Photo-reactivity of *endo*-Dicyclohexadiene (*endo*-1,4,4a,7,8,8a-Hexahydro-1,4-ethanonaphthalene)

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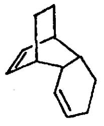
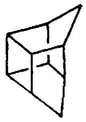
Summary The apparent unreactivity of *endo*-dicyclohexadiene to intramolecular cycloaddition is ascribed to the flexibility of the dienophile unit and the ring size of the diene unit, but not to inefficient sensitization.

AMONG numerous reports of intramolecular photo-cycloaddition of non-conjugated olefins,[1] it is well known that *endo*-dicyclohexadiene (**1**) does not react photochemically in the presence of various sensitizers,[2] whereas *endo*-dicyclopentadiene (**2**) readily forms the cage isomer (**3**).[3] Becker and Konar suggested that the inertness of (**1**) may be attributable to inefficient sensitization.[4] In order to clarify this, the photo-reaction of (**1**) in the presence of acetic acid has now been studied.

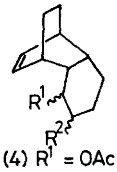


(1)

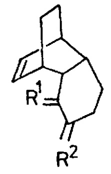
(2)



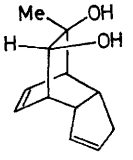
(3)



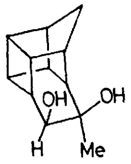
(4) $R^1 = OAc, R^2 = H$
(5) $R^1 = H, R^2 = OAc$



(6) $R^1 = O, R^2 = H_2$
(7) $R^1 = H_2, R^2 = O$



(8)



(9)

A solution of (**1**) in toluene and AcOH was irradiated (100 W high pressure Hg lamp, N_2, 20 h) to give a mixture of the isomeric acetates (**4**) and (**5**) in 34% yield. When acetone was used as a sensitizer, essentially the same mixture was obtained (11%). This mixture was treated with 5% NaOH, followed by Jones oxidation to give the isomeric ketones (**6**) [ν 1705 cm^{-1}; semicarbazone, m.p. 227—229 °C (decomp.)] and (**7**) [ν 1715 cm^{-1}; semicarbazone, m.p. 222—223 °C (decomp.)] in a ratio of 3:2 and 90% yield. Since these ketones could not be differentiated by spectral methods, deuterium exchange reactions were examined. Thus on treatment of (**6**) and (**7**) with MeOD in the presence of NaOMe at room temperature for 2 days, the significant peaks 176 (M^+) and 97 (C_6H_9O) observed in the mass spectra of both (**6**) and (**7**) were shifted to 179 and 100, and to 180 and 101, respectively,† thus indicating that structures (**6**) and (**7**) were correct. In addition, (**6**) was obtained by the reaction (180 °C, 8 h) of cyclohexenone and cyclohexadiene.

These results show that energy transfer from an excited sensitizer to the double bond of the dienophile unit in (**1**) actually occurs, promoting the double bond to its unstable *trans* geometry, which is sensitive to the addition of acetic acid.[5] Thus, when (**8**),‡ whose cyclopentene ring is restricted to the *cis* geometry, was irradiated (acetone, Pyrex, 10 h), a cycloaddition product (**9**) [m.p. 76—79 °C] was obtained though in only 20% yield.

Furthermore, the marked difference between the reactivities of (**2**)[3] and (**8**) towards photo-cycloaddition suggests that the ring size of the diene unit also plays a role.[6]§

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† The photo-reaction of (**1**) occurred selectively at the double bond of the dienophile unit, because ketones derived from alternative routes were not obtained. They should incorporate two deuterium atoms (see also G. L. Buchanan, *Chem. Soc. Rev.*, 1974, **3**, 41).

‡ This compound (**8**) (m.p. 58—60 °C) was prepared by $LiAlH_4$ reduction of the corresponding ketone [*cf.* D. M. Bratby and G. I. Fray, *J. Chem. Soc.* (*C*), 1971, 970], together with the isomeric *trans*-diol (m.p. 175—178 °C).

§ The photolysis of tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene gives similar results (personal communication from Dr. E. Ōsawa).

[1] W. L. Dilling, *Chem. Rev.*, 1966, **66**, 373; 1969, **69**, 845.
[2] D. Valentine, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1964, **86**, 5202.
[3] G. O. Schenck and R. Steinmetz, *Chem. Ber.*, 1963, **96**, 520.
[4] H.-D. Becker and A. Konar, *Tetrahedron Letters*, 1972, 5177; H.-D. Becker, *Annalen*, 1973, 1675.
[5] See also J. A. Marshall, *Accounts Chem. Res.*, 1969, **2**, 33.
[6] See also R. D. Miller and D. Dolce, *Tetrahedron Letters*, 1972, 4541.