

Cyclobutadiene

By S. MASAMUNE,* M. SUDA, H. ONA, and L. M. LEICHTER

(Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada)

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 findings⁶ 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.

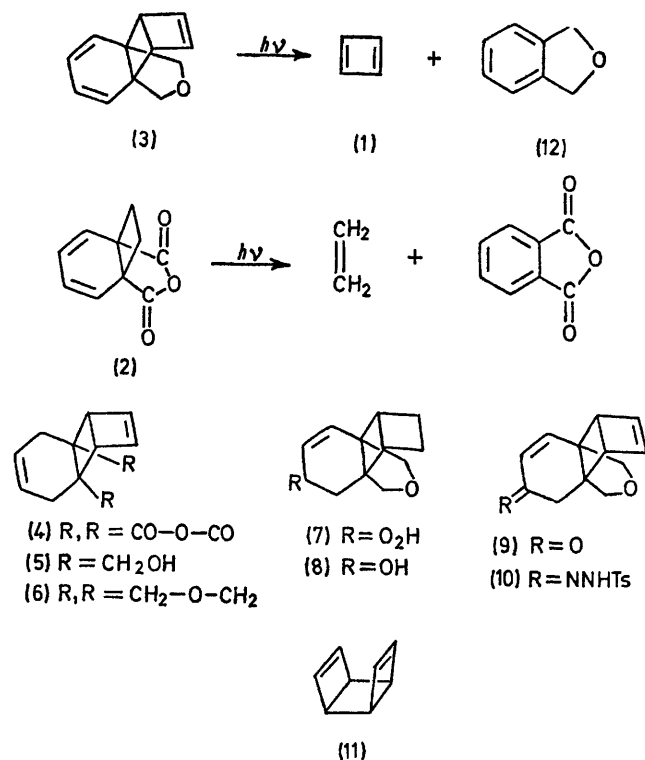
Reaction of 3,6-dihydrophthalic anhydride with tri-carbonylcyclobutadieneiron effected by ceric ammonium nitrate⁷ gave an adduct (4),† m.p. 157–158°, which was reduced with lithium aluminium hydride to provide the corresponding diol (5), m.p. 132.5–134.5°. Intramolecular cyclization of (5) proceeded 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 methyl-lithium⁸ afforded the desired triene (3), m.p. ca. 30°.

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[4,2,0,0²,5]-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 ($\epsilon \approx 100$)[‡] and tailing to 400 nm to that of the parent cyclobutadiene. Since the presence of (12) was readily recognizable in the two spectra, the

† 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 complica-

tions that may arise in the presence of transition metals as previously noted.

We thank Mr. K. Morio for his skilful technical assistance and the National Research Council for financial support.

(Received, 7th September 1972; Com. 1555.)

¹ W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Comm.*, 1967, 497.

² F. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *J. Amer. Chem. Soc.*, 1969, **91**, 1875.

³ E. Hedaya, I. S. Krull, R. D. Miller, M. E. Kent, P. F. D'Angelo, and P. Schissel, *J. Amer. Chem. Soc.*, 1969, **91**, 6880. *cf.*, P. H. Li and H. A. McGee, jun., *Chem. Comm.*, 1969, 592.

⁴ G. Maier and F. Bosslet, *Tetrahedron Letters*, 1972, 1025. G. Maier and M. Schneider, *Angew. Chem. Internat. Edn.*, 1971, **10**, 809. G. Maier, G. Fritsch, and B. Hoppe, *ibid.*, 1970, **9**, 529.

⁵ R. D. Miller and E. Hedaya, *J. Amer. Chem. Soc.*, 1969, **91**, 5401. S. F. Nelsen and J. P. Gillespie, *Tetrahedron Letters*, 1969, 5059.

⁶ S. Masamune and N. Darby, unpublished observation; *e.g.*, G. Schröder, *Chem. Ber.*, 1964, **97**, 3140.

⁷ L. Reeves, J. Henery, and R. Pettit, *J. Amer. Chem. Soc.*, 1969, **91**, 5888.

⁸ W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *J. Amer. Chem. Soc.*, 1968, **90**, 4762.