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Photoreactivity in δ-keto-β,γ-enones: oxa-di-π-methane (ODPM) rearrangements from states other than T_1(π, π*)

B.C. Maiti, R. Singh, S. Lahiri *

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

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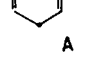
Abstract

The phototransformations of tricyclic β, γ-enones with substitutions on the π bond (**10a–10c**) have been studied. All of them were found to yield only the corresponding oxa-di-π-methane-rearranged products **11a–11c** on direct as well as on sensitized irradiation. Quenching studies suggest that states other than the lowest triplet are involved in the cases of **10a** and **10b**.

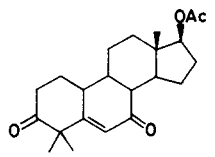
Keywords: δ-keto-β,γ-enones; Photoreactivity; Quenching; Oxa-di-π-methane rearrangement

1. Introduction

The behavioural dichotomy that has been observed in the phototransformation of β,γ-enones, whereby a 1,3-acyl shift takes place on direct irradiation and a 1,2-acyl shift (oxa-di-π-methane or (ODPM) rearrangement) on sensitized irradiation [1–5], is characterized by an intricate structure–reactivity relationship. The synthetic aspects of the latter type of rearrangement have been extensively reviewed in recent years [5–11]. A modified correlation of excited state and reactivity for this class of compounds and a model for empirical prediction of reactivity for bicyclo[2.2.2]oct-5-en-2-one systems have been furnished by Demuth [10,11]. The energy correlation of excited state and reactivity prefers a π,π* configuration in either the S_2 or T_1 state for the 1,2-acyl shift, whereas an S_1 or T_2 state of n,π* configuration is preferred for the 1,3-acyl shift. While this correlation applies fairly well for most of the β,γ-enone systems, Rogers and coworkers reported what is currently the only exception, where a T_2 state of n,π* configuration is shown to be involved in the photo-1,2-acyl shift [12,13]. In comparison with the vast amount of available data related to the photochemistry of β,γ-enones, data on δ-keto-β,γ-enones are rather scarce in the literature. The spatial arrangement **A** for such systems, with the sp^3 carbon either fully substituted or as a bridgehead, has been suggested as one with noticeably enhanced ODPM reactivity.



A



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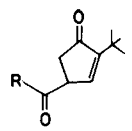
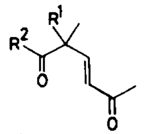


R = Ph or CMe_3

2



R^1=Me or $CHMe_2$

R^2=$CHMe_2$ or Me

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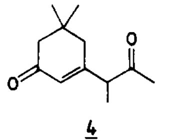

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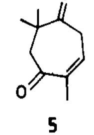

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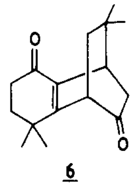

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An efficient $S_1 \rightarrow T_1$ intersystem crossing (ISC) has been suggested for such systems **1–6**, bringing about the ODPM reaction even with no sensitizer. Unlike **1** [14], **2** [15] and **6** [16] which underwent exclusively ODPM rearrangement even on direct irradiation, **3–5** [17] always gave some amount of 1,3-acyl shift products. Besides these two types of products, in the case of **5** a dimer has also been reported to be a major product. The acyclic compounds **3** were found to have a wavelength-dependent ODPM reactivity. Amongst the cyclic systems, **5** has been reported to give only the dimer on acetophenone sensitization. Compound **7**, with a minor variation in substitution pattern, has been reported to behave in a different manner (Scheme 1) [18]. No ODPM-rearranged (Scheme 1) product has been reported from this reaction. From these results it is apparent that the substitution pattern does play a role even in such a spatial arrangement as type **A**. Because of our interest in the photochemistry of such

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* Corresponding author.

