Diphenylamine·Borane, A New Stable Amine·Borane with Remarkable Hydroborating and Reducing Properties

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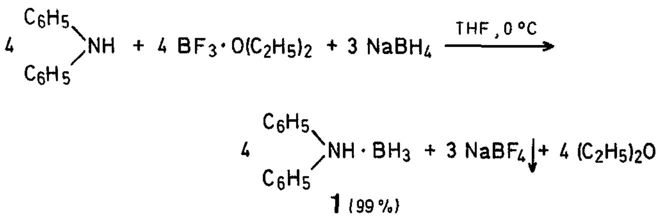
Diphenylamine·borane (**1**), a new amine·borane[1], can be easily prepared from sodium borohydride, boron trifluoride etherate, and diphenylamine in tetrahydrofuran at 0 °C; filtration and solvent evaporation affords **1** as a white crystalline compound (m.p. 86 °C).



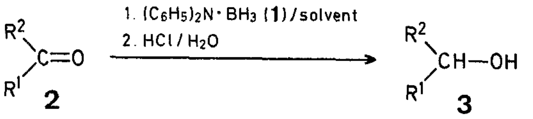
Reagent **1** is a remarkably stable source of borane (BH_3). It has interesting advantages over other borane adducts such as $BH_3·THF$ (a commercially available borane[2]) because it can be prepared in a pure form, it is solid and stable to air, and it can be stored in the cold over long periods of time without showing decomposition. Reagent **1** is more reactive than aliphatic amine-boranes and almost as reactive as $BH_3·THF$. It can be used in tetrahydrofuran, dichloromethane, and hydrocarbon solvents.

The convenient applicability of diphenylamine·borane (**1**) is due to its physical properties since reactive borane adducts are generally difficult to handle and store. For example, $BH_3·THF$ has to be stored as a dilute solution (2 molar) in tetrahydrofuran (3% weight of BH_3), i.e., in a solvent which is cleaved by BH_3 at room temperature.

Diphenylamine·borane (**1**) is an exceptionally reactive amine·borane and it has more convenient characteristics than aliphatic amine·boranes which are usually less reactive in hydroboration reactions and react only at elevated temperatures[3,4], with the assistance of boron trifluoride etherate[5], or in acidic medium[6]. The high reactivity may be rationalized by the electron-withdrawing effect of the phenyl groups which weakens the coordination of the N-atom and thus makes the borane more acidic and reactive.

The structure of compound **1** was confirmed by mass-, I.R.-, and ^{11}B-N.M.R. spectrometry. The molecular ion found ($m/e = 183$) agreed with the calculated value. The I.R. spectrum shows the presence of B—H bonds, an N—H bond, and a B←N coordination bond. The ^{11}B-N.M.R. spectrum of **1** in tetrahydrofuran shows two quartets of approximately equal intensity assigned to **1** and $BH_3·THF$ complex, respectively. The latter assignment shows that reagent **1** may be considered as a crystalline source of $BH_3·THF$. The ^{11}B-N.M.R. spectrum of **1** in benzene reveals the formation of diborane so that **1** partially dissolved in benzene can be used as a source of diborane, B_2H_6.

The reaction of **1** with ketones without solvent sets in almost instantly and is highly exothermic. Since amine·borane **1** is sufficiently reactive in solvents such as hexane and dichloromethane it is preferentially used in these solvents in which its reactions can be better controlled. In certain cases, tetrahydrofuran may be a better solvent due to better solubilizing properties. The optimum reaction conditions for the reduction of aldehydes or ketones (**2**) with reagent **1** were found to be a substrate/borane ratio of 1.5 and a reaction time of 1 h at 0 °C and 1 h at room temperature.



