Tetrahedron. Vol. 31, pp 239 to 244 Pergamon Press 1975 Printed in Great Britain

MEDIUM-SIZED CYCLOPHANES—XVII

TETRA-, HEXA-, OCTA- AND DECAHYDROPYRENES FROM [2.2]METACYCLOPHANE. TRANSANNULAR DEHYDROGENATION, ISOMERIZATION, AND DISPROPORTIONATION REACTIONS BY MEANS OF BENZOYL PEROXIDE, METAL SALTS AND SULFURIC ACIDS[1]

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(Received in Japan 15 October 1974; Received in UK for publication 24 October 1974)

Abstract—[2.2]Metacyclophane (**1**) undergoes a variety of reactions according to the reagents and conditions. These include (1) substitution (path a), (2) transannular dehydrogenation (path b and c), (3) cycloisomerization (path d) and (4) transannular hydrogenation. A brief summary of these reactions is presented.

The diversity of the reactions of **1** is further explored using benzoyl peroxide (BPO), cupric chloride, aluminum chloride, other metal salts, H_2SO_4 and FSO_3H. With BPO or cupric chloride, one-electron transfer mechanism is postulated. This involves a tautomeric ion pair formed by the intramolecular arylation with an aryl cation radical. A supporting evidence in favor of the mechanism is presented from experiments using various metal salts in different solvents.

On the contrary, the reaction with aluminum chloride gives decahydropyrene (**8**) and octahydropyrene (**11**) together with cycloisomerization product **5** and dehydrogenation products **2**, **3** and **4**. When treated with $AlCl_3$–HCl **1** gives similar products as above but the product ratios are quite different. The major product is **5** but only a trace amount of **8** is formed. The reaction with H_2SO_4 or FSO_3H also produce **2**, **4**, **5** and **11**. Some mechanistic evidence in favor of the disproportionation reaction is presented.

Extensive studies on the reaction of [2.2]metacyclophane (**1**) and derivatives have revealed three major reaction types (Scheme 1). These are substitution (path a),[1,2] transannular dehydrogenation (path b and c),[1-3] and transannular isomerization (path d).[4] Due to ready transannular reactions the substitution reaction (path a) is rarely observed in metacyclophane compounds.[1,2,5,6]

Electrophilic,[3a,b] photolytic,[3c] and some radical[3d] reactions produced 4,5,9,10-tetrahydropyrene (**2**) in a good yield (path b and c). Further substitution or dehydrogenation was observed as a secondary process (e.g. **2**→**3**→**4**). Treatment with iodine, on the other hand, gave 1,2,3,3a,4,5-hexahydropyrene (**5**) in a quantitative yield (path d).[4]

As other examples of the transannular reaction, Lehner and Langer[7] obtained perhydropyrene on catalytic hydrogenation of **1**. Dehydrogenation over Pd–C gave pyrene as reported by Baker *et al.*[8] The same authors described the formation of **5** from **1** by the reaction of aluminum chloride.[8]

To find out the scope of the reaction and to obtain the mechanistic evidence we have studied the reaction of **1** with metal salts and acids.

As the result, detailed studies of the aluminum chloride reaction have revealed a new type of reaction giving rise to hydropyrenes and pyrene by disproportionation. The similar reaction was observed by the action with sulfuric acid and fluorosulfonic acid. These took place via protonation of the substrate. On the other hand one-electron oxidants such as cupric chloride caused dehydrogenation into **2**. In this paper these two types of reactions are described.

