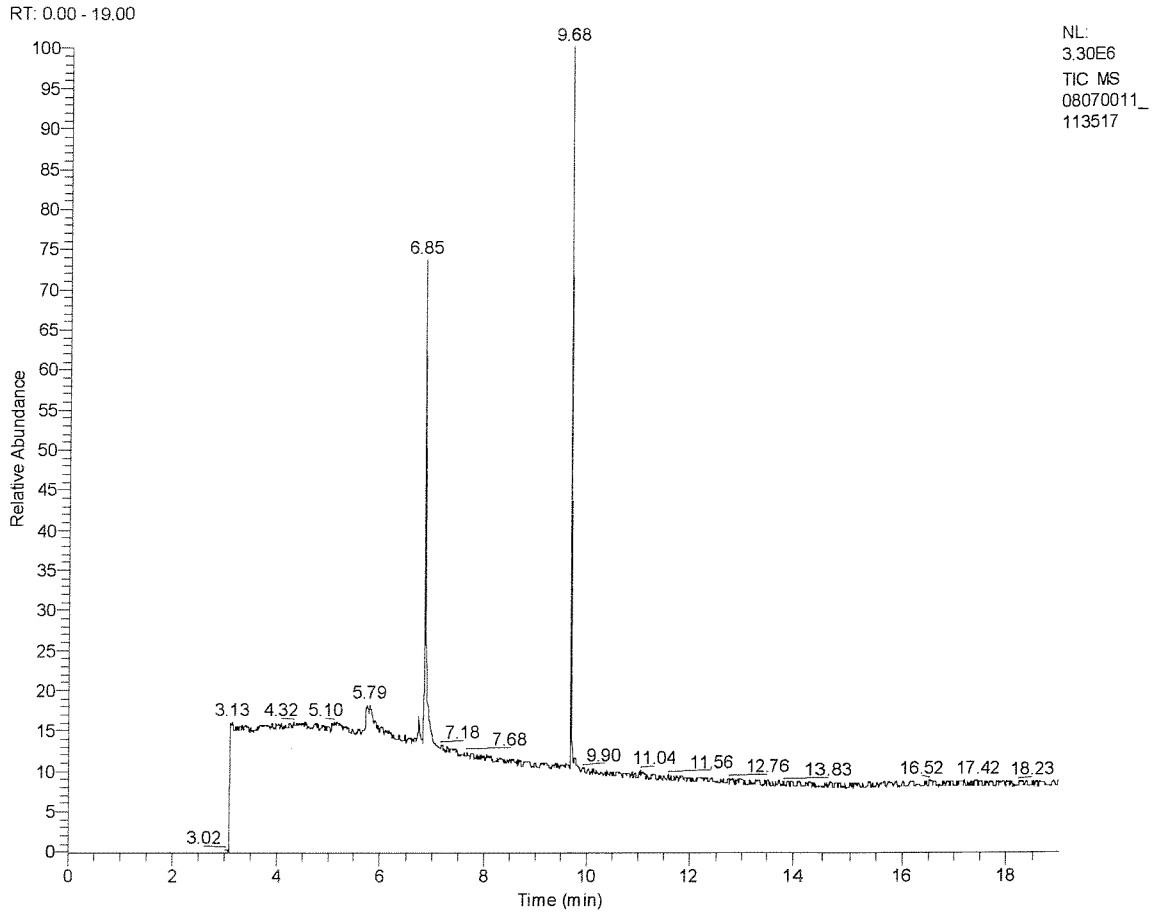


Figure 4.5.2.2.5 *GC-MS analysis of aliquot removed from the organic wash of the electrolysis solution of iodobenzene and toluene.*

The mass spectra corresponding to the peaks in the gas chromatogram, *ibid,* are shown in Table 4.5.2.2.1.

The peak with a retention time of 6.85 minutes had a molecular ion of 150 Da and showed an intense daughter ion daughter ion, with a m/z value of 43 Da. The parent ion, of 150 Da, could be benzyl acetate, whilst the daughter ion of m/z 43 Da, was the acetyl cation fragment which was a feature of aromatic esters[44]. Hence one product may be a derivative of benzyl acetate. Benzyl acetate has a retention time of 9.6 minutes on the hplc column, therefore it did not account for the two minor peaks seen in Figure 4.5.2.2.1.

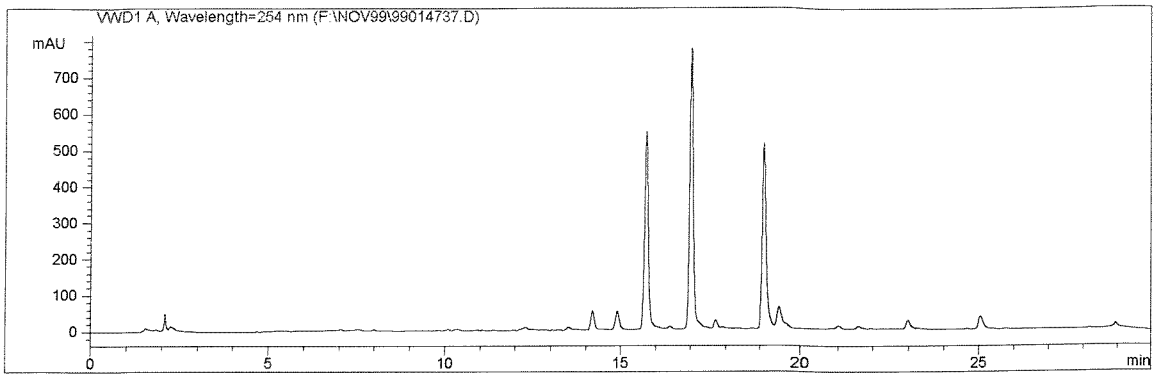
The chemical selectivity and current efficiency, of the electrolysis of iodobenzene and toluene, with respect to the 4-methylphenylphenyliodonium iodide was 71 and 20 % respectively.

Retention Time	**6.85**		**9.68**	
	m/z	Relative Intensity / %	m/z	Relative Intensity / %
	150	30	76	22
	77	34	126	23
	90	36	153	29
	43	66	232	70
	91	73	234	70
	108	100	152	100

Table 4.5.2.2.1

4.5.2.3 Summary of the Synthesis of 4-Methylphenylphenyliodonium Salt

It was apparent that 4-methylphenylphenyliodonium iodide was successfully electrosynthesised from iodobenzene and 4-iodotoluene, but not from the coupling of 4-iodotoluene and benzene. The hplc chromatograms recorded at the end of the electrolysis are shown in Figure 4.5.2.3.1.



Chromatogram of a solution of original composition of 0.2 M 4-iodotolunene and 0.3 M benzene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride, after 3.0 F of charge had been passed at a constant current of 5 mA/cm^2.

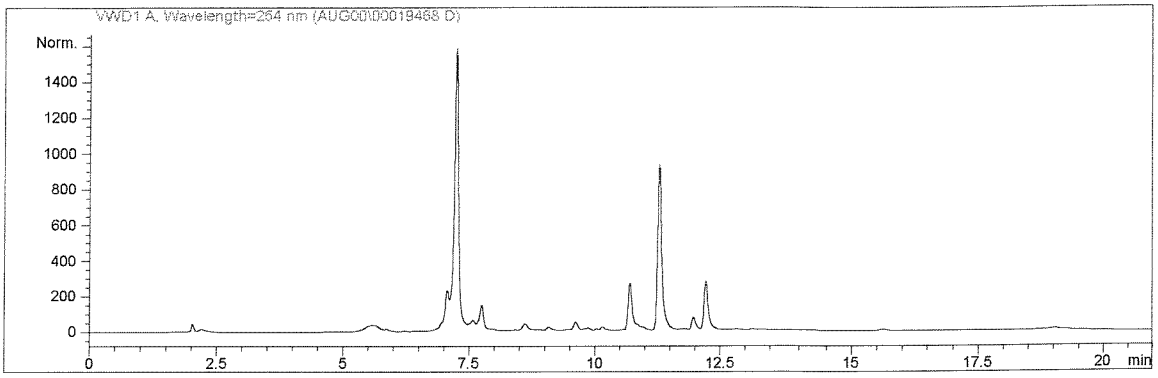
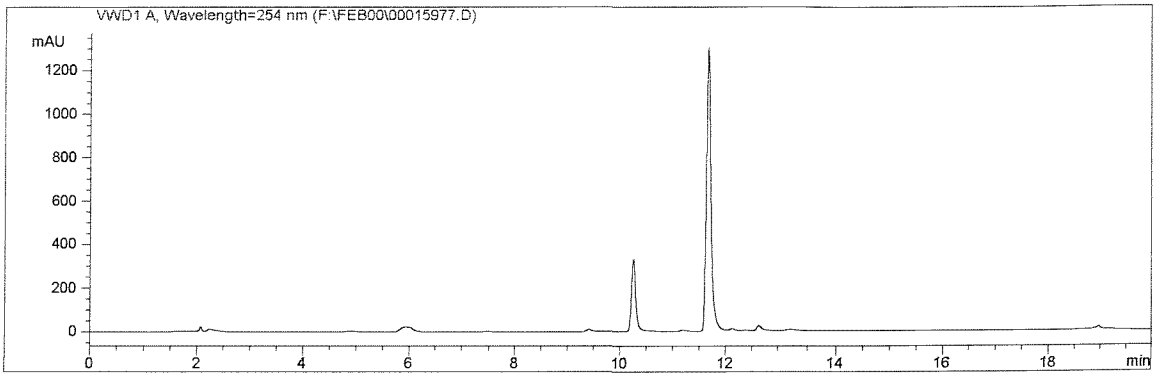


Figure 4.5.3.2.1. *Chromatogram of a solution of original composition 0.2 M iodobenzene and 0.3 M toluene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O, after a charge of 1.5 F was passed at a constant current of 5 mA/cm^2.*

The electrolysis of 4-iodotoluene and benzene gave a hplc which showed 3 main peaks; 19.0, 17.0 and 15.7 minutes. The peak at 19 minutes was for 4-iodotoluene, whilst the other two peaks were due to 4-iodobenzylacetate and 4-iodobenzaldehyde. The chromatogram corresponding to the electrolysis of iodobenzene and toluene contained two major product peaks; with retention times of 11.3 and 7.3 minutes. The peak at 7. 3 minutes was due to the iodonium product. It must be noted that the two chromatograms were recorded with different elution gradients, so peaks are not directly comparable, but it was clear from the chromatograms that there was no sign of the iodonium product from the electrolysis of 4-iodotoluene but a strong signal corresponding to the iodonium product was seen in the chromatogram of iodobenzene and toluene.

4.5.3 Electrolysis of Iodobenzene and Benzene

The carbon felt anode cell was charged with a solution of 0.2 M 4-iodobenzene and 0.3 M benzene in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride. A galvanostat was set to deliver a current of 800 mA, after sixty minutes the current had fallen to 570 mA and after 270 minutes had fallen to 130 mA, as the resistance of the cell increased. This probably indicates strong filming of the anode. During the electrolysis the solution was constantly stirred and aliquots of reaction mixture were removed for hplc analysis to monitor the consumption of starting material and identify any products. The electrolysis was stopped when 2.6 F of charge had been passed. Figure 4.5.3.1 shows that the hplc chromatograms recorded before and after the electrolysis.



Chromatogram of a solution with original composition 0.2 M 4-iodobenzene and 0.3 M benzene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O.

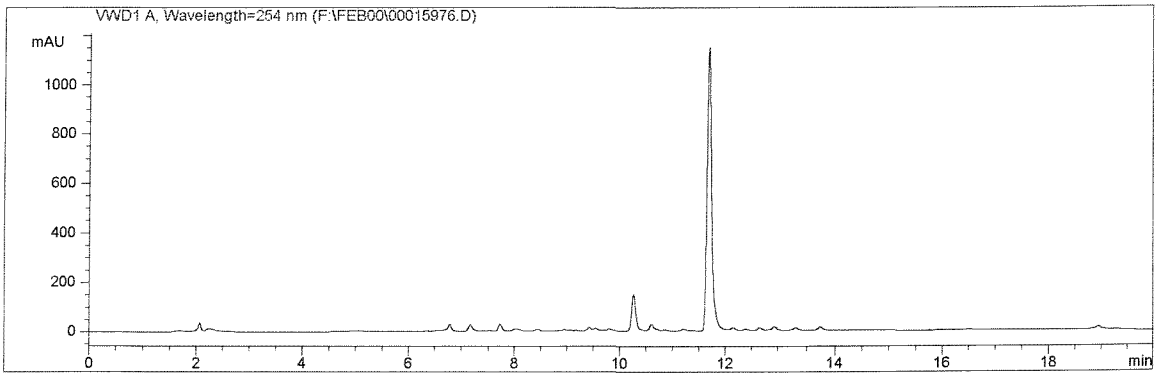


Figure 4.5.3.1 *Chromatogram of a solution with original composition 0.2 M 4-iodobenzene and 0.3 M benzene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O., after 2.6 F of charge was passed at a constant current of 5mA/cm^2.*

Consideration of the hplc traces shown in Figure 4.5.3.1 showed that there was hardly any change in the peak heights for iodobenzene and benzene. Aliquots was removed and diluted with acetonitrile for electrospray mass spectroscopy. The electrospray mass spectrum showed a three ions whose relative intensities were higher than 10 %, see Table 4.5.3.1.

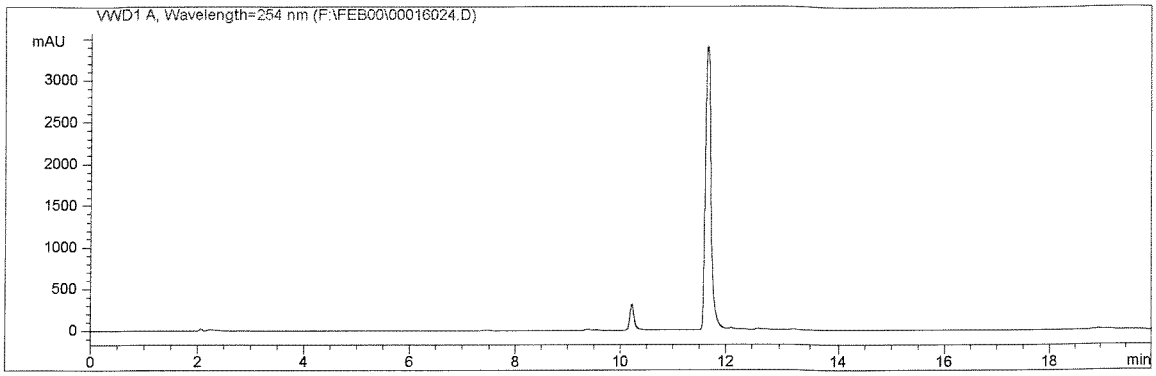
Relative Intensity %	**m/z**
20	394.3
21	281
100	393.2

Table 4.5.3.1

The ion with an m/z value of 281 was what expected for diphenyliodonium cation Work up of the reaction mixture led to no precipitate. Hence the diphenyiodonium salt is only formed in trace amounts.

The electrolysis was repeated with a lower current of 400 mA and Figure 4.5.3.2 shows the hplc response before and after electrolysis. Again little reactant was consumed. Aliquots was removed and diluted with acetonitrile for electrospray mass spectroscopy. The electrospray mass spectrum showed a three ions whose relative intensities were higher than 10 %, see Table 4.5.3.2. The ion with an m/z value of 281 was what expected for diphenyliodonium cation.

In view of there being no change in the hplc response on passing a current the reaction was not worked up.



Chromatogram of a solution with original composition 0.2 M iodobenzene and 0.3 M benzene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O.

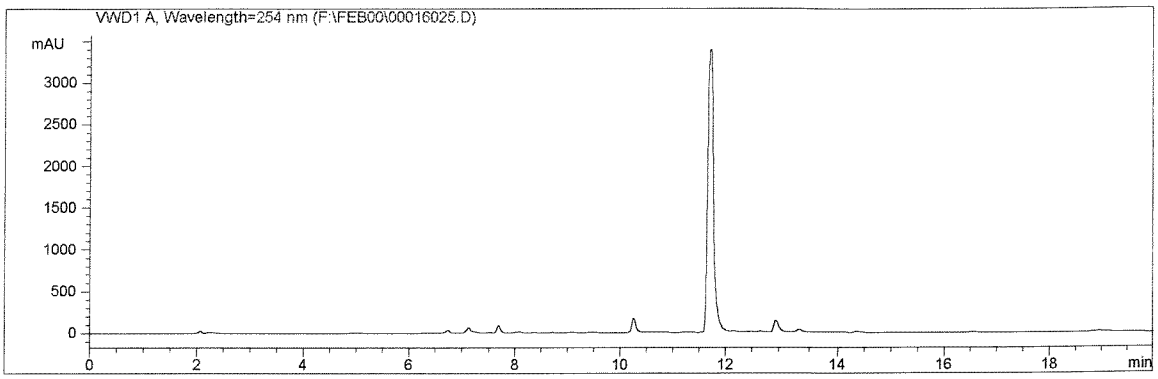


Figure 4.5.3.2 *Chromatogram of a solution with original composition 0.2 M iodobenzene and 0.3 M benzene in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O, after a charge of 1.4 F was passed.*

It was concluded that a trace amount of diphenyliodonium cation may have been formed, because of the ion at 281 m/z seen by positive ion electrospray mass spectroscopy, but there was not enough of a reaction for it to be discernible by hplc analysis or to allow product isolation.

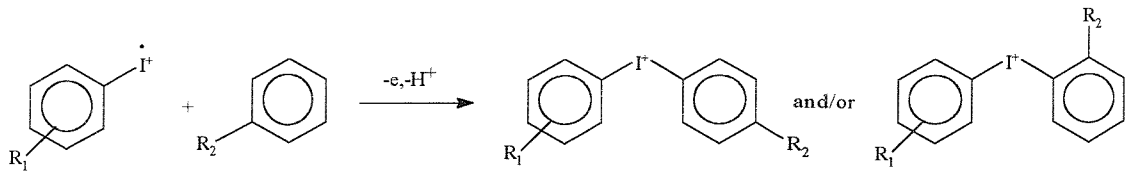
Relative Intensity %	**m/z**
20	394.3
21	281
100	393.2

Table 4.5.3.2

4.5.4 Summary of the Electrosynthesis of Alkyl Substituted Diaryliodonium Salts

The electrochemical synthesis of a number of alkyl substituted diaryliodonium salts has been described, *ibid.*. Table 4.5.4.1 is a summary of these electrolyses

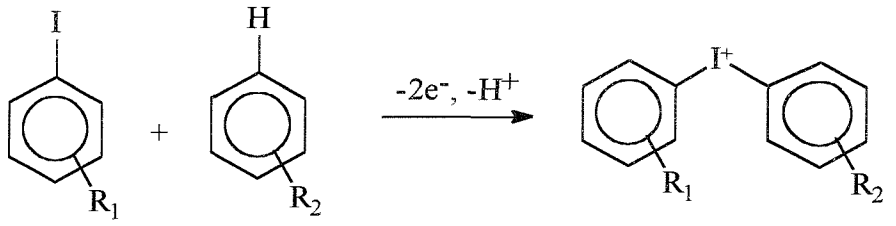
It was clear from the summary that the electrolysis conditions favoured the coupling of alkyl substituted aryl iodides with alkyl substituted arenes. The alkyl group and the iodine atom in the aryl iodide have fixed positions on the phenyl ring and as expected these positions were seen to be retained in the product. The alkyl-arene was expected to undergo nucleophilic attack by the aryl iodide cation radical in the 2 or 4 position, thus two isomers were possible in the electrolysis product, see Scheme 4.5.3.1.



Scheme 4.5.3.1

In the series of electrolyses of alkyl substituted aryl iodides and alkyl substituted arenes, only 4-iodotoluene and toluene coupled to give the *para* isomer 4,4'-dimethyldiphenyliodonium cation and the *ortho* isomer 2,4'-dimethyldiphenyliodonium cation, in the ratio 9:1. It may be that the bulky nature of the alkyl groups in the rest of the series excludes the *ortho* isomer, because of the steric hindrance of the *ortho* position relative to the *para* position. Similarly it was found that the coupling of iodobenzene and toluene lead to two isomers, 4-methylphenyliodonium and 2-methyphenylphenyliodonium cation, in the ratio of ca. 12:1. There was no evidence from the ^{1}H-NMR of an alkyl benzene being coupled in the *meta* position relative to the alkyl group which was consistent with Kitamuras[9] observation. It is of interest that 4-methylphenylidonium cation was successfully electrosynthesised from iodobenzene and toluene but not from 4-iodotoluene and benzene. Also iodobenzene would not couple with benzene. It was therefore apparent that for efficient synthesis of aryl iodides and arenes the aryl iodide did not necessarily need to be substituted with an electron donating group, but it was necessary for the arene to be activated by

substitution with such a group.



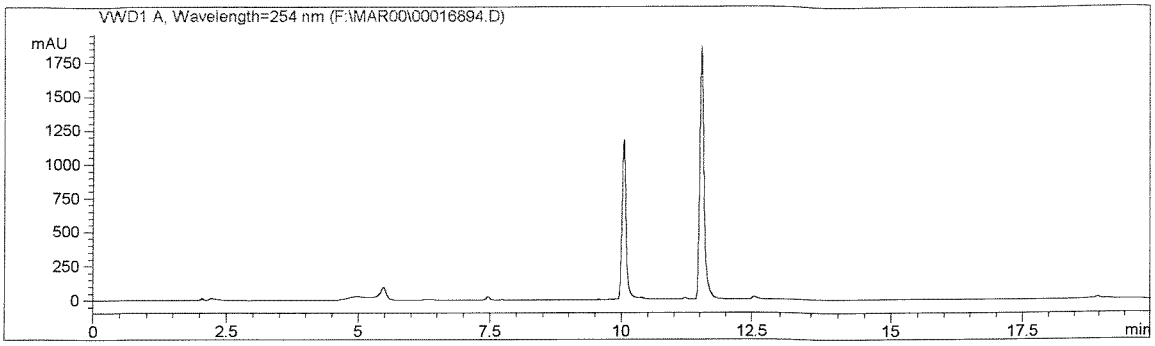
R_1	R_2	Chemical Selectivity %	Current efficiency %
H	H	no iodonium salt isolated	no iodonium salt isolated
4-Me	H	no iodonium salt isolated	no iodonium salt isolated
H	Me	71	20
4-Me	4-Me	92	46
3-Me[a]	4-Me	83	27
2-Me	4-Me	77	37
4-Me	4-Et	71	22
4-Me	4-*i*-Pr	78	22
4-Me	4-*t*-Bu	92	44
4-*t*-Bu	4-Me	48	14
4-*t*-Bu	4-*t*-Bu	52	31

Table 4.5.4.1.