The reductions of cyclohexanone and acetophenone with reagent **1** in hexane were monitored by ^{11}B-N.M.R. spectrometry. After 2 hours, the signals of **1** had disappeared. In the case of cyclohexanone, two new signals were observed: one at $\delta = +17$ ppm which was assigned to the boric ester **4c** and one at $\delta = +22.6$ ppm (~10%) which was assigned to the boronic ester **5c**. In the case of acetophenone, a new sig-

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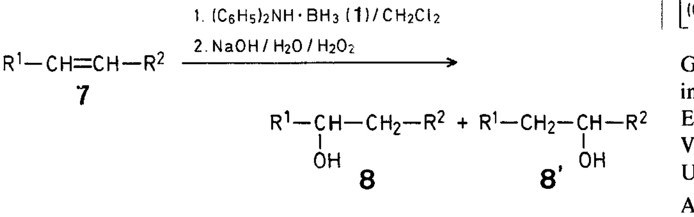
nal was found at $\delta = +30.4$ ppm which may be attributed to the boronic ester **5f** or to the aminoboronic ester **6f.**

Thus, it may be concluded that the reaction proceeds via the intermediacy of boric or boronic esters which are cleaved to the alcohols **3** during the acidic work-up.

The stereoselectivity of the reduction of ketones with reagent **1** was studied using 2-methylcyclohexanone **(2d)** and 4-*t*-butylcyclohexanone **(2e)** as substrates (Table 1). The results are very similar to those obtained with $BH_3 \cdot THF$ as reducing agent.

Reagent **1** was found to be highly reactive in the hydroboration of alkenes **(7)**, the yields of alcohols **(8)** obtained after oxidative work-up being similar to those obtained with $BH_3 \cdot THF$ as hydroborating agent (Table 2).



$$\underset{\mathbf{7}}{R^1{-}CH{=}CH{-}R^2} \xrightarrow[2.\ NaOH/H_2O/H_2O_2]{1.\ (C_6H_5)_2NH \cdot BH_3\ (1)/CH_2Cl_2} \underset{\mathbf{8}}{R^1{-}\underset{OH}{CH}{-}CH_2{-}R^2} + \underset{\mathbf{8'}}{R^1{-}CH_2{-}\underset{OH}{CH}{-}R^2}$$

The regioselectivity of the hydroboration of alkenes **7** with reagent **1** is also comparable to that obtained with $BH_3 \cdot THF$ as hydroborating agent (Table 3).

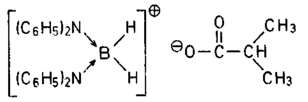
The hydroboration of styrene with reagent **1** in hexane was followed by ^{11}B-N.M.R. spectrometry. Three signals were observed 1 h after the reaction had started: one signal at $\delta = +94$ ppm which was attributed to the trialkylborane, a second one at $\delta = +54$ ppm which may be attributed to the aminodialkylborane, and a third signal at $\delta = +34.6$ ppm which was assigned to triaminoborane. Part of the hydrides is lost by the formation of aminoboranes.

The reactivity of reagent **1** towards carboxylic acids, anhydrides, and esters was also investigated (Table 4). Acids **(9)**, butanoic anhydride, and ethyl butanoate (as an example of a purely aliphatic ester) were reduced to the alcohols ***(10)*** whereas succinic anhydride, phthalic anhydride, and alkyl benzoates did not react.

$$\underset{\mathbf{9}}{R{-}COOH} \xrightarrow[2.\ H_2O]{1.\ (C_6H_5)_2NH \cdot BH_3\ (1)/THF} \underset{\mathbf{10}}{R{-}CH_2OH}$$

R = alkyl, aryl

The reduction of 2-methylpropanoic (isobutyric) acid with reagent **1** in dichloromethane was followed by ^{11}B-N.M.R. spectrometry. The formation of diisobutyl boronate [$\delta = +19$ ppm (60%)] and a signal [$\delta = +1.5$ ppm (33%)] attributed to the boronium ion **11** were observed. The existence of this boronium ion may well account for the low yields found in the reduction of carboxylic acid derivatives.



