Reduction of Polycyclic Arenes by >BH Boranes, III[1]

Partial Hydrogenation: From Anthracene to Coronene

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Reduktion kondensierter Arene mit >BH-Boranen, III[1]. – Partielle Hydrierung: Anthracen bis Coronen

Tetrapropyldiboran(6) (TPDB) katalysiert die Hydrierung polycyclischer Arene [z. B. Anthracen (**A**), Tetracen (**TET**), Pyren (**PY**), Perylen (**PER**) oder Coronen (**C**)] unter Wasserstoff-Druck bei 200°C. In einigen Fällen können sehr hohe Ausbeuten an Hydroarenen erzielt werden [z. B. Tetrahydroanthracen (**4H-A**), Octahydroanthracen (**8H-A**), Dodecahydrotetracen (**12H-TET**), Tetrahydropyren (**4H-PY**), Hexahydroperylen (**6H-PER**) oder Hexahydrocoronen (**6H-C**)]. Neben unterschiedlichen kleinen Mengen an Perhydroarenen bilden sich nach langer Reaktionszeit aus sämtlichen Arenen auch C–C-Spaltungsprodukte.

We reported in a recent publication on the >BH borane additions onto arene >C=C< bonds[2]. It was shown that tetraethyl- or tetrapropyldiborane(6) (TEDB and TPDB, respectively), add with differing ease to naphthalenes, anthracene (**A**), and a number of other condensed arenes. At 180–200°C and with molecular hydrogen the borylated hydroarenes initially formed readily underwent further hydrogenolysis of the B–C bonds releasing the hydroarene and regenerating the hydroborane catalyst[1]. Applied to naphthalene and its derivatives, it was demonstrated that the boron containing reagents act as very effective catalysts for the preparation of tetralins[1]. In this contribution we describe the application of the >BH borane catalyst to the partial hydrogenation of more highly condensed arenes and show that in terms of general applicability (rates, simplicity, yields, and selectivity) this reaction is at least comparable to some of the other recently published hydrogenation procedures[3–23].

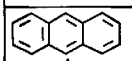
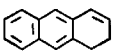
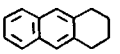
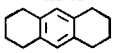
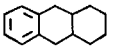
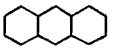
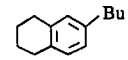
Results and Discussion

I. Linearly *ortho*-Fused Arenes

a) *Anthracene* (**A**): Table 1 summarizes the results of the hydroboration of **A** in the presence of TPDB (substrate to borane ratio ≈ 3:1) at 200°C and 90 bar of H_2 gas pressure. Aliquots taken from the autoclave at intervals during the reaction were analyzed by GC and GC-MS. The results show a rapid buildup of 1,2,3,4-tetrahydroanthracene (**4H-A**). After 1.5 hours **4H-A** has reached its peak concentration. Following the near complete conversion of all **A** to **4H-A**, at a slower rate 1,2,3,4,5,6,7,8-octahydroanthracene (**s8H-A**) is formed. Longer reaction times result in progressive degradation of **8H-A**. Small amounts of *cis*- and *trans*-1,2,3,4,4a,9,10,10a-octa- and *cis* and *trans* isomers of dodecahydroanthracenes (**u8H-A** and **14H-A**, respectively) are also formed. The sources for the di- and hexahydroanthracenes (**2H-A** and **6H-A**, respectively) found intermediatly are the corresponding monoborylated tetra- and octahydroanthracenes, which partially accumulate and are readily dehydroborated in the injection port of the gas chromatograph[1]. Longer reaction times result in slow isomerization of **s8H-A** into **u8H-A** and also in the formation of a large number of C–C bond scission products. Amongst these 6-butyltetralin has been identified.

Utilizing these results, **4H-A** and **s8H-A** have been obtained in large preparative scale reactions in 87 and 90% isolated yields. Anthracene has previously been hydrogen-

Table 1. Hydrogenation of anthracene (**A**)[a]

