Reduction of Polycyclic Arenes by $>$BH-Boranes, II[1a)]

Borane Catalyzed Hydrogenation of Naphthalenes to Tetralins

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Tetrapropyldiborane(6) (TPDB) and triethylborane (TEB) catalyze the regioselective and partial hydrogenation of naphthalene (N) and a number of substituted naphthalenes at 170–200°C and hydrogen pressures of 25–100 bar. Tetralin (T) is formed quantitatively. Naphthalene derivatives are mainly hydrogenated in the least substituted ring. In the case of alkyl substituents, Lewis acid catalyzed migration and, to a lesser extent C–C bond rupture, lower the yield of the main tetralin derivative. Chlorinated naphthalenes and at the O-atom derivatized naphthols undergo also partial loss of the chloro or oxygen functional groups. The initially added borane acts only as a precatalyst and is slowly converted to catalytically active polyboranes of as yet unknown structures.

Reduktion kondensierter Arene mit $>$BH-Boranen, II[1a)]. – Boran-katalysierte Hydrierung von Naphthalinen zu Tetralinen

Tetrapropyldiboran(6) (TPDB) und Triethylboran (TEB) katalysieren bei 170–200°C und Wasserstoff-Drucken von 25–100 bar die regioselektive und partielle Hydrierung von Naphthalin (N) sowie von zahlreichen substituierten Naphthalinen. Tetralin (T) wird aus N quantitativ gebildet. Naphthalin-Derivate lassen sich bevorzugt im nicht oder weniger substituierten Ring hydrieren. Nebenreaktionen der Tetralin-Bildung sind Lewis-Säure-katalysierte Alkyl-Wanderungen und in geringem Umfang auch C–C-Spaltungen. Chlorierte Naphthaline sowie am Sauerstoff-Atom derivatisierte Naphthole reagieren mit H_2/Boran unter partiellem Verlust der Chlor-Atome bzw. der O-Funktion. Das eingesetzte Boran ist eine Katalysator-Vorstufe, aus der während des Erhitzens langsam katalytisch wirksame Polybor-Verbindungen unbekannter Struktur gebildet werden.

The facile addition of $>$BH-borane reagents to carbon–carbon and to carbon–heteroatom multiple bonds has rendered them most versatile as tool for organic synthesis. Hitherto it has been assumed that the $>C=C<$ bonds of arenes are inert towards attack by these reagents. We have now shown that di- and polycyclic arenes react readily with borane reagents such as tetraethyl- and tetrapropyldiborane(6) (TEDB and TPDB, respectively) at about 140°C forming borylated hydroarenes[1)]. Utilizing these results and combining them with the knowledge that B–C bonds can be hydrogenized under H_2 pressure at $T > 140°C$[2)] and in light of the divergent results reported in recent years on the catalytic hydrogenation of these systems using various hetero- or homogeneous catalysts[3)], it was hoped that by this method a more predictable, controllable, and efficient route (not involving heavy metal catalysis) to regioselectively hydrogenated polycyclic hydroarenes will become available.

Herein we report details of our studies (with scope and limitations of the method) on the partial hydrogenation of naphthalene (N) and some of its derivatives to tetralins using hydrogen in the presence of organoboranes. The extension of this procedure to the higher polycyclic arenes will be described in a subsequent publication.

Results and Discussions

Table 1 summarizes the results obtained for the hydrogenation of N and some of its derivatives under our standard procedure using TPDB in heptane as catalyst at 200°C and with an initial hydrogen pressure of 100 bar and 4 h reaction time.

While the conversion of N to tetralin (T) is excellent and essentially quantitative, the hydrogenation of naphthalene derivatives leads to the formation of product mixtures in which generally one component predominates with fair to good yields. Hydrogenation occurs preferentially at the unsubstituted ring. Besides the problem of regioselectivity, other factors, too, diversify the products formed and thus lower the yields of the main products. The isomerization of alkyl substituent(s) at the aromatic ring (cf. Table 1, entries 2–12) is probably induced by the Lewis acid character of the borane catalyst and occur independently of the hydrogenation step[4)]. Another sidereaction of some importance is the C–C bond rupture[5,6)], which in the case of 2,6-dimethylnaphthalene leads to the formation of up to 12% of 6-methyltetralin (Table 1, entry 12). This C–C bond cleavage can also lead to ring cleavage and thus formation of alkylbenzene(s), e.g., butylbenzene from naphthalene. Since tetralin is stable under these conditions it must be assumed, that the C–C bond rupture occurs at the stage of the at least partially hydroborated intermediate. While the extent of these reactions is usually insignificant (ca. 1–2%) for simple alkylnaphthalenes, it plays a major role for acenaphthene and acenaphthylene (Table 1, entries 13 and 14).

