Tetrahedron Letters No. 6, pp 501 - 504, 1974. Pergamon Press. Printed in Great Britain.

LAYERED COMPOUNDS. XIX.1) NOVEL REARRANGEMENT OF TRIPLE-LAYERED [2.2]PARACYCLOPHANE WITH FRIEDEL-CRAFTS ACIDS

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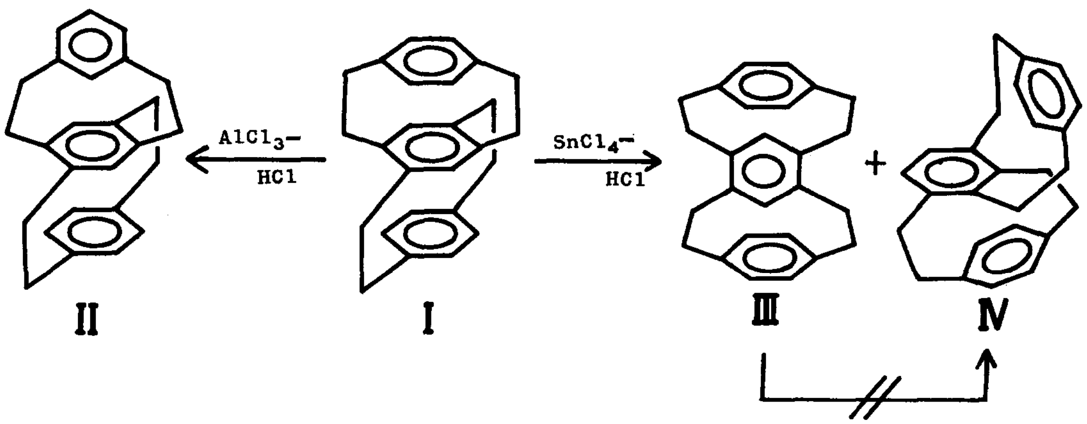
(Received in Japan 12 November 1973; received in UK for publication 28 December 1973)

In the previous papers of this series, we have reported the syntheses and properties of multilayered [2.2]paracyclophanes.2) The increased electronic interaction and the highly strained structure of those compounds prompted us to further investigation.2,3) The present communication reports unique skeletal rearrangements of triple-layered [2.2]paracyclophane (I) with several Friedel-Crafts acids.

Cram reported an interesting rearrangement of [2.2]paracyclophane to [2.2]metaparacyclophane with aluminum chloride-hydrogen chloride catalyst and described it as a result of decreasing the π-π repulsion.4) Treatment of more severely strained triple-layered [2.2]-paracyclophane (I) with the same acid produced mainly metapara triple-layered cyclophane II, formed by migration of a bridge in one of the outer benzene rings, along with small portions of



two isomeric products, III and IV, formed by bridge migration in the inner benzene ring. On the other hand, when a large excess of stannic chloride-hydrogen chloride was used as a catalyst, a mixture of migration products, III and IV, was obtained in a 80% yield besides polymeric substance, but neither starting material nor migration product II was appreciably detected. Being treated with titanium tetrachloride or boron trifluoride as a Lewis acid, I afforded also III and IV in the nearly same yield and ratio as in the case of stannic chloride. Treatment with hydrogen fluoride at 0°C gave lower yield of triple-layered compounds mixture containing IV as main product. These results are summarized in Table 1.

Table 1. Rearrangement conditions of cyclophane I. All reactions were carried out in methylene chloride.

Friedel-Crafts Acid	Temperature	Time	Yield	Product Ratios[a]
$AlCl_3$-HCl	-17°C	15 min	51 %	I(3%) + II(76%) + III(11%) + IV(10%) III:IV = 52:48
$SnCl_4$-HCl	29°C	30 min	80 %	III(54%) + IV(46%)
	30°C	180 min	64 %	III(55%) + IV(45%)
$TiCl_4$-HCl	29°C	30 min	72 %	III(54%) + IV(46%)
	29 ~ 31°C	180 min	69 %	III(48%) + IV(52%)
BF_3-HCl	-17°C	60 min	recovery of starting material	
	29 ~ 31°C	30 min	74 %	I(15%) + III(47%) + IV(38%) III:IV = 55:45
	30 ~ 34°C	180 min	79 %	III(53%) + IV(47%)
HF	0°C	20 min	20 %	I(13%) + III(11%) + IV(76%)

a) determined by 100 MHz NMR analysis.

For separating the mixture of III and IV into its components, the mixture was subjected to fractional crystallization with benzene to afford most of less soluble isomer III, and further recrystallization of the resulting residue gave two kinds of colorless crystals, plates of III and prisms of IV. After picking out with a tweezers, they were recrystallized separately. The cyclophanes II and III thus obtained are quite identical with those previously reported in all respects.[5] A new type of cyclophane, IV, possessing an inner benzene ring of

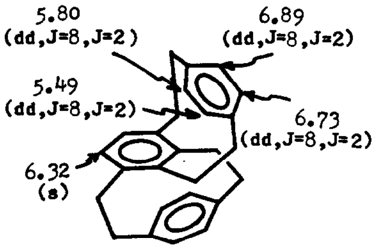


Fig. 1. NMR data of IV in $CDCl_3$ (δ value; J, cps)

prehnitene framework crystallizes as colorless prisms from benzene-n-hexane, m.p. 209~210°C (partly sublimed), mass m/e 338 (M^+), 233, 104; UV λ_{max} (ε) 238 sh (10200), 280 sh (490), 285 (600), 293 nm (530). The NMR data are shown in Fig. 1.