Compound	% (GC) Products					Mass spectra
	1h	1.5h	2h	3h	4.5h	[rel. abundance (%)]
 **A**	38.1	4.2	-	-	-	178 (M^+, 100), 176(20), 89(15)
 **2H-A**	12.0	6.6	0.8	0.5	-	180 (M^+, 100), 179(80), 178(66), 165(65), 152(15)
 **4H-A**	45.0	81.8	38.6	7.3	0.5	182 (M^+, 100), 167(25), 165(25), 154(40), 141(30)
 **s8H-A**	-	4.8	54.8	86.1	90.3	186 (M^+, 100), 158(80), 145(40), 143(35), 129 (45), 115(25)
 **u8H-A**	-	-	-	0.4*	1.7*	186 (M^+, 100), 104(80)
 **14H-A**	-	-	-	1.0*	0.8*	192 (M^+, 95), 150(25), 135(100), 121(40), 81 (65), 67(80), 41(100)
 **buT**	-	-	-	0.7	2.1	188 (M^+, 25), 145(100), 131(30), 91(20)

* Sum of isomers. – [a] 6.0 g (33.7 mmol) of A, 1.4 g (11.8 mmol) of TPDB, 60 ml of toluene.

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ated over heavy metal-[4] and in recent years by using a variety of homogeneous catalysts[3,5–14]. Lewis acids such as $ZnCl_2$ or $AlCl_3$[15] and $H_2O \cdot BF_3/(CH_3CN)_2PtCl_2$[16] have also been employed as catalysts. Except one report in the older literature using Raney nickel[17], all previous methods, at least in the reaction times used, are reported to yield mixtures containing varying amounts of **2H-A**, **4H-A**, and **8H-A**.

b) *9-Phenylanthracene* (**pA**): Table 2 shows that the rate of formation of 1,2,3,4-tetrahydro-9-phenylanthracene (**4H-pA**) from **pA** is only slightly faster than that of 1,2,3,4,5,6,7,8-octahydro-9-phenylanthracene (**8H-pA**) at a reaction temperature of 200°C. By decreasing the temperature to 180°C an acceptable yield of **4H-pA** can be obtained after three hours.

Table 2. Hydrogenation of 9-phenylanthracene (**pA**)[a]

Compound	% (GC) Products					Mass spectra
	1h	2h	3h	4h	5h	[rel. abundance (%)]
Ph **pA**	44.3	6.9	1.0	-	-	254 (M^+, 100), 253(47), 252(40), 126(19)
Ph **4H-pA**[b]	40.5	32.4	10.8	1.0	-	258 (M^+, 100), 215(20)
Ph **8H-pA**	11.4	57.9	84.4	93.8	94.5	262 (M^+, 100), 234(22)

[a] 1.0 g (3.9 mmol) of **pA**, 0.30 g (2.5 mmol) of TPDB, 20 ml of toluene. — [b] When the reaction temperature was decreased to 180°C, the yield of **4H-pA** after 3 h was 70%.

Table 3. Hydrogenation of 9,10-dimethylanthracene (**9,10-dmA**)[a]

Compound	% (GC) Products			Mass spectra
	1h	2h	3h	[rel. abundance(%)]
9,10-dmA	23.5	0.8	-	206 (M^+, 100), 191(34)
4H-9,10-dmA	62.1	25.1	-	210 (M^+, 100), 195(85), 180(20), 165(25)
8H-9,10-dmA	9.3	60.3	72.5	214 (M^+, 68), 199(100), 176(10), 157(15)

[a] 1.0 g (4.8 mmol) of **9,10-dmA**, 0.40 g (3.3 mmol) of TPDB, 20 ml of toluene.

c) *9,10-Dimethylanthracene* (**9,10-dmA**): The rate of conversion of **9,10-dmA** to 1,2,3,4-tetrahydro-9,10-dimethylanthracene (**4H-9,10-dmA**) is significantly slower than its further reaction to 1,2,3,4,5,6,7,8-octahydro-9,10-dimethylanthracene (**8H-9,10-dmA**). By carefully monitoring the reaction progress **4H-9,10-dmA** may be obtained in 74% yield after 30 minutes reaction time (see Table 3). On further exposure **8H-9,10-dmA** is found in 72% yield.

Table 4. Hydrogenation of 1,4-dimethylanthracene (**1,4-dmA**)[a]

Compound	% (GC) Products			Mass spectra
	1.75h	2.5h	6h	[rel. abundance (%)]
Me Me **4H-1,4-dmA**	91.7	50.0	0.3	210 (M^+, 100), 195(55), 182(25), 165(35)
Me Me **4H-iso-dmA**	0.3	19.4	1.9	210 (M^+, 100), 195(60), 182(32), 165(30)
Me Me **8H-iso-dmA**	2.9*	10.0*	26.1*	214 (M^+, 80), 199(35), 157(20), 132(100), 119(70)

* Sum of isomers. — [a] 0.90 g (4.3 mmol) of **1,4-dmA**, 0.40 g (3.3 mmol) of TPDB, 20 ml of toluene.