Naphthalenes carrying aromatic substituents (Table 1, entries 15–17) do not undergo isomerization or C–C bond ruptures, and high yields of the corresponding biphenyl de-

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Table 1. Hydrogenation products of naphthalenes catalyzed by tetrapropyldiborane(6) (TPDB)

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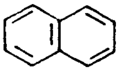
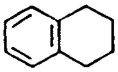
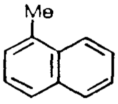
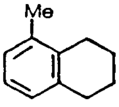
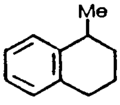
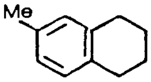
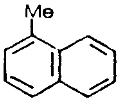
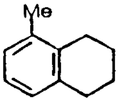
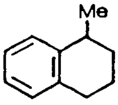
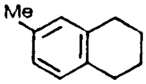
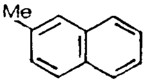
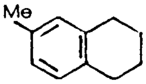
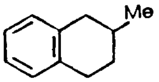
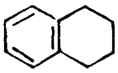
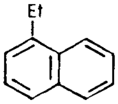
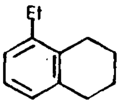
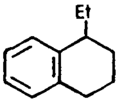
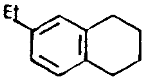
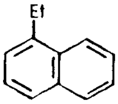
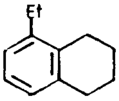
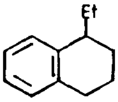
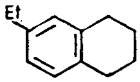
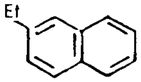
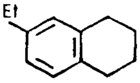
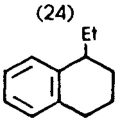
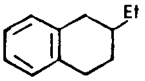
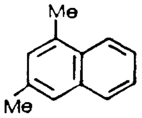
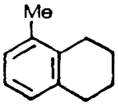
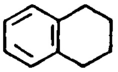
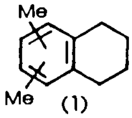
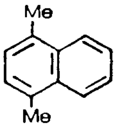
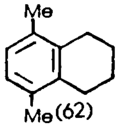
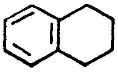
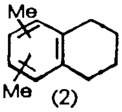
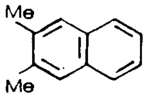
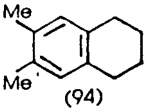
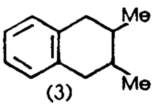
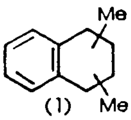
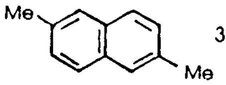
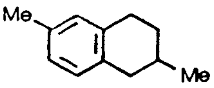
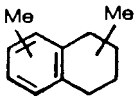
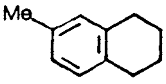
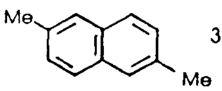
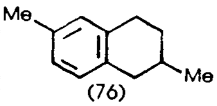
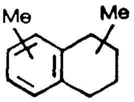
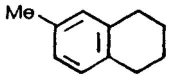
1		78	12	 (99)		
2		14	18	 (18)	 (17)	 (53)
3		20	3	 (76)	 (21)	 (1)
4		14	12	 (85)	 (14)	 (<1)
5		32	12	 (44)	 (20)	 (28)
6		20	3	 (70)	 (24)	 (3)
7		32	12	 (72)	 (10)	 (11)
8		13	12	 (89)	 (3)	 (1)
9		13	6	 (62)	 (25)	 (2)
10		32	12	 (94)	 (3)	 (1)
11		32	12	 (66)	 (6)	 (12)
12		32	4	 (76)	 (4)	 (7)