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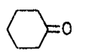
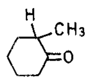
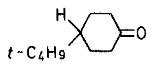
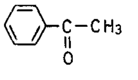
G.L.C. analyses were carried out on a Varian Aerograph Model 1400 instrument. Mass spectra were measured at 70 eV on a Hitachi-Perkin Elmer RMV-7H instrument. ^{11}B-N.M.R. spectra were measured on a Varian XL-100A-12FT-16K spectrometer and I.R. spectra on a Pye Unicam Sp1000 instrument.

All glassware, syringes, and needles were dried in an oven at 130 °C for 4 h prior to use. The glassware was assembled hot and allowed to cool under a dry nitrogen atmosphere. Dichloromethane was distilled from calcium hydride. Benzene and hexane were dried with and distilled from sodium. Tetrahydrofuran was dried by distillation from lithium aluminium hydride.

Diphenylamine · borane (1):

In a 250 ml three-necked flask equipped with a stirrer, two dropping funnels, and a nitrogen inlet connected to a mercury bubbler, sodium

Table 1. Reduction of Aldehydes and Ketones **(2)** to Alcohols **(3)** with Diphenylamine · Borane **(1)**

Substrate **2**[a]	Solvent	Product **3**	Yield [%][b]		b.p./torr [°C]	
			using **1**	using $BH_3 \cdot THF$	found	reported
a n-C_6H_{13}–CHO	THF	heptanol	80		66–72°/20	176°/760[8]
	hexane		82			
b $n\text{-}C_6H_{13}{-}\underset{O}{\overset{\Vert}{C}}{-}CH_3$	THF	2-octanol	91	90[c]	86–88°/20	180°/760[8]
	hexane		81			
c 	THF	cyclohexanol	91	92[c]	56–58°/20	161.1°/760[8]
	CH_2Cl_2		88			
	hexane		90			
d 	THF	2-methyl-cyclohexanol	85[c]	87 (*cis*/*trans* = 32/68)[c]	60–63°/12	60°/12[8]
	hexane		83 (*cis*/*trans* = 31/69)			
e 	hexane	4-*t*-butyl-cyclohexanol	85 (*cis*/*trans* = 14/86)	90 (*cis*/*trans* = 10/90)[c]	110–115°/15	110°/15[9]
f 	THF	1-phenylethanol[d]	91		86–88°/10	87.2°/10[8]
	CH_2Cl_2		96			
	hexane		88			

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[a] Ratio substrate/borane = 1.5; reaction time: 1 h at 0 °C, 1 h at 20 °C.

[b] Yield of isolated product of >97% purity (G.L.C. analysis; carbowax 20 M, 20% on chromosorb W, 80–100 mesh).

[c] Yields obtained in our comparative experiments.

[d] For compounds which are sensitive to acidic treatment, the amine was removed by column chromatography.

[e] Mixture of *cis/trans* isomers.

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borohydride (1.71 g, 45 mmol) and tetrahydrofuran (60 ml) are placed under a nitrogen atmosphere. The flask is cooled in an ice bath and boron trifluoride etherate (6.3 ml, 50 mmol) is added dropwise, over 75 min, from one of the dropping funnels. Stirring at 0 °C is continued for 30 min. Then, a solution of diphenylamine (7.6 g, 45 mmol) in tetrahydrofuran (20 ml) is added dropwise, over 5 min, from the other dropping funnel. Sodium tetrafluoroborate formed in the reaction is filtered off and the solvent is evaporated in vacuo to give **1** as a white crystalline compound; yield: 8.2 g (99%); m.p. 85 °C.

M.S.: $m/e = 183$ (M^+).

I.R. (KBr): $\nu = 3173$ (N—H); 2377, 2326, 2296 (B—H); 1137 cm^{-1} (B←N coordination bond).

^{11}B-N.M.R. (THF/BF_3·etherate = 0): $\delta = -11.5$ (q, $J_{B,H} = 81$ Hz); -0.3 ppm (q, $J = 102$ Hz).