Table 5. Hydrogenation of 9-bromoanthracene (**brA**)[a]

Compound	% (GC) Products		Mass spectra
	1.5h	3.5h	[rel. abundance (%)]
Br **brA**	18.3	0.6	258 (M^+, 100), 177(63), 151(25), 88(55)
Pr **prA**	15.2	-	220 (M^+, 30), 191(100), 189(25)
A	39.2	-	see Table 1
4H-A	6.5	-	see Table 1
Pr **4H-prA**	2.8	0.8	224 (M^+, 60), 196(22), 195(100), 165(32)
8H-A	-	59.1	see Table 1
Pr **s8H-prA**	-	10.7	228 (M^+, 58), 200(22), 199(85), 185(100)

[a] 0.60 g (2.3 mmol) of **brA**, 0.40 g (3.3 mmol) of TPDB, 10 ml of toluene.

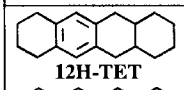
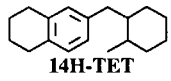
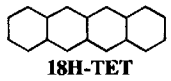
d) *1,4-Dimethylanthracene* (**1,4-dmA**): Short-time hydrogenation of **1,4-dmA** gives 1,2,3,4-tetrahydro-5,8-dimethylanthracene (**4H-1,4-dmA**) in 91% yield (see Table 4). The isomeric 1,2,3,4-tetrahydro-1,4-dimethylanthracene is only a minor component. Longer reaction times produce mainly a mixture of four isomeric octahydrodimethylanthracenes (**8H-dmA**). The very similar characteristic mass spectral

fragmentation pattern (loss of C_6H_{10} from the molecular ion) in each of the four isomers suggests that the two unsubstituted rings are hydrogenated, giving rise to a *cis/trans* mixture in addition to a methyl migration, possibly to the 3-position[1]. The preference for hydrogenation of the unsubstituted rings and also the alkyl migration have previously been observed for alkylnaphthalenes[1]. In addition to these octahydroanthracenes a larger number of not further identified C–C bond scission products are also formed.

e) *9-Bromoanthracene* (**brA**): As previously observed for the halonaphthalenes[1], **brA** is first mainly dehalogenated followed by subsequent conversion to **4H-A** or **8H-A** (see Table 5). Major side products are the 1,2,3,4-tetra- and 1,2,3,4,5,6,7,8-octahydro-9-*n*-propylanthracenes (**9pr-4H-A**) and (**9pr-s8H-A**), respectively[18] (compare ref.[3]).

f) *Tetracene* (**TET**): The hydrogenation of tetracene gives mainly (73%) 1,2,3,4,4a,5,7,8,9,10,12,12a-dodecahydrotetracene (**12H-TET**). Additionally, small amounts (5.5%) of three isomers of perhydrotetracene (**18H-TET**) and a number of C–C bond scission products are also formed. Two of the latter have probably the isomeric structures shown in Table 6, based on their mass spectral fragmentation pattern.

Table 6. Hydrogenation of tetracene (**TET**)[a]

Compound	% (GC) Products 16h	Mass spectra [rel. abundance (%)]
 **12H-TET**	72.6	240 (M^+, 100), 212(10), 158(50), 145(50)
 **14H-TET**	8.6	242 (M^+, 20), 146(100), 97(40), 55(40)
 **18H-TET**	5.5*	246(M^+, 100), 189(65), 135(45), 95(80), 81(70)

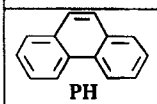
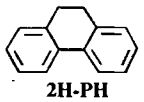
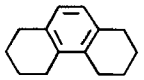
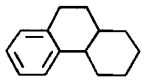
* Sum of isomers. – [a] 0.40 g (1.6 mmol) of **TET**, 0.40 g (3.3 mmol) of TPDB, 10 ml of toluene.

II. Angularly *ortho*-Fused Arenes

a) *Phenanthrene* (**PH**): Although in stoichiometric reactions with >BH boranes no hydroboration of **PH** has been achieved, a slow >BD/>CH exchange reaction with >BD borane reagents had indicated some reactivity of this arene[2]. In conjunction with molecular hydrogen at 200°C and in presence of catalytic amounts of >BH boranes hydrogenation of **PH** is readily achieved. Thus after three hours reaction time a mixture consisting of mainly 9,10-dihydro- and lesser amounts of *sym*- and *unsym*-octahydrophenanthrenes (**2H-PH**, **s8H-PH**, and **u8H-PH**, respectively) is formed (see Table 7). Longer reaction times do not result in significant changes of the product composition, suggesting that **2H-PH** is not an intermediate in the reaction to the **8H-PH** stereoisomer (compare also refs.[3,4,8,12,14,15]).