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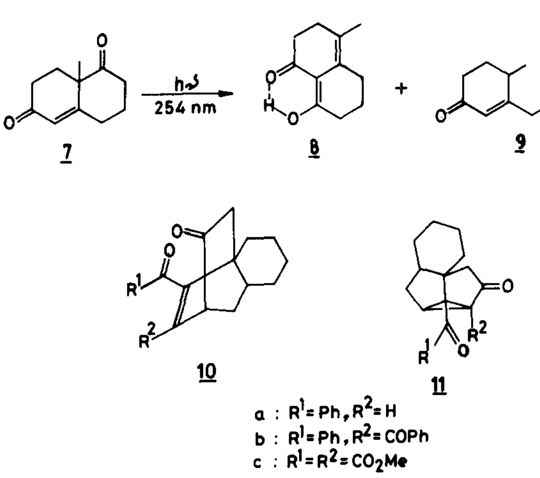


Scheme 1.

systems, we undertook the present work (i) to study the steady state photoreaction of a rigid tricyclic δ-keto-β,γ-enone (**10a**), (ii) to probe the probable reaction cascade when the π bond in such a system is also part of another chromophore (**10b**) and (iii) to compare the results with another electron-withdrawing substituent at the γ position (**10c**).

2. Experimental details

The starting materials **10a**–**10c** were prepared by a previously reported procedure [19]. All melting points were uncorrected and were determined in a Gallenkamp apparatus. IR spectra were recorded on a Perkin–Elmer 298 spectrometer. Electronic spectra were recorded on a Hitachi 200-20 UV spectrophotometer using ethanol as solvent. NMR spectra were recorded on a Varian XL-200, Brucker AC-200 or Varian EM 360 spectrometer using tetramethylsilane as internal standard. The petroleum ether (PE) used was the fraction of b.p. 60–80 °C. Solvents for steady state photolysis experiments were purified, dried and distilled before use.

*2.1. Steady state photolysis of **10a**–**10c***

Steady state irradiation experiments were carried out with solutions of the starting materials in various solvents (110 ml). These were degassed with argon for 10–15 min and photolysed using mainly a Hanovia medium pressure mercury lamp (450 W) for various time periods with a Pyrex filter. Solvents were removed and the residues were chromatographed over a silica gel column. Table 1 summarizes the time periods and yields of the various reactions.

*2.1.1. Irradiation of **10a***

In benzene. A solution of **10a** (300 mg, 1.07 mmol) in dry benzene was irradiated for 30 min. The residue was eluted with 15% EtOAc in PE to give a solid which on recrystallization from a mixture of ether and PE gave white crystals of **11a** (250 mg, 83%), m.p. 77 °C. Anal. Calc. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.58; H, 7.27. IR (KBr) ν_{max}: 1710, 1660 cm^{-1}. UV (EtOH) λ_{max}: 250 nm (log ε 4.02), 284 (2.90). ^{1}H NMR (CDCl$_3$) δ: 0.9–1.5 (m, 5H), 1.5–1.85 (m, 4H), 2.1–2.4 (m, 3H), 2.41–2.65 (m, 3H), 7.45–7.7 (m, 3H), 7.8–7.95 (m, 2H).

In methanol. From **10a** (480 mg, 1.71 mmol), white crystals of **11a** (400 mg, 73%), m.p. 77 °C (mmp 77 °C), were obtained. Further elution of the column with 20% EtOAc in PE gave a solid which on recrystallization from methanol and PE gave white crystals of **12** (60 mg, 11%), m.p. 149 °C. Anal. Calc. for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.47; H, 7.63. IR (KBr) ν_{max}: 3430, 3300, 1705 cm^{-1}. UV (EtOH) λ_{max}: 222 nm (log ε 3.61), 260 (2.53), 283 (2.23). ^{1}H NMR (CDCl$_3$) δ: 0.8–1.3 (m, 4H), 1.4–1.65 (m, 6H), 1.7–2.5 (m, 6H), 2.9 (s, 1H), 3.7 (dd, *J* 10 and 5 Hz, 1H), 3.9 (dd, *J* 10 and 5 Hz, 1H), 7.3–7.7 (m, 5H).

In acetone. From **10a** (300 mg, 1.07 mmol), white crystals of **11a** (260 mg, 87%), m.p. 77 °C (mmp 77 °C), were obtained.

*Irradiation of **11a** in methanol.* Elution of the residue obtained from **11a** (400 mg, 1.42 mmol) with 20% EtOAc in PE gave **12** (150 mg, 34%), m.p. 148 °C (mmp 147–148 °C). Further elution gave back 200 mg of **11a**.

