PREPARATION AND REACTIONS OF BICYCLO-[3,3,1]-NONA DIENEDIONES AND RELATED COMPOUNDS

by

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ABSTRACT

FACULTY OF SCIENCE

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Some bicyclo-[3,3,1]-nona dienediones have been synthesised and their structures rigorously assigned. A comparison was drawn between the ultraviolet spectra of these compounds and those of other unsaturated ketones. It was seen that there was interaction between the two α,β-unsaturated ketone chromophores in these compounds.

Reduction of the bicyclo-[3,3,1]-nona-3,6-diene-2,8-diones with magnesium and mercuric chloride in pyridine yielded tricyclo-$[3,3,1,0^{2,8}]$-nonadiones. However direct hydrogenation of these dienediones resulted in the addition of hydrogen to the olefinic double bonds and to the keto groups.

Photolysis of the bicyclo-[3,3,1]-nona-3,7-diene-2,6-diones gave good yields of triasteranediones. These photorearrangements occurred by two successive 1,2-acyl shifts which occurred both under direct irradiation and under sensitised irradiation. Examination of other photoproducts of these dienediones showed that 1,3-acyl shifts occurred. Also isolated were compounds formed by overall 1,5-acyl shifts. Mechanistic aspects of these photoreactions are briefly discussed.

ACKNOWLEDGMENTS

I would like to express my sincere thanks to my supervisor **Dr.** J. M. Mellor for his help and guidance. Also to other members of the University who have been helpful and to the typist Mrs. S. Bell.

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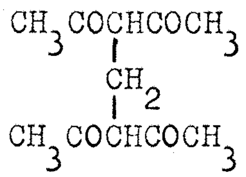
CONTENTS

CHAPTER I

BICYCLO- [3,3,1] -NONA DIENEDIONES AND RELATED COMPOUNDS

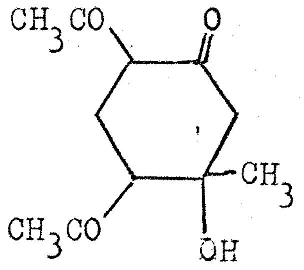
INTRODUCTION

It has been reported by Knoevenagel[1] that the reaction of formaldehyde with acetylacetone in ethyl alcohol gives a product m.p. 41.5-42.5°C, formed from two molecules of acetylacetone and one of formaldehyde. This has been reported[2] to be the tetraketone (1). He found that the reaction of formaldehyde with acetylacetone in ethyl alcohol in the presence of an amine base yielded a different compound, $C_{11}H_{16}O_4$, m.p. 87-89°C, which more recently[2,3] has been assigned the structure (2). He gave it the name "methylenebisacetylacetone" and found that on dehydration in warm concentrated sulphuric acid it produced a bright yellow compound, $C_{11}H_{12}O_2$, m.p. 125-127°C, to which the structure (3) was tentatively assigned. Knoevenagel[1] also reported the preparation of compounds (4), (5) and (6). However, structures have never been rigorously assigned to these unsaturated ketones.



$$\begin{array}{c} CH_3COCHCOCH_3 \\ | \\ CH_2 \\ | \\ CH_3COCHCOCH_3 \end{array}$$

(1)



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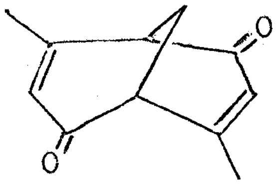
The present work is concerned with these unsaturated ketones and similar compounds. It was of interest to find if the structures assigned by Knoevenagel to these ketones were correct. As the yellow colour of these compounds is unlikely to be a result solely of the conjugation of unsaturated ketone, it was interesting to find out what other physical and chemical properties they had which differed from those of a simple $\alpha\beta$-unsaturated ketone.



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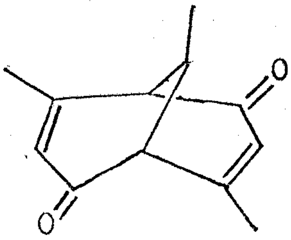

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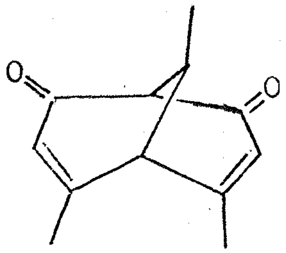

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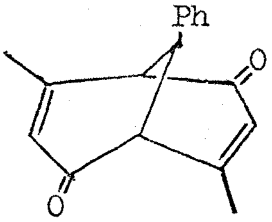

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The aims of the present work were

(a) to repeat the synthesis of these unsaturated ketones by the method of Knoevenagel and also isolate any minor products by column chromatography.

(b) to assign structures to them using modern methods, such as nuclear magnetic resonance spectroscopy.

(c) to examine their physical properties. In particular, it was intended to compare their ultraviolet spectra with those of other compounds possessing similar chromophores within the molecule.

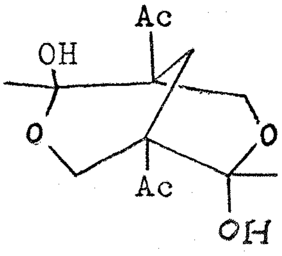
(d) to investigate their chemical reactivity. By using different methods of reduction it was intended to obtain a variety of products from these highly unsaturated compounds. The nature of some of the products would show if a homoconjugative interaction exists between the two enone chromophores.

(e) to study the photochemistry of these compounds (Chapter II of this thesis).

DISCUSSION

(a) Syntheses

A number of crystalline products are reported to have been obtained from the reaction between formaldehyde and acetylacetone. In the presence of an amine catalyst Knoevenagel[1] and later Wilson[2] obtained compound (2). Kennedy and McMurray[4] obtained a compound, $C_{12}H_{18}O_5$, m.p. 90.5°C, (8), a second compound $C_{13}H_{20}O_6$, m.p. 136°C, (7) and a third compound $C_{19}H_{28}O_8$, m.p. 180°C, (9).



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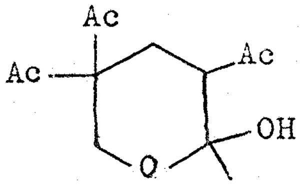

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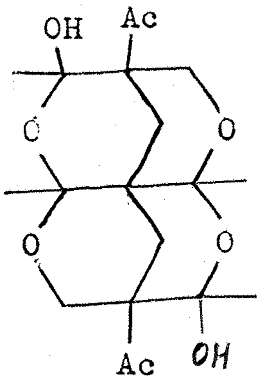
In the absence of an amine catalyst Knoevenagel[1] obtained compound (1) and Wilson[2] obtained two tautomeric compounds viz. compound (1) and a compound $C_{11}H_{16}O_4$, m.p. 55-56°C, (10). Wilson[2] found that when compounds (1) or (10) were treated with an amine catalyst compound (2) was formed.

In the present work it was decided to obtain compound (1). The reaction of formaldehyde with acetylacetone in the absence of an amine catalyst gave a yellow oil. Cooling of the oil in an acetone/dry ice mixture gave white crystals of compound (1), m.p. 37-41°C[1]. These crystals changed into an oil in 24 hours, possibly due to the formation of some of the tautomeric compound (10)[2]. When a sample of the crude product was chromatographed another compound, m.p. 77-79°C was obtained. This compound was not characterised. Without further purification, the yellow oil obtained from the above reaction was taken for the next step in the synthesis. Dehydration of this oil by refluxing in benzene containing toluene-p-sulphonic acid gave the diketone $C_{11}H_{12}O_2$, m.p. 128-130°C (3) in 45% yield. A second dehydration product, $C_{11}H_{12}O_2$, m.p. 156-158°C (11) was obtained in 25% yield by chromatography of the reaction mixture.



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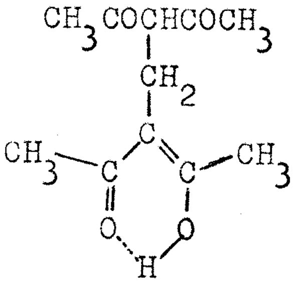

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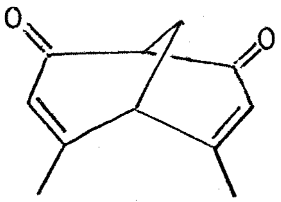

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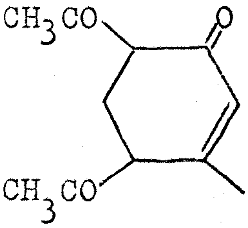
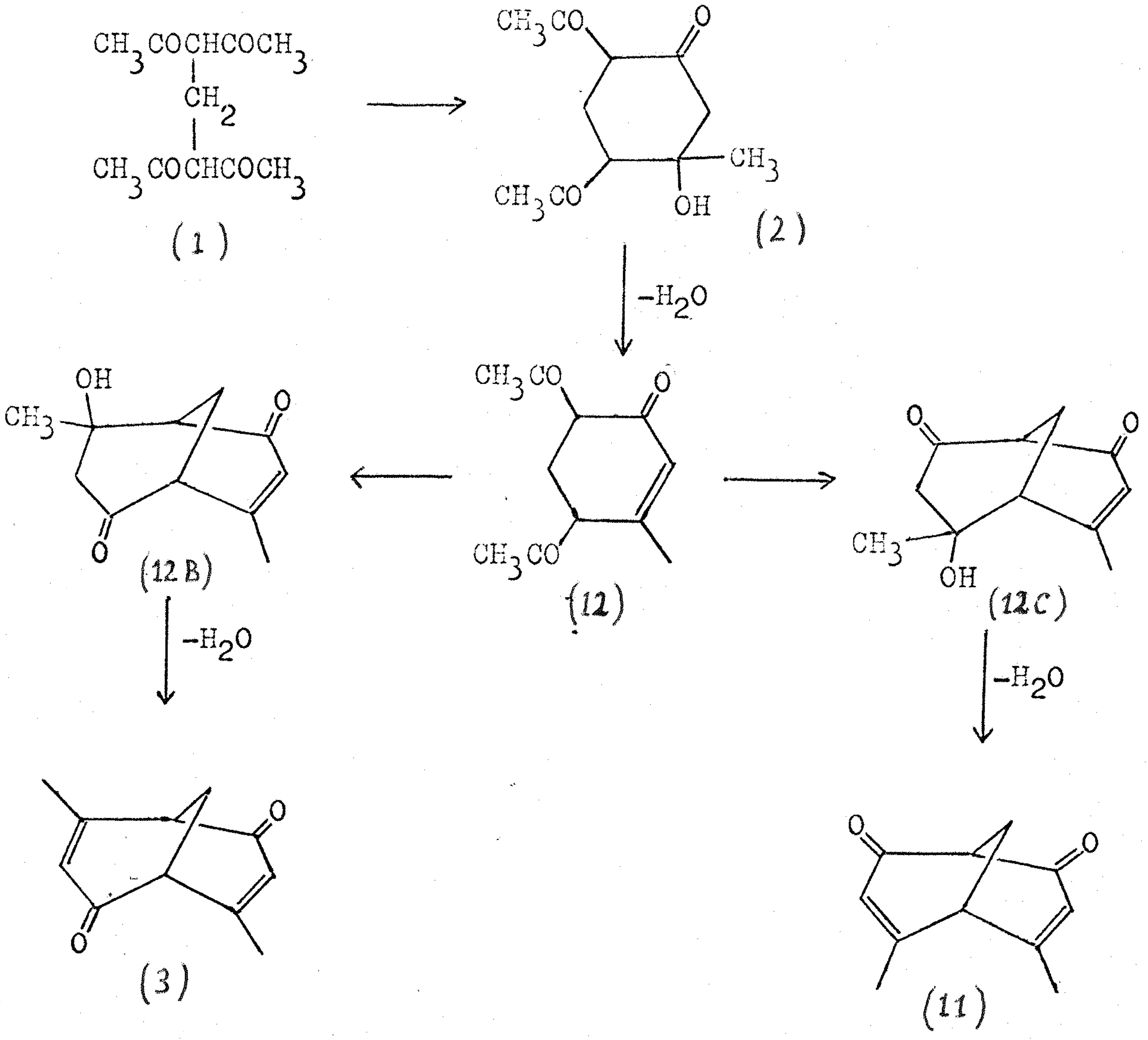


(12)

The formation of the products may be represented in Scheme A. That this scheme properly describes the formation of the dehydration products is clear from the dehydration of the tetraketone (1) in acetic acid containing hydrochloric acid. Then the major product, obtained by chromatography, is the monocyclic compound[1] $C_{11}H_{14}O_3$, m.p. 70-75°C, (12).

Scheme A



In benzene containing toluene-p-sulphonic acid, the ketone (12) is further dehydrated to give products (3) and (11) in the ratio 2:1 respectively. The monocyclic compound (12) was characterised as follows.

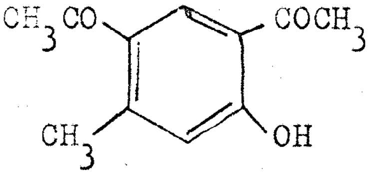
Mass spectrum gave the molecular ion $M^{+}194$. Infra red indicated the presence of the saturated carbonyl group ($\nu_{\text{max.}}$ 1710 cm.^{-1}) and the hydrogen bonded unsaturated carbonyl group ($\nu_{\text{max.}}$ 1650-1590 cm.^{-1}). The nuclear magnetic resonance spectrum shows only one vinyl hydrogen resonance at 3.97 τ and three methyl groups resonating separately at 7.80τ, 7.92τ and 8.01τ. These spectroscopic observations are in accord with the structure (12).

By using different methods of dehydration of the tetraketone (1), the ratio of the products was found to alter. Besides the two methods mentioned above, four other methods of dehydration were studied:

warming in concentrated sulphuric acid, refluxing in acetic acid containing toluene-p-sulphonic acid, refluxing in acetic acid containing hydrobromic acid and refluxing in acetic acid containing sulphuric acid.

