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# THE ROLE OF SINGLET AND TRIPLET STATES IN THE PHOTOCHEMISTRY OF EUCARVONE[1]

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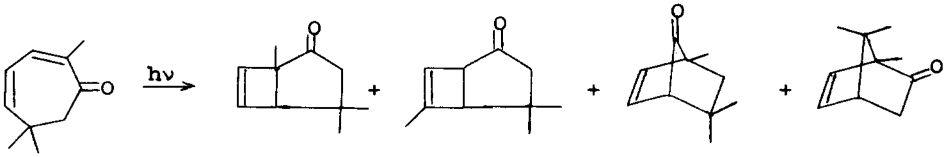
Previous investigations have shown that eucarvone (1) is slowly converted photochemically into a mixture of isomers (2-5) whose composition is solvent dependent.[4,5,6] Mechanisms have been suggested for these isomerizations, although no work has been reported specifying the nature of the excited states and intermediates involved in these reactions. This paper concerns details of the conversion of 1 to 2, which is the main reaction of eucarvone in all twelve of the solvents studied.



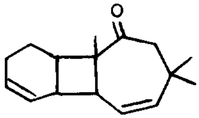
1 2 3 4 5

The quantum yield $\varphi$ for formation of 2 from 1 in benzene at 313nm is $2.5 \times 10^{-3}$, at a conversion of 1.4% of eucarvone. Competitive photolyses of 1 in a merry-go-round (MGR) apparatus[7] (Pyrex filter) indicate that $\varphi$ for disappearance of 1 increases in polar as opposed to non-polar solvents, but the material balance in terms of products 2-5 is poorer in the polar media. In dioxane-water mixtures, the formation of other products, not identified, increases with the water content. The solvent effect supports the contention that dipolar intermediates are involved in these reactions.[4,5,6] The absence of hydrogen abstraction reactions in good H-donor solvents (e.g., toluene and 2-propanol) supports this suggestion. From the absorption spectra, the lowest triplet is expected to have a $\pi,\pi^*$ configuration.

Conversion of 1 to 2 could be effected with triplet sensitizers with $E_T$ greater than 62 kcal/mole,[8] while quenching was observed with compounds when $E_T$ is less than 61 kcal/mole, suggesting that $E_T$ for eucarvone is 61 ± 1 kcal/mole. The efficiency of reaction using high energy sensitizers was not different from that on direct photolysis, indicating that the inefficiency of the conversion of 1 to 2 is mainly due to processes occurring after intersystem crossing to the triplet manifold.

Quantitative quenching experiments in benzene (MGR) were carried out with 1,3-cyclohexadiene ($E_T$ 54)[9] and piperylene ($E_T$ 57-59),[9,10] following the extent of formation of 2 by careful glc analysis, with only 4.3% conversion to 2 in tubes without added quencher. With both quenchers, efficient quenching was seen at low quencher concentrations (Stern-Volmer slope 110 $M^{-1}$), but the plots leveled off to a constant value of $\Phi_o/\Phi$ below 0.01 M quencher. Such an effect has been seen in other systems,[11,12] and indicates formation of product from two excited states, only one of which is quenchable. The simplest explanation is that both singlet and triplet excited states are reactive intermediates in formation of 2 from 1, with about 60% reaction from the singlet. By subtracting the singlet contribution, a linear Stern-Volmer plot was constructed for the triplet part of the reaction, with a slope of 380 $M^{-1}$ for both quenchers. This slope is significantly higher than that found in the total quantum yield plots, which is to be generally expected, although this has not always been taken into account in calculating triplet rate constants.[11] From this latter slope, using a diffusion-controlled quenching rate constant of $5 \times 10^9$ $M^{-1}$ $sec^{-1}$, a triplet lifetime of $7.6 \times 10^{-8}$ sec is calculated. From $\Phi_{triplet}$ of $1.03 \times 10^{-3}$, rate constants $k_{rT}$ (isomerization of the triplet) $= 1.4 \times 10^4$ $sec^{-1}$ and $k_{dT}$ (triplet decay) $=$ $1.3 \times 10^7$ $sec^{-1}$ are calculated. The latter seems high for triplet radiationless decay to the ground state,[13] and is consistent with a triplet relaxation process involving twisting around the double bonds.[14]

Quenching of eucarvone triplets by 1,3-cyclohexadiene (CHD) gave in addition to CHD dimers (the expected products of triplet energy transfer to CHD)[15] two new products in the ratio 10:1 which were isolated by column chromatography. The major component was shown by mass spectroscopy to be a 1:1 adduct of CHD and 1. Spectral data on the adduct indicated that the carbonyl group was unconjugated and, with hydrogenation data, indicated that there were two double bonds. The complete analysis allowed assignment of structure 6 to the adduct. Photolysis of eucarvone with cyclohexene gives a product which on hydrogenation gives the same product as hydrogenation of 6, and furthermore photolysis of 2 in the presence of CHD gives a product other than



6

6, so that several other possible structures for 6 could be excluded. The minor product 7, m/e 310, is an adduct of 1 to two molecules of CHD, but photolysis of 6 in the presence of excess CHD gives a mixture of oxetanes and no 7.

If the formation of adduct 6 and triplet energy transfer from 1 to CHD to give ultimately diene dimers[15] take place from the same excited state, the ratio of the yields of 6 and diene dimers ought to remain the same as the CHD concentration is increased. On the other hand, if triplet 1 gives an intermediate (e.g., a *cis, trans* isomer of 1)[17,18] which is a precursor of 2 and 6, the ratio of adducts to diene dimers ought to decrease with increasing CHD concentration. The results of a careful glc analysis of the photolysis reaction products in thoroughly degassed solutions of 1 in benzene as the CHD concentration was increased show a smooth *increase* in the ratio of 6 + 7 to the diene dimers, from a value of 1.45 at 0.001 M CHD to 5.3 at 0.100 M CHD*. This result indicates that the major adduct 6 arises from an intermediate which is a precursor to that triplet state of 1 which can transfer triplet excitation to CHD. Since the Stern-Volmer plots level off at high CHD concentrations, the possibility is excluded that the precursor to 6 is a singlet state. It therefore appears that adduct 6 arises from reaction of an upper triplet state with CHD. Although reactions of ketones *via* upper triplet states have been postulated in some cases,[19,20] this was not a totally satisfactory hypothesis, and in at least one instance this proposal has since been discredited.[14,21] The postulate of involvement of upper triplets in the photochemistry of 1 therefore must be considered tentative, and will be the subject of further investigation.

*Following completion of this work, a similar result was reported with propionaldehyde: T. Kubota, *et al*, Chem. Commun., 1462 (1969).

Full details of this study will be published elsewhere.

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