Tetrahedron Letters No. 13, pp 1153 - 1156, 1975. Pergamon Press. Printed in Great Britain.

TRIPLET PHOTOSENSITIZATION OF 2-NORBORNENONE AND OTHER β,γ-UNSATURATED KETONES

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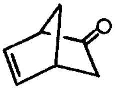
(Received in USA 17 January 1975; received in UK for publication 24 February 1975)

The diversity of photochemical reactions exhibited by β,γ-unsaturated ketones[1] (β,γ-UK's) has prompted us to examine the triplet state properties of some representative compounds. The following conclusions have emerged from this study 1) 2-norbornenone (1) undergoes an unusual triplet sensitized 1,3-acyl shift. 2) The previously reported[2] phosphorescence data for 1 and 2 are erroneous. 3) Formation of an excited complex accounts for much of the interaction between β,γ-UK's and aromatic ketone triplet sensitizers.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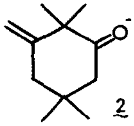
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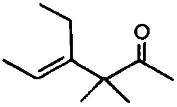
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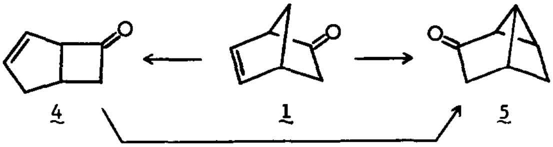
Quantum yields for ketone disappearance and for product appearance in the triplet sensitized irradiation of compounds 1-3 are shown in Table I. Contrary to the usual behavior of β,γ- UK's,[1] triplet 1 gives a considerable amount of the 1,3-acyl shift product 4[3] in addition to the reported[4] oxadi-π-methane product 5. Although one is tempted to attribute this result to singlet sen-



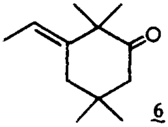

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Table I. Triplet Sensitization of Compounds 1-3

Ketone	Conc., M	Sensitizer	Conc., M	Φ_{-K}[a]	Φ_P[b]	% Reacted
1	0.036	acetone[c]	solvent	0.40	4 0.18, 5: 0.16	25.6
1	0.051	acetophenone[d]	0.021	0.14	4. 0.013, 5: 0.13	71.3
1	0.051	benzophenone[d]	0.068	0.071	4: 0.006, 5· 0.042	45.0
2	0.050	acetophenone[d]	0.20	0.0051	0.00	2.5
2	0.049	benzophenone[d]	0.050	0.0066	0.00	3.3
3	0.10	acetone[c]	solvent	0.24	0.20[e]	26.0
3	0 097	acetophenone[d]	0.066	0.08[f]	0.08[e,f]	6.3
3	0.093	benzophenone[d]	0.057	0.03	0.01[e]	5.1

a) quantum yield for ketone disappearance determined by vpc using internal standards b) quantum yield for appearance of specified product c) irradiated at 313 nm d) irradiated at 366 nm in benzene e) Z-3 f) corrected for incomplete light absorption by sensitizer sitization or to direct light absorption by 1, these explanations are ruled out by the very short singlet lifetime of aromatic ketones[5] and by the fact that 1 does not absorb at 366 nm where benzophenone and acetophenone were irradiated. Only two cases of a triplet sensitized 1,3-acyl shift have been reported previously.[6,7]

When the acetone sensitized photolysis of 1 was monitored by periodic withdrawal of aliquots, it was discovered that the yield of 5 increases dramatically at longer irradiation times, as shown in Figure 1. Similar experiments using acetophenone and benzophenone at 366 nm gave plots of the same general shape, so that the Φ_P values in Table I are valid only for the percent reaction indicated. These results suggest that 4 is rearranged to 5 during the irradiation.[8] One can always write a reasonable mechanism for transformation of a β,γ-UK and its 1,3-acyl shift product to the same cyclopropyl ketone but both reactions have seldom been observed.[9] Its occurrence in the present rigid compounds is expected[10,11] and was confirmed by independent irradiation of 4 with acetophenone. Coupled with the difficulty of separating 4 from 1 by vpc or tlc, the conversion of 4 to 5 explains why the triplet sensitized 1,3-acyl shift was missed in previous work.[4,12]

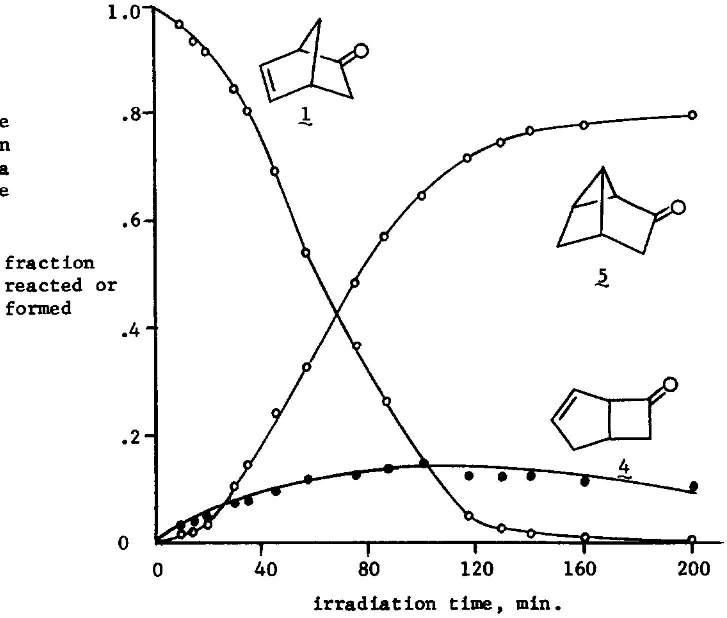

Figure 1. The acetone sensitized irradiation of 2-norbornenone as a function of time. The lamp was turned on at time = 0.