The crude product from each method of dehydration was examined by g.l.c. This showed that the formation of the moncyclic ketone (12) was rapid in all experiments. Subsequent dehydration was most easily achieved with hydrobromic acid in glacial acetic acid or with toluene-p-sulphonic acid in benzene. Little ($<$ 5%) of 4,6-dimethylbicyclo-[3,3,1]-nona-3, 6-dione-2,8-dione (11) was formed in acetic acid while in benzene the ratio of

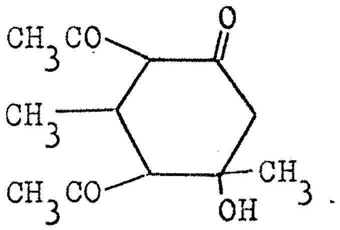
(3) to (11) was 2:1. Further dehydration of the monocyclic ketone (12) was so slow in acetic acid containing hydrochloric acid that this medium was used in order to obtain compound (12). Complete dehydration was also difficult to achieve in cencentrated sulphuric acid. The monocyclic ketone (12) readily oxidises in air to form the compound (13), small quantities of which were isolated by column chromatography of the dehydration products. Compound (13) is identified by its melting point, 108-109°C (lit[1],m.p. 112°C)



(13)

and by its spectra. The nuclear magnetic resonance spectrum shows two identical methyl group resonances at 7.42τ and one methyl group resonance at 7.33τ. The hydroxyl hydrogen resonates at -2.45τ and the two aromatic hydrogens at 1.8τ and 3.2τ. The ultra violet spectrum shows high intensity absorption at short wavelength, $\lambda_{max.}$ 244 mm. (ε 37,000), due to the aromatic nature of the compound. These spectroscopic data agree with the structure (13).

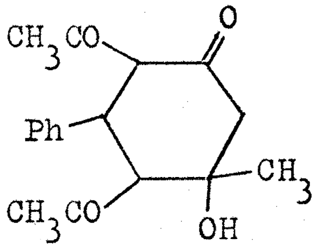
Knoevenagel[1] showed that reaction of acetaldehyde with acetylacetone in the presence of an amine catalyst gave an adduct, $C_{12}H_{18}O_4$, m.p. 108°C, described as "ethylidenebisacetylacetone" which on dehydration in hydrochloric acid gave two compounds, $C_{12}H_{14}O_2$, m.p. 136°C and $C_{12}H_{14}O_2$, m.p. 64°C. The adduct is probably the triketo



(14)

alcohol (14) by analogy to compound (2) which was described as "methylenebisacetylacetone". This preparation was repeated except that the dehydration of the adduct was carried out in glacial acetic acid containing hydrobromic acid. It was possible by chromatography to isolate the two products $C_{12}H_{14}O_2$, m.p. 71-72°C (4) and $C_{12}H_{14}O_2$, m.p. 131-132°C (5).

Knoevenagel[1] again described the reaction of benzaldehyde with acetylacetone in the presence of an amine catalyst to give a product, $C_{17}H_{20}O_4$, m.p. 166°C which he called "benzlidenebisacetylacetone" and which on dehydration in hydrochloric acid gave the product $C_{17}H_{16}O_2$, m.p. 154°C (6). This preparation was also repeated but it was possible to obtain two adducts. Recrystallisation from ethanol gave the tetraketone, $C_{17}H_{20}O_4$, m.p. 165-166°C (16) and recrystallisation from ether and petroleum ether gave the triketo alcohol $C_{17}H_{20}O_4$, m.p. 144-145°C (15). These compounds were distinguished by n.m.r. Compound (16) showed four



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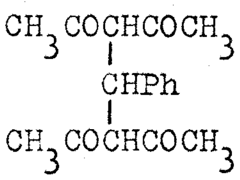
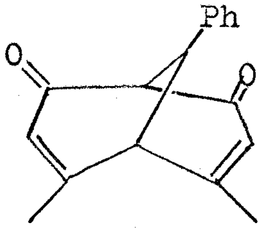


$$\begin{array}{c} CH_3COCHCOCH_3 \\ | \\ CHPh \\ | \\ CH_3COCHCOCH_3 \end{array}$$

(16)

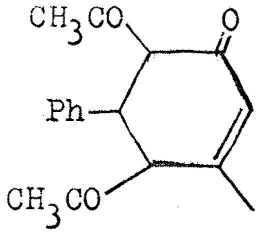
methyl groups in identical environment giving a single resonance at 7.83τ, while compound (15) showed only three methyl signals resonating at 8.33τ, 8.38τ and 8.75τ. By dehydration of compound (15) in benzene containing toluene-p-sulphonic acid and then chromatography it was possible to isolate two products, $C_{17}H_{16}O_2$, m.p. 154-155°C (6) and $C_{17}H_{16}O_2$, m.p. 196-198°C (17) in the ratio 2:1 respectively.



(17)

Dehydration of the tetraketone (16) under the same conditions again gave products (6) and (17) in the ratio 2:1. Hence it may be deduced that in all of these syntheses the dehydration can be performed on either the triketo alcohol or the tetraketone adducts. This gives support to scheme (A) as representing the formation of the dehydration products.

The dehydration of the adduct (15) was performed separately in warm concentrated sulphuric acid, in refluxing glacial acetic acid containing hydrochloric acid, in refluxing glacial acetic acid containing hydrobromic acid and in refluxing benzene containing toluene-p-sulphonic acid. The crude product in each case was analysed by g.l.c. It was seen that in sulphuric acid and in acetic acid containing hydrochloric acid the major product was the monocyclic ketone (18).



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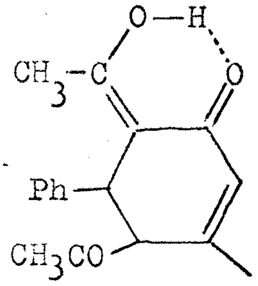


(18B)

In acetic acid containing hydrobromic acid the major product was the ketone (6) with minor products ketone (17) (<5%) and monocyclic ketone (18) (< 5%). In benzene the ratio of (6) to (17) was 2:1.

The monocyclic ketone (18) is characterised by its spectra. $\nu_{max.}$ 1710 cm.$^{-1}$ indicates a saturated carbonyl group and $\nu_{max.}$ 1590 cm.$^{-1}$ agrees with the presence of a hydrogen bonded unsaturated carbonyl group. In the n.m.r. spectrum the phenyl group appears as a resonance at 2.6 to 2.8τ. The vinyl hydrogen resonance appears as a multiplet at 3.85τ and the vinyl methyl group as a doublet (J = 1.5 Hz) at 8.16τ, coupling with the vinyl hydrogens. The two acyl groups resonate as singlets at 7.75 and 8.08τ. Two of the remaining hydrogens resonate as doublets at 5.72 and 6.80τ and their identical coupling constants (J = 1.5 Hz) suggest that they are on adjacent carbon atoms. The remaining hydrogen did not show any sharp resonance, possibly due to the equilibrium between the two tautomers (18) and (18B). Further support for this structural assignment is obtained by analogy to the monocyclic ketone (12). For both compounds (12) and (18) the similarity of their infra red and nuclear magnetic spectra is remarkable. Their methods of preparation are identical and dehydration of each compound yields similar types of products. Finally the existence of an equilibrium between the two tautomers (18) and (18B) would explain the difficulty in obtaining a crystalline sample of this compound.

(b) Structural assignment

The dehydration products of the acetylacetone-formaldehyde adduct are also formed from the monocyclic ketone (12). Further dehydration of this ketone (12) can lead either to the bicyclicketone (3) which has a C_{2v} symmetry or to the bicyclic ketone (11) which has a symmetry plane. In each of the bicyclic ketones the n.m.r. spectrum (see Table I) shows a single resonance attributable to two methyl groups at 8.01τ in compound (3) and at 7.85τ in compound (11). This is consistent with the structures given. A distinction between the two structures may be made by consideration of the other resonances in the n.m.r. spectra. For the compound (3) of C_{2v} symmetry the two bridgehead hydrogens resonating at 6.92τ (2H) are equivalent, and this structure is assigned to the compound m.p. 128-130°C, which also has a resonance at 7.30τ (2H). For the compound (11), characterised by a symmetry plane, the two bridgehead hydrogens are nonequivalent and resonate at 7.04τ and 6.63τ. This structure is therefore assigned to the compound, m.p. 156-158°C, which also has a resonance at 7.28τ (2H). The original structural assignment made by Knoevenagel[1] for the compound (3) is therefore correct.

Table I

N.m.r. data for bicyclo-[3,3,1]-nona-3,7-diene-2,6-diones and bicyclo-[3,3,1]-3,6-diene-2,8-diones.

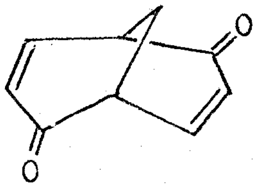
Compound	Hydrogens (value, multiplicity and coupling constant in Hz)							Methyls		
	1-H	2-H	3-H	5-H	6-H	7-H	9-H	C-4	C-6(C-8)	C-9
(19)	6.68dt $J_{12}=7$ $J_{19}=2.5$	2.98q $J_{23}=10$ $J_{12}=7$	4.13d $J_{23}=10$	As 1-H	As 2-H	As 3-H	7.25t $J_{19}=J_{59}$ $=2.5$			
(3)	6.92t $J_{19}=3$		4.37m	As 1-H		As 3-H	7.30t $J_{19}=J_{59}$ $=3$	8.01d J=2	As C-4	
(4)	7.12d $J_{19}=2.5$		4.35m	As 1-H		4.35m	7.00m	8.03d J=2	As C-4	8.80d J=6
(6)	6.56d $J_{19}=3$		4.42m	As 1-H		4.27m	5.88t $J_{19}=J_{59}$ $=3$	8.06d J=2	7.92d J=2	
(11)	7.04t $J_{19}=3$		4.35m	6.63t $J_{59}=3$		As 3-H	7.28t $J_{19}=J_{59}$ $=3$	7.85d J=2	As C-4	
(5)	7.27m		4.30m	6.85m		4.30m	7.10m	7.92d J=2	7.85d J=2	8.82d J=6.5
(17)	6.72t $J_{19}=2.5$		4.33m	6.14m		4.21m	5.79t $J_{19}=J_{59}$ $=2.5$	7.98d J=2	7.76d J=2	

d = doublet, t = triplet, q = quartet, m = multiplet, dt = doublet of triplets.

In a similar way compound (6) is distinguished from compound (17) and compound (4) from compound (5). In each pair of compounds, that with the higher melting point shows two non-equivalent bridgehead hydrogens but the lower melting point compounds show two equivalent bridgehead hydrogens.

The analysis of the n.m.r. spectra of these diketones is straightforward but for one point. In the compound (3) the signals of 1-H and 5-H, which are equivalent, must be distinguished from the signal of 9-H. It might be expected that 1-H and 5-H in (3) would have a chemical shift intermediate between 1-H and 5-H in (11). For compounds (4) and (6) the chemical shifts of 1-H and 5-H, at 7.12τ and 6.56τ respectively, confirm this expectation. Therefore for the compound (3) the signal at 6.92τ, intermediate between the bridgehead hydrogen resonances of compound (11) at 6.63τ and 7.04τ, is then assigned to the equivalent bridgehead hydrogens, 1-H and 5-H. The signal at 7.30τ is assigned to the hydrogens 9-H at the bridge.

The validity of these assignments is reinforced by consideration of the n.m.r. spectrum of the diketone (19).



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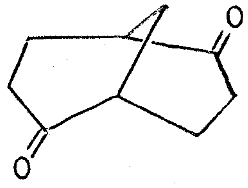
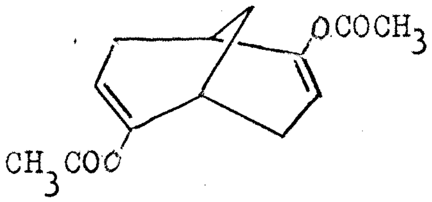


(20)

Here the bridgehead hydrogens are further split by the neighbouring vinyl hydrogens and therefore appear as a doublet of triplets with $J_{1,2}$ 7 Hz and $J_{1,9}$ 2.5 Hz.

The chemical shift of the bridgehead hydrogens in (19) at 6.68 τ and of the bridge hydrogens at 7.26 τ are in close accord with the above structural assignments.

The diketone (19) was prepared from the diketone (20). Bromination of the compound (20)[5] in acetic acid followed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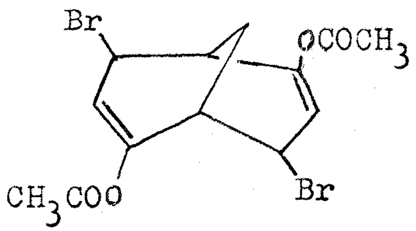

(22)

by dehydrobromination of the intermediate bromoketones under a variety of conditions failed to give a satisfactory yield of the compound (19). However conversion of the compound (20) to the dienol acetate (21)[6] permitted allylic bromination[7] with N-bromosuccinimide under carefully controlled conditions to give a mixture of bromo-enol acetates (22). Without further purification, the crude bromo-enol acetates (22) were hydrolysed and the α,β-unsaturated diketone (19) isolated by chromatography.

Bromination of the dienol acetate (21) with N-bromosuccinimide by refluxing in carbon tetrachloride followed by hydrolysis gave a mixture of bromo-compounds with a very low yield ($< 5\%$) of the required product (19). Chromatography of the crude products gave a dibromo-ketone, $C_9H_8O_2Br_2$ (M^+ 306, 308 and 310), m.p. 210-216°C and a monobromo-ketone, $C_9H_9O_2Br$ (M^+ 228 and 230), m.p. 185-187°C as major products. Structures were not assigned to these bromo-compounds. However when bromination of the dienol acetate (21) with N-bromo-succinimide was performed in carbon tetrachloride kept rigidly at 76°C, subsequent hydrolysis gave the dienedione (19) as the major product (50% overall yield). It was noticed that bromination in vigorously refluxing carbon tetrachloride was accompanied by a brown colour in the solution whereas bromination at 76°C gave only a pale yellow colour to the solution which became colourless again after 30 minutes. It seems that allylic bromination[7] is achieved by a low concentration of bromine and that this low concentration is maintained by careful temperature control of the reaction mixture.

(c) Ultra violet spectra

The yellow colour of all the bicyclo- [3,3,1]-nonadienediones prepared in this work indicates an interaction between the two rigidly held enone chromophores. In Table 2 the U.V. spectra of the dienediones are listed together with those of a number of compounds of similar structure.

