

Hydrogenation of Aromatic Hydrocarbons by Al/Ti Reagents

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Treatment of anthracene (**A**) with LiAlH₄ (LAH) at 150°C under atmospheric pressure gives 9,10-di- and 1,2,3,4-tetrahydroanthracene (**2H-A** and **4H-A**). At 160–200°C and under hydrogen pressure (10–90 bar) a number of simple and polycyclic aromatic compounds [e. g. toluene, naphthalene (**N**), **A**, phen-

anthrene (**PH**), and pyrene (**PY**)] are converted to fully or partially hydrogenated arenes. Addition of small amounts of TiCl₄ or TiCl₃ and the choice of solvents (heptane or glymes) have marked effects on the reaction. The pair triethylaluminium/TiCl₄ acts also as efficient hydrogenation catalyst.

Alkylaluminium hydrides²⁾ and LAH (lithium aluminium hydride) in conjunction with titanium and zirconium catalysts³⁾ have been successfully used to effect hydroalumination of olefines. Aluminium compounds as part of complex transition metal containing reagents have also been reported to be effective in the hydrogenation of arenes^{4,5)}. A case of application of aluminium hydrides for either stoichiometric or catalytic hydroalumination or hydrogenation of aromatic hydrocarbons has previously not been reported. The success in using organoboranes as reagents for the hydroboration⁶⁾ or as catalysts^{7,8)} for the hydrogenation of polycyclic arenes has led to the utilization of aluminium reagents for the reduction or reductive hydrogenation of arenes. In this paper are presented the results of the stoichiometric and catalytic hydrogenation of a number of simple and polycyclic arenes by LAH and other aluminium reagents.

Results and Discussions

Heating of anthracene (**A**) in the presence of an excess of LAH in nonane at 140°C for 36 hours results in the formation of 9,10-dihydroanthracene (**2H-A**) in 68.5% yield. When, in analogy to the hydroalumination reactions of olefins²⁾, a quantity of titanium tetrachloride (TiCl₄) is also added to the reaction mixture 1,2,3,4-tetrahydroanthracene (**4H-A**) is formed in 14.9% yield in addition to **2H-A**. The use of LAD (lithium aluminium deuteride), followed by protolytic workup leads to the formation of partially deuterated products (Table 1, entry 1).

The deuterium distributions observed in **A** and **2H-A** show that besides addition of the reagent to the 9,10 positions of **A** and **2H-A** a significant exchange process at other sites also takes place. The presence of relatively large amounts of D₀ and D₁ dihydroanthracenes cannot be rationalized by in situ D/H exchange reactions. Treatment of the products obtained by reaction of **A** with LAH, with deuterium oxide, either with and without added TiCl₄,

Table 1. Reaction of anthracene (**A**) with LAD/H₂O or LAH/D₂O in nonane at 140°C (n. m. = not measured)

Exp. No	A mmol	Reduc. agent (mmol)	time h	hydrolyzed by	Product (%)	Relative D content (~%)					
						D ₀	D ₁	D ₂	D ₃	D ₄	D ₅
1	3.3	LAH/TiCl ₄ (11.9/1.9)	36	H ₂ O	A (76.6)	15	30	29	17	6	2
					2H-A (19.6)	14	24	35	14	10	3
					4H-A (2.9)	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
2	5.6	LAH (26.3)	36	D ₂ O	A (31.5)	100	-	-	-	-	-
					2H-A (68.5)	85	8	8	-	-	-
3	11.2	LAH/TiCl ₄ (26.3/4.2)	36	D ₂ O	A (58.9)	100	-	-	-	-	-
					2H-A (25.8)	80	9	11	1	-	-
					4H-A (14.9)	100	-	-	-	-	-

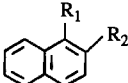
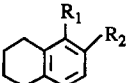
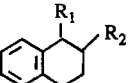