The titration of reagent **1** with water (evolution of 3 equiv of hydrogen = 100%) is carried out in a 500 ml round-bottom flask equipped with a magnetic stirrer and connected to a gasimeter. A solution of reagent **1** (0.351 g, 1.92 mmol) in tetrahydrofuran (2 ml) is placed in the flask, water (1 ml) is added, and hydrogen evolution measured: 5.53 mmol of H_2, corresponding to a purity of **1** of 96%.

Hydroboration of Styrene with Diphenylamine·Borane (1) in Dichloromethane; Typical Hydroboration Procedure:

Reagent **1** (95.5% pure; 13.386 g, 0.070 mol) and dichloromethane (100 ml) are placed in a 200 ml round-bottom flask fitted with stirrer and connected to a mercury bubbler. The reaction is performed under a nitrogen atmosphere. The solution is cooled to 0 °C and styrene (11 ml, 0.096 mol) is added slowly. The mixture is stirred for 1 h at 0 °C and for 1 h at 20 °C. Then, aqueous 3 molar sodium hydroxide (24 ml) is added followed by a 30% hydrogen peroxide solution (24 ml) (exothermic reaction). The organic phase is separated and the aqueous phase extracted with dichloromethane (4 × 100 ml). The organic phases are combined and the diphenylamine is removed by column chromatography on silica gel (J. T. Baker, 60-200 mesh) using hexane as eluent. Evaporation of the solvent gives a mixture of *1-phenylethanol* (17%) and *2-phenylethanol* (83%) (as determined by G.L.C. analysis; carbowax 20 M, 20% on chromosorb W, 80-100 mesh); yield: 10 g (86%); b.p. 95 °C/10 torr.

Table 2. Alcohols (**8**+**8'**) by Hydroboration of Alkenes (**7**) with Diphenylamine·Borane (**1**)

Substrate 7[a]		Solvent	Yield [%] of 8+8'[b]		b.p./torr [°C]	
R^1	R^2		using 1	using BH_3·THF	found	reported[8]
n-C_6H_{13}	H	THF	81[e]	85[c]	100°/20	98°/19[f]
		CH_2Cl_2	86[e]			
		hexane	70[e]			
C_6H_5	H	THF	84[d,e]	86[c]	94-97°/10	97.4°/10[g]
		CH_2Cl_2	86[d,e]			
		hexane	82[d,e]			
—$(CH_2)_4$—		THF	90		56-58°/20	161.1°/760
		hexane	78			
C_6H_5	CH_3	THF	85[c]		95-98°/10	98°/10[h]
		hexane	81[c]			

[a] Ratio substrate/borane = 1.5; reaction time: 1 h at 0 °C, 1 h at 20 °C.

[b] Yield of isolated product of >97% purity (G.L.C. analysis; Carbowax 20M, 20% on chromosorb W, 80-100 mesh).

[c] Yields obtained in our comparative experiments.

[d] For compounds which are sensitive to acid treatment, the amine was removed by column chromatography.

[e] Mixture of isomers **8**+**8'**.

[f] 1-Octanol.

[g] 2-Phenylethanol.

[h] 1-Phenyl-1-propanol.

Table 3. Ratio of Isomeric Alcohols **8**+**8'** obtained from the Hydroboration of Alkenes (**7**) with Diphenylamine·Borane (**1**)

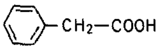
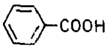
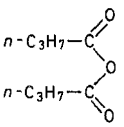
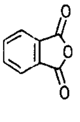
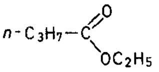
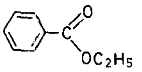
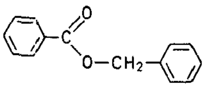
R^1	R^2	Isomers 8 and 8'		Content [%] in the Product[b,c]			
				using 1			using BH_3·THF[7]
				Hexane	CH_2Cl_2	THF	THF
n-C_6H_{13}	H	8	1-octanol	96	98	95	[a]
		8'	2-octanol	4	2	5	[a]
C_6H_5	H	8	1-phenylethanol	19	17	17.5	19
		8'	2-phenylethanol	81	83	82.5	81
C_6H_5	CH_3	8	1-phenyl-2-propanol	9		12	15
		8'	1-phenyl-1-propanol	91		88	85

[a] Hydroboration of 1-hexene with BH_3·THF proceeds with 94% of boron attack at C-1[7].