Table 2

U.V. spectral maxima of bicyclo- [3,3,1] -nonadienediones and related compounds

Compound	Maxima (nm.)	$\varepsilon_{max.}$	Solvent	Reference
(23)	225 320	10,000 36	EtOH	8
(23)	217 342	12,000 27	Isooctane	8
(24)	235 311	13,200 47	MeOH	8
(24)	225 337	14,200 31	Isooctane	8
(19)	229 270 (sh) 349	8,000 1,570 560	EtOH	
(3)	236 330 350 366 381	11,950 770 770 513 206	Hexane	
(3)	237 268 (sh) 280 (sh) 344	16,850 1,720 900 975	EtOH	
(4)	238 268 (sh) 348	14,250 1,432 758	EtOH	

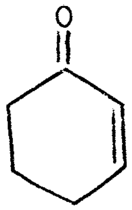
Table 2 (cont'd)

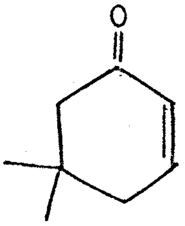
Compound	Maxima (nm.)	$\varepsilon_{max.}$	Solvent	Reference
(6)	237	15,700	EtOH	
	270 (sh)	2,185		
	348	835		
(25)	230	3,200	EtOH	9
	283	567		
	351	92		
(25)	228 (sh)	2,075	Cyclohexane	9
	273	539		
	343 (sh)	52		
	359	69		
	374	64		
	395	28		
(26)	225	5,720	EtOH	10
	263	704		
	351	137		
(27)	226	7,900	MeOH	11
	338	108		
(11)	224	27,700	EtOH	
	239 (sh)	11,000		
	272	1,640		
	320 (sh)	228		
	335	200		
	362	170		
(5)	221	30,640	EtOH	
	239 (sh)	12,780		
	271 (sh)	2,157		
	335	209		
	367	197		
(17)	223	19,600	EtOH	
	240 (sh)	9,800		
	270 (sh)	2,700		
	336	225		
	362	200		

sh = shoulder

The spectra of the bicyclo-[3,3,1]-nona-3,7-diene-2,6-diones and the bicyclo-[3,3,1]-nona-3,6-diene-2,8-diones show common features. The $\pi \longrightarrow \pi^*$ transition is unexceptional both in position and intensity.

The $n \rightarrow \pi^*$ transition of both series of diones is shifted to longer wavelength by comparison with the simple cyclohexenones (23)[8] and (24)[8] and also shows considerable


(23)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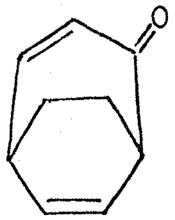
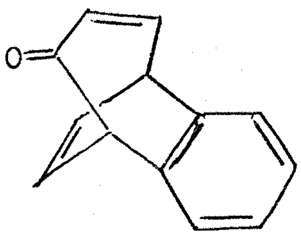

(25)

enhancement. In ketones (25), (26) and (27) which have similar structural features, a comparable shift and enhancement are observed.[9-11] Vibrational structure is noted in the $n \rightarrow \pi^*$ transition and is particularly marked in diketones (11), (5) and (17).

The shift enhancement of the $n \rightarrow \pi^*$ transition of α,β-unsaturated ketones, by comparison with simple saturated ketones, are well known. The present results suggest that the β,γ double bond causes a similar shift and enhancement of the $n \rightarrow \pi^*$ transition of β,γ-unsaturated ketones.

A maximum or shoulder at 270nm. is also observed in these dienediones and in the related α,β-unsaturated ketones (25) and (26). This band is doubtless that observed in certain β,γ-unsaturated ketones[12] of similar structure. The interaction of the two enone chromophores is reflected in the photochemistry of these diene-diones (see Chapter II of this thesis).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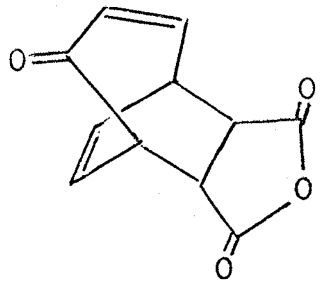
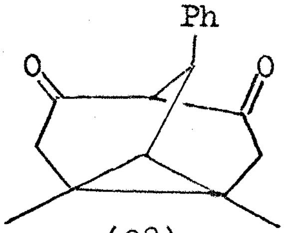
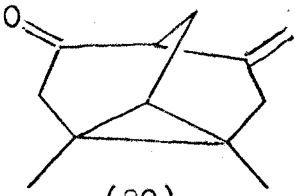

(27)

(d) Reduction

The proximity of the two enone chromophores permits a homoconjugative interaction. This was illustrated by the pinacol reduction of ketone (17). The reduction was carried out with magnesium and mercuric chloride in pyridine under nitrogen and led smoothly to the formation of the tricyclo- $\left[3,3,1,0^{2,8}\right]$ -nonadione (28) in 70% yield.



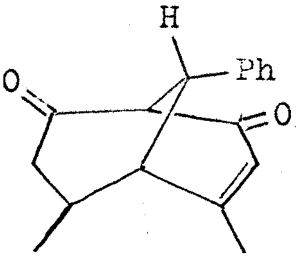
(28)



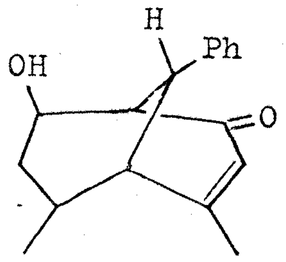
(29)

The product was characterised by the molecular ion $M^+ = 254$ and ν_{max} 1720 cm^{-1}. The n.m.r. spectrum shows no resonance attributable to a vinyl hydrogen but two methyl signals at 8.57 τ and 8.66 τ and a cyclopropyl hydrogen at 8.80 τ were observed. Similarly, reduction of ketone (11) gave the tricyclic ketone (29), characterised by $M^+ = 178$, ν_{max} 1720 cm^{-1} and the n.m.r. spectrum. Resonance of the two methyl groups as one signal at 8.78 τ indicated a product with an element of symmetry. No resonance attributable to a vinyl hydrogen was observed and the cyclopropyl hydrogen was observed to resonate at 9.10 τ. Although the intramolecular pinacol reduction of saturated ketones[13] and the intermolecular pinacol reduction of α,β -unsaturated ketones[14] are known, this represents another extension to the pinacol reduction.

When reduction of ketone (17) was brought about by molecular hydrogen at one atmosphere pressure in the presence of a platinum catalyst, two products, $C_{17}H_{18}O_2$, m.p. 150-151°C (30) and



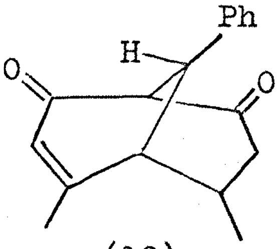
(30)



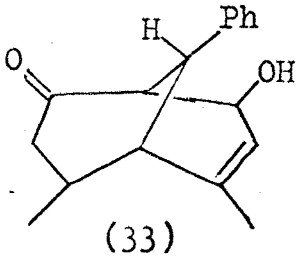
(31)

$C_{17}H_{20}O_2$, m.p. 151-152°C (31) were formed. The infra red spectrum of product (30) showed $\nu_{max.}$ 1710 cm^{-1}, attributable to the saturated carbonyl group and 1660 cm^{-1}, attributable to the unsaturated carbonyl group. The n.m.r. spectrum shows no resonance attributable to a hydroxyl group. One methyl group resonates at 8.80τ (d J = 7 Hz), the coupling constant indicating a methyl group adjacent to one hydrogen. The other methyl group resonates at 7.97τ (d J = 1.5 Hz), the small coupling constant indicating no adjacent hydrogen. Resonance attributable to only one vinyl hydrogen was observed. The product (31) was characterised by i.r. and n.m.r. $\nu_{max.}$ 1650 cm^{-1} indicates the presence of an unsaturated carbonyl group. Resonance of the hydroxyl hydrogen was observed at 6.9τ, shifting to 6.8 τ on dilution. Only one vinyl hydrogen resonance was observed at 3.92τ. One methyl group resonates at 8.13τ (d J= 1.5 Hz), the small coupling constant indicating the absence of an adjacent hydrogen. The other methyl group, resonating at 8.94τ (d J = 7 Hz), must be adjacent to a hydrogen because of the large coupling constant.

As analysis of compound (30) has shown the formula to be $C_{17}H_{18}O_2$, it is clearly formed by the addition of hydrogen across one double bond. Two isomers, (30) and (32), are possible, the phenyl group on the bridge probably determining



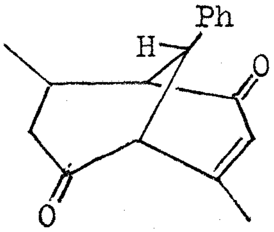
(32)



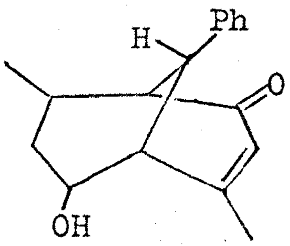
(33)

which double bond is attacked. As only one of these isomers was isolated it is apparent that the phenyl group is offering steric hindrance to hydrogenation at one of the double bonds. Hence structure (30) is assigned to the product m.p. 150-151°C. Compound (31) of molecular formula $C_{17}H_{20}O_2$ is seen from spectroscopic analysis to contain a hydroxyl group as well as only one ethylenic double bond. Hence it appears to have been formed from compound (30) by the addition of hydrogen at one of the keto groups. Again it is reasonable to expect that the compound most likely to be formed is (31) rather than (33) due to the steric hindrance of the phenyl group. Hence structure (31) is assigned to the product m.p. 151-152°C. However a complete stereoanalysis has not been performed on compounds (30) and (31).

Hydrogenation of compound (6) using molecular hydrogen at one atmosphere in the presence of a platinum catalyst gave two major products (34) and (35). These products were characterised



(34)



(35)

in a similar manner to the compounds (30) and (31). Again it was noticed that the phenyl group offered steric hindrance to hydrogenation of one of the unsaturated enone chromophores.

EXPERIMENTAL

I.r. spectra were measured in solution in chloroform with a Unicam S.P. 200 spectrophotometer. N.m.r. spectra were measured in deuteriochloroform solution (unless otherwise stated) with a Varian A 60 and/or a Varian HA 100 spectrometer. Chemical shifts are expressed in τ values (T.M.S. = 10). Bands were observed as sharp singlets except where the following designations are used: d = doublet, t = triplet, q = quartet, m = multiplet, dt = doublet of triplets. Coupling constants (J) are expressed in Hz units. U.v. spectra were measured with a Unicam S.P. 800 spectrophotometer, employing ethanol solutions unless otherwise stated. Molecular ion (M^+) values were obtained with a A.E.1. M.S.12 mass spectrometer. Micro analysis were performed by Dr. G. Weiler and Dr. F. B. Strauss (Oxford). Column chromatography was carried out on activated silica gel (Grace 100-200 mesh), using 30 g. for each gram of organic material. Eluting solvents used were mixtures of diethyl ether and petroleum spirit b.p. 40-60°C and of diethyl ether and chloroform, unless otherwise stated. G.l.c. was carried out on a 5% CDMS column on chromosorb W at 180°C or 200°C. T.l.c. was carried out on Merck silica gel (Stahl) using mixtures of benzene and ethyl acetate as chromatography solvents and the position of compounds was shown by developing in iodine vapour. Melting points are recorded uncorrected. The term "petrol" represents petroleum spirit (b.p. 40-60°C). The term "ether" represents di-ethyl ether (M & B boiling range 34-36°C).

Bicyclo- [3,3,1] -nona-3,7-diene-2,6-dione (19).

The dione (20)[5] (10.83 g.) was dissolved in a mixture of acetic anhydride (200 ml) and acetyl chloride (50 ml) and heated under reflux for 3 hours. The solvent was removed initially at atmospheric pressure and finally under reduced pressure. The product was isolated by column chromatography with elution of ether/petrol (15:85), to give the dienol acetate (21)[6] as a white solid (7.76 g). Recrystallisation from ether/petrol yielded white needles (5.62 g), m.p. 78-80°C; $\nu_{max.}$ 1740 cm.$^{-1}$. The dienol acetate (21) (4.52 g) was stirred in a solution of N-bromosuccinimide (4.99 g) in carbon tetrachloride (400 ml) at 76°C for 6 hours. After cooling to room temperature, the precipitate of succinimide was removed by filtration and washed with further carbon tetrachloride. The combined filtrate and washings were evaporated under reduced pressure to give a yellow oil (6.52 g), ν_{max} 1760 cm^{-1}. The yellow oil was dissolved in a mixture of ethanol (100 ml), water (100 ml) and 10 M hydrochloric acid (3ml) and heated under reflux for 30 minutes. The solvent was removed under reduced pressure and the product isolated by column chromatography. Elution with ether/petrol (30:70) gave bicyclo-[3.3.1]-nona-3,7-diene-2,6-dione (19) (1.85 g) as a white solid. Recrystallisation from ether/petrol gave white prisms, m.p. 81-83°C (Found: C, 73.0%; H, 5.4%. $C_9H_8O_2$ requires C, 73.0%; H, 5.4%); M^+ 148: ν_{max} 1678 cm^{-1}; λ_{max}229 (ϵ 8,000) and 349 nm. (ϵ 560); τ 2.98 (2H q J = 10 Hz and 7 Hz), 4.13 (2H d J = 10 Hz), 6.68 (2Hdt J = 7 Hz and2.5Hz), 7.25 (2H t J =2.5Hz).

4,8,9-Trimethylbicyclo-[3,3,1]-nona-3,7-diene-2,6-dione (4) and 4,6,9-Trimethylbicyclo-[3,3,1]-nona-3,6-diene-2,8-dione (5)

Acetylacetone (20 g.) and acetaldehyde (4.4 g.) were dissolved in ethyl alcohol (50 ml.) and cooled to 0°C. Diethylamine (1 ml.) in ethyl alcohol (4 ml.) was then added to the reaction mixture. After 6 days at 0°C the solvent was evaporated off under reduced pressure and the crude residue was dissolved in glacial acetic acid (100 ml.) containing hydrobromic acid (10 ml. of 45%). The solution was heated under reflux for 12 hours, concentrated under reduced pressure and the residue partitioned between chloroform (30 ml. x 2) and water (50 ml.). The combined chloroform layers were washed successively with potassium bicarbonate solution and with water and dried with anhydrous sodium sulphate. The solvent was removed to afford a crude residue which was then chromatographed. Elution with ether/petrol (30:70) afforded 4,8,9-trimethylbicyclo- [3,3,1] -nona-3,7-diene-2,6-dione (4) (5.86g.). Recrystallisation from ether/petrol gave yellow crystals, m.p. 71-72°C (lit.,[1] m.p. 64°C); M^+ 190; $\nu_{max.}$ 1670 and 1635 $cm.^{-1}$; $\lambda_{max.}$ 238 (ε 14,250), 268 (ε 1,432) and 348 nm. (ε 758); τ 4.35 (2H m), 7.0 (1H m), 7.12 (1Hd J = 2.5 Hz), 8.03 (6H d J = 2 Hz) and 8.80 (3H d J = 6 Hz).

