

THE PHOTOLYSIS OF ADDUCTS DERIVED FROM *o*-CHLORANIL

A NEW ROUTE TO DIHYDROBARRELENES

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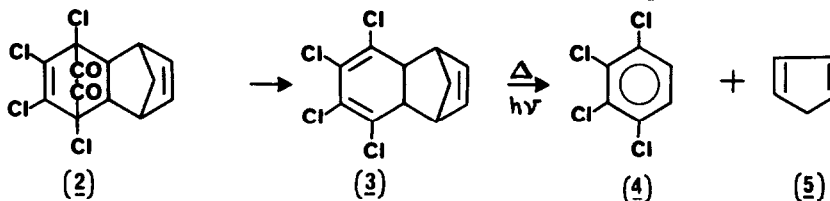
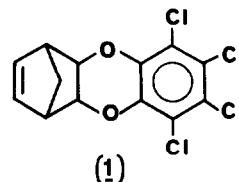
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(Received in UK 9 November 1971; accepted for publication 9 December 1971)

Recent reports(1) have shown that bridged α -diketones can be eliminated under photochemical conditions, although such systems are known to be quite thermally stable. This fact, together with the known reactivity of *o*-benzoquinones in cycloaddition reactions(2), lead us to investigate their use in photoaromatization reactions**.

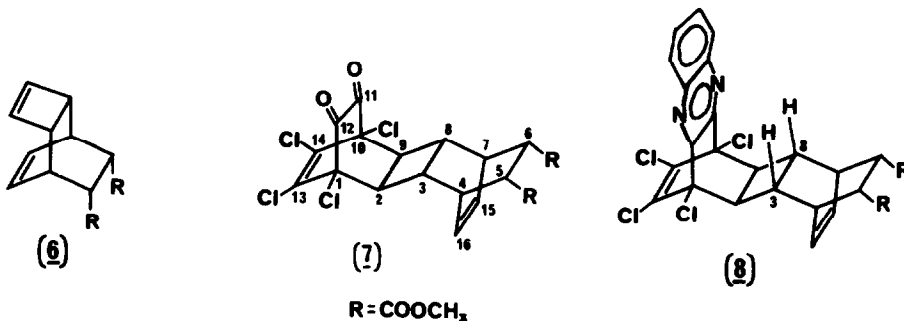
o-Chloranil reacts with norbornadiene in refluxing benzene to form a mixture of two 1:1 adducts (ratio 3:1). The major yellow-coloured isomer, m.p. 166° was the bridged α -diketone (2) [i.r. 1756, 1740 cm^{-1} , quinoxaline derivative m.p. 199°]; the minor product (colourless), m.p. 150° (no carbonyl in i.r.) was assigned the 1,4-dioxene structure (1).



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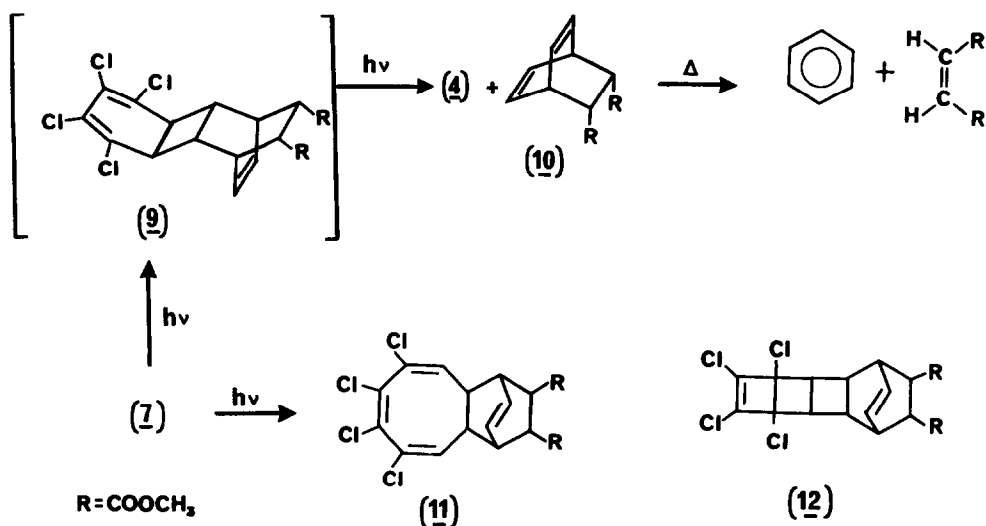
** *o*-Chloranil is typical of the class of dienes which display reverse electron demand in $\pi 4s + \pi 2s$ cycloaddition reactions (3). We reasoned that such a diene complements the normal electronic requirements of the dienones usually used by our group in photoaromatization reactions (4). Further, the long wavelength $n \rightarrow \pi^*$ transition of the α -diketone allows selective irradiation of this chromophore; the generated tetrachlorocyclohexadiene also displays considerable absorption above 300nm, which has experimental advantages.