4.6 Electrolysis of 4-Iodoanisole and Anisole

An extension of our efforts to synthesize a series of diaryliodonium analogues was to extend the oxidative coupling to alkoxy substituted iodonium salts. In pursuit of this goal the electrolysis of 4-iodoanisole and anisole was carried out.

The beaker cell was filled with a solution of 0.2 M 4-iodoanisole and 0.3 M anisole in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride. The electrolysis was carried out at a current density of 5 mA/cm^2 at the carbon felt anode, until 1.6 F of charge was passed. Figure 4.6.1 shows that the hplc chromatograms recorded before and after the electrolysis.



Chromatogram of a solution of 0.2 M 4-iodoanisole and 0.3 M anisole in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride.

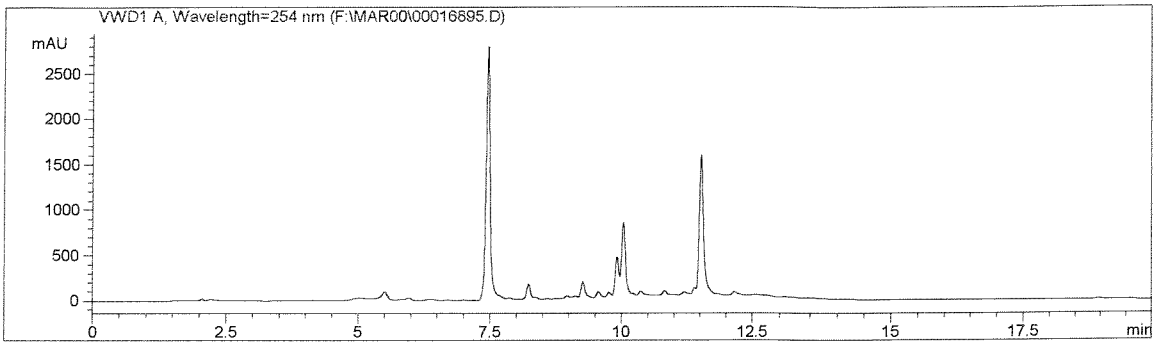


Figure 4.6.1. *Chromatogram of a solution of 0.2 M 4-iodoanisole and 0.3 M anisole in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride. After a charge of 1.6 F had been passed at a constant current density of 5 mA/cm^2.*

The hplc chromatograms in Figure 4.6.1 show that there was consumption of the starting material and the was the production of a major peak at ca. 7.5 minutes. Also an additional small peak was seen at ca. 5.5 minutes even before any charge was passed. Aliquots was removed and diluted with acetonitrile for electrospray mass spectroscopy, after the electrolysis. The electrospray mass spectrum showed a single ion of m/z 341 Da, that was expected for the dimethoxydiphenyliodonium cation. The reaction mixture was worked up in accordance with the standard procedure. The addition of potassium iodide caused the immediate precipitation of crystals. The crystals were separated and dried on a filter paper. A 0.71 g yield of material was found. The ^{1}H-NMR spectrum was recorded, see Figure 4.6.2.

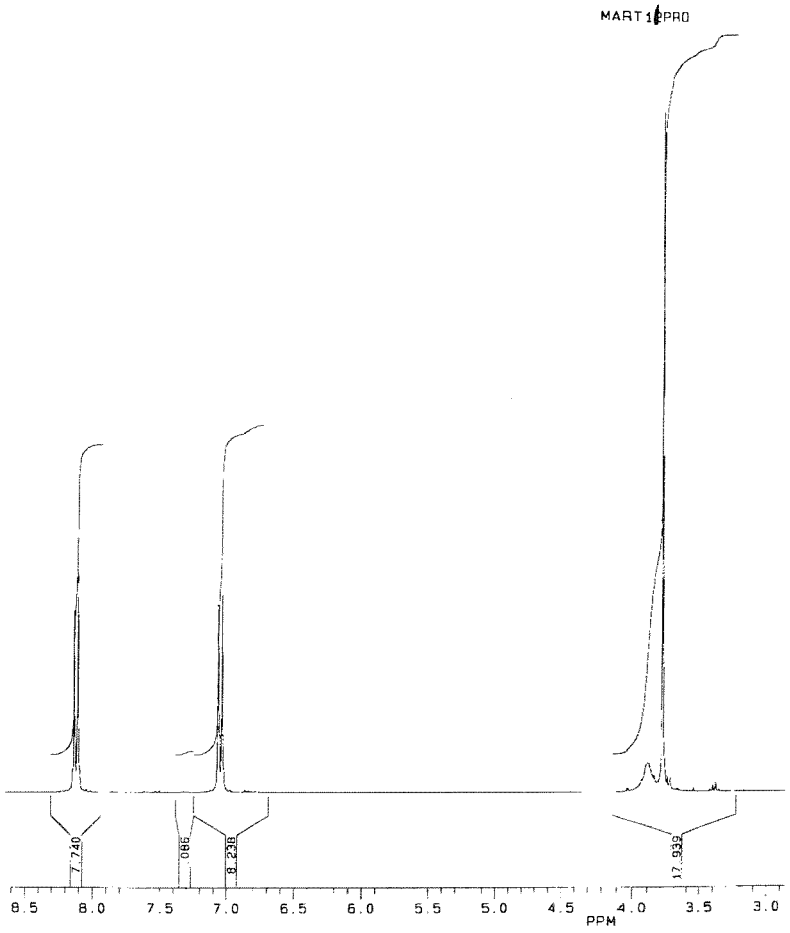


Figure 4.6.2 *^{1}H-NMR spectrum of the material isolated from the electrolysis of 4-iodoanisole and anisole.*

The ^{1}H-NMR spectrum contained three signals; 8.11, 7.04 and 3.8 ppm, with the ratio of the integral values being 2:2:3 respectively. The signals in the aromatic region were doublets, which would suggest that the aromatic rings were *para* substituted. The singlet at 3.8 ppm has a chemical shift value, which would suggest that it was adjacent to an electronegative atom , such as oxygen. Considering the ratio of the signal, at 3.8 ppm and its chemical shift value it was assigned to the protons on a methoxy group. The ^{1}H-NMR spectrum were compared to that of 4-methoxyphenylphenyliodonium triflate, synthesised by the method of Kitamura[9], see Section 2.4.3. This similarly

contained a doublet at 8.2 ppm and 7.1 ppm and a singlet at 3.8 ppm. The ^{1}H-NMR spectrum was also compared to that of 4,4'-dimethyldiphenyliodonium iodide. The pattern of peaks in the spectra of 4,4'- dimethyldiphenyliodonium iodide and the isolated material was very similar, except that the chemical shift values had changed to similar values to the chemical shifts in methoxyphenylphenyliodonium triflate. It would be expected that 4,4-dimethoxydiphenyliodonium iodide would have the same pattern of peaks as 4,4'-dimethyldiphenyliodonium iodide, but those peaks would occur at different chemical shift values because of the replacement of a methyl group by a methoxy group.

It was noted that there were no additional peaks in the spectrum of 4,4-dimethoxydiphenyliodonium iodide which could be assigned to the 2,4'-dimethoxydiphenyliodonium iodide isomer.

The ^{13}C-NMR and DEPT-135 spectra, of the material isolated after the electrolysis of 4-iodoanisloe and anisole were recorded, see Figure 4.6.3 and Figure 4.6.4 respectively.

Figure 4.6.3 *^{13}C-NMR spectrum of the material isolated from the electrolysis of 4-iodoanisole and anisole*

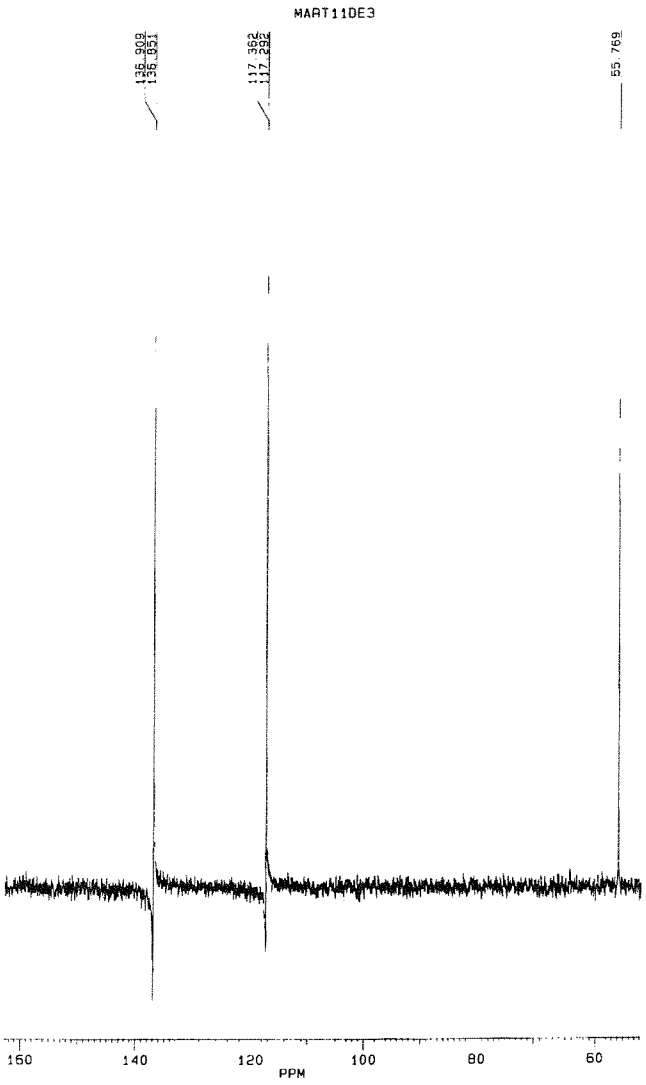


Figure 4.6.4 *DEPT-135 spectrum of the material isolated from the electrolysis of 4-iodoanisole and anisole.*

A comparison of the ^{13}C-NMR and DEPT-135 spectra was carried out.

The ^{13}C-NMR spectrum showed five signals; 161.7, 136.9, 117.3 107.1 and 55.8 ppm.

The DEPT-135 spectrum similarly showed three signals; 136.9, 117.3 and 55.8 ppm.

The signals at 161.7 and 107.1 were assigned to aromatic quaternary carbon atoms, whilst the signals at 136.8 and 117.3 were assigned to aromatic methine carbon atoms. The signal at 55.7 was characteristic of a methoxy carbon atom. The pattern of the

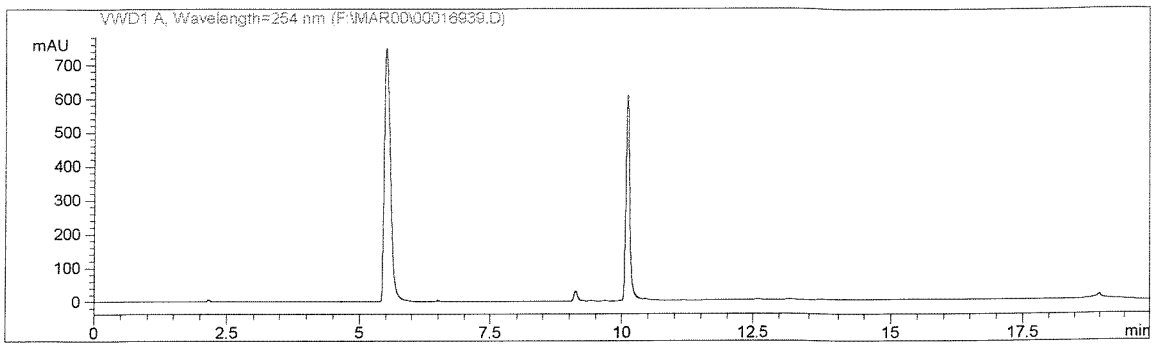
peaks in the ^{13}C-NMR was similar to that seen for the 4,4'-dimethyldiphenyliodonium cation.

The chemical selectivity, of the electrolysis of 0.2 M 4-iodoanisole and 0.3 M anisole, was determined to be 42 % and the current efficiency 9 %, with respect to the isolated 4,4'-dimethoxydiphenyliodonium salt.

4,4'-Dimethoxyldiphenyliodonium iodide. ^{1}H NMR (300 MHz, d^{6}-DMSO); δ 8.11 (d, J = 8.8, 4H), 7.04 (d, J = 9.56, 4H), 3.8 (s, 6H): ^{13}C NMR (300 MHz, d^{6}-DMSO): δ 161.54,136.71, 117.14, 114.22, 55.71: MS (ES) calcd. for $C_{14}H_{14}O_2I^+$ 341, found 341.

The NMR spectrum did not have additional peaks which could be attributable to isomers of the iodonium salt. This was consistent with Kitamura[9] and Kazmierczak[6] observations, who had similarly coupled iodobenzene (III) with anisole and had only isolated the 4-methoxyphenylphenyiodonium cation. It was suggested that this resulted from the enhanced steric and/ or inductive factors of the methoxy substituent[6].

We had previously seen an improvement in yield of 4,4'-dimethydiphenyliodonium salt, when the acetic anhydride content of the solvent, acetic acid/ 5 % sulfuric acid, was raised to 25 % , see Section 4.4.1. A 0.3 M solution of anisole in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride was prepared and immediately an aliquot was removed and diluted with acetonitrile for analysis by hplc. A series of such aliquots were then removed at regular time intervals. The chromatograms for the solution at t = 0 and t =10 minutes are shown in Figure 4.6.5.



Chromatogram of a solution with an original composition of 0.3 M anisole in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O. Sample was taken from the freshly prepared solution.

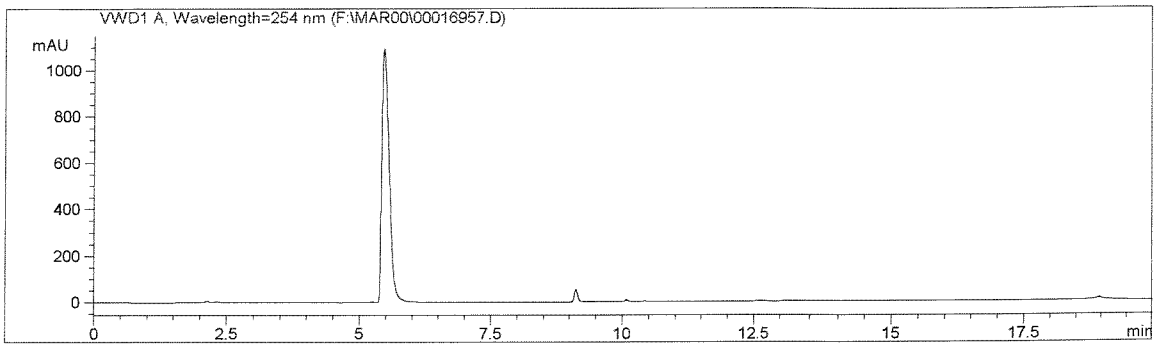


Figure 4.6.5 *Chromatogram of a solution of 0.3 M anisole in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O. Sample was taken 10 minutes after the solution was prepared.*

It was seen that in the freshly prepared solution, t = 0, there were two peaks in the chromatogram, with elution times of 5.5 and 10.5 minutes. The peak at 10.5 minutes was assigned to the anisole. After a period of 10 minutes only one major peak was seen , elution time 5.5 minutes, with the anisole peak all but gone. It was clear that anisole was undergoing a relatively rapid homogenous reaction comparable to the time scale of an electrolysis. It was previously noted that a fresh solution of 4-iodoanisole and anisole in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride similarly showed this peak, see Figure 4.6.1, but the peak was very much smaller.

The following protocol was adopted to isolate the reaction product; the reaction mixture was partitioned between an aqueous phase and diethyl ether. The diethyl ether phase was separated and then dried with anhydrous magnesium sulfate. The hydrated magnesium sulfate was then removed by filtration and the diethyl ether was removed

under vacuum. A clear oil was left; a sample of which was diluted with acetonitrile for hplc analysis, see Figure 4.6.6.

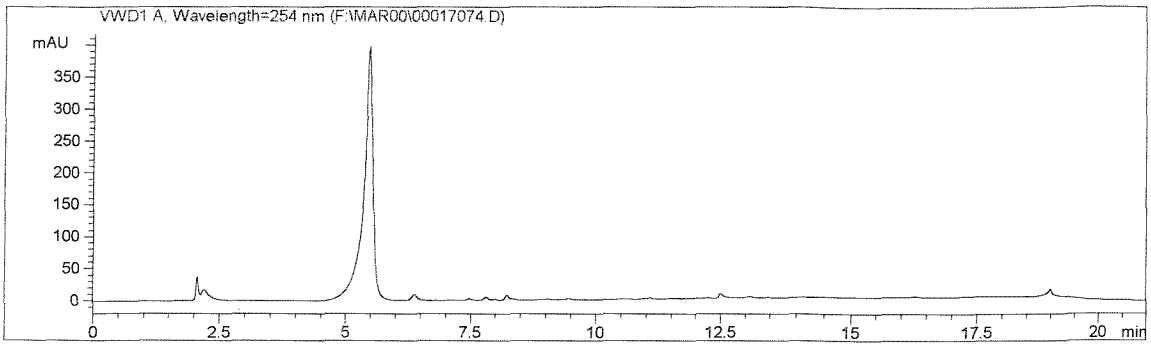
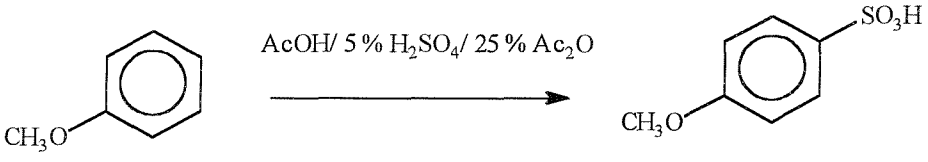


Figure 4.6.6 *Chromatogram of a solution of oil separated from the solution of original composition 0.3 M anisole in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O.*

A sample of the oil was diluted with acetonitrile/water 0.1 % ammonia and analysed by negative ion electrospray mass spectrometry and showed a peak ion of 187 Da. The ^{1}H-NMR and C^{13}-NMR spectra were recorded. The aromatic region of the ^{1}H NMR and ^{13}C-NMR showed that the ring was *para* substituted, and that one of the substituents was a methoxy group whilst the other group did not contain any carbon atoms.
A structure consistent with these conclusions is 4-methoxybenzenesulfonic acid. The calculated m/z for the conjugate base of the acid was 187 Da, which was seen by negative electrospray mass spectroscopy. The reaction is summarised in Scheme4.6.1.

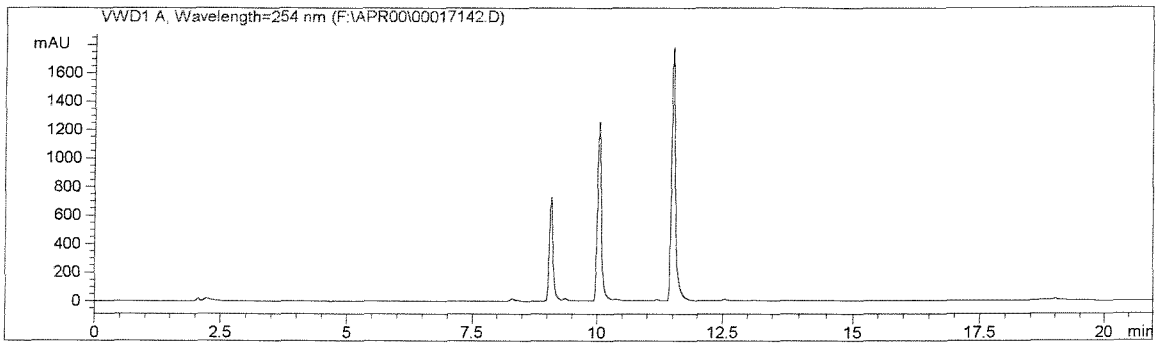


Scheme 4.6.1

4-Methoxybenzenesulfonic acid.^{1}H NMR (300 MHz, d^6-DMSO); δ 7.55 (d, J = 8.8, 2H), 6.89 (d, J = 8.8, 2H), 3.75 (s, 3H): ^{13}C NMR (300 MHz, d^6-DMSO): δ 159.66, 139.82, 127.20, 113.04, 55.28: MS (ES negative ion) calcd. for $C_7H_6O_4S^-$ 187, found 187.

The sulfonation of aromatic rings can be carried out with a number of reagents and solvent systems[31], but the solvent system identified in our work is an example of a relatively mild system. Parker [32], similarly carried out the monosulfonation of anisole in the *para* position, using a concentration of 0.88 M anisole in trifluoroacetic acid/ 8 % sulfuric acid, this solution was not so dissimilar to the one used in our experiment.

An alternative approach that avoids the possibility of sulfonation was to change the electrolyte system to acetic acid/ 8 % fluoroboric acid/ 2 % acetic anhydride:
The electrolysis cell with a graphite cathode, was charged with a solution of 0.2 M 4-iodoanisole and 0.3 M anisole in acetic acid/ 8 % sulfuric acid/ 2 % acetic anhydride. Constant current electrolysis was performed using a current of 400 mA (current density at the anode was ca. 5 mA cm^{-2}). Figure 4.6.7 shows that the hplc recorded before and after the electrolysis.



Chromatogram of a solution with original composition 0.2 M 4-iodoanisole and 0.3 M anisole in AcOH/ 8 % HBF_4/ 2 % Ac_2O.

