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THE NATURE OF THE REACTIVE EXCITED STATES IN THE PHOTOCHEMICAL BÜCHI REARRANGEMENT OF BICYCLO [3.2.0]HEX-6-EN-2-ONES[1]

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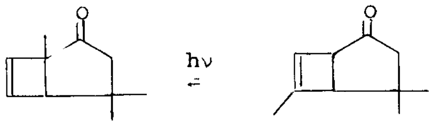
The photochemical sigmatropic change of order [1,3] shown in the equilibration of compounds 1 and 2 was first observed by Büchi and Burgess,[4] and has since been shown to be a general reaction of bicyclic β,γ-unsaturated ketones.[5] Our observations bear on the mechanistic details of this type of photochemical rearrangement, and are of interest in comparison with recent related reports from other laboratories.



1 2

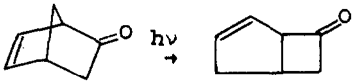
Compound 1 was prepared by photoisomerization of eucarvone.[4,6] The quantum yield for isomerization of 1 to 2 at 313 nm in benzene was found to be 0.041, with the conversion below 5.0%. The reaction could be effected in a wide variety of solvents, with extensive side reactions occurring in methanol, ethanol, highly aqueous dioxane-water mixtures, chloroform and carbon tetrachloride, using Pyrex-filtered light. In all solvents, the equilibrium mixture of 1 and 2 was well on the side of 2, in contrast with the earlier report[4] that the equilibrium was 4:1 in favor of 1.[*] The ratio of 1:2 was accurately determined by glc in comparison with prepared mixtures of pure 1 and 2, and the analyses were reproducible.

[*] Note, however, the discrepancy in ref. 4 in this ratio as reported in the text and in the experimental section.

Triplet sensitization studies were carried out on a merry-go-round apparatus[7] using Pyrex-filtered light, with solutions such that the sensitizers absorbed greater than 90% of the incident light. Sensitization was observed with triplet sensitizers of triplet energy above 65 kcal/mole, while quenching was seen with compounds whose triplet energy was below 62 kcal/mole. The triplet energy of 1 can therefore be estimated at 63 ± 1 kcal/mole.

Quantitative quenching experiments were carried out using piperylene and 1,3-cyclohexadiene, and as in similar studies of the eucarvone photoisomerization[6] curved Stern-Volmer plots were obtained. From the plateau value of Φ_o/Φ , one can determine that the isomerization originates from the singlet state to the extent of 74% (cyclohexadiene data) to 78% (piperylene data), with the balance of reaction from a quenchable triplet state. The fact that triplet energy transfer occurred was confirmed by formation of cyclohexadiene dimers,[8] detected by glc. There were significant differences between the initial slopes in the Stern-Volmer plots, indicating more efficient quenching by 1,3-cyclohexadiene, ($k_q\,\tau = 34.1$) than piperylene ($k_q\,\tau = 25.2$) consistent with results with a number of other cyclic unsaturated ketones.[9] However, these initial slopes are only lower limits to the true Stern-Volmer slopes for triplet quenching, as noted earlier.[6] Quenching plots for the triplet portion of the reaction alone[6] could not be constructed in this case because of the imprecision of the difference between total and singlet quantum yields, since the singlet contribution to reaction is close to 80%. This precluded the calculation of meaningful triplet lifetimes and rate constants for triplet processes.

These data are to some extent in disagreement with data on some related β,γ-unsaturated ketones. It was recently reported[10] that the photochemical [1,3] sigmatropic rearrangement of 3 to 4[11] can not be brought about using triplet sensitization, which leads instead to a new product derived from 3. Also, the photochemical 1,3-acyl shift in 5, which leads to racemization of optically active starting material, can not be quenched by piperylene or naphthalene, and triplet sensitized reaction of 5 again leads to a new product.[12] In both instances, it is concluded that the [1,3]-sigmatropic rearrangement occurs exclusively from the excited singlet state, and that intersystem crossing to the triplet on direct excitation of 3 or 5 is of negligible importance. Detailed quantum yield and quenching data in both cases will be needed before meaningful comparison with our somewhat conflicting results on the interconversion of 1 and 2 can be made.



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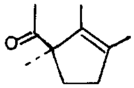

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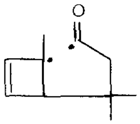
Photolysis of 1 in benzene in the presence of excess 1,3-cyclohexadiene did not give cyclobutane-type adducts as found with eucarvone.[6] It was concluded that oxetanes were formed on the basis of disappearance of the carbonyl band in the infrared spectra of the isolated adducts and the appearance of strong bands at 1040-1050 cm^{-1} characteristic of oxetanes.[13] No further structural studies were carried out on these compounds. This difference in behavior is probably due to a change in configuration of the reactive triplet from π,π^* for eucarvone[6] to n,π^* in the case of 1.

The lowest excited singlet state of 1 is clearly an n,π^* state, from the absorption spectrum of 1, λ_{max}^{MeOH} 303 nm, ϵ 174. Since the quantum yield for reaction from the singlet is approximately 0.03, intersystem crossing to the triplet manifold is probably 97% efficient, assuming no radiationless decay from the excited singlet. Apparently decay to the ground state from the lowest triplet state competes effectively with photoisomerization. Ring cleavage of the triplet to give a diradical 6 may be reversible, regenerating 1 in its ground state in competition with rearrangement to 2. Such an effect has been proposed to explain the observed inefficiency of photoreactions of a number of cyclopentanones and cyclohexanones in solution.[14]

Full details will be published elsewhere in the near future.



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