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PII: S0040-4039(15)30208-2
DOI: <http://dx.doi.org/10.1016/j.tetlet.2015.10.012>
Reference: TETL 46841

To appear in: *Tetrahedron Letters*

Received Date: 8 September 2015
Revised Date: 2 October 2015
Accepted Date: 4 October 2015

Please cite this article as: Zhang, Y., An, Y., Sun, J., Ding, A., Wang, Y., Rios, R., Guo, H., Catalyst-Free Photocyclopropanation of Dibromomalonates with Alkenes: An Approach to Multisubstituted Cyclopropanes, *Tetrahedron Letters* (2015), doi: <http://dx.doi.org/10.1016/j.tetlet.2015.10.012>

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Tetrahedron Letters
journal homepage: www.elsevier.com

Catalyst-Free Photocyclopropanation of Dibromomalonates with Alkenes: An Approach to Multisubstituted Cyclopropanes

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ARTICLE INFO

ABSTRACT

Article history:

Received

Received in revised form

Accepted

Available online

We report herein a novel photocyclopropanation of dibromomalonates with alkenes in the presence of Hünig base. This protocol provides an environmentally benign approach for the synthesis of multisubstituted cyclopropanes, since no catalyst is required. The Photo-induced Electron Transfer (PET) from Hünig base to dibromomalonate is the key process during this transformation.

Keywords:

Photochemistry

Cyclopropanation

Catalyst-free

Cyclopropane

Mechanism

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Functionalized cyclopropanes are commonly found in many natural products and pharmaceutical compounds, which exhibit broad spectrum biological activities.¹ Due to the special properties of the smallest three-membered ring, cyclopropane derivatives are also important building blocks in organic synthesis.^{2,3} Accordingly, much attention has been paid to construct the structure of cyclopropane. Several methods have been developed in this field.⁴ One of the most classic approaches is Simmons-Smith Reaction which requires more than one equivalent of zinc or copper to form a carbene intermediate and then insert into an alkene (Scheme 1a).⁵ Sulfur ylides are also effective reagents for the synthesis of cyclopropanes (Scheme 1b).⁶ Diazoethane may proceed [3+2] cycloaddition with a carbon-carbon double bond and the following photodecomposition to form a three-membered ring (Scheme 1c).⁷ Moreover, transition metal carbenoids, like Au carbenoids (Scheme 1d),⁸ also show high catalytic activity in the cyclopropanation of enyne derivatives.

Recently, our group reported a visible light induced cyclopropanation employing Visible Light Photoredox Catalyst (VLPC) and we proposed a photoinduced double-SET process which afforded the key carbanion intermediate in this transformation (Scheme 2).⁹ This reaction employed visible light as energy source and could be carried out in the open air,

a. Simmons-Smith Reaction

b. Cyclopropanation via sulfur ylides

c. Cyclopropanation via diazomethane

d. Cyclopropanation via Au carbenoids

Scheme 1. Classic methods for the synthesis of cyclopropane derivatives.

showing environmental benignness and operational easiness. However, transition metal catalyst was still required, although its amount was catalytic. Taking these thoughts, we reconsidered the reaction process: The excited $\text{Ru}(\text{bpy})_3^{2+}$ resulted from the irradiation of visible light could get an electron from Hünig base to form $\text{Ru}(\text{bpy})_3^+$. Then the Single Electron Transfer (SET) from highly reductive $\text{Ru}(\text{bpy})_3^+$ to dibromomalonate afforded a bromomalonate radical. Subsequently, the second SET from $\text{Ru}(\text{bpy})_3^+$ to bromomalonate radical gave the corresponding malonate carbanion. The Michael addition of malonate carbanion to alkene and subsequent intramolecular nucleophilic substitution led to the final cyclopropane product. In fact, VLPC was just a media for the SET from amine to dibromomalonate. Obviously, it will be better, if this SET process occurs without any catalyst. As reported in the literature,¹⁰ amine could be excited under high energy UV irradiation. The excited amine might be a good single electron donor.¹⁰ Thus, we assumed that we might apply UV irradiation, instead of the combination of visible light and VLPC to realize the SET process from amine to

dibromomalonate. If succeeded, the same cyclopropanation might be achieved without any catalyst, showing much better environmental benignness. Herein, we wish to report our recent results on a UV light induced catalyst-free cyclopropanation of dibromomalonates with alkenes under mild reaction conditions.