Table 1 *(Continued)*

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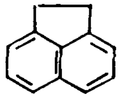
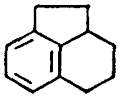
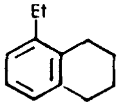
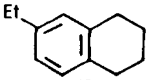
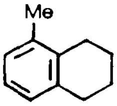
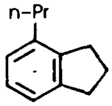
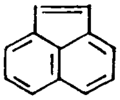
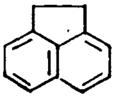
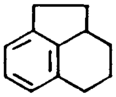
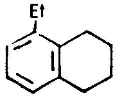
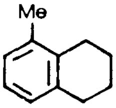
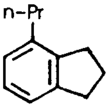
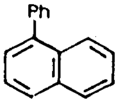
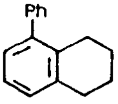
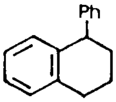
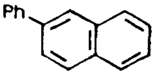
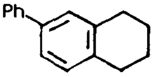
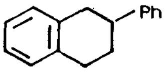
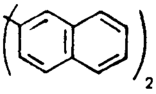
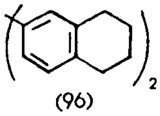
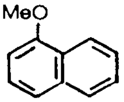
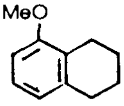
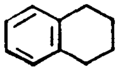
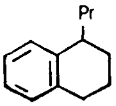
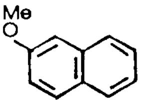
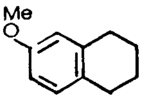
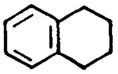
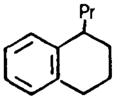
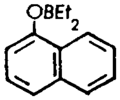
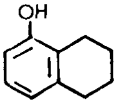
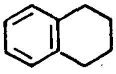
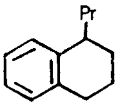
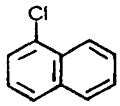
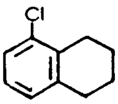
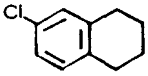
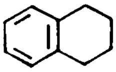
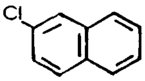
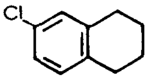
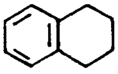
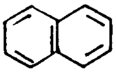
13		33	12	 (14)  (34)  (8)  (1)  (36)
14		32	12	 (12)  (7)  (13)  (17)  (29)
15		10	6	 (91)  (4)
16		10	6	 (95)  (4)
17		4	6	 (96)
18		32	12	 (39)  (54)  (2)
19		32	12	 (31)  (68)  (1)
20		35	12	 (14)  (68)  (2)
21		31	12	 (38)  (6)  (53)
22		25	6	 (75)  (21)  (3)

rivatives are readily obtained. The partial loss of the alkoxy and chlorine substituents observed (Table 1, entries 18 – 22) are probably the result of a hydrogenation-elimination-hydrogenation sequence (anisole and chlorobenzene are virtually unreactive under these conditions).

Although we have not attempted to optimize the yields of the main components formed in the hydrogenation of the substituted naphthalenes, preliminary results (cf. Table 1, entries 2, 3, 5, 6, and 11, 12) indicate that by increasing the ratio of the substrate to catalyst some of the side reactions can be subdued.

A series of experiments were, however, performed to determine the limiting factors for the hydrogenation of N. The results are presented in Table 2.

It can be seen (entries 1 – 4) that the reaction is truely catalytic. From these results it can be estimated that each borane molecule is involved in about 20 catalytic turnovers (TON) (calcd. assuming two catalytic steps for each naphthalene molecule) in a reaction time of 4 h. When the time was extended to 12 h, the TON increased to 140. The threshold temperature, in agreement with that observed earlier for B – C bond hydrogenations[2], appears to be somewhat above 150°C (entry 7). At a starting hydrogen pressure of ca. 10 bars, the reaction is still relatively efficient (entry 11). A high yield of tetralin is also obtained in the short reaction time of 0.5 h (entry 13). The reaction performs well in both aliphatic and aromatic solvents (toluene is not appreciably hydrogenated under these conditions) but is retarded in polar solvents such as THF (entry 15). Other boranes such as tetraethyldiborane(6) (TEDB) and triethylborane (TEB) can also be effective catalysts (entries 16 and 17). However, amine – boranes such as triethylamine – borane (TEAB) (en-

Table 2. Effect of variation of reaction conditions on the hydrogenation of naphthalene

Exp.[a] No.	Type of borane	mmol borane (mg)	Solvent	Temp. (°C)	Pressure (bar)	Time (h)	Yield (tetralin) %	Recovered (naphthalene) %
1	TPDB[b]	12.0	heptane	200	100	4	98.9	0
2	TPDB[b]	3.0	heptane	200	100	4	98.7	0.1
3	TPDB[b]	1.5	heptane	200	100	4	94.2	5.8
4	TPDB[b]	0.3	heptane	200	100	4	7.2	92.7
5	TPDB[b]	0.06	heptane	200	100	4	0	100
6	TPDB[b]	6.0	heptane	170	100	4	96.7	3.4
7	TPDB[b]	6.0	heptane	150	100	4	1.5	97.6
8	TPDB[b]	3.0	heptane	200	50	4	99.1	0.4
9	TPDB[b]	3.0	heptane	200	25	4	91.1	6.9
10	TPDB[b]	3.0	heptane	200	20	4	83.4	14.6
11	TPDB[b]	3.0	heptane	200	10	4	66.4	33.6
12	TPDB[b]	3.0	heptane	200	100	2	99.6	0.4
13	TPDB[b]	3.0	heptane	200	100	0.5	85.6	14.4
14	TPDB[b]	12	toluene	200	100	4	98.9	0.4
15	TPDB[b]	6.0	THF	200	100	4	57.7	28.1
16	TEDB[c]	12.0	heptane	200	100	4	98.1	0
17	TEB[c]	14.0	heptane	200	100	4	96.9	0
18	TEAB[e]	13.0	heptane	200	100	4	1.2	90.6
19	TEAB[e]	13.0	heptane	240	100	4	77.4	8.1
20	SPB[f]	(400)	heptane	200	100	4	70.0[g]	0
21	SPBA[h]	(400)	heptane	200	100	4	23.7	73.2
22	LPB[i]	(400)	heptane	200	100	4	70.9[g]	0