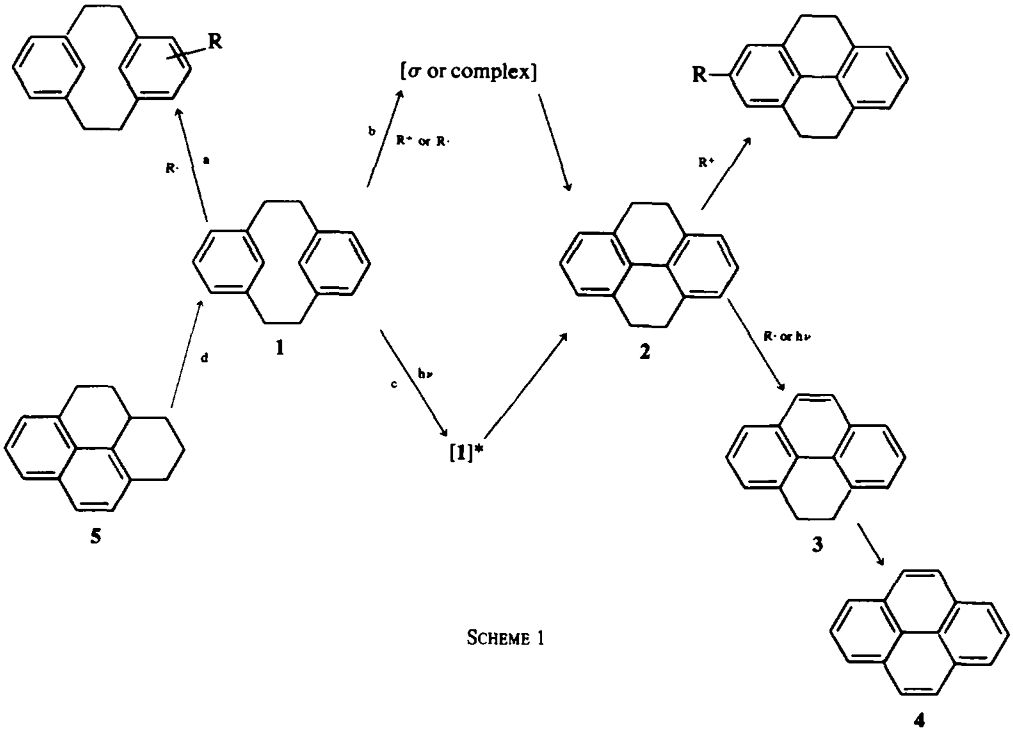
RESULTS AND DISCUSSION

The transannular dehydrogenation of [2.2]*metacyclophane* (**1**)

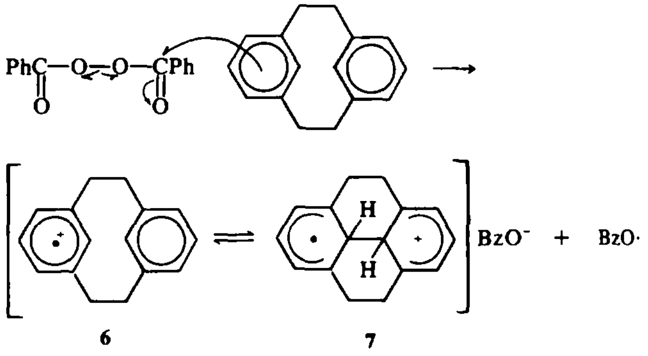
The treatment of **1** with aroyl peroxide and cupric chloride gave **2**, **3**, and **4** (total yield, *ca* 12%) in addition to substituted **1**.[1,2] Each aroyl peroxide and cupric chloride was found to be effective for the transannular dehydrogenation.

Although benzoyl peroxide (BPO) gave only 2% yield of **2**, cupric chloride in acetonitrile (80° for 20 hr) produced 20% of **2** and a small amount of **3**.[1,2] Competitive experiments using several alkyl derivatives revealed the dependence of reaction rates upon the ionization potential of the substrates. It was also found that the reaction is favored in polar solvents. These results suggest involvement of an ionic intermediate produced by a one-electron-transfer process. Surprisingly the dehydrogenation with BPO occurred even at 40° although in a low yield (~3%).

With BPO as an oxidant, Scheme 2 can be postulated: Induced decomposition[9] of BPO with **1** gives valence tautomer **6** and **7** via one-electron transfer. Ready electron transfer from **1** is favored by a lower ionization potential, 8·41 eV,[10] compared with simple arenes (*cf* *m*-xylene, 8·71 eV) and also by the formation of transannular



SCHEME 1



$$7 \xrightarrow[-H\cdot]{-H^+} 2$$

SCHEME 2

tautomer 7. Deprotonation and hydrogen abstraction from 7 leads to 2.