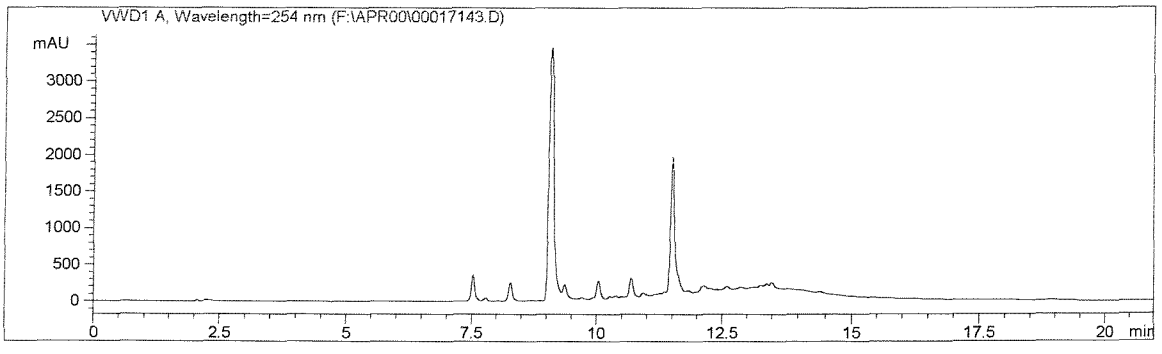


Figure 4.6.7 *Chromatogram of a solution with original composition 0.2 M 4-iodoanisole and 0.3 M anisole in AcOH/ 8 % HBF_4/ 2 % Ac_2O, after 1.8 F of charge was passed at a constant current of 5mA/cm^2.*

Consideration of the hplc response shown in Figure 4.6.7 show that there were three peaks present before any charge was passed. The peaks at 10.0 and 11.5 minutes were assigned to anisole and 4-iodoanisole respectively. The additional peak was seen at 9 minutes. At the end of the electrolysis nearly all the anisole had been lost and the peak at 9 minutes together with a small peak at 7.5 minutes was seen on the chromatogram. It was noted, from the electrolysis of 4-iodotoluene and toluene, that the dimethyldiphenyliodonium cation had an elution time of ca. 7.5 minutes. An aliquots was removed from the reaction mixture and diluted with acetonitrile for positive ion electrospray mass spectroscopy analysis. The electrospray mass spectrum showed a single ion of m/z 341 Da, that was expected for the dimethoxyldiphenyliodonium cation. The reaction mixture was then worked up using the standard procedure. The addition of the potassium iodide solution, caused an immediate precipitation of white powder. This material was separated on the filter paper, and dried to give a yield of 1.94 g. The ^{1}H-NMR, ^{13}C-NMR, and DEPT-135 analysis was carried out. The spectra were compared to those previously recorded for 4,4'-dimethoxydiphenyliodonium iodide and were clearly the same. It was noted that there were again no peaks which may be assigned to the 2,4'-dimethoxydiphenyliodonium iodide. A current efficiency of 25 % was calculated

The diethyl ether solution, was reduced in volume under vacuum to a dark oil. This oil was diluted in dichloromethane and submitted for GC-MS analysis. Figure 4.6.8 shows the recorded GC-MS chromatogram.

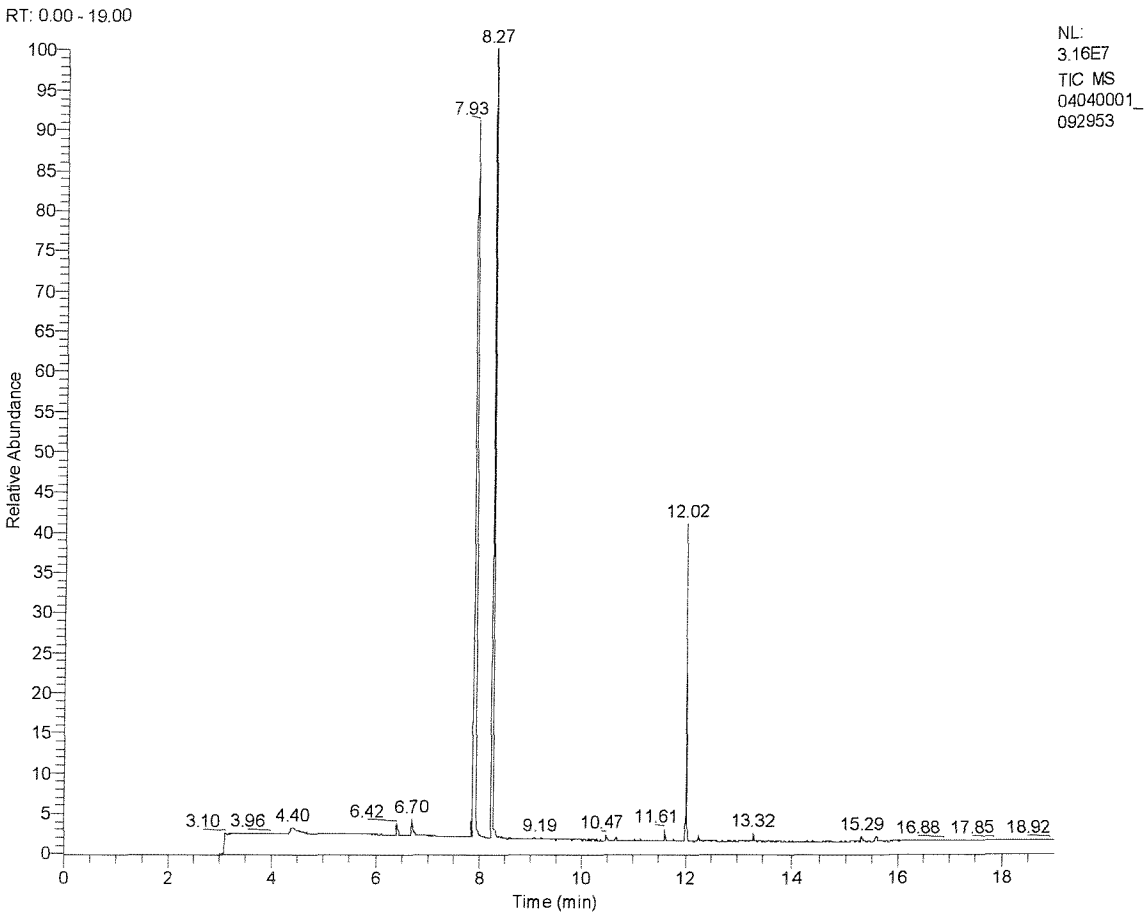


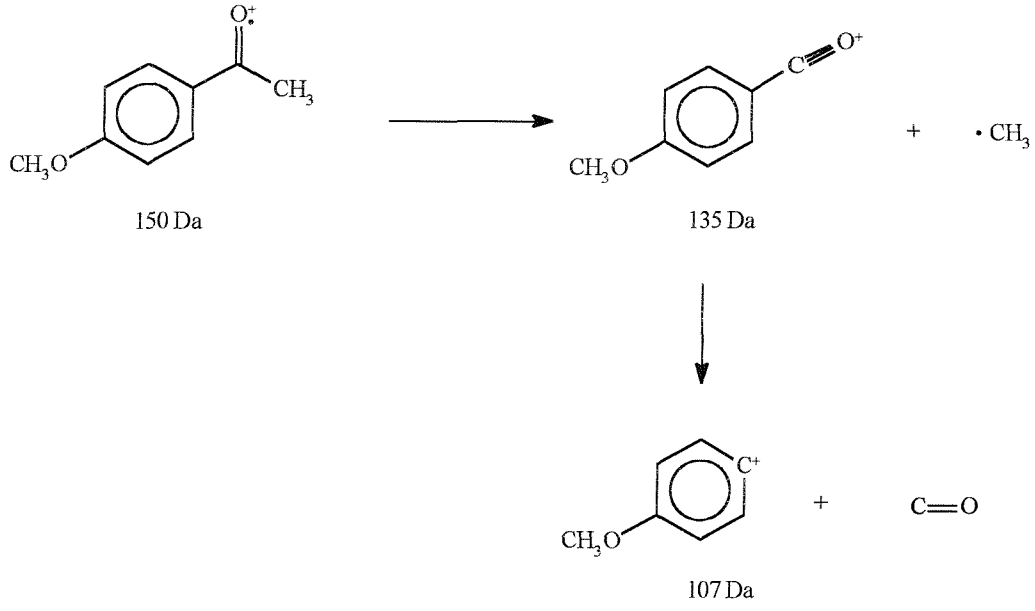
Figure 4.6.8 *Chromatogram of the dichloromethane wash after the electrolysis of a solution of an original composition of 0.2 M 4-iodoanisole and 0.3 M anisole in AcOH/ 8 % HBF_4/ 2 % Ac_2O.*

The corresponding mass spectra of the peaks in the chromatogram are shown in Table 4.6.1.

Retention Time	7.93		8.27		12.02	
	m/z	Relative Intensity / %	m/z	Relative Intensity / %	m/z	Relative Intensity / %
	38	32	107	31	115	8
	64	36	63	31	169	9
	50	40	92	41	141	10
	92	42	77	58	228	12
	234	58	150	59	242	25
	63	100	135	100	227	100

Table 4.6.1

An analysis of the GC-MS chromatogram was carried out; the peak at 7.93 minutes was identified as the starting material, 4-iodoanisole. The peak at 8.27 minutes was seen to have a molecular ion at 150 Da and fragmented to give daughter ions at 135 Da and 107 Da. The two daughter ions have molecular weights equal to 150 - CH_3 and 150 - $COCH_3$. The loss of a methyl group and an acetyl group is characteristic of an acetophenone[44] It was therefore proposed that the peak eluted at 8.27 minutes was the molecule 4-methoxyacetophenone, whose molecular weight was 150 Da. The proposed fragmentation of 4-methoxyacetophenone is summarised in Scheme 4.6.2.



Scheme 4.6.2

The third peak seen by on the GC-MS had a retention time of 12.02, the heaviest ion in the corresponding mass spectrum had a m/z value of 242 Da. A speculative molecular formulae for this ion was $C_{15}H_{14}O_3$. There was an intense daughter ion with a m/z value of 227 Da, which could result from the loss of a methyl group, 15 Da, which was a characteristic of an acetophenone[44].

An hplc chromatogram of a commercial sample of 4-methoxyacetophenone was recorded, see Figure 4.6.8.

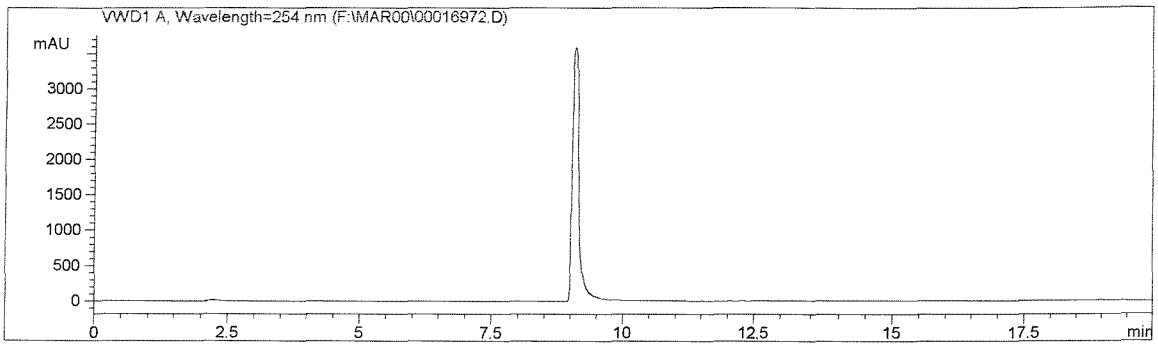
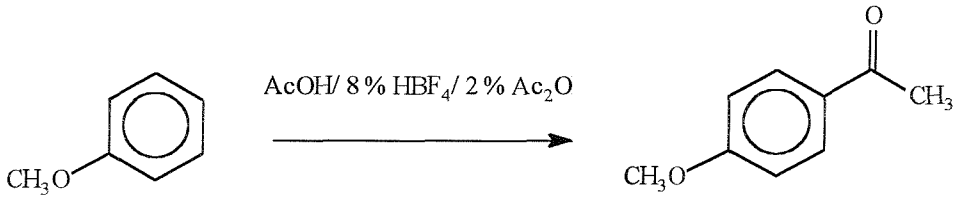


Figure 4.6.8 *Chromatogram of a solution of 4-methoxyacteophenone in acetonitrile.*

The retention time of 4-methoxyacetophenone was ca. 10.9 minutes, this was the elution time seen for the third peak seen in the chromatogram after the solution of 4-iodoanisole had been allowed to stand. When this evidence was taken into account along side that gathered from the GC-MS analysis it was apparent that anisole was undergoing a Friedel-Craft type acylation under the reaction conditions. This is shown in Scheme 4.6.3.



Scheme 4.6.3

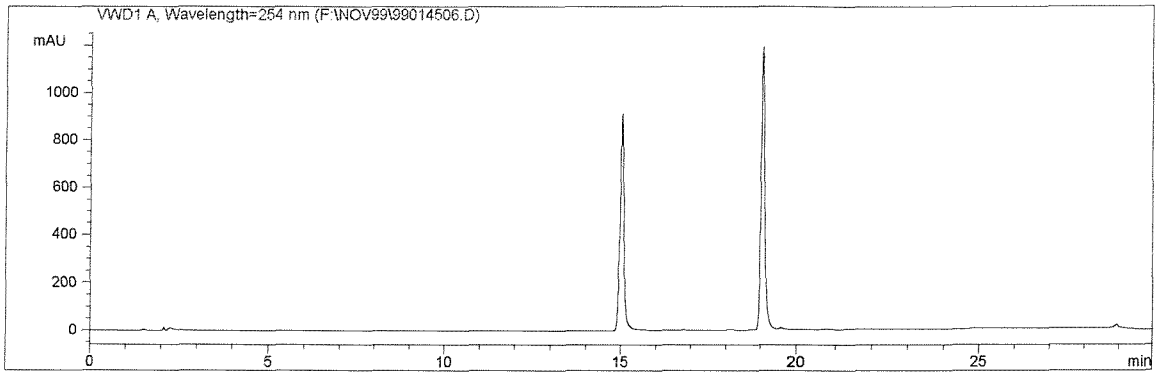
A review[31] of the Friedel-Craft acylation of anisole would suggest that the *para* position was the favoured site for electrophilic substitution.

Therefore a competing chemical reaction was taking place in competition with the electrolysis of 4-iodoanisole and anisole in acetic acid/ 8 % fluoroboric acid/ 2 % acetic anhydride.

The current efficiency of this reaction was limited by the competing chemical reaction that anisole had with the solvent system to form 4-methoxybenzophenone. There was no evidence for the coupling between 4-iodoanisole and 4-methoxybenzophenone.

4.7 Electrolysis of 4-Iodotoluene and Fluorobenzene

A electrolysis of 0.2 M 4-iodotoluene and 0.3 M fluorobenzene in acetic acid/ 5 % sulfuric acid/ 10 % acetic anhydride was carried out where the current density at the anode was ca. 5 mA cm^{-2}. Figure 4.7.1 shows that the hplc chromatograms recorded before and after the electrolysis.



The chromatogram of a solution of original composition of; 0.2 M 4-iodotoluene and 0.3 M fluorobenzene in AcOH/ 5 % H_2SO_4/ 10 % Ac_2O

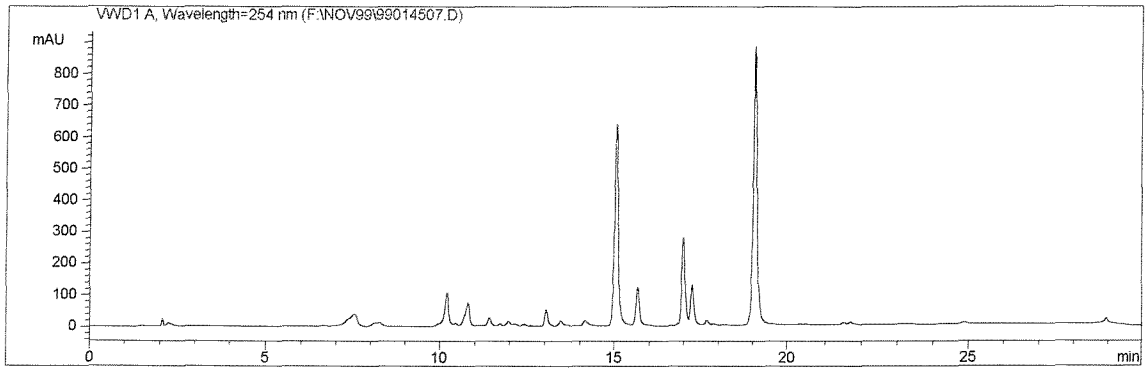


Figure 4.7.1 *The chromatogram of a solution of original composition of; 0.2 M 4-iodotoluene and 0.3 M fluorobenzene in AcOH/ 5 % H_2SO_4/ 10 % Ac_2O, after a charge of 1.6 F was passed at 400 mA constant current.*

The hplc chromatograms showed that there was a small decrease in the peak heights of the starting material and the formation of several new compounds. Aliquots was removed and diluted with acetonitrile for electrospray mass spectroscopy. The electrospray mass spectrum showed a three ions whose relative intensities were higher than 20 %, see Table 4.7.1.

Relative Intensity %	**m/z**
60	313.1
65	351.2
100	309.1

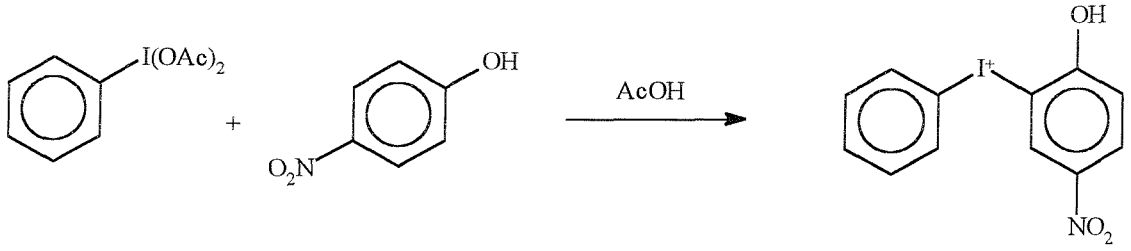
Table 4.7.1

The ion with an m/z value of 313 was what expected for fluorophenylmethylphenyliodonium cation

After the standard work up procedure the addition of the potassium iodide caused a brown oil to appear, but no identifiable material was isolated.

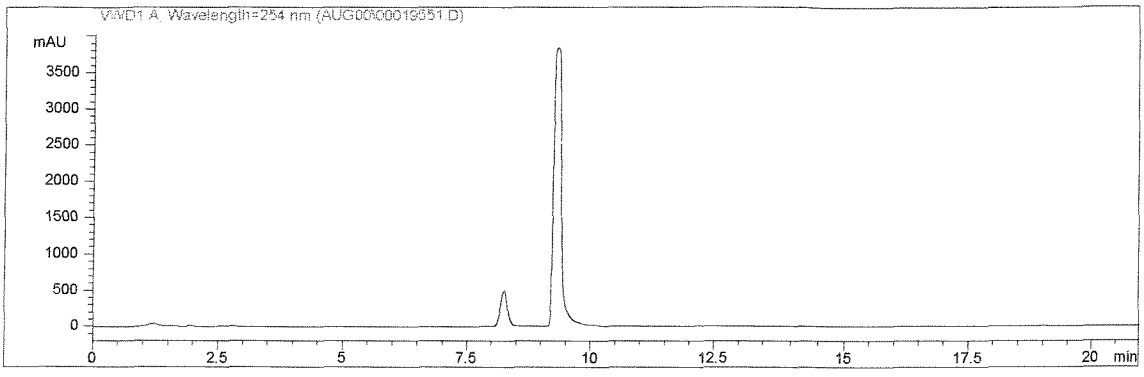
4.8 Electrolysis of 4-Iodotoluene and 4-Nitrophenol

Beringer[32] *et al* reported that the condensation of iodosylbenzene or [(diacetoxy)iodo]benzene with phenol in acid conditions were uniformly unsuccessful and only resulted in 4-iododiphenyliodonium salt. A hydroxydiphenyliodonium salt was reported was prepared by the condensation of (diacetoxyiodo)benzene with 4-nitrophenol in acetic acid. The success of the condensation was assisted in part by the decreased susceptibility of the phenol to oxidation resulting from the presence of the nitro group, see Scheme 4.8.1.



Scheme 4.8.1

An attempt to parallel the work of Beringer was undertaken. A 100 cm^3 solution of 0.3 M concentration of 4-nitrophenol in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride was prepared. An aliquot was removed immediately and diluted with acetonitrile and submitted for hplc analysis, a second aliquot was removed after one hour and similarly analysed, see Figure 4.8.1.



Chromatogram of a fresh solution of original composition 0.3 M 4-nitrophenol in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride

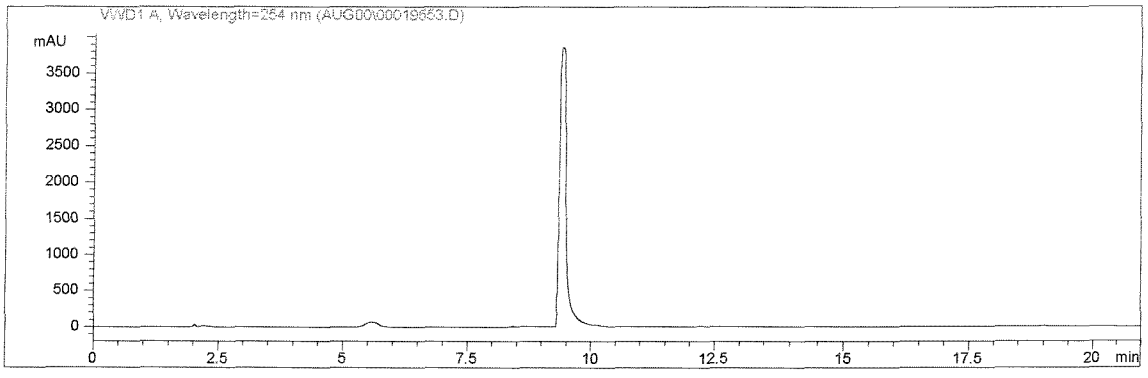


Figure 4.8.1 *Chromatogram of a solution of original composition 0.3 M 4-nitrophenol in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride, after 1hour.*

It was clear that in the freshly prepared solution of 4-nitrophenol there were two peaks at 8.3 and 9.3 minutes. The peak with the elution time of 8.3 minutes was identified as 4-nitrophenol although most had already undergone reaction. After one hour the second chromatogram shows that the 4-nitrophenol had completely gone.

A 1 cm^3 sample of the solution was removed and the solution was partitioned between dichloromethane and water. The dichloromethane phase was separated and an aliquot was further diluted with dichloromethane and submitted for GC-MS analysis, see Figure 4.8.2.