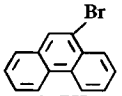
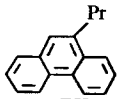
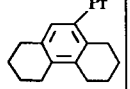
b) *9-Bromophenanthrene* (**brPH**): The hydrogenation of **brPH** under the above conditions is more sluggish than of **PH**. After 10 hours the main component in the product mixture is **s8H-PH** in 55% yield (see Table 8). **2H-PH** is present only as a minor component. Obviously the initial presence of a bulky substituent on the central ring of **PH** hinders the approach of the borane catalyst to the olefin-like C-9/C-10 double bond. Hydrogenation is thus thought to be initiated at one of the terminal rings, followed by fast dehalogenation to give 1,2,3,4-tetrahydrophenanthrene (**4H-PH**) as a further reactive intermediate (compare also ref.[3]).

Table 7. Hydrogenation of phenanthrene (**PH**)[a]

Compound	% (GC) Products			Mass spectra [rel. abundance (%)]
	2h	4h	22h	
 **PH**	66.3	1.7	0.5	178 (M^+, 100), 176(15), 89(12)
 **2H-PH**	14.5	48.0	41.7	180(100), 179(60), 178 (38), 165(25), 89(15)
 **s8H-PH**	8.3	22.5	17.1	186(100), 158(80), 145 (40), 143(35), 129(22)
 **u8H-PH**	4.8*	19.8*	21.5*	186 (M^+, 100), 158(20), 143(90), 129(100), 104(40)

* Sum of isomers. – [a] 6.0 g (33.7 mmol) of **PH**, 1.4 g (11.7 mmol) of TPDB, 30 ml of toluene.

Table 8. Hydrogenation of 9-bromophenanthrene (**brPH**)[a]

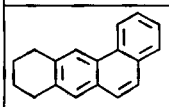
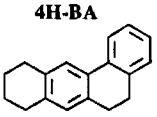
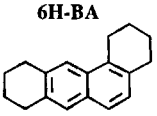
Compound	% (GC) Products		Mass spectra [rel. abundance (%)]
	2h	10h	
 **brPH**	2.5	-	258 (M^+, 100), 177(32)
PH	43.0	0.6	see Table 7
 **prPH**	3.3	3.0	220 (M^+, 25), 191(100)
 **8H-prPH**	1.5	3.2	228 (M^+, 50), 200(15), 199(75), 185(100)
2H-PH	3.7	8.3	see Table 7
s8H-PH	24.0	55.0	see Table 7
u8H-PH	4.8*	16.0*	see Table 7

* Sum of isomers. – [a] 2.0 g (7.8 mmol) of **brPH**, 1.4 g (11.7 mmol) of TPDB, 15 ml of toluene.

c) *Benz[a]anthracene* (**BA**): In **BA** both the linear and nonlinear fused structural features are present. It could be expected that 8,9,10,11-tetrahydrobenz[*a*]anthracene (**4H-**

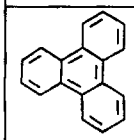
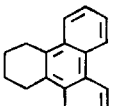
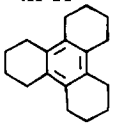
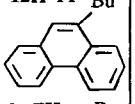
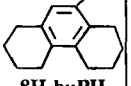
BA) would be the initial product. After four hours reaction time 5,6,8,9,10,11-hexahydrobenz[*a*]anthracene (**6H-BA**) is found as the major product (60%) (see Table 9). **4H-BA** and the octa- and dodecahydro derivatives (**8H-BA** and **12H-BA**) are formed in small amounts (compare refs.[3,4,9,19]).

Table 9. Hydrogenation of benzo[*a*]anthracene (**BA**)[a]

Compound	% (GC) Products 4h	Mass spectra [rel. abundance (%)]
 **4H-BA**	13.4	232 (M^+, 100), 204(45), 191(20), 189(17)
 **6H-BA**	60.0	234 (M^+, 100), 206(30), 191(35), 165(15)
 **8H-BA**	2.6	236 (M^+, 100), 108(35), 195(25), 165(25), 28(95)
12H-BA	17.8*	240 (M^+, 100), 197(80), 158(20), 141(50)

* Sum of isomers. – [a] 0.50 g (2.2 mmol) of **BA**, 0.40 g (3.3 mmol) of TPDB, 20 ml of toluene.

