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A Highly Selective Transannular Route to *trans-trans*-1,2,3,3a,4,5,9,10,10a,10b-Decahydropyrenes from [2.2]Metacyclophanes

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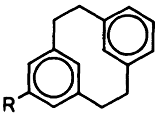
The treatment of [2.2]metacyclophanes with aluminum chloride gave a variety of hydropyrenes as the results of dehydrogenation, cycloisomerization, and disproportionation reactions. With ethylaluminum dichloride, however, a highly selective reaction occurred to give *trans-trans*-1,2,3,3a,4,5,9,10,10a,10b-decahydropyrene. Revised structures were presented for *cis-cis-* and *trans-trans*-decahydropyrenes based on ^{13}C NMR and X-ray crystallographic analyses.

We have reported[1] that the treatment of [2.2]-metacyclophane (**1a**) with aluminum chloride in carbon disulfide gives a variety of hydropyrenes, arising from three types of transannular reactions; 1) dehydrogenation (**2a**, **3a**, and **4a**), 2) cycloisomerization (**5a**), and 3) hydrogenation *via* disproportionation (**6a** and **7a**). The type-1 reaction occurred quite readily due to an anomalously low anodic potential of **1a**[2] by the action of various one-electron oxidants and other electron-transfer conditions.[3] The selective formation of **5a** through the type-2 reaction was best achieved by the reaction of **1a** with iodine.[4]



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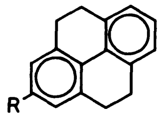

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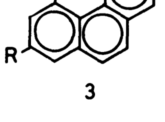

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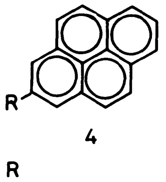

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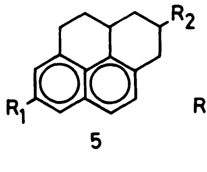
	R
a	H
b	Me



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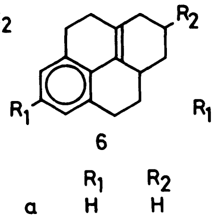

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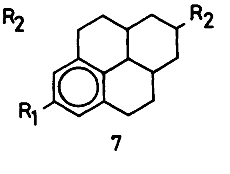

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	R1	R2
a	H	H
b	Me	H
c	H	Me

In this paper we describe the selective formation of the type-3 products, especially decahydropyrene (*cf.* **7a**) by using ethylaluminum dichloride. We also report the stereochemistry of the decahydropyrene studied by the NMR spectrometry and by the X-ray crystallographic analysis.

The Reaction of [2.2]Metacyclophane with Aluminum Chloride. Baker and co-workers[5] have reported the formation of 1,2,3,3a,4,5-hexahydropyrene (**5a**) by the reaction of **1a** with aluminum chloride in carbon disulfide. When we repeated the reaction we obtained a complex mixture of products, **2a**, **3a**, **4a**, **5a**, **6a**, and **7a**. By carrying out the reaction under various conditions[1] we have shown that the initial products are 1,2,3,3a,4,5,9,10-octahydropyrene (**6a**), **5a**, and 4,5,9,10-tetrahydropyrene (**2a**). Upon further contact with aluminum chloride, 1,2,3,3a,4,5,9,10,10a,10b-decahydropyrene (**7a**) was formed by the disproportionation of **6a**.

Table 1 shows the product ratio obtained from the transannular reaction of **1a** and **1b** with 4 equiv aluminum chloride in carbon disulfide for 3 h at room temperature. The analyses of the products were performed by GC–MS by using an OV-1 column for gas chromatography. When hydrogen chloride was passed through the mixture, the cycloisomerization product **5a** became the major product.