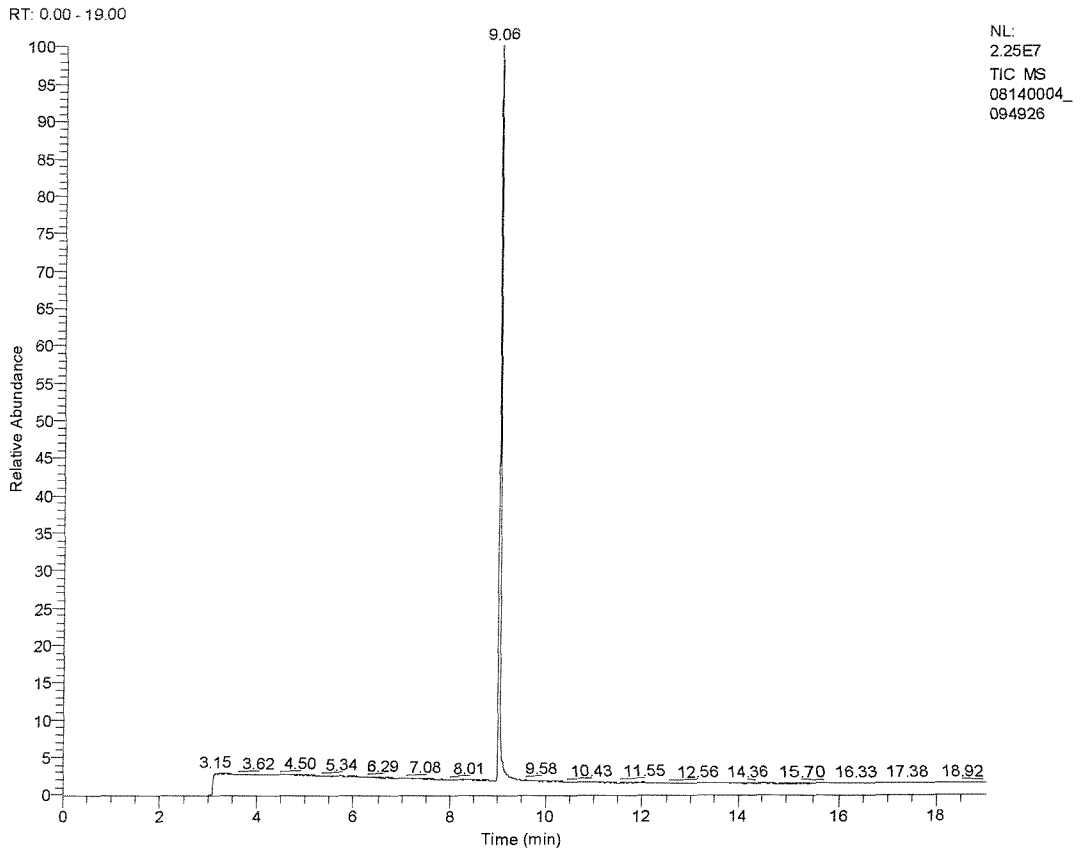


Figure 4.8.2 *GC-MS analysis of the material formed after phenol was left to stand in a solution of AcOH/ 5 % H_2SO_4/ 25 % Ac_2O.*

The gas chromatogram showed only one peak which was expected from the hplc out, see Figure 4.8.1. The corresponding electron impact mass spectra of the eluted compounds is shown in Table 4.8.1

Retention Time	**9.06**
m/z	Relative Intensity / %
64	31
39	43
109	44
64	50
63	54
43	100

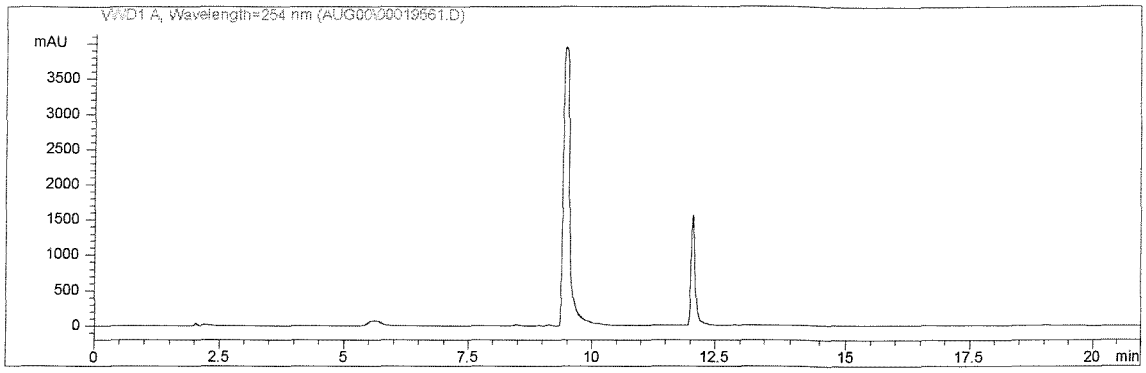
Table 4.8.1

The base peak had a m/z value of 43 Da, which was characteristic of an acetyl group. The parent molecular ion had an m/z value of 181 Da and a relative intensity of 10 %. A daughter ion was seen of m/z value 139 Da, which is the loss of CH_2CO and had a relative intensity of 23 %. The loss of CH_2CO was characteristic of an aryl acetate[44]. There are two further ion of m/z values 109 and 93 Da, which corresonded to 139-NO and 139-NO_2 respectively. These ions, 109 and 93 indicate that a nitro group was present in the molecule[44].

The starting material was 4-nitrophenol in a strong solution of acetic anhydride and considering the GC-MS evidence, then it was concluded that the peak in the hplc chromatogram at 9.3 minutes was 4-nitrophenyl acetate.

Into the remaining reaction solution , ca 99 cm^3, of acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride containing ca. 0.3 M 4-nitrophenyl acetate was added 4.36 g of 4-iodotoluene. The concentration of 4-iodotoluene was therefore ca. 0.2 M.

The electrolysis cell with a graphite cathode, surrounded by a carbon felt anode (approximate surface area of 80 cm^2) was charged with the solution. A constant current electrolysis was performed at 298 K, by maintaining a current of 400 mA (current density at the anode was ca. 5 mA cm^{-2}), between the two electrodes until the charge passed corresponding to 1.5 F had passed. Figure 4.8.3 shows that the hplc chromatograms recorded before and after the electrolysis.



The chromatogram of a solution of composition of 0.2 M 4-iodotoluene and 0.3 M 4-nitrophenyl acetate in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O

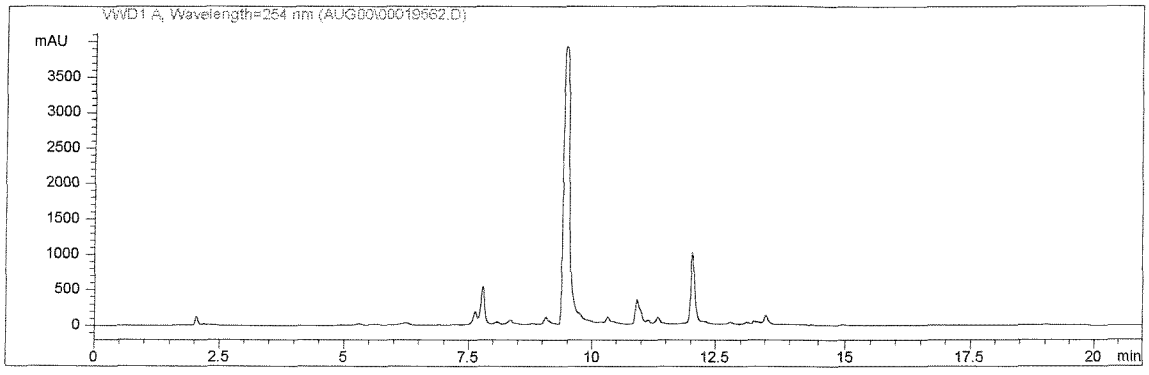


Figure 4.8.3 *The chromatogram of a solution of original composition of; 0.2 M 4-iodotoluene and 0.3 M 4-nitrohenyl acetate in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O, after a charge of 1.5 F was passed at a constant current of 5 mA/cm^2.*

Consideration of the chromatogram showed that there was a 37 % reduction in peak height of 4-iodotoluene. A small peak was seen to appear during the electrolysis at 7.8 minutes, which was in the region where iodonium cations are seen to elute. An aliquot of the reaction mixture was removed at the end of the electrolysis and diluted with acetonitrile for positive ion mass spectroscopy analysis. The mass spectrum showed two peaks whose relative intensities was greater than 20 %, see Table 4.8.2.

Relative Intensity %	**m/z**
83	309
100	398

Table4.8.2.

There was a base peak of m/z value 398 Da that was expected for the iodonium salt synthesised from the coupling of 4-iodotoluene and 4-nitrophenyl acetate.
The reaction mixture was worked up in the usual way. After the addition of the potassium iodide solution, a fine precipitation of a brown powder was seen. This material was separated on the filter paper, and dried. A 200 mg yield of material was recorded. The ^{1}H-NMR spectrum was recorded and is shown in Figure 4.8.5.

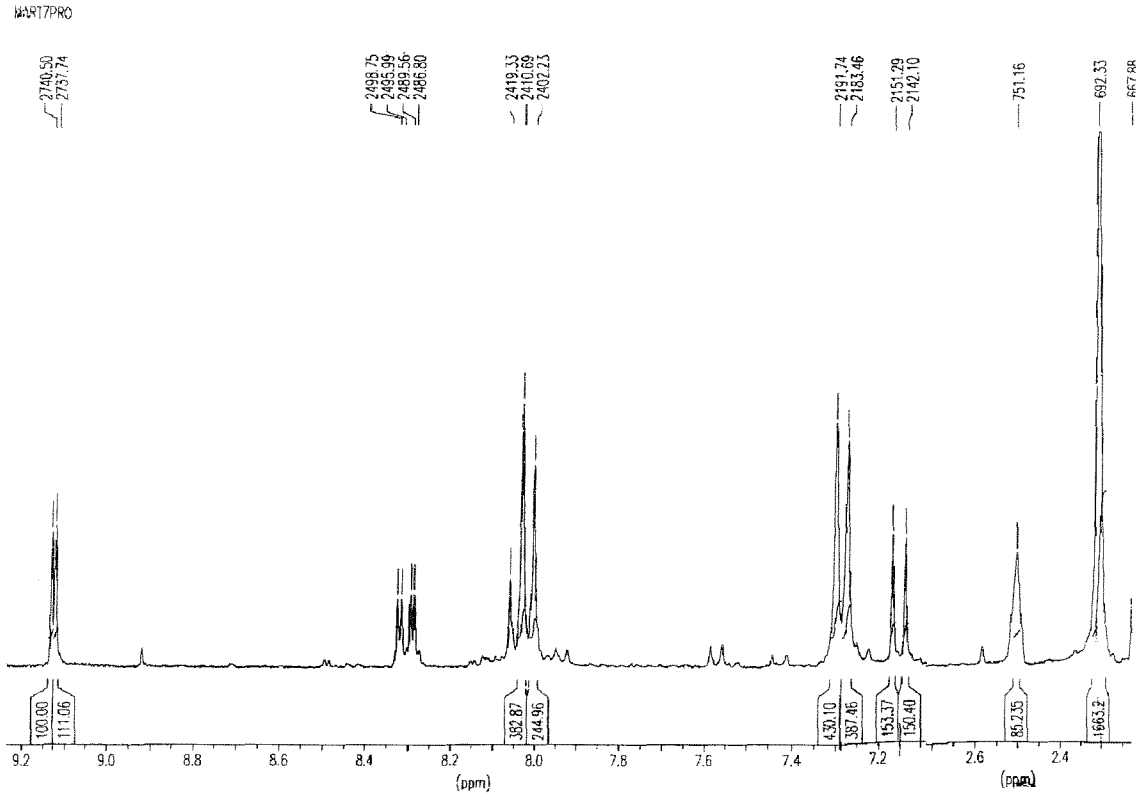
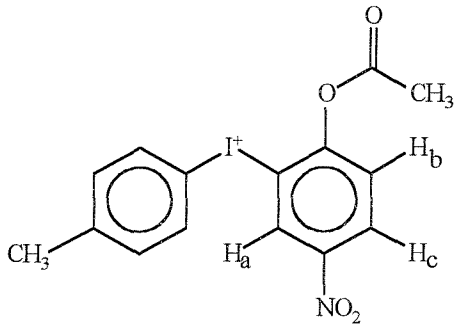


Figure 4.8.5 *Material isolated after the electrolysis of 0.2 M 4-iodotoluene and 0.3 M 4-nitrohenyl acetate in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O*

In the ^{1}H-NMR spectrum six distinct signals were seen at; 9.13, 8.30, 8.03, 7.30, 7.15, 2.30, with integral values ratio of 1:1:2:2:1:6. The doublet peaks at 8.03 and 7.30 were assigned to a phenyl ring that was *para* substituted with a methyl group and an iodonium group. The remaining three peak in the aromatic region were assigned to the remaining aromatic protons in accordance with Table 4.8.3.



Proton	Chemical Shift Value
a	9.13
b	8.30
c	7.15

Table 4.8.3

The integral ration of the peak at 2.30 would suggest that proton atoms in the two methyl groups had co-incidental chemical shift values.

The chemical selectivity and current efficiency were 5.4 and 2.4 % respectively.

The diethyl ether phase was reduced in volume and diluted with dichloromethane, an aliquot was removed and further diluted. The GC-MS chromatogram was recorded, see Figure 4.8.6.

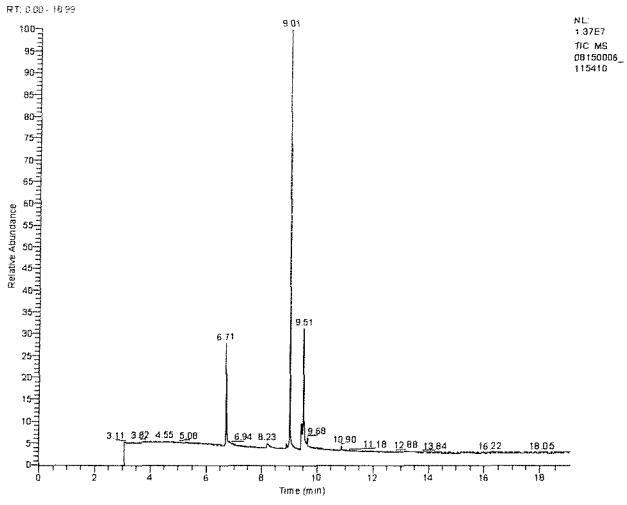


Figure 4.8.6 *GC chromatogram of a dichloromethane extraction of the electrolysis solution of 4-iodotoluene and 4-nitrophenyl acetate.*

The corresponding mass spectra are shown in Table 4.8.4

Retention Time	**6.71**		**9.01**		**9.51**	
	m/z	Relative Intensity / %	m/z	Relative Intensity / %	m/z	Relative Intensity / %
	89	24	64	10	90	37
	39	32	139	11	217	39
	65	41	65	17	276	47
	63	45	63	17	234	60
	91	95	39	16	89	94
	218	100	43	100	43	100

Table 4.8.4

The peaks with retention times of 6.71, 9.01 and 9.51 were identified as 4-iodotoluene, 4-nitrophenyl acetate and 4-iodobenzyl acetate respectively, by consideration of previous gas chromatograms and electron impact mass spectra.

The structure of the material isolated, 2-acetoxy-4-nitrophenyl-4'-methylphenyliodonium iodide was decided upon by considering how the functional groups on the aromatic ring in 4-nitrophenyl acetate would influence the site of attack by the electrophilic 4-iodotoluene cation radical. The acetoxy group activates positions *ortho* and *para* to itself towards electrophilic substitution, but the *para* position is blocked by the nitro group. The nitro group deactivates all ring positions, but deactivates the *meta* position less than those positions *ortho* and *para* to itself. Therefore in the molecule 4-nitrophenyl acetate it was the 2 position that was most susceptible to electrophilic substitution.

Chapter 5

Results and Discussion: Cyclic Hypervalent Iodoarenes

5.1 Introduction

This chapter reports the voltammetry of aryl iodides whose oxidation lead to cyclic hypervalent compounds by *intra* molecular cyclisation.

5.2 Electrochemistry of 2-Iodobiphenyl

5.2.1 Voltammetry of 2-Iodobiphenyl

The voltammograms of 2-iodobiphenyl in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride was recorded at a vitreous carbon rotating disc electrode, see Figure 5.2.1.1.

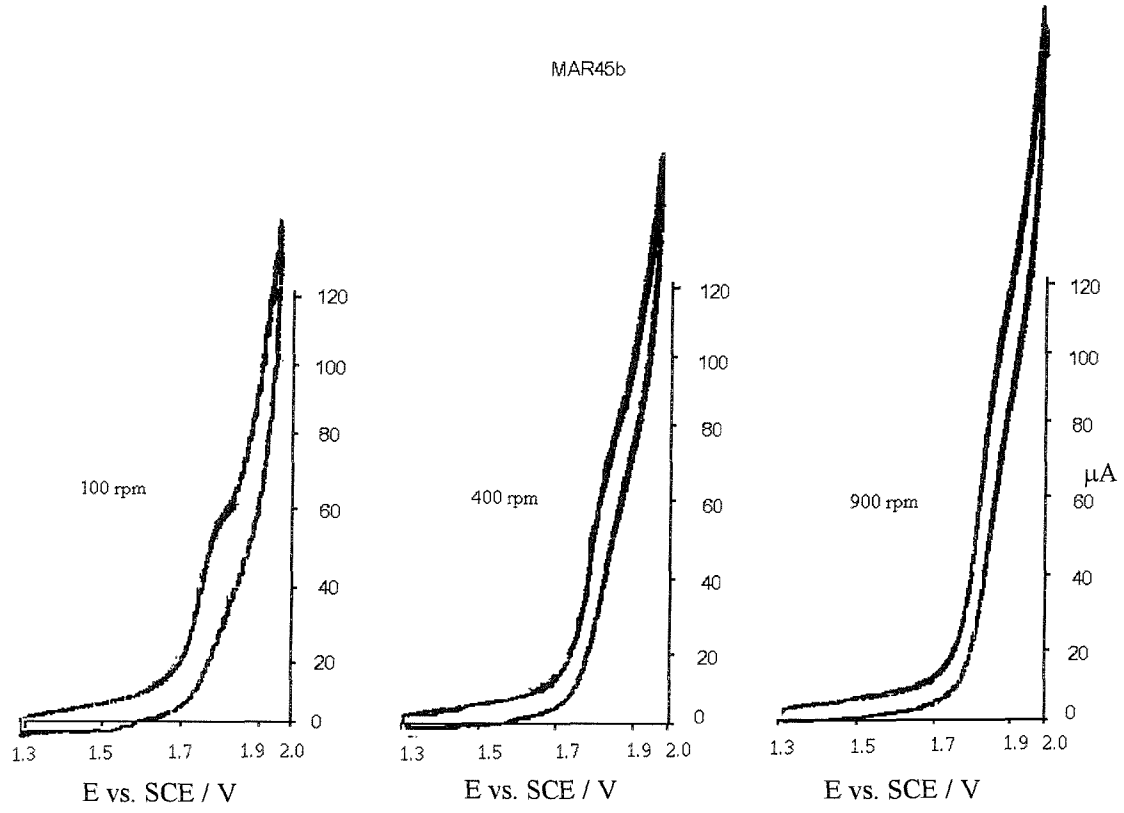


Figure 5.2.1.1 *Voltammogram of a freshly prepared solution of 2-Iodobiphenyl at a 1mM concentration in AcOH/ 5% H_2SO_4/ 2 % Ac_2O recorded at a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s.*

A wave was seen at a rotation rate of 100 rpm, with a half wave potential of 1.80 V vs. SCE, but which became less clear as the rotation rate was increased. There was little hysteresis between the forward and the back scan. The limiting current was seen to be dependent upon rotation rate. The wave recorded at a rotation rate of 400 rpm was investigated using Tomes analysis, see Figure 5.2.1.2. The gradient of the line was 91 mV. The expected gradient for a reversible two electron transfer was 29.5 mV. Thus it was concluded that the oxidation of 2-iodobiphenyl was irreversible. It was seen that the wave height of 2-iodobiphenyl was almost twice that measured for 4-iodotoluenes oxidation waves, but the oxidation of 2-iodobiphenyl took place at a higher anodic potential than 4-iodotoluene and therefore probably suffered increased distortion from the background current, see Section 3.2.1.

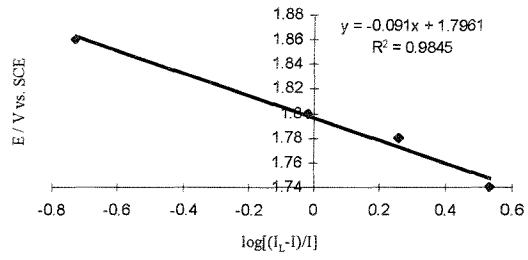
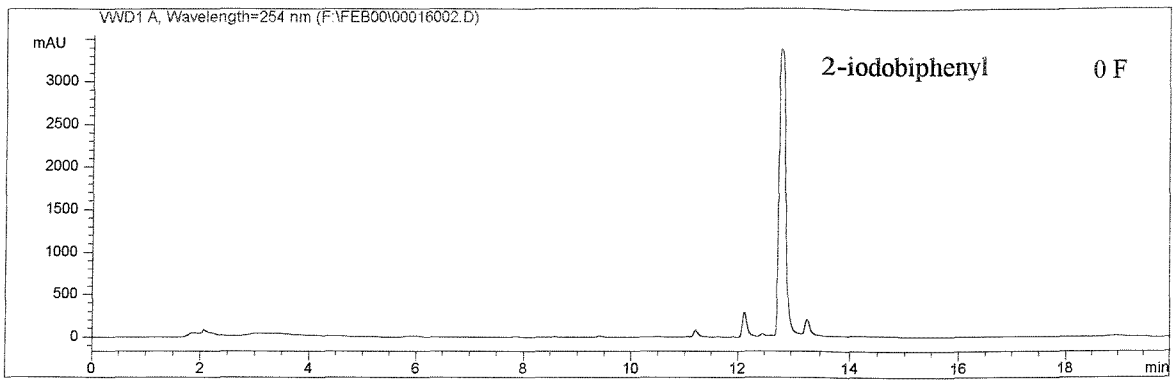


Figure 5.2.1.2 *Tomes analysis of the E vs. the log[(I$_L$- I)/I] for a freshly prepared solution of 2-Iodobiphenyl at 1mM concentration in AcOH/5 % H_2SO_4/2 % Ac_2O using a vitreous carbon rotating disc electrode (diameter 3mm), platinum counter electrode, scan rate 0.02V/s. Data was taken from the voltammogram recorded at 400 rpm in Figure 5.2.1.1.*

5.2.2 Electrolysis of 2-Iodobiphenyl

The beaker cell described previously, see Section 2.2.2, was charged with a 100 cm^3 solution of 0.2 M 2-iodobiphenyl in acetic acid/ 25 % acetic anhydride/ 5 % sulfuric acid. The electrolysis was performed at a current density of 5 mA/ cm^2 until a charge of charge of 1.6 F was passed. The electrolysis was analysed by removal of aliquots from the solution at the beginning and the end of the electrolysis and these were diluted with acetonitrile before being analysed by hplc, see Figure 5.2.2.1.