Table 10. Hydrogenation of triphenylene (**TP**)[a]

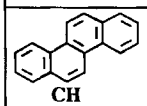
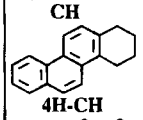
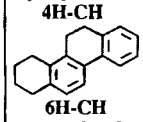
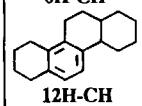
Compound	% (GC) Products 7h	Mass spectra [rel. abundance (%)]
 **TP**	50.0	228 (M^+, 100), 226(25), 114(15), 113(18)
 **4H-TP**	12.2	232 (M^+, 100), 215(20), 204(75), 191(30), 101(15)
 **12H-TP** Bu	3.6	240 (M^+, 100), 212(35), 211(30), 199(32), 198 (45), 197(30), 141(20)
 **buPH** Bu	15.0	234 (M^+, 65), 192(50), 191(100), 178(42), 165(20)
 **8H-buPH**	1.7	242 (M^+, 40), 199(100), 185(80), 157(30)

[a] 0.50 g (2.2 mmol) of **TP**, 0.40 g (3.3 mmol) of TPDB, 10 ml of toluene.

d) *Triphenylene* (**TP**): The rate of hydrogenation of **TP** is slow. After seven hours only 50% conversion is observed (see Table 10). The tetra- and dodecahydrotriphenylenes (**4H-TP** and **12H-TP**) constitute only the lesser amounts. The C–C bond scission products such as 9-butylphenanthrene and 9-butyl-1,2,3,4,5,6,7,8-octahydrophenanthrene (**buPH** and **s8H-PH**, respectively) are also formed (compare also refs.[4,6]).

e) *Chrysene* (**CH**): Table 11 shows the changes in the product composition during the hydrogenation of **CH** for various times. The first major product formed is 1,2,3,4-tetrahydrochrysene (**4H-CH**). After two hours the concentration of **4H-CH** begins to decrease, instead the concentration of 1,2,3,4,5,6-hexahydrochrysene (**6H-CH**) increases, reaching a maximum after four hours. From the beginning, small amounts of two isomers of 1,2,3,4,4a,7,8,9,10,11,12,12a-dodecahydrochrysene (**12H-CH**) are also formed. Their concentration increases in the final stages of the hydrogenation process (compare also refs.[4,8]).

Table 11. Hydrogenation of chrysene (**CH**)[a]

Compound	% (GC) Products						Mass spectra
	$^3/_4$h	$1^1/_2$h	2h	3h	4h	$5^1/_2$h	[rel. abundance (%)]
 **CH**	58.9	34.3	22.4	7.3	3.6	-	228 (M^+, 100), 226 (27)
 **4H-CH**	28.3	35.5	24.4	13.5	6.8	2.4	232 (M^+, 100), 204 (75), 191(20)
 **6H-CH**	6.7	18.3	37.0	54.6	61.0	59.8	234 (M^+, 100), 206 (30), 191(35)
 **12H-CH**	-	3.7*	8.3*	14.0*	17.9*	21.9*	240 (M^+, 100), 212 (15), 197(60), 183 (20), 141(30)

* Sum of isomers. – [a] 0.30 g (1.3 mmol) of **CH**, 0.30 g (2.5 mmol) of TPDB, 15 ml of toluene.

III. *ortho*- and *peri*-Fused Arenes

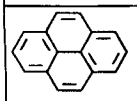
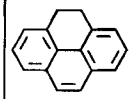
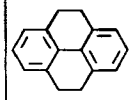
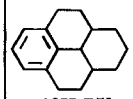
a) *Pyrene* (**PY**): The reaction times for the complete hydrogenation of the smallest of the *ortho*- and *peri*-fused arene **PY** is 24 hours. The main product is 4,5,9,10-tetrahydropyrene (**4H-PY**) in 76% yield (see Table 12), 4,5-dihydropyrene (**2H-PY**) is only a minor component. Two isomeric decahydropyrenes (**10H-PY**) are also formed in small amounts (compare also refs.[3,4,8,12,19–21]).

