CHEMISTRY LETTERS, pp. 1405-1406, 1976. Published by the Chemical Society of Japan

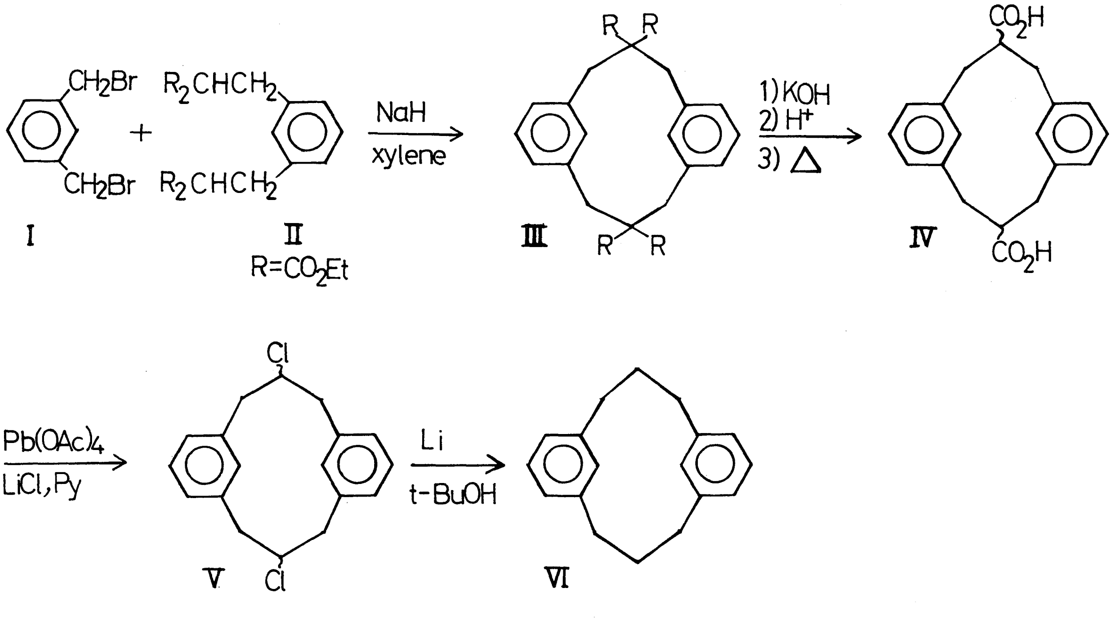
SYNTHESIS OF [3.3] METACYCLOPHANE

Teruo SHINMYOZU, Takahiko INAZU, and Tamotsu YOSHINO
Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki 6-10-1, Higashi-ku, Fukuoka 812

[3.3]Metacyclophane was synthesized by hydrolysis of tetraethyl [3.3]metacyclophane-2,2,11,11-tetracarboxylate (III), followed by decarboxylative chlorination and reduction. Compound III was obtained by the coupling reaction of m-bis(bromomethyl)benzene (I) and tetraethyl m-diethylbenzene-ω,ω,ω′,ω′-tetracarboxylate (II) in the presence of sodium hydride as a base under high dilution conditions.

The synthetic methods and structures as well as chemical and physical properties of [2.2]metacyclophanes1) have been widely investigated, but no useful synthetic methods of [3.3]metacyclophanes have been found as yet. We wish to report the first synthesis of [3.3]metacyclophane, a parent compound of [3.3]metacyclophane series.

When m-bis(bromomethyl)benzene (I) and tetraethyl m-diethylbenzene-ω,ω,ω′,ω′-tetracarboxylate (II) were added to sodium hydride in refluxing xylene under modified conditions of those described by Vögtle,2) there were obtained the desired tetraester (III) (the cyclic dimer) and the higher cyclic oligomers (the tetramer and the hexamer). After purification by chromatography on silica gel, III was isolated in 5.4 % yield. III; colorless plates from ether, mp 126.2-126.8°C. Found: C, 68.58; H, 6.93 %; mol wt(MS, M^+), 524. Calcd for $C_{30}H_{36}O_8$: C, 68.69; H, 6.92 %; mol wt, 524.6. PMR($CDCl_3$, δ): 1.38(t, 12H), 3.19(s, 8H), 4.33(q, 8H), 5.54(broad s, 2H), 7.02(m, 6H). UV(cyclohexane): 264.6(ε, 430), 271 nm(sh, 360).



After alkaline hydrolysis of III, the resulting tetracarboxylic acid was pyrolyzed to give a dicarboxylic acid (IV) (mp 240-242.5°C) in 86 % yield from III. IV was treated with lead tetraacetate[3)] and lithium chloride in pyridine to give a dichloride (V) in 75 % yield. V; colorless needles from ethanol, mp 180-182°C. Found: C, 70.64; H, 6.13 %; mol wt(MS, M^+), 304. Calcd for $C_{18}H_{18}Cl_2$: C, 70.83; H, 5.94 %; mol wt, 305.2. PMR($CDCl_3$,δ): 2.50-3.70(m, 8H), 4.0-4.8(m, 2H), 6.75, 6.90(m, 8H). The dichloride (V) was treated with lithium and tert-butanol in refluxing THF to give [3.3]metacyclophane VI in 61 % yield. VI; colorless plates from metanol, mp 79-80°C. Found: C, 91.22; H, 8.55 %; mol wt(MS, M^+), 236. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53 %; mol wt, 236.3. PMR($CDCl_3$,δ): 1.8-2.4(m, 4H), 2.75(t, 8H), 6.50-7.0 (m, 8H). UV(Cyclohexane): 216(sh, 9950), 226(sh, 6270), 256(sh, 473), 261(sh, 343), 266(sh, 240), 275(sh, 146) and 282 nm(sh, 103).

The yield of III in the coupling reaction is not so high, but this may be covered by the fact that the starting materials are readily available. This synthetic method has been successfully applied to other cyclophane systems, such as [3.3]paracyclophanes, [3.3]metaparacyclophanes and [3.3]naphthalenophanes.[4)] The method appears to be general for syntheses of [3.3]cyclophanes and also to have merit especially for the preparation of cyclophanes in which the two moieties of the cyclophane molecule are dissimilar each other. The synthetic studies and the spectral properties of [3.3]cyclophane systems are now under investigation.

Reference

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2) F. Vögtle and M. Zuber, Synthesis, 1972, 543; they reported the synthesis of octaethyl [3.3.3.3]metacyclophane-2,2,11,11, 20,20,29,29-octacarboxylate by slow addition of I and II to an excess sodium hydride in refluxing toluene, but they did not succeed in isolation of III. R. W. Griffin, Jr. and R. A. Coburan, Tetrahedron Lett., 2571 (1964); they obtained diethyl [3.2]metacyclophane-2,2-dicarboxylate by the reaction of 3,3′-bis(bromomethyl)bibenzyl and diethyl malonate using sodium hydride as a base.

3) J. K. Kochi, J. Am. Chem. Soc., 87, 2500 (1965).

4) To be published.

(Received October 23, 1976)