Tetrahedron Letters No.10, pp. 1255-1259, 1968. Pergamon Press. Printed in Great Britain.

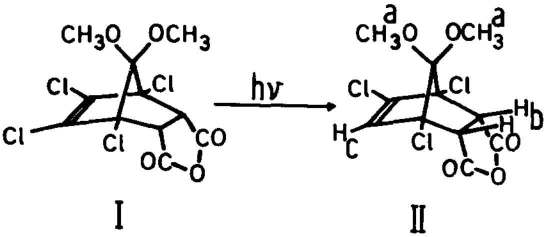
REACTION-PATH SELECTIVITY : CAGE FORMATION VERSUS PHOTODECHLORINATION IN SOME ALICYCLIC SYSTEMS.

C.M. Anderson, J.B. Bremner*, I.W. McCay and R.N. Warrener†

Department of Chemistry, School of General Studies,
Australian National University, Canberra, A.C.T. 2600,
Australia.

(Received in UK 28 November 1967)

Although a number of polychlorinated cage structures have been synthesised via photocycloaddition processes (1), it has only recently been observed that photodechlorination sometimes occurs (2). In our own studies related to the influence of substituents and leaving groups on the photo-aromatisation of cyclohexa-1,3-diene derivatives (3), we have also encountered this photodechlorination reaction. We report here our results on the tetrachloro ketals, (I) and (VI).



Irradiation (4) of the tetrachloro compound (I) (5) in ether solution with ultraviolet light of wavelength greater than 210mμ (vycor filter), yielded the monodechlorinated derivative (II), m.p. 158-159°, as the major

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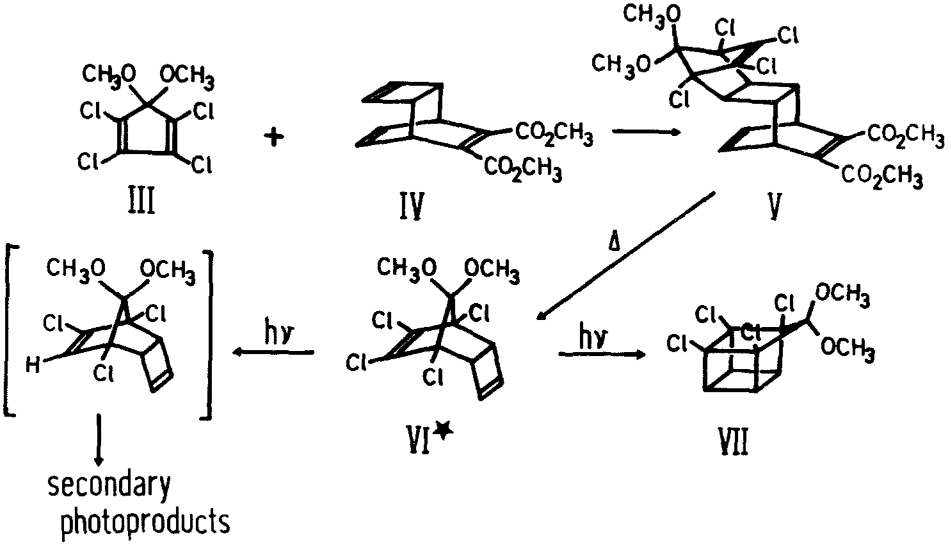
*Present address: Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138, U.S.A.

†To whom enquiries should be directed. Present address: Department of Chemistry, University of Washington, Seattle, 98105, U.S.A.

photoproduct. The structure of (II) was supported by elemental analysis and by spectral data. The 'H-n.m.r. spectrum in d^6-DMSO exhibited resonances at 6.50, 6.42 (3H,3H singlets), 5.95 (2H singlet), and 3.21 τ (1H singlet), assigned to the protons Ha, Hb, and Hc respectively, and is consistent with Cl/H exchange occurring at the vinylic position.

