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PHOTODIMERISATION OF 1,4-CYCLOHEXADIENE-1,2-DICARBOXYLIC ANHYDRIDE*

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The nature of the interaction between the double bonds in the 1,4-cyclohexadiene and norbornadiene systems is currently of interest.[1a,b] The photochemistry of this latter system has attracted considerable attention[2] while the photochemistry of the 1,4-cyclohexadiene system has been less well-noted. Prinzbach *et al.* reported the formation of the compound 1 on irradiation of 1,4-cyclohexadiene-1,2-dicarboxylic anhydride (2).[3] In a previous paper,[4] it was reported that the product mixture is largely polymeric. However, a small amount (10 %) of a high-melting cage dimer (3) was isolated.

The photochemistry of the 1,4-cyclohexadiene 2 has been examined here in further detail. In addition to the cage dimer 3, irradiation[5] of 2 in dioxane solution (0.67 M) gives the dimer 4 in a 5-10 % yield. The structure of 4 was established by single crystal X-ray crystallography.[6] Mp 327-328° (evac. capillary, from DMSO). Nmr (DMSO-d_6, TMS, δ-units): 2.40 d J = 1.5 Hz (8 H), 5.8 t J = 1.5 Hz (4 H). Ir (cm^{-1}): 1830, 1780 (C=O, cyclic anhydride); 1635 (alkene). Mass spectrum: parent ion *m/e* = 300, base peak *m/e* = 150. Irradiation[5] of 2 in diethyl ether solution gives a precipitate of complex composition. The dimer 5 was isolated (5-10 %) by sublimation of this precipitate. The structural assignment is then based on its spectral properties: Nmr (DMSO-d_6, TMS, δ-units): 2.45 m (10 H), 5.90 s (2 H). Ir (cm^{-1}): 1850, 1790 (C=O, cyclic anhydride), 1640 (alkene). Mass spectrum: parent ion *m/e* = 300, base peak *m/e* = 150. Mp 265-270°. The head-to-tail *anti*-structure 5 is preferable to the head-to-tail *syn* isomer 6 since the dimer is inert to irradiation in dioxane solution. The *syn* isomer 6 should be expected to close the cage dimer 3 on further irradiation.

Quenching experiments show that formation of the dimers 3 and 4 is unaffected by oxygen. However, the formation of the cage dimer 3 is quenched by piperylene. At a piperylene concentration of 0.15 M, the yield of 3 is reduced to half its initial value.[7] Quenching takes

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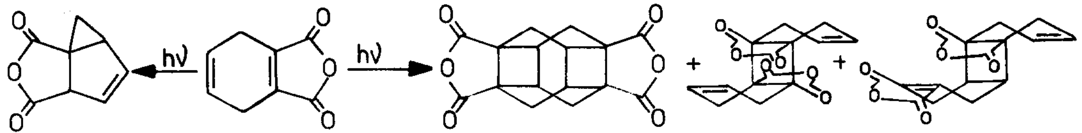
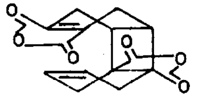
* Cycloaddition reactions, part 6. Part 5: Ref. 4

place at rather high concentrations of piperylene, and it is not possible to draw any conclusions here with respect to the multiplicity of the excited species involved in the reaction, since both singlets and triplets could be quenched. Further, irradiation of 2 in acetone- or benzene solution and in dioxane solution in the presence of benzophenone or acetophenone did not increase the formation of dimers but resulted in complex product mixtures.

The cage dimer 3 may be formed in a one-quantum process or *via* an intermediate open head-to-tail *syn* dimer 6, undergoing a second photochemical closure. The formation of such an intermediate could not be detected. On the other hand, a one-quantum process might constitute a concerted *homo* ($\pi^2_s + \pi^2_s + \pi^2_s + \pi^2_s$)-cycloaddition.[8] The 1,4-cyclohexadiene 2 has been shown to undergo this type of photocycloaddition with dimethylacetylene.[9] A similar reaction takes place between 1,4-cyclohexadiene and acetylenedicarboxylic acid.[10]



1 2 3 4 5



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REFERENCES

1. (a) R. Hoffmann, E. Heilbronner, and R. Gleiter, *J. Amer. Chem. Soc.*, 92 706 (1970).
(b) M.J.S. Dewar and J.S. Wasson, *ibid.*, 92 3506 (1970).

2. G. Kaupp and H. Prinzbach, *Helv. Chim. Acta*, 52 956 (1969).

3. E. Druckrey, M. Arguelles, and H. Prinzbach, *Chimia*, 20 432 (1966).

4. G. Ahlgren, B. Åkermark, and R. Karlsson, *Acta Chem. Scand.*, 25 753 (1971); See also G. Fritz, Dissertation, Universität Karlsruhe 1972.

5. A Rayonet reactor equipped with 300 nm lamps and vycor vessels were used.

6. R. Karlsson, to be published.

7. The slope of the Stern-Vollmer plot is *ca.* 5 l/mol.

8. In this particular case, a correlation diagram shows that such a reaction is forbidden according to the Woodward-Hoffmann rules.

9. R. Askani, *Chem. Ber.*, 98 3618 (1965).

10. M. Takahashi, Y. Kitahara, I. Murata, T. Nitta, and M.C. Woods, *Tetrahedron Lett.*, 3387 (1968).