Chromatogram of a solution of 0.2 M 2-iodobiphenyl in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O

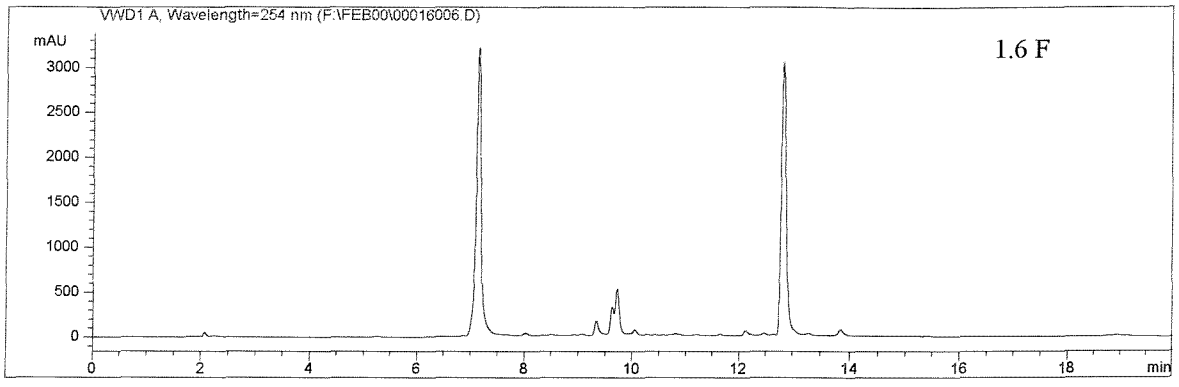


Figure 5.2.2.1 *The chromatograms recorded after a specified charge had been passed. The solution had an initial composition of; 0.2 M 2-iodobiphenyl in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O*

Consideration of the hplc chromatograms shown in Figure 5.2.2.1 show that there was consumption of the starting material and the production of a major peak at ca. 7.1 minutes. At the end of the electrolysis a precipitate was seen on the carbon felt anode, on the graphite cathode and on the bottom of the beaker. The suspension was filtered and the material sticking to the electrodes was carefully scrapped on to the filter paper. The slightly off white material was washed with diethyl ether whilst still on the paper and then dried. A yield of 0.63 g was recovered. A sample of this recovered material was then analysed by ^{1}H-NMR, see Figure 5.2.2.2.

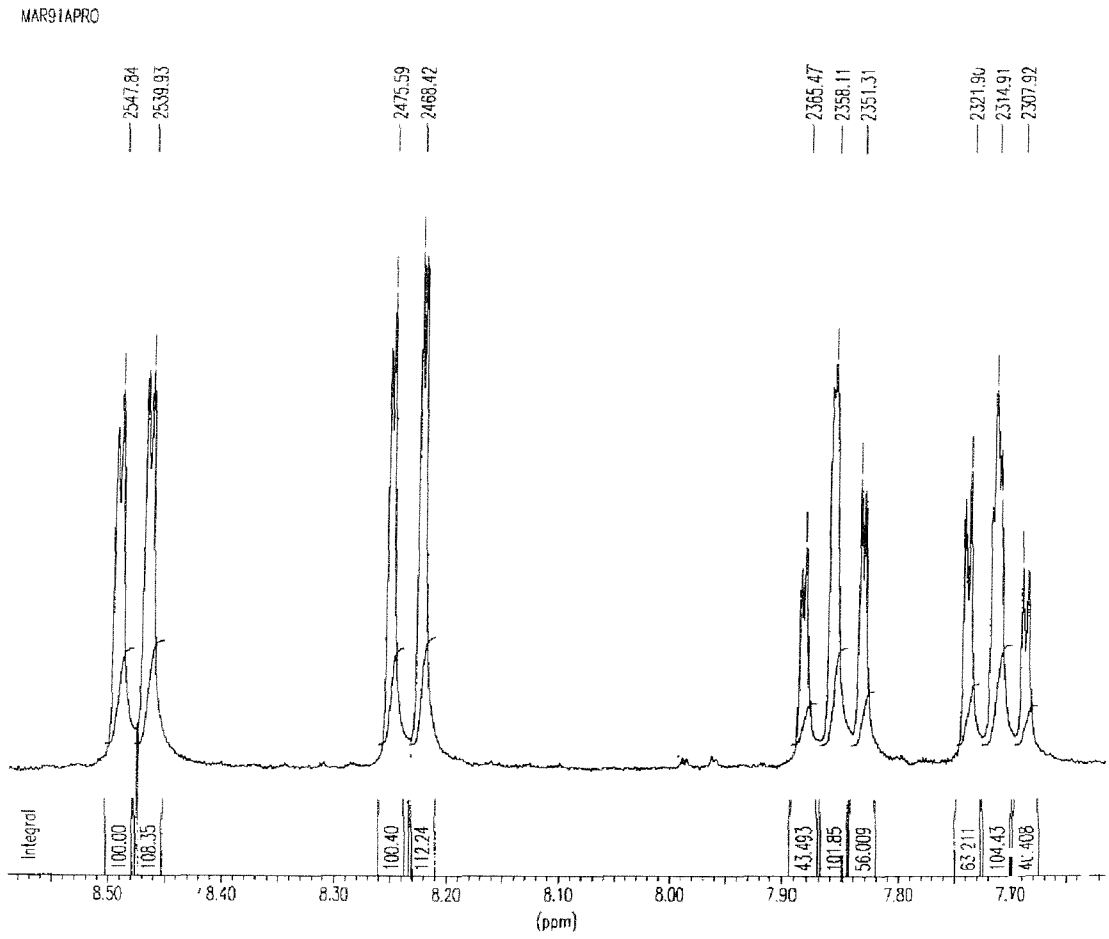


Figure 5.2.2.2. *The ^{1}H-NMR spectrum of material filtered from the electrolysis of 2-iodobiphenyl.*

Four peaks were seen in the aromatic region of the ^{1}H-NMR spectrum, with no high field signals. The ratio of the signal intensity was 1:1:1:1. The presence of these four signals suggested an aromatic ring that was di-substituted. The ^{13}C-NMR and DEPT-135 spectra of the filtered material were similarly recorded, see Figure 5.2.2.3 and Figure 5.2.2.4 respectively.

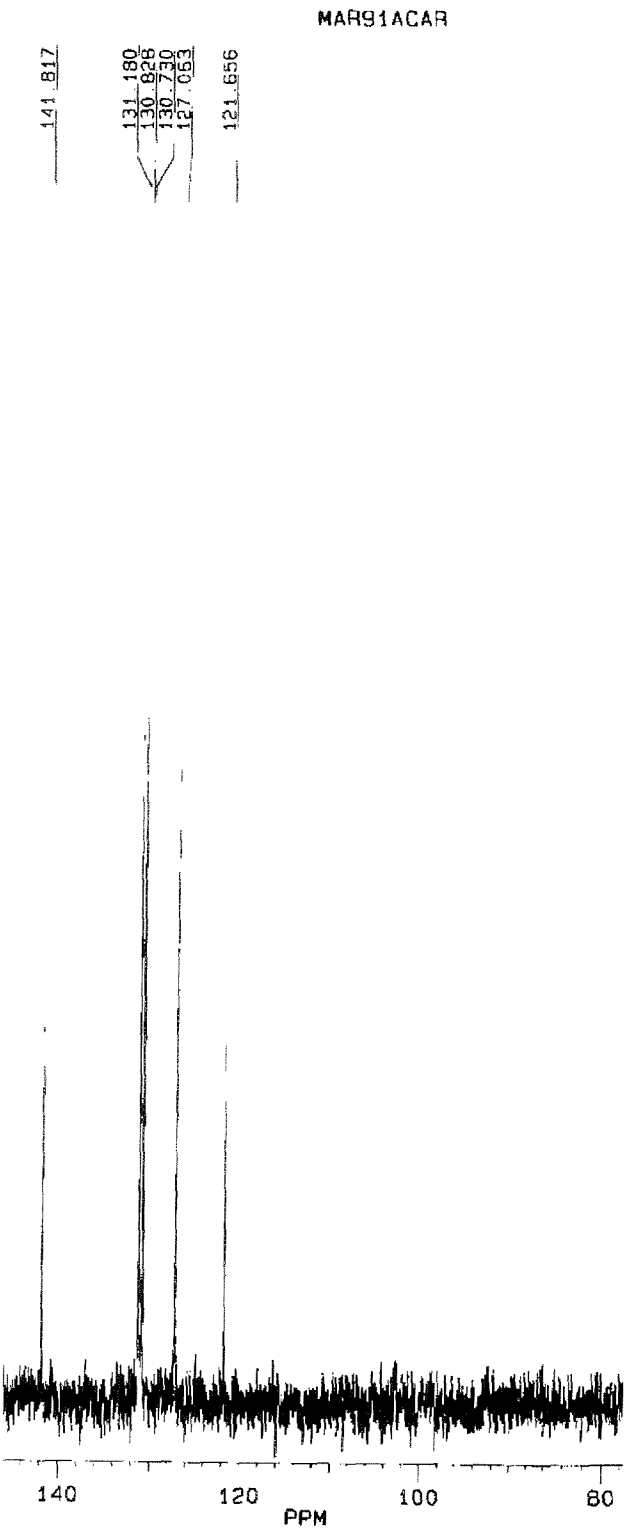


Figure 5.2.2.3. *The ^{13}C-NMR spectrum of material filtered from the electrolysis of 2-iodobiphenyl*

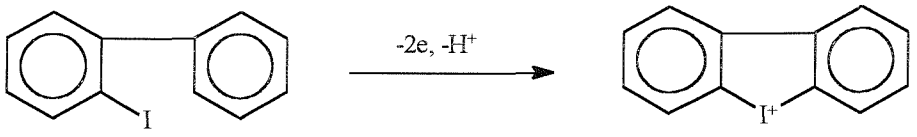
The ^{13}C-NMR spectrum showed six signals in the aromatic region also the spectrum was consistent with the ^{1}H-NMR spectrum as there were no signals in the high field region.

Figure 5.2.2.4. *The DEPT-135 spectrum of material filtered from the electrolysis of 2-iodobiphenyl.*

The DEPT-135 spectrum showed four signals; 131.18, 130.83, 130.73, 127.06 ppm. These signals were of similar chemical shift value to those seen in the ^{13}C-NMR.

The ^{13}C-NMR spectrum contained two additional signals, at 141.82 and 121.66 ppm, which were not seen in the DEPT-135 spectrum, therefore it was apparent that these signals were due to the resonance of quaternary carbon atoms. Consideration of the ^{13}C-NMR and DEPT-135 spectra showed that the material contained an aromatic ring which was substituted in two positions. The NMR spectra showed only signals that were associated with an aromatic system, which was di-substituted. A sample of the isolated material was analysed by positive ion electrospray mass spectroscopy. A single ion with a m/z value of 279 Da was seen.

Considering that the starting material was 2-iodobiphenyl then it was logical to assume that the compound had undergone *intra* cyclisation to the dibenziodolium cation, see Scheme 5.2.2.1, in parallel with that seen in analogous organic reaction , see Section 1.3.2.3.



Scheme 5.2.2.1

Dibenziodolium bisulfate. ^{1}H NMR (300 MHz, d^{6}-DMSO);δ 8.48 (d, J = 7.9, 2H), 8.28 (d, 7.2, 2H), 7.85 (app t, J = 7.1, 2 H), 7.70 (app t, J= 7.0, 2H): ^{13}C NMR (300 MHz, d^{6}-DMSO): δ 141.81, 131.18, 130.82, 130.73, 127.06, 121.65, : MS (ES) calcd. for $C_{12}H_8I^+$ 279, found 279.

The filtrate which was separated was then reduced in volume *in vacuo* until it was a dark oil. The oil was then separated between diethyl ether and water. The aqueous phase was then treated with potassium iodide, 3g dissolved in a minimum amount of water. The addition of potassium iodide caused the immediate precipitation of an light yellow powder. This was separated and dried on a filter paper, 3.74 g of material was isolated. The ^{1}H-NMR spectrum was recorded, see Figure 5.2.2.5.

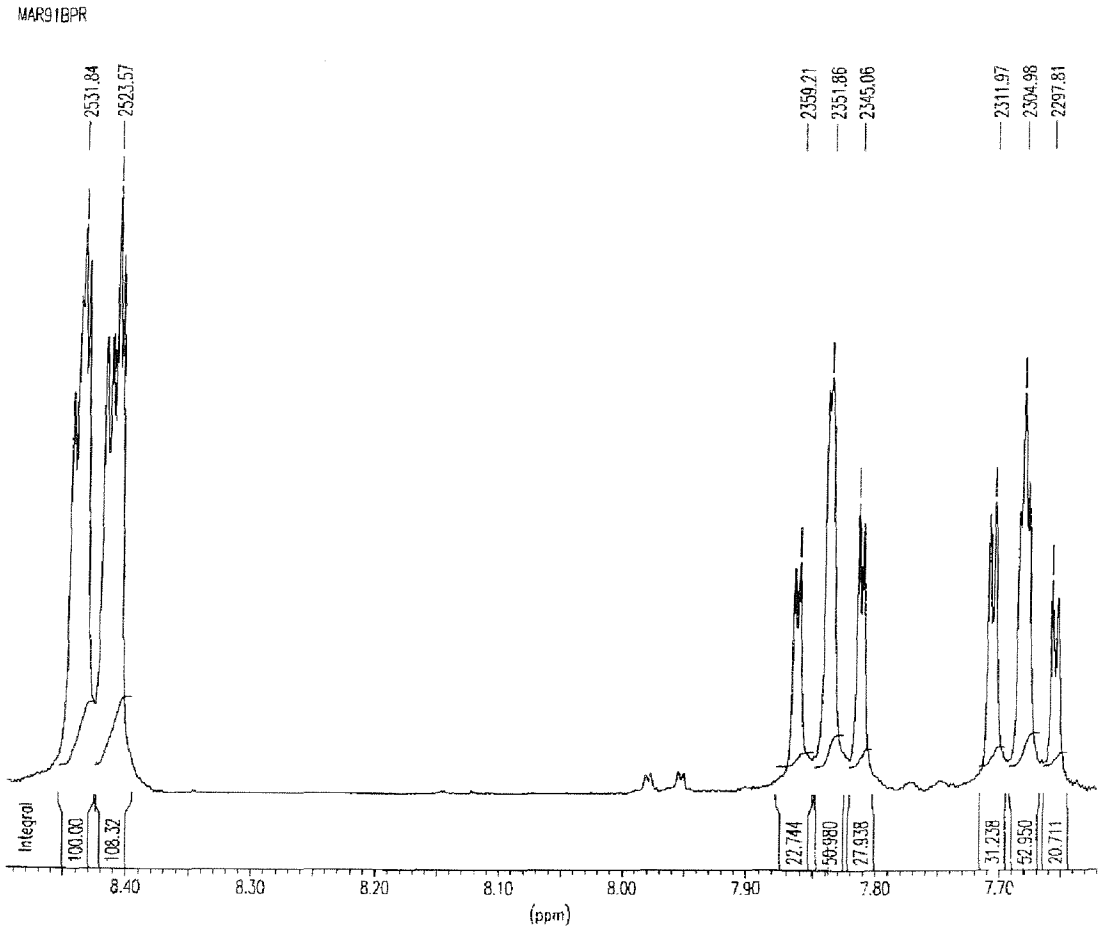


Figure 5.2.2.5 *The ^{1}H-NMR spectrum of material precipitated after the addition of potassium iodide after the electrolysis of 2-iodobiphenyl.*

The ^{1}H-NMR spectrum was compared to that in Figure 5.2.2.2. It was apparent that the spectrum were similar in appearance to the dibenziodolium bisulfate, but the isolation as the iodide had caused a change in the chemical shift values. A sample of the material was analysed by positive ion mass spectroscopy, a single ion with a m/z value of 279 Da was seen. The ^{1}H-NMR spectrum of dibenziodolium iodide was reported in the literature[29]. The chemical shift values were compared to those in Figure 5.2.2.2. It was apparent that the chemical shift values of were very similar to those quoted in the literature.

Dibenziodolium iodide. ^{1}H NMR (300 MHz, d^{6}-DMSO);δ 8.41 (app d, J = 7.4, 4H), 7.84 (app t 7.1, 2H), 7.68 (app t, J = 7.1, 2 H): ^{13}C NMR (300 MHz, d^{6}-DMSO): δ 141.84, 131.09, 130.83, 130.76, 127.01, 121.69: MS (ES) calcd. for $C_{12}H_8I^+$ 279, found 279.

A chemical selectivity of 75 % and current efficiency of 67 % was recorded, with respect to the combined yields of dibenziodolium bisulfate and dibenziodolium iodide.

A 100 cm^3 volume of 0.1 M concentration of 2-iodobiphenyl in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride was electrolysed at a constant current of 3 mA/ cm^2. A total charge of 1.1 F was passed. At the end of the electrolysis there was a precipitate on the electrodes and at the bottom of the beaker. The material was collected on a filter paper, then washed with diethyl ether and dried on the paper. A yield of 0.38 g was recorded. The ^{1}H-NMR spectrum was recorded and was identical to that of dibenziodolium bisulfate. The carbon felt anode was washed with hot methanol. The methanol was then removed *in vacuo.* An orange precipitate was collected and dried. A yield of 1 g was recorded. A ^{1}H-NMR of the material showed that it to was dibenziodolium bisulfate. The filtrate was similarly reduced in volume under vacuum to a dark oil. The oil was then partitioned between diethyl ether and water. The aqueous phase was then treated with potassium iodide, 3 g dissolved in a minimum amount of water. There was a small precipitation which was similarly collected on the filter paper. A yield of 0.089 g was recorded. The ^{1}H-NMR spectrum was recorded and the material was identified as dibenziodolium iodide by comparison with Figure 5.2.2.5. The chemical efficiency and chemical selectivity was 46 and 60 % respectively.

A summary of the electrolyses of 2-iodobiphenyl is made in Table 5.2.2.1.

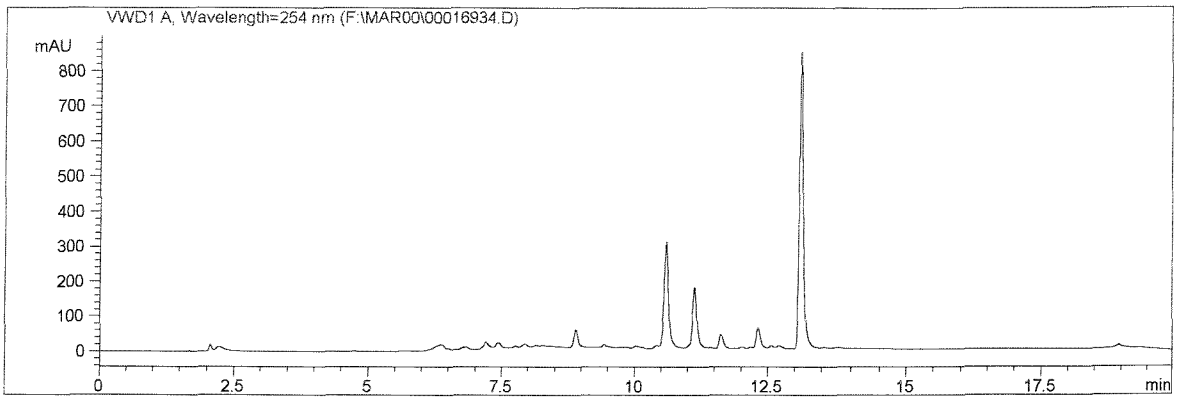
Cell Conditions	**Chemical Selectivity %**	**Current Efficiency %**
0.1 M 2-Iodobiphenyl, AcOH/ 5 %H_2SO_4/ 2 % Ac_2O	60	46
0.2 M 2-Iodobiphenyl, AcOH/ 5 %H_2SO_4/ 25 % Ac_2O	75	67

Table 5.2.2.1

5.3 Electrolysis of 2-Iodophenylphenylmethane

A solution of ca. 0.075 M concentration of 2-iodophenylphenylmethane in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride was prepared. The beaker cell, described in Section 2.2.2, was charged with the solution and an electrolysis was carried out, at a current density of 5 mA/ cm^2, until a charge of 1.6 F was passed. An aliquot of the reaction mixture was removed at the beginning and at the end of the electrolysis and submitted for hplc analysis, see Figure 5.3.1.

It was apparent that before any charge was passed there were several compounds in the solution other than 2-iodophenylphenylmethane, which had an elution time of ca. 13.1 minutes. After the electrolysis the stating material peak had diminished considerable. An aliquot was removed and diluted with acetonitrile and analysed by positive ion electrospray mass spectroscopy. A single ion of m/z value 293 Da was seen.



