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The Effects of Triplet Sensitizers' Energies on the Photoreactivity of β,γ -Unsaturated Methyl Ketones

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Remarkable Observations on Triplet-Sensitized Reactions. The Di- π -methane Rearrangement of Acyclic 1,4-Dienes in the Triplet Excited State

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ABSTRACT



$R^1 = \text{C}_6\text{H}_5$, 4-MeOC₆H₄; $R^2 = \text{C}_6\text{H}_5$, 4-CNC₆H₄; CN, Me, H; $R^3 = \text{C}_6\text{H}_5$, 4-CNC₆H₄, Me, H
Sens.: Acetophenone, 3-Methoxyacetophenone, Thioxanthone, 4-Phenylbenzophenone, Chrysene

Previous studies have led to the conclusion that a large majority of acyclic 1,4-dienes do not undergo photochemical di- π -methane (DPM) rearrangement under triplet-sensitized irradiation. The results of a detailed analysis of these processes demonstrate that a series of these compounds do indeed undergo highly efficient DPM rearrangement from their triplet excited states when suitable triplet sensitizers are used.

Sensitization is a standard method used to promote triplet excited state reactivity in molecules that do not undergo rapid intersystem crossing from singlet excited states that are populated by light absorption. This topic is discussed in great detail in all photochemical textbooks and monographs.¹ According to the literature, the main requirement to promote a triplet-sensitized reaction is efficient energy transfer from the sensitizer to the reactant molecule. Once this process has occurred, the triplet of the reactant is formed and the corresponding reaction takes place. As far as we are aware, there are no precedents indicating that the reaction pathway followed by a molecule would depend on the type of sensitizer that is used to generate the triplet excited state.

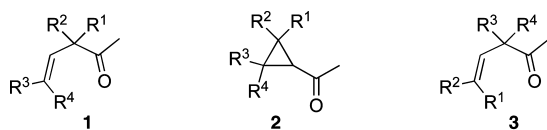
However, recent studies carried out in our laboratory have demonstrated that acyclic β,γ -unsaturated ketones undergo different reactions in the triplet excited state depending on the nature of the triplet sensitizer used to promote the

reaction.² Thus, ketones **1**, which had been previously described as unreactive toward oxadi- π -methane (ODPM) rearrangement, undergo this reaction in high yields when sensitizers with triplet energies slightly above the triplet energies of the acceptor alkene unit of the enone are used. In contrast, in the presence of sensitizers with much higher triplet energies, ketones **1** do not react to afford the corresponding ODPM products **2**, but instead, *E/Z* isomerization takes place exclusively. Additionally, when the triplet energies of the sensitizers are slightly lower than those of the alkene groups in **1**, enones **3**, derived by 1,3-acyl migration, are generated along with cyclopropyl ketones **2**, resulting from the ODPM rearrangement (Figure 1).²

The results obtained in studies with ketones **1** are unprecedented and prompted us to investigate the possible influence of triplet sensitizers on the photoreactivity of related acyclic 1,4-dienes. Observations reported in the literature demonstrate that most of the dienes undergo DPM rearrangement on direct irradiation, while triplet-sensitized

(1) For example, see: (a) Calvert G. J.; Pitts J. N. *Photochemistry*; John Wiley: New York, 1996. (b) Turro N. J. *Modern Molecular Photochemistry*; Benjamin Cummings Publishing Company: Menlo Park, CA, 1978. (c) Gilbert A.; Baggot J. *Essential of Molecular Photochemistry*; Blackwell Scientific Publications: Oxford, 1991.

(2) Armesto, D.; Ortiz, M. J.; Agarrabeitia, A. R.; El-Boulifi, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 7739.



- 1a, 2a, 3a:** $R^1 = R^2 = \text{Me}$; $R^3 = \text{C}_6\text{H}_5$; $R^4 = \text{H}$
1b, 2b, 3b: $R^1 = R^2 = (\text{CH}_2)_4$; $R^3 = \text{C}_6\text{H}_5$; $R^4 = \text{H}$
1c, 2c, 3c: $R^1 = R^2 = \text{Me}$; $R^3 = R^4 = \text{C}_6\text{H}_5$
1d, 2d, 3d: $R^1 = R^2 = \text{Me}$; $R^3 = R^4 = \text{CN}$
1e, 2e, 3e: $R^1 = R^2 = \text{Me}$; $R^3 = (\text{Me})_2\text{C}=\text{CH}$; $R^4 = \text{H}$

Figure 1. Starting enones (**1**) and photoproducts (**2**) and (**3**) from our previous study.²

irradiation typically brings about exclusive *Z/E* isomerization of the alkene moiety.³ The observations described below show that this conclusion cannot be generalized.

