Cyclobutanol-to-Fragmentation Ratios for the Singlet and Triplet States in the Photochemistry of *cis*-2-Propyl-4-t-butylcyclohexanone

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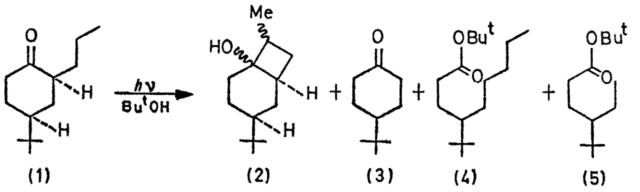
Summary In the Type II photochemical reactions of *cis*-2-propyl-4-t-butylcyclohexanone, the ratio of cyclobutanols to fragmentation products is 13:87 for the singlet-state reaction and 68:32 for the triplet-state reaction, showing that, in the latter state at least, there is a noticeable stereoelectronic effect on the fragmentation reaction.

PHOTOLYSIS of ketones having a hydrogen atom on C-4 is well known[1,2] to give a fragmentation product and a cyclobutanol. These products are now called[1] the Type II products, and both are known to be produced from both the singlet and the triplet states. Recently some interest has been shown in the proportion of these two types of product. One factor which has occasionally been cited[1–3] is the possibility that, in the fragmentation reaction, there is a need for continuous overlap of the orbitals involved. The requirement for cyclobutanol formation is not expected to be so dependent upon the orientation of the 2,3-bond, and hence a high cyclobutanol-to-fragmentation ratio will be expected of ketones in which the 2,3-bond is held more or less rigidly in an orientation unfavourable to fragmentation. Several cases of ketones' giving an unusually high proportion of cyclobutanols have been found,[3,4] most of which can readily, but not uniquely, be explained by this hypothesis.

The ketone we have used is *cis*-2-propyl-4-t-butylcyclohexanone (**1**), which has already been studied briefly by Turro and Weiss.[5] This ketone has the fragmenting bond equatorial in the cyclohexane ring. It is, therefore, unfavourably oriented for fragmentation; yet Turro and Weiss observed fragmentation and did not report on the formation of any cyclobutanols. On photolysis in degassed t-butyl alcohol,[†] this ketone gave seven identifiable products: all four possible cyclobutanols (**2**), 4-t-butylcyclohexanone (**3**) (the fragmentation product), and two t-butyl esters (**4** and **5**) (the Type I products from **1** and **3**). There was no detectable aldehyde production, although aldehydes are usually major products;[6,8,9] but small amounts of two unidentified products have not been characterised.



When piperylene was added, very little of the Type I products (**4** and **5**) was produced; it had been expected, on the basis of earlier reports[6,8] that these products with cyclohexanones are formed from the triplet state. Moreover, in the presence of piperylene two of the cyclobutanols were not produced, and the ratio of cyclobutanols to fragmentation products was changed from 35:65 for the unquenched reaction to 13:87 for the quenched. If, as is usual, we equate the unquenchable reaction with singlet-state reaction, we can see that the cyclobutanol-to-fragmentation ratio (13:87) is not very different from that usually observed for the singlet-state reaction of open-chain ketones (*e.g.* 7:93 for hexan-2-one,[10]

[†] Medium-pressure mercury lamp, Pyrex apparatus, 27°; the quantum yield for unquenched fragmentation was approximately 0·05, in line with the low values (0·016—0·04) found[6] for other 2-alkylcyclohexanones. Turro and Weiss used cyclohexane as a solvent. A change to t-butyl alcohol is expected[7] to increase the quantum efficiency of the triplet-state reaction but to have little effect on the singlet-state reaction. It is also expected to reduce somewhat the cyclobutanol-to-fragmentation ratio for the triplet-state reaction.

2 98 for octan-2-one,[7b] and 10:90 for octan-4-one[7c]) Thus the unpropitious orientation in this case would not seem to be much of a constraint upon the singlet-state reaction

A Stern–Volmer plot between 0 5M and 1·7M piperylene had a slope of 0 04,‡ which probably represented singlet quenching [11] Extrapolation to zero concentration of quencher indicates that 15% of the fragmentation reaction is taking place from the triplet state § From this figure of 15%, we calculate that the cyclobutanol-to-fragmentation ratio for the triplet-state reaction is 68:32 This ratio is clearly higher than those usually found for the triplet-state reaction in open-chain ketones (*e g* 30:70 for hexan-2-one [10] 13:87 for octan-2-one,[7b] 16:84 for octan-4-one,[7c] and between 10:90 and 20.80 for valerophenone[3a 13]) Thus the unpropitious orientation in this case is a much more noticeable constraint upon the triplet-state reaction than upon the singlet-state reaction We also note that the least equivocal examples[3a–d] in the literature, in which the orientation of the fragmenting bond has been seen to affect the ratio, are reactions which are solely from the triplet state

The singlet-state reaction, whether it is concerted[1] or not,[12b 13–15] is so exothermic that it is relatively insensitive to the orientation of the orbitals, the triplet-state reaction, on the other hand, is likely to be less exothermic and to have a higher activation energy for both closure and fragmentation reactions of the intermediate diradical [15] This would explain the fact that the cyclobutanol-to-fragmentation ratio is generally higher for the triplet-state reaction than for the singlet-state reaction Our ratios, derived from the ketone (**1**), are higher than those of open-chain ketones for the triplet-state reaction, and they are probably higher for the singlet-state reaction too If so, it may be that in energetic terms an orientation unfavourable to fragmentation affects the singlet-state reaction and the triplet-state reaction equally Because the triplet-state reaction in open-chain ketones generally has the higher cyclobutanol-to-fragmentation ratio (30:70 for hexan-2-one), any change in that ratio is more noticeable than a similar change in the smaller ratio (7:93 for hexan-2-one) of the singlet-state reaction We cannot, therefore, conclude that the singlet-state reaction is insensitive to the orientation of the fragmenting bond, but the errors both in our work¶ and in the work of others, and the uncertainty over the choice of a representative open-chain ketone, do leave our results open to that interpretation Perhaps the most striking outcome of our work, in addition to the clear observation that at least the triplet-state reaction is affected by the orientation of the fragmenting bond, is how small a constraint this feature is in energetic terms, apparently little more than about 1 kcal /mole

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‡ The small slope of our Stern–Volmer plot for singlet quenching is reasonable, since t-butyl alcohol is more viscous than the solvents used[11 12] in earlier work where slopes in the range 0 08 to 0 26 have been reported.

§ Turro and Weiss found that the fragmentation was "unaffected by up to 0 9M piperylene" in their solvent, cyclohexane.

¶ The ratios measured, and the derived ratios reported here, are all reproducible to within 2—3%.

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