Scheme 2. Visible light induced cyclopropanation

The initial attempt was carried out employing diethyl 2,2-dibromomalonate **1a** and 2-benzylidenemalononitrile **2a** as the model substrates. We found that the desired product cyclopropane derivative **3aa** was obtained in a 40% NMR yield under simple photo irradiation at $\lambda = 365$ nm in the presence of 2 equiv. of Hünig base in CH_3CN at room temperature (entry 1, Table 1). Encouraged by this result, we further increased the photo irradiation energy (entries 2-4, Table 1), among which photo irradiation at $\lambda = 185\&254$ nm gave 57% NMR yield in shorter time (entry 4, Table 1). Next, a screen of the solvent revealed that the photocyclopropanation could proceed in many solvents (entries 5-10, Table 1), and the reaction in methanol showed the highest yield and the shortest reaction time (entry 10, Table 1). Then some other amines were tested as well, however, no improvement was observed (entries 11-14, Table 1). We also tried to reduce the amount of Hünig base, which led to the corresponding decreased yield (entries 15 and 16, Table 1). No desired product was found without Hünig base (entry 17, Table 1). Finally, the reaction was carried out under air atmosphere. Almost the same yield was generated (entry 18, Table 1). Considering that reaction without light gave **3aa** in only 16% isolated yield after full conversion according to literature reports (entry 19, Table 2),²⁷ the UV irradiation indeed played an essential role in this cyclopropanation. Thus, Condition A (**1**, **2** (2 equiv.), *i*-Pr₂NEt (2 equiv.), methanol, UV ($\lambda = 185\&254$ nm), and rt) was applied for further studies.

With the optimal conditions in hand, the substrate scope of this photocyclopropanation was studied with a series of dibromomalonate derivatives and alkenes (Table 2). The electronic effect of the aromatic rings in **2** was explored firstly. Those with strong electron-withdrawing groups, such as methoxycarbonyl (entry 1, Table 2), trifluoromethyl (entry 2, Table 2), and nitro (entries 3-5, Table 2), showed good yields. Good yields were also obtained for weak electron-withdrawing group, like fluorine (entry 6, Table 2) and chlorine (entry 7, Table 2), substituted substrates. Alkenes with weak electron-donating groups, like alkyl (entries 9-13, Table 2) and phenyl (entry 14, Table 2), gave good yields, too. As for strong electron-

Table 1. Optimization of the reaction conditions ^a

Entry	λ (nm)	Solvent	Amine (equiv.)	Time (h)	Yield (%) ^b
1	365	CH ₃ CN	<i>i</i> -Pr ₂ NEt (2)	4.5	40
2	313	CH ₃ CN	<i>i</i> -Pr ₂ NEt (2)	4.5	52
3	254	CH ₃ CN	<i>i</i> -Pr ₂ NEt (2)	4	54
4	185&254	CH ₃ CN	<i>i</i> -Pr ₂ NEt (2)	3.5	57
5	185&254	CH ₂ Cl ₂	<i>i</i> -Pr ₂ NEt (2)	4.5	15
6	185&254	CHCl ₃	<i>i</i> -Pr ₂ NEt (2)	5.5	7
7	185&254	THF	<i>i</i> -Pr ₂ NEt (2)	6	29
8	185&254	EtOAc	<i>i</i> -Pr ₂ NEt (2)	5	11
9	185&254	EtOH	<i>i</i> -Pr ₂ NEt (2)	4.5	73
10	185&254	MeOH	<i>i</i> -Pr ₂ NEt (2)	2.5	90
11	185&254	MeOH	<i>i</i> -Pr ₂ NH (2)	4	64
12	185&254	MeOH	NEt ₃ (2)	4	69
13	185&254	MeOH	Pyrrolidine (2)	4	57
14	185&254	MeOH	Pyridine (2)	4	trace ^c
15	185&254	MeOH	<i>i</i> -Pr ₂ NEt (1)	5	49
16	185&254	MeOH	<i>i</i> -Pr ₂ NEt (0.5)	4.5	33
17	185&254	MeOH	--	6	trace
18 ^d	185&254	MeOH	<i>i</i> -Pr ₂ NEt (2)	2	91 (90) ^e
19 ^f	dark	MeOH	<i>i</i> -Pr ₂ NEt (2)	32	16 ^e

^a All reactions were carried out using **1a** (0.2 mmol), **2a** (0.4 mmol), and amine in deaerated solvent (10 mL) irradiated by a Matrix-10 reactor with sixteen ultraviolet lamps (10 W per lamp) under Argon atmosphere. ^b The yield was determined by ¹H NMR (400 MHz) analysis with CH₂Br₂ (0.2 mmol) as internal standard. ^c Some unidentified byproducts were formed. ^d The reaction was carried out under air atmosphere. ^e Isolated yield. ^f See reference 9.

donating group, like alkoxy (entries 15–18, Table 2) and acetoxy (entry 19, Table 2), the yields decreased slightly. Then other dibromomalonates **1b** and **1c** were applied in this photocyclopropanation. The desired products were formed in good yields (entries 20 and 21, Table 2).