That this is not a simple radical reaction has been shown by the inertness of 1 toward t-butoxy and α-cyanoisopropyl radicals. These are effective for the transannular dehydrogenation only under photoirradiation.[3d] As another evidence in favor of the above scheme, 1 gave 2 when treated with diisopropyl peroxydicarbonate.

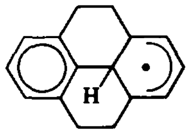
Dehydrogenation via the ion-pair mechanism for 1 is favored by the inertness of the benzylic position for a radical attack. As expected, no cyclization reaction occurred with acyclic model, 3,3′,4,4′-tetramethoxybibenzyl, which, on treatment with BPO, underwent normal radical abstraction reaction.

When cupric chloride is used the reaction proceeds in the following way:

$$CuCl_2 \xrightarrow{+e^-} [CuCl_3] \longrightarrow CuCl + Cl^-$$

$$1 \xrightarrow{-e^-} 6 \rightleftharpoons 7$$

$$7 \xrightarrow{-H^+}$$



$$\xrightarrow[-H^+]{-e^-} 2$$

SCHEME 3

One-electron transfer from the substrate to cupric chloride produces the ion pair similar to the BPO case except that the counter ion is $[CuCl_2]^{\cdot -}$, which expels a chloride anion. Two-stage deprotonation occurs directly from **7** and via further oxidation with cupric chloride as shown in Scheme 3.

The arylation with an aryl cation radical intermediate meets recent studies on the inter- and intramolecular aryl coupling reactions. Norman *et al*[11] have observed intermolecular aryl coupling reactions through the cation radical using lead tetraacetate. As more related cases to ours intramolecular cyclization with tris-(*p*-bromophenyl)ammoniumyl hexachloroantimonate has been reported.[12] We have confirmed that with lead tetraacetate **1** was converted to **2** in a quantitative yield.

The reaction proceeded in ethanol as well as acetonitrile but no reaction occurred in methyl acetate. A marked dependence of the reaction rates in the dielectric constants[13] of the solvents is another testimony for the involvement of the charged species such as **6** and **7**.

The reaction of **1** with several metal salts are summarized in Table 1. As expected from the above scheme, no reaction occurred with cuprous chloride. Although **2** was formed with ferric chloride in acetonitrile, no reaction occurred with titanium (IV), mercuric, or stannic chlorides.

Table 1. Reaction of **1** with metal halides

Metal Halide	Solvent	Temp, °C	Time, hr	Yield of **2**, %[a]
$CuCl_2$	MeCN	80	20	20·1
$CuCl_2$	EtOH	80	20	19·6
$CuCl_2$	AcOMe	80	20	trace
$FeCl_3$	MeCN	80	20	8·5
CuCl	MeCN	80	20	trace
$TiCl_4$	CS_2	reflux	3	0
$HgCl_2$	EtOH	80	20	trace
$SnCl_4$	CS_2	reflux	3	0
$Pb(OAc)_4$	CF_3CO_2H–CH_2Cl_2	0	15	~100

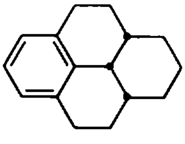
[a] The yield of **2** was determined by VPC.

The disproportionation reaction of [2.2]*metacyclophane* (1)

When aluminum chloride was used entirely different reaction occurred. The complex mixture obtained by the reaction of **1** and aluminum chloride in carbon disulfide contained **4** (20%), **5** (6%), small amounts of **2** and **3** together with two new products, which were found to be 1,2,3,3a,4,5,9,10,10a,10b-decahydropyrene (**8**) and 1,2,3,3a,4,5,9,10-octahydropyrene (**11**). Earlier, Baker *et al*[8] reported the formation of **5** in 52% under essentially the same conditions. No mention is given to the rest of the materials.

The structure of 1, 2, 3, 3*a*, 4, 5, 9, 10, 10*a*, 10*b*-*decahydropyrene* (**8**). Column chromatography on silica gel—silver nitrate eluted by hexane afforded a compound, mp 53·5–54·5°, with a parent ion peak *m/e* 212. IR spectrum showed absorptions due to three vicinal aromatic hydrogens. Analytical figures suggested **8–10** as possible structures.

