# Synthesis of [2. 1. 1. 1. 1]Paracyclophane

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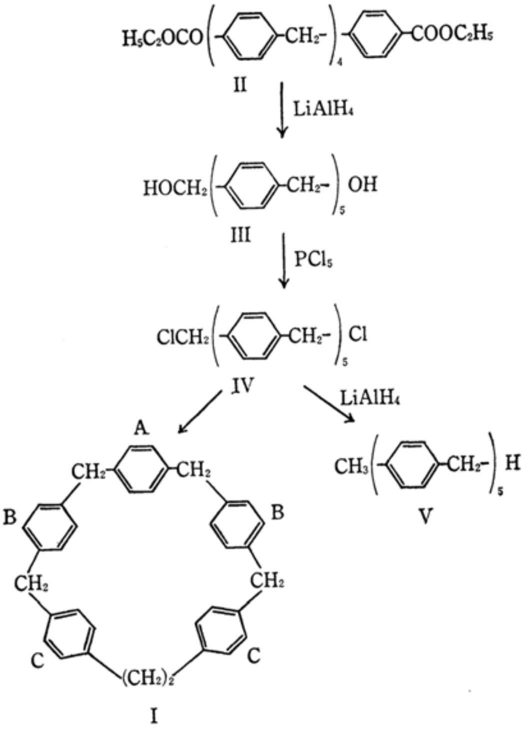
Because of its ability to form clathrates or charge-transfer complexes, the macro-ring compound I, which is furnished with an empty space of an appropriate size at the center of the molecule, is of particular interest. The synthesis of [2.1.1.1.1]-paracyclophane, I, will here be reported. This may be the first example of a paracyclophane constructed with five benzene rings and intervening methylene bridges. The large ring formation by the intramolecular Wurtz-type reaction of a compound with two halogen atoms at mutually unfavorable sites in a molecule may also be novel.



An ester, II,1) was reduced with lithium aluminum hydride to a carbinol, III, mp 203—205°C (Found: C, 86.53; H, 7.04%. Calcd for $C_{36}H_{34}O_2$: C, 86.71; H, 7.12%). This carbinol was then converted by phosphorus pentachloride to a chloride, IV, mp 182.5—183°C (Found: C, 80.47; H, 6.02%. Calcd for $C_{36}H_{32}Cl_2$: C, 80.74; H, 6.02%). The Wurtz reaction of the IV chloride using a sodium tetraphenylethylene adduct in tetrahydrofuran under a nitrogen atmosphere at room temperature and under high dilution conditions afforded the compound I, mp 257°C (Found: C, 92.73; H, 6.96%; mol wt (Rast), 495. Calcd for $C_{36}H_{32}$: C, 93.06; H, 6.94%; mol wt, 464.62) in a 5% yield. The cyclic structure of I was confirmed by a study of its IR and NMR spectra. The IR spectrum of did not show the absorption band at 1380 $cm^{-1}$ which was observed in the case of the open-chain analog, V, mp 153°C. The NMR spectrum consisted of three sets of absorption bands which were consistent with the I structure: a singlet of methylene protons at $\tau$ 6.26, a singlet of ethylene protons at $\tau$ 7.13, and three peaks, at $\tau$ 3.13, $\tau$ 3.20, and $\tau$ 3.29, identified as aryl protons of the A, B, and C rings respectively. The UV spectra of the ring compound I and of the open-chain analog V showed no marked difference in the pattern of absorption bands or of $\lambda_{max}$ (I: 267.5 m$\mu$, log $\varepsilon=3.58$. V: 267.5 m$\mu$, log $\varepsilon=3.20$ in ethanol); the benzene rings in I were found not to be distorted from planarity and not to give rise to a marked trans-spatial overlap of the $\pi$-orbitals of the rings.

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1) The synthesis of the II ester was reported at the Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.