Irradiation (5) of the diketone (2) at 0° formed a high yield of cyclopentadiene (isolated as the *N*-methylmaleimide derivative) and 1,2,3,4-tetrachlorobenzene (4). A similar result was achieved thermally, but fragmentation was slow even at 155° [$t_{0.5} = ca. 52$ hrs]. The triene (3) is the presumed intermediate in each experiment, but because of its thermal instability (6) [$t_{0.5}^{54.5^\circ} = 10.5$ mins; $t_{0.5}^{34.5^\circ} = 106$ mins] with respect to fragmentation to (4) and (5), this could be confirmed only in the photochemical experiment. Thus brief irradiation of the diketone (2) yielded the triene (3) which was isolated by layer chromatography (silica/*n*-hexane) in 82% yield and shown to be identical with that reported by Mackenzie and Lay (6). Separate photolysis of this product at 0° slowly formed (4) and (5)*. Control experiments confirmed that triene (3) was stable at this temperature in the absence of ultra-violet light.



Cycloaddition with the cyclobutene dienophile (6) formed the bridged α -diketone adduct (7), m.p. 281° [i.r. 1765, 1725 cm^{-1}] as the sole product. The stereochemistry of the adduct followed from consideration of its p.m.r. spectrum [p.m.r. (CDCl_3) δ p.p.m.; 1.97 (2H, m, $\text{C}_{3,8}$ -H); 2.62 (2H, d, $\text{C}_{2,9}$ -H); 2.85 (2H, s, $\text{C}_{5,6}$ -H); 3.13 (2H, m, $\text{C}_{4,7}$ -H); 3.60 (6H, s, OCH_3); 6.55 (2H, t, olefinic)] and of its quinoxaline derivative (8) (m.p. 290°). The 3,8-cyclobutyl protons in the quinoxaline were shielded ($\Delta\nu$ 0.58 p.p.m.) relative to those in (7) which supports the stereochemistry depicted.

* Heavy atom induced intersystem crossing to the triplet state by the chlorine atoms should facilitate this fragmentation, since a similar fragmentation is known to be triplet sensitized (7).



Irradiation (5) of the α -diketone (7) again proceeded smoothly to form 1,2,3,4-tetrachlorobenzene (5) and the dihydrobarrelene (10) (m.p. 54-5°; 63% yield) together with the ring opened product (11) (12%). The structure of the dihydrobarrelene followed from the mode of formation, spectral data [p.m.r. (CDCl_3) δ p.p.m.; 2.95 (2H, br. s, $\text{C}_{7,8}\text{-H}$); 3.66 (6H, s, OCH_3); 3.93 (2H, m, $\text{C}_{1,4}\text{-H}$); 6.4-6.6 (4H, 2 x q, olefinic); m/e 222] and its facile thermal fragmentation ($t_{0.5}^{60}$ 6 hrs) into benzene and dimethyl maleate. The stereospecificity of this fragmentation is consistent with the known (8) orbital-symmetry requirements in concerted $\pi 4s + \pi 2s$ pericyclic reactions.

The reaction of the intermediate* (9) is concentration dependent. In dilute solution, fragmentation to (4) and (10) and ring opening (non-concerted?) to (11) are predominant, whereas in more concentrated solution, significant formation of the pentacyclic valence-isomer (12) is observed. A similar concentration dependent perispecificity has been noted in the irradiation of *trans*-9,10-dihydronaphthalene (10).

* While compound (9) has not been isolated, its presumed intermediacy follows from the isolation of valence isomers (11) m.p. 197-9° and (12) m.p. 157-8° and its logical fragmentation to (4) and (10). In a related series, all three valence-isomers corresponding to (9), (11) and (12) have been isolated and characterized, and these will be reported at a later date (9).

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5. Hanovia 450 W, Hg lamp, pyrex filter, N₂ atmosphere, benzene solution. Compound (2), 250 mg/75mls, 2 hrs; Compound (7), a) 300 mg/70 ml, 4 hr, b) 1.0 g/125 ml, 4 hr.
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