b) *Perylene* (**PER**): The next higher homologue, the pentacyclic **PER**, forms mainly 1,2,3,10,11,12-hexa- and *cis*/*trans*-1,2,3,3a,4,5,6,7,8,9,9a,10,11,12-tetradecahydroperylene (**6H-PER** and **14H-PER**, resp.) in 26.8 and 24.7% yields, respectively. C–C bond scissions reaction of these leads to products with the probable structures (MS fragmentation) shown in Table 13 (compare also ref.[22]).

c) *Coronene* (**C**): Finally, we applied this reaction to the hydrogenation of **C**. After six hours reaction time,

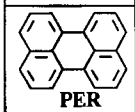
besides lesser amounts of di- and tetrahydrocoronene, and 1,2,5,6,9,10-hexahydrocoronene (**2H-C**, **4H-C**, and **6H-C**, respectively) is the main reaction product (50%) (see Table 14). Trace quantities of more highly hydrogenated coronenes could also be detected. On increasing the reaction times the ratio of these latter components progressively increase. After 86 hours they constitute the major components (compare also ref.[23]).

Table 12. Hydrogenation of pyrene (**PY**)[a]

Compound	% (GC) Products					Mass spectra [rel. abundance (%)]
	3h	7h	11h	17h	21.5h	
 **PY**	80.0	26.4	6.8	1.6	0.8	202 (M^+, 100), 101 (35), 100(25)
 **2H-PY**	10.9	28.3	17.2	9.3	7.2	204 (M^+, 62), 203 (61), 202(100), 201 (20), 200(22), 101 (40)
 **4H-PY**	1.8	34.0	59.9	69.4	71.9	206 (M^+, 100), 205 (60), 203(30), 189 (15), 188(17), 178 (17), 165(15)
 **10H-PY**	-	1.5*	4.2*	6.5*	7.8*	212 (M^+, 60), 184 48), 169(100)

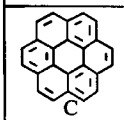
* Sum of isomers. — [a] 1.0 g (29.7 mmol) of **PY**, 0.40 g (3.3 mmol) of TPDB, 15 ml of toluene.

Table 13. Hydrogenation of perylene (**PER**)[a]

Compound	% (GC) Products		Mass spectra [rel. abundance (%)]
	3h	6h	
 **PER**	14.8	-	252 (M^+, 100), 250(25), 126(20), 125(18)
 **6H-PER**	68.8	26.8	258 (M^+, 100), 229(15), 228(16), 215(18), 114 (20)
 **14H-PER**	3.1	24.7	266 (M^+, 100), 238(90), 223(45), 210(32), 195 (15), 165(25)
 **8H-PER**	9.5	16.9	260 (M^+, 100), 231(75), 217(20), 215(20), 202 (15)
 **8H-BN**	5.0	4.7	262 (M^+, 100), 234(55), 219(20)
 **16H-PER**	>0.5*	~8.2*	268 (M^+, 15), 255(100)

* Sum of isomers. — [a] 0.40 g (1.6 mmol) of **PER**, 0.60 g (5.0 mmol) of TPDB, 20 ml of toluene.

Table 14. Hydrogenation of coronene (**C**)[a]

Compound	% (GC) Products			Mass spectra [rel. abundance (%)]
	6h	10h	86h	
 **C**	15.5	6.4	3.5	300 (M^+, 100), 299(25), 298(22), 150(40), 149(35)
 **2H-C**	5.5	4.0	1.5	302 (M^+, 100), 301(55), 300(98), 299(20), 298 (30), 150(55)
 **4H-C**	16.5	14.5	3.5	304 (M^+, 100), 303(40), 302(41), 301(45), 300 (70), 152(15), 151(25), 150(50), 149(30)
 **6H-C**	50.0	4.9	11.5	306 (M^+, 100), 305(45), 304(30), 303(25), 302 (30), 301(35), 300(50), 150(40), 149(25)
10H-C	2	5	15.5	310 (M^+, 100), 309(25), 308(25), 282(20), 281(20)
14H-C	5*	5*	12*	314 (M^+, 100), 313(25), 286(20)
 **18H-C**	3*	7*	22*	318 (M^+, 100), 317(35), 316(18), 290(20)
 **24H-C**	n.o	n.o	2*	324 (M^+, 100), 28(40)

* Sum of isomers. — [a] 0.40 g (1.3 mmol) of **C**, 0.60 g (5.0 mmol) of TPDB, 20 ml of toluene.

Experimental

GC: Siemens Sicromat 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 7A. — MS: Varian MAT CH 7. — ^{1}H NMR: Bruker AC 200. — For sources of the borane reagent see ref.[2].