The effect of a substituent at C-5 was then investigated. Under similar conditions as above, 5-methyl-[2.2]metacyclophane (**1b**) also gave a complexed mixture. Compared with **1a**, the yields of **6** and **7** decreased while the yields of **2** and **5** increased marked-

TABLE 1. THE REACTION OF [2.2]METACYCLOPHANE (**1a**) AND (**1b**) WITH $AlCl_3$ OR $AlCl_3$–HCl

Compound	Hydropyrenes/%					
	Tetra-, **2**	Di-, **3**	**4** (Pyrene)	Hexa-, **5**	Octa-, **6**	Deca-, **7**
1a[a)]	1	—	20	6	30	43
1a[a,b)]	—	—	3	84	12	1
1b	40	10	5	25	18	2
1b[c)]	1	—	2	95	2	1

a) Ref. 1. b) $AlCl_3$–HCl reflux. c) $AlCl_3$–HCl room temperature.

ly. For **5**, **6**, and **7**, two isomeric products are possible, namely the b or c types according to the direction of reaction. The ^{1}H NMR of the products showed the presence of an aromatic methyl resonance at around δ 2.2—2.5 and, hence, these were **5b**, **6b**, and **7b** but not **5c**, **6c**, and **7c**. When hydrogen chloride was passed through the mixture the major product was **5b**.

Selective Formation of Decahydropyrene. The Lewis acid strength of ethylaluminum compounds were found to be as follows:[6)]

$$AlCl_3 > EtAlCl_2 > Et_2AlCl,\ Et_3Al$$

While aluminum chloride was too reactive for **1a** to induce a selective disproportionation reaction, **1a** was inert toward triethylaluminum as well as diethylaluminum chloride.

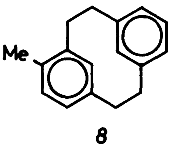
Ethylaluminum dichloride has been generated *in situ* using the following scheme:[7)]

$$Et_2AlCl + TiCl_4 \longrightarrow EtAlCl_2 + EtTiCl_3$$

Ethyltitanium trichloride formed was unstable and the evolution of ethylene among others was noticed.[8)] As a control experiment, compound **1a** was found to be stable toward titanium tetrachloride.

When compound **1a** was treated with the reagent formed from 3 equiv each of diethylaluminum chloride and titanium tetrachloride in benzene under reflux for 3 h, nearly equal amounts of **2a** and **7a** were produced. Compound **7a** was found to be a single stereoisomer by the ^{13}C NMR spectrum and gas chromatography using an SE-30 column. The stoichiometric consideration requires a hydrogen donor other than **1a** to give **7a** since only two hydrogens are evolved to form **2a** while the formation of **7a** requires four. Presumably, the ethylaluminum reagent is responsible for the hydrogen source to form highly hydrogenated **7a**.

The directional selectivity on the formation of isomeric decahydropyrenes was tested using methyl-substituted [2.2]metacyclophanes, **1b**, **8**, and **9**. It has been found[1,9)] that an alkyl substituent on [2.2]metacyclophane exerts different effects according to the position of substitution. With cycloisomerization, for example, a C-5 alkyl group as in **1b** directs the hexahydropyrene formation while preserving a substituted aryl ring. The C-4 and 6 alkyl groups as in **8** and **9** lead the hydrogenation of a substituted aryl ring, presumably through the additional strain effect of the methyl group on the bridging methylene group.[1,9)]



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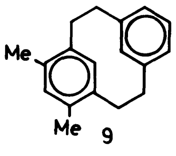

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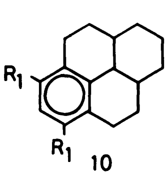

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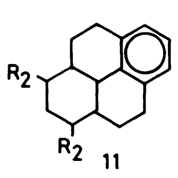

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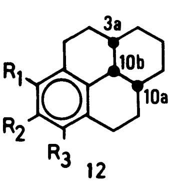
	R_1	R_2
a	Me	H
b	Me	Me

5-Methyl derivative **1b**, upon treatment with 3 equiv diethylaluminum chloride and titanium tetrachloride in benzene, gave an exclusive formation of **7b**, no isomeric **7c** being detected. 4-Methyl derivative **8**, on the other hand, gave a mixture of products **10a** and **11a** in a ratio of 4:6 as analyzed by gas chromatography and ^{1}H NMR. 4,6-Dimethyl derivative **9** gave, under similar conditions, a mixture of **10b** (75%) and **11b** (25%). Here again, the methyl group next to the bridging methylene group forced the formation of the product with a hydrogenated substituted aryl ring similar to the case of cycloisomerization.

