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Evidence for a Discrete Biradical Intermediate in the Photolysis of 2,3-Dimethylcyclohexanone

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Summary The photolysis of *cis*- and *trans*-2,3-dimethylcyclohexanone in methanol–benzene leading *via* the triplet state to the ester (E) and aldehydes (A) is shown by kinetic analysis probably to proceed through a common discrete biradical (R) which is also responsible for the photoepimerisation: quantitative data bearing on the fate of the biradical are provided.

There are conflicting reports in the literature[1–5] as to whether the photochemical ring-opening and hydrogen-transfer reactions of cycloalkanones are concerted or stepwise in nature. Recent results[3] for 2-methylcyclohexanone were taken to indicate that the process is stepwise, but the fact that a mixture of geometrical isomers of the unsaturated aldehyde is formed, and not a single isomer as was originally reported,[4,5] is not sufficient evidence to prove a non-concerted pathway, since there may be two concerted pathways involving different conformations of the excited state or involving the transfer of hydrogen from conformationally different positions. We present evidence which more strongly supports the biradical mechanism, and which shows that photoepimerisation[1,6] occurs through the same biradical.

We partially separated the *trans*- and *cis*-isomers of 2,3-dimethylcyclohexanone, (I) and (II), by preparative g.l.c., and irradiated them in solution in 2·8% v/v methanol in benzene in a merry-go-round apparatus under conditions of equal light absorbance. Figures 1 and 2 show the variation of reactant and product concentrations with time. In both irradiations the same ratio (1·0 : 2·1) of stereoisomers of the unsaturated aldehyde was formed, and, unless the ratios of two concerted pathways for each epimer are fortuitously equal, this strongly suggests a mechanism involving a common (biradical) intermediate.

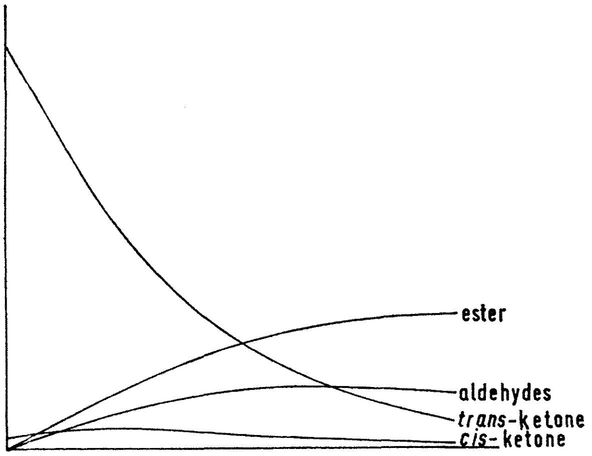


Figure 1. *Irradiation of* trans-2,3-*dimethylcyclohexanone.*

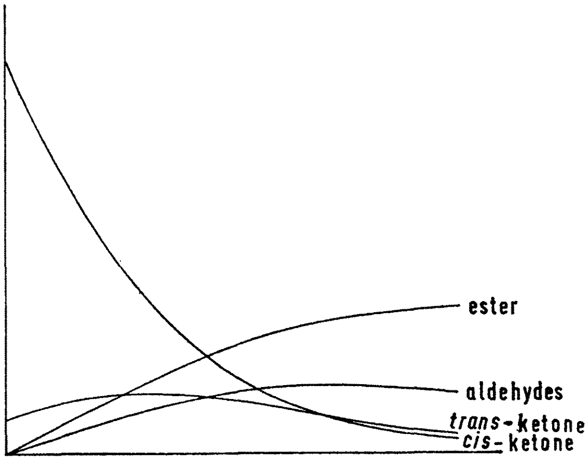
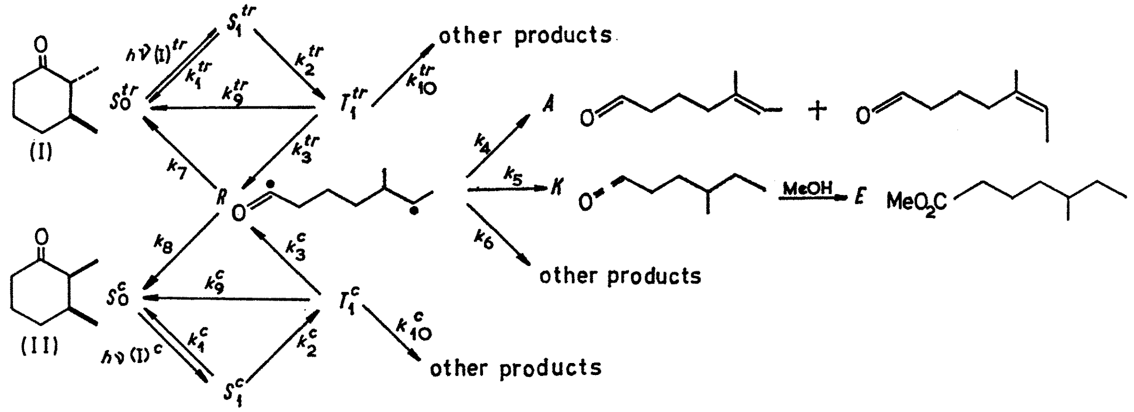


Figure 2. *Irradiation of* cis-2,3-*dimethylcyclohexanone*



SCHEME

A reaction scheme can be set up and kinetic equations derived. S_0, S_1, T_1 represent the ground state, first excited singlet state, and lowest triplet state of the ketone, and the superscripts *tr* and *c* refer to the *trans-* and *cis*-isomers. *R* represents the biradical intermediate, *A* the mixture of unsaturated aldehydes, *K* the keten primary product, and *E* the ester into which it is converted. Quenching experiments show that all the photoisomerisation processes occur through the triplet state. Application of the steady-state approximation to the species S_1^{tr}, S_1^{c}, T_1^{tr}, T_1^{c} and *R* leads to useful expressions for the rates of formation of the different species if it is assumed that $[k_2^{tr}/k_2^{tr} + k_1^{tr})]$ $[k_3^{tr}/(k_3^{tr} + k_9^{tr} + k_{10}^{tr})] = [k_2^{c}/(k_2^{c} + k_1^{c})]$ $[k_3^{c}/(k_3^{c} + k_9^{c} + k_{10}^{c})]$. This assumption is justified on the grounds that the initial rate of formation of either ester or aldehyde is the same for both epimers of the starting ketone.

The measured values of the initial slopes of the time curves for each species enable consistent ratios of the rate constants k_{4-8} to be calculated, and the results in their most useful form are:

$$k_4/k_5 = 0{\cdot}65$$
$$k_7/k_8 = 2{\cdot}6$$
$$(k_7 + k_8)/(k_4 + k_5 + k_6 + k_7 + k_8) = 0{\cdot}33$$
$$k_6/(k_4 + k_5 + k_6) = 0{\cdot}40$$

Thus approximately one-third of the biradicals undergo ring-closure to the ground-state ketones, and the preference for closure to the *trans*-ketone over closure to the *cis*- involves a factor of 2·6 [*cf.* the thermal equilibrium[7] of (I) and (II) which leads to a *trans*:*cis* ratio of about 4·0]. Since the measured total yield of aldehydes and ester based on ketone consumed is about 60%, and since k_6 is approximately 40% of $(k_4 + k_5 + k_6)$, it seems that all the photoreactions of the ketones occur through the biradical, and that the triplet does not undergo reactions other than ring-opening to any great extent.

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