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PHOTOCHEMISTRY OF CYCLOBUTANECARBOXALDEHYDE

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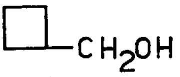
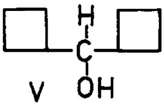
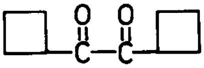
The gas phase photolysis of aliphatic aldehydes and ketones has been studied extensively.[1] Relatively little attention has however been paid to the photochemistry of aliphatic aldehydes in solution. Some quantitative studies on the Norrish type II process of non-cyclic aliphatic aldehydes have been made by Coyle.[2] Therefore we began systematic attempts to study the photolysis of cycloalkanecarboxaldehydes. Preliminary results on the photolysis of cyclopropanecarboxaldehyde in solution have been reported by Overwater.[3]

We now report on the liquid phase photolysis of cyclobutanecarboxaldehyde (I), which is the first cyclic aldehyde with γ-hydrogens and which therefore would allow a Norrish type II process. Oxygen free solutions of I (0.3 M) in benzene or neohexane were irradiated with a 300 nm source.[4] The identified products were: carbon monoxide (II), cyclobutane (III), cyclobutylmethanol (IV), dicyclobutylmethanol (V), dicyclobutylethanedione (VI) and 1,2-dicyclobutyl-1-hydroxyethanone (VII). The compounds II and III were identified on the basis of their GSC- and GLC-retention times respectively by comparison with authentic samples.[5] The compounds IV - VII were isolated by preparative GLC and their structures assigned on the basis of IR-, NMR- and mass spectra. These products account for ~70% of the converted cyclobutanecarboxaldehyde. No evidence for the formation of the possible Norrish type II products 4-pentenal and bicyclo-[1.1.1]pentan-2-ol was obtained, the upper limit being 1% of the sum of the primary products V and VII.


IV


V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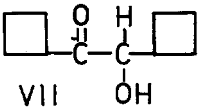

VII

The dependence of the formation of the non-gaseous products on the photolysis time was determined at -60°, 0° (neohexane), 40° (neohexane and benzene), and 60° (benzene).[6] The results are the same for benzene and neohexane. The results for 0° and 40°C are shown in Fig. 1. For the compounds IV and VI there is an induction period; these compounds are apparently formed in secondary reactions probably from VII (cf. the relative amounts of IV, VI and VII).

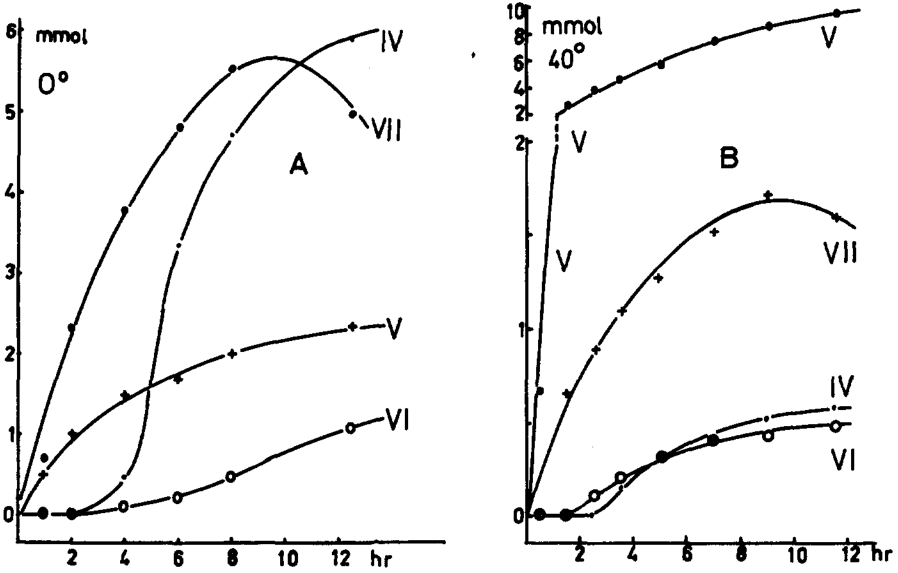


Fig. 1 Dependence of product formation on irradiation time.

Information about the nature of the excited state(s) leading to the reaction products was obtained by carrying out the photolysis in the presence of the triplet quenchers cis-piperylene and naphthalene. In the presence of a sufficient amount of each quencher, the formation of III, IV, V and VI was completely suppressed, while the formation of VII was only partially reduced. Apparently III - VI are most probably formed from the excited triplet state, and VII from both the singlet and triplet state. The Stern-Volmer plot[7] for the formation of III, using cis-piperylene as quencher, is shown in Fig. 2. The triplet lifetime τ_T was calculated from the slope of Fig. 2 to be 70 ns.