In addition to decahydropyrenes, these reactions afforded approximately equal amounts of the corresponding tetrahydropyrenes, **2b**[10)] from **1b**, 1-methyl- and 1,3-dimethyl-4,5,9,10-tetrahydropyrenes[10)] from **8** and **9**, respectively.

Isomeric structures between **7b** and **7c**, and also **10** and **11**, could be assigned based on both ^{1}H NMR and mass spectrometry. Aromatic methyl compounds, **7b**, **10a**, and **10b** showed singlets around δ 2.2, while aliphatic methyl derivatives **7c**, **11a**, and **11b** showed doublets in the expected region. A base peak in mass spectrometry also gives the difference; namely, base peaks for aromatic methyl and aliphatic methyl compounds were found to be M-15 and M-28, respectively (Table 3).

Stereochemistry of Decahydropyrene. The decahydropyrene **7a** can exist in three stereoisomers, namely *cis-cis*-compound **12a**, *trans-trans*-compound **13a**, and *cis-trans*-**14**. Compounds **12a** and **13a** are *meso* type while **14a** is a *dl*-type.



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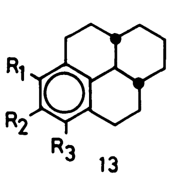

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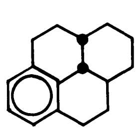

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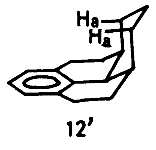
	R_1	R_2	R_3
a	H	H	H
b	H	Me	H
c	Me	H	H
d	Me	H	Me



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Lehner and co-worker obtained[11)] a decahydropyrene, mp 129 °C, by the hydrogenation of **1a** over rhodium on alumina catalyst and assigned a *trans-trans*-structure **13a** based on the NMR evidence. We obtained[1)] a deca-

Table 2. ^{13}C NMR data for decahydropyrenes (**12a**), (**12d**), and (**13a**)—(**13d**)

Compound	Aliphatic Carbons				Aromatic Carbons	
	3a,10a	10b	CH_2	Me	quat.	ArH
12a[a]	35.68	39.75	28.47, 26.06 25.74, 25.24		136.22, 134.12	126.22, 125.00
13a[b]	38.11	47.93	34.29, 30.76 29.14, 25.73		136.11, 135.95	126.13, 125.39
13b	38.47	47.93	34.45, 31.00 29.26, 25.97	21.06	136.07, 135.01 133.02	127.06
13c	38.30 37.45	48.24	34.36, 30.81 30.79, 29.08 27.02, 25.73	19.49	135.76, 134.41 133.53, 126.79	127.20, 126.11
12d	35.64	40.34	28.41, 26.06 24.91, 23.61	19.47	133.60, 133.07 131.82	128.73
13d	37.58	48.47	34.33, 30.75 26.77, 25.58	19.22	135.69, 133.21 131.77	129.99

a) Lehner's decahydropyrene; Ref. 10. b) Our decahydropyrene; Ref. 1: Data reported in Ref. 1 need to be modified as tabulated as pointed out by Hansen *et al.*[12)]

Table 3. 1,2,3,3a,4,5,9,10,10a,10b-Decahydropyrenes

Compound	Mp/θ_{m}/°C	M^+	Base Peak	Formula	Found %		Calcd %	
					C	H	C	H
13a[a]	53.5—54.5	212	184 (M−28)					
13b	93—94	226	211 (M−15)	$C_{17}H_{22}$	89.82	9.97	90.20	9.80
11a	oil	226	198 (M−28)	$C_{17}H_{22}$	90.15	9.73	90.20	9.80
13c	oil	226	211 (M−15)					
13d	97—98	240	225 (M−15)	$C_{18}H_{24}$	89.66	10.01	89.94	10.06
12d	(75—85[b])	240	225 (M−15)	$C_{18}H_{24}$	89.86	10.19	89.94	10.06
11b	oil	240	212 (M−28)					

a) Ref. 1. b) Mp of the mixture, **12d** and **13d**.