*2.1.2. Irradiation of **10b***

In benzene. A solution of **10b** (250 mg, 0.65 mmol) in dry benzene was irradiated for 5.5 h. Elution of the residue with 20% EtOAc in PE afforded a white solid which on recrystallization from ether gave white crystals of **11b** (113 mg, 45%), m.p. 172 °C. Anal. Calc. for $C_{26}H_{24}O_3$: C, 81.22; H, 6.29. Found: C, 80.98; H, 6.11. IR (KBr) ν_{max}: 1730, 1670 cm^{-1}. UV (EtOH) λ_{max}: 254 nm (log ε 4.44), 357 (2.31). ^{1}H NMR (CDCl$_3$) δ: 1.0–1.40 (m, 4H), 1.40–1.90 (m, 6H), 2.18–2.70 (m, 3H), 3.26 (dd, *J* 6 and 2 Hz, 1H), 7.44–7.72 (m, 6H), 7.80–8.02 (m, 4H).

In methanol. From **10b** (250 mg, 0.65 mmol), **11b** (138 mg, 55%), m.p. 172 °C (mmp 172 °C), was obtained.

Table 1
Results of phototransformations of **10a**–**10c**

Starting compound	Solvent	Irradiation time (h)	Yield (%)
10a	Benzene	0.5	83
	Methanol	0.5	73 (**11a**) 11 (**12**)
	Acetone	0.5	87
10b	Benzene	5.5	45
	Methanol	5.0	55
	Acetone [a]	5.0	60
10c	Benzene	3.0	78
	Methanol	3.0	75
	Acetone	3.0	71
11a	Methanol [b]	1.0	34 (**12**)

[a] A Hanovia 100 W mercury lamp has been used; [b] no product was formed in the presence of oxygen.

Table 2
Quantum yields of phototransformations of **10a–10c**

Compound/ irradiation time (s)	Quantum yield ϕ				
	In benzene	In cyclohexane	In acetone	In methanol	In acetonitrile
10a/30	Ar (0.36) O_2 (0.32) Naph (0.33)	Ar (0.39) O_2 (0.36)	Ar (0.38) O_2 (0.13) [a] Naph (0.12)	Ar (0.34) O_2 (0.38) Naph (0.33)	
10b/150	Ar (0.049) O_2 (0.049) Naph (0.047)		Ar (0.052) O_2 (0.032) Naph (0.037)	Ar (0.052) O_2 (0.036) Naph (0.051)	Ar (0.055) O_2 (0.038) Naph (0.052)
10c/120	Ar (0.073) O_2 (0.05) Naph (0.038)	Ar (0.082) O_2 (0.036)	Ar (0.072) O_2 (0.008) Naph (0.005)	Ar (0.074) O_2 (0.059) Naph (0.029)	

[a] Remained unaffected when 350 nm was used.

In acetone. Irradiation of **10b** (160 mg, 0.41 mmol) with a Hanovia 100 W mercury lamp for 5 h gave **11b** (100 mg, 60%), m.p. 172 °C (mmp 172 °C).

2.1.3. Irradiation of 10c

In benzene. A solution of **10c** (450 mg, 1.54 mmol) in dry benzene was irradiated for 3 h. Elution of the residue with 20% EtOAc in PE gave a solid which on recrystallization from a mixture of ether in PE gave white crystals of **11c** (350 mg, 78%) m.p. 65–66 °C. Anal. Calc. for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.77; H, 7.29. IR (KBr) ν_{max}: 1735, 1720 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.0–1.40 (m, 4H), 1.6–1.95 (m, 4H), 1.97–2.50 (m, 5H), 3.00 (dd, *J* 7 and 2 Hz, 1H), 3.72 (s, 3H), 3.75 (s, 3H).

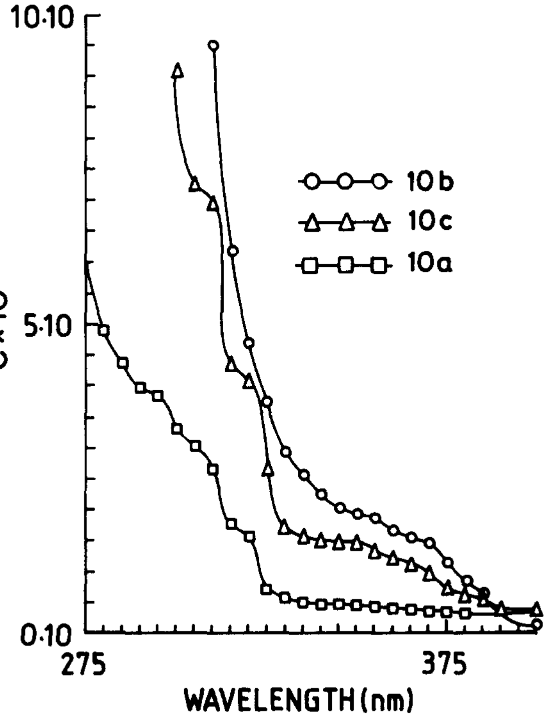


Fig. 1. Absorption spectra of **10a–10c**.

