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[2.2.2.2]ORTHOPARACYCLOPHANE[16]

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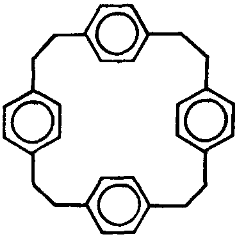
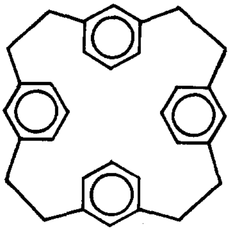
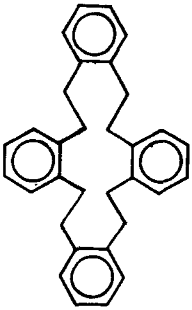
In years past several authors have reported the preparation of macrocyclic compounds containing aromatic rings of various substitution patterns bridged by ethylene and/or methylene units (1-6). Interest in these compounds stems from studies of the physical properties of these molecules and their various conformations, and also from the possibility of forming novel inclusion or charge transfer compounds using these structures as organic backbones. A modified Wurtz coupling reaction has been the most widely used method for preparing such compounds with ethylene bridges (1,2,4,7) resulting, for example, in 1-14% yields of macrocycles I, (1) II, (6,7) and IV (2). Compound III has been made by multi-Wittig reaction.[15] Compound IV has also been made via



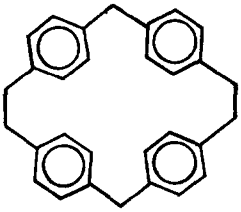
I



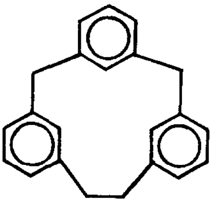
II



III

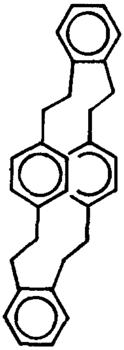


IV

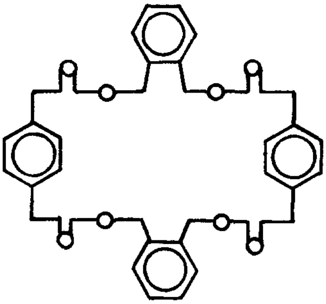


V

a copper(I) coupling reaction in slightly better yield (8), and V was the product of an aromatic electrophilic substitution (4). We now wish to report the preparation of a new compound in this series, [2.2.2.2]orthoparacyclophane(VI), which was prepared by photodecarboxylation of tetraester VII. Photodecarboxylation is a process that has been investigated in some detail (9), and in fact, in a previous communication we reported the extrusion of carbon dioxide from a benzylic bislactone upon uv irradiation, resulting in the formation of [2.2]paracyclophane in good yield (10).



VI



VII

Starting material was prepared by condensing diargentous p-phenylene diacetate with α,α'-dibromo-o-xylene in refluxing acetonitrile (5×10^{-3}M), or by slow addition of a solution of the dibromide to a suspension of the silver salt in the same solvent at reflux. The cyclic benzylic tetraester, bis-o-xylylene bis-p-phenylenediacetate (VII) was isolated by thick-layer chromatography (silica gel, chloroform) in 24% yield and, after recrystallization from chloroform/methanol, it exhibited physical characteristics consistent with the assigned structure (m.p. 197-198°C, MW: Calc. 592, Found: 595±30 (11); lR(KBr): 1740 (s, c=o); NMR ($CDCl_3$, 60MHz,TMS) σ's: 7.44, 7.24, 5.08, 3.51 singlets of equal intensity).

Hydrocarbon VI was prepared by irradiating a solution of 100 mg VII in 100 ml freshly distilled 1,2-dimethoxyethane in a Rayonet reactor at 2537Å (4 hrs, 5°C, N_2). The product was isolated (31 mg, 44%) by preparative thin-layer chromatography (silica gel, chloroform) and recrystallized from chloroform/hexane or acetonitrile. Side products were detected by TLC, but none were isolated in large enough quantities to characterize. The compound assigned as structure VI exhibited physical characteristics consistent with assigned structure:[16]

M.P.: 159-160°C

Anal.: $(C_{32}H_{32})$C,H

MW: Calc.: 416; Found: 428±20 (11)

MS: m/e$^+$ 416 (parent ion), 207 (paracyclcphanyl), 119-115(ethyl tolyl), 104(xylylen
91(tropylium)

IR(KBr): cm^{-1} 3000, 2950, 2930, 1515, 1490, 1450, 1420, 815, 750

UV(EtOH): $\lambda_{max}(\varepsilon)$ 253(368), 257(488), 261(538), 266(690), 274(564), 288(sh), 296(s)

NMR(CD_2Cl_2, TMS, 90MHz)σ's: 7.17(s,8H), 6.84(s,8H), 2.74-2.08(m,16H)

The mass spectrum confirms the molecular weight assignment and exhibits a fragmentation pattern typical of ethylene bridged cyclophanes (12). Although their exact origin is unclear, very strong IR bands at 815 and 750 cm^{-1} have been previously associated with cyclophane structures (1). The presence of the benzene fine structure in the UV spectrum supports the prediction based on CPK molecular models that the benzene rings of VI are planar (13). In the NMR spectrum of VI, the δ 6.8 singlet seems to correspond to the aromatic singlet of I (1c), leaving the signal at 7.17 to be assigned to the ortho bridged ring. There is considerable precedent for ortho-disubstituted aromatic rings to give rise to sharp singlets in the NMR (14). In addition, the symmetrical multiplet assigned to the ethylene bridge indicates that all the bridges are the same, requiring an alternating sequence of ortho and para bridged rings.

In related systems we have isolated intermediate, partially decarboxylated cyclophanes (3). We therefore believe that the mechanism for the formation of VI is the sequential extrusion of the four carbon dioxide molecules, followed in each instance by recombination of the resultant diradical (9). Further experiments on photochemical decarboxylation of large ring systems and the chemistry of VI are in progress.

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(16) Simultaneous with the submission of this paper, there was another report of the title compound: B. Thulin, O. Wennerström, and I. Somfai, Acta. Chem. Scan, 1978, B32, 109. The spectral data appear to be comparable, but this previous paper reports a melting point of 248-252°C (from carbon tetrachloride-methanol?).

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