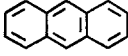
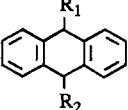
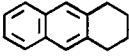
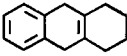
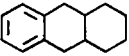
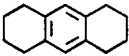
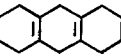
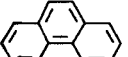
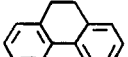
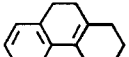
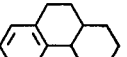
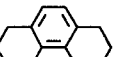
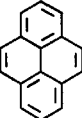
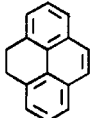
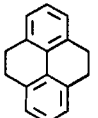
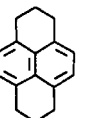
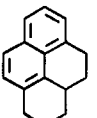
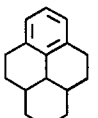
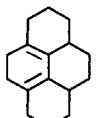
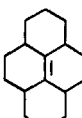
leads to partially mono- and dideuterated products of **2H-A** (Table 1, entries 2 and 3). This indicates the presence of significant amounts of hydroalumination products prior to hydrolysis.

Expecting a facile hydrogenolysis of C–Al bonds at higher temperatures by pressurized molecular hydrogen⁹⁾ in analogy to the >BH borane catalyzed arene hydrogenations^{7,8)}, the reaction was carried out under H₂ pressure at 200°C in an autoclave. The products obtained from the hydrogenations of naphthalene (**N**), some of its derivatives, anthracene (**A**), phenanthrene (**PH**), and pyrene (**PY**) are shown in Table 2.

The reaction conditions used and the product yields obtained are listed in Table 3.

Heptane solutions of **N** are completely converted into a mixture of *cis*- and *trans*-decalins (**c-D** and **t-D**) on treatment with the LAH/TiCl₄ catalyst pair for 30 hours (Table 3, entry 1). With shorter reaction times increasing yields of tetralin (**T**) and an octahydronaphthalene [probably Δ⁹-oc-

Table 2. Formulas of arenes and of hydrogenation products obtained

Arene	Hydrogenation products						
 <p>N, $R_1=R_2=H$ 1-mN, $R_1=Me, R_2=H$ 2-mN, $R_1=N, R_2=Me$ 2-cN, $R_1=H, R_2=Cl$ 1-moN, $R_1=OMe, R_2=H$</p>	 <p>T, $R_1=R_2=H$ 1-mT, $R_1=Me, R_2=H$</p>	 <p>5-mT, $R_1=Me, R_2=H$ 6-cT, $R_1=H, R_2=Cl$</p>	 <p>O</p>				
 <p>A</p>	 <p>2H-A, $R_1=R_2=H$ m-2H-A, $R_1=Me, R_2=H$ m₂-2H-A, $R_1=R_2=Me$</p>	 <p>4H-A</p>	 <p>6H-A</p>	 <p>u8H-A</p>	 <p>s8H-A</p>	 <p>10H-A</p>	
 <p>PH</p>	 <p>2H-PH</p>	 <p>6H-PH</p>	 <p>u8H-PH</p>	 <p>s8H-PH</p>			
 <p>PY</p>	 <p>2H-PY</p>	 <p>4H-PY</p>	 <p>s6H-PY</p>	 <p>u6H-PY</p>	 <p>10H-PY</p>	 <p>12H-PY</p>	 <p>14H-PY</p>

taline (**O**) are obtained (Table 3, entries 2–4). By lowering the reaction temperature to 160 °C the conversion rate is reduced significantly, especially the further hydrogenation of **T** to **O** or **D** (Table 3, entries 5, 6).

No reaction is observed in the absence of LAH. The conversion rate is reduced at low H₂ pressure, and only traces of **T** are formed upon the application of N₂ pressure (Table 3, entries 7–10). The reaction rate is influenced by the concentration of the titanium reagent, low conversion being observed in its absence (Table 3, entries 11 and 12). When deuterium gas pressure is used, the highly deuterated **T** is formed (up to D₁₂), and the partial H/D exchange of hydrogen atoms of **N** indicates the formation and involvement of an intermediate Al–D species as the hydrogenation agent (Table 3, entry 13).

