Cyclobutano[*a*]indene: A Highly Reactive Strained Olefin which Plays a Key Trapping Role in the Photodecomposition of a Polycyclic α-Dione

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Cyclobutano[*a*]indene is characterised for the first time and shown to undergo a selection of cycloaddition reactions, including self-dimerisation to a [π2 + π2] dimer whose structure has been confirmed by single crystal *X*-ray analysis.

Cyclobutano[*a*]indene (**4**) is a highly reactive molecule formed by rearrangement of 2*H*-indene-2-spiro-cyclopropane (**3**) which, to date, has only been reported as a transient intermediate. Some time ago we reported that photolysis of the polycyclic α-dione (**1**) led to a mixture of two dimers which appeared to result from the dimerisation of (**4**).[1] We now report the structure of these dimers, offer proof of the intermediacy of the title indene (**4**), and elucidate the role of the latter in the photodecomposition of α-dione (**1**).

The structure of the minor dimer (m.p. 88—89 °C), formed by photodecomposition of α-dione (**1**) in hexane or tetrahydrofuran (THF) was shown to have the head to head *anti* structure (**6**)† by single crystal *X*-ray structure determination (ORTEP structure shown in Figure 1);‡ the other dimer (m.p. 98—99 °C) is assigned§ the head to head *syn* structure (**7**).† Confirmation of the structures (**6**) and (**7**) lends positive support for the intermediacy of (**4**).

The successful characterisation of (**4**) was achieved by working in dilute solution. Accordingly solutions of (**4**) were prepared by photolysis of the α-dione (**1**) (10^{-3} M) in hexane. The resultant ultraviolet spectrum ($\lambda_{max.}$ 268, 272, 277 nm) is very similar to that of 2,3,4,4a-tetrahydro-1*H*-fluorene, which contains the same chromophore.[2] Chemical support for (**4**) was obtained only after some difficulty, by catalysed hydrogenation (Adams catalyst) of moderately concentrated solutions of (**4**); the difficulty being the propensity of (**4**) to dimerise to (**6**) and (**7**) under these conditions. The derived dihydroderivative (**5**) was stable and identical with authentic material.[3]

Cyclobutano[*a*]indene is a highly reactive molecule which undergoes a variety of cycloaddition reactions. This has helped unravel the complex photochemistry of α-dione (**1**). Thus photolysis of (**1**) (5×10^{-2} M, THF, 0 °C) leads not only to the [π2 + π2] dimers (**6**) and (**7**) but also to the *endo*-[π4 + π2] adduct (**8**)† (m.p. 114—115 °C); the latter results from reaction of the initially formed (**3**) with (**4**). At even lower temperatures (10^{-2} M, diethyl ether, −80 °C) the

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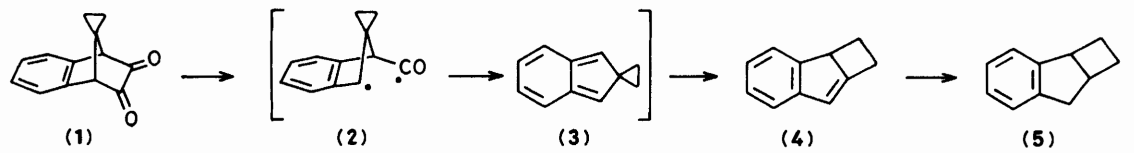
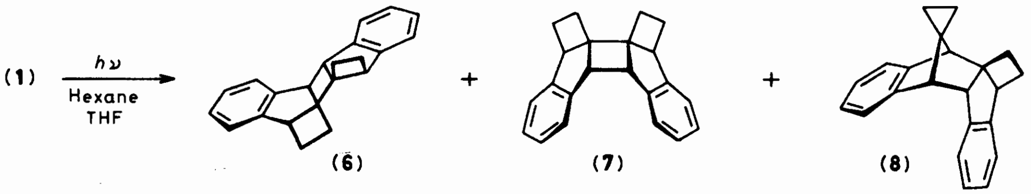
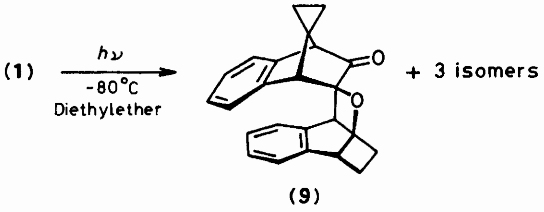
† All new compounds, with the exception of (**4**), gave satisfactory elemental analysis and consistent spectral data (i.r., ^{1}H and ^{13}C n.m.r.).