Proton-decoupled CMR spectrum determined by a pulse FT mode showed ten resonance lines, four aromatic and six aliphatic carbons (Table 2). With an off-resonance technique low-field resonances at 134·5 and 134·4 ppm were assigned to the carbons bearing no hydrogens and the rest to protonated carbons.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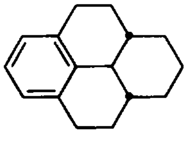
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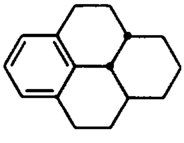
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Symmetry consideration eliminates **10** as the possible structure, which requires more resonance lines. Recently, Lehner *et al*[7] obtained a decahydropyrene, m.p. 129°, by the hydrogenation of **1** and assigned the structure **9**. Our decahydropyrene is different from that of Lehner *et al* as compared by retention times of gas chromatography.† Compared with **8**, **9** has a flatter conformation and should have a higher melting point. The decahydropyrene we obtained can best be represented by structure **8**.

The structure of 1,2,3,3*a*,4,5,9,10-*octahydropyrene* (**11**). We also obtained a compound, mp 76–77°, by column chromatography on silica gel-silver nitrate. Mass spectrum, *m/e* 210, IR spectrum, and analytical data suggest an octahydropyrene structure. It was identical with the product obtained by the reduction of tetrahydropyrene **2** with sodium-amyl alcohol according to Coulson.[14] Coulson obtained a product, mp 68°, which he erroneously assigned the decahydropyrene structure (**8**, **9**, or **10**). The reduction, however, was found to be stopped at the octahydropyrene stage. This was also confirmed by Lehner *et al.*[7]

Table 2. CMR spectra, TMS as a reference, ppm[a]

Compd	Aromatic and ethylenic carbons	Aliphatic carbons
8	134·5, 134·4, 124·9, 124·1	46·8, 37·0, 33·2 29·7, 28·0, 24·6
11	134·8, 134·3, 130·8, 128·3, 126·6, 125·9	35·4, 31·8, 31·6, 31·2, 29·8, 29·3, 28·0. 22·2

[a] Spectra were measured in $CDCl_3$ using a Varian XL-100 spectrometer.

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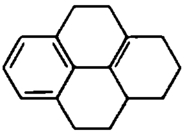
† We are indebted to Dr. Lehner for providing us with a specimen of **9**.

There are three possible structures **11**–**13** (stereochemistry not shown). The octahydropyrene we obtained had no vinyl proton absorption in the PMR. In the CMR spectrum it showed eight aromatic and ethylenic carbon resonances and eight aliphatic carbon resonances (Table 2). Of the eight sp^2 carbons five are quarternary and three are protonated. These spectral features are satisfied only with **11**. Conjugated structure by UV maxima, 220 and 276 nm (hexane).



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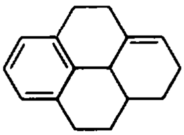

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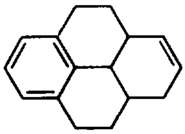

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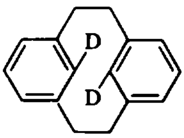
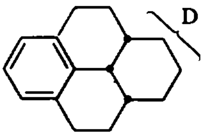
Table 3 summarizes the reaction of **1** with aluminum chloride. Since the reaction is heterogeneous the product ratio is influenced by stirring and other experimental conditions. Reaction was repeatedly carried out under similar reaction conditions and reproducability was confirmed to be generally good (yield variation with ±5%).

Product ratios are dependent on the initial concentration of the substrate. With three different concentrations, $9{\cdot}7\times10^{-3}$, $9{\cdot}7\times10^{-2}$ and $6{\cdot}5\times10^{-2}$ M, not much variation was observed in the yields of **2**, **3**, **4** and **11**. But **8** increased in a more concentrated mixture whereas **5** increased in low concentration. The total yield of hydrogenated products, **8** and **11**, was 44, 64, and 73%, respectively, for each runs.

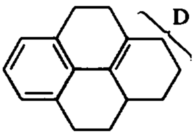
The same reaction was carried out using a deuterated substrate, [2.2]metacyclophane-8,16-d_2 (**1/D**).[4] Table 4 summarizes deuterium distribution among **8/D** and **11/D**.[4] Table 4 summarizes deuterium distribution among **8/D** and **11/D** as determined by mass spectrometry using the Biemann's method.[15] Starting from dideuterated precursor (77%) more than three deuteriums are introduced into **8** (17%) and **11** (16·6%).