Polar solvents should be expected to increase the reaction rate by increasing the solubility of LAH. Using tetrahydrofuran or monoglyme as solvents only slight conversions are obtained (Table 3, entries 14 and 15).

As can be seen in the case of 1-methylnaphthalene (**1-mN**) (Table 3, entries 16 and 17) substituents on the naphthalene ring appreciably reduce the reaction rate. The unsubstituted ring is preferentially hydrogenated. Furthermore, the formation of small amounts of 2- and 6-methyltetralins (**2-mT** and **6-mT**) suggests the partial initial Lewis acid-catalyzed isomerization of **1-mN** to 2-methylnaphthalene (**2-mN**). This is supported by the presence of traces of **2-mN** in the product mixture.

2-Chloro- and 1-methoxynaphthalene (**2-cN** and **1-moN**, respectively) appear to first undergo dechlorination or de-

methoxylation. Presumably, this also leads to partial inactivation of the catalyst (Table 3, entries 18 and 19).

As described above, without hydrogen pressure the polycyclic arene **A** is only sluggishly hydrogenated by LAH or by LAH/TiCl₄ to yield mainly **2H-A**. By application of hydrogen pressure it can be smoothly converted within three hours into a mixture consisting of 1,2,3,4,5,6,7,8-octahydroanthracene (**s8H-A**) as the predominant product and the unsymmetrical octahydroanthracene (**u8H-A**), **2H-A** and decahydroanthracene (**10H-A**) as the major by-products. A slight reduction of the reaction temperature and time results in the formation of **2H-A** followed by **4H-A** as the main products. Without TiCl₄ only **2H-A** is formed (Table 2, entries 20–22).

The relatively facile further conversion of **2H-A** to more highly hydrogenated anthracenes (Table 3, entry 23) shows that it is an intermediate in the reactions involving TiCl₄.

The use of diglyme as the solvent in the absence of TiCl₄ results in a reduced conversion. Besides small amounts of 9-methyl- and 9,10-dimethyl-9,10-dihydroanthracenes (**m-2H-A** and **m₂-2H-A**, respectively) mainly **2H-A** is obtained. In the presence of TiCl₄ **4H-A** is formed in satisfactory yield (Table 3, entries 24 and 25).

In the absence of TiCl₄ phenanthrene is unreactive in hexane but reacts slowly in diglyme to give mainly 9,10-dihydrophenanthrene (**2H-PH**). In the presence of TiCl₄ nearly complete conversion is observed after a reaction period of 10-hours yielding a mixture of symmetrical and unsymmetrical octa-, a hexahydrophenanthrene (**s8H-PH**, **u8H-PH**, **6H-PH**) and **2H-PH** (Table 3, entries 26–28).

Table 3. Reaction conditions and product yields from hydrogenation of di- and polynuclear arenes catalyzed by LiAlH₄ (LAH) and titanium(IV) chloride