[b] For the total yields see table 2.

[c] The isomer ratio was determined by G.L.C. analysis (Carbowax 20 M, 20% on chromosorb W, 80-100 mesh).

Table 4. Reduction of Carboxylic Acids (**9**) and Derivatives to Alcohols (**10**) using Diphenylamine·Borane (**1**)

Carboxylic acid (9) or Derivative	Ratio Substrate/ Borane	Yield [%][a] of Primary Alcohol (10)	b.p./torr [°C]	
			found	reported[8]
$H_3C-CH_2-CH_2-COOH$	1/2	61	18-20°/20	117°/760
 $(H_3C)_2CH-COOH$	1/2	72	12-14°/20	108°/760
	1/2	75	97°/10	97°/10
	1/2	67	93°/10	93°/10
	1/4	56	18-20°/20	117°/760
	1/4	no reaction		
	1/4	no reaction		
 $n\text{-}C_3H_7-C(=O)-OC_2H_5$	1/2	77[b] (butanol)	18-20°/20	117°/760
	1/2	no reaction		
	1/2	no reaction		

[a] Yield of isolated product. Purity (G.L.C.): >95%. No unreacted starting material was recovered.

[b] 18% of starting material was recovered with the alcohol. The mixture was not separated.

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Reduction of 2-Octanone with Diphenylamine · Borane (1) in Tetrahydrofuran; Typical Reduction Procedure:

Reagent 1 (95.5% pure; 12.87 g, 0.067 mol) and tetrahydrofuran (75 ml) are placed in a 200 ml round-bottom flask fitted with stirrer and connected to a mercury bubbler. The reaction is performed under a nitrogen atmosphere. The solution is cooled to 0 °C and 2-octanone (15 ml, 0.096 mol) is added slowly. The mixture is then stirred for 1 h at 0 °C and for 1 h at 20 °C. Tetrahydrofuran is evaporated and the residual solid resuspended in hexane (60 ml). Concentrated hydrochloric acid (37.5%; 26 ml, 4 equiv) is added and diphenylamine hydrochloride is filtered off. The filtrate is washed with saturated sodium hydrogen carbonate solution (30 ml) and dried with sodium sulfate. The solvent is evaporated and the residual product purified by distillation; yield of *2-octanol:* 10.45 g (84%); b.p. 130 °C/580 torr (Ref.[8], b.p. 180 °C/760 torr). [2-Octanol thus obtained was pure according to G.L.C. analysis (carbowax 20 M, 20% on chromosorb W, 80–100 mesh)].

Analogous procedures are used for the reduction of other carbonyl compounds (Table 1) and of carboxylic acids and derivatives (Table 3).

Reduction of 2-Methylcyclohexanone (2d) with Borane · Tetrahydrofuran Complex (BH_3·THF) in Tetrahydrofuran; Typical Procedure:

A solution of BH_3·THF (0.9 ml, 1.88 molar, 0.0017 mol) is placed in a 25 ml round-bottom flask fitted with stirrer and connected to a mercury bubbler. The reaction is performed under a nitrogen atmosphere. The solution is cooled to 0 °C and 2-methylcyclohexanone (0.462 g, 0.004 mol) is added slowly. The mixture is then stirred for 1.5 h at 0 °C. After the reaction has subsided the mixture is hydrolyzed with water (5 ml) and the products are extracted with dichloromethane (4 × 50 ml). The extract is evaporated and the isomer ratio of *cis*- to *trans*-2-methylcyclohexanol determined by G.L.C. analysis (Diglycerol, 5% on chromosorb W, 80–100 mesh).

Received: November 9, 1981
(Revised form: May 11, 1982)

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