1/D



8/D



11/D

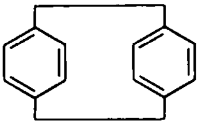
When the reaction of **1** and aluminum chloride was carried out in the presence of an excess of tetralin, the total of **8** and **11** amounted 82% while the yield of pyrene decreased to 8·4%. These results are best interpreted by disproportionation reaction mechanism.

With reaction times of 0·5–1 h in carbon disulfide, no significant change in product distribution is observed. After 3 h, however, **4**, **8** and **11** increased and **2**, **3** and **5** became minor products.

To find out initial reaction product(s), **1** was treated with aluminum chloride in tetrachloroethylene at −2° for 30 min. The reaction mixture contained **2** (2·3%), **4** (1·3%), **5** (4·5%), and **11** (4·7%), the rest of the material being recovered. On treatment with aluminum chloride in carbon disulfide **11** gave **8** in 43% yield (3 hr) together with **2**, **3**, **4** and **5** recovering 27% of **11**. From these we can assume that the reaction produces **2**, **5** and **11** as the initial products. Compound **8** is formed by disproportionation of **11** giving **2**, **3** and **4** at the same time. In fact, aluminum chloride catalyzes the disproportionation of **11** to **8**, **2**, **4** and **5**.

When dry hydrogen chloride was passed through the reaction mixture product distribution differed markedly. The results are summarized in Table 5. The reaction produced **5** (major) and **11**. The product pattern appears to be more closely related to the Baker's experiment. It is probable that the aluminum chloride used by these authors was an $AlCl_3$–HCl type.

Cram *et al*[16] used $AlCl_3$–HCl for a skeletal rearrangement of [2.2]paracyclophane (**14**) to [2.2]metaparacyclophane (**15**) whereby obtaining **5**. Combination of these and the present experiments establish a series of reactions **14**→**15**→**1**→**5**+**11**.



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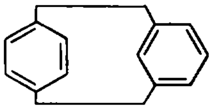

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Protonation appears to be essential to the formation of **5** and **11**. When **1** was treated with conc. sulfuric acid at room temperature **2**, **4**, **5** and **11** were obtained (Table 6). Similarly the reaction with fluorosulfonic acid in carbon tetrachloride produced **2**, **4**, **5** and **11**. When benzene was used as a solvent a large amount of diphenyl sulfone was produced.

With 85% sulfuric acid **5** was formed in 3–4% together with a trace amount of **2**, the rest being recovered. Neither **11** nor sulfonated products was formed. Both **2** and **5** on treatment with conc. sulfuric acid did not produce **8** or **11** in the control experiments. These results clearly indicate neither **2** nor **5** is the precursor for **11**. It is possible that **11**

Table 3. Reaction of **1** with aluminum chloride[a]

Compd **1** mmol	$AlCl_3$ mmol	CS_2 ml	Time hr	Products, %					
				8	**11**	**5**	**2**	**3**	**4**
0·486	4	5	3	42·8	30·4	5·7	trace	1·0	20·2
0·500	4	5	3	36·5	32·4	14·0	trace	trace	17·1
0·493[b]	4	5	3	24·4	57·6	9·6	0	0	8·4
0·979	8	15	3	32·3	31·2	13·7	trace	trace	22·9
0·487	8	50	3	14·7	29·5	31·6	4·0	2·3	17·9
0·983	8	15	1	22·0	26·0	21·7	11·0	2·8	16·5
1·02	8	15	0·5	22·4	24·3	21·9	20·5	trace	11·0
0·978[c]	8		0·5	0	4·7	4·5	2·3	0	1·3

[a] The reaction was carried out at reflux except for the one carried out in tetrachloroethylene.

[b] Tetralin was added.

[c] The reaction was carried out at −2° in tetrachloroethylene.