Exp. No	Substrate/ mmol	LiAlH ₄ mmol	TiCl ₄ mmol	Solvent (ml)	H ₂ (bar)	Temp. (°C)	Time (h)	Products (% yield)	Recovered substrate (%)
1	N/15.6	28.9	7.3	H/20	90	200	30	T(0.1); c-D(69.0); t-D(28.8)	-
2	N/15.6	28.9	7.3	H/20	90	200	9	T(51.1); c-D(29.5); t-D(11.6); O(7.3)	-
3	N/15.6	28.9	7.3	H/20	90	200	3	T(59.4); c-D(25.7); t-D(8.6); O(5.0)	0.4
4	N/15.6	28.9	7.3	H/20	90	200	2	T(83.9); D(6.7*)	9.3
5	N/15.6	28.9	7.3	H/20	90	180	2	T(86.0); c-D(5.0); t-D(1.3); O(1.3)	5.9
6	N/15.6	28.9	7.3	H/20	90	160	2	T(59.2); c-D(1.1) t-D(0.5)	38.9
7	N/15.6	2.6	7.3	H/20	90	200	3	T(15.9)	84.0
8	N/15.6	-	7.3	H/20	90	200	3	-	99.5
9	N/15.6	28.9	7.3	H/20	10	200	3	T(77.7); D(1.7*)	20.0
10	N/15.6	28.9	7.3	H/20	N ₂ /50	200	15	T(6.0)	93.3
11	N/15.6	28.9	0.46	H/20	90	200	3	T(50.6)	49.4
12	N/15.6	28.9	-	H/20	90	200	3	T(6.9)	92.7
13	N/15.6	14.5	3.8	H/20	D ₂ /40	200	3	T(89.3)*	10.7
14	N/15.6	28.9	7.3	THF/20	90	200	3	T(3.2)	90.3
15	N/15.6	28.9	7.3	MG/20	90	200	65	T(2.3)	94.5
16	1-mN/14.1	28.9	7.3	H/20	90	200	3	5-mT(30.8); 6-mT(0.7); 1-mT(7.6)	55.6
17	1-mN/14.1	28.9	7.3	H/20	90	200	8	5-mT(53.8); 6-mT(13.8); 1-mT(15.5); 2-mT(2.9)	7.0 2-mN(1.6)
18	2-cN/12.3	28.9	7.3	H/20	90	200	3	N(17.9); T(80.7); 6-cT(0.1)	0.2
19	1-moN/12.7	28.9	7.3	H/20	90	200	3	N(40.9); T(7.6)	27.4
20	A/11.2	28.9	7.3	H/20	90	200	3	s8H-A(52.3); u8H-A(2.5*); 4H-A(5.0); 10H-A(10.0); 2H-A(28.0)	0.8
21	A/11.2	28.9	7.3	H/20	90	190	2	s8H-A(14.4); u8H-A(2.3*); 4H-A(20.5); 10H-A(2.0); 2H-A(48.5)	12.0
22	A/11.2	28.9	-	H/10	90	200	16	2H-A(90.7); 4H-A(3.7)	0.5
23	2H-A/11.1	28.9	7.3	H/20	90	200	3	s8H-A(50.6); u8H-A(2.8*); 6H-A(12.7)	22.8
24	A/11.2	1.1	-	DG/10	90	200	18	4H-A(2.2); 2H-A(50.0); m-2H-A(11.4); m ₂ -2H-A(1.0)	29.0
25	A/11.2	1.1	1.1	DG/10	90	200	18	4H-A(79.2); 2H-A(4.2); m-2H-A(9.7)	3.6
26	PH/11.2	10.5	-	H/25	90	200	16	-	99.0
27	PH/11.2	10.5	-	DG/20	90	200	48	2H-PH(76.1); 6H-PH(3.0)	13.3
28	PH/11.2	28.9	3.2	H/20	90	200	10	s8H-PH(36.4); u8H-PH(16.4*); 6H-PH(6.4); 2H-PH(18.8)	6.5
29	PY/5.0	14.5	-	H/10	90	200	30	4H-PY(25.7); s6H-PY(44.4); u6H-PY(14.4); 2H-PY(7.7)	-
30	PY/5.0	14.5	3.7	H/10	90	200	30	12H-PY(10.4*); 10H-PY(55.7*); 4H-PY(2.1); 14H-PY(11.1*)	2.0
31	PY/5.0	14.5	-	MG/10	90	200	30	4H-PY(54.8); 2H-PY(24.5)	-
32	PY/5.0	14.5	3.7	MG/10	90	200	30	s6H-PY(3.0); 4H-PY(1.3); 2H-PY(13.7)	53.4

* Sum of isomers; H = heptane; MG = monoglyme; DG = diglyme

a) Approximate % deuterium isotope content:	b) Approximate % deuterium isotope content:
D ₀ D ₂ D ₂ D ₃ D ₄ D ₅ D ₆ D ₇ -D ₁₂	D ₀ D ₁ D ₂ D ₃ -D ₆
5 4 8 23 30 15 8 Σ 6	74 19 5 Σ 2