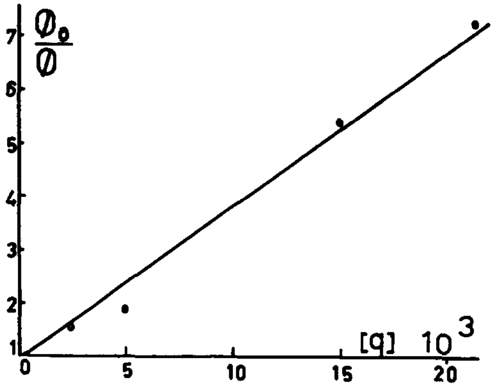
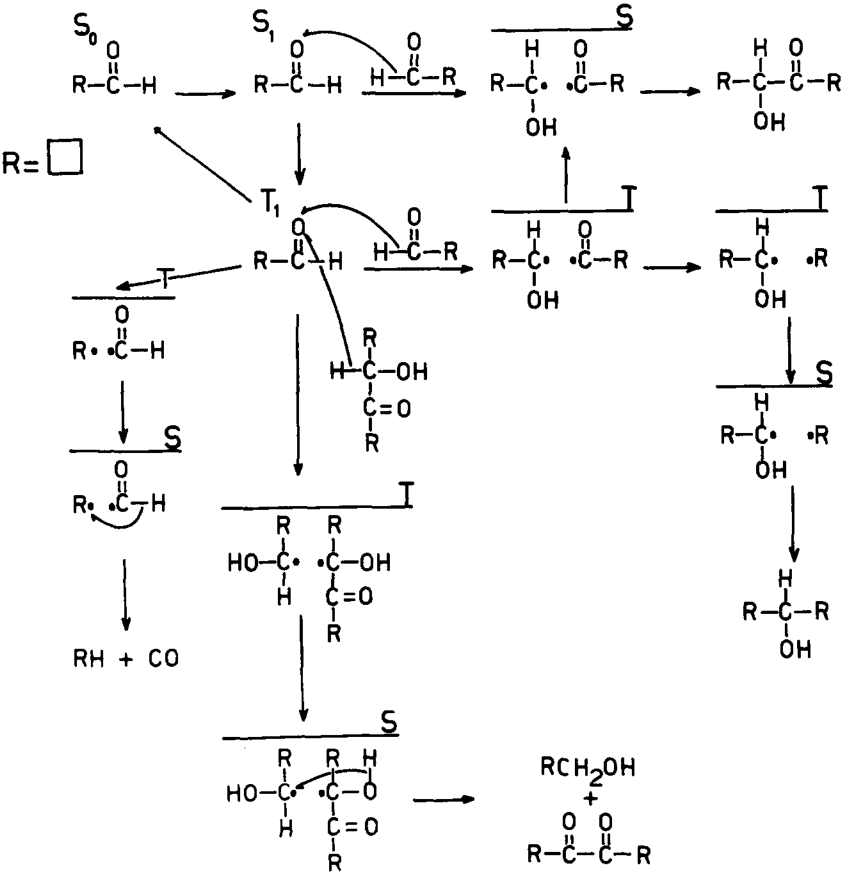
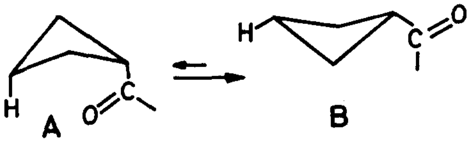


Fig. 2 Stern-Volmer plot for the formation of cyclobutane.

The yield of the products III - VII was found to be the same for benzene and for carbon tetrachloride as solvent. As carbon tetrachloride is a well-known radical scavenger,[8,9] this result implies that the formation of III - VII does not involve free radicals. This leaves the possibility of a concerted type of reaction, or of a reaction via radical pair intermediates. The present experiments do not permit us to express a preference for one of these possibilities. For the photolysis of benzaldehyde Cocivera[9] and Closs[10] have established by CIDNP the presence of a triplet type intermediate radical pair. Furthermore it is well established that excited carbonyl compounds very efficiently abstract hydrogen from suitable donors, with formation of ketyl radicals. We therefore incline towards the radical pair explanation. The formation of the reaction products can then be formulated as :[11]



With cyclobutanecarboxaldehyde there is no evidence for γ-H abstraction by the carbonyl group. This result may be explained in terms of the conformation(s) of excited I. The cyclobutane ring is puckered by about 30°. This implies that (excited) I can occur in two conformations, A and B. We may expect that only a small fraction of I is in the conformation A, in which γ-H abstraction can proceed via a favourable six membered ring transition state. In fact, a very low rate for γ-H abstraction has also been reported for cyclobutyl phenyl



ketone,[13] the unimolecular rate constant being only k_r=5.5 x 10^3 sec^{-1}. This low rate has been explained by the almost exclusive occurrence of conformer B. exo-5-Benzoylbicyclo[2.1.1]hexane, on the other hand, which is locked in the A conformation, has a relatively high unimolecular rate constant for γ-H abstraction, viz. k_r=3.9 x 10^8 sec^{-1}.

The absence of γ-H abstraction also accounts for the longer triplet lifetime of the present substrate (70 ns), compared with that of hexanal[2] (6.2 ns).

Acknowledgements

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References

1. J.G. Calvert and J.N. Pitts "Photochemistry", Wiley, 1966, pg 368 - 427.
2. J.D. Coyle, J.Chem.Soc.(B), 2254 (1971).
3. J.J.I. Overwater, Thesis (University of Amsterdam) 1969, chapter 7.
4. Rayonet Photochemical Reactor with merry-go-round attachment (MGR-100).
5. CO was identified on 0.75 m column molsieves 5A + 4.5 m Porapak Q, at 25°, cyclobutane was identified on 10 m column 33% dimethylsulfolane, at 0°.
6. GLC analysis was carried out on 1.8 m column 3% SE-30, at 50 - 150°.
7. N.J. Turro, "Molecular Photochemistry", Benjamin, 1967, p 94.
8. S. Winstein and F.H. Seubold, J.Amer.Chem.Soc., 69, 2916 (1947).
9. M. Cocivera and A.M. Trozzolo, ibid. 92, 1772 (1970).
10. G.L. Closs and D.R. Paulson, ibid. 92, 7229 (1970).
11. The ratio of the secondary products IV and VI increases significantly with increasing irradiation time. This may be explained in terms of disappearance of VI by e.g. photodihydrodimerization.[12]
12. J. Kelder and H. Cerfontain, Tetrahedron Lett., 1307 (1972).
13. A. Padwa and W. Eisenberg, J.Amer.Chem.Soc., 94, 5852, 5859 (1972).