[a] In all experiments 2.0 g (15.6 mmol) of naphthalene was employed. – [b] TPDB = tetrapropyldiborane(6). – [c] TEDB = tetraethyldiborane(6). – [d] TEB = triethylborane. – [e] TEAB = triethylamine – borane. – [f] SPB = solid polyborane. – [g] In this reaction about 15% of *n*-butylbenzene was also formed. – [h] SPBA = solid polyborane that has been exposed to air for 24 h. – [i] LPB = liquid polyborane.

try 18) are only active at higher temperatures producing also a large number of sideproducts including *n*-butylbenzene and *cis*- and *trans*-decalines.

When the reactions were catalyzed by large amounts of borane, as shown in entry 1 of Table 2, the product solution was very turbid. Filtration of this suspension gave a small amount of a light grey solid[7], which showed a very strong >B−H band at $\tilde{\nu}$ = 2550 cm^{-1} in its IR spectrum. This solid, which was extremely insoluble in all of the nonprotic solvents tested, had an active hydride content of ca. 2%. This is more then twice the amount employed in the starting borane (ca. 0.86%). A similar solid could be obtained when a solution of TPDB in heptane was heated to 200°C under hydrogen pressure for 4 h. Elemental analysis of the solid gave an approximate elemental composition of $(C_2H_{12}B_9)_x$[8] probably with a poly- or carborane-type structure (SPB). From the filtrate of this reaction product, a liquid fraction could also be obtained on evaporation of the solvent under vacuum. This liquid fraction (LPB) had a similar IR spectrum as found for the solid polyborane but was of a lower hydride content (ca. 1.5%). Longer reaction times produced solid and liquid polyboranes of other compositions. Thus, the ^{11}B-NMR spectrum of the liquid fractions, depending on its prior history, showed a complex set of signals ($\delta \approx +20$ to -35) with variable integral intensities. Thus, a sample obtained after a reaction time of 4 h showed higher intensities of the signals at lower fields, while the product obtained after a reaction time of 14 h showed a higher concentration of the borane components with signals at higher fields. These high-field signals can be assigned to boron atoms in a chemical environment similar to those found in the highly condensed carboranes[9]. Notably, the two very narrow and intense peaks at $\delta = -11.9$ and -14.5 (integral ratio 1:1) are reminiscent of the carborane $(CH_3)_4C_4B_4H_4$[10].

The formation of these solid and liquid polymeric boranes (SPB and LPB, respectively) during the hydrogenation reactions implied that they may be the active catalytic species involved. Indeed, when they were used as catalysts, an efficient conversion of naphthalene was observed (Table 2, entries 20−22). However, only ca. 70% of the product was tetralin. In the remaining complex mixture *n*-butylbenzene in ca. 15% concentration could be identified. The formation of relatively large amounts of sideproducts (when the hydrogenation is catalyzed by these polyboranes) suggests a different mode of action for these than for the tetraalkyldiboranes, or for species formed directly thereof. The polyborane catalyzed C−C bond rupture leading to the formation of *n*-butylbenzene (usually absent in the diborane catalyzed hydrogenation of naphthalene) is probably also the source of the dealkylated products of the hydrogenation of alkylnaphthalenes.

The transformation of the initially added borane TPDB into a catalytically active species is also clearly evident from the induction periods of up to 1 h as revealed in the results of a preliminary kinetic analysis of this reaction at 200°C. This is shown in Figure 1.

Figure 1 also summarizes the results of several experiments with different initial TPDB concentrations and shows that after the induction period an approximately pseudo-first-order rate is established in all cases for this reaction. From a plot of these pseudo-first-order rate constants vs. the initial TPDB concentrations it can be seen that, while the rates vary linearly with the added borane, the rate increases are significantly less than proportional to the added >BH-borane units.