General Procedure for the Hydrogenation of the Arenes: The substrate, 0.10–10 g, dissolved or suspended in 10–100 ml of toluene solution containing 0.50–2.0 g (2.5–16.8 mmol) TPDB was placed in a 200-ml stainless steel autoclave with magnetic stirring. The autoclave was charged with 90 bar of hydrogen and heated to an external temperature of 200°C. Where appropriate, 0.5-ml samples were removed at set times through an auxiliary capillary valve and analyzed by GC or GC-MS. After cooling to room temp., the gas was vented. The suspension formed on exposure to air was filtered from the solid polyboranes formed. Where possible the products were isolated in pure form by simple crystallization from ethanol or another appropriate solvent. When complex mixtures were present separation and purification were carried out by preparative thicklayer chromatography [Commercial silica-gel plates, 2 mm thick (Merck)] with hexane, or hexane/dichloromethane as solvent.

Structural assignments of the products were made in the following ways: (a) If one of the main components could be purified by crystallization or by TLC: by direct comparision with known compounds (in some cases independently prepared by known hydrogenation procedures) or by the combined analysis of their MS (see Tables 1–14) and ^{1}H-NMR spectra (see Table 15). (b) In other cases and in the case of most of the minor components: by comparison with the fragmentation pattern of known compounds (MS spectral library). (c) In a few cases on the basis of analysis of MS fragmentation patterns only.

Table 15. ^{1}H-NMR data for various partially hydrogenated polycyclic arenes

Compound	δ ^{1}H (200 MHz, $CDCl_3$)
4H-A	7.82 (dd, 2H), 7.61 (s, 2H), 7.47 (dd, 2H), 3.03 (m, 4H), 1.91 (m, 4H)
s8H-A	6.85 (s, 2H), 2.79 (m, 8H), 1.85 (m, 8H)
4H-pA	7.85 (d, 1H), 7.68 (s, 1H), 7.59 (dd, 1H), 7.52 (m, 2H), 7.42 (m, 1H), 7.29 (m, 4H), 3.11 (t, 2H), 2.67 (t, 2H), 1.86 (m, 4H)
s8H-pA	7.65 (m, 3H), 7.42 (dd, 2H), 7.18 (s, 1H), 3.06 (t, 4H), 2.57 (t, 4H), 1.95 (m, 8H)
4H-9,10-dmA	7.95 (dd, 2H), 7.30 (dd, 2H), 2.82 (m, 4H), 2.44 (s, 6H), 2.76 (m, 4H)
8H-9,10-dmA	2.95 (m, 8H), 2.36 (s, 6H), 2.05 (m, 8H)
4H-5,8-dmA	7.85 (s, 2H), 7.21 (s, 2H), 3.10 (m, 4H), 2.70 (s, 6H), 1.88 (m, 4H)
12H-TET	6.70 (s, 2H), 2.64 (m, 6H), 2.30 (m, 2H), 1.70 (m, 8H), 1.24 (m, 4H), 0.94 (m, 2H),
s8H-PH	7.06 (d, 2H), 2.97 (m, 4H), 2.76 (m, 4H), 2.00 (m, 4H)
6H-BA	7.79 (d, 1H), 7.49 (s, 1H), 7.30 (m, 1H), 7.24 (m, 2H), 6.97 (s, 1H), 2.85 (m, 8H), 1.88 (m, 4H)
6H-CH	7.79 (d, 1H), 7.49 (s, 1H), 7.30 (dd, 1H), 7.24 (m, 2H), 6.97 (s, 1H), 2.85 (m, 8H), 1.88 (m, 4H)
2H-PY	7.50 (dd, 2H), 7.35 (s, 2H), 7.20 (m, 4H), 3.09 (s, 4H)
4H-PY	6.95 (m, 6H), 2.88 (s, 8H)
6H-PER	8.55 (d, 2H), 7.48 (dd, 2H), 7.33 (d, 2H), 3.12 (t, 4H), 3.09 (t, 4H), 2.09 (m, 4H)
8H-PER	7.16 (d, 2H), 7.09 (dd, 2H), 6.94 (d, 2H), 3.51 (m, 2H), 7.81 (m, 4H), 2.52 (m, 2H), 2.15 (m, 2H), 1.90 (m, 4H)
12H-PER	2.51 (m, 10H), 1.84 (m, 12H), 1.15 (m, 4H)
6H-C	7.33 (s, 6H), 3.2 (s, 12H)

The procedures below for the hydrogenation of anthracene (**A**) to either **4H-A** or **s8H-A** demonstrate the utility of this method for preparative purposes.