Chromatogram of 0.075 M concentration of 2-iodophenyphenylmethan in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O

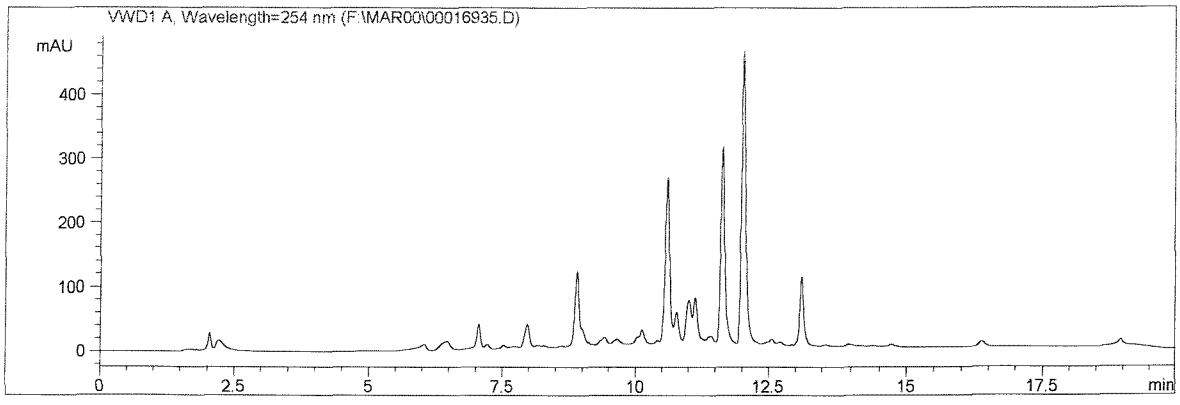


Figure 5.3.1 *Chromatogram of a solution of original composition of 0.075 M concentration of 2-iodophenyphenylmethane in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O, after 1.6 F was passed.*

The electrodes were washed with methanol, and were subsequently combined with the reaction mixture. The solvent was removed *in vacuo.* The resulting oil was partitioned between diethyl ether and water. The aqueous phase was separated and treated with potassium iodide, 3 g dissolved in a minimum amount of water. A fine precipitate was seen, which was collected and dried on a filter paper. A yield of 126 mg was recorded. The ^{1}H-NMR spectrum of the isolated material is shown in Figure 5.3.2.

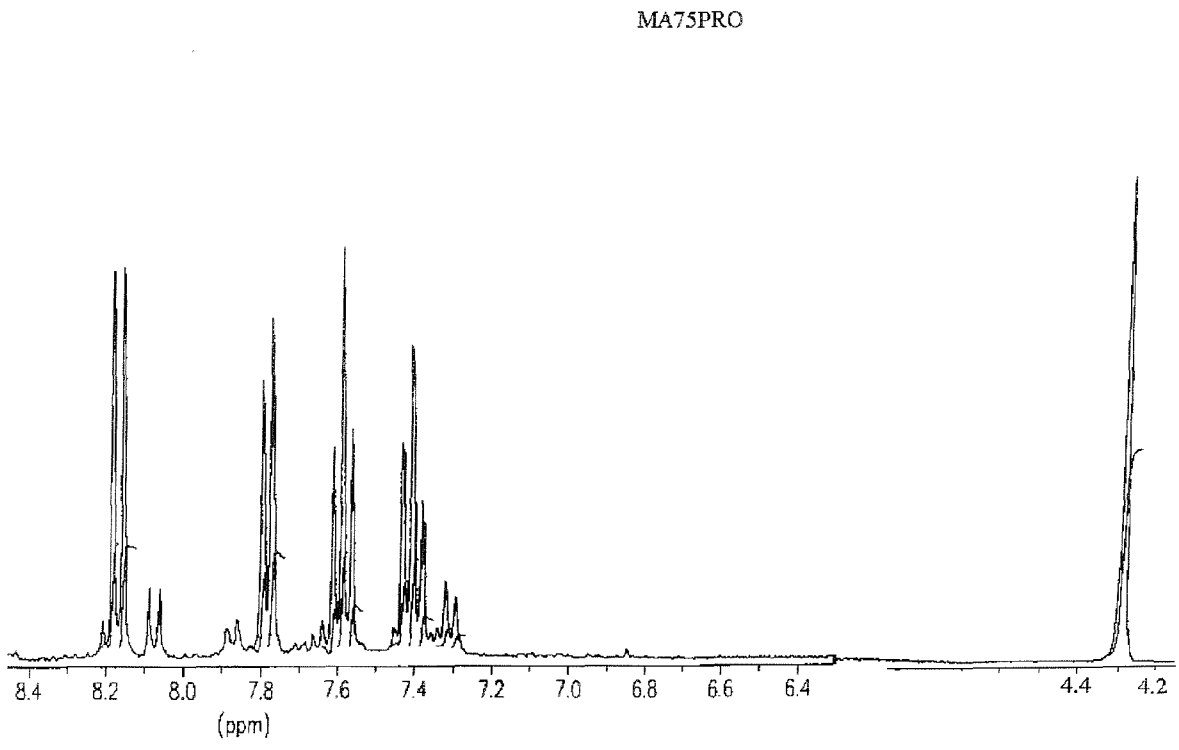
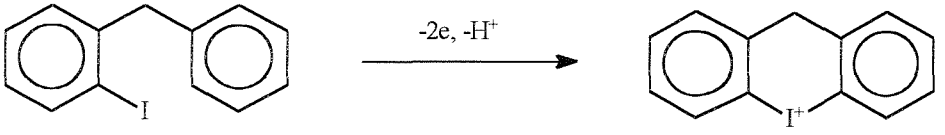


Figure 5.3.2 *The ^{1}H-NMR spectrum of the material precipitated by the addition of potassium iodide after the electrolysis of 2-iodophenyphenylmethane.*

The ^{1}H-NMR spectrum was contained 5 main resonance signals; four signals in the aromatic region and a signal at 4.30 ppm, which was the chemical shift value for benzyl protons. The aromatic signals and the signal at 4.30 ppm were all of equal intensity. The ^{1}H-NMR spectrum showed that the aromatic splitting pattern was identical to that in Figure 5.2.2.2, for the dibenziodolium cation. A sample of the material was analysed by positive ion electrospray and showed again one of ion of m/z value 293 Da. The isolated

material was therefore identified as 10H-dibenziodininium iodide[4]. The expected molecular weight for the cation was 293 Da, which fitted the mass spectroscopy data. The isolated material was the result of an intra molecular cyclisation of the 2iodophenylphenylmethane, see Scheme 5.3.1.



Scheme 5.3.1

5.4 Electrochemistry of 2-Iodobenzoic Acid

5.4.1 Voltammetry of 2-Iodobenzoic acid

A 1 mM concentration of 2-iodobenzoic acid in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride was prepared. Figure 5.4.1.1 shows a cyclic voltammogram recorded at a scan rate of 20 mV/ s and starting at a potential of 0.8 V vs. SCE.

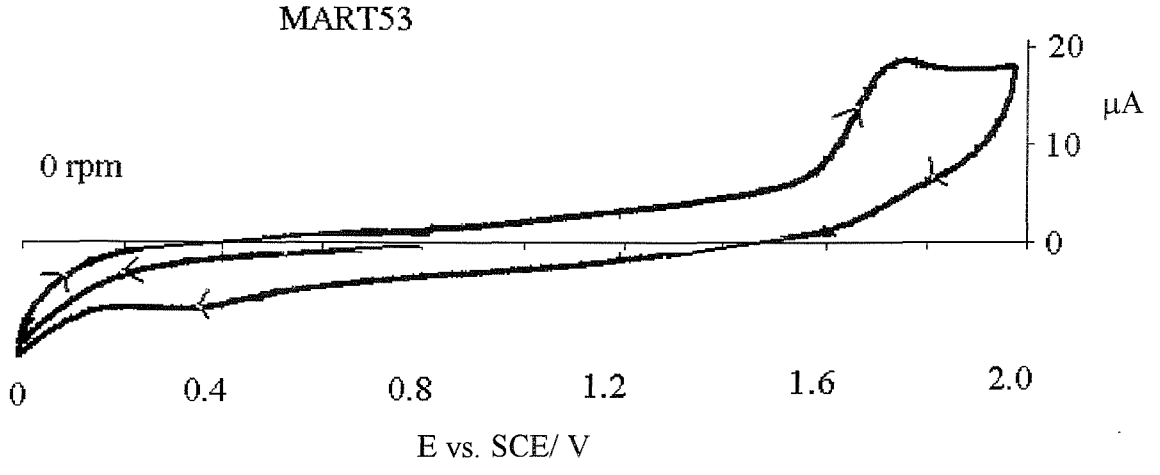


Figure 5.4.1.1. *The cyclic voltammogram of 1 mM 2-iodobenzoic acid in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O at a vitreous carbon electrode at a scan rate of 20 mV/s.*

Consideration of the cyclic voltammogram , *ibid,* showed that there was a small cathodic current on the first scan from 0.8 to 0 V vs. SCE, then on the scan from 0 to 2.0 V vs. SCE there was an oxidation peak with a half wave potential of ca. 1.66 V vs. SCE. On the

back scan from 2.00 V to 0 V vs. SCE there was now a reduction peak with a half wave potential of ca. 0.48 V vs. SCE. It was apparent that there was no reduction of 2-iodobenzoic acid on the first scan from 0.8 to 0 V vs. SCE, but after the oxidation in the region 1.7 V vs. SCE there was a reduction of the product on the back scan.
The voltammogram of the 1mM solution of 2-iodobenzoic acid in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride was also investigated using the vitreous carbon rotating disc electrode, see Figure 5.4.1.2.

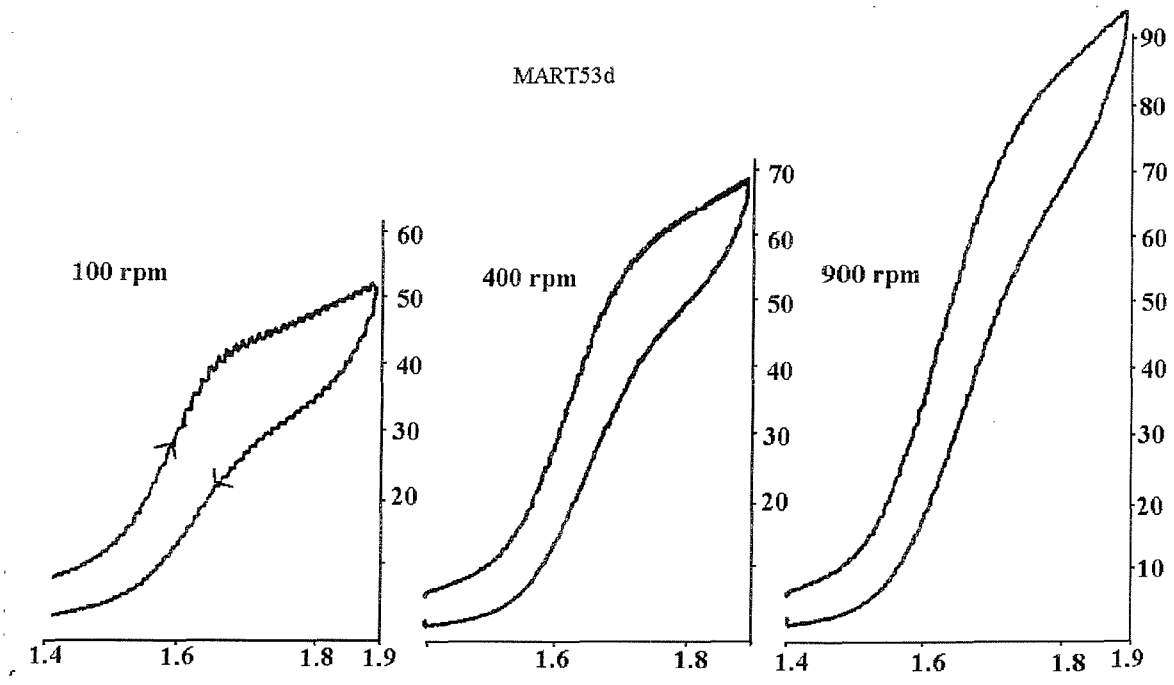


Figure 5.4.1.2. *The voltammograms of 1 mM 2-iodobenzoic acid in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O at a vitreous carbon electrode at a scan rate of 20 mV/s.*

It was apparent from the voltammetry that there was an oxidation wave with a half wave potential of 1.62 V vs. SCE and that the limiting cure was dependent on the rotation rate of the electrode. The value of $E_{3/4}$-$E_{1/4}$, for the voltammogram recorded at a rotation rate of 400 rpm, was calculated to be 100 mV. It was apparent from the Tomes analysis that the oxidation of 2-iodobenzoic acid was irreversible.

5.4.2 Electrolysis of 2-Iodobenzoic Acid.

A 100 cm^3 solution of 0.1 M 2-iodobenzoic acid in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride was prepared and a galvanostatic current at 3 mA/ cm^2 was passed until a charge of 6 F was passed, at a carbon felt anode. The chromatogram of the solution at the beginning and at the end of the electrolysis was recorded, see Figure 5.4.2.1.

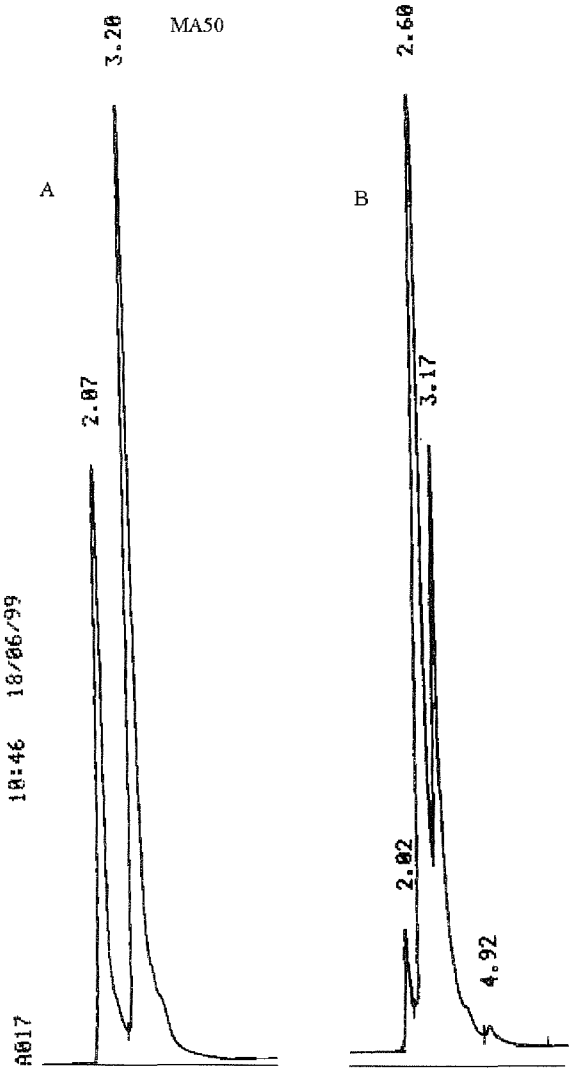


Figure 5.4.2.1 *A) Chromatogram of a solution of 0.1 M 2-iodobenzoic acid in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O.*

B) Chromatogram of solution of original composition 0.1 M 2-iodobenzoic acid in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O. Recorded after a charge of 6 F was passed.

The peak at ca. 2.1 minutes was due to the solvent, whilst the peak at ca. 3.1 was due to the 2-iodobenzoic acid. It was apparent over the course of the electrolysis that a new peak developed with a retention time of ca. 2.6 minutes.

At the end of the electrolysis the reaction mixture was diluted with 300 cm^3 of diethyl ether and 100 cm^3 of 1.0 M sodium hydroxide. The solution was left standing for 3 hours. After which a precipitate had formed at the aqueous phase and organic phase interface. The precipitate was separated by filtration and dried on the paper. An isolated yield of 1 g was recorded. The ^{1}H-NMR was recorded, see Figure 5.4.2.2.

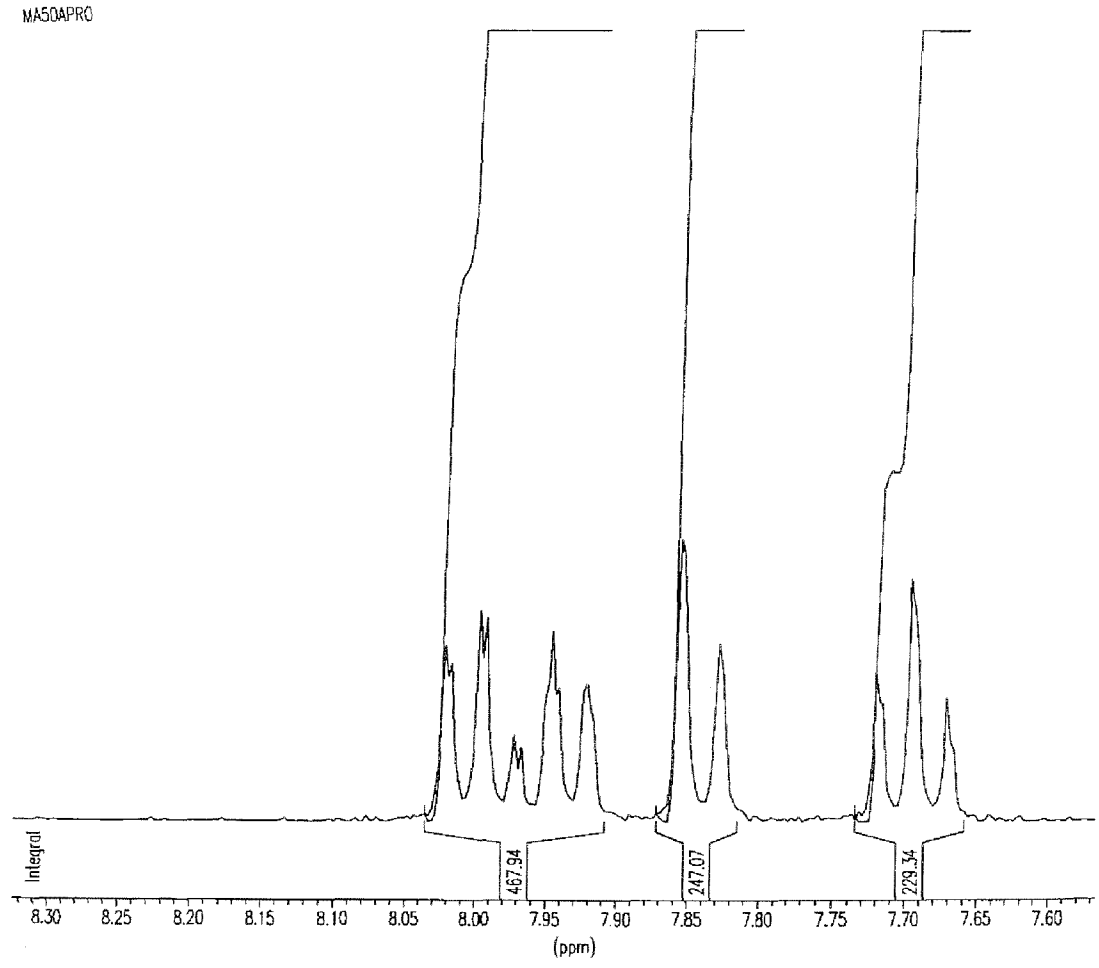
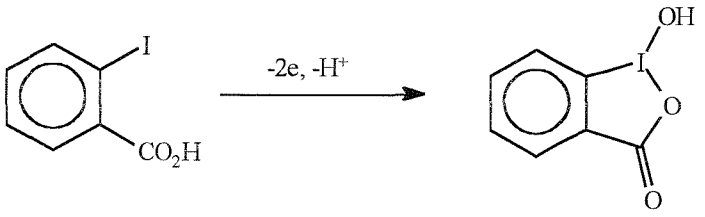


Figure 5.4.2.2 *The ^{1}H-NMR spectrum of material precipitated by the addition of diethyl ether and sodium hydroxide solution to the electrolysis solution of 2-iodobenzoic acid.*

The spectrum, *ibid*, was compared to the ^{1}H-NMR of a proprietary sample of 2-iodosylbenzoic acid (*Sigma*). The ^{1}H-NMR of the material isolated from the electrolysis of

2-iodobenzoic acid was identical to that recorded for 2-iodosylbenzoic acid. Scheme 5.4.2.1 shows the reaction of 2-iodobenzoic acid to give 2-iodosylbenzoic acid. The actual mechanism must also involve an oxygen source.



Scheme 5.4.2.1

The mother liquors were left standing over night and further material precipitated. This was separated and dried on the filter paper. A yield of 3.16 g was recorded. The ^{1}H-NMR spectrum was recorded and a comparison with the ^{1}H-NMR of the proprietary sample of 2-iodosylbenzoic acid demonstrated that it too was 2-iodosylbenzoic acid.

The chemical selectivity and current efficiency was calculated to be 100 % and 12 % respectively.

5.4.3 Voltammetry of 2-Iodosylbenzoic acid

A solution of 1mM concentration of 2-iodosylbenzoic acid in acetic acid/ 5 % sulfuric acid/ 25 acetic anhydride was prepared and a cyclic voltammogram was recorded between the potential limits of 0 and 2.0 V starting at a potential of 0.9 V vs. SCE. The scan rate throughout was 20 mV/ s, see Figure 5.4.3.1.

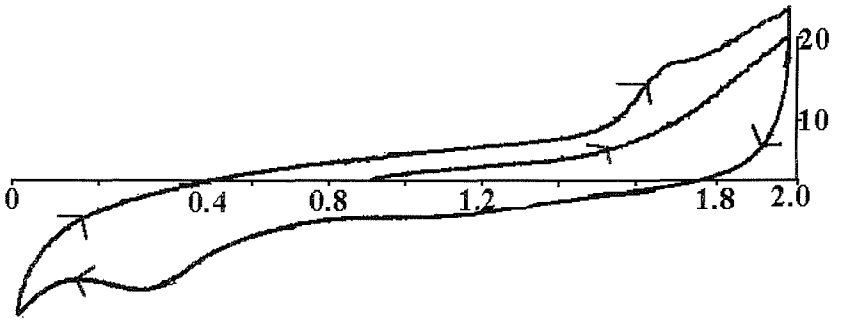


Figure 5.4.3.1 *The cyclic voltammogram of a 1mM concentration of 2-iodosylbenzoic acid in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O at a vitreous carbon electrode (diameter 3mm).*

On the first scan from 0.9 V to 2.0 V vs. SCE there was a smooth increase in anodic current. On the back scan there was a cathodic peak corresponding to the reduction of 2-iodosylbenzoic acid, with a half wave potential of 0.48 V vs. SCE. When the potential was raised back to 2.0 V there was an anodic wave with a half wave potential of ca. 1.66 V vs. SCE. This peak corresponded to the oxidation of the product of the material formed by the reduction of 2-iodosyl benzoic acid.

The 1 mM solution of 2-iodosylbenzoic acid was further investigated at the vitreous carbon electrode , but where the electrode was now rotated. The potential was swept between the limits of 0.8 and -0.1 V vs. SCE at a scan rate of 20 mV/s, see Figure 5.4.3.2.