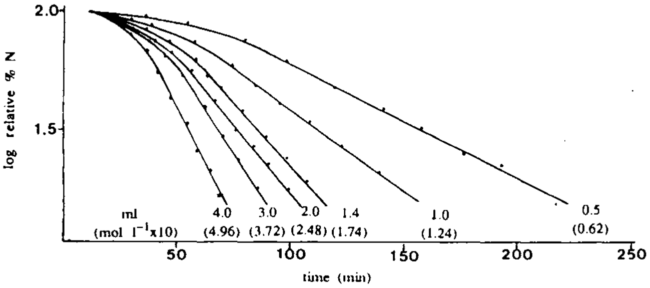


Fig. 1. Plot of logarithm of relative % of N vs. time at 200 C for various TPDB concentrations

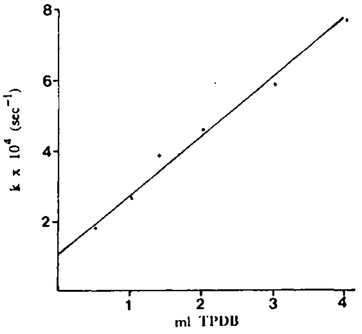


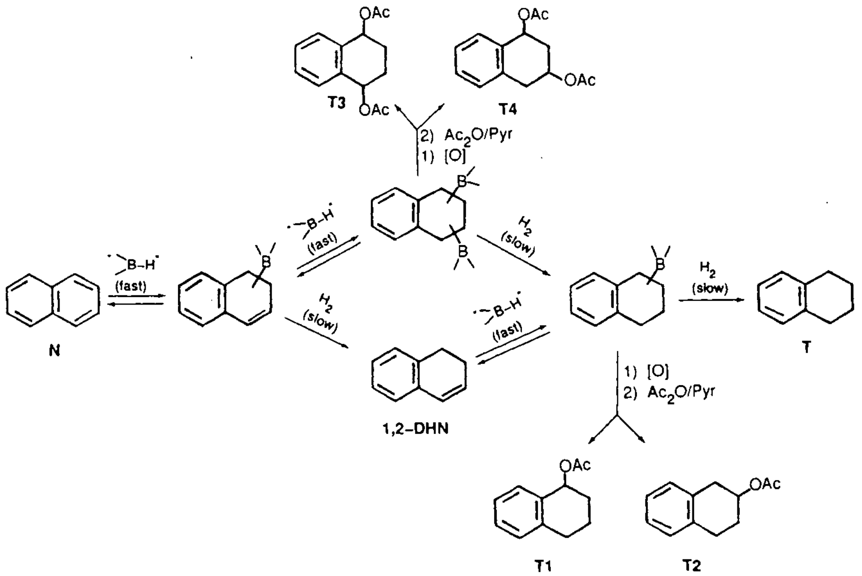
Fig. 2. Plot of first-order rate constants vs. ml of TPDB

In fact, the slope of the straight line in Figure 2 indicates that only about one half of the boron atoms added end up on catalytically active sites. These results, however informative, are at present insufficient for forwarding a structural concept for this "polyborane" catalyst.

These investigations, extended to a slightly lower (190°C) and a slightly higher (210°C) temperature, showed, as expected, that at least in this temperature range, the rates approximately double for every 10°C rise of the reaction temperature. From these results an approximate[11] value of 35 kcal/mol could also be calculated for the activation energy.

Finally, the kinetic experiments also revealed that when the TPDB:N ratio was high an intermediate slowly accumulated (up to 6%), the concentration of which decreased again towards the final stages of the reaction. This intermediate was identified (GC-MS) as 1,2-dihydronaphthalene (1,2-DHN). In one experiment (TPDB:N ratio ca. 1:4), the reaction was interrupted after 1 h, the volatile components removed at 50°C/0.0001 Torr, and the viscous, slightly yellow residue oxidized with alkaline dihydrogen peroxide and *O*-acetylated with Ac_2O/Py[1]. The products, analyzed by GC-MS, consisted of 1- and 2-acetoxytetralins [T1 (30.7%) and T2 (53%), respectively] as well as 1,4- and 1,3-diacetoxytetralines [T3 (3.5%) and T4 (10.1%), respectively].

Scheme 1. Probable reaction pathway of N and oxidation/*O*-acetylation products of the intermediate borylated tetralins



These results suggest that at high borane concentrations the rates of the hydrogenolysis reaction steps are significantly lower than of the steps leading to borane addition to the aromatic and the olefinic C=C bonds. This would lead to the accumulation of the borylated tetralins (detected as the corresponding *O*-acetyltetralins). The steps leading to the formation of tetralin can thus be summarized as in Scheme 1; it also shows the products T1–T4 of the oxidation/*O*-acetylation workup of the intermediate borylated tetralins.

