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

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The photochemistry of β,γ-unsaturated ketones has been a topic of great interest to organic photochemists for many years.[1] The results of studies in this area show that these substances undergo a 1,3-acyl migration on direct irradiation and an oxa-di-π-methane (ODPM) rearrangement in the presence of triplet sensitizers. Both processes usually occur with high chemical and quantum efficiencies and high degrees of stereoselectivity.[1] As a result, the photochemical 1,3-acyl migration and ODPM rearrangement reactions have found important synthetic applications.[1] Despite the fact that a large majority of β,γ-unsaturated ketones undergo triplet-state ODPM reactions, some acyclic compounds in this series, even those having substitution patterns that are known to favor this reaction, are unreactive.[1a] For example, it has been reported that the β,γ-unsaturated ketones **1a**,[2] **1b**[3] **1c**,[4] and **1d**[2] do not undergo the ODPM rearrangement in the presence of acetophenone or 3-methoxyacetophenone. Instead, under these conditions **1a** and **1b** undergo alkene *E*/*Z* isomerization.

To gain a better understanding of this unusual behavior, we have carried out a more detailed study in which we have probed the photochemistry of enones **1a**–**e** by using a variety of other triplet sensitizers. The results arising from this effort reveal that these acyclic β,γ-unsaturated ketones do indeed undergo the ODPM process when the triplet energies of the sensitizers used to promote the reaction are close to those of the triplet states of the alkene moieties, and that the ODPM reactivity of these substrates is intimately related to the features of the triplet formed in the energy-transfer processes.

In this study, solutions of β,γ-unsaturated ketones **1a**–**e** containing sensitizers of varying triplet energies[5] (acetophenone: $E_T = 74$ kcal mol^{-1}; 3-methoxyacetophenone: $E_T = 71$ kcal mol^{-1}, depending on the absorption properties of the enone; thioxanthone: $E_T = 63$ kcal mol^{-1}; 4-phenylbenzophe-

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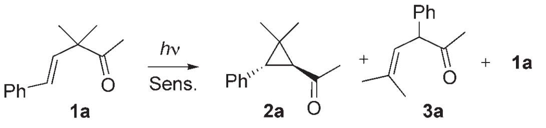
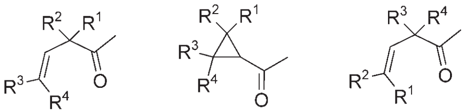
none: $E_T = 61$ kcal mol^{-1}; chrysene: $E_T = 57$ kcal mol^{-1}) were irradiated in an immersion apparatus through Pyrex using a 400-W medium-pressure mercury arc lamp. The results of an earlier study showed that irradiation of the β,γ-unsaturated ketone **1a**[2] (the E_T of the styrene chromophore is about 62 kcal mol^{-1})[5] with acetophenone triplet sensitization (E_T = 74 kcal mol^{-1}) for 5 h led to 91 % recovery of the enone as a 1:1 mixture of *E* and *Z* isomers. In contrast, irradiation of **1a** (1:2 mixture of *E* and *Z* isomers) in CH_2Cl_2 with thioxanthone ($E_T = 63$ kcal mol^{-1}) as the sensitizer for 8.5 h resulted in formation of the ODPM product (*E*)-**2a** (50 %) and recovered starting material **1a** (20 %), as a 2:3 mixture of *E*- and *Z*-isomers (Scheme 1). Likewise, irradiation of **1a** (1:2, *E*/*Z*) with 4-phenylbenzophenone ($E_T = 61$ kcal mol^{-1}) as sensitizer for 8.5 h promoted formation of the ODPM product (*E*)-**2a** (10 %), the 1,3-acyl migration product **3a** (28 %), and recovered starting material **1a** (35 %), as a 2:5 mixture of *E* and *Z* isomers (Scheme 1). In this case, three different types of photochemical reactions, namely *E*/*Z* isomerization, ODPM rearrangement, and 1,3-acyl migration, take place from the triplet excited state of **1a**, a phenomenon rarely observed in photochemistry.[6] Finally, when the photoreaction of **1a** was carried out with chrysene ($E_T = 57$ kcal mol^{-1}) as the triplet sensitizer, **3a** (6 %) and recovered starting material **1a** (56 %, 1:6 mixture of *E* and *Z* isomers) were isolated (Scheme 1).