hydropyrene, mp 53.5—54.5 °C, by the disproportionation of **1a**. It was also a *meso*-type compound similar to that of Lehner, as examined by ^{13}C NMR. In view of Lehner's results, we tentatively assigned a *cis-cis*-structure **12a**.[1)] Later, Hansen *et al.* obtained[12)] both of these by the cathodic reduction of tetrahydropyrene **2a** in DMF in the presence of a proton donor. The *dl*-type compound **14** was also reported by Hansen *et al.*[12)]

Table 2 summerizes the ^{13}C NMR data for isomeric decahydropyrenes obtained by Lehner *et al.* and by us. The assignment was achieved by an intensity consideration, the off-resonance spectrum, and by a comparison with reported data. Compared with our product, Lehner's decahydropyrene showed a general upfield shift of corresponding resonances. For example, two quaternary carbon resonaces and three out of four methylene carbon resonances showed upfield shifts of 2—8 ppm while aromatic signals were almost similar. The upfield shift of the 10b carbon amounted to almost 8 ppm. This was taken as evidence that Lehner's product had a more congested structure compared to our decahydropyrene.[13)] Our product showed a clear triplet in the ^{1}H NMR spectra, determined at 500 MHz at 1.845 ppm with J=11.3 Hz. This was assigned to the 10b proton which had antiperiplaner vicinal protons (possible only for **13a**, but not for **12a**). From this evidence, we concluded that the assignment must be revised. The Lehner's product was **12a** not **13a**, and our product was **13a** but not **12a**. This assignment appeared to be consistent with the hydrogenation experiment carried out by Lehner for **1a**. They obtained[14)] a perhydropyrene possessing *cis-cis*-structure as the partial structure expected from one-sided hydrogenation.

Our decahydropyrenes **7b** and **10a** are best represented by **13b** and **13c**, respectively. The ^{13}C resonances of the 10b carbon for **13b** and **13c** were δ 47.93 and 48.24, respectively, expected from a *trans-trans*-structure. Decahydropyrene **10b**, obtained from **9**, was found to be a mixture of both **12d** and **13d** (mp 75—85 °C as a mixture), almost in equal amounts. These were separated by repeated chromatography on alumina containing silver nitrate. This separated **13d** (mp 97—98 °C) as a fast eluting fraction which was followed by *cis-cis*-compound **12d**. By gas chromatography on OV-1, the elution order was reversed and **12d** became the fast moving fraction. Compound **12d** showed an upfield shift of the 10b carbon resonance by about 8 ppm compared with **13d**. Also, **12d** showed a high-field multiplet in the ^{1}H NMR at 0.80—1.40 ppm, which in the case of **13d** occurred at 1.05—1.50 ppm. Axial protons Ha in 12′ must be responsible for the upfield shift due to a ring-current

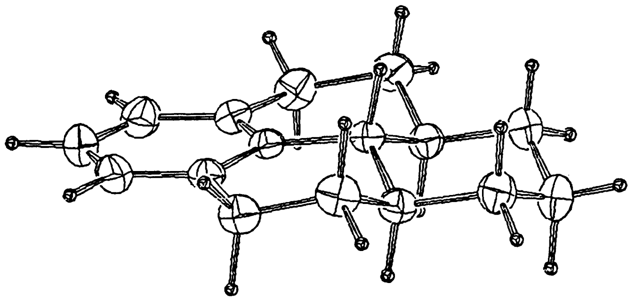

Fig. 1. ORTEP drawing of the structure of **13a**, thermal ellipsoid of 30% probability.

effect.

Conclusive evidence was obtained by the X-ray crystallographic analysis of **13a**. The crystal data for **13a** are as follows: $C_{16}H_{20}$, M=212.32, monoclinic, space group C2/c, a=19.139(15), b=9.970(8), c=15.311(10) Å, β=123.34(9)°, U=2440.8 Å^3, Z=8, D_c=1.155 g cm^{-3}. The structure was solved by the direct method. Least-squares refinement of the atomic positional and thermal parameters converged at R=0.06 using 2467 refractions. A view of the molecular structure is shown in Fig. 1.