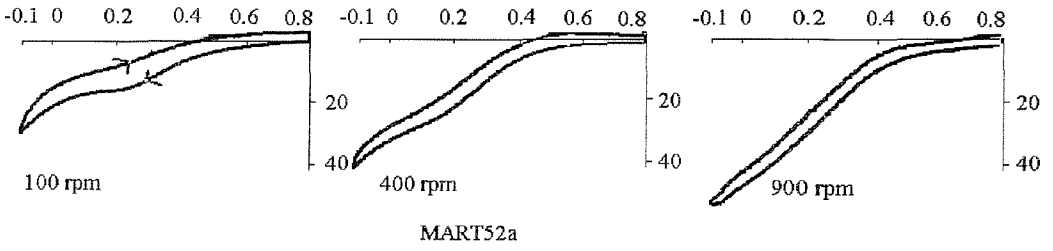


Figure 5.4.3.2 *The voltammogram of a 1mM concentration of 2-iodosylbenzoic acid in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O at a vitreous carbon rotating disc electrode (diameter 3mm).*

The voltammograms, *ibid*, show that the limiting current was dependent on rotation rate of the electrode. A quantitative analysis was not carried out as the waves were distorted by the hydrogen evolution, which is know to take place at the vitreous carbon electrode at potentials lower than 0 V vs. SCE.

5.4.4 Comparison of the Voltammetry of 2-Iodobenzoic Acid and 2-Iodosylbenzoic Acid.

Figure 5.4.4.1a and Figure 5.4.4.1b show the voltammograms of 2-iodobenzoic and 2-iodosylbenzoic acid respectively.

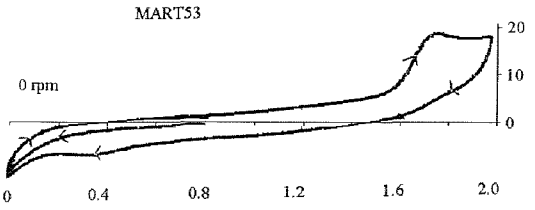


Figure 5.4.4.1a. *The cyclic voltammogram of 1 mM 2-iodobenzoic acid in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O at a vitreous carbon electrode at a scan rate of 20 mV/s.*

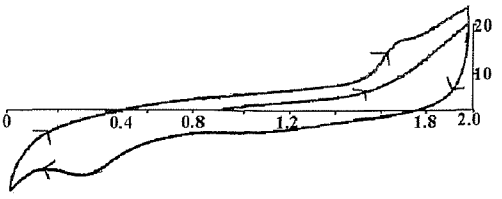
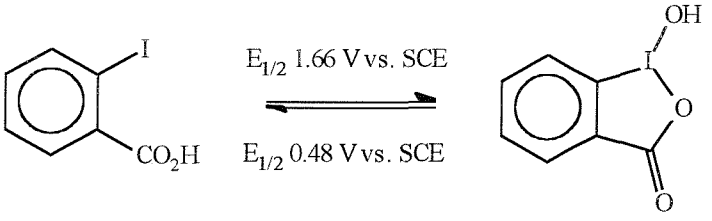


Figure 5.4.4.1b *The cyclic voltammogram of a 1mM concentration of 2-iodosylbenzoic acid in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O at a vitreous carbon electrode (diameter 3mm).*

A comparison of the voltammograms of 2-iodobenzoic acid and 2-iodosylbenzoic acid showed that they were very similar. Both voltammograms contained an oxidation event whose half wave potential was ca. 1.66 V vs. SCE. Similarly both voltammograms contained a cathodic peak whose half wave potential was ca. 0.48 V vs. SCE. Considering that an electrolysis of 2-iodosbenzoic acid formed 2-iodosylbenzoic acid in quantitative yield, it was apparent that a the vitreous carbon disc electrode 2-iodobenzoic acid was oxidised to 2-iodosylbenzoic acid. Also at the vitreous carbon disc electrode 2-iodosylbenzoic acid was seen to be reduced to 2-iodobenzoic acid, see Scheme 5.4.4.1



Scheme 5.4.4.1

The voltammetry of 2-iodosyl benzoic showed that it was not possible to further oxidise the compound at potentials below 2.0 V vs. SCE. Therefore it was not possible to oxidise 2-iodosyl benzoic acid to 2-iodylbenzoic acid using the procedures developed in this work.

CONCLUSIONS

The electrolysis of 4-iodotoluene and toluene was chosen as the reaction with which to investigate the effect of the electrolysis conditions on the yield of the diaryliodonium salt. It was seen that the acetic anhydride content of the solvent influenced the products of the electrolysis. The chemical selectivity of the electrolysis, with respect to the diaryliodonium salt, increased from 46 % to 96 % on raising the acetic anhydride content from 2 % to 25 %. At low concentrations of acetic anhydride two side products were identified; 4-iodobenzyl acetate and 4-iodobenzaldehyde. It was clear from hplc analysis that their production was suppressed as the acetic anhydride content was raised. The electrolysis of 4-iodotoluene in the absence of an arene in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride was seen by hplc analysis to give a good yield of 4-iodobenzyl acetate, but when the acetic anhydride content of the cell was raised to 25 % a similar electrolysis showed hardly any production of 4-iodobenzyl acetate.

The effect of acid on the electrolysis of 4-iodotoluene and toluene was similarly studied. Fluoroboric acid and sulfuric acid were seen to promote the chemical selectivity of the electrolysis towards the diaryliodonium salt, whilst methanesulfonic acid facilitated the production of 4-iodobenzyl acetate, 4-iodobenzaldehyde and an unknown compound. It was noted that the acetic acid/ 5 % methanesulfonic acid/ 2 % acetic anhydride was a considerably less conducting medium. Trifluoromethanesulfonic acid gave an intermediate result with respect to the dimethyldiphenyliodonium cation when present as the supporting electrolyte.

A series of electrolysis of 4-iodotoluene and toluene were carried out, but where the current density was changed. It was seen that a relatively low current density of 5 mA/ cm^2 was the optimum current density. This was probably due to the limited rate of mass transport in the simple beaker cell. The isolated dimethyldiphenyliodonium cation was characterised by mass spectroscopy and NMR, it was apparent that two isomers were present; 4,4'-dimethyldiphenyliodonium salt and 2,4'-dimethyldiphenyliodonium salt, in the ratio 9:1.

A series of electrolysis were carried out in order to determine whether the formation of diaryliodonium salts by the anodic oxidation of mixtures of aryl iodide and arene in a media consisting of acetic acid/ acetic anhydride and anhydrous acid was generally applicable. When the arene had alkyl substituents it was possible to synthesize symmetric and asymmetric iodonium salts with good chemical selectivity and current efficiencies. It was also possible to carry out the *intra*-molecular cyclisation of 2-iodobiphenyl and 2-iodophenylphenylmethane to their respective cyclic iodonium salts. The investigation of the reaction with other aryl iodides and arene showed the following limitations.

1. The oxidation of the aryl iodide must occur at a lower potential than the arene. Similarly at a lower potential than the rapid oxidation of the solvent medium. This avoids passivation of the electrode and competing reactions.
2. The ring substituents must be resistant to facile oxidation.
3. Electron donating substituents in the arene appear to be critical so that the arene is sufficiently nucleophilic to trap the aryl iodide cation radical.
4. Both the aryl iodide and the arene must be resistant to homogenous chemical reactions.

The choice of solvent for an electrolysis was determined by the mixture of substrates. For example, the optimum solvent for the electrolysis of 4-iodotoluene and toluene was acetic acid/ 25 % acetic anhydride/ 8 % fluoroboric acid. In contrast this medium was unsuitable for electrolysis involving anisole, because it was reactive to the solvent mixture. Electrolysis involving anisole were best carried out in acetic acid/ 2 % acetic anhydride/ 5 % sulfuric acid. It was noted that the 4,4'-dimethoxydiphenyliodonium cation was the only isomer isolated from the electrolysis of 4-iodoanisole and anisole. Similarly when 4-iodotoluene was coupled with an alkyl substituted arene, whose substituent was larger than a methyl group, the isolated iodonium salt had only the 4,4'-dialkyldiphenyliodonium isomer present and not the 2,4'-dialkyldiphenyliodonium isomer. This was due to the increased steric and/or inductive factors of the substituents.

The electrolysis procedure describes a truly single step method to the synthesis of diaryliodonium salts, from proprietary starting materials. The method developed for

isolation of the iodonium salts was quick and simple. The method compared well to published organic synthesis strategies and is more attractive as a method for scale up. The methodology was transferred to the electrosynthesis of 2-iodosylbenzoic acid from 2-iodobenzoic acid, which was achieved in excellent yield. Preparation of further analogues may be achieved readily as the 2-iodobenzoyl chloride is commercially available. It has been shown[46] that the acid chloride can be coupled with natural amino acids or their methyl ester. These N- substituted 2-iodobenzamides could be oxidised to give chiral hypervalent reagents.

The voltammetry indicates that oxidation of the carbon anode and/or intercalation of anions into the carbon anode was a competing reaction to the formation of the diaryliodonium salts. This did not have a detrimental effect on the carbon felt used for electrolysis as it was possible to re-cycle the felt without effecting the result of the next electrolysis.

The media developed in this work was successful, because they combined a number of properties. They are non-nucleophilic and probably stabilised cationic intermediates by solvation. Many organic compounds are soluble. It also has acceptable conductivity and offers simple counter electrode chemistry i.e. hydrogen evolution. A review[59] of anodic coupling reactions shows that many are carried out in acetonitrile, which is not suitable for scale up. It will be of interest to see if similar couplings can be improved upon in the acetic acid based media.

APPENDIX 1

Results and Discussion: Triarylsulfonium Salts

A.1 Introduction

Having established that acetic acid/ acetic anhydride/ strong acid was well suited to anodic coupling reactions. A brief study was made of the possibility of coupling aryl sulfides to aromatic hydrocarbons.

A.2 Voltammetry of Phenyl Sulfide

A 1 mM concentration of phenyl sulfide in acetic acid/ 5 % sulfuric acid/ 25 % acetic anhydride was prepared. The voltammograms of the solution were recorded at a rotating vitreous carbon disc electrode, between the limits of 1.1 and 1.5 V vs. SCE, at a scan rate of 20 mV/s, see Figure A.2.1.

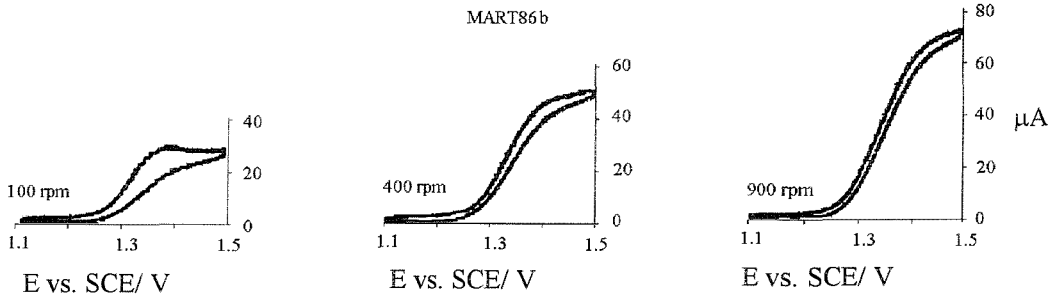


Figure A.2.1 *Voltammetry of a solution of 1 mM phenyl sulfide in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O, measured using a vitreous carbon RDE (diameter 3 mm), scan rate = 20 mV/s.*

The well formed wave in the voltammograms had a half wave potential of 1.32 V vs. SCE. The limiting current was seen to be dependent on rotation rate of the electrode. An analysis of $E_{3/4}$ - $E_{1/4}$ gave a value of 70 mV. Therefore the oxidation of phenyl sulfide was irreversible, if it was a two electron process.

A second series of voltammograms were similarly recorded, but where the upper potential limit was raised to 1.7 V vs. SCE, see Figure A.2.2.

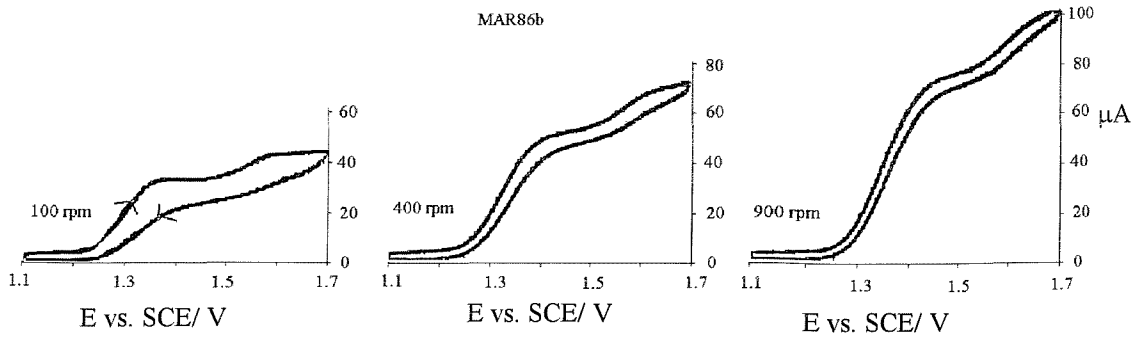


Figure A.2.2 *Voltammetry of a solution of 1 mM phenyl sulfide in AcOH/ 5 % H_2SO_4/ 25 % Ac_2O, measured using a vitreous carbon RDE (diameter 3 mm), scan rate = 20 mV/s.*

It was apparent that by raising the upper limit, a second oxidation wave was seen, with a half wave potential of 1.55 V vs. SCE. The value for $E_{3/4}$ - $E_{1/4}$ for the second wave was ca. 0.12 V, so the second oxidation in the voltammogram of phenyl sulfide was similarly irreversible. The ratio of the wave heights between the first and second wave was 5:1.

The voltammogram of phenyl sulfide was again recorded between the limit 1.1 and 1.7 V vs. SCE at a rotation rate of 400 rpm. An aliquot of *tert*-butylbenzene was then added to the working electrode compartment and a voltammogram was recorded. This was continued until the concentration of *tert*-butylbenzene in the working electrode compartment was ca. 7mM. The addition of *tert*-butylbenzene caused no change in the appearance of either wave in the voltammogram of phenyl sulfide.

A.3 Electrolysis of Phenyl Sulfide

A 100 cm^3 solution of 0.2 M diphenyl sulfide in acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride was prepared . An aliquot was removed and immediately diluted with acetonitrile for hplc analysis, see Figure A.3.1.

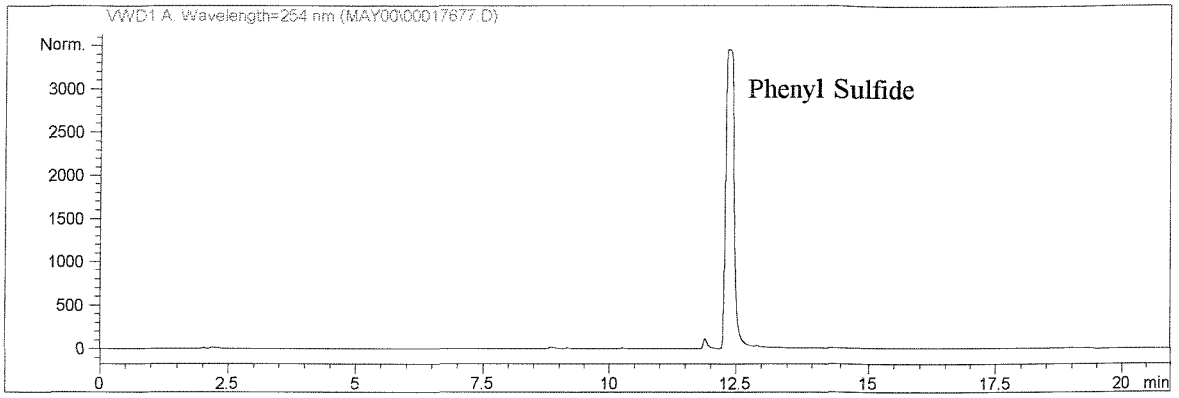


Figure A.3.1 *Chromatogram of a solution of 0.2 M phenyl sulfide in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O.*

A single peak was seen with an elution time of 12.3 minutes. After 16 hours a second aliquot was removed and similarly diluted and analysed by hplc, see Figure A.3.2.

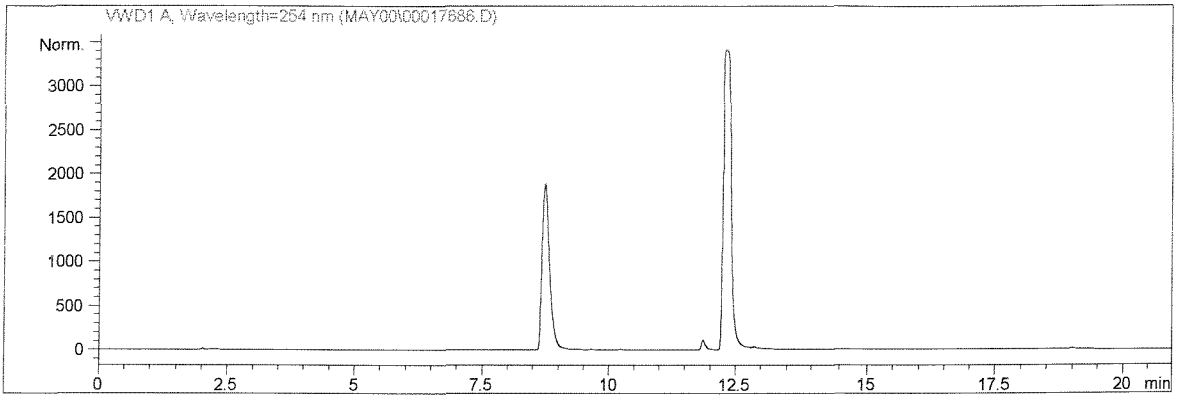


Figure A.3.2 *Chromatogram of a solution with an original composition of 0.2 M phenyl sulfide in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O.*

A second peak was now seen, with an elution time of 8.7 minutes. To the solution was added equal volumes of water and dichloromethane. An aliquot was removed from both the organic and aqueous phase and anlaysed by hplc. The starting material, phenyl sulfide, was seen to be present in the dichloromethane phase whilst the product was present in the aqueous phase. The aqueous phase was separated and reduced in volume under vacuum. The subsequent oil was loaded on top of a column of silica. The material was then eluted through the column with a mobile phase of dichloromethane and methanol in the ratio 4:1. The fractions containing the eluted compound were combined and the solvent was removed again under vacuum. The resulting material was a clear oil. To the oil was added

diethyl ether. This addition caused a precipitation of white 'fluffy' crystals. The precipitate was separated and dried on the filter paper. A sample of the precipitate was dissolved in acetonitrile and was analysed by hplc, see Figure A.3.3.

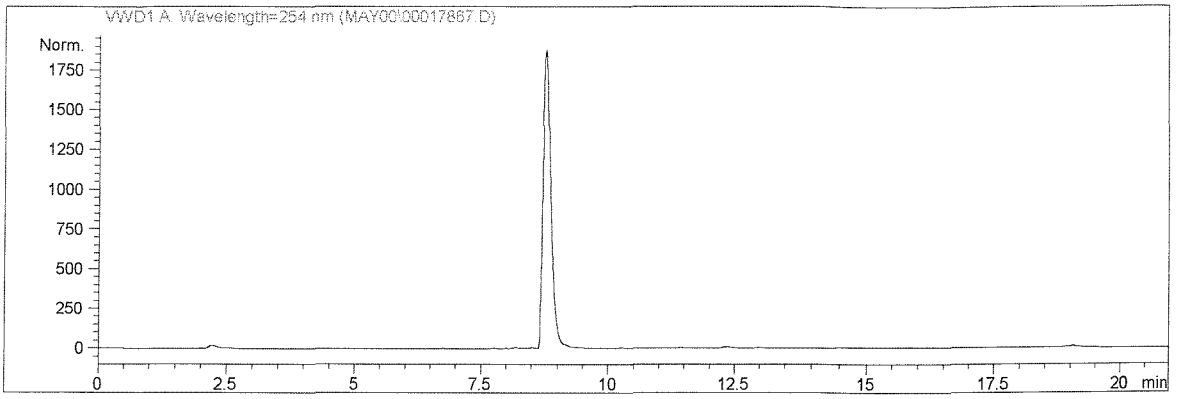
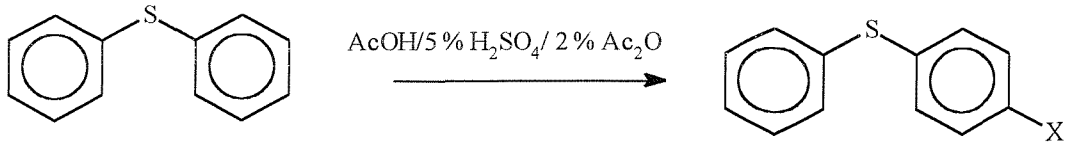


Figure A.3.3 *Chromatogram of the material isolated from the solution with an original composition of 0.2 M phenyl sulfide in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O.*

The recovered material had the same elution time as the product seen in Figure A.3.2. A sample of the material was dissolved in acetonitrile and a few drops of dilute ammonia solution were added. This sample was then analysed by negative ion electrospray mass spectroscopy. A single ion was seen, with a m/z value of 265 Da. A further sample was dissolved in deuterated DMSO and analysed by ^{1}H-NMR, see Figure A.3.4.

Figure A.3.4 *^{1}H-NMR of the material isolated from the solution of phenyl sulfide in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O.*

A pertinent feature of the ^{1}H-NMR spectrum was a pair of doublet signals at 7.59 and 7.27 ppm, whose coupling constant was 8.3 Hz. The chemical shift value of the signals and their splitting pattern suggested that the material contained an aromatic ring that was *para* substituted. The apparent quartet centred at a chemical shift value of 7.36 ppm had a signal intensity five times that of the doublet at 7.59 ppm.. This suggested that the isolated compound contained an aromatic ring that was mono substituted. Scheme A.3.1 shows a possible structural moiety that would explain the ^{1}H-NMR spectrum.



Scheme A.3.1

The parent ion seen in the negative ion mass spectrum would be consistent with X being a sulfonic acid group. The ^{1}H-NMR spectrum contained no other protons signals, which suggested that the 'X' functionality did not contain 'static' protons, but did not exclude 'mobile' protons; such as those found on acid functionalities.

