The Type 2 Photoelimination Reaction of 2-Alkylcycloalkanones

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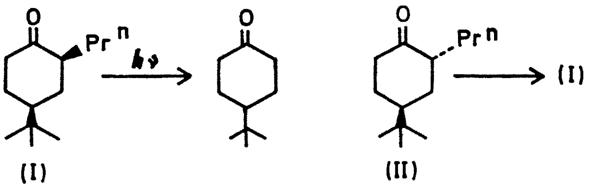
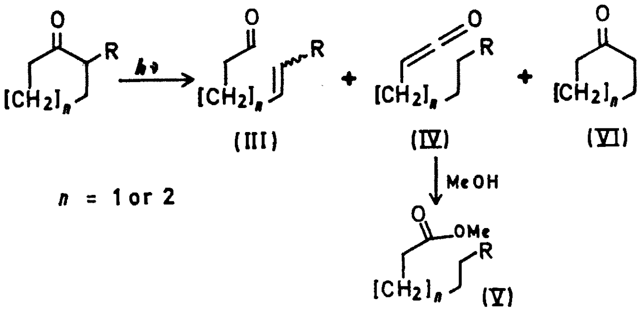
Summary A type 2 photoelimination reaction occurs in both the singlet and triplet excited states of certain 2-alkyl-cyclopentanones and -cyclohexanones, and the rate constant for the reaction of triplet 2-isobutylcyclopentanone is not significantly different from that for an acyclic ketone.

THERE are few reports[1-4] of the Norrish type 2 photoelimination reaction for simple 2-alkylcyclohexanones. Turro and Weiss[4] report that *cis*-2-n-propyl-4-t-butylcyclohexanone (I) gives 4-t-butylcyclohexanone on photolysis, whereas the *trans*-isomer (II) undergoes only a slow photoepimerisation to (I) under the same conditions, and conclude that there is a stereoelectronic requirement for the type 2 process. The work described here concerns the type 2 photoelimination in the solution-phase photochemistry of 2-alkyl-cyclopentanones and -cyclohexanones. Alkyl-substituted cyclopentanones and cyclohexanones were prepared, and irradiated in solution in benzene or methanol using light of wavelength *ca.* 300 nm. The products were the expected unsaturated aldehyde (III), the ester (V) derived by attack of methanol on the first-formed keten (IV), and, in some cases, the unsubstituted cycloalkanone (VI). The percentage yields of type 2 product based on the total amount of identified product (aldehyde + ester + type 2 product) are given in Table 1.





If it is assumed that the overall rate constant for formation of ring-opened products is approximately constant for a given ring-size, then two trends are apparent. First, that as the hydrogen which is abstracted in the type 2 process is changed from primary to secondary to tertiary, so the type 2 process competes more effectively with the formation of ring-opened products. This reflects an increase in the rate of the hydrogen-abstraction process as the C–H bond broken in the abstraction step becomes weaker, and a similar result was found in the acyclic systems.[5] The second trend is that as the number of abstractable hydrogens of a given type is increased, so the type 2 process again competes more efficiently with the other processes. This effect is much greater than would be expected on simple statistical grounds, doubtless because of the intervention of a conformational effect associated with the 2-substituent.

TABLE 1. *Percentage of type 2 elimination product*

Substituent	Cyclopentanone	Cyclohexanone
2-Et[a]	< 1	< 1
2-Et-4-Bu^t	—	< 1
2-Pr^n	< 1	65
2-Pr^i	< 1	14
2-Pr^i-5-Me	—	17
2-Bu^i	20	77
2-Bu^t	—	49

[a] Measured in benzene as solvent; other compounds measured in MeOH.

The type 2 process is less favoured in the cyclopentanone than in the cyclohexanone series, and the observation that the ring-opening process for a cyclopentanone has a higher rate constant than the same process for the corresponding cyclohexanone[6–8] is sufficient to account for the observed differences if the rate constant for abstraction of a given type of hydrogen is of the same order of magnitude for the two ring-sizes. The present result that 2-n-propylcyclopentanone does not undergo a type 2 reaction to any appreciable extent in solution is in agreement with the finding of Turro and Weiss,[3] and in contrast to the results obtained by Srinivasan[2] for the photolysis of the neat liquid.

The type 2 reaction could be only partially quenched using piperylene as a triplet quencher, so that both singlet and triplet excited states of the ketone are involved in this reaction, as in the acyclic systems.[5,9] A major difference between the cyclic and acyclic systems is that, for a given type of abstracted hydrogen and a given solvent, there is a greater percentage of singlet reaction in the type 2 processes for the cyclic systems. The quenching of the triplet part of the type 2 reaction follows Stern–Volmer kinetics, and the Stern–Volmer slopes (Table 2) are in each case the same within experimental error as those for the other triplet processes (formation of aldehyde and formation of ester).

TABLE 2. *Stern–Volmer slopes* (M^{-1}, MeOH *solvent*)

2-Bu^i-cyclopentanone	..	0·9
2-Pr^n-cyclohexanone ..	..	6—7
2-Bu^i-cyclohexanone ..	..	13
2-Bu^t-cyclohexanone	..	10—11

These slopes are equal to the ratio of rate constants $k_q/\Sigma k_T$, where k_q M^{-1} sec.$^{-1}$ is the bimolecular quenching rate constant, and Σk_T sec.$^{-1}$ is the sum of the rate constants for the unimolecular processes undergone by the triplet state. If the difference between the slopes for 2-isobutylcyclopentanone (0·9 M^{-1}) and for 2-ethyl- or 2-n-propyl-cyclopentanone (1·4 or 1·2 M^{-1}) arises solely because of effective competition of the type 2 process in the isobutyl compound, a value of 1—2 $\times$ 10^9 sec.$^{-1}$ can be estimated for the rate constant for hydrogen-abstraction in 2-isobutylcyclopentanone (using a value of 5×10^9 for k_q). This is remarkably similar to the value for the rate constant for abstraction of a tertiary hydrogen in the acyclic methyl ketones (1×10^9 sec.$^{-1}$).[5]

It is difficult to assess the effect of solvent on the type 2 process in these systems because of the secondary reactions undergone by the type 2 product even at quite low conversions. The substitution of methanol for benzene as solvent for the photolysis of 2-n-propylcyclohexanone leads to an increase in the quantum yield of triplet type 2 reaction whilst the singlet type 2 reaction remains unaffected.

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