Table 4. Deuterium distribution, %[a]

Compd	d_0	d_1	d_2	d_3	d_4	d_5
1/D	1·7	21·3	77·0			
8/D	22·6	34·4	25·9	12·2	3·5	1·3
11/D	21·7	34·4	27·3	12·8	3·8	0

[a] Deuterium content was determined by mass spectrometry using the Biemann's method.[15]

Table 5. Reaction of **1** with $AlCl_3$–HCl[a]

Compd **1** mmol	Temp, °C	Time, hr	Products, %					
			8	**11**	**5**	**2**	**3**	**4**
1·06	reflux	3	trace	33·0	59·2	trace	0	7·8
1·00	reflux	1	1·3	12·2	84·0	0	0	2·5
0·990	19	1	1·5	22·7	42·9	16·0	8·0	8·8

[a] The reaction was carried out in carbon disulfide (15 ml).

is formed by a protonation step different from that gives **2** and **5**.

Sulfonated products accounted for 35–50% throughout the experiments. With a longer reaction time, **5** increased slightly whereas **2**, **4** and **11** remained almost constant. The reaction with fluorosulfonic acid is quite similar to the reaction with sulfuric acid as shown in Table 6.

In summary, two types of reactions were differentiated: while $AlCl_3$–HCl, H_2SO_4, and FSO_3H were found to give **2**, **3**, **4**, **5** and **11**, aluminum chloride alone gave further reaction product **8** formed from **11** by further disproportionation.

EXPERIMENTAL

Methods. PMR spectra were obtained on a Hitachi R-20B spectrometer. CMR spectra were recorded on a Varian XL-100 spectrometer and determined by a pulse FT mode using $CDCl_3$ as a solvent. Chemical shifts are shown in δ values (ppm) downfield from TMS. Mass spectra were obtained on a Hitachi RM-50 or a Hitachi RMU-6E mass spectrometer with ionization current of either 10 eV (for deuterium content determination) or 70 eV. To determine deuterium content, contribution of ^{13}C was corrected through M + 1 to M + 4 using average values of three scans.[15] IR and UV spectra were recorded on a Hitachi EPI-G2 or a 215 Hitachi Grating Infrared Spectrophotometer and a Hitachi EPS-3T photometer, respectively. Gas chromatographic analyses were performed on a Hitachi K-53 equipped with a flame-ionization detector using 3 mm by 1 m or 2 m stainless steel column packed with SE-30 or Apiezon grease L both on Daichrom A. All melting points were obtained in liquid bath and uncorrected.

Materials. Compound **1** was prepared as previously described[3b] and was purified by sublimation followed by column chromatography and recrystallization from EtOH, mp 132–3°. Compound

Table 6. Reaction of **1** with sulfuric and fluorosulfuric acids[a]

Compd **1** mmol	Solvent, ml	Acid, ml (%)	Time, hr	Products, %				
				11	**5**	**2**	**4**	Recovery
0·50	C_6H_6, 6	H_2SO_4, 6 (conc)	2	5·2	12·7	3·4	5·6	trace
0·49	C_6H_6, 6	H_2SO_4, 6 (conc)	1	10·0	25·0	5·5	3·9	5·1
0·49	C_6H_6, 6	H_2SO_4, 6 (conc)	0·5	11·1	16·8	6·4	5·3	24·4
0·48	C_6H_6, 6	H_2SO_4, 6 (85)	25	9	4·2	trace	0	95·8
0·48	C_6H_6, 6	H_2SO_4, 6 (82)	11·5	0	3·1	trace	0	96·9
0·48	C_6H_6, 6	H_2SO_4, 6 (82)	4	0	0·8	trace	0	99·2
0·26	CCl_4, 3	FSO_3H,[b] 3	0·5	12·1	26·5	6·4	9·1	0

[a] The reaction was carried out at room temperature (~18°).

[b] Aldrich Chemical Co. Inc.