The ^{13}C-NMR and DEPT-135 spectrum were similarly recorded, see Figure A.3.5 and Figure A.3.6 respectively.

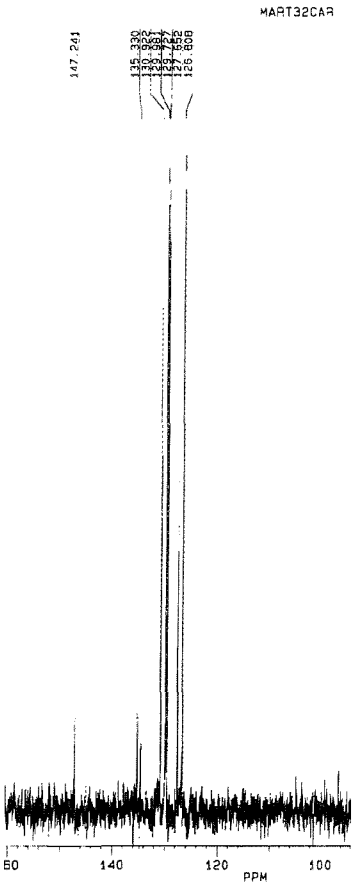


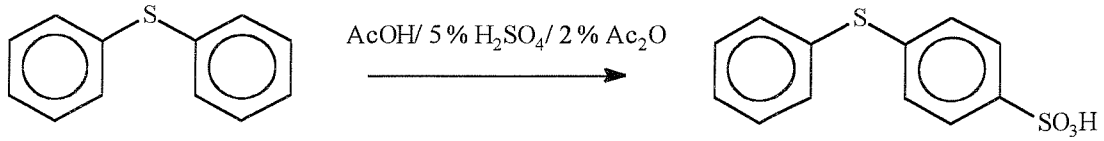
Figure A.3.5 *^{13}C-NMR of the material isolated from the solution of phenyl sulfide in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O*

The ^{13}C-NMR contained 8 signals which was consistent with the structure shown in Scheme A.3.1.

Figure A.3.7 *DEPT-135 spectrum of the material isolated from the solution of phenyl sulfide in AcOH/ 5 % H_2SO_4/ 2 % Ac_2O.*

There were 5 signals in the DEPT-135 spectrum which was in line with the structure suggested in Scheme A.3.1.

The DEPT-135 and ^{13}C-NMR spectra gave no indication of a carboxylic acid functionality. It was shown in Section 4.6 that anisole was partially derivatised when standing in a solution of acetic acid/ 5 % sulfuric acid/ 2 % acetic anhydride to 4-methoxybenzene sulfonic acid. It was similarly suggested that the phenyl sulfide reacted to form 4-phenylsulfide sulfonic acid when left standing in the same solution, see Scheme A.3.2.



Scheme A.3.2

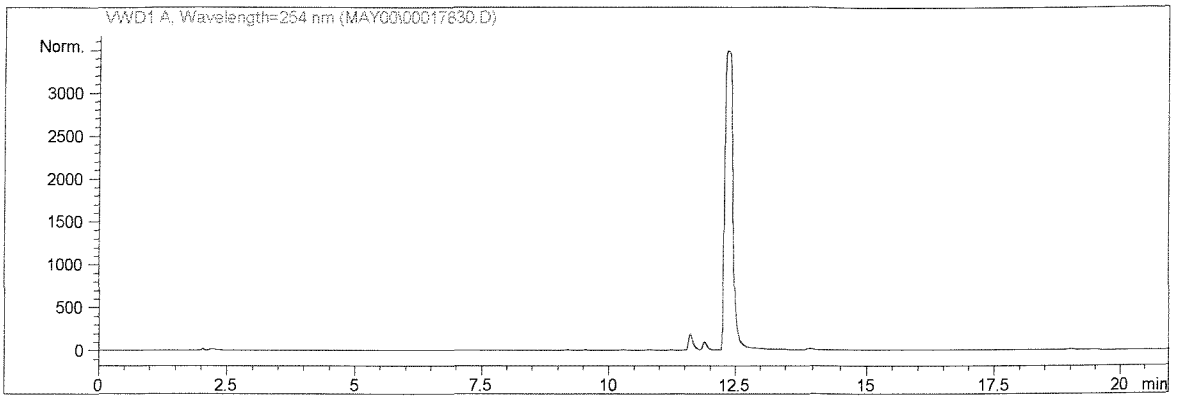
The sulfonic acid moiety does not contain any carbon atoms which was in line with the evidence form the ^{13}C-NMR spectrum and as stated, *ibid*, the molecular weight of the sulfonic acid was consistent with the mass spectrum recorded.

Phenyl sulfide-4- sulfonic acid. ^{1}H NMR (300 MHz, d^6-DMSO); δ 7.59 (d, J = 8.3, 2H), 7.36 (appar. q, 5H), 7.27 (d, J = 8.3, 2H): ^{13}C NMR (300 MHz, d^6-DMSO): δ 147.24, 135.33, 134.50, 130.92, 129.98, 129.72, 127.65, 126.80: MS (ES negative ion) calcd. for $C_{12}H_9O_3S_2^-$ 265, found 265.

It may be noted that the sulfonation reaction was very slow compared to the time scale of an electrolysis.

A 100 cm^3 solution of 0.2 M phenyl sulfide in acetic acid/ 8 % fluoroboric acid/ 2 % acetic anhydride was prepared. An aliquot was removed and analysed by hplc. A single peak was seen, with an elution time of 12.3 minutes, which was identified as phenyl sulfide. A second sample was taken from the solution after 6 hours and similarly analysed. There was again one peak still in the hplc at 12.3 minutes, therefore the phenyl sulfide was stable. The beaker cell, described in Section 2.2.2, was charged with the solution, *ibid*, and a galvanostatic electrolysis was carried out at a current density of 5 mA/cm^2, until a charge

of 3219 C had passed. An aliquot was removed from the solution at the beginning and end of the electrolysis to monitor the progress of the reaction , see Figure A.3.8.



Chromatogram of a solution of composition 0.2 M in AcOH/ 8 % HBF_4/ 2 % Ac_2O

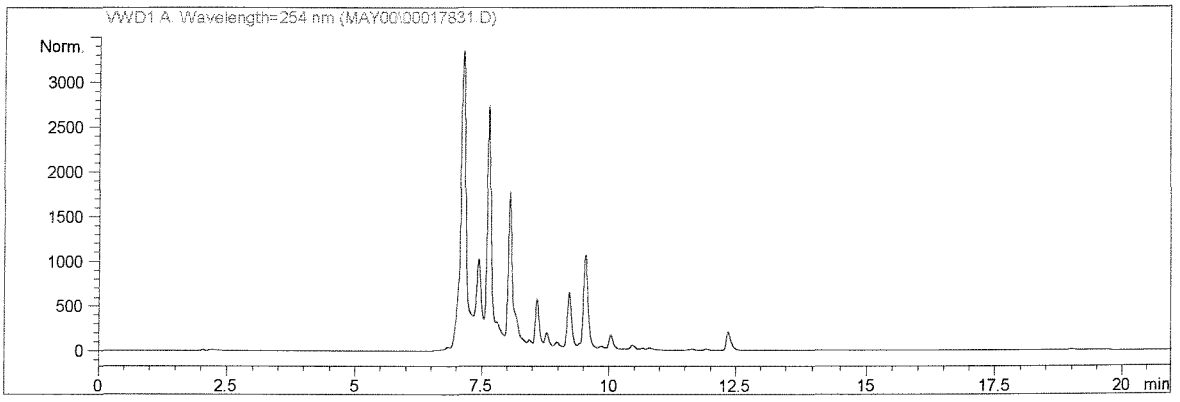
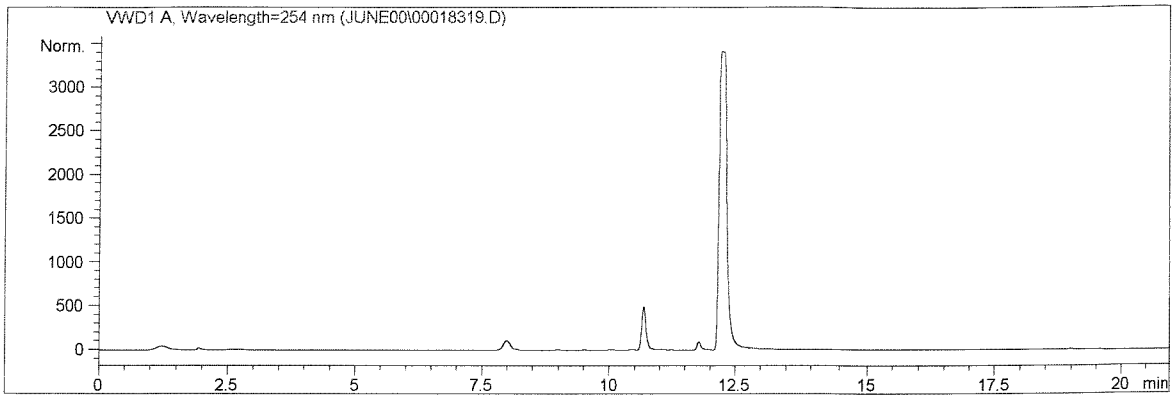


Figure A.3.8 *Chromatogram of a solution of initial composition 0.2 M phenyl sulfide in AcOH/ 8 % HBF_4/ 2 % Ac_2O, after a charge of 3219 C was passed at a current density of 5 mA/cm^2.*

It was apparent from comparing the chromatograms, *ibid*, that the starting material was all but consumed and 7 new peaks had been formed during the electrolysis. The obvious lack of selectivity of the electrolysis under galvanostatic control meant the reaction was abandoned.

The potentiostatic cell, described in Section 2.2.3, was charged with a 25 cm^{3}solution of acetic acid/ 8 % fluoroboric acid/ 2 % acetic anhydride. Into the working electrode compartment was added a 0.83 cm^3 volume of phenyl sulfide and a 0.80 cm^3 of toluene. The concentration of phenyl sulfide and toluene was ca. 0.2 M and 0.3 M respectively in the working electrode compartment. The solution was stirred with a magnetic stirrer and

an aliquot was removed for hplc analysis. A potential of 1.2 V vs. SCE was applied to the working graphite disc electrode, and a charge of 410 C was passed over a period of 13 hours. At the end of the electrolysis an aliquot was removed from the working electrode compartment and analysed by hplc, see Figure A.3.9.



Chromatogram of a solution of composition ca. 0.2 M phenyl sulfide and ca. 0.3 M toluene in AcOH/ 8 % HBF_4/ 2 % Ac_2O

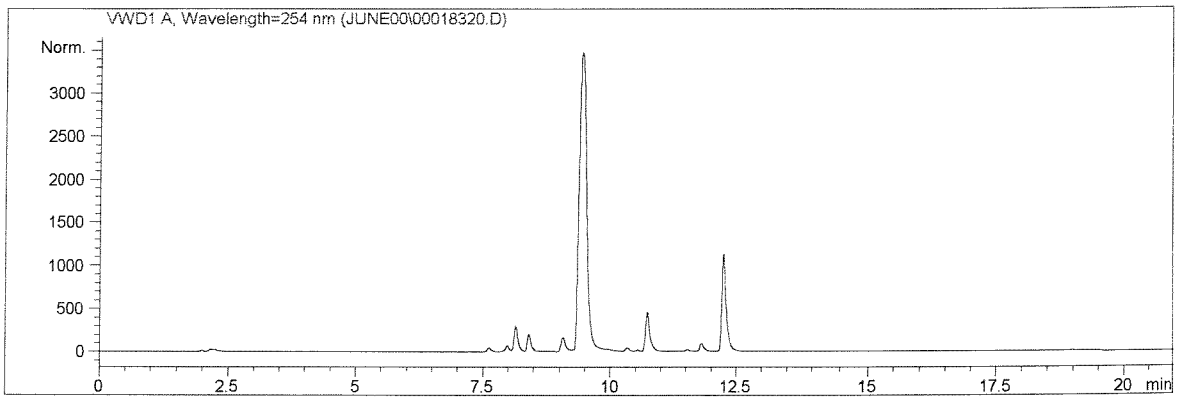


Figure A.3.9 *Chromatogram of a solution of original composition of ca. 0.2 M phenyl sulfide and ca. 0.3 M toluene in AcOH/ 8 % HBF_4/ 2 % Ac_2O, after a charge of 410 C was passed at 1.2 V vs. SCE.*

It was apparent from the hplc analysis that a major product peak had developed during the electrolysis, with a retention time of 9.5 minutes. There was a large depletion in the peak height of phenyl sulfide, elution time 12.2 minutes, but no depletion in the toluene peak height, elution time 10.7 minutes. An aliquot was removed from the reaction mixture and diluted with acetonitrile. The sample was submitted for positive ion mass spectroscopy analysis. A single ion of m/z value 371 Da was seen.

The reaction mixture was reduced in volume under vacuum, to a dark oil. The oil was partitioned between diethyl ether and water. The aqueous phase was separated and treated

with potassium iodide, 0.83 g dissolved in a minimum amount of water. The addition of potassium iodide caused a precipitation of brown powder. This was collected and dried on the filter paper. A yield of 0.65 g of material was recorded. A hplc analysis of the sample was carried out, see Figure A.3.10.

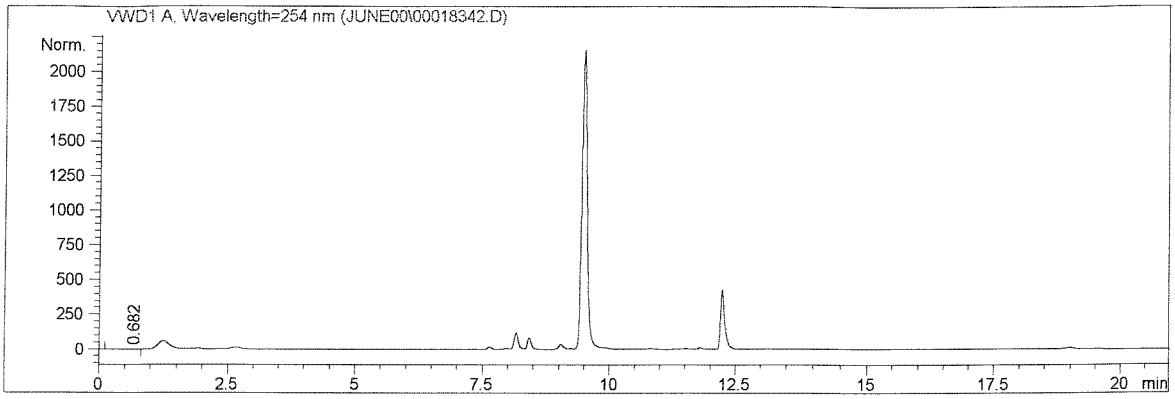


Figure A.3.10 *Chromatogram of the material isolated after the electrolysis of phenyl sulfide and toluene at a potential of 1.2 V vs. SCE.*

The chromatogram was seen to contain two peaks; the peak at 9.5 minutes was the product peak, whilst the peak at 12.4 minutes was phenyl sulfide. Considering that the material was isolated from the aqueous phase and had been washed with diethyl ether it was unexpected that the sample still showed the presence of phenyl sulfide. It was suggested that the product was perhaps unstable and had decomposed on the hplc column and in doing so regenerated phenyl sulfide.

The isolated material was analysed by ^{1}H-NMR, see Figure A.3.11.

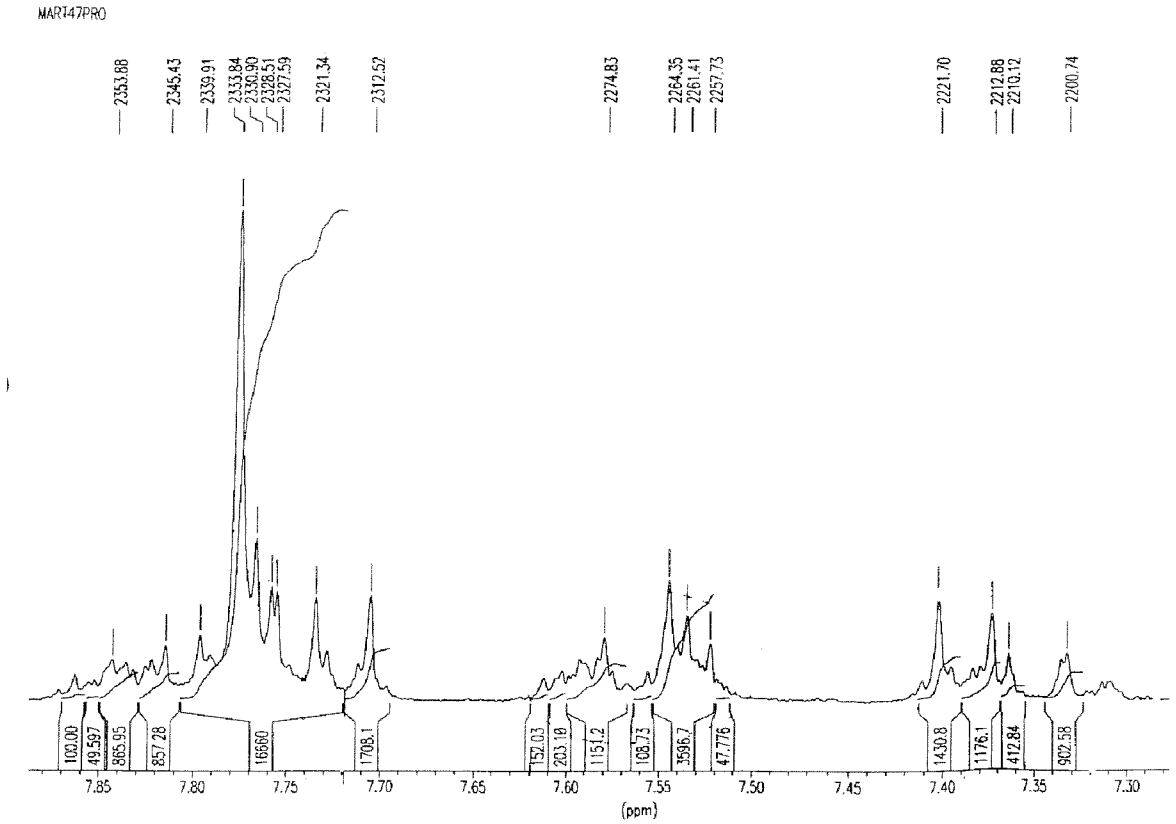
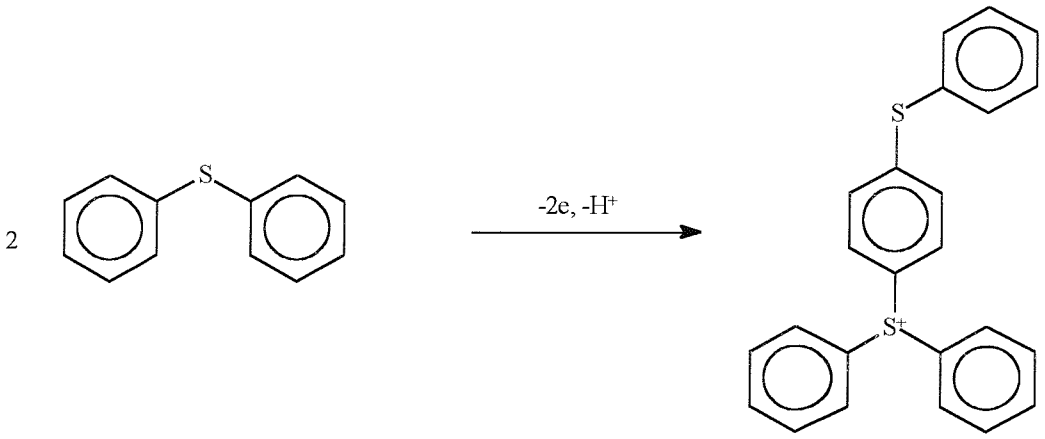


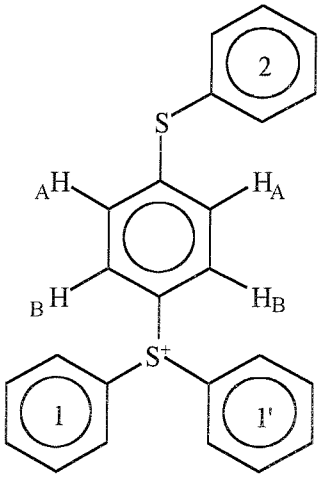
Figure A.3.11 *^{1}H-NMR spectrum of material isolated after the electrolysis of phenyl sulfide and toluene*

The ^{1}H-NMR of phenyl sulfide was similarly recorded and compared to the spectrum, *ibid.* It was apparent that the material did not contain peaks that were attributable to phenyl sulfide, as its peaks were seen in a muliplet between 7.25 and 7.40 ppm.. Positive ion electrospray analysis of the material showed again an ion of m/z value 371 Da. Consideration of the litriture[55] on the potentiostatic electrolysis of phenyl sulfide suggested that a possible product was the result of a self coupling reaction of phenyl sulfide, see Scheme A.3.3.



Scheme A.3.3

Considering Figure A.3.11, there were a pair of doublet signals in the ^{1}H-NMR signal, at 7.39 and 7.72 ppm. Both signals had a coupling constant of 8.8 Hz and the signals were of equal intensity. These signals were assigned to protons H_A and H_B, see Scheme A.3.4.



Scheme A.3.4

The multiplet signal between the limits of 7.74 and 7.80 ppm, in Figure A.3.11, was in the ratio 5:1 to the doublet signal at 7.39. The intensity of the signal would suggest that there were 10 protons in the signal. The down field position of the signals would suggest that the ring was directly substituted with an electron with drawing group. The multiplet was therefore assigned to the protons in rings 1 and 1', in Scheme A.3.4. The remaining multiplet between 7.62 and 7.51 ppm was in the ratio 5:2 to the signal at 7.39 ppm, therefore the signal was assigned to ring 2, which contained 5 protons. The assigned

cation structure would have a molecular weight of 371 Da, which was the ion seen by positive ion mass spectroscopy.

The electrosynthesis of *p*-(phenylthio)phenyl sulfonium salt from phenyl sulfide was previously reported by Torii[41] and Magno[55], see Section 1.6.

The coupling of phenyl sulfide and toluene was not possible in the pipe cell, because phenyl sulfide was a stronger nucleophile and so would react quicker with the phenyl sulfide cation radical so giving the self coupled product as opposed to the cross coupled product.

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