Elution with ether afforded 4,6,9-trimethylbicyclo-[3,3,1]-nona-3,6-diene-2,8-dione (5) (4.27 g.). Recrystallisation from chloroform/ether gave yellow crystals, m.p. 131-132°C (lit.,[1] m.p. 136°C); M^+ 190; $\nu_{max.}$ 1680, 1655 and 1635 $cm.^{-1}$; $\lambda_{max.}$ 221 (ε 30,640), 239 (ε 12,780), 271 (ε 2,157), 335 (ε 209) and 367 nm. (ε 197); τ 4.30 (2H m), 6.85 (1H m), 7.10 (1H m), 7.27 (1H m), 7.85 (3H d J = 2 Hz), 7.92 (3H d J = 2 Hz) and 8.82 (3H d J = 6.5 Hz).

3,5-Diacetylheptane-2,6-dione (1)

Acetylacetone (436 g) was dissolved in ethyl alcohol (220 ml) containing 40% formalin (154 ml) and left at 20°C for 3 days. The solvent was then removed under reduced pressure to give crude 3,5-diacetylheptane-2,6-dione (1) (209 g); $\nu_{max.}$ 1720 and 1700 cm^{-1}.
On leaving the crude product at 0°C for 2 days crystals appeared. Filtration followed by washing with ethanol yielded white crystals (1.4 g), m.p. 37-41°C (lit.,[1] m.p. 41.5-42.5°C).

2,4-Diacetyl-5-methlcyclohex-5-ene-1-one (12)

Crude 3,5-diacetylheptane-2,6-dione (1) (5 g) was heated under reflux for 20 hours in glacial acetic acid (100 ml) with 10 M hydrochloric acid (1.5 ml). The solvent was removed under reduced pressure and the residue was chromatographed. Elution with ether/petrol (50:50) gave 4,8-dimethylbicyclo-[3,3,1]-nona-3,7-diene-2,6-dione (3) (500 mg) and elution with petrol/ether (60:40) gave 2,4-diacetyl-5-methylcyclohex-5-ene-1-one (12) (1.85 g). Recrystallisation from ether/petrol gave yellow needles of 2,4-diacetyl-5-methylcyclohex-5-ene-1-one (12), m.p. 70-75°C (lit.,[1] m.p. 75°C) (Found: C, 68.6%; H, 6.25%. $C_{11}H_{14}O_3$ requires C, 68.73%; H, 6.29%.); M$^+$ 194; $\nu_{max.}$ 1710 and 1650-1590 cm^{-1}; $\lambda_{max.}$ 225 (ε 9,750) and 338 nm. (ε 6,220); $\lambda_{max.}$ in ethanolic sodium hydroxide 312 (ε 7,450) and

358 nm. (ε 9,750); τ 1.8 (1H s), 3.97 (1H m), 6.82 (1H m), 7.20 (2H m), 7.80 (3H s), 7.92 (3H s) and 8.01 (3H d J= 3Hz).

4,8-Dimethylbicyclo- [3,3,1] -nona-3,7-diene-2,6-dione (3) and 4,6-dimethylbicyclo- [3,3,1] -nona-3,6-diene-2,8-dione (11).

(a) Dehydration with toluene-p-sulphonic acid in benzene. Crude 3,5-diacetylheptane-2,6-dione (1) (177 g) was heated under reflux in dry benzene (440 ml) containing toluene-p-sulphonic acid (8.9 g) and water was removed using a Dean and Stark separator. After three days removal of water was complete and the cooled solution was washed with water, dried with anhydrous sodium sulphate and the solvent removed under reduced pressure. The orange coloured residue was analysed by g.l.c. and the products separated by column chromatography.

In ether/benzene (2:98):2,4-diacetyl-5-hydroxytoluene (13) (3.9 g), m.p. 108-109°C from ether/petrol (lit.,[1] m.p. 112°C), M^+ 192; ν_{max} 1680 and 1650 cm^{-1}; $\lambda_{max.}$ 244 (ε 37,000) and 318 nm. (ε 3,500); $\lambda_{max.}$ in ethanolic sodium hydroxide 252 (ε 24,000) and 313 nm. (ε 24,800); τ-2.45 (1H s), 1.8 (1H s), 3.2 (1H s), 7.33 (3H s) and 7.42 (6H s).

In ether/benzene (15:85): 4,8-dimethylbicyclo- [3,3,1] -nona-3,7-diene-2,6-dione (3) (45.6 g), m.p. 128-130°C from ether/petrol (lit.,[1] m.p. 125-127°C) (Found: C, 74.9%; H 6.9%. $C_{11}H_{12}O_2$ requires C, 75.0%; H, 6.9%); M^+ 176; $\nu_{max.}$ 1670 and 1635 cm^{-1}; $\lambda_{max.}$ 237 (ε 16,850), 268 (ε 1,720) and 344 nm. (ε 975); $\lambda_{max.}$ in n-hexane 236 (ε 13,650),

305 (ε 722), 330 (ε 750), 350 (ε 580), 366 (ε 530) and 385 nm. (ε 207);
τ 4.37 (2H m), 6.92 (2H t J = 3 Hz). 7.30 (2HtJ = 3 Hz), 8.01 (6H d J = 2 Hz).

In ether/benzene (20:80): a substance which was not identified (14.49 g). Recrystallisation from ether/petrol yielded yellow crystals, m.p. 135-137°C; M^+ 176.

In ether/benzene (75:25): 4,6-dimethylbicyclo- [3,3,1]-nona-3,6-diene-2,8-dione (11) (21.3 g). Recrystallisation from chloroform/ether gave yellow crystals of (11), m.p. 156-158°C (Found: C, 75.0%; H, 6.9%. $C_{11}H_{12}O_2$ requires C, 75.0%; H, 6.9%); M^+ 176; ν_{max} 1680, 1655 and 1630 cm^{-1}; $\lambda_{max.}$ 224 (ε 27,700), 272 (ε 1,640), 320 (ε 228), 335 (ε 200) and 362 nm. (ε 170); $\lambda_{max.}$ in diglyme 265 (ε 1,875), 330 (ε 140), 345 (ε 145) and 372 nm. (ε 152);
τ 4.35 (2H m), 6.63 (1H t J = 3 Hz), 7.04 (1H t J = 3 Hz), 7.28 (2H t J = 3 Hz) and 7.85 (6H d J = 2 Hz).

(b) Dehydration in acetic acid.

(i) Crude 3,5-diacetylheptane-2,6-dione (1) (2 g) was heated under reflux in glacial acetic acid (50 ml) containing toluene-p-sulphonic acid (25 mg) for 24 hours. The solution was concentrated under reduced pressure, cooled and the residue partitioned between water (50 ml) and ether (50 ml). The ethereal layer was separated, washed with saturated potassium hydrogen carbonate solution and dried with anhydrous sodium sulphate. The resulting solution was analysed by g.l.c.

(ii) Crude 3,5-diacetylheptane-2,6-dione (1) (1 g) was heated under reflux in glacial acetic acid (25 ml) containing 10 M hydrochloric acid (0.5 ml) for 24 hours. The crude product was poured into water (50 ml) and extracted with ether (50 ml x 2). After neutralising with saturated potassium hydrogen carbonate solution, the ethereal extract was dried with anhydrous sodium sulphate, filtered and analysed by g.l.c.

(iii) Crude 3,5-diacetylheptane-2,6-dione (1) (1 g) was treated under the same conditions using 40% hydrobromic acid (0.5 ml) instead of 10M hydrochloric acid. Again the products were analysed by g.l.c.

(iv) Crude 3,5-diacetylheptane-2,6-dione (1) (2 g) was heated under reflux in glacial acetic acid (50 ml) containing concentrated sulphuric acid (2.5 ml) for 6 hours. The crude product was poured into water (100 ml) and extracted with ether (50 ml x 2). The combined ethereal layers were combined and washed with aqueous potassium hydrogen carbonate solution, dried with anhydrous sodium sulphate and analysed by g.l.c.

(c) Dehydration in sulphuric acid.

Crude 3,5-diacetylheptane-2,6-dione (1) (2 g) was dissolved in 5 M sulphuric acid (5 ml) and left for 24 hours at 20°C. The solution was poured into water (100 ml) and purification as before (b(iv)) afforded a yellow oil which was analysed by g.l.c.

Dehydration of 2,4-diacetyl-5-methylcyclohex-5-ene-1-one (12).

2,4-Diacetyl-5-methylcyclohex-5-ene-1-one (12) (380 mg.) was heated under reflux in benzene (150 ml.) containing toluene-p-sulphonic acid (32 mg.) for 18 hours. The cooled solution was washed with water (50 ml. x 2), dried with anhydrous sodium sulphate and the solvent removed to give a crude residue which was analysed by g.l.c. and chromatographed on silica gel. The following fractions were eluted and identified by infra red spectroscopy: in ether/petrol (20:80), 2,4-diacetyl-5-hydroxytoluene (13) (32 mg.); in ether/petrol (30:70), 4,8-dimethylbicyclo-[3,3,1]-nona-3,7-diene-2,6-dione (3) (103 mg.); in ether/petrol (50:50), 2,4-diacetyl-5-methylcyclohex-5-ene-1-one (12) (124 mg.); and in ether/petrol (75:25), 4,6-dimethylbicyclo-[3,3,1]-nona-3,6-diene-2,8-dione (11) (75 mg.).

3,5-Diacetyl-4-phenylheptane-2,6-dione (16) and 2,4-diacetyl-5-methyl-3-phenylcyclohexan-5-ol-1-one (15).

Acetylacetone (20 g.) and benzaldehyde (10.6 g.) were dissolved in ethyl alcohol (60 ml.) and after cooling to 0°C diethylamine (1 ml.) in ethyl alcohol (4 ml.) was added. After two days the product was filtered and washed with ethanol to give a white solid (17.4 g.). Recrystallisation from ethyl alcohol yielded 3,5-diacetyl-4-phenylheptane-2,6-dione (16) as white needles (8.2 g.), m.p. 165-166°C; M^+ 288; $\nu_{max.}$ 1720 and 1700 cm.$^{-1}$; $\lambda_{max.}$ 258 (ϵ 310), 264 (ϵ 290) and 290 nm. (ϵ 247); $\lambda_{max.}$ in ethanolic sodium hydroxide 233 (ϵ 16,760) and 304 nm. (ϵ 3,327). τ 2.6-2.7 (5H m), 6.3 (1H m), 7.33-7.43 (2H m) and 7.83 (12H s).

The solvent was removed from the mother liquor to give a white solid. Recrystallisation from ether/petrol yielded 2,4-diacetyl-5-methyl-3-phenylcyclohexan-5-ol-1-one (15) as white crystals (4.5 g.), m.p. 144-145°C; M^+ 288; $\nu_{max.}$ 1695 and 1600 cm.$^{-1}$; $\lambda_{max.}$ 290 nm. (ε 6,300); $\lambda_{max.}$ in ethanolic sodium hydroxide 305 nm. (ε 11,100); τ 2.6-2.8 (5H m), 5.85 (1H d J = 10 Hz), 7.13 (1H d J = 10 Hz), 7.45 (2H s), 8.33 (3H s), 8.38 (3H s) and 8.75 (3H s).

2,4-Diacetyl-5-methyl-3-phenylcyclohex-5-ene-1-one (18).

The ketone (15)^1 (195 mg.) was heated under reflux in glacial acetic acid (25 ml.) containing 1 OM hydrochloric acid (0.5 ml.) for 18 hours. The resulting solution was poured into water (100 ml.), extracted with ether (50 ml. x 2), dried over anhydrous soldium sulphate. The solvent was removed and the product isolated by column chromatography. Elution with ether/petrol (28:80) gave 2,4-diacetyl-5-methyl-3-phenylcyclohex-5-ene-1-one (18) as a yellow non-crystallisable oil (50 mg.); $\nu_{max.}$ 1700 and 1590 cm.$^{-1}$; τ 2.6-2.8 (5H m), 3.85 (1H m), 5.72 (1H d J = 1.5 Hz), 6.8 (1H d J = 1.5 Hz), 7.75 (3H s), 8.08 (3H s) and 8.16 (3H d J = 1.5 Hz).

4,8-dimethyl-9-phenylbicyclo-[3,3,1]-nona-3,7-diene-2,6-dione (6) and 4,6-dimethyl-9-phenylbicyclo-[3,3,1]-nona-3,6-diene-2,8-dione (17).

(a) Dehydration with toluene-p-sulphonic acid in benzene.

The ketone (15)^1, m.p. 166°C, (77 g.) was heated under reflux in dry benzene (500 ml) containing toluene-p-sulphonic acid (5 g) and water was removed using a Dean and Stark water separator. After three days the solution was cooled and the solvent removed to give a crystalline product which was then analysed by g.l.c. Recrystallisation from benzene/ethyl alcohol afforded pale yellow crystals of 4,8-dimethyl-9-phenybicyclo- [3,3,1] -nona-3,7-diene-2,6-dione (6) (37 g), m.p. 153-154°C (lit.,[1] m.p. 154°C). (Found: C, 81.1%; H, 6.4%. $C_{17}H_{16}O_2$ requires C, 80.9; H, 6.4%.)1 M^+ 252; $\nu_{max.}$ 1660 and 1630 cm.$^{-1}$; $\lambda_{max.}$ 237 (ϵ 15,700) and 348 nm. (ϵ 835); $\lambda_{max.}$ in diglyme 237 (ϵ 15,450), 335 (ϵ 640), 350 (ϵ 775) and 362 nm. (ϵ 630); τ 2.6-2.85 (5H m), 4.27 (1H m), 4.42 (1H m), 5.88 (1H t J = 3 Hz), 6.56 (2H d J = 3Hz), 7.92 (3H d J = 2 Hz), 8.06 (3H d J = 2 Hz).

