Photosensitisation in the Photolysis of Saturated Ketones

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The cyclobutanol : fragmentation ratio was measured for the Type II photoreactions of cis-2-propyl-4-t-butyl-cyclohexanone as a function of solvent. The ratio measured for acetone as a solvent is the same as that for the reaction taking place entirely in the triplet state. It is concluded that acetone can photosensitise the triplet state reactions of saturated ketones.

In the work described in the preceding paper,[1] we measured the cyclobutanol : fragmentation ratios in the Type II photochemistry of some saturated ketones. We were particularly interested in separating the ratios for the singlet-state and triplet-state reactions. The former was relatively easy to measure: we simply added piperylene to quench the triplet state reaction in the usual way. For the latter, however, we had to adopt a very time-consuming method, involving both measurements of absolute yields of products as a function of quencher concentration, and extrapolating to zero quencher concentration. It would have been much simpler if we could have adopted the photochemist's usual approach to this problem, which is to use a photo-sensitiser in order to populate only the excited triplet state of the substrate. The problem in our case was that the only photosensitisers which were sure to have a high enough triplet energy to photosensitise saturated ketones (>80 kcal mol^{-1}) were molecules such as benzene. However, it was not easy to use them because of the difficulties of arranging for the photosensitiser to absorb all the light. Furthermore, aromatic molecules can photosensitise singlet-state reactions, so there was no certainty that they would work for our purposes.

One other photosensitiser, namely acetone (E_T 80—81 kcal mol^{-1}),[2] was a possible candidate. It is easy simply by using acetone as the solvent, to ensure tha

[1] I. Fleming, A. V. Kemp-Jones, W. E. Long, and E. J. Thomas, preceding paper.

[2] R. F. Brokman and D. R. Kearns, *J. Chem. Phys.*, 1964, 40 1038.

the sensitiser absorbs most of the light; but in this case the unknown factor was whether acetone had enough triplet energy. Photosensitisation of αβ-unsaturated ketones is very common, and βγ-unsaturated ketones have also been photosensitised by acetone.[3] It is likely that the interactions of the double bonds make such ketones more susceptible to photosensitisation than saturated ketones. Thus E_T for several βγ-unsaturated ketones [4] is in the range 74—78 kcal mol⁻¹.

In this paper we show that acetone can be used to photosensitise the reactions of saturated ketones, and that therefore, we now have a simple method for measuring the cyclobutanol : fragmentation ratios for the triplet state Type II reaction in these compounds.

(1)   (2)
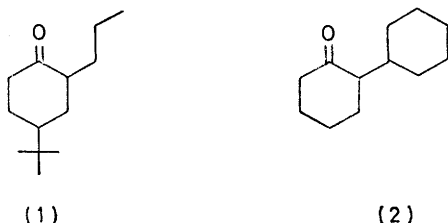
The cyclobutanol : fragmentation ratio in the Type II photochemistry of the ketone (1) is very different in the singlet and triplet states. For the former, in t-butyl alcohol, it is 13 : 87, and for the latter it is 73 : 27.[1] It is therefore potentially a good indicator with which to measure the proportion of reaction going by way of the triplet state.

We have measured the cyclobutanol : fragmentation ratio for the ketone (1) as a function of solvent. The major effect of changing the solvent should be to change the proportion of the reaction going by way of the triplet rather than the singlet state. The more the reaction takes place from the triplet state, the higher will be the cyclobutanol : fragmentation ratio. This assumes that the solvent has a relatively small effect on the ratio in each individual excited state. Such an assumption was justified partly by our observation that the ratio for the singlet state was very similar in t-butyl alcohol (13 : 87) [1] and in piperylene (18 : 82), and partly by the finding [5] that the cyclobutanol : fragmentation ratio in a triplet-state reaction did not change in going from benzene to acetonitrile as a solvent.