The 1,4-dienes, **4a**,⁴ **4d**,⁵ and **4g**⁶ probed in this study (Figure 2) have been reported to undergo DPM rearrange-



- 4a, 5a:** $R^1 = R^2 = R^3 = \text{C}_6\text{H}_5$
4b, 5b: $R^1 = \text{C}_6\text{H}_5$; $R^2 = R^3 = \text{Me}$
4c, 5c: $R^1 = \text{C}_6\text{H}_5$; $R^2 = R^3 = \text{H}$
4d, 5d: $R^1 = \text{C}_6\text{H}_5$; $R^2 = \text{CN}$; $R^3 = \text{H}$
4e, 5e: $R^1 = \text{C}_6\text{H}_5$; $R^2 = 4\text{-CNC}_6\text{H}_4$; $R^3 = \text{H}$
4f, 5f: $R^1 = \text{C}_6\text{H}_5$; $R^2 = 4\text{-MeOC}_6\text{H}_4$; $R^3 = \text{H}$
4g, 5g: $R^1 = 4\text{-MeOC}_6\text{H}_4$; $R^2 = R^3 = 4\text{-CNC}_6\text{H}_4$

Figure 2. Starting dienes (**4**) and DPM photoproduct (**5**).

ments to afford the respective vinylcyclopropanes **5a**, **5d**, and **5g** on direct irradiation. However, they are described as unreactive in the DPM mode when subjected to triplet-sensitized conditions. Compound **4b**⁷ is known to undergo inefficient DPM rearrangement, and **4c**⁵ affords **5c** in 16% yield when benzophenone is employed as a triplet sensitizer. The photoreactivity of dienes **4e** and **4f** under direct and triplet-sensitized irradiation conditions is described for the first time in this work. These two dienes are readily synthesized by using standard procedures starting from 2-(1,3-dithian-2-yl)-2-methylpropanal.⁸

Solutions of the dienes in CH_2Cl_2 were irradiated using a 400 W medium-pressure Hg arc lamp and a Pyrex filter. The

following sensitizers with the corresponding triplet energies⁹ were used: acetophenone ($E_T = 74 \text{ kcal mol}^{-1}$), 3-methoxyacetophenone ($E_T = 71 \text{ kcal mol}^{-1}$), thioxanthone ($E_T = 63 \text{ kcal mol}^{-1}$), 4-phenylbenzophenone ($E_T = 61 \text{ kcal mol}^{-1}$), and chrysene ($E_T = 57 \text{ kcal mol}^{-1}$). The irradiation times, yields of products, and recovered starting materials are summarized in Table 1. Contrary to the literature precedent, all of these substances undergo the DPM rearrangement from their triplet excited states when an appropriate sensitizer is used (Table 1).

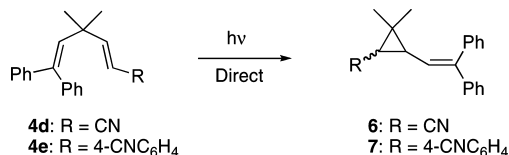
The results obtained for compound **4a** are consistent with our previous observations on the triplet photoreactivity of β,γ -unsaturated ketones. Thus, low energy sensitizers such as thioxanthone, 4-phenylbenzophenone, and chrysene promote the DPM reaction affording **5a** in low yield. Higher irradiation times result in a decrease in the yield of recovered starting material without increasing the yield of the DPM product. However, the reaction does not occur when high energy sensitizers are used. Zimmerman and Mariano⁴ had reported previously that **4a** lacks DPM reactivity when chlorobenzene ($E_T = 82 \text{ kcal mol}^{-1}$),⁹ propiophenone ($E_T = 74.6 \text{ kcal mol}^{-1}$),⁹ and benzophenone ($E_T = 68.8 \text{ kcal mol}^{-1}$) are used as triplet sensitizers.⁹ In agreement with these results, irradiation of **4a** using 3-methoxyacetophenone gives **5a** in very low yield (4%).