The mother liquors, on crystallisation from chloroform/ ether afforded a second dione. Recrystallisation from benzene gave 4,6-dimethyl-9-phenylbicyclo- [3,3,1] -nona-3,6-diene-2,8-dione (17) as pale yellow crystals (7.5 g), m.p. 196-198°C. (Found: C, 81.1%; H, 6.5%. $C_{17}H_{16}O_2$ requires C, 80.9%; H, 6.4%); M^+ 252; $\nu_{max.}$ 1685, 1655 and 1635 cm^{-1}; $\lambda_{max.}$ 223 (ϵ 19,600), 270 (ϵ 2,700), 336 (ϵ 225) and 362 nm. (ϵ 200); $\lambda_{max.}$ in diglyme 270 (ϵ 6,440), 345 (ϵ 197) and 370 nm. (ϵ 164); τ 2.6-2.9 (5H m), 4.21 (1H m), 4.33 (1H m), 5.79 (1H t J = 2.5 Hz), 6.14 (1H m), 6.72 (1H t J = 2.5 Hz), 7.76 (3H d J = 2 Hz), 7.98 (3H d J = 2 Hz).

(b) Dehydration in acetic acid.

The ketone (15)[1], m.p. 166°C, was heated in acetic acid with hydrochloric acid or hydrobromic acid as dehydration catalyst in a similar manner to that used for the dehydration of 3,5-diacetyl-heptane-2,6-dione. The products were analysed by g.l.c.

(c) Dehydration in sulphuric acid.

The ketone (15)[1], m.p. 166°C, (208 mg) was mixed with concentrated sulphuric acid and left at 20°C for 18 hours. The crude product was purified as before and analysed by g.l.c.

Dehydration of 3,5-diacetyl-4-phenylheptane-2,6-dione (16).

3,5-diacetyl-4-phenylheptane-2,6-dione (16) was heated separately in acetic acid containing toluene-p-sulphonic acid and in benzene containing toluene-p-sulphonic acid in a similar manner to that used for the dehydration of the ketone (15)[1], m.p. 166°C. The products were analysed by g.l.c.

Dehydration of 2,4-diacetyl-5-methyl-3-phenylocyclohex-5-ene-1-one (18).

Crude 2,4-diacetyl-5-methyl-3-phenylcyclohex-5-ene-1-one (18) (50 mg) was heated under reflux in benzene (50 ml) containing toluene-p-sulphonic acid (20 mg) for 18 hours. The cooled solution was washed with water, dried with anhydrous sodium sulphate and analysed by g.l.c.

2,8-dimethyltricyclo $[3,3,1,0^{2,8}]$-nonane-4,6-dione (29).

4,6-dimethylbicyclo- $[3,3,1]$ -nona-3,6-diene-2,8-dione (11) (1.32 g), mercuric chloride (1.02 g) and magnesium (0.18 g) were stirred at 0°C in pyridine (20 ml) under nitrogen for 18 hours. After filtration, the residue was washed with a little pyridine, the washings and filtrate combined and concentrated under reduced pressure.

The concentrate was diluted with water (100 ml) and the products were extracted into chloroform (50 ml x 2). The chloroform solution was washed with 0.5 M hydrochloric acid (50 ml), with sodium carbonate solution (50 ml) and with water (50 ml) and dried with anhydrous sodium sulphate. Evaporation of the solvent gave a yellow oil (1 g) which was chromatographed on silica gel. Elution in ether/petrol (50:50) afforded the reduction product (29) (510 mg). Recrystallisation from ether/petrol gave crystals of (29), m.p. 54-56°C. M^+178; (Found: C, 74.0%; H, 7.9%. $C_{11}H_{14}O_2$ requires C, 74.1%; H, 7.9%) $\nu_{max.}$ 1720 cm^{-1}; $\lambda_{max.}$ 315 nm. (ϵ 375); τ 6.82 (1H t J = 3 Hz), 7.32 (4H s), 7.54 (2H t J = 3 Hz), 8.78 (6H s), 9.10 (1H t J = 3 Hz). Elution in ether gave the starting material (11) (300 mg).

2,8-dimethyl-9-phenyltricyclo-$[3,3,1,0^{2,8}]$-nonane-4,6-dione.(28)

4,6-dimethyl-9-phenylbicyclo-$[3,3,1]$-nona-3,6-diene-2,8-dione (17) (12 g), mercuric chloride (4.5 g) and magnesium (1.4 g) were stirred at 0°C in pyridine (150 ml) under nitrogen for 36 hours. After filtration and concentration of the filtrate under reduced pressure, water (100 ml) was added. The products were extracted with ether (50 ml x 2) and the combined ether solutions washed with 0.5M hydrochloric acid (50 ml)., then with sodium carbonate solution (50 ml) and finally with water (50 ml). After drying with anhydrous sodium sulphate, the solvent was removed to give a crystalline product. Recrystallisation from chloroform/petrol gave powdery crystals of the reduction product (28). (9.7 g), 162-163°C (Found: C, 79.9%; H, 7.1%. $C_{17}H_{18}O_2$ requires C, 80.3%; H, 7.1%); M^+ 254; $\nu_{max.}$ 1720, 1695 and 1600 cm^{-1}; $\lambda_{max.}$ 252 (ϵ 620), 258 (ϵ 520), 265 (ϵ 420), 287 (ϵ 250), 297 (ϵ 250) and 315 nm. (ϵ 226); τ 2.5-2.9 (5H m), 6.09 (1H t J = 3 Hz), 6.62 (1H d J = 3 Hz), 7.25 (2H s), 7.32 (2H s), 8.57 (3H s), 8.66 (3H s) and 8.80 (1H m).

Hydrogenation of 4,8-dimethyl-9-phenylbicyclo-[3,3,1]-nona-3,7-diene-2,6-dione (6)

4,8-dimethyl-9-phenylbicyclo-[3,3,1]-nona-3,7-diene-2,6-dione (2.04 g) was dissolved in ethyl acetate (30 ml) and hydrogenated at 1 atmosphere pressure in the presence of Adam's catalyst (117 mg). When hydrogen (490 ml) had been absorbed the mixture was filtered and the solvent removed. The products were separated by column chromatography.

Elution with ether/petrol (50:50) gave 4,8-dimethyl-9-phenylbicyclo-[3,3,1]-nona-3-ene-2,6-dione (34) as a white solid (370 mg). Recrystallisation from ether/petrol yielded white crystals of (34) (180 mg), m.p. 128-129°C (Found: C, 79.57%; H, 7.45%. $C_{17}H_{18}O_2$ requires C, 80.28%; H, 7.13%.); $\nu_{max.}$ 1690 and 1640 cm^{-1}; $\lambda_{max.}$ 250 (ϵ 5,835) and 307 nm. (ϵ 880); τ 2.6-2.9 (1H m), 3.93 (1H s), 6.50 (1H t J = 1.5 Hz), 6.53 (1H d J = 1.5 Hz), 6.19 (1H s), 7.53 (2H s), 8.14 (3H d J = 1.5 Hz) and 8.89 (3H m).

Elution with ether gave 4,8-dimethyl-6-hydroxy-9-phenylbicyclo-[3,3,1]-nona-3-ene-2-one (35) as a white solid (916 mg). Recrystallisation from ether yielded (35) as white crystals (580 mg). m.p. 129-130°C (Found: C, 79.68%; H, 7.83%. $C_{17}H_{20}O_2$ requires C, 79.65%; H, 7.86%); $\nu_{max.}$ 1655 cm^{-1}; $\lambda_{max.}$ 250 (ε 9,300) and 325 nm. (ε 86); τ 2.6-30 (5H m), 3.93 (1H s), 5.80 (1H m), 6.88 (2H s), 7.34 (2H s), 8.05 (3H d J = 1.5 Hz) and 9.0 (3H d J = 7 Hz).

Hydrogenation of 4,6-dimethyl-9-phenylbicyclo- [3,3,1] -nona-3,6-diene-2,8-dione (17).

4,6-dimethyl-9-phenylbicylo- [3,3,1] -nona-3,6-diene-2,8-dione (1.45 g) was dissolved in ethyl acetate (30 ml) and hydrogenated at one atmosphere pressure in the presence of Adam's catalyst (100 mg). When hydrogen (300 ml) had been absorbed the mixture was filtered, the solvent removed and the products separated by column chromatography.

Elution with ether/petrol (50:50) gave 4,6-dimethyl-8-hydroxy-9-phenylbicyclo- [3,3,1] -nona-3-ene-2-one (31) as a white solid (550 mg). Recrystallisation from ether/petrol yielded (31) as white crystals (350 mg), m.p.151-152°C (Found: C, 79.65%; H, 7.61%. $C_{17}H_{20}O_2$ requires C, 79.68%; H, 7.86%); $\nu_{max.}$ 1650 cm^{-1}; $\lambda_{max.}$ 247 (ε 9,200) and 330 nm. (ε 85); τ 2.7-3.0 (5H m), 3.72 (1H s), 5.00 (1H m), 6.86 (1H s), 7.00 (2H d J = 6 Hz), 7.28 (1H s), 8.13 (3H d J = 1.5 Hz) and 8.94 (3H d J = 7 Hz).

Elution with ether afforded 4,6-dimethyl-9-phenylbicyclo- [3,3,1] -nona-3-ene-2,8-dione (30) as a white solid (610 mg).

Recrystallisation from ether/petrol yielded (30) as white crystals (400 mg), m.p. 150-151°C (Found: C, 79.83%; H, 7.27%. $C_{17}H_{18}O_2$ requires C, 80.28%; H, 7.13%; $\nu_{max.}$ 1710 and 1660 cm^{-1}; $\lambda_{max.}$ 235 (ε 7,340), 250 (ε 7,340) and 332 nm. (ε 150); $\lambda_{max.}$ in diglyme 232 (ε 9,800), 247 (ε 7,930), 330 (ε 108), 342 (ε 126), 358 (ε 101) and 370 nm. (ε 47); τ 2.6-3.0 (5H m), 3.90 (1H s), 6.25 (1H s), 6.38 (1H t J = 3 Hz), 6.94 (1H s), 7.52 (2H s), 7.97 (3H d J = 2 Hz), 8.80 (3H d J = 7 Hz).

CHAPTER II

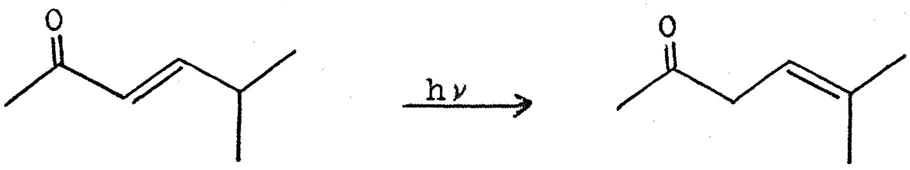
Photochemistry of the bicyclo- [3,3,1] -nona dienediones

INTRODUCTION

The photochemistry of unsaturated ketones has been extensively investigated. This chapter is concerned with the photochemistry of the dienediones (3), (6) and (19) which may be considered as α,β-unsaturated ketones or as β,γ-unsaturated ketones. It was therefore interesting to find out whether these dienediones underwent photoreactions similar to those reported for α,β-unsaturated ketones or yielded photoproducts resembling those obtained from β,γ-unsaturated ketones. It is appropriate also to consider reported photoreactions of α,β-unsaturated ketones which are simultaneously β,γ-unsaturated ketones.

(i) Photoreactions of α,β-unsaturated ketones.

Yang and Jorgenson[15] reported that the α,β-unsaturated ketone (36) underwent ready interconversion to the β,γ-unsaturated ketone (37). They[16] also reported the photoisomerisation of the eneone (38) to the cyclopropane compound (39).



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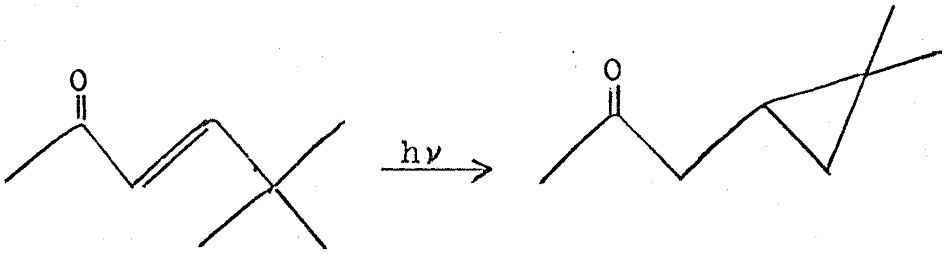
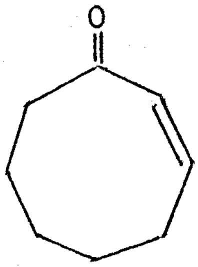


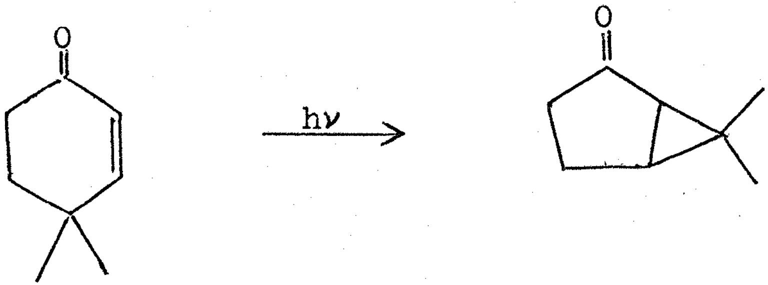
(38) (39)

Other types of photo-induced rearrangement in α,β -unsaturated ketones are also known. One of these is the cis-trans isomerism about the double bond. Eaton and Lin[17] found that irradiation of cis-2-cyclooctenone(40)



(40)

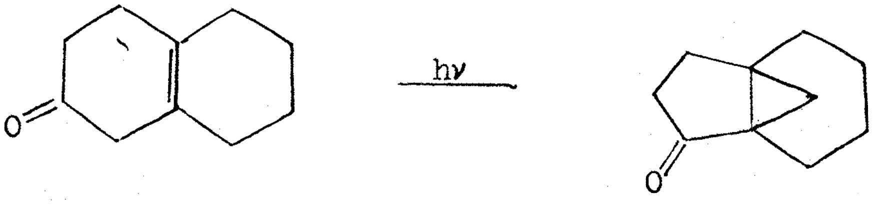
produced an equilibrium mixture containing trans-2-cyclooctenone. However cis-trans isomerism has not been found to occur in six membered or smaller ring systems because of the ring strain produced. A fourth type of rearrangement has been reported[18] by irradiating the ketone (41) in t-butyl alcohol. In this case one of the major products was (42).