It is very likely that the borylated intermediates, as shown in Scheme 1, are in an equilibrium with their aromatic/olefinic precursors N and 1,2-DHN, respectively. The small amounts of 1,2-DHN observed during the kinetic experiments (cf. above) can, therefore, be regarded as a dehydroboration product (formed by the high temperatures in the injection port of the GC) of the monohydroborated tetraline species present in the reaction mixture.

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 7 A. – MS: Varian MAT CH 7. – ^{1}H, ^{11}B, and ^{13}C NMR: Bruker AC 200. – For sources of the borane reagents used in this work cf. ref.[1].

General Procedure for the Hydrogenation of Naphthalene (N) *and its Derivatives:* Solutions of the substrates (2–10 g) dissolved in 40–100 ml of the appropriate solvent (heptane, toluene, or THF) were added under argon to a thoroughly dried 200-ml stainless-steel rocking autoclave followed by 0.01–2.00 ml of the borane catalyst (TPDB, TEDB, Et_3B, Et_3N-BH_3). The autoclave was charged with 10–100 bar of hydrogen and heated to the desired temperature (150–240°C) for 0.5–4.0 h. After cooling to room temp., the pressure decrease generally corresponded to an uptake of more than two equivalents of hydrogen (dissolution of the propane formed from the catalyst). After venting the gas, the liquid suspension was filtered from the solid polyboranes formed and the filtrate subjected to GC and GC-MS analysis (cf. Tables 1 and 2). In some cases, the main product could be isolated and purified by vacuum distillation (e.g., tetralin) or by recrystallization (e.g., 2-phenyltetralin).

Structural assignements of the products were made in the following ways: (a) if one of the main components could be purified by distillation, crystallization, or preparative GC, by direct comparison with known compounds or analysis of their ^{1}H- and ^{13}C-NMR and mass spectra; (b) in other cases and for most of the minor components, by establishing common GC retention times and superimposition of fragmentation patterns (MS spectral library); (c) in a few cases, on the basis of MS fragmention patterns only.

The selected procedures below for the hydrogenation of naphthalene, 2-phenylnaphthalene, and 2,3-dimethylnaphthalene demonstrate the viability of this reaction for preparative purposes.

Tetralin: A solution of 10.0 g (78.1 mmol) of N and 1.5 g of TPDB (12.6 mmol >BH-borane) in 100 ml of heptane was placed in the autoclave, pressurized to 100 bar with H_2 gas, and heated at 200°C for 4 h. On cooling, a pressure drop of 65 bar (calcd. 38 bar) was observed. The colourless product solution (for results of GC analysis cf. Table 1) was fractionally distilled to give T (9.1 g, 88%), b.p. 95°C/11 Torr, n_D^{23} = 1.5405. – GC: 98.9% T. – ^{13}C NMR (CD_2Cl_2): δ = 137.7 (s), 129.6 (d), 125.9 (d), 30.0 (t), 24.0 (t). – ^{1}H NMR (CD_2Cl_2): δ = 7.21 (s, 4H), 2.92 (m, 4H), 1.95 (m, 4H). – MS (70 eV): *m/z* (%) = 132 (48) [M^+], 104 (100).

6-Phenyltetralin: A solution of 2.0 g (9.8 mmol) of 2-phenylnaphthalene and 0.75 g of TPDB (6.3 mmol >BH-borane) in 100 ml of heptane was placed in the autoclave, pressurized to 100 bar with H_2 gas and heated at 200°C for 4 h. On cooling, a pressure decrease of 20 bar (calcd. ca. 5 bar) was observed. After removal of solvent (for GC analysis of crude product cf. Table 1) the residue was distilled to give 6-phenyltetralin (1.8 g, 88%), b.p. 85–90°C/0.01 Torr (ref.[12] 97°C/0.5 Torr). – GC: 98.1%. – ^{13}C NMR (CD_2Cl_2): δ = 141.6 (s), 138.8 (s), 138.0 (s), 137.2 (s), 129.9 (d), 129.1 (d), 128.0 (d), 127.3 (d), 127.2 (d), 124.5 (d), 30.0 (t), 29.6 (t), 23.8 (t, 2C). – ^{1}H NMR (CD_2Cl_2): δ = 7.6 (dd, 2H), ca. 7.4 (m, 5H), 7.14 (d, 1H), 2.80 (m, 4H), 1.83 (m, 4H). – MS (70 eV): *m/z* (%) = 208 (100) [M^+], 180 (68), 165 (16).