Experimental

[2.2]Metacyclophane Derivatives. Compounds **1a**,[1)] **1b**,[10)] and **9**[10)] were prepared as described in the literature.

2,11-Dithia-5-methyl[3.3]metacyclophane. α,α'-Dibromo-*m*-xylene was treated with thiourea in ethanol and then with a potassium hydroxide solution to give *m*-xylene-α,α'-dithiol. Benzene solution (600 cm^3) of 4-methyl-α,α'-dichloro-*m*-xylene (17.8 g, 94 mmol), prepared by bischloromethylation of toluene, was dropped slowly into a solution of the dithiol (16 g, 94 mmol) and sodium hydroxide (8 g, 0.2 mol) in benzene (400 cm^3)–ethanol (1000 cm^3) during 72 h under reflux. The solvent was then evaporated, and washed dichloromethane extracts were passed through a silica-gel column. The bis(sulfide) was thus obtained in a 52% yield: pale yellow needles from ethanol–water–hexane, mp 86—88 °C: NMR ($CDCl_3$) δ=2.15 (3H, s, Me), 3.6 (8H, m, CH_2), and 6.5—6.9 (7H, m, ArH).

Found: C, 71.24; H, 6.41; S, 22.13%. Calcd for $C_{17}H_{18}S_2$: C, 71.28; H, 6.33; S, 22.39%.

4-Methyl[2.2]metacyclophane (8). The above bis(sulfide) was converted to bis(sulfone), 2,11-dithia-5-methyl[3.3]-metacyclophane 2,2,11,11-tetraoxide, by oxidation with 30% hydrogen peroxide in benzene–acetic acid at room temperature. The pyrolysis of bis(sulfone) at 550 °C gave **8** (mp 70—72 °C) after chromatography on silica gel: NMR ($CDCl_3$) δ=2.35 (3H, s, Me), 2.05 and 3.07 (8H, m, CH_2), 4.2—4.3 (2H, m, C-8H and C-16H), and 6.9—7.4 (7H, m, ArH).

Found: C, 91.81; H, 8.15%. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16%.

The Reaction of 5-Methyl[2.2]metacyclophane (1b) with Aluminum Chloride. The reaction was carried out at room temperature according to the reported method.[1)] Analyses of products were carried out by GC–MS using OV-1 (1 m) column. The results are summerized in Table 1.

The Reaction of [2.2]Metacyclophanes with Ethylaluminum Dichloride. a) 1,2,3,3a,4,5,9,10,10a,10b-Decahydropyrenes: As an example the reaction of **1a** with ethylaluminum dichloride is shown. A solution of **1a** (104 mg, 0.5 mmol), diethylaluminum chloride (180 mg, 1.5 mmol), and titanium tetrachloride (285 mg, 1.5 mmol) in benzene (5 cm^3) was stirred at room temperature for 3 h. Column chromatography on alumina eluted with hexane gave **13a** (45 mg, 42%) and **2a** (46 mg, 45%).

Compounds **1b**, **8**, and **9** were treated in a similar manner. Melting points, mass spectra, analytical data, and ^{13}C NMR of decahydropyrenes are shown in Tables 2 and 3.

b) 1-Methyl-4,5,9,10-tetrahydropyrene: The compound was obtained from **8** as an oily material. ^{1}H NMR ($CDCl_3$) δ= 2.30 (3H, s, Me), 2.82 (8H, s, CH_2), 6.97 (2H, s, ArH), and 7.05 (3H, s, ArH). Mass spectrum, *m/z* 226.

Found: C, 92.25; H, 7.65%. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32%.

Other hydropyrenes were characterized by comparing with the authentic materials reported before.[2,10)]

Measurements. ^{1}H NMR spectra were determined on a JEOL GX-500 spectrometer and ^{13}C NMR spectra were measured on a JEOL GX-400 or on a Varian XL-300 spectrometers. X-ray crystallographic analysis was carried out on a Philips automated difractometer (graphite monochromated Cu $K\alpha$ radiation, λ=1.5418 Å; θ—2θ scan method, θ_{max} 78°).

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