In methanol. From **10c** (460 mg, 1.57 mmol), white crystals of **11c** (350 mg, 75%), m.p. 65 °C (mmp 65 °C), were obtained.

In acetone. From **10c** (570 mg, 1.60 mmol) also, **11c** (355 mg, 71%), m.p. 66 °C (mmp 65–66 °C), was obtained.

2.2. Periodate oxidation of 12

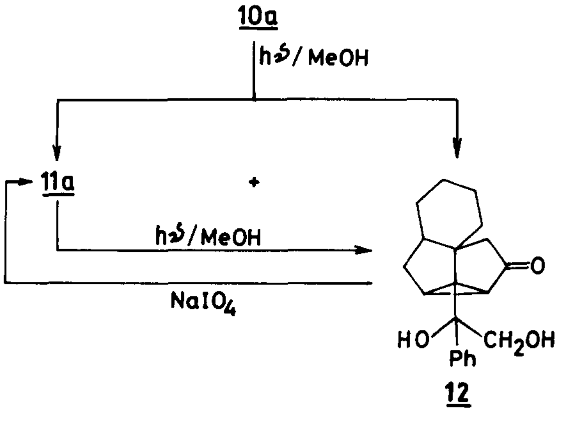
To a solution of **12** (100 mg, 0.32 mmol) in methanol (6 ml) and water (1.5 ml), sodium periodate (90 mg, 0.4 mmol) was added and the mixture was stirred for 20 h at room temperature. After removal of methanol the reaction mixture was extracted with ether and the solvent was removed. The residue was chromatographed over silica gel. Elution with 10% EtOAc in PE gave **11a** (75 mg, 84%), m.p. 77 °C (mmp 77 °C).

2.3. Quenching studies of the phototransformation

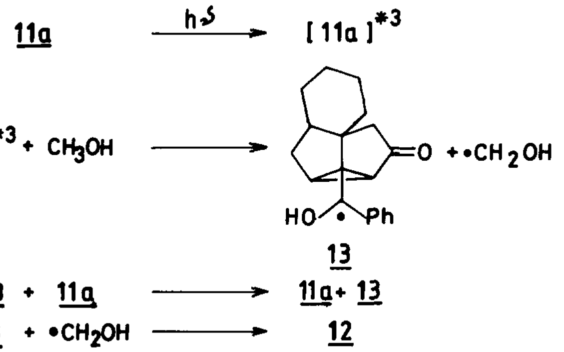
Standard solutions (about 3×10^{-3} M) of **10a–10c** were prepared in benzene, cyclohexane, acetone, methanol and acetonitrile. From these solutions, 15 ml aliquots were irradiated in the presence of argon, oxygen and naphthalene (about 1.5×10^{-2} M) in a Rayonet photoreactor using a merry-go-round at $\lambda\approx300$ nm. The time of irradiation for each set was so chosen so as to bring about 20%–30% conversion of the starting material (Table 2). Comparative phototransformations (%) were calculated by NMR spectroscopy and quantum yields for product formation were determined by uranyl oxalate actinometry ($\phi_{C_2O_4^{2-}}$ was 0.57 at 302 nm [20]).

3. Results and discussion

Like all other β,γ-enones, the absorption spectra of **10a–10c** showed an increased intensity in the n,π^* region (Fig. 1). As has been reported [16] for δ-keto compounds, **10a** and **10b** also showed additional absorptions around $\lambda\approx350$ nm.



Scheme 2.



Scheme 3.

