

## 7,8-Dimethylenecyclo-octa-1,3,5-triene

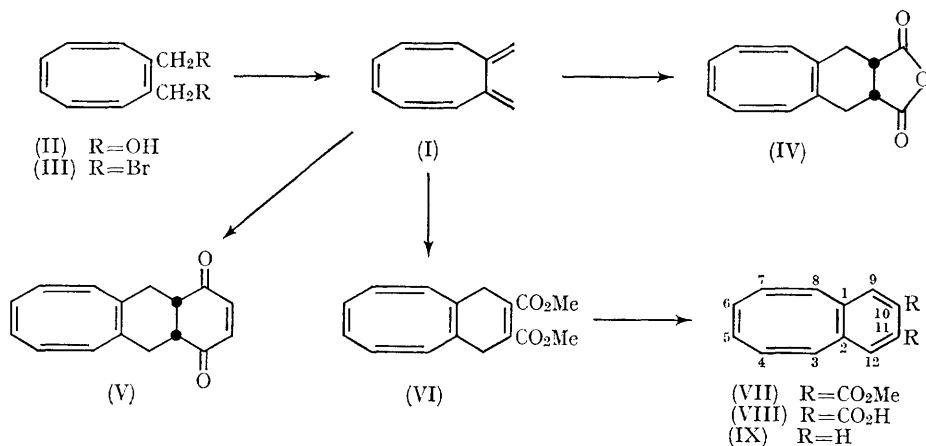
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We report the synthesis of 7,8-dimethylenecyclo-octa-1,3,5-triene (I), a higher vinylogue of 3,4-dimethylenecyclobutene<sup>1</sup> and of *o*-xylylene (5,6-dimethylenecyclohexa-1,3-diene).<sup>2</sup> Compound (I) is not only of interest *per se*, but also as a valuable intermediate for the synthesis of fused cyclo-octatetraene derivatives.

1,2-Bishydroxymethylcyclo-octatetraene (II)<sup>3</sup> on treatment with phosphorus tribromide and pyridine at 0—20° yielded 53% of 1,2-bisbromomethylcyclo-octatetraene (III), m.p. 65—66°.<sup>4</sup> Debromination of (III) in dimethylformamide with zinc at room temperature produced (I) in practically quantitative yield.

The exocyclic double bonds of (I) constitute a conjugated diene system, which reacts readily with a variety of dienophiles to form substituted dihydro- and tetrahydrobenzocyclo-octatetraenes. This behaviour is in marked contrast to the reactions of 1,2-diphenyl-3,4-dimethylenecyclobutene.<sup>6</sup>

The reaction of (I) with maleic anhydride in boiling cyclohexane led to 9,10,11,12-tetrahydrobenzocyclo-octatetraene-*cis*-10,11-dicarboxylic anhydride (IV), m.p. 144—145°, in 37% yield. The structure of (IV) follows from the n.m.r. spectrum (CDCl<sub>3</sub>, 100 Mc./sec.), which showed peaks at  $\tau$  4.17, 4.22 (6H) due to the vinylic protons, at  $\tau$  6.55 (2H) due to the methine protons, and at



7,8-Dimethylenecyclo-octa-1,3,5-triene (I) is an unstable yellow oil, which polymerises rapidly on standing. The mass spectrum exhibited a molecular ion peak at  $m/e$  130, and a base peak at  $m/e$  129. The ultraviolet spectrum [ $\lambda_{\max}$  (EtOH) 269  $m\mu$  ( $\epsilon$  3,400)] closely resembles that of cyclo-octa-1,3,5-triene.<sup>5</sup> The infrared spectrum (neat) showed maxima at 3080 (m), 3000 (s), 1720 (m), 1650 (w), 1600 (m), 1580 (m), 1460 (m), 1430 (m), 1400 (w), 1180 (s), 900 (vs), 800 (s), and 660 (s)  $\text{cm}^{-1}$ . The n.m.r. spectrum (CCl<sub>4</sub>; 100 Mc./sec.) exhibited peaks at  $\tau$  3.67, 3.79 (2H) and at  $\tau$  4.13, 4.22, 4.24 (4H) due to the ring protons, as well as at  $\tau$  4.92, 4.93 (2H), and 5.17, 5.18 (2H) due to the methylene protons.

$\tau$  7.48 (4H) arising from the methylene protons. In a similar manner, (I) reacted with *p*-benzoquinone to give 34% of the adduct (V), m.p. 123—124°, and with dimethyl acetylenedicarboxylate to form 52% of methyl 9,12-dihydrobenzocyclo-octatetraene-10,11-dicarboxylate (VI), m.p. 79.5—80.5° (no  $\lambda_{\max}$  > 210  $m\mu$ ).

In order to obtain a known cyclo-octatetraene derivative, the adduct (VI) was dehydrogenated with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in boiling benzene, whereby methyl benzocyclo-octatetraene-10,11-dicarboxylate (VII), m.p. 60.5—61.5°,  $\lambda_{\max}$  (EtOH) 242  $m\mu$  ( $\epsilon$  22,800), was obtained in 80% yield. Base hydrolysis of this ester gave the corresponding dicarboxylic acid

(VIII), m.p. 175—178° dec., which was decarboxylated with copper chromite at 260—270° to form benzocyclo-octatetraene (IX) in low yield. Compound (IX) was obtained as colourless prisms, m.p. 49—50°,  $\lambda_{\max}$  (cyclohexane) 243 m $\mu$  (lit.<sup>7</sup>

m.p. 50—51°,  $\lambda_{\max}$  ca. 245 m $\mu$ ) and could be converted to the silver nitrate adduct, m.p. 153—156° (lit.<sup>7</sup> m.p. 150—155°).

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<sup>2</sup> *Inter al.*, L. A. Errede, *J. Amer. Chem. Soc.*, 1961, **83**, 949; D. A. Ben-Efraim and F. Sondheimer, *Tetrahedron Letters*, 1963, 313; M. Avram, I. G. Dinulescu, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *Tetrahedron*, 1963, **19**, 309.

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<sup>4</sup> Satisfactory microanalytical and mass-spectral data were obtained for all new solid compounds.

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