(41) (42)

(ii) Photoreactions of β,γ-unsaturated ketones.

Many β,γ-unsaturated ketones are also found to be photosensitive and again different reactions are possible. Williams and Ziffer[19] reported ketone (43) yielding the product (44). This represents a 1,2-acyl shift instead of the 1,2-alkyl shift which compound (41) undergoes under similar conditions. The ketone (45) has been reported[20] to undergo a photo-induced 1,3-acyl shift to give the ketone (46). This is a reversible reaction [20].



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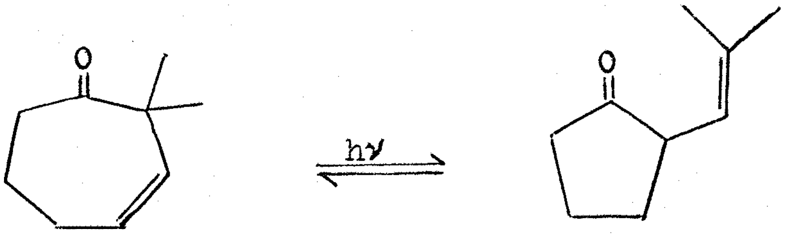
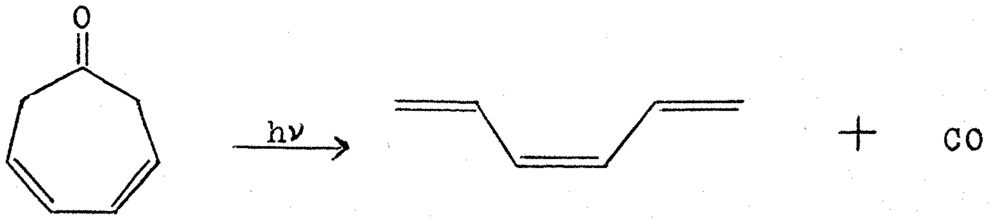


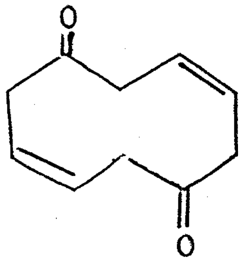
(45) (46)

In contrast to these reactions the ketone (47) is reported[21] to undergo decarbonylation under ultra violet irradiation yielding the hydrocarbon (48).



(47) (48)

However, irradiation of the dienedione (49) is reported[22'] to cause cyclization, yielding the dione (50).



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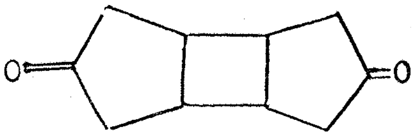
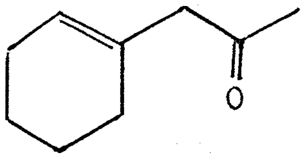


(50)

A different photoprocess has been reported by Dalton and Chan[23] for the ketone (51). Intramolecular alkylic γ-hydrogen abstraction occurs with the subsequent formation of the cyclobutanol (52).



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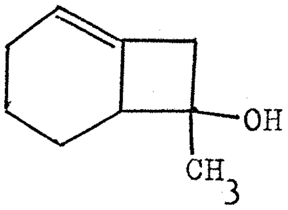
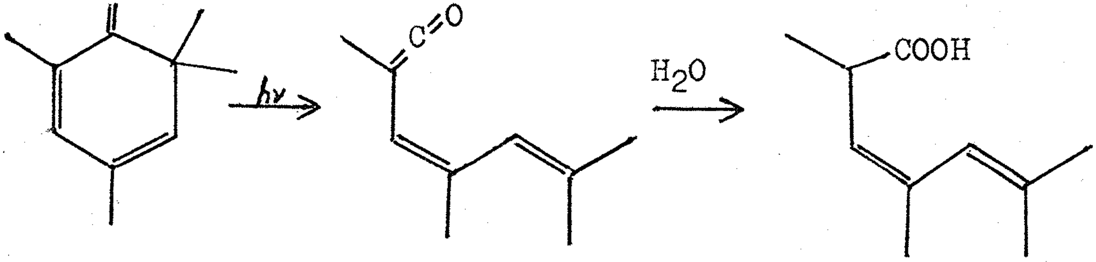


(52)

<u>(iii) Photoreactions of α,β-unsaturated ketones which are sumultaneously β,γ-unsaturated ketones.</u>

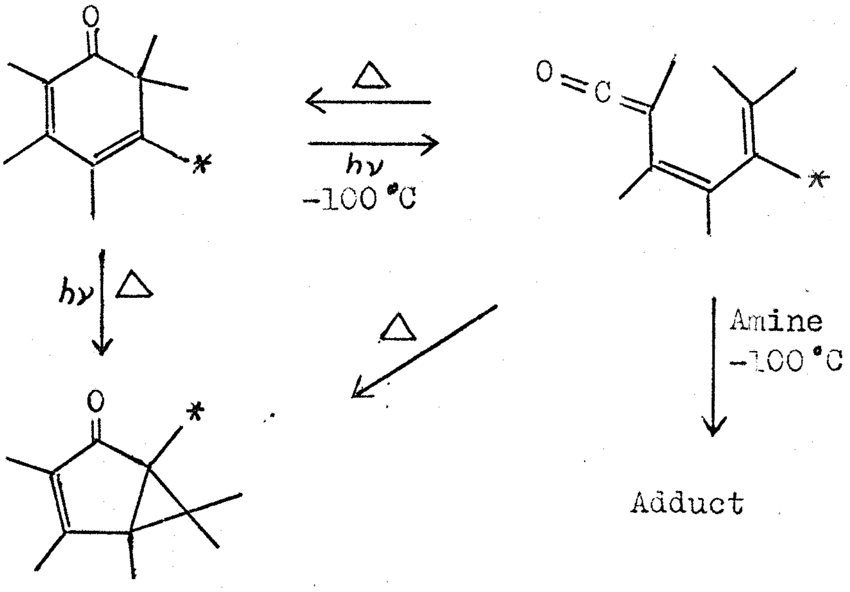
Bartone and Quinkert[24] reported that the dienone (53) yielded the acid (54) when irradiated in moist ether.



(53) (54)

Hart, Collins and Waring[25] reported only one photoproduct (56) from the dienone (55) using either dry or moist ether as solvent. Labelling the C-5 methyl group showed that the reaction involved a 1,2-acyl shift rather than a methyl migration. The same product (56) was also isolated by Griffiths and Hart[26] but they also found that the ketene intermediate (57) was formed by low temperature photolysis. Thus the formation of the compound (56) is possible by cycloaddition in the ketene (57) as well as by a 1,2-acyl shift. They[26] also reported that the rate of formation of either product (56) or (58) was greater in ethanol as solvent than in the less polar ether or hexane.

(55)



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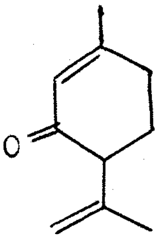
(56)

(58)

A different dieneone (59) is reported by Erman and Gibson[27] to undergo cycloaddition, yielding the ketone (60).



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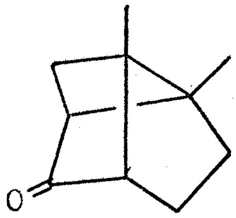
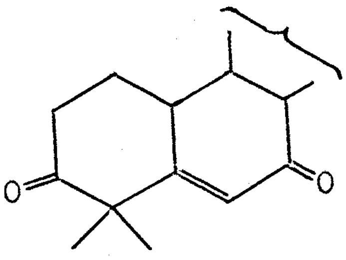


(60)

Domb and Schaffner[28] reported that irradiation of the enedione (61) led to the 1,2-acyl migration product (62).



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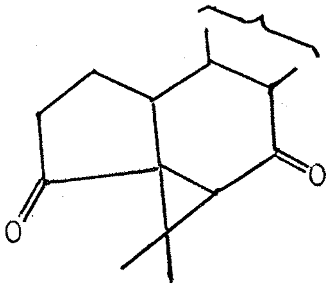
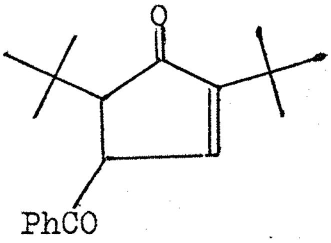


(62)

The enedione (63) is reported[29] also to undergo a 1,2-acyl shift when irradiated to form the cyclopropyl isomer (64).



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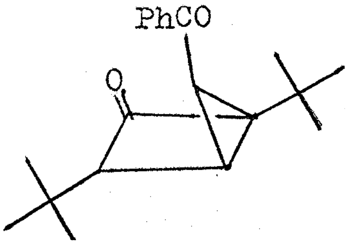


(64)

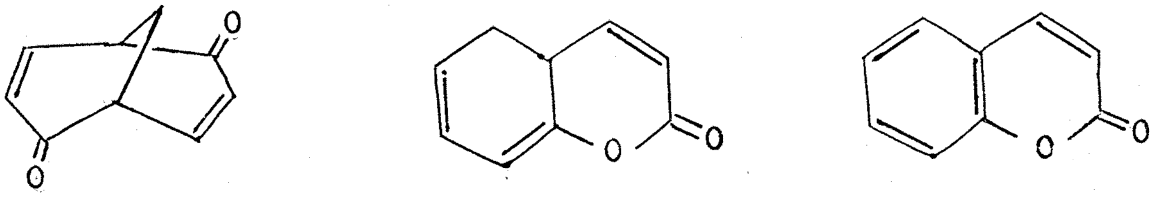
The aim of the present work was to isolate and characterise the photoproducts formed by ultraviolet irradiation of bicyclo-[3,3,1]-nona dienediones. It was also intended to examine the mechanism of these photoreactions and to discover if different photoproducts were produced when the reaction conditions were altered.

DISCUSSION

(a) Identification of the Photoproducts

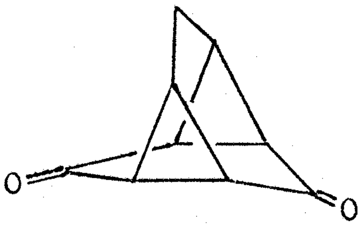
Irradiation of the dienedione (19) in benzene through quartz led to the rapid disappearance of starting material. Chromatographic separation afforded two major products. One, coumarin (66) was identified by its melting point, m.p. 69-70°C (lit.[30] 67-67.5°C) and by a comparison of its nuclear magnetic resonance spectrum with that in "Varian Nuclear Magnetic Resonance Spectra Catalogue"[31]. A thin layer chromatogram of the crude product showed only a trace of coumarin in the mixture but revealed the presence of a third compound which was not isolated by column chromatography. It can therefore be inferred that this third compound is the precursor of coumarin and the reaction may be represented by Scheme B. Here the dienedione (19) undergoes a photo-induced 1,5-acyl shift to give the dihydrocoumarin (65) which suffers atmospheric oxidation during the chromatographic separation, readily aromatising to coumarin. Further support for this Scheme is given later in this thesis in considering the photoproducts of 4,8-dimethyl-[3,3,1]-nona-3,7-diene-2,6-dione (3).

Scheme B



(19) (65) (66)

The second photoproduct was found to be the triasteranedione (67). This was characterised by its melting point and spectra. Its nuclear magnetic resonance spectrum showed no vinyl hydrogen resonance. Its mass spectrum showed that it was isomeric with the starting material (19). Its infra red spectrum has a single peak at ν_{max} 1690 cm.$^{-1}$ thus agreeing with the presence of two identical carbonyl groups. Confirmation that it was the triasteranedione (67) was obtained by comparison with an authentic sample (identical t.l.c. behaviour and no depression of the mixed melting point)[32]. The triasteranedione (67) may be formed by two possible routes: (a) by two successive 1,2-acyl shifts, typical of the



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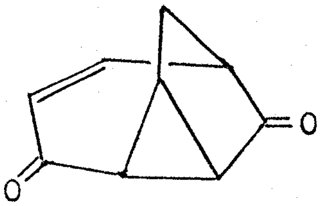
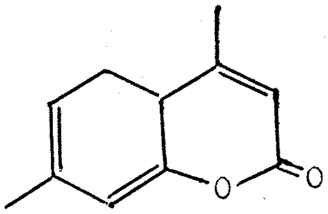


(68)

photochemistry of β,γ-unsaturated ketones[33], via the intermediate (68), or (b) by two successive 1,2-alkyl shifts, typical of the photochemistry of α,β-unsaturated ketones[34], via the same intermediate (68). It is not possible, at this stage, to decide which route the reaction takes. However, a discrimination between the two routes is made later in this thesis when the photoproducts of 4,8-dimethyl-9-phenylbicyclo-[3,3,1]-nona-3,7-dienedione (6) are considered.

The dione (3) undergoes similar rearrangements to those of the dione (19) under ultra violet irradiation, yielding two major photoproducts. One, the dihydrocoumarin (69), was rapidly oxidised and in a chromatographic separation was isolated as 4,7-dimethylcoumarin (70)



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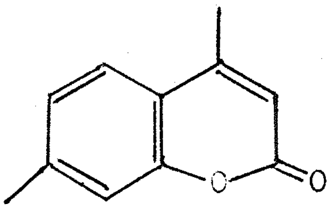
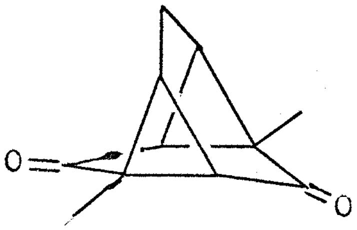


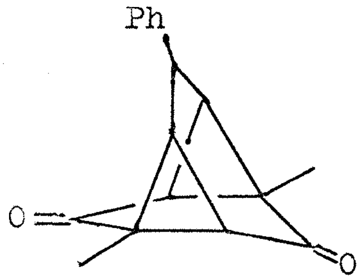
(70)

The oxidation was followed by t.l.c. and g.l.c. analysis of one of the chromatographic fractions. Initial analysis showed compounds (69) and (70) to be present in equal quantities. However after exposure to the atmosphere for fifteen minutes an increase in the quantity of 4,7-dimethylcoumarin (70) was observed, the ratio being 1:3 for compounds (69) and (70) respectively and after two days the dihydrocoumarin had completely disappeared. This gives further support for Scheme B. 4,7-dimethylcoumarin was identified by its melting point, m.p. 133-134°C (lit.[35] 132°C) and by its spectroscopic data. Its n.m.r. spectrum, which bears a remarkable resemblance to that of coumarin shows the three aromatic hydrogens resonating at 2.5-3.0 τ, the other vinyl hydrogen at 3.8 τ and the two methyl hydrogens at 7.58 τ. To confirm this identification a comparison with an authentic sample[35] showed identical t.l.c. behaviour and no depression of the mixed melting point.