The conversion of [2.2]paracyclophane to [2.2]metaparacyclophane was explained in terms of release of strain and relative basicity of polyalkyl benzenes, e.g., m-dialkyl > p-dialkyl.4)

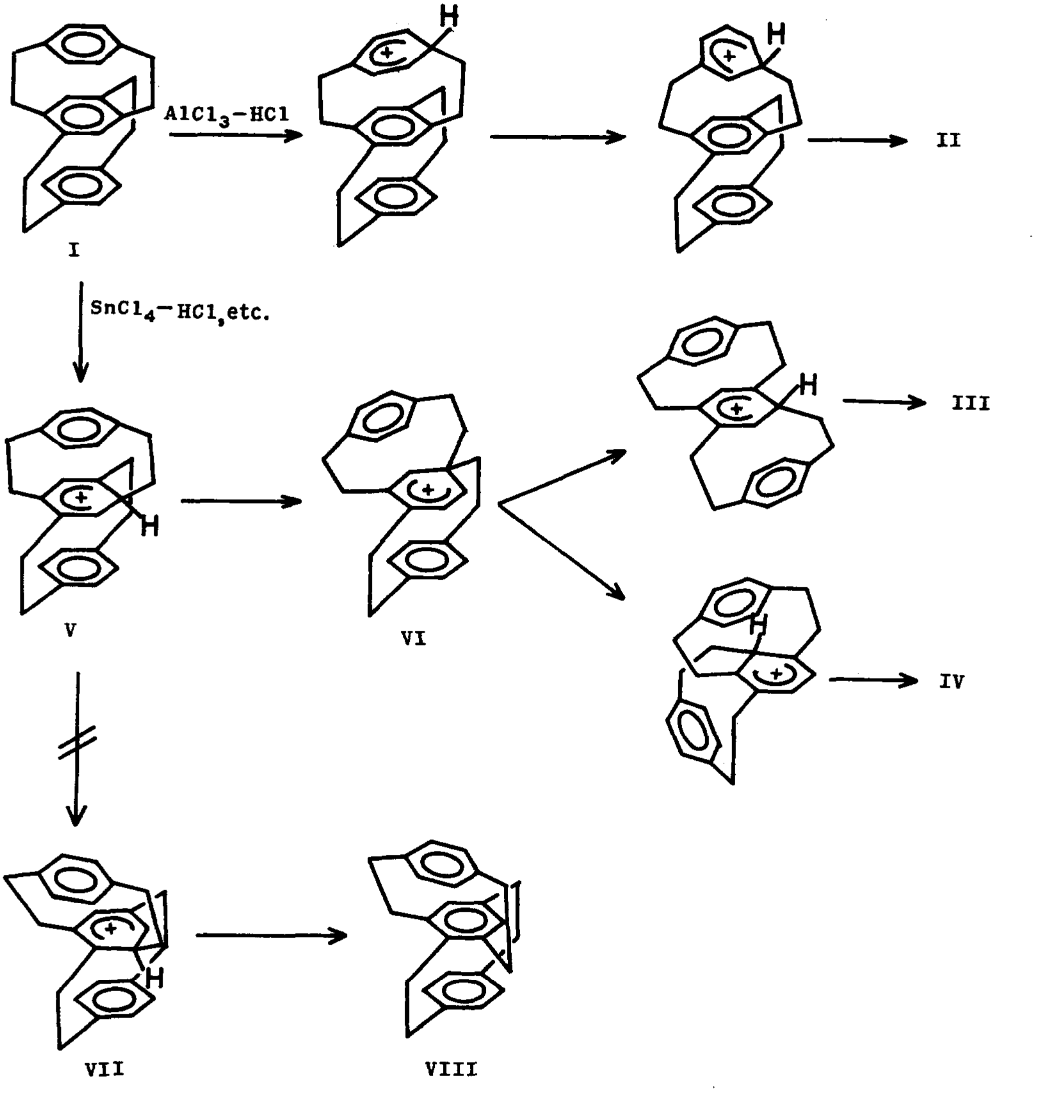


Fig. 2. A reaction mechanism of the rearrangements of I to II, III, and IV.

The rearrangement of triple-layered [2.2]paracyclophane also is probably interpreted by the same driving forces as for double-layered one. We propose a mechanism of the rearrangement as shown in Fig. 2. In the course of the rearrangement of I to III and IV, the initial stage would be the protonation at one of the bridgehead carbons in the inner benzene ring, which is more deformed and stronger basic than the outer rings, to form a cation V. The methylene bridge at the protonated bridgehead carbon is then moved intramolecularly by 1,2-shift to give a cation VI. The cation VI is presumed to be common intermediate for the formation of III and IV, since the product ratios of III:IV were generally constant regardless of catalysis species and reaction times as seen in Table 1, and no further rearrangement of III to IV was observed under the same conditions. Then the cation VI converts to two rearranged cations through the corresponding way of subsequent bridge migration, followed by deprotonation to produce III and IV. The rearrangement of the cation V to a cation VII is considered to proceed hardly because a supposed cyclophane VIII is strained to much larger extent compared with III and IV. In the rearrangement with an excess of aluminum chloride-hydrogen chloride catalyst, the preferred protonation at the bridgehead in the outer benzene ring may be associated with both the acidity and bulkiness of the protonic acid.

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