6,7-Dimethyltetralin: A solution of 5.0 g (32.0 mmol) of 2,3-dimethylnaphthalene and 1.5 g of TPDB (12.6 mmol >BH-borane) in 100 ml of heptane was placed in the autoclave, pressurized to 100 bar with H_2 gas, and heated at 200°C for 4 h. On cooling, a pressure decrease of 30 bar (calcd. 16 bar) was observed. After removal of the solvent (for GC results of crude product cf. Table 1) the residue was distilled to give 6,7-dimethyltetralin (4.1 g, 80%), b.p. 50 to 60°C/0.001 Torr (ref.[13] 127°C/13 Torr). – GC: 94.5%. – ^{13}C NMR (CD_2Cl_2): δ = 134.8 (s), 133.9 (s), 130.6 (d), 29.5 (t), 24.2 (t), 19.0 (t). – ^{1}H NMR (CD_2Cl_2): 6.95 (s, 2H), 2.85 (m, 4H), 2.35 (s, 6H), 1.90 (m, 4H). – MS (70 eV): *m/z* (%) = 160 (60) [M^+], 145 (100), 132 (36).

Preparation of Solid Polyboranes (SPB) *and Liquid Polyboranes* (LPB): A solution of 7.2 g of TPDB (8.67‰ Hydride-H) (62.4 mmol $\rangle$BH-borane) in 20 ml of heptane was heated at 200 bar of H_2 to 200°C for 4 h. On cooling, a pressure decrease of 27 bar was observed. The product suspension was filtered; light yellow solid (SPB), 0.9 g, m.p. >300°C. – IR (KBr): $\tilde{\nu}$ = 2550 cm^{-1}. Active hydride content (reaction with 2-ethylhexanol at 150°C): 2%.

$(C_2H_{12}B_9)_x$	Calcd.	C 18.0	H 9.07	B 72.93
	Found	C 16.51	H 8.49	B 72.40

The filtrate from above gave on evaporation of the volatiles i. vac. 0.12 g of a light yellow oil (LPB). – IR (film): $\tilde{\nu}$ = 2550 cm^{-1}. – Active hydride content: 1.5%. – ^{11}B NMR: δ_B = +20 to −35, with peaks at −5 (br.), −11.9 (s), and −14.5 (s).

Kinetic Experiments: A solution of 10 g (78 mmol) of N in 50 ml of toluene together with 0.5–4.0 ml (0.37–2.90 g) of TPDB (8.67‰ Hydride-H) (3.1–24.3 mmol $\rangle$BH-borane) was introduced under argon into a thoroughly dried, magnetically stirred 200-ml autoclave, pressurized with H_2 to 90 bar, placed in an electrically heated mantle, and rapidly (10–15 min) heated to 190–210°C. T_0 was arbitrarily chosen 2–3 min after constancy of the internal temp. Samples (ca. 0.5 ml) were removed at intervals through a sampling valve and analyzed by GC.

Detection of Reaction Intermediates as Acetoxy Derivatives T1, T2, T3, *and* T4: A solution of 10 g (78 mmol) of N and 3.9 g of TPDB (8.67‰ Hydride-H) (33.8 mmol $\rangle$BH-borane) in 50 ml of toluene was treated under hydrogen pressure at 200°C as described above. After 1 h, the reaction was terminated (^{11}B NMR: br. signal with peaks at $\delta \approx$ 40, 29.5, 22.5, and 9.3) and the products, after removal of the volatile components at 50°C/0.0001 Torr (3.2 g), were oxidized with alkaline H_2O_2 and *O*-acetylated with Ac_2O/Py[1] yielding 1.3 g of *O*-acetylated tetralins analyzed by GC: T1 (30.7%), T2 (53.0%), T3 (3.5%), and T4 (10.1%).

