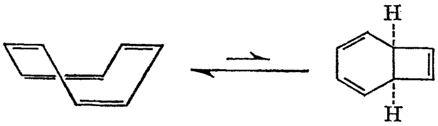
A Stable Bicyclo[4,2,0]octatriene[1]

LEO A. PAQUETTE* and J. CHRISTOPHER PHILIPS
(*Department of Chemistry, The Ohio State University, Columbus, Ohio* 43210)

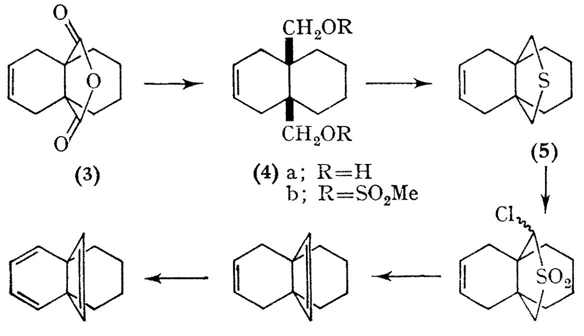
ALTHOUGH cyclo-octatetraene (**1**) is 99·99% monocyclic at 100°, its reaction with dienophiles occurs by kinetically controlled (4 + 2) π cycloaddition to its valence tautomer (**2**). Interest in such reactions derives from the unusual structural elements in (**2**) and the present inability to observe directly the presence of (**2**) in the tautomeric mixture. Several attempts to prepare bicyclo[4,2,0]octatriene (**2**) have been reported. The most successful route has been that based on the debromination of cyclo-octatetraene dibromide;[3] however, only impure samples of (**2**) [u.v. maxima at 273 (ϵ 3100) and 277 nm. (ϵ 3000)] were obtained because of the extreme thermal instability of the triene relative to (**1**). Three groups have noted that irradiation of (**1**) gives rise to absorption in the 281—283 nm. region which has been attributed to (**2**).[4] We now illustrate a new synthetic entry to the bicyclo[4,2,0]octatriene system which has provided access to a stable derivative of (**2**).



(1) **(2)**

Reduction of Δ^2-octalin-9,10-dicarboxylic anhydride (**3**)[5] with lithium aluminium hydride and treatment of resulting diol (**4a**), m.p. 145—147°,[†] with methanesulphonyl chloride in pyridine at 0—10° gave rise to (**4b**), m.p. 124·5—125·5°,[†] in 62% overall yield. This dimesylate was readily transformed in 77% yield to the sulphide (**5**), m.p. 85—87°,[†] by means of anhydrous sodium sulphide in hexamethylphosphoramide (HMP) solution at 120°. This sulphide was further characterized as its sulphone, m.p. 138—140°.[†][6] As before,[7] the use of HMP, in contrast to a variety of other solvents, permitted efficient displacement at the neopentyl carbon atoms with a minimum of side-reactions. The α-chloro-sulphone (**6**), m.p. 127—134°,[†] was prepared in 96% yield by chlorination of (**5**) with 1 equiv. of *N*-chlorosuccinimide followed by direct oxidation with 2 equiv. of monoperphthalic acid in ether solution. Ramberg–Bäcklund rearrangement[8] of (**6**) with powdered potassium t-butoxide in anhydrous tetrahydrofuran at ambient temperatures led to the formation of tricyclo-[4,4,2,0]dodeca-3,11-diene (**7**) in 56% yield. The n.m.r. spectrum of (**6**) displays the expected signals for the cyclobutene and vinyl protons at δ 5·90 (singlet, 2H) and 5·75 (multiplet, 2H), respectively, in addition to the broad multiplets attributable to the allylic (δ 1·87, 4H) and saturated methylene protons (δ 1·57, 8H).