The study was extended to diene **4b**, a compound that was previously reported to undergo the DPM reaction on benzophenone-sensitized irradiation yielding cyclopropane **5b** in ca. 5% yield.⁷ However, contrary to the results obtained in the previous investigation with **4a**, the chemical efficiency of the reaction increases considerably when sensitizers of higher and lower energy than benzophenone ($E_T = 68.8 \text{ kcal mol}^{-1}$)^{4,9} are used, reaching a maximum 80% yield when thioxanthone is employed. No reaction is observed to take place under chrysene-sensitized irradiation conditions (Table 1).

Diene **4c** has been reported to undergo DPM reaction upon benzophenone-sensitized irradiation to afford **5c** in 16% yield.⁵ The results obtained in the current effort show that the yield of **5c** increases considerably when 3-methoxyacetophenone, thioxanthone, and 4-phenylbenzophenone are used as sensitizers, but decreases when acetophenone or chrysene sensitization are employed (Table 1).

The photoreactivity of **4d** was previously reported by Zimmerman and Klun,⁵ who showed that direct irradiation affords cyclopropane **6** (Scheme 1) while acetophenone-

Scheme 1



sensitized irradiation brings about *E/Z* isomerization of the alkene solely.

(3) Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, *96*, 3065–3112.
 (4) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718–1727.

(5) Zimmerman, H. E.; Klun, R. T. *Tetrahedron* **1978**, *34*, 1775–1803.
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(7) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6259–6267.

(8) Taylor, E. C.; LaMattina, J. L. *Tetrahedron Lett.* **1977**, *24*, 2077–2080.

(9) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

Table 1. Reaction Conditions and Yields of Isolated Products in the Triplet-Sensitized Irradiation of Acyclic 1,4-Dienes

substrate	irrad time (h)	triplet sensitizer (E_T , kcal mol ⁻¹)	DPM (yield, %) <i>E/Z</i> (ratio)	recovered S.M. (yield, %) <i>E/Z</i> (ratio)
4a	4	propiophenone ⁴ (74.6)		4a
4a	4	3-methoxyacetophenone (71.0)	5a (4)	4a (93)
4a	4	thioxanthone (63.0)	5a (15)	4a (71)
4a	4	4-phenylbenzophenone (61.0)	5a (25)	4a (72)
4a	4	chrysene (57.0)	5a (15)	4a (70)
4b	3	acetophenone (74.0)	5b (43)	4b (38)
4b	3	3-methoxyacetophenone (71.0)	5b (38)	4b (48)
4b	3	thioxanthone (63.0)	5b (80)	4b (3)
4b	3	4-phenylbenzophenone	5b (47)	4b (52)
4b	3	chrysene (57.0)		4b (83)
4c	3	acetophenone (74.0)	5c (12)	4c (68)
4c	3	3-methoxyacetophenone (71.0)	5c (36)	4c (51)
4c	3	thioxanthone (63.0)	5c (39)	4c (45)
4c	3	4-phenylbenzophenone (61.0)	5c (49)	4c (49)
4c	3	chrysene (57.0)	5c (9)	4c (81)
(<i>E</i>)- 4d	3	acetophenone (74.0)		4d (97) <i>E/Z</i> (1:1)
(<i>E</i>)- 4d	3	3-methoxyacetophenone (71.0)	5d (47) <i>E/Z</i> (1:4)	4d (39) <i>E/Z</i> (1:1)
(<i>E</i>)- 4d	3	thioxanthone (63.0)	5d (89) <i>E/Z</i> (2:1)	4d (2) <i>E/Z</i> (1:1)
(<i>E</i>)- 4d	3	4-phenylbenzophenone (61.0)	5d (30) <i>E/Z</i> (5:1)	4d (50) <i>E/Z</i> (9:1)
(<i>E</i>)- 4d	3	chrysene (57.0)		4d (83) <i>E/Z</i> (5:4)
(<i>E</i>)- 4e	1.5	acetophenone (74.0)		(<i>E</i>)- 4e (88)
(<i>E</i>)- 4e	1.5	3-methoxyacetophenone (71.0)	(<i>E</i>)- 5e (20)	(<i>E</i>)- 4e (69)
(<i>E</i>)- 4e	1.5	thioxanthone (63.0)	(<i>E</i>)- 5e (18)	(<i>E</i>)- 4e (75)
(<i>E</i>)- 4e	1.5	4-phenylbenzophenone (61.0)	(<i>E</i>)- 5e (55)	(<i>E</i>)- 4e (40)
(<i>E</i>)- 4e	1.5	chrysene (57.0)	(<i>E</i>)- 5e (8)	(<i>E</i>)- 4e (85)
4f <i>E/Z</i> (3:5)	2	acetophenone (74.0)		4f (80) <i>E/Z</i> (2:1)
4f <i>E/Z</i> (3:5)	2	3-methoxyacetophenone (71.0)	5f (40) <i>E/Z</i> (1:1)	4f (47) <i>E/Z</i> (10:1)
4f <i>E/Z</i> (3:5)	2	thioxanthone (63.0)	5f (10) <i>E/Z</i> (1:1)	4f (75) <i>E/Z</i> (10:1)
4f <i>E/Z</i> (3:5)	2	4-phenylbenzophenone (61.0)	5f (38) <i>E/Z</i> (1:1)	4f (48) <i>E/Z</i> (10:1)
4f <i>E/Z</i> (3:5)	2	chrysene (57.0)	5f (25) <i>E/Z</i> (1:1)	4f (69) <i>E/Z</i> (10:1)
4g	3	acetophenone (74.0)	5g (14)	4g (70)
4g	3	3-methoxyacetophenone (71.0)	5g (30)	4g (54)
4g	3	thioxanthone (63.0)		4g (90)
4g	3	4-phenylbenzophenone (61.0)	5g (36)	4g (56)
4g	3	chrysene (57.0)	5g (73)	4g (20)

