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### HEXALOCYCLOPENTANTADIENES IV. SYNTHESIS AND PYROLYSIS OF OCTABROMO-3a,4,7,7a-TETRAHYDROMETHANOINDENE-1,8-DIONE

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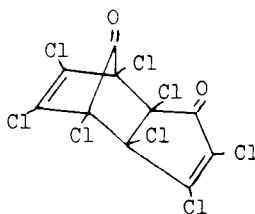
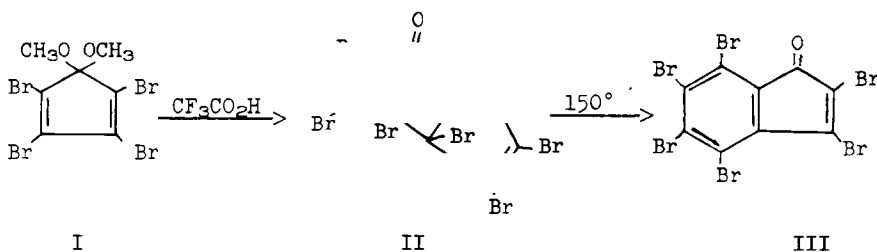
HEXAHALOCYCLOPENTADIENES IV. SYNTHESIS AND PYROLYSIS  
OF OCTABROMO-3a,4,7,7a-TETRAHYDROMETHANOINDENE-1,8-DIONE

R. G. Pews

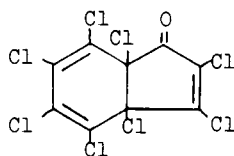
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1,2,3,4-Tetrabromo-5,5-dimethoxycyclopentadiene (I) from hexabromocyclopentadiene has recently been prepared.<sup>1</sup> We now report the synthesis and pyrolysis of octabromo-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione (II).



IV



V

The pyrolysis of III at 150° in benzene solution gave hexabromoindone in 75% yield. Under these conditions, the analogous chlorine compound, IV, yields octachloro-3a,7a-dihydroindone (V) which may be transformed to hexachloroindone with stannous chloride.<sup>2</sup>

EXPERIMENTAL

Ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 15, and are reported in mμ. Infrared spectra were

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obtained with a Beckman IR-9 spectrometer. The mass spectra were obtained on a CEC-21-110B (Direct Probe) instrument. The melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected.

Octabromo-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione (II). - 1,2,3,4-Tetrabromo-5,5-dimethoxycyclopentadiene 25 g (0.0565 mole) and trifluoroacetic acid (100 ml) were heated and stirred to reflux for 1 hr. The reaction was cooled to room temperature and poured onto ice. The white precipitate was filtered, dried and recrystallized from hexane-ethyl acetate to give 18g (82%) of a white solid, m.p. 200-201° (dec).<sup>3</sup> UV max (hexane) 223 m $\mu$  ( $\epsilon$ , 14,850), 270 m $\mu$  ( $\epsilon$ , 8,750); IR (split mull) 1821 and 1842 (C=O, bridged), 1729 cm<sup>-1</sup> (C=O,  $\alpha,\beta$ -unsaturated). The mass spectrum gave a molecular weight of 784 (Br<sup>79</sup>) and the correct isotope ratio for eight bromine atoms in the molecule.

Anal: Calcd for C<sub>10</sub>Br<sub>8</sub>O<sub>2</sub>: C, 15.18; H, 0.00; Br, 80.78. Found: C, 15.40; H, <0.30; Br, 80.50.

Hexabromoindone (III). - Octabromo-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione 5g (0.0063 mole) and benzene (25.0 ml) were heated at 150° in a Fisher-Porter reactor for 17 hrs. After cooling, the reaction mixture was removed from the reactor and the solvent evaporated under reduced pressure to give a bright orange solid which on recrystallization from ethyl acetate gave 3.5g (75%) product, m.p. 196-198° (dec).<sup>3</sup> UV max (hexane) 266 and 276 m $\mu$  (overlap,  $\epsilon$ , 30,000); IR (split mull) 1729 cm<sup>-1</sup> (C=O); and 1656, 1545 and 1518 cm<sup>-1</sup> (aromatic ring modes and C=C).

Anal: Calcd for C<sub>9</sub>Br<sub>6</sub>O: C, 17.88; H, 0.00; Br, 79.47. Found: C, 18.10; H, < 0.20; Br, 79.60.

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#### REFERENCES

1. R. G. Pews, C. W. Roberts and C. R. Hand, *Tetrahedron* 26, 1771 (1970).
2. T. Zincke and W. Pfaffendorf, *Ann.*, 394, 3 (1912).
3. The TGA and DTA curves of II and III showed that the melting points were not for the same compound.

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