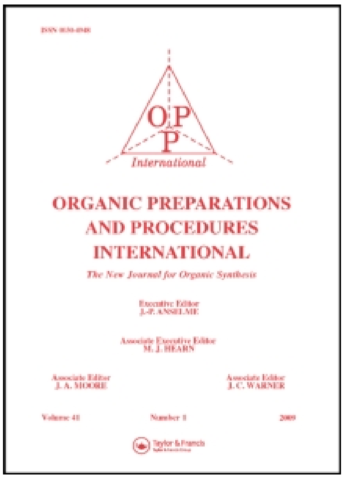


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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

R. G. Pews[a]
[a] Halogens Research Laboratory, The Dow Chemical Company, Midland, Michigan

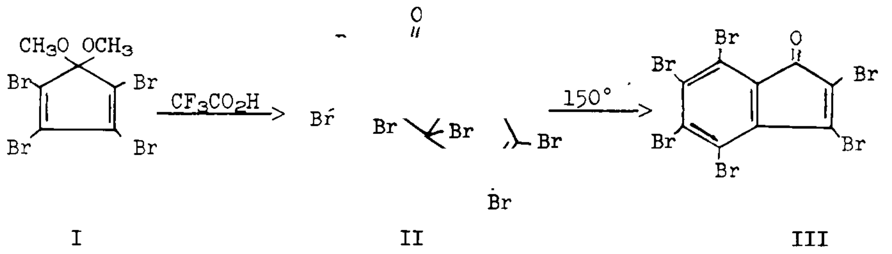
To cite this Article Pews, R. G.(1971) 'HEXALOCYCLOPENTANTADIENES IV. SYNTHESIS AND PYROLYSIS OF OCTABROMO-3a,4,7,7a-TETRAHYDROMETHANOINDENE-1,8-DIONE', Organic Preparations and Procedures International, 3: 1, 37 — 38
To link to this Article: DOI: 10.1080/00304947109356029
URL: http://dx.doi.org/10.1080/00304947109356029

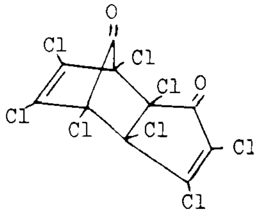
ORGANIC PREPARATIONS AND PROCEDURES INT. 3(1), 37-38 (1971)

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

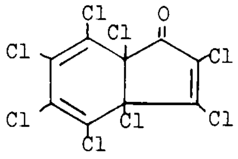
R. G. Pews
Halogens Research Laboratory
The Dow Chemical Company, Midland, Michigan 48640

1,2,3,4-Tetrabromo-5,5-dimethoxycyclopentadiene (I) from hexabromocyclopentadiene has recently been prepared.[1] 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.[2]

EXPERIMENTAL

Ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 15, and are reported in mμ. Infrared spectra were 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).[3] UV max (hexane) 223 mμ (ε, 14,850), 270 mμ (ε, 8,750); IR (split mull) 1821 and 1842 (C=O, bridged), 1729 cm^{-1} (C=O, α,β-unsaturated). The mass spectrum gave a molecular weight of 784 (Br^{79}) and the correct isotope ratio for eight bromine atoms in the molecule.

Anal: Calcd for $C_{10}Br_8O_2$: 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.)[3]. UV max (hexane) 266 and 276 mμ (overlap, ε, 30,000); IR (split mull) 1729 cm^{-1} (C=O); and 1656, 1545 and 1518 cm^{-1} (aromatic ring modes and C=C).

Anal: Calcd for C_9Br_6O: C, 17.88; H, 0.00; Br, 79.47. Found: C, 18.10; H, < 0.20; Br, 79.60.

ACKNOWLEDGMENTS

The author is grateful to Dr. L. Shadoff for the mass spectral data, to Mr. R. Nyquist for determining the infrared spectra, to Mr. J. Simek for determining the ultraviolet spectra and to Mr. L. Swim and his associates for the elemental analyses reported herein. I am also indebted to N. DeHaas for technical assistance.

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.

(Received July 27, 1970)