In clear contrast with the earlier observations, 3-methoxyacetophenone-sensitized irradiation of (*E*)-**4d** in CH₂Cl₂ for 3 h leads to efficient production of the DPM product **5d**⁵ (47%). When thioxanthone is used as sensitizer, the reaction affords **5d** in a much higher 89% yield. DPM reaction of (*E*)-**4d** also takes place when 4-phenylbenzophenone is employed although with lower efficiency (30%). Finally, when chrysene sensitization is used, the only reaction observed is *E/Z* isomerization (83%, *E/Z* 5:4) (Figure 2 and Table 1).

The study was extended to include the diene (*E*)-**4e**. Direct irradiation of this substance using Pyrex filtered light for 45 min results in formation of vinylcyclopropane (*E*)-**7** (77%) and recovered starting material (*E*)-**4e** (21%) (Scheme 1). Acetophenone-sensitized irradiation of (*E*)-**4e** results in recovered starting material (88%) only. However, when 3-methoxyacetophenone, thioxanthone, 4-phenylbenzophenone, and chrysene are used as triplet sensitizers, the DPM photoproduct (*E*)-**5e** is generated in variable yields (Figure 2 and Table 1). The highest yield of **5e** (55%) is obtained when 4-phenylbenzophenone is used as sensitizer.

An interesting observation made in the study of **4d** and **4e** is the change in the regiochemical course of the DPM reaction depending on which excited state (singlet or triplet) undergoes the rearrangement reaction. Thus, direct irradiation of **4d** and **4e** affords the respective cyclopropanes **6** and **7** which contain the electron-withdrawing cyano or 4-cyanophenyl groups on the cyclopropane ring. However, on triplet-sensitized irradiation, cyclopropanes **5d** and **5e**, having the electron-withdrawing groups attached to the residual double bond, are obtained. These results are in good agreement with those arising from previous work on the influence of two electron-withdrawing groups at position 1 of the 1,4-diene of the DPM rearrangement.^{10,11} However, as far as we are aware, these are the first examples of triplet DPM rearrangements in acyclic 1,4-dienes that have only one electron-withdrawing group at C-1.

(10) Zimmerman, H. E.; Armesto, D.; Amezuza, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367–6383.