In order to gain information on the multiplicity of the excited state involved in this photodechlorination reaction, (I) was photolysed in ether solution at wavelengths greater than 290mμ, in the presence of benzophenone as a triplet sensitiser [E_T = 69 k cal/mole (6)], but no change was observed. The exact role of the solvent is not clear in these reactions.



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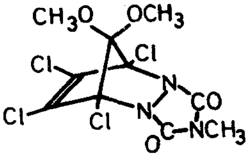
[*] Preparation of (VI)·. This preparation is given in some detail as it represents an alternative approach to these systems. The method of Pettit and co-workers (7) utilising cyclobutadiene cycloadditions was not successful in our hands. In the initial Diels-Alder addition, the triene (IV), (8), reacted exclusively at the cyclobutene double bond to form the adduct (V), m.p. 186° (54% yield), on refluxing in chloroform for 50 hrs. The retro Diels-Alder fragmentation was effected by heating (V) at 195-205° for 15 mins., and the cyclobutene (VI), m.p. 80-81° (100% yield) isolated by chromatography in carbon tetrachloride solution on silica gel. The reaction is quite general, and has been used to prepare a number of related bi- and tricyclo products containing a cyclobutene ring (9).

It is noted for example that no reaction occurs upon irradiation of compound (I) in benzene or iodobenzene under similar conditions. This may be interpreted in one of two ways. On the one hand it may indicate that the reaction occurs via the singlet state, but that the energy of this species may be insufficient to allow abstraction of the H-atom from the aromatic solvent; or that benzene is acting as a triplet sensitiser (E_T = 85 k cal/mole), although this is known to be an inefficient process(6). These results suggest that, in the formation of (II), Cl/H exchange occurs in the following sequence: (i) excitation of (I) to the singlet state or to a high energy triplet state (i.e. > 85 k cal/mole) (ii) H-abstraction from the solvent (iii) elimination of Cl.

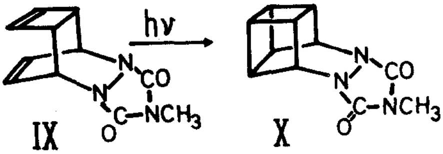
However, further support that Cl/H exchange in dichloro-vinylic systems occurs via the singlet state is forthcoming from the reactions of (VI). Irradiation of (VI) in acetone solution [E_T = 76 k cal/mole (6); vycor filter], a solvent which is both a triplet sensitiser and possible H-donor, produced a near quantitative yield of the homocubane derivative, (VII), m.p. 123°. Barborak and Pettit recently noted (7) a similar cyclisation during synthetic studies of the homocubyl ring system. Attempts to effect this reaction in ether solution, using benzophenone as a triplet sensitiser, were frustrated due to the preferential interaction of the benzophenone with the solvent (10). This difficulty was overcome by irradiation of (VI) in carbon tetrachloride solution (benzophenone; pyrex filter) to give (VII), affording added confirmation that the cage-formation reaction is triplet sensitised.

By way of contrast, a preliminary investigation of the major product from the photolysis of (VI) under non-triplet sensitising conditions (ether solution; vycor filter), indicated that only vinylic chlorine/hydrogen exchange had occurred. However, the reaction is complicated by secondary photochemical reactions, and a definitive structure for this photoproduct must await further experimentation.

Also consistent with the foregoing multiplicity assignments are the reactions of (VIII) and (IX). Irradiation of (IX) (11) in acetone (vycor filter) gave the cage compound (X), m.p. 111-113°C, while irradiation of (VIII) (12), under conditions which lead to dechlorination in (I), was without effect. Possibly, the urazole-ring acts as a selective singlet quencher, thus preventing the singlet reaction (dechlorination) in one case, but allowing the triplet reaction (cage formation) in the other.



VIII



IX X

No 1,2,3,4-tetrachlorobenzene could be detected in the photoproducts from either (I) or (VI), although it could possibly be formed by elimination of the ketal as dimethoxycarbene and subsequent fragmentation of the anhydride (3) or cyclobutene (9) groups. While this general type of elimination has been observed (13) on pyrolysis of norbornadiene ketals, no photolytically induced process has been reported (14).

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