Like most of the class **A** type of compounds, irradiation of **10a** in benzene and acetone using $\lambda > 254$ nm produced the ODPM-rearranged tetracyclic ketone **11a** in quantitative yield within 30 min. No other product could be identified from this reaction. The structure of **11a** was confirmed from its analytical and spectral data. In methanol a methanol addition product **12** has also been isolated in minor quantity. The structure of **12** was confirmed from its analytical and spectral data. One of its two –OH protons appeared in the NMR spectrum as a singlet at δ 2.9 and the other one was submerged in the multiplet around δ 1.5. The two protons were exchangeable on shaking with D_2O. The methylene protons appeared as double doublets at δ 3.7 and 3.9. The structure was further confirmed from the fact that on periodate oxidation this diol gave back **11a**. Irradiation of **11a** in methanol gave **12** (Scheme 2), which confirmed its secondary nature of formation from irradiation of **10a**. The mechanism of formation of **12** from **11a** may be explained by invoking the formation of the ketyl radical **13** from the triplet state of **11a**, which then transfers hydrogen to the ground state ketone **11a**, followed by formation of the coupled product **12** (Scheme 3). Complete quenching of the formation of **12** from **11a** has been observed in the presence of oxygen, which further supports this mechanism.

Since all the starting tricyclic compounds and the resulting tetracyclic products were inseparable by gas chromatography (GC) as well as by high performance liquid chromatography (HPLC), the quantum yields in all cases were determined from their NMR data.

The quantum yields of product formation from **10a** using $\lambda \approx 300$ nm in benzene and acetone were found to be very similar (Table 2). A similar ϕ value in cyclohexane eliminated any probability of sensitization of **10a** by benzene in this transformation. Interestingly, although oxygen and naphthalene did not affect the reactions in benzene and cyclohexane, the reaction in acetone was found to be quenched by their presence.

From these results we suggest two possible pathways for **10a** → **11a** transformation: (i) via an $S_2(\pi,\pi^*)$ state and/or (ii) via a $T_1(\pi,\pi^*)$ state. Although for such a class of compounds an efficient ISC from S_1 to T_1 has generally been preferred in the literature [14–17], leading to ODPM rearrangement, from the differential results in our quenching studies we prefer to involve the S_2 state for the transformation of **10a** in solvents other than acetone. (The small difference in ϕ values in methanol was due to the formation of the side product **12**.) Koppes and Cerfontain arrived at a similar conclusion from their studies on photochemical reactivities of cyclic α-phenyl-β,γ-enones [21].

Quenching of the reaction in acetone by triplet quenchers might be explained in two ways: either **10a**^{*3} was quenched by the quenchers and/or quenching of acetone itself prevented the formation of the excited state of **10a** by energy transfer. In fact, when this experiment was repeated with $\lambda \approx 350$ nm, where acetone was transparent, ϕ remained unquenched in the presence of oxygen. Such an observation suggested, like most of the reported **A** class of compounds, that energy transfer from acetone triplet to **10a** led to the direct formation of a $T_1(\pi,\pi^*)$ state (path (ii)) which then underwent ODPM rearrangement. When this energy transfer path was hindered by using the higher wavelength, route (i) was followed by the ketone.

Next we took up the photochemistry of **10b** where the π bond of the enone was also part of another chromophore. The reason for considering such a system was to examine the effect of juxtaposition of two homoconjugated chromophores in bringing about their photochemical transformations.

Irradiation of **10b** in benzene, methanol and acetone gave a fairly good yield of the ODPM product **11b** (Table 1). In contrast with its monobenzoyl analogue **10a**, phototransformation of **10b** was found to require a much longer time in this case and the yield was also comparatively lower. The structure of the product **11b** was confirmed from its analytical and spectral data. The cyclopropyl H appeared as a double doublet in the NMR spectrum at δ 3.26.

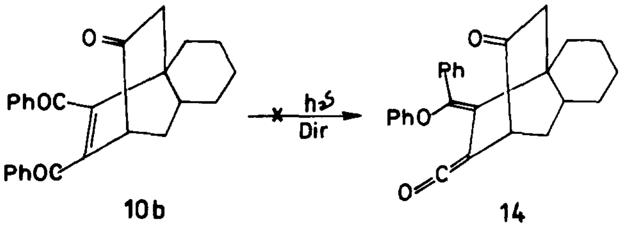
The quantum yields of product formation from **10b** were found to be comparable in benzene, acetone, methanol and acetonitrile ($\phi \approx 0.05$, Table 2). Here again the results of the quenching studies were rather intriguing. While both oxygen and naphthalene were found to quench the phototransformation in acetone, the phototransformations in methanol and acetonitrile were quenched only by oxygen and not by naphthalene. On the other hand, the reaction in benzene remained unaffected by both quenchers. As has been suggested for **10a**, the phototransformation of **10b** in acetone also appeared to proceed from the lowest triplet state via an energy transfer route. Non-quenching of the phototransformation in benzene by the triplet quenchers supported our earlier assumption that an S_2 state was involved in such a case.

