Cyclobutadiene

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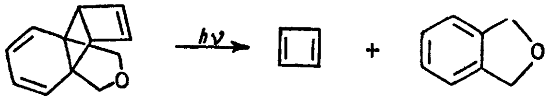
Summary Photolysis of compound (**3**) in a matrix provides phthalan (**12**) and cyclobutadiene.

Because of the short life-time ($t_{\frac{1}{2}}$ = 2—10 ms)[1,2] of cyclobutadiene (**1**) in the gas phase (10—100 μ), the accurate spectral observation of this elusive species demands[2,3] the construction of an appropriate precursor which upon photolysis provides (**1**) in a matrix *exclusively* and *efficiently*. Although alkyl substituted cyclobutadienes have been generated in this manner,[4] all experiments designed thus far to isolate the parent hydrocarbon (**1**) for the spectral characterization have apparently been unsuccessful.[5] Earlier findings[6] that irradiation splits compound (**2**) quantitatively into ethylene and phthalic anhydride led us to examine the photochemistry of compound (**3**) at low temperatures. We now describe the synthesis and photochemical behaviour of (**3**) and record what we believe is the u.v. spectrum of cyclobutadiene.

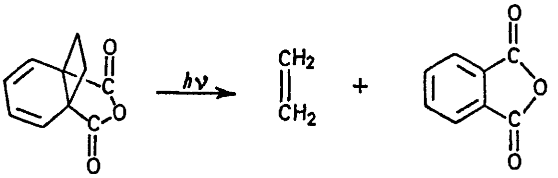
Reaction of 3,6-dihydrophthalic anhydride with tricarbonylcyclobutadieneiron effected by ceric ammonium nitrate[7] gave an adduct (**4**),† m.p. 157—158°, which was reduced with lithium aluminium hydride to provide the corresponding diol (**5**), m.p. 132·5—134·5°. Intramolecular cyclization of (**5**) proceeded smoothly with the aid of 1 mole of tosyl chloride in pyridine to give a liquid ether (**6**) which was photochemically oxygenated in the presence of Methylene Blue.

Brief treatment of the resulting hydroperoxide (**7**) with lithium aluminium hydride gave the corresponding hydroxy-compound (**8**) which was in turn oxidized with manganese dioxide to afford a liquid ketone (**9**).

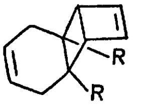
Treatment of a mixture (**10**) of the *syn*- and *anti*-tosylhydrazones derived from (**9**) with 3 equivalents of methyllithium[8] afforded the desired triene (**3**), m.p. *ca.* 30°.



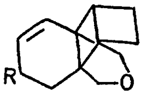
(**3**) (**1**) (**12**)



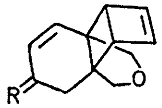
(**2**)



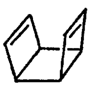
(**4**) R,R = CO—O—CO
(**5**) R = CH$_2$OH
(**6**) R,R = CH$_2$—O—CH$_2$



(**7**) R = O$_2$H
(**8**) R = OH



(**9**) R = O
(**10**) R = NNHTs



(**11**)

Irradiation (5 min) of a solution of (**3**) in deuteriated tetrahydrofuran at −100° with a low pressure mercury lamp (2537 Å) provided exclusively *syn*-tricyclo[4,2,0,0^{2,5}]-octa-3,7-diene (**11**) and phthalan (**12**) (n.m.r. and g.l.p.c.). When (**3**) was photolysed in a 2-methyltetrahydrofuran matrix at *ca.* −175°, a faint yellow colour developed immediately and disappeared upon warming. The products were again solely (**11**) and (**12**). The difference between two u.v. spectra taken before and after the warming represents that of the reactive species which dimerized to give (**11**). Thus we attribute the broad absorption with a maximum around 300—305 nm (ε ≃ 100)‡ and tailing to 400 nm to that of the parent cyclobutadiene. Since the presence of (**12**) was readily recognizable in the two spectra, the

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† Spectral data of all new compounds are in accord with the structures assigned.

‡ The molar extinction coefficient was calculated on the basis of the quantitative conversion of (**3**) into (**1**).

possibility that (**1**) formed a complex with (**12**) is virtually excluded. We believe that this instance represents the first spectral characterization of (**1**) and active investigations are underway to generate (**1**) with equal efficiency from other sources in order to confirm the above results. Photolysis of (**3**) obviously provides a means of defining the physical and chemical properties of (**1**) free from complications that may arise in the presence of transition metals as previously noted.

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