A similar sensitivity to the solvent and to the presence of the titanium reagent is observed in the slow conversion of pyrene. In hexane prolonged hydrogenation leads to a mixture of partially hydrogenated pyrenes, ranging from 4,5-

dihydropyrene (2H-PY) to small amounts of perhydro isomers. In the presence of TiCl₄ the more highly hydrogenated derivatives are increasingly formed. From the mixtures 1,2,3,6,7,8-hexa- and *cis*- or *trans*-1,2,3,3a,4,5,5a,7,8-deca-

hydropyrene (**6H-PY** and **10H-PY**, respectively) are isolated in sufficient amounts by thick layer chromatography. Surprisingly, the presence of TiCl_4 retards the reaction in monoglyme. The mixture consists mainly of a multitude of methylated hydropyrenes. In the absence of TiCl_4 only **2H-PY** and 4,5,9,10-tetrahydropyrene (**4H-PY**) are formed (Table 3, entries 29–32).

The facile formation of decalins from naphthalene suggests that in contrast to the borane-catalyzed hydrogenation of arenes^{7,8)} the LAH/ TiCl_4 reagent may also be used in the hydrogenation of simple benzene derivatives. Indeed, toluene and biphenyl are reduced to methylcyclohexane, phenylcyclohexane and bicyclohexyl, resp. (Table 4, entries 1 and 2). The reaction rates show a marked dependence on the number of substituents present on the benzene ring. This is evident from experiment 3 (Table 4), in which an approximately equimolar mixture of benzene, toluene, and *p*-xylene have been hydrogenated. The hydrogenated products cyclohexane, methylcyclohexane, and *cis/trans*-1,4-dimethylcyclohexane are approximately found in the ratio 15:3:1.

Table 4. Hydrogenation of monocyclic arenes by LAH and titanium(IV) chloride^{a)}

Exp. No	Substrate	mmol	Products (% yield)	Recovered substrate (%)
1	toluene	13.0	methylcyclohexane (48.6)	49.8
2	biphenyl	12.9	phenylcyclohexane (59.4), bicyclohexyl (14.7)	26.3
3	<i>p</i> -xylene	8.3	dimethylcyclohexane (3.0*)	97
	toluene	9.1	methylcyclohexane (14.5)	85.5
	benzene	11.4	cyclohexane (47.2)	52.5

* Sum of isomers.

^{a)} Reactions were carried out in hexane (20 ml) using 28.9 mmol of LAH, 7.3 mmol of TiCl_4 and 90 bar H_2 pressure at 200 °C for 3 h.

The preliminary results listed in Table 5 show that hydrogenation activity is not restricted to the LAH/ TiCl_4 reagent. The use of other titanium or zirconium reagents such as TiCl_3 or bis(cyclopentadiene)zirconium dichloride (Cp_2ZrCl_2) in the hydrogenation of N cleanly leads to the formation of tetralin.

While sodium dihydridobis(2-methoxyethoxy)aluminate (NAH), a reagent soluble in nonpolar organic solvents⁹⁾, proved to be unreactive in the hydrogenation of arenes, trialkylaluminium reagents such as triethylaluminium in conjunction with TiCl_4 appear to be very efficient catalysts (Table 5, entries 6–8)¹⁰⁾.