The other photoproduct was the triasteranedione (71), recognised by the resemblance of its spectroscopic data to those of the triasteranediones (67) and (72).



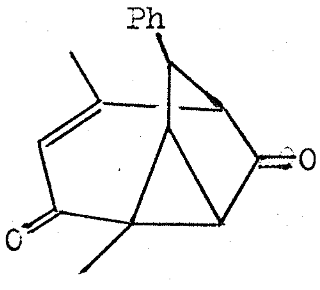
(71)



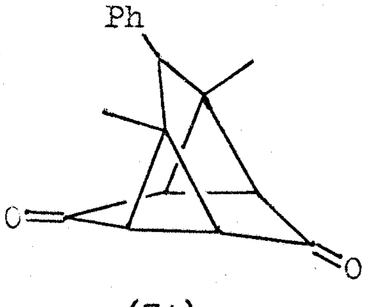
(72)

The triasteranedione (72) was formed by the irradiation of 4,8-dimethyl-9-phenylbicyclo-[3,3,1]-nona-3,7-diene-2,6-dione (6) and isolated by column chromatography yielding pale yellow crystals, m.p. 146-148°C. It was characterised by spectroscopic methods. Its mass spectrum shows the molecular ion $M^{+}252$, thus indicating this product to be isomeric with the starting material (6). Its infra red spectrum ($\nu_{max.}$ 1685cm.$^{-1}$) and its ultra violet spectrum ($\lambda_{max.}$ 252nm. (ε 600) and 290nm. (ε 200) are similar to those of the triasteranedione (67) and are consistent with structure (72). No vinyl hydrogen resonance is observed in its nuclear magnetic resonance spectrum.

Two successive 1,2-acyl shifts[33] via the intermediate(73) would lead to the formation of the triasteranedione (72). However, two successive 1,2-alkyl shifts[34] would lead to the formation of the triasteranedione (74). A discrimination between the two pathways is possible by an examination of



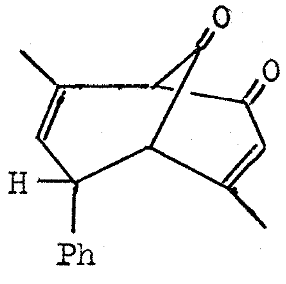
(73)



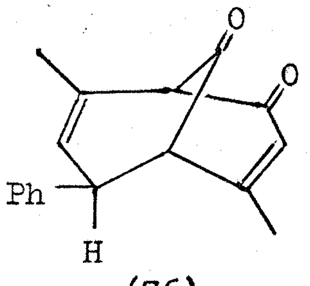
(74)

the nuclear magnetic resonance spectra of the triasteranedione, m.p. 146-148°C. In deuteriochloroform the two methyl signals are separated by 3.2 Hz but in pyridine the same methyl signals are separated by 1.6 Hz. Hence the signals arise from two methyl groups in different environments and as the triasteranedione (74) is characterised by a plane of symmetry this structure must be rejected. Further, in pyridine the signal of the benzylic proton at 6.17τ appears as a triplet (J = 1.5 Hz). Structure (72) is therefore assigned to the triasteranedione, m.p. 146-148°C. Hence the photorearrangement must have proceeded by two successive 1,2-acyl shifts and each of these shifts corresponds to a photochemically allowed ($\sigma^2 + \pi^2$) addition as a concerted process. Formation of triasteranediones (67) and (71) is assumed to follow the same pathway. Although the syntheses of triasteranes[32,36] are known, the photorearrangement constitutes another useful method of generation of this strained skeleton.

Two further photoproducts (75), m.p. 146-148°C and (76), m.p. 170-172°C, were obtained from the ketone (6). Both have similar spectroscopic characteristics. Their



(75)



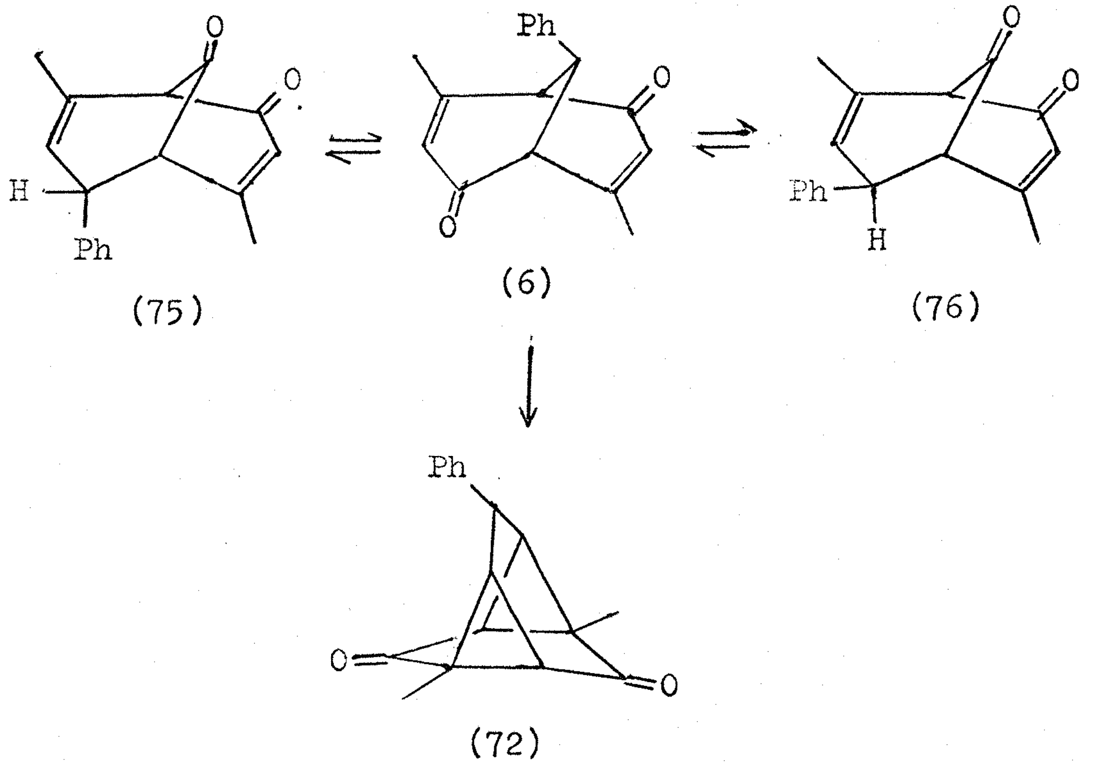
(76)

infra red spectra shows an α,β -unsaturated keto group

($\nu_{\text{max.}}$ 1675 cm.$^{-1}$) and a saturated keto group ($\nu_{\text{max.}}$ 1725 cm.$^{-1}$). Mass spectroscopy shows their molecular ions M^+ 252. Their nuclear magnetic resonance spectra shows that each product has two vinyl protons with separate resonances. Hence they are bicyclic compounds. A distinction between the two structures is made by considering their nuclear magnetic resonance spectra. For the dione m.p. 146-148°C the coupling constant between the benzylic proton at 5.76 τ and the adjacent bridgehead proton at 6.62 τ is 6.3 Hz, whereas for the dione m.p. 170-172°C no coupling between the benzylic proton at 6.06 τ and the bridgehead proton at 6.96 τ is observed. Therefore structure (75) is assigned to the dione m.p. 146-148°C and structure (76) to the dione m.p. 170-172°C. Coupling constants in a similar system have been reported[37] to be 6.4 Hz and 0 Hz respectively. Further, the methyl group situated at the β position of the α,β-unsaturated ketone (75) is shielded by the endo phenyl group. Thus the signal of this methyl group is situated at 8.89 τ whereas in the ketone (76) this signal is at 7.81 τ. This confirms the assignment of structures (75) and (76) which are formed by 1,3-acyl shifts.

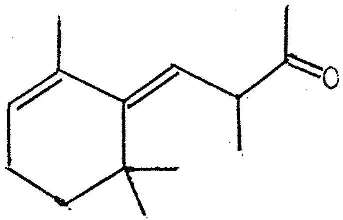
The rearrangements yielding the diones (75) and (76) were found to be reversible. Thus irradiation of either of these diones (75) or (76) gave a mixture of all three diones (6), (75) and (76) together with the triasteranedione (72). However, prolonged irradiation increases the relative proportion of the triasteranedione (72) in the reaction mixture, thus suggesting that this 1,2-acyl shift is not reversible. Indeed, irradiation of the triasteranedione (72) failed to give any of the other isomers. Thus the photorearrangements may be represented by Scheme C.

Scheme C

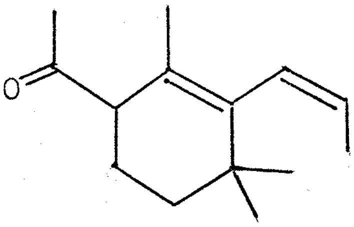


The triasteranedione (72) could be formed from all three diendiones (6), (75) and (76). Two successive 1,2-acyl shifts in any one of them would produce the triasteranedione (72). However, mechanistic aspects of the photoreactions discussed later indicate that the dienedione (6) is structurally the most favoured to undergo this change.

From identification of the photoproducts of bicyclo[3,3,1]-nona-3,7-diene-2,6-diones three different kinds of photorearrangement have been observed. The 1,3-acyl shifts which produced the dienediones (75) and (76) have been found[38] to occur in many β,γ-unsaturated ketones. Formation of the triasteranediones (67), (71) and (72) by 1,2-acyl shifts is in agreement with the reported[28, 29] photoproducts of other β,γ-unsaturated ketones which are simultaneously α,β-unsaturated ketones. On the other hand, formation of the dihydrocoumarins (65) and (69) by apparent 1,5-acyl shifts is unusual. However, an analogy may be drawn between this and the 1,5-acyl shift reported[47] by van Wageningen, van Noort and Cerfontain. They[47] found that irradiation of the ketone (86) in alcohol or in acetone yielded the ketone (87).



(86)

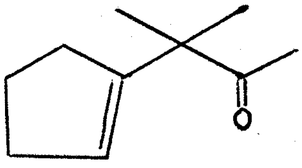


(87)

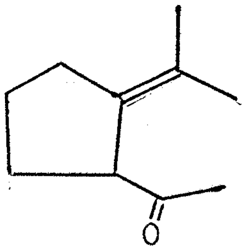
(b) Mechanistic Aspects of the Photoreactions

In order to find out if any other photoproducts could be obtained, photolysis of the dienedione (6) was performed in various solvents. Besides benzene, both methanol and glacial acetic acid were used as solvents. The same photoproducts were isolated in all three cases. This would suggest that the mechanism of the reaction is not altered by a change of solvent. It also excludes the possibility of a ketene intermediate[26] as this would form an adduct with methanol. However, it was observed that the disappearance of starting material (6) and the formation of photoproducts (75), (76) and (72) was about twice as rapid in the polar solvents, methanol and acetic acid, than in the less polar benzene. The same effect of solvent on the rate of reaction has been observed in similar photorearrangements[26].

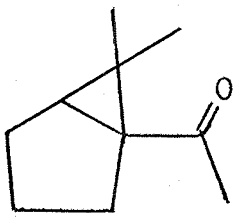
Reports on the photochemistry of β,γ-enones indicate that a 1,3-acyl shift results from a singlet state.[38,39,40,41] However, irradiation of the dienedione (6) in acetone results in 1,2-acyl shifts giving compounds (75) and (76). Prolonged irradiation gave a good yield of the triasteranedione (72), thus agreeing with Scheme C. It is therefore assumed that here is an example of a triplet 1,3-acyl shift as well as a triplet 1,2-acyl shift. One other example of a 1,3-acyl shift is reported[42] by Engel and Schexnayder, who found that irradiation of the β,γ-unsaturated ketone (77) in acetone yielded a mixture of two photoproducts (78) and (79). It seems,



(77)



(78)



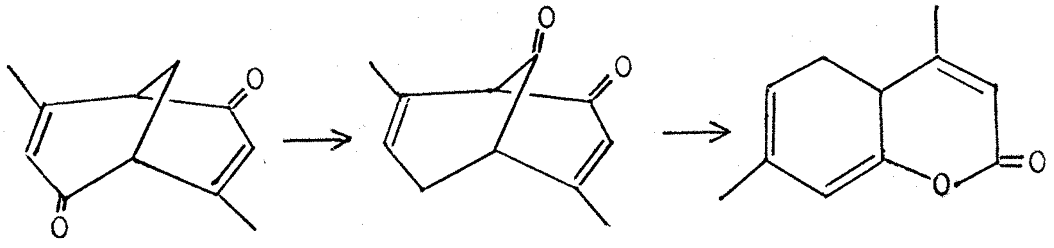
(79)

therefore, that in these compounds intersystem crossing occurs faster than any singlet induced reaction.

Houk, Northington and Duke[38] have calculated that a β,γ-unsaturated ketone should undergo a 1,3-acyl shift from an excited triplet provided it was a n-π^* excited state. Also they have shown that a 1,2-acyl shift should occur from a π-π^* excited triplet. However, Hancock and Grider[43] have shown that in a wide selection of β,γ-unsaturated ketones the lowest triplet state is a π-π^* excitation. It is therefore suggested that the dienedione (6) triplets undergo both 1,2-acyl shifts and 1,3-acyl shifts. It is not possible, at this stage, to comment on the possible character of the triplet in (6). The 1,2-acyl and 1,3-acyl shifts in the dienediones (3) and (19) are assumed to occur also from excited triplets.