Next, alkenes **4** with different configurations were employed to gain stereochemistry information of this photocyclopropanation. As shown in Scheme 3, reactions under Condition A with either **Z-4** or **E-4** gave the same product **trans-5** in similar yields. No **cis-5** was formed in either case. These results might indicate a free bond rotation during the reaction process (*vide infra*), which led to a favored configuration of **trans-5** in both cases. For further consideration of possible isomerization of **Z-4** or **E-4** before cyclization, the unconsumed alkenes **Z-4** and **E-4** were recovered and no isomerization of the double bond was obtained by ¹H NMR analysis. This observation further proved that the initial isomerization of alkene under UV irradiation did not take place at all and the change of the configuration (**Z-4** to **trans-5**) should only occur in the cyclization step. This also negated the possibility that the excitation of the alkene was the initial step for the whole procedure, since such excitation must lead to the isomerization of **Z-4** into **E-4**.¹¹

With these results in hand, we further studied the mechanism. The ultraviolet-visible spectra of **1a**, **2a**, and Hünig base (see Figure S1 in SUPPLEMENTARY DATA) showed clearly that

Table 2. The photocyclopropanation under Condition A ^a

Entry	1 (R)	2 (Ar)	Time (h)	3	Yield (%) ^b
1	1a (Et)	2b (4-COOMeC ₆ H ₄)	3	3ab	89
2	1a (Et)	2c (4-CF ₃ C ₆ H ₄)	1.5	3ac	87
3	1a (Et)	2d (4-NO ₂ C ₆ H ₄)	1.5	3ad	85
4	1a (Et)	2e (3-NO ₂ C ₆ H ₄)	1.5	3ae	78
5	1a (Et)	2f (2-NO ₂ C ₆ H ₄)	2	3af	80
6	1a (Et)	2g (4-FC ₆ H ₄)	2	3ag	80
7	1a (Et)	2h (4-ClC ₆ H ₄)	2	3ah	81
8	1a (Et)	2a (C ₆ H ₅)	2	3aa	89
9	1a (Et)	2i (4-MeC ₆ H ₄)	2	3ai	86
10	1a (Et)	2j (3-MeC ₆ H ₄)	2	3aj	86
11	1a (Et)	2k (2-MeC ₆ H ₄)	2	3ak	87
12	1a (Et)	2l (4-EtC ₆ H ₄)	2	3al	79
13	1a (Et)	2m (4- <i>i</i> -PrC ₆ H ₄)	1.5	3am	84
14	1a (Et)	2n (4-PhC ₆ H ₄)	2.5	3an	83
15	1a (Et)	2o (4-MeOC ₆ H ₄)	2.5	3ao	73
16	1a (Et)	2p (3-MeOC ₆ H ₄)	2.5	3ap	70
17	1a (Et)	2q (2-MeOC ₆ H ₄)	2	3aq	72
18	1a (Et)	2r (4-EtOC ₆ H ₄)	3	3ar	70
19	1a (Et)	2s (4-AcOC ₆ H ₄)	2.5	3as	67
20	1b (Me)	2a (C ₆ H ₅)	2	3ba	86
21	1c (<i>i</i> -Pr)	2a (C ₆ H ₅)	2.5	3ca	77

^a All reactions were carried out using **1** (0.2 mmol), **2** (0.4 mmol), and *i*-Pr₂NEt (0.4 mmol) in deaerated methanol (10 mL) irradiated by a Matrix185-10 reactor with sixteen ultraviolet lamps (10 W per lamp, $\lambda = 185&254$ nm) at rt under air atmosphere. ^b Isolated yield.

all these three components absorb light at $\lambda = 185$ nm and 254 nm. Nevertheless, as discussed above, the fact that no isomerization of the recovered alkene **4** was detected (Scheme 3) proved that the excitation of alkene **2** was not the key step during this transformation. On the other hand, the observation that no cyclopropane was formed without Hünig base (entry 17, Table 2) suggested that the direct excitation of dibromomalonate **1** could only lead to decomposition. Thus, the electron transfer starting from Hünig base under the excitation of UV light¹⁰ seemed to be the most reasonable. The Photon-induced Electron Transfer (PET) from Hünig base to dibromomalonate could result in several intermediates which were listed below.