It may be argued here that an efficient ISC from the singlet **10b** to a too short-lived triplet state might also give the same results. We disprove this argument as follows. The reaction in acetone was found to be quenched by triplet quenchers, which suggests that the triplet may really not be such a short-lived one. Furthermore, quenching of the phototransformation in acetone by naphthalene ruled out the probability of its lowest triplet state being of lower energy than that of naphthalene. Thus the observation that in polar solvents such as methanol and acetonitrile the reactions were found to be quenched by oxygen but remained unaffected by naphthalene suggested an involvement of a triplet state higher than $T_1(\pi,\pi^*)$ in these cases.

Although involvement of a $T_2(n,\pi^*)$ state to bring about ODPM rearrangement in β,γ-enones [12,13] is considered to be a rather exceptional case, a similar probability has also been considered by Oren and Fuchs [22] to explain the phototransformations in δ,ϵ-unsaturated-β,γ-enones. In fact, in the case of **10b**, quenching of the 1,2-acyl shift by oxygen but not by naphthalene in polar solvents is best explained by involving a higher triplet state, namely $T_2(n,\pi^*)$. This state is likely to be energetically raised in polar solvents and may thus be attained from $S_2(\pi,\pi^*)$ by a favourable ISC. Any effective spectroscopic study could not be taken up with these ketones because of their non-emitting nature.

When the π bonds of bicyclo[2.2.2]oct-2-ene or bicyclo[2.2.2]-oct-5-en-2-one systems are substituted by two benzoyl groups, the photoreactions are mostly reported to occur from the dibenzoylalkene part [23–27]. Surprisingly, from **10b**, no such 1,5-phenyl migration product (**14**) arising from the phototransformation of the dibenzoylalkene part could be identified (Scheme 4).

Substitution of the γ position with an electron acceptor is expected to enhance the ODPM reactivity in rigid β,γ-enones. Thus substitution of a carbomethoxy group at this position has been reported to lead to a sensitized ODPM reaction in bicyclo[2.2.2]-oct-5-ene-2-one [28]. Similar results have also been reported for β,γ-dicarbomethoxy derivatives [26,29]. Since in the case of a highly rigid tricyclic β,γ-dibenzoyl derivative (**10b**) the irradiation results were different from those in a bicyclic system, we took up the case of **10c** to compare its irradiation results.



10b 14

Scheme 4.

Although dicarbomethoxy-substituted bicyclic compounds are reported not to yield ODPM-rearranged products on direct irradiation, a similar tricyclic compound **10c** on irradiation in the presence of benzene, methanol or acetone produced exclusively the ODPM-rearranged tetracyclic product **11c** in moderate yields (Table 1). The structure of **11c** was confirmed from its analytical and spectral data. The cyclopropyl H in **11c** appeared as a double doublet at δ 3.0 in the NMR spectrum.

The quantum yields of product formation were similar in benzene, cyclohexane, acetone and methanol. Triplet quenchers such as oxygen and naphthalene quenched the phototransformation in all cases. Quenching studies indicated a $T_1(\pi,\pi^*)$ state to be involved in all these cases. A rigid geometry probably favoured an ISC from the singlet to the lowest triplet state in this case even on direct irradiation.

Comparing our results and those for the other acyclic δ-keto-β,γ-enones (**1**, **2**, **4–7**), we are tempted to conclude here that the part of the generalization dealing with the tendency of the bicyclic **A** class of compounds to yield ODPM-rearranged products from either an $S_2(\pi,\pi^*)$ or a $T_1(\pi,\pi^*)$ state and not from any other state does not arise because of the inability of these states to undergo such rearrangement; rather, it arises because of the availability of more facile processes from these states. This reasoning might also be valid for other γ-substituted compounds, depending on the nature of the substituent and the rigidity of the molecule. Thus in the case of (E)-1-cyano-3,3,5-trimethylhex-1-ene-4-one the ODPM rearrangement has been concluded to arise from an S_2 or $T_2(n,\pi^*)$ state [30]. On the other hand, the configurational rigidity in **10c** facilitated an ISC from the S_1 state to T_1, favouring an ODPM rearrangement even on direct irradiation.

Acknowledgements

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