Acetophenone	—	—	91%
Thioxanthone	50%	—	20%
4-Phenylbenzophenone	10%	28%	35%
Chrysene	—	6%	56%

Scheme 1. Photoreactivity of enone **1a** using different triplet sensitizers. Sens. = sensitizer.

To the best of our knowledge, these unusual observations, which suggest that the excited-state reaction pathways followed by enone **1a** depends on the triplet energy of the sensitizer, are unprecedented. In order to determine if this behavior is observed with other β,γ-unsaturated ketones, the photochemistry of ketones **1b**–**e** was also explored. We found that (*E*)-**1b** behaves in a similar manner to **1a** in photoreactions promoted by the triplet sensitizers listed above. The only difference observed in this case is that the ODPM photoproduct **2b** is also formed in low yield, along with **3b** as the major product, when chrysene is used as triplet sensitizer (Scheme 2 and Table 1). The diphenylvinyl chromophore in **1c** has a triplet energy of about 53–62 kcal mol^{-1},[7] and irradiation of **1c** with 3-methoxyacetophenone ($E_T = 71$ kcal mol^{-1}) as the sensitizer leads to recovered starting material



1 **2** **3**

1a, **2a**, **3a**: $R^1 = R^2 = Me$, $R^3 = Ph$, $R^4 = H$
1b, **2b**, **3b**: $R^1 = R^2 = (CH_2)_4$, $R^3 = Ph$, $R^4 = H$
1c, **2c**, **3c**: $R^1 = R^2 = Me$, $R^3 = R^4 = Ph$
1d, **2d**, **3d**: $R^1 = R^2 = Me$, $R^3 = R^4 = CN$
1e, **2e**, **3e**: $R^1 = R^2 = Me$, $R^3 = (Me)_2C{=}CH$, $R^4 = H$

Scheme 2. Starting enones and photoproducts.

Table 1: Reaction conditions and yields of isolated products in the irradiation of β,γ-unsaturated ketones **1** in the presence of triplet sensitizers.

Substrate	Irrad. time [h]	Triplet sensitizer	Estimated ΔE_{D-A} [kcal mol^{-1}]	ODPM (yield [%])	1,3-Acyl migration (yield, [%])	Starting material (yield [%])
1a	5	acetophenone	12	–	–	91[2]
1a	8.5	thioxanthone	1	**2a** (50)	–	20
1a	8.5	4-phenylbenzophenone	−1	**2a** (10)	**3a** (28)	35
1a	8.5	chrysene	−5	–	**3a** (6)	56
1b	11	acetophenone	12	–	–	83[a]
1b	11	thioxanthone	1.7	**2b** (68)	–	30
1b	11	4-phenylbenzophenone	−1	**2b** (51)	**3b** (15)	15
1b	11	chrysene	−5	**2b** (8)	**3b** (22)	65
1c	11	3-methoxyacetophenone	13[b]	–	–	80[4]
1c	10	thioxanthone	5[b]	**2c** (39)	–	45
1c	10	4-phenylbenzophenone	3[b]	**2c** (20)	**3c** (10)	56
1c	10	chrysene	−1[b]	–	**3c** (23)	40
1d	14	acetophenone	14	–	–	60[2]
1d	25	thioxanthone	3	**2d** (39)	–	50
1d	25	4-phenylbenzophenone	1	**2d** (16)	**3d** (6)	63
1d	25	chrysene	−3	**2d** (10)	**3d** (8)	40
1e	5.5	3-methoxyacetophenone	12	–	–	72
1e	5.5	thioxanthone	4	**2e** (20)	–	32
1e	5.5	4-phenylbenzophenone	2	**2e** (53)	**3e** (7)	20
1e	5.5	chrysene	−2	**2e** (23)	**3e** (30)	27

[a] Reinvestigated by us. Compound **1b**[3] was previously reported without experimental details. [b] An average energy value of 58 kcal mol^{-1} [7] was used for the triplet energy of the diphenylvinyl unit present in **1c**.

(80 %) exclusively.[4] When thioxanthone is used as sensitizer, **1c** reacts to form the ODPM photoproduct **2c** (39 %) exclusively, and both **2c** (20 %) and **3c** (10 %) are obtained when the process is sensitized by 4-phenylbenzophenone. Finally, the chrysene-sensitized photoreaction of **1c** gives only **3c** (23 %) (Scheme 2 and Table 1).