The formation of the dihydrocoumarins (65) and (69) from the dienediones (19) and (3) respectively appears to result from 1,5-acyl shifts. An explanation of this unusual type of reaction is possible by analogy to the 1,3-acyl shift occurring in the dienedione (6). A slow 1,3-acyl shift, followed by a second fast 1,3-acyl shift would result in a dihydrocoumarin as shown in Scheme D.

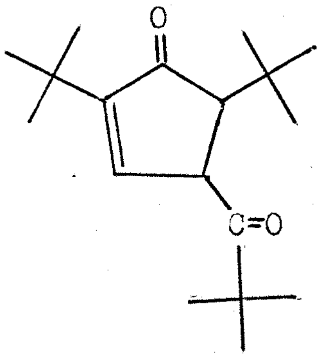
Scheme D



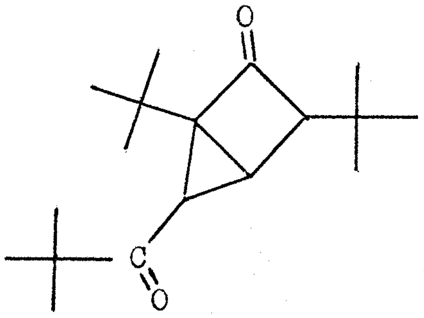
(3) (80) (69)

The relative rates of these steps would explain why the intermediate compound (80) was not isolated.

There is one structural aspect of the 1,2-acyl shift which is of interest here. Although many β,γ-unsaturated ketones undergo 1,2-acyl shifts in the presence of a photosensitizer,[40,41] it has been shown by Houk, Northington and Duke[38] that direct irradiation (n - π*) rarely gives this shift in β,γ-unsaturated ketones. An exception to this generalisation is found in the direct irradiation of α,β-unsaturated ketones which are simultaneously β,γ-unsaturated ketones. Domb and Schaffner[28] found that the enedione (61) gave a 1,2-acyl shift when irradiated in dioxan in a pyrex tube. Also Matsuura and Ogura[44] reported the formation of compound (82) on irradiating the enedione (81) in the benzene using a pyrex filter. Hence it seems that the second keto moiety

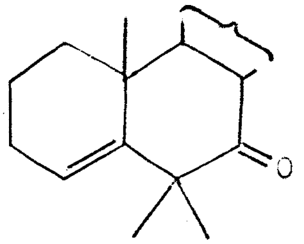


(81)

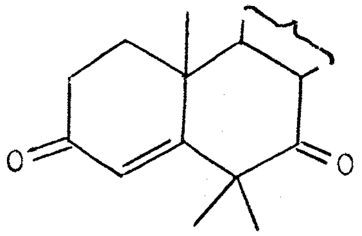


(82)

encourages the 1,2-acyl shift and this aspect is borne out by the findings of Sato et al[45] who reported that irradiation of the eneone (83) in acetone with a pyrex filter afforded no photoproducts whereas the enedione (84) gave a 1,2-acyl shift photoproduct.

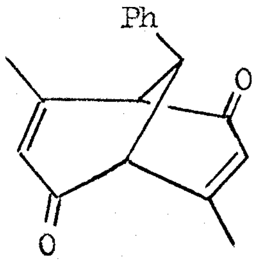


(83)

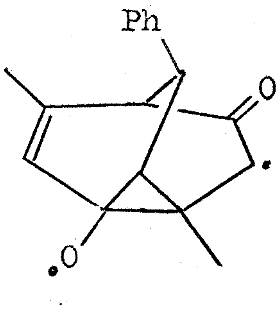


(84)

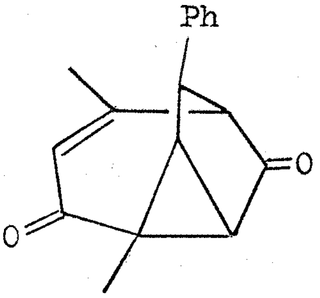
Recent findings[28,45,46] suggest that the 1,2-acyl shift occurs by an oxa-di-π-methane mechanism rather than by asymmetry allowed concerted ($\sigma^2+\pi^2$) cycloaddition. By this mechanism, the first step is the formation of the biradical (85) which then forms the cyclopropyl compound (73). Then by a second oxa-di-π-methane mechanism the triasteranedione (71) is formed. It is worth noting that each of the biradicals formed by this mechanism is stabilised by the second keto group, thus suggesting that the dienedione (6) rather than the dienediones (75) and (76) undergoes two successive 1,2-acyl shifts to form the triasteranedione (72).



(6)



(85)



(73)

It is clear from this work that there is an interaction between the two α,β-unsaturated ketone chromophores in the compounds (3), (6) and (19). In fact, the photoproducts of these compounds resemble those formed from β,γ-unsaturated ketones rather than those formed from α,β-unsaturated ketones. However, unlike the photoreactions of many other β,γ-unsaturated ketones, both the 1,2-acyl shifts and the 1,3-acyl shifts result from triplet states and occur simultaneously.

EXPERIMENTAL

Unless otherwise stated all photo-irradiations were conducted with a M.B.W. 125W U.V. arc. The compound to be irradiated was dissolved in benzene (crystalline BDH standard) and placed in an internally water cooled pyrex photolyser, the temperature being maintained at about 30°C. The absence of air was ensured by a continuous stream of nitrogen bubbling through the solution. The photolyses were monitored by t.l.c. and i.r. analysis. In other respects the experimental procedures and results are recorded as in Chapter I.

Photolysis of Bicyclo-[3,3,1]-nona3,7-diene-2,6-dione (19)

The crude dione (19) (3 g.) in solution in benzene (300 ml.) was irradiated for 24 hours. After removing the solvent under reduced pressure, the products were separated by column chromatography.

Elution with benzene/chloroform (30:70) gave coumarin (30 mg.). Recrystallisation from benzene afforded white crystals, m.p. 69-70°C (lit[30] 67-67.5°C) ; τ 2.28 (1H d J = 10 Hz), 2.5-2.9 (4H m), 3.58 (1H d J = Hz); $\nu_{max.}$ 1720 cm.$^{-1}$, 1610 cm.$^{-1}$.

Elution with chloroform yielded the triasteranedione, tetracyclo-$[3,3,1,0^{1,7},0^{3,5}]$-nona-2,6-dione (67), (1.75 g.) which on recrystallisation from chloroform/ether yielded a cream coloured crystalline material (1.15 g.), m.p. 154-155°C; M^+ 148, $\nu_{max.}$ 1690 cm.$^{-1}$; $\lambda_{max.}$ 288 nm (ε 105);

τ 7.58-7.63 (8H m). The recrystallised sample was compared (mixed m.p. and t.l.c.) with an authentic sample of triasteranedione[32] and found to be identical.

Photolysis of 4,8-Dimethyl bicyclo-[3,3,1]-nona-3,7-diene-2,6-dione (3)

The dione (3) (1.05 g.) was dissolved in benzene (300 ml.) and irradiated for 66 hours. The solvent was removed and the products separated by column chromatography.

Elution with ether/petrol (15:85) afforded 4,7-dimethyl coumarin (70) (131 mg.). It was recrystallised from ether/petrol to give white needles (80 mg.), m.p. 133-134°C (lit.[35] 132°C); $\nu_{max.}$ 1720, 1700 and 1625 cm.$^{-1}$; τ 2.5-3.0 (3H m), 3.80 (1H s), 7,58 (6H m); mixed m.p. with an authentic sample 133-134°C. (The authentic sample of 4,7-dimethyl coumarin was obtained by reacting ethyl acetoacetate with m-cresol in the presence of concentrated sulphuric acid[35]).

Elution with ether/petrol (25:75) gave an oil, consisting mainly of the dimethyl dihydrocoumarin (69) (127 mg.), $\nu_{max.}$ 1720 cm.$^{-1}$. It was rapidly oxidised to 4,7-dimethyl coumarin on exposure to the atmosphere, the change being followed by t.l.c. and g.l.c. analysis.

Elution with ether/petrol (50:50) returned the starting material (3) (285 mg.).

Elution with ether/petrol (75:25) yielded the triasteranedione, 1,5-dimethyl tetracyclo- $[3,3,1,0^{1,7},0^{3,5}]$-nona-2,6-dione (59) (206 mg.) as an oil. M^+ 176; $\nu_{max.}$ 1670 cm.$^{-1}$; $\lambda_{max.}$ 277 nm. (ε 662); τ 7.96 (2H m), 8.06 (4H m), 9.06 (6H s).

Photolysis of 4,8-dimethyl-9-phenylbicyclo- [3,3,1] -nona-3,7-diene-2,6-dione (6)

The dione (6) (5.0 g.) in solution in benzene (300 ml.) was irradiated for 5 days. After removing the solvent under reduced pressure the products were separated by column chromatography.

Elution with ether/petrol (15:85) gave the dione (75) (426 mg.). Crystallisation from ether/petrol gave yellow crystals (180 mg.), m.p. 146-148°C; M^+ 252; $\nu_{max.}$ 1725 cm.$^{-1}$; $\lambda_{max.}$ 328 nm. (ε 256); τ 2.64-2.96 (5H m), 3.89-3.94 (1H m), 4.41 (1H s), 5.65-5.86 (1H m), 6.50 (1H s), 6.62 (1H q J = 6.3 Hz and 1.3 Hz), 8.09 (3H q J = 2.6 Hz and 1.5 Hz), 8.88 (3H d J = 1.3 Hz).

Further elution with ether/petrol (15:85) gave the dione (76) (512 mg.). Recrystallisation from ether/petrol yielded yellow crystals (208 mg.), m.p. 170-172°C; (Found C, 80.66%; H, 6.38%. $C_{17}H_{16}O_2$ requires C, 80.92%; H, 6.39%); M^+ 252; $\nu_{max.}$ 1675 cm.$^{-1}$; $\lambda_{max.}$ 325 nm. (ε 223); τ 2.66-2.92 (5H m), 3.97-4.01 (1H m), 4.60 (1H d J = 3.3 Hz), 6.00-6.14 (1H m), 6.46 (1H s), 6.95 (1H s), 7.81 (3H D J = 1.4 Hz), 8.14 (3H t J = 1.6 Hz).

Elution with ether/petrol (25:75) returned the starting material (6) (1.85 g.).

Elution with ether/petrol (50:50) afforded the triasteranedione, 1,5-dimethyl-9-phenyltetrachclo- $[3,3,1,0^{1,7}0^{3,5}]$ -nona-2,6-dione (72) (1.203 g.). Recrystallisation from ether yielded pale yellow crystals (800mg.), m.p. 146-148°C; (Found C, 80.90%; H, 6.18%. $C_{17}H_{16}O_2$ requires C, 80.92%; H, 6.39%); M^+ 252; $\nu_{max.}$ 1685 cm.$^{-1}$; $\lambda_{max.}$ 252 nm. (ε 600) and 290 nm. (ε 200); τ 2.6-2.9 (5H m), 6.17 (1H s); 7.68 (4H m), 8.69 (3H s), 8.72 (3H s).

Photolysis of 4,8-dimethyl-9-phenylbicyclo- [3,3,1] -nona-3,7-diene-2,6-dione in methanol

The dione (6) (1.90 g.) was dissolved in methanol (300 ml.) and irradiated for 30 hours. After removal of the solvent, a column chromatographic separation gave the dione (75) (210 mg.), the dione (76) (464 mg.), starting material (6) (244 mg.) and the triasteranedione (72) (540 mg.).

Photolysis of 4,8-dimethyl-9-phenylbicyclo- [3,3,1] -nona-3,7-diene-2,6-dione in acetic acid

A solution of the dione (6) (1.93 g.) in glacial acetic acid (300 ml.) was irradiated for 24 hours. After removal of the solvent, a column chromatographic separation afforded the dione (75) (190 mg.), the dione (76) (460 mg.), the dione (6) (200 mg.) and the triasteranedione (72) (757 mg.).

Photolysis of 4,8-dimethyl-9-phenylbicyclo- [3,3,1] -nona-3,7-diene-2,6-dione (6) using a triplet quencher

The dione (6) (458 mg.) was dissolved in ether (300 ml.)

containing 1-methyl naphthalene (670 mg.) and irradiated for 22 hours. Separation of the products by column chromatography and identification by t.l.c. and i.r. afforded the dione (75) (19 mg.), the dione (76) (22 mg.), starting material (6) (29 mg.) and the triasteranedione (72) (260 mg.). No new products were isolated.

Photolysis of 4,8-dimethyl-9-phenylbicyclo-[3,3,1]-nona-3,7-diene-2,6-dione (6) through quartz

(a) Benzene solvent. The dione (6) (932 mg.) was dissolved in benzene (300 ml.) and irradiated for 10 hours through quartz, using a 450-W Hanovia Type 6744 mercury lamp. Separation of the products by column chromatography and identification by t.l.c. and i.r. gave the dione (75) (35 mg.), the dione (76) (38 mg.), starting material (6) (46 mg.) and the triasteranedione (72) (375 mg.). No new products were isolated.

(b) Acetone solvent. The dione (6) (1.03 g.) was dissolved in acetone (300 ml.) and irradiated through quartz as before, for 5 hours. Separation of the products by column chromatography and identification by t.l.c. and i.r. afforded the dione (75) (50 mg.), the dione (76) (56 mg.), starting material (6) (55 mg.) and the triasteranedione (72) (658 mg.). Again no new products were isolated.

Photolysis of the dione (75)

The dione (75) (15 mg.) in solution in benzene (1 ml.)

was placed in a stoppered pyrex flask with air excluded and irradiated. The reaction was monitored by g.l.c. (230°C), i.r. and t.l.c. After 5 hours the mixture of products consisted of the dione (76) (~ 2%), the starting material (75) (~ 90%), the dione (6) (~ 4%) and the triasteranedione (72) (~ 2%). After 13 hours the triasteranedione (72) was the major product (~ 80%).

Photolysis of the dione (76)

The dione (76) in solution in benzene (1 ml.) was irradiated in a pyrex flask with air excluded. Again the reaction was monitored by g.l.c. (230°C), i.r. and t.l.c. After 5 hours the composition of the mixture of products consisted of the starting material (76) (~ 90%), the dione (75) (~ 3%), the dione (6) (~ 5%) and the triasteranedione (72) (~ 2%). After 13 hours the major product was the triasteranedione (72) (~ 80%).

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