1,2,3,4-Tetrahydroanthracene (**4H-A**) *(Preparative Scale):* A suspension of 17.8 g (0.10 mol) of **A** and 4.0 g (33.6 mmol) of TPDB in 100 ml of toluene was placed in a 200-ml rocking autoclave, pressurized to 80 bar with H_2 gas, and heated to 200°C for 1.5 h. On cooling a pressure drop of 55 bar (calcd. 48 bar) was observed. The slightly yellow solution was evaporated to dryness and the residue recrystallized twice from ethanol to give **4H-A** (15.9 g, 87%), m.p. 101–102°C. For mass and ^{1}H-NMR spectra see Tables 1 and 15.

1,2,3,4,5,6,7,8-Octahydroanthracene (**s8H-A**) *(Preparative Scale):* A suspension of 17.8 g (0.10 mol) of **A** and 4.0 g (33.6 mmol) of TPDB in 100 ml of toluene was placed in a 200-ml rocking autoclave, pressurized with 140 bar of H_2 gas, and heated to 200°C for 5 h. On cooling a pressure drop of 130 bar (calcd. 120 bar) was observed. The dark yellow-brown solution was evaporated to dryness and the residue recrystallized twice from ethanol to give **s8H-A** (16.8 g, 90%), m.p. 71–72°C. For mass and ^{1}H-NMR spectra see Tables 1 and 15.

CAS Registry Numbers

A: 120-12-7 / **C**: 191-07-1 / **TPDB**: 22784-01-6 / **4H-A**: 2141-42-6 / **s8H-A**: 1079-71-6 / *cis*-**u8H-A**: 64363-88-8 / *trans*-**u8H-A**: 77341-12-9 / **14H-A**: 6596-35-6 / **buT**: 30654-45-6 / **2H-A**: 58746-82-0 / **pA**: 602-55-1 / **4H-pA**: 13225-66-6 / **8H-pA**: 125379-29-5 / **9,10-dmA**: 781-43-1 / **4H-9,10-dmA**: 94573-50-9 / **8H-9,10-dmA**: 42173-25-1 / **1,4-dmA**: 781-92-0 / **4H-1,4-dmA**: 125379-30-8 / **4H-iso-dmA**: 125379-31-9 / **8H-iso-dmA**: 125379-32-0 / **brA**: 1564-64-3 / **4H-prA**: 101580-33-0 / **s8H-prA**: 125379-33-1 / **TET**: 92-24-0 / **12H-TET**: 125379-34-2 / **14H-TET**: 125379-35-3 / **18H-TET**: 64302-84-7 / **PH**: 85-01-8 / **2H-PH**: 776-35-2 / **s8H-PH**: 5325-97-3 / **u8H-PH**: 16306-39-1 / **brPH**: 573-17-1 / **prPH**: 17024-03-2 / **8H-prPH**: 125379-36-4 / **BA**: 56-55-3 / **4H-BA**: 67064-62-4 / **6H-BA**: 67064-61-3 / **8H-BA**: 93872-28-7 / **12H-BA**: 125379-37-5 / **TP**: 217-59-4 / **4H-TP**: 5981-10-2 / **12H-TP**: 1610-39-5 / **bu-PH**: 10394-57-7 / **8H-buPH**: 16703-29-0 / **CH**: 218-01-9 / **4H-CH**: 2091-90-9 / **6H-CH**: 2091-91-0 / **12H-CH**: 1610-22-6 / **PY**: 129-00-0 / **2H-PY**: 6628-98-4 / **4H-PY**: 781-17-9 / **10H-PY**: 55821-21-1 / **PER**: 198-55-0 / **6H-PER**: 7350-92-7 / *cis*-**14H-PER**: 125379-38-6 / *trans*-**14H-PER**: 125379-42-2 / **8H-PER**: 14930-91-7 / **8H-BN**: 1154-14-9 / **16H-PER**: 125379-39-7 / **2H-C**: 107716-56-3 / **4H-C**: 125413-07-2 / **6H-C**: 113845-11-7 / **10H-C**: 125379-40-0 / **14H-C**: 122764-04-9 / **18H-C**: 125379-41-1 / **24H-C**: 54171-94-7 / **prA**: 1498-77-7

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[346/89]