When a purified sample of (**7**) was treated with a refluxing carbon tetrachloride solution of *N*-bromosuccinimide (slightly more than 1 equiv.) followed by powdered potassium t-butoxide in anhydrous tetrahydrofuran at 25°, the desired triene (**8**)[†] was readily isolated after preparative scale v.p.c. separation from unchanged (**7**). The colourless noncrystalline hydrocarbon exhibits u.v. absorption (in iso-octane) at 268 (ϵ 2400) and (sl inflection) 276 nm. (ϵ 2100)



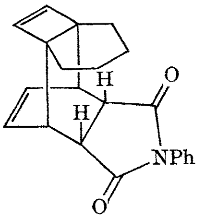
(3) (**4**) a; R=H
b; R=SO_2Me (5)

(**7**) (**6**) (8)

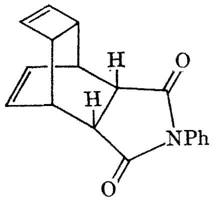
[†] Satisfactory elemental analyses (± 0·3%) and spectra were obtained for all new compounds reported herein.

and an n.m.r. spectrum which consists of three sets of signals: δ 5·88 (singlet, 2H, cyclobutene protons), 5·53 (A_2B_2 pattern, 4H, cyclohexadiene protons), and 1·50 (broadened singlet 8H, methylene protons). The fine details of this n.m.r. spectrum remained unchanged over a substantial temperature range (40—165°); not unexpectedly, therefore,[9] the tetramethylene bridge in (**8**) causes sufficient constriction to guarantee the absence of valence tautomerism to a cyclo-octatetraene derivative for reasons of steric strain. Lastly, the structural assignment was established unequivocally by catalytic hydrogenation of (**8**) to the previously characterized tricyclo[4,4,2,0]dodecane.[7,10]

These results show that a thermally stable bicyclo[4,2,0]-octatriene is capable of existence. By way of contrast, irradiation of ether solutions of (**8**) with 2537 Å light led to the rapid formation of tetralin and acetylene. This observation gives support to the earlier contention that the low-yield photolysis of (**1**) to benzene and acetylene proceeds *via* (**2**).[4a,11] In addition, the triene (**8**) reacts readily with *N*-phenylmaleimide in refluxing benzene solution to afford the adduct (**9**), m.p. 195—197°,† in 90% yield. Cyclo-octatetraene is totally unreactive under such conditions.‡



(**9**)



(**10**)

We thank the National Institutes of Health for a Fellowship (to J.C.P.)

(*Received, March* 31*st*, 1969; *Com.* 456.)

---

‡ Using *o*-dichlorobenzene as solvent, (10) m.p. 237—239°,† was formed in 87% yield.

[1] Previous paper: L. A. Paquette and R. W. Houser, *J. Amer. Chem. Soc.*, 1969, **91**, in the press.

[2] R. Huisgen and F. Mietzsch, *Angew. Chem.*, 1964, **76**, 36; *Angew. Chem. Internat Edn.*, 1964, **3**, 83.

[3] E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem.*, 1964, **76**, 432; *Angew. Chem. Internat. Edn.*, 1964, **3**, 442.

[4] (a) E. Migirdicyan and S. Leach, *Bull. Soc. chim. belges*, 1962, **71**, 845; (b) G. J. Fonken, *Chem. and Ind.*, 1963, 1625; (c) E. H. White, E. W. Friend, jun., R. L. Stern, and H. Maskill, *J. Amer. Chem. Soc.*, 1969, **91**, 523.

[5] K. Alder and K. H. Backendorf, *Ber.*, 1938, **71B**, 2199.

[6] Compare J. Altman, E. Babad, J. Pucknat, N. Reshef, and D. Ginsburg, *Tetrahedron*, 1968, **24**, 975.

[7] L. A. Paquette and J. C. Philips, *Tetrahedron Letters*, 1967, 4645.

[8] For reviews of this subject, see (a) L. A. Paquette, *Accounts Chem. Res.*, 1968, **1**, 209; (b) L. A. Paquette in "Mechanisms of of Molecular Migrations, vol. 1," ed. B. S. Thyagarajan, Interscience, New York, 1968, pp. 121—156.

[9] L. A. Paquette and J. C. Philips, *J. Amer. Chem. Soc.*, 1968, **90**, 3898.

[10] (a) E. Vogel, W. Maier, and J. Eimer, *Tetrahedron Letters*, 1966, 655; (b) J. J. Bloomfield and J. R. S. Irelan, *ibid.*, 2971; (c) J. Altman, E. Babad, J. Itzchaki, and D. Ginsburg, *Tetrahedron*, 1967, Suppl. **8**, 279.

[11] (a) I. Tanaka, S. Miyakawa, and S. Shida, *Bull. Chem. Soc. Japan*, 1951, **24**, 119; (b) I. Tanaka and M. Okuda, *J. Chem. Phys.*, 1954, **22**, 1780.