1/D was also prepared as previously described[4] and was purified by sublimation followed by column chromatography on alumina and recrystallization from EtOH, mp 132–3°, IR (KBr) 2230 cm^{-1}. (For deuterium content see Table 4.) Compound **11** was prepared by reducing **2** according to Coulson's method[14] and was purified by column chromatography followed by recrystallization from MeOH; colorless needles, mp 76–77°, *m/e* 210, IR (KBr) 755 and 775 cm^{-1}. UV (hexane) 220 (ϵ = 19200), 227 (18300), 235 (13700), 268 (10800), and 276 (10900) nm. PMR; δ 7·1–6·8 (m, 3H), 2·9–2·6 (m, 4H), and 2·4–1·0 (m, 11H). CMR signals are shown in Table 2. (Found: C, 91·41; H, 8·60. Calcd for $C_{16}H_{18}$: C, 91·38; H, 8·62%). Commercial **2** was purified by column chromatography and recrystallization from EtOH, mp 137–8°,[3b] purity being checked by VPC (>99%). Anhydrous metal halides obtained by drying over P_2O_5 were employed. CuCl was prepared by described method.[17]

The reaction of compound **1** *with metal halides.* In a sealed tube a soln of 62·6 mg (0·3 mmole) of **1** and 40·7 mg (0·3 mmole) of $CuCl_2$ in 3 ml of MeCN was warmed at 80° for 20 hr. After washing with water, the mixture was analyzed by VPC (Apiezon grease L and SE-30 both on Daichrom A). The reaction was studied using other solvents and various metal halides as summarized in Table 1.

The reaction of compound **1** *with aluminum chloride.* With stirring, a mixture of 201·7 mg (0·97 mmole) of **1** and *ca* 1 g (8 mmole) of $AlCl_3$ in 15 ml of CS_2 was refluxed for 3 hr. The mixture was poured on ice and was extracted with benzene. Benzene extract was washed with dil HCl, water, and $NaHCO_3$ aq, repeatedly. Dried, concentrated, and then passed through silica gel–silver nitrate column (hexane).

First elute was **8** which was followed by **11**. Compounds **2**, **5**, **3**, and **4** were eluted successively. Compound **8** was recrystallized from MeOH and obtained as colorless needles, mp 53·5–54·5°, IR (KBr) 742 and 762 cm^{-1}, and *m/e* 212. (Found: C, 90·22; H, 9·31. Calcd for $C_{16}H_{20}$: C, 90·49; H, 9·51%). CMR spectra are shown in Table 2. Octahydropyrene **11**, *m/e* 210, was obtained as colorless needles, mp 76–7°, which did not depress the mp on admixture with the octahydropyrene prepared by the Coulson's method. Several experiments are summarized in Table 3. The reaction of **1**/D with $AlCl_3$ was carried out as above. **8**/D and **11**/D were isolated by column chromatography on silica gel–silver nitrate. Quantitative analyses were performed by VPC.

The reaction of compound **1** *with* $AlCl_3$–HCl. Dry HCl gas was passed through a suspension of *ca* 1 g (8 mmol) of $AlCl_3$ in 15 ml of CS_2 for 15 min. To this was added 206·4 mg (0·99 mmole) of **1**, and the mixture was stirred for 1 hr at room temp (~19°). After being poured on ice benzene extract was washed with $NaHCO_3$ aq and water, dried, concentrated, and then passed through silica gel–silver nitrate column (hexane). Compounds **11** and **5** were isolated and confirmed by comparison with the authentic materials. Other pyrenes were identified by comparing the retention times with those of the authentic materials. The reaction was studied under several conditions as shown in Table 5. The reaction was analyzed by VPC.

The reaction of compound **1** *with sulfuric acid.* A soln of 201·8 mg (0·97 mmole) of **1** in 6 ml benzene and 6 ml conc H_2SO_4 were stirred for 1 hr at room temp (~18°). The mixture was poured on ice and washed with $NaHCO_3$ aq and water. The products were subjected to column chromatography on alumina, eluted with hexane, to give **2**, **4**, **5** and **11**. Octahydropyrene **11** which was identified with the Coulson's octahydropyrene was recrystallized from MeOH and obtained as colorless needles, mp 76–77°, IR (KBr) 755 and 775 cm^{-1}, and *m/e* 210. Other pyrenes were confirmed by comparison of the retention times with those of the authentic materials. Table 6 shows the results under varying conditions. Quantitative analyses were performed by VPC. With FSO_3H, CCl_4 instead of benzene was used as solvent. The rest of conditions was similar as above. When benzene was used a large amount of diphenyl sulfone resulted.

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