Conclusions

Although in no case optimized, the results presented in this paper show that LAH may be used for the partial or complete hydrogenation of arenes. In most cases the activation by titanium or zirconium co-catalyst causes an increase of the hydrogenation rate and changes the product composition. The slight but significant differences in the products formed in reactions catalyzed by TiCl_3 indicate

Table 5. Hydrogenation of arenes catalyzed by aluminium and Ti/Zr reagents^{a)}

Exp. No	Substrate (mmol)	Al reagent (mmol)	Ti/Zr reagent (mmol)	Time h	Products (% yield)	Recovered substrate (%)
1	N (15.6)	LAH (28.9)	TiCl_3 (7.0)	3	T(45.5)	54.0
2	N (15.6)	LAH (28.9)	TiCl_3 (7.2)	15	T(95.0), D(3.6*)	0
3	A (11.2)	LAH (28.9)	TiCl_3 (7.0)	3	s8H-A(9.2), 4HA(8.0), 2H-A(65.3)	8.0
4	N (15.6)	LAH (28.9)	Cp_2ZrCl_2 (7.3)	3	T(99)	1
5	N (15.6)	NAH ^{b)} (35.0)	TiCl_4 (7.3)	3	-	100
6	N (15.6)	AlEt_3 (7.3)	-	3	-	100
7	N (15.6)	AlEt_3 (7.3)	TiCl_4 (7.3)	3	T(48.4), O(1.5),	32.1
8	N (15.6)	AlEt_3 (29.2)	TiCl_4 (7.3)	3	T(53.9), O(2.2), D(37.6*)	0.7

* Sum of isomers.

^{a)} Reactions were carried out in hexane (20 ml) with 90 bar H_2 pressure and 200 °C. — ^{b)} NAH = sodium dihydridobis(2-methoxyethoxy)aluminate.

that TiCl_4 is not converted into the latter under these reaction conditions.

The use of a polar solvent such as THF, mono- or diglyme to increase the solubility of LAH often appears to have adverse effects on the conversion rates and may also lead to the formation of methylated hydroarene byproducts. Also, since the soluble aluminium hydride $\text{NaAlH}_2(\text{OCH}_2\text{-CH}_2\text{OMe})_2$ ⁹⁾, in contrast to LAH, shows no activity, it is concluded that solubility is not a determining factor. The stoichiometric reactions using $\text{LAD}/\text{H}_3^+\text{O}$ and $\text{LAH}/\text{D}_3^+\text{O}$ indicate that hydroalumination by LAH or by an intermediate aluminium hydride species should be considered as the initiating step of the process. Al–C bond hydrogenolysis by in-situ formed active hydrogen atoms or by molecular hydrogen terminates the reaction. The active role of external molecular hydrogen becomes evident in experiments performed under nitrogen or at low hydrogen pressures. This has further been demonstrated by the formation of deuterated tetralin when deuterium gas pressure was applied. The necessity for using a relatively large excess of LAH in most cases implies, therefore, that in a competing reaction some of the LAH employed may be converted into an inactive aluminium species. It can be assumed that the known slow decomposition of LAH at atmospheric pressure and at higher temperatures (> 125 °C)¹¹⁾ is this competing reaction. When hydrogenations are fast (< 1 h), as those of simple olefins, with both LAH/ TiCl_4 and $\text{AlEt}_3/\text{TiCl}_4$ relatively efficient catalysis with more than 100 turnover cycles have been observed¹²⁾.

Experimental

GC: Siemens Sicomat 1, SE-54 and OV-1 capillary columns, programmed at 8 °C/min 30–300 °C. — GC-MS: Perkin-Elmer

F 22/Varian MAT CH 7 A. — MS: Finnigan MAT-311 A. — ^1H NMR: Bruker AC 200. — All operations prior to the hydrogenations were carried out under strictly dry oxygen-free argon. The products were generally identified as described earlier^{6–8}. **s6H-PY** and **10H-PY** were identified by their mass and ^1H -NMR spectra and **12H-PY** by its mass spectrum only.

Partially Deuterated Anthracene (A) and 9,10-Dihydroanthracene (2H-A) from LiAlD₄ and TiCl₄: A suspension of 0.59 g of **A**, 0.5 g of LAD, and 0.36 g of TiCl₄ in 10 ml of nonane was heated at 140°C for 36 h. The solution was poured carefully onto crushed ice and slowly hydrolyzed with dil. HCl. After filtration from a black solid material the organic layer was separated, dried and the solvent removed in vacuo. The residue (0.56 g) was analyzed by GC-MS. (For results see Table 1, entry 1.)