The effect of changing the solvent can be seen in the Table. The highest cyclobutanol : fragmentation ratio (76 : 24) is indeed found in acetone; it is actually slightly higher than the value found for the triplet state reaction in t-butyl alcohol (73 : 27), but this could be either experimental error or a small solvent effect on the cyclobutanol : fragmentation ratio in the triplet state. What is clear is that acetone gives a high cyclobutanol : fragmentation ratio neither because it is the most polar solvent (acetonitrile is more polar), nor because it is the most basic solvent (pyridine is a lot

more basic). The lowest cyclobutanol : fragmentation ratio is, of course, that in piperylene. It seems safe to conclude that the reactions in acetone and piperylene are essentially triplet state and singlet state reactions respectively.

Solvent	Dielectric constant	Dipole moment	Cyclo-butanol : fragmen-tation ratio	% Reaction going *via* triplet state [a]
Piperylene-10% t-butyl alcohol			18 : 82 [b,c]	0
Cyclohexane-10% t-butyl alcohol			23 : 77 [b,c]	6 [d,e]
Cyclohexane	2.02	0	28 : 72 [b]	9 [d,e]
Benzene-10% t-butyl alcohol	~2.28	~0	29 : 71 [b,f]	10 [d]
t-Butyl alcohol	10.9	1.66	34 : 66 [g,h]	14 [d]
Hexane	1.89	0.08	46 : 54 [f]	28 [d]
Hexane-10% t-butyl alcohol			50 : 50 [e,f]	3 [d]
Acetonitrile-10% t-butyl alcohol			43 : 57 [h]	24 [d]
Acetonitrile	36.2	3.92	53 : 47 [b,c]	38 [d]
Pyridine-10% t-butyl alcohol	~12.3	~2.19	54 : 46 [c,h,i]	40 [d]
Dioxan	2.21	0	58 : 42 [f]	48 [d]
Dioxan-10% t-butyl alcohol			62 : 38 [c,h]	58 [d]
Acetone	20.7	2.88	76 : 24 [b]	100 [j]
Acetone-10% t-butyl alcohol			82 : 18 [b,c]	100 [j]

[a] 100m_t of equation (1) in ref. 1. [b] Average of two runs. [c] Allowing for further photolysis of the fragmentation product [*i.e.* (3) ⟶ (4) in ref. 1]. [d] Calculated using equation (1) in ref. 1, and assuming that f_s and f_t do not change with solvent. The numbers in this column will not therefore be reliable. [e] Addition of piperylene to this mixture caused no measurable change in the cyclobutanol : fragmentation ratio. [f] One run only. [g] Compare 35 : 65 measured earlier, as described in ref. 1. [h] Average of three runs. [i] Pyridine itself obscured the g.l.c. trace, so the reaction mixture was dissolved in ether, washed with dilute acid, and the ether solution injected into the g.l.c. machine. [j] Since the ratio is >73 : 27, the equation would lead to an answer >100%. The 100% in this column is therefore assumed, see text.

We also measured the cyclobutanol : fragmentation ratio in the photolysis of the ketone (2). In this case, we have [1] only a very approximate value for the triplet state reaction in t-butyl alcohol, somewhere between 70 : 30 and 90 : 10. The cyclobutanol : fragmentation ratio in acetone containing 10% t-butyl alcohol was found to be 80 : 20, confirming that the ratio for the triplet state reaction is indeed in this region.

EXPERIMENTAL

The photolysis conditions, precautions, g.l.c. analysis, and apparatus are described in the preceding paper.[1] Runs were usually reproducible to ±3%. Each solvent was photolysed alone to make sure that no new peaks interfered with the analysis. It is still possible that new photoproducts from reaction of the ketone (1) and the solvent interfered with the analysis, but no changes of peak shapes were observed.

[3] P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, 1972, **94**, 4357.

[4] P. S. Engel, M. A. Schexnayder, and W. V. Phillips, *Tetrahedron Letters*, 1975, 1157.

[5] J. A. Barltrop and J. D. Coyle, *J. Amer. Chem. Soc.*, 1968, **90**, 3584.