Firstly, a free radical mechanism was proposed as shown in Scheme 4. The PET from excited Hünig base to **1** led to a free radical **6** along with the release of Br[•]. The radical addition of **6** with **2** afforded radical intermediate **7** which underwent another PET to give a di-radical **8**. The final radical coupling yielded cyclopropane **3**.

To check the possibility of the above mechanism, reactions with radical scavengers were carried out under Condition A (Scheme 5). The addition of 1 equiv. of TEMPO resulted in a decreased yield. Further increasing the amount of TEMPO to 5 equiv. led to similar result. Next, BHT was used instead of TEMPO. The reaction showed similar efficiency and yield with 1 equiv. of BHT. Lower yield was observed with 5 equiv. of BHT compared with reactions employing TEMPO. Oxygen was also employed as radical scavenger and led to 82% yield. Considering that reactions with radical scavengers led to a decreased yield, radical might participate in the reaction pathway. On the other

Scheme 3. Photocyclopropanation of two stereoisomeric alkenes **Z-4** and **E-4**

Scheme 4. Free radical involved mechanism

Scheme 5. Effect of radical scavenger

Scheme 6. Carbene involved mechanism

hand, neither 5 equiv. of radical scavengers nor O_2 could completely inhibit this transformation, which might indicate that radical species were not the predominant intermediate during this reaction process. Additionally, a dark reaction after 5 minutes' photo irradiation was also carried out yielding only 19% of **3aa** (See Scheme S1 in SUPPLEMENTARY DATA), which ruled out a radical chain reaction mechanism,⁹ since similar result was obtained in dark reaction (entry 19, Table 1).

Next, a carbene involved mechanism was considered (Scheme 6). In the first step, radical **6** was generated by PET as mentioned above. Then the second PET afforded a carbene intermediate **9**. Carbene **9** could proceed a direct insertion to alkene **2** yielding the final product **3**.

Our previous study showed that a reported carbene precursor was not capable for this transformation.⁹ For detailed discussion,

both singlet and triplet carbenes should be considered. Firstly, the direct insertion of a singlet carbene with **Z-4** could only lead to **cis-5**, since there should be no bond rotation taking place in such process.¹² But this is obviously opposite with the observation of reaction using alkene **Z-4** (Scheme 3). Thus, singlet carbene species might not be involved in this reaction procedure. A triplet carbene involved cyclopropanation might form **trans-5** from **Z-4**, however, it should be easily quenched by oxygen¹³ or TEMPO.¹⁴ But this reaction was not sensitive to air and the results discussed in Scheme 5 suggested this reaction could not be quenched by TEMPO completely. So a triplet carbene was not the key intermediate, either. Thus, these two kinds of carbenes might not be the key intermediate during this transformation.

Compared with the above carbene involved mechanism, the second PET to radical **6** might alternatively generate a carbanion intermediate **10**. Its Michael addition to alkene **2** followed by intramolecular nucleophilic substitution would finally give the desired product **3** (Scheme 7).⁹ Since a carbanion intermediate is relatively stable in air,⁹ and a free bond rotation of **11** is reasonable for the transformation from **Z-4** to **trans-5**,⁹ this carbanion mechanism might be a possible reaction pathway for this photocyclopropanation. Additionally, only a minority of radical **6** could be trapped with radical scavenger during its transformation to carbanion **10**, which might be an explanation for why radical scavenger could partly inhibit this reaction (Scheme 5).

Scheme 7. Carbanion involved mechanism

In summary, we have developed a UV light induced catalyst-free cyclopropanation of dibromomalonates with alkenes at room temperature under air atmosphere, which provides a novel method for the synthesis of multisubstituted cyclopropanes. The high yields and environmentally friendly features of this reaction show great potential on organic synthesis. Several possible mechanisms were proposed and examined. Carbanion might be the key intermediate in the whole process. However, the mechanism is still not clear. Further studies in this field are in progress in our group.

Acknowledgments

We greatly acknowledge the financial support from National Basic Research Program of China (973 Program, 2012CB720300), International Science & Technology Cooperation Program of China (2014DFE40130), Shanghai Rising-Star Program (14QA1400500), and Science and Technology Commission of Shanghai Municipality (14ZR1407300).

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