General Procedure for the Catalytic Hydrogenation of Arenes: Solutions or suspensions of the substrate in the appropriate solvent (for quantities see Tables 3–5) were placed in a dry and argonized 100-ml magnetically stirred or 200-ml rocking stainless steel autoclave followed by the aluminium and titanium or zirconium reagents. The autoclave was charged with hydrogen and heated at the temperatures and for the times shown in Tables 3–5. The products were isolated by carefully adding crushed ice, followed by dil. HCl. The slurry was filtered and washed with ether. From the ether layer, after evaporation of the solvents, the product mixture was obtained in 90–100% yield.

Isolation of 1,2,3,6,7,8-Hexahydropyrene (s6H-PY): A suspension of 1.0 g (5.0 mmol) of **PY** and 0.55 g (14.5 mmol) of LAH in 10 ml of heptane was placed in a dry and argonized 100-ml autoclave, pressurized with 90 bar of H₂ gas, magnetically stirred, and heated to 200°C for 30 h. On cooling a pressure drop of about 5 bar was observed. To the product solution about 10 g of crushed ice was added followed by 5 ml of 2 N HCl. The dark suspension was filtered through a sintered glass funnel, the organic layer separated, and the aqueous phase washed twice with diethyl ether. After drying with Na₂SO₄ the combined organic phase gave 0.94 g of a pale yellow solid. (For GC analysis see Table 3, entry 29). The solid was further purified on preparative thick-layer plates (commercial silica-gel plates, 2 mm thick (Merck) with hexane/EtOAc (4:1). The major front-running fraction gave on elution 0.36 g (35%) of **s6H-PY**. Twice recrystallized from hexane, m.p. 134.5–135.5°C (ref.¹³) 132–134°C. — ^1H NMR: δ = 6.9 (s, 4H), 3.05 (t, 8H), 2.00 (q, 4H). — MS: m/z (%) = 208 (100) [M⁺], 180 (20), 165 (40).

Isolation of 1,2,3,3a,4,5,5a,6,7,8-Decahydropyrene (10H-PY): As above, a suspension of 1.0 g (5.0 mmol) of **PY** and 0.55 g (14.5 mmol) of LAH in 10 ml of heptane together with 0.7 g (3.7 mmol) of TiCl₄ was placed in a 100-ml autoclave, pressurized with 90 bar of H₂ and heated at 200°C for 30 h. After workup 0.93 g of a pale yellow viscous hydrogenation product was obtained. (For GC analysis see Table 3, entry 30). The viscous product was further purified as described above by preparative TLC. The main front-running fraction gave on elution 0.42 g (40% yield) of a colourless liquid (GC/MS 95% of **10H-PY**). — ^1H NMR: δ = 7.0 (s, 2H), 2.90 (m, 4H), 2.70 (m, 2H), 2.19 (m, 4H), 1.95 (m, 4H), 1.30 (m, 4H). — MS: m/z (%) = 212 (65) [M⁺], 184 (48), 169 (100).

CAS Registry Numbers

N: 91-20-3 / **A**: 120-12-7 / **1-mN**: 90-12-0 / **2-mN**: 91-57-6 / **2-cN**: 91-58-7 / **1-moN**: 2216-69-5 / **PH**: 85-01-8 / **PY**: 129-00-0 / **s6H-PY**: 1732-13-4 / **10H-PY**: 55821-21-1 / LAH: 16853-85-3 / NAH: 7646-69-7 / Cp₂ZrCl₂: 1291-32-3 / TiCl₄: 7550-45-0 / TiCl₃: 7705-07-9 / AlEt₃: 97-93-8 / toluene: 108-88-3 / biphenyl: 92-52-4 / *p*-xylene: 106-42-3 / benzene: 71-43-2

¹ Part III: see ref.⁸.

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