Ketone 2 was essentially inert to triplet sensitization but this material is assumed[11] from studies on 6 to undergo degenerate olefin cis-trans isomerization. Since 3 bears a marked structural resemblance to 6, it is hardly surprising that it also cis-trans isomerizes using all three sensitizers.

An unexpected feature of Table I is the considerably reduced quantum yield of acetophenone sensitization relative to acetone. The triplet energies of 1 and 2 have been reported[2] to lie at 69.5 and 70.7 kcal mol^{-1}. Since acetophenone (E_T = 74 kcal mol^{-1}) should transfer efficiently to these compounds and therefore give as high a quantum yield as acetone, we decided to measure the energy transfer rate constants. This was conveniently done by quenching of aromatic ketone phosphorescence in fluid solution at room temperature.[13] The results of this study, summarized in Table II, immediately show that the rate constants fall short of the diffusion controlled limit by at least an order of magnitude. These values are incompatible with a triplet energy for **1**-**3** of less than 74 kcal mol^{-1}.

Table II. Quenching of Aromatic Ketone Phosphorescence[a]

Sensitizer	Quencher	Conc., M	I_o/I[b]	10^8 k_q, M^{-1} sec^{-1}
acetophenone[c]	diene[d]	2.00×10^{-5}	2.10	70[e]
"	**1**	1.00×10^{-3}	4.97	5.1
"	**2**	1.00×10^{-3}	2.60	2.0[f]
"	**3**	1.00×10^{-3}	1.31	0.39
benzophenone[g]	diene[d]	2.00×10^{-5}	3.17	70[e]
"	**1**	2.00×10^{-3}	1.41	0.13
"	**2**	2.00×10^{-3}	2.10	0.36
"	**3**	1.00×10^{-3}	3.05	1.3

a) solvent--acetonitrile, degassed four times and sealed in quartz cells b) ratio of intensity without quencher to that with quencher c) 0.01 M, excitation λ 346 nm, emission λ 435 nm d) 2,5-dimethyl-2,4-hexadiene e) assumed diffusion controlled value, used to calculate the other entries f) agrees with value determined (1.1×10^8) for quenching of acetophenone photoreduction in isopropanol, calculated using the data of ref. 14 g) 0.005 M, excitation λ 358 nm, emission λ 450 nm

The reported[2] triplet energy of **1** and **2** is based on phosphorescence spectroscopy, however, our independent examination of these compounds gave very different results. By continued purification of **1**, we were able to reduce its emission to essentially zero in EA or MCIP at 77 K. **2** was purified by a) low temperature recrystallization from hexane and then from methanol, b) preparative tlc, and c) preparative vpc, followed in each case by bulb-to-bulb distillation. Using our best sample and a Hitachi MPF-2A phosphorimeter at its maximum sensitivity, the slits had to be opened to 22 nm in order to see any emission. Even then, the excitation spectrum did not resemble the absorption spectrum and the emission spectrum varied drastically with excitation wavelength and solvent. We conclude that the emission was not due to **2** and that phosphorescence spectroscopy provides no information on the triplet energy of this compound.

Comparison of the data in Table I with those in Table II raises the question of why the quantum yields decrease with sensitizer energy while k_q remains large enough that energy transfer should be the predominant fate of triplet sensitizer. Even in the most unfavorable case, the decay rate of benzophenone triplet[15] in benzene is 1.7×10^5 sec^{-1} while the rate of quenching by **1** is $1.3 \times 10^7 \times 0.051 = 6.7 \times 10^5$ sec^{-1}. Thus energy transfer should be 80% efficient and Φ_{-K} should be much higher than the observed 0.071. Furthermore, the acetophenone results suggest that E_T of **1**-**3** lies above 74 kcal mol^{-1}, yet k_q for benzophenone (E_T = 68.9) is far too large for such endothermic energy transfer. These observations suggest that β,γ-UK's can interact with triplet sensitizers in some manner besides energy transfer. Formation of an excited complex $(SK)^{*3}$ is an attractive possibility because even simple olefins are known to quench aromatic ketone triplets with rate constants in the 10^7-10^8 range by this mechanism.[16,17] In the present systems, we postulate that formation of $(SK)^{*3}$ competes with energy transfer to the β,γ-UK. $(SK)^{*3}$ in turn can lead to reaction of sensitizer with the β,γ-UK, as was found in 3,4,5,6,7,8-hexahydronaphthalen-2(1H)-one[18] or to radiationless decay, which would account for the high quenching rates but low quantum yields with benzophenone (cf. Tables I and II). The competition between energy transfer and excited complex formation probably depends on the relative triplet energy of sensitizer and β,γ-UK and on their donor--acceptor properties.

Acknowledgment: The authors are grateful to the National Science Foundation for financial support. We thank Drs. Jeffrey I. Seeman and H. Ziffer for the samples of 2-norbornenone.

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