Photochemical Rearrangement of *cis,anti,cis*-Tricyclo[5,3,0,$0^{2,6}$]deca-4,9-diene-3,8-dione: a New Approach to Cubane Precursors

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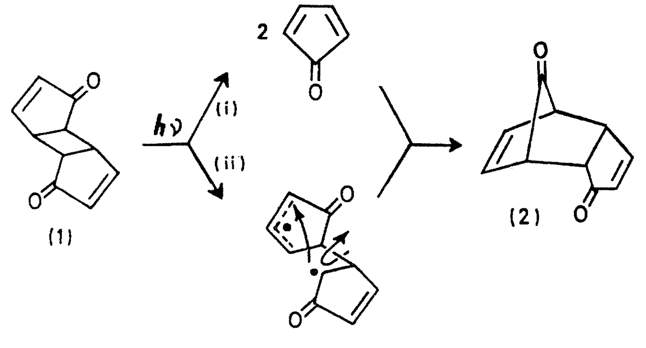
Summary The photochemical rearrangement of *cis,anti,-cis*-tricyclo[5,3,0,$0^{2,6}$]deca-4,9-diene-3,8-dione to *endo*-dicyclopentadienone is shown to occur by an intramolecular path.

WE have found that the title compound[1] (**1**) upon u.v. irradiation† is converted in good yield into *endo*-dicyclopentadienone[2] (**2**). Two economic pathways along which this transformation might proceed are: (i) two-bond cleavage[3] to cyclopentadienone followed by thermal Diels–Alder dimerization of this very reactive diene, and (ii) one-bond cleavage followed by internal reorganization.[4]

These paths are readily distinguishable by way of a labelling experiment. Photorearrangement of the dideuteriated compound (**3**) along path (i) or along (ii) would lead to quite different distributions of the label in the product. Most notably from the analytical (n.m.r.) view, reaction by path (i) would lead to material averaging half protium–half deuterium at position 2; whereas reaction *via* path (ii) would give product with only deuterium at that position. The labelled compound (**3**) was prepared by



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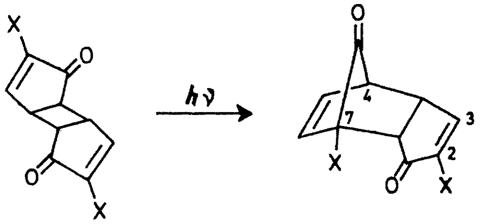
† In benzene or methylene chloride with light of $\lambda > 3000$ Å.

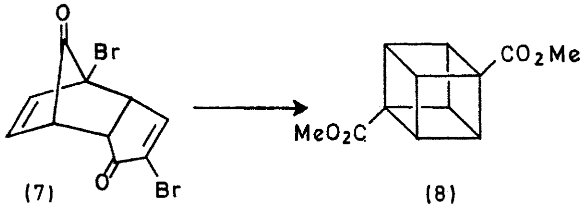
reaction of (**1**) with 55 weight-% dideuteriosulphuric acid in deuterium oxide. Irradiation of (**3**) gave material having only (>90%) deuterium at position 2. This result establishes that the dominant rearrangement path is intramolecular [path (ii)].



(3) X = D
(5) X = Br

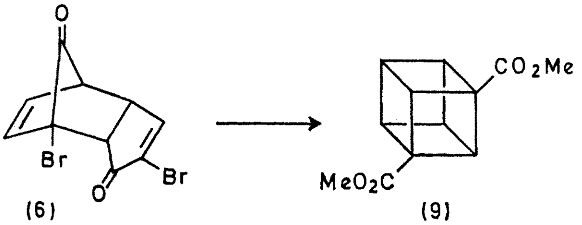
(4) X = D
(6) X = Br

We have used such photochemical rearrangements in a novel way. Irradiation‡ of (**5**) [m.p. 220° (decomp.); i.r. ν (mull) 1700 (C=O) and 1575 cm^{-1} (C=C–Br)], prepared by bromination–dehydrobromination of compound (**1**), gives the 2,7-dibromide (**6**). This structure is assigned by analogy to the rearrangement of (**3**) to (**4**) and is fully consistent with the spectral data: i.r. ν (CH_2Cl_2) 1800 (bridge C=O), 1715 (conjugated C=O), and 1575 cm^{-1} (C=C–Br); n.m.r. δ ($CDCl_3$) 7·45 (3-H, 1H, d, *J* 3 Hz), 6·3 (2H, m), 3·8—3·2 (2H), and 3·1 p.p.m. (1H, d, *J* 6·5 Hz).§ The 2,7-dibromide (**6**) is a positional isomer of the 2,4-dibromide (**7**), a key intermediate in the synthesis of 1,4-dimethoxycarbonylcubane (**8**) reported by us some years ago.[5] Examination of that synthesis shows that introduction of (**6**) into the sequence will lead to 1,3-dimethoxycarbonylcubane (**9**). We have now prepared 1,3-dimethoxycarbonyl cubane by exactly that route.[6]



(7)

(8)



(6)

(9)

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‡ Dibromide (**5**) is extraordinarily insoluble. For this reason alone the irradiation was carried out on a dilute solution of (**5**) in trifluoroacetic acid.

§ This n.m.r. spectrum is identical to that recorded for compound (**4**) except for the broadening due to deuterium coupling and minor changes in chemical shifts.

[1] P. E. Eaton, *J. Amer. Chem. Soc.*, 1962, **84**, 2344.

[2] C. H. DePuy, M. Isaks, K. L. Eilers, and G. F. Morris, *J. Org. Chem.*, 1964, **29**, 3503. The systematic name for compound (**2**) is *endo*-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione.

[3] *cis,anti,cis*-Tricyclo[5,3,0,0^{2,6}]deca-3,9-diene, and *endo*- and *exo*-dicyclopentadiene all revert to cyclopentadiene upon sensitized irradiation; P. E. Eaton and T. W. Cole, jun., unpublished results.

[4] A concerted shift would be allowed, but see R. L. Cargill, B. M. Gimarc, D. M. Pond, T. Y. King, A. B. Sears, and M. R. Willcott, *J. Amer. Chem. Soc.*, 1970, **92**, 3809.

[5] P. E. Eaton and T. W. Cole, jun., *J. Amer. Chem. Soc.*, 1964, **86**, 962.

[6] Material prepared in this way is identical to that prepared by J. C. Barborak, L. Watts, and R. Pettit (*J. Amer. Chem. Soc.*, 1966, **88**, 1328) using another modification of the original route into the cubane system. We thank Dr. Pettit for a sample of his material.