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The absence of *E/Z* isomerization of the 4-cyanophenylvinyl unit in the triplet-sensitized reactions of diene **4e** is surprising. However, this observation is consistent with literature precedents that show that the *E/Z* isomerization of 4-cyanostilbenes occurs only from their singlet excited states.¹²

In order to determine whether 1,4-dienes with electron-donor groups at C-1 would also undergo DPM rearrangement in the triplet manifold, the photochemical reactivity of compound **4f** with 4-methoxyphenyl substitution at C-1 was investigated. Direct irradiation of **4f** (*E/Z*, 3:5) generates **5f** (22%, *E/Z* 1:1) and recovered starting material **4f** (54%, *E/Z* 3:2). In contrast, acetophenone-sensitized irradiation of **4f** leads to *E/Z* isomerization of the alkene unit, exclusively. However, when 3-methoxyacetophenone, thioxanthone, 4-phenylbenzophenone, or chrysene are used as sensitizers, **4f** undergoes DPM reaction to generate photoproduct **5f** with the respective efficiencies displayed in Table 1.

The formation of **5f** in the sensitized irradiation of **4f** represents the first example of a triplet DPM rearrangement in an acyclic 1,4-diene that contains an electron-donating group at C-1. In this instance, the regiochemistry of the reaction does not depend on the multiplicity of the excited state, and cyclopropane **5f**, with the 4-methoxyphenyl group attached to the vinyl unit, is obtained from both direct and triplet-sensitized irradiation promoted reactions.

The study was extended to include 1,4-diene **4g** that has two 4-methoxyphenyl groups at C-1 and two 4-cyanophenyl substituents at C-5. The photochemistry of **4g** was previously described by Zimmerman and Welter.⁶ These authors observed that DPM rearrangement of **4g** takes place on direct irradiation to yield **5g** (30%) and that this substance is unreactive under 3-methoxyacetophenone-sensitized irradiation conditions.

In contrast with these previous observations, the results of the current studies show that acetophenone-sensitized irradiation of **4g** affords the DPM photoproduct **5g** (14%). Likewise, when 3-methoxyacetophenone and 4-phenylbenzophenone are used as sensitizers, **5g** is obtained in 30% and 36% yield, respectively. However, irradiation with thioxanthone as a triplet sensitizer leads to recovery of starting material (90%). Finally, chrysene-sensitized irradiation of **4g** efficiently yields the DPM product **5g** (73%) (Figure 2 and Table 1). The regiochemistry of the triplet-DPM reaction in this instance is the same as that previously reported for the direct irradiation reaction of **4g**.⁶ These results are surprising in light of the fact that **4g** undergoes efficient DPM rearrangement with sensitizers

of high triplet energy (acetophenone and 3-methoxyacetophenone) and low triplet energy (4-phenylbenzophenone and chrysene) but that the reaction does not occur when thioxanthone is used (Table 1).

In summary, previous studies of the photochemistry of acyclic 1,4-dienes led to the establishment of the general rule of thumb that these substances undergo DPM rearrangements on direct irradiation via the singlet excited states, whereas their triplet excited states lead to *Z/E* isomerization, exclusively.³ However, the results obtained in the current effort show that these substrates do indeed undergo DPM reactions on triplet-sensitized irradiation via the triplet excited state and that the chemical efficiencies of the triplet processes depend on the nature of the sensitizer used. Although our previous studies with related unsaturated ketones suggested that a possible correlation exists between the triplet energy of the sensitizer and the photoreactivity observed, the observations made in this study demonstrate that this correlation does not apply to dienes **4**. Therefore, other factors (still unknown) must play an important role in the outcome of triplet-sensitized reactions of acyclic 1,4-dienes. We have tried to correlate the reactivity observed with different physical constants of the sensitizers and the dienes without success. In an attempt to obtain information about this issue, diene **4a** was irradiated in *t*-BuOH. The results indicate that significant differences in the reactivity profile of **4a** do not exist for reactions in CH₂Cl₂ or the *t*-BuOH. It is clear that additional studies are needed to clarify the influence of sensitizer type and triplet energy on the triplet reactivity of 1,4-dienes. Nevertheless, the obvious consequence of the investigation described above is that other compounds that have been previously reported to be unreactive in their triplet excited states might actually be reactive when suitable triplet sensitizers are used.

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Supporting Information Available: Experimental procedures for the synthesis of dienes **4e** and **4f** and photolysis of **4a–g**. Analytical and spectroscopic data for all photoproducts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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