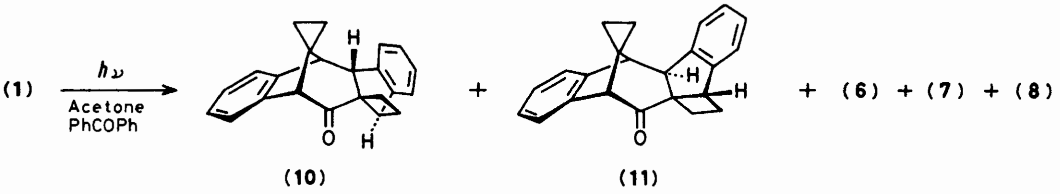
‡ Crystals of *anti*-dimer (**6**), $C_{22}H_{20}$, are monoclinic, space group $P2_1/c$, $a = 11.477(4)$, $b = 10.495(3)$, $c = 14.583(3)$ Å, $\beta = 114.0(1)°$, $Z = 4$. Intensity data [2255 reflections, 1556 with $I > 3\sigma(I)$] were collected on a Picker FACS-1 diffractomer (graphite monochromated Mo-K_α radiation, θ—2θ scan). Carbon atoms were located using the MULTAN series of programs and hydrogen atoms from difference Fourier syntheses. The structure was refined by full-matrix least squares with anisotropic thermal parameters for carbon and isotropic parameters for hydrogen atoms to $R = 0.039$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

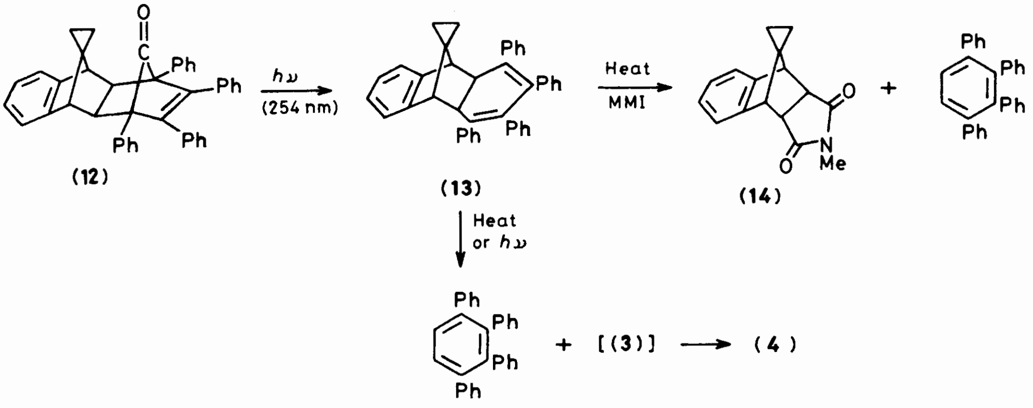
§ A comparison was made with a number of head to head (H,H) and head to tail (H,T) cyclobutane dimers derived from indenes. The cyclobutane proton (Hcb) resonance in H,H *anti*-dimers range from δ 3.35 to 3.75, whereas H,H *syn*-dimers range from δ 4.00 to 4.42. The aromatic proton resonances (Har) were also valuable guides: *anti* dimers giving resonances centred around δ 7.2—7.5, while *syn*-dimers are at δ 6.8—7.0. Relevant data for (**6**): Hcb δ 3.8—3.9, Har 7.2—7.3 and (**7**) Hcb δ 4.07, Har 6.9—7.1 thus supporting the structural assignment.











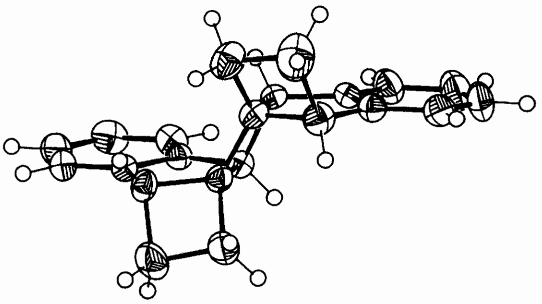


Figure 1. ORTEP diagram of cyclobutane dimer (**6**).

bisdecarbonylation step is less efficient and a mixture of four isomeric oxetanes[4] is formed by [π2 + π2] reaction of (**4**) with α-dione (**1**), of which (**9**)† is typical (^{13}C n.m.r. δ 87.1, 90.6 p.p.m. oxetane C's).

The most important result in regard to understanding the steps in the sensitised photodecomposition of (**1**) (5×10^{-2} M, 0 °C, benzophenone, acetone) is the ability of cyclobutano-[*a*]indene to act as a trap for the monocarbonyl species (**2**). Formation of the oily ketones (**10**)† and (**11**)† represents the first case where bimolecular trapping of a monocarbonyl species has been reported, and only the second case where stepwise carbon monoxide loss from an α-diketone has been recorded.[5,6]

The diene (**13**)†¶ served as a more accessible precursor to cyclobutano[*a*]indene. Thus heating (**13**) in xylene solution

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¶ The adduct (**12**) (m.p. 182—183 °C) was prepared in 60% yield by heating benzonorbornadiene-7-spiro-cyclopropane with tetracyclone in xylene solution at reflux for 3 days. Irradiation (254 nm, 0 °C, acetone) of (**12**) formed the diene (**13**) (m.p. 174—175 °C) in 80% yield.

(10^{-2} M) yielded dimers (**6**) and (**7**) in 76% yield. Again the intermediacy of (**3**) could be established by conducting the decomposition of (**13**), as above, in the presence of two equivalents of *N*-methylmaleimide (MMI), whence (**14**), the known 1 : 1 adduct[1] of (**3**) and MMI, was formed in 80% yield. Fragmentation of (**13**) was also observed to occur photochemically.

Thus cyclobutano[*a*]indene is readily generated by either thermal or photochemical processes and thus available for chemical use or as a versatile trapping agent.

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