The photochemical behavior of dicyano-substituted enone **1d**, which has a triplet energy of about 60 kcal mol^{-1},[7] also follows the general pattern described above. Thus, the acetophenone-sensitized reaction of this substrate leads to recovered starting material (60 %) only.[2] With thioxanthone, the photoreaction of **1d** gives the ODPM product **2d** (39 %) exclusively, and with 4-phenylbenzophenone **2d** (16 %) and **3d** (6 %) are obtained. Finally, chrysene sensitization also transforms **1d** into **2d** (10 %) and **3d** (8 %) (Scheme 2 and Table 1).

The photochemistry of β,γ-unsaturated ketone **1e**, which contains a piperylene group ($E_T = 59$ kcal mol^{-1}),[5] was studied to test the generality of this novel reactivity profile. Irradiation of **1e** (1:6 mixture of *E* and *Z* isomers) with 3-methoxyacetophenone as the sensitizer gives rise to *E*/*Z* isomerization (3:2, *E*/*Z*) only. However, with thioxanthone the ODPM product **2e** (20 %) is formed in addition to recovered starting material **1e** (3:2 mixture of *E*- and *Z*-isomers). With 4-phenylbenzophenone as the triplet sensitizer, **2e** (53 %) and **3e** (7 %) are generated along with recovered **1e** (1:1, *E*/*Z*). Chrysene sensitization ($\Delta E_{D-A} \approx -2$ kcal mol^{-1}) also affords **2e** (23 %), **3e** (30 %), and **1e** (3:1, *E*/*Z*) (Scheme 2 and Table 1).

In summary, we have explored triplet-sensitized reactions of the acyclic β,γ-unsaturated methyl ketones **1a–e** by using sensitizers with different triplet energies. It has been reported that **1a–d**[2–4] do not undergo an ODPM rearrangement when acetophenone and 3-methoxyacetophenone are used as triplet sensitizers: under these conditions, **1a** and **1b** instead undergo alkene *E*/*Z* isomerization. Enone **1e** behaves similarly in that it undergoes *E*/*Z* isomerization exclusively when irradiated in the presence of 3-methoxyacetophenone as triplet sensitizer. Both of the sensitizers used in these processes have triplet energies that are about 12 kcal mol^{-1} higher than those of the alkene moieties present in the β,γ-unsaturated enones. In contrast, photoreactions of enones **1a–e** with triplet sensitizers having triplet energies that are about 5 and 1 kcal mol^{-1} higher than those of the alkene triplets follow ODPM rearrangement pathways to afford cyclopropyl ketones **2a–e** (Scheme 2). An ODPM rearrangement still takes place (albeit inefficiently) even when the triplet energies of the sensitizer are slightly lower (ca. −1 to −5 kcal mol^{-1}) than those of the alkene groups in **1a–e**, and a new process involving 1,3-acyl migration to form enones **3a–e** (Scheme 2) becomes competitive.

These results clearly show that the energy of the triplet sensitizer plays an important role in determining the outcome of triplet-sensitized reactions of β,γ-unsaturated ketones **1a–e**. The reactivity patterns suggest that, regardless of their triplet energies, all sensitizers promote photo-*E*/*Z* isomerization of the alkene moiety. However, the "hot" triplet excited states, with a large excess of vibrational energy, that are formed when sensitizers with a high triplet energy are used deactivate by *E*/*Z* isomerization exclusively. "Warm" triplet excited states of the alkene chromophores in the β,γ-unsaturated ketones are formed upon lowering the triplet energy of the sensitizer, and these undergo ODPM rearrangements in addition to the *E*/*Z* isomerization, and sensitizers that have a triplet energy close to that of the alkene groups give "cold" triplet excited states that undergo *E*/*Z* isomerization, 1,3-acyl migration, and ODPM rearrangement. Finally, when the energy of the sensitizer is slightly lower than that of the alkene, the efficiency of the ODPM rearrangement reaction path falls or is totally suppressed and *E*/*Z* isomerization and 1,3-acyl migration become the main routes followed.

It is interesting to view the conclusions presented above in the context of basic photochemical principles. Triplet sensitization is a standard method to promote triplet reactivity in molecules that do not undergo spontaneous intersystem crossing from their singlet excited states. This topic is discussed in great detail in all standard photochemical textbooks and monographs.[8] However, no reports exist, to the best of our knowledge, in the massive amount of literature on this topic that show that triplet excited states generated by intermolecular energy transfer can undergo different reactions depending on the energy of the triplet sensitizer used. Consequently, the generality of these novel findings and the accuracy of our mechanistic postulates will be tested in further studies we plan to carry out in this area.

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