CAS Registry Numbers

naphthalene: 91-20-0 / 1-methylnaphthalene: 90-12-0 / 1-ethyltetralin: 13556-58-6 / 2-methylnaphthalene: 91-57-6 / 2-methyltetralin: 3877-19-8 / 2-ethylnaphthalene: 939-27-5 / 1,3-dimethylnaphthalene: 575-41-7 / 1,4-dimethylnaphthalene: 571-58-4 / 2,3-dimethylnaphthalene: 581-40-8 / 2,6-dimethylnaphthalene: 581-42-0 / 5-ethyltetralin: 42775-75-7 / 1-phenylnaphthalene: 605-02-7 / 2-phenylnaphthalene: 612-94-2 / 2,2′-binaphthyl: 612-78-2 / 1-methoxynaphthalene: 2216-69-5 / 2-methoxynaphthalene: 93-04-9 / 1-chloronaphthalene: 90-13-1 / 2-chloronaphthalene: 91-58-7 / tetralin: 119-64-2 / 5-methoxytetralin: 2809-64-5 / 1-methyltetralin: 1559-81-5 / 6-methyltetralin: 1680-51-9 / 6-ethyltetralin: 22531-20-0 / 2-ethyltetralin: 32367-54-7 / 5,8-dimethyltetralin: 14108-88-4 / 6,7-dimethyltetralin: 1076-61-5 / 2,3-dimethyltetralin: 21564-92-1 / 2,6-dimethyltetralin: 7524-63-2 / dimethyltetralin: 51855-29-9 / 5-phenyltetralin: 67064-63-5 / 1-phenyltetralin: 3018-20-0 / 6-phenyltetralin: 41284-88-2 / 2-phenyltetralin: 29422-13-7 / 5-methoxytetralin: 1008-19-1 / 6-methoxytetralin: 1730-48-9 / 5-hydroxytetralin: 529-35-1 / triethylborane: 150-46-9 / triethylamine–borane: 1722-26-5 / tetrapropyldiborane(6): 22748-01-6 / tetraethyldiborane(6): 12081-54-8 / 1-ethylnaphthalene: 1127-76-0 / 1,8-ethanonaphthalene: 83-32-9 / 1,8-ethenonaphthalene: 208-96-8 / 1-(diethylboryloxy)naphthalene: 118761-47-0 / 1,8-ethanotetralin: 480-72-8 / 4-propylindene: 92013-16-6 / 6,6′-bitetralin: 118761-48-1 / 5-chlorotetralin: 3468-80-2 / 1-acetyloxytetralin: 21503-12-8 / 2-acetyloxytetralin: 71601-10-0 / 1,4-diacetyloxytetralin: 79909-37-8 / 1,3-diacetyloxytetralin: 118761-49-2 / 6-chlorotetralin: 35337-44-1

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[1] [1a] R. Köster, W. Schüßler, M. Yalpani, *Chem. Ber.* **122** (1989) 677, preceding. – [1b] T. Lunow, Max-Planck-Institut für Kohlenforschung, Mühlheim an der Ruhr, 1987/1988; results taken in part from the *Diplomarbeit*, Fachhochschule Niederrhein, Abteilung Chemie, Krefeld 1987.

[2] [2a] R. Köster, *Angew. Chem.* **68** (1956) 383. – [2b] R. Köster, *Umwandlungen von Organobor-Verbindungen* in *Methoden der Organischen Chemie* (Houben-Weyl-Müller), 4th ed., vol. XIII/3c (R. Köster, Ed.), p. 230, Thieme, Stuttgart 1984, and references cited therein.

[3] I. Amer, H. Amer, R. Ascher, J. Blum, Y. Sasson, P. C. Vollhardt, *J. Mol. Cat.* **39** (1987) 185, and references cited therein.

[4] When 5-methyltetralin was subjected under the standard conditions to the hydrogenation reaction, a 24% isomerization to 6-methyltetralin was observed.

[5] During the haloboration of alkylbenzenes and polystyrene with dihaloboranes ($HBHal_2$) at 150°C, extensive rupture of the C–C bond of the alkyl substituent has been observed in some cases, cf. P. Paetzold, J. Hoffmann, *Chem. Ber.* **113** (1980) 3724.

[6] The C–C bond rupture, usually a sidereaction during haloboration of alkylarenes[5], assumes a major proportion when trialkylboranes or tetraalkyldiboranes(6) under a hydrogen pressure of 200 bar act in stoichiometric reactions at 180°C or in substoichiometric reactions at 300°C on a number of diarylmethanes and -ethanes. In these reactions, which also result in varying amounts of partial or complete hydrogenation of some of the aromatic rings, reaction times of 16–54 h have been employed, cf. E. Osthaus, M. W. Haenel, in *Proceed. Intern. Conf. Coal Sci.* (J. A. Moulijn, K. A. Nater, H. A. G. Chermin, Eds.), p. 765, Elsevier, Amsterdam 1987; cf. also E. Osthaus, *Dissertation*, Ruhr Universität, Bochum 1986.

[7] [7a] Similar (white-yellow) amorphous solids with varying elemental compositions have also been isolated and reported earlier[6,7b] and shown to posses some catalytic activity for C–C bond cleavage reactions[6]. – [7b] R. Köster, *Angew. Chem.* **70** (1958) 743.

[8] In ref.[6] an elemental composition of $(CH_2B)_x$ is given for the solid polyborane.

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[10] Cf. ref.[9], p. 606.

[11] The accuracy of values of the rate constants, and the activation energy are limited by the inaccuracies (±2°C) of the temperature controls of our autoclave heating mantle.

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[285/88]