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Unusual rapid hydroboration of alkenes using diborane in chlorohydrocarbon solvents[†]

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Abstract

Diborane dissolves in chlorohydrocarbon solvents, such as dichloromethane, 1,2-dichloroethane and 1,1,2,2-tetrachloroethane to form ~0.5 M solutions of B_2H_6. In these solutions, diborane is in equilibrium with solvent–BH_3 adducts (8–15%) and these solutions hydroborate representative olefins almost instantaneously, even at −16°C. The alcohol products can be obtained by standard oxidation of these organoboranes. © 2000 Elsevier Science Ltd. All rights reserved.

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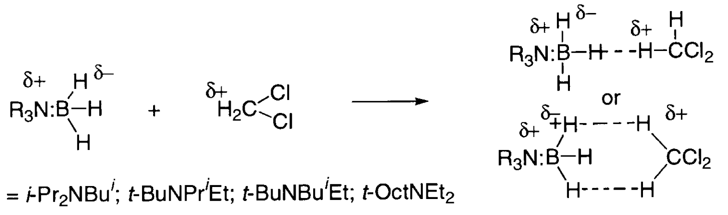
The hydroboration of olefins using diborane in the absence of solvent is sluggish requiring elevated temperatures and long reaction periods.[1] However, in coordinating solvents such as diglyme, ether and THF, the reaction is rapid and quantitative.[2] Whereas in non-coordinating solvents such as hydrocarbons, hydroborations do not occur or they occur very slowly. Recently, during our hydroboration studies of representative olefins using some new, highly reactive amine–borane adducts in various solvents, unusual rate retardation was observed in dichloromethane solvent with some amine–borane adducts.[3] It is quite intriguing as with other borane–Lewis base adducts such as $Me_2S{:}BH_3$, the rates of hydroborations in dichloromethane are comparable to those in *n*-pentane and diethyl ether.[4] In order to understand this unusual slow hydroboration reaction in dichloromethane with the amine–borane adducts, we carried out detailed studies and explained the rate retardation considering dipolar interactions between dichloromethane and amine–borane, as described in Eq. (1).



R_3N = i-Pr_2NBu^i; t-$BuNPr^iEt$; t-$BuNBu^iEt$; t-$OctNEt_2$

(1)

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During these studies, a closer look was taken at the reactivity of diborane[5] in dichloromethane, as no useful data has been reported on the hydroboration of olefins using diborane in dichloromethane. To our delight, it was noted that diborane dissolves in dichloromethane to form solutions ~0.5 M in B_2H_6. More interestingly, the ^{11}B NMR examination showed the presence of ~8–10% of the $CH_2Cl_2{:}BH_3$ adduct (+2.4ppm, q). Also, this solution of diborane in dichloromethane hydroborated 1-octene instantaneously, even at −16°C (ice–salt mixture), to the trialkylborane stage (Eq. (2)).

$$\begin{array}{ccc} \mathrm{CH_2Cl_2} + \mathrm{B_2H_6} & \rightleftharpoons & \mathrm{CH_2Cl_2{:}BH_3} \\ & \Big\downarrow \text{ 3 1-octene, -16 °C, 5min} & \\ & (\mathrm{octyl})_3\mathrm{B} & \end{array} \qquad (2)$$

The hydroboration of other representative olefins, such as 1-decene, 2-methyl-1-butene, β-pinene, cyclohexene, α-pinene and 2,3-dimethyl-2-butene were also carried out under similar conditions. The less hindered 2-methyl-1-butene, β-pinene and cyclohexene were instantaneously hydroborated to the trialkylborane stage, while hindered α-pinene and 2,3-dimethyl-2-butene were hydroborated to the monoalkyl stage instantaneously at −16°C, with further hydroboration being slow.[6] The results are presented in Table 1.

Table 1
Hydroboration of representative olefins using diborane in dichloromethane[a]

Olefin	Reaction time[b] (min)	Product(s)[c]	Yield (%)[d]
1-Octene[e]	5	1-Octanol/2-octanol (94/6)	89
1-Decene[e]	5	1-Decanol/2-decanol (94/6)	91
2-Methyl-1-butene[e]	5	2-Methyl-1-butanol/2-methyl-2-butanol (99/1)	86
β-Pinene[e]	5	Myrtanol	90
Cyclohexene[f]	5	Cyclohexanol	92
α-Pinene[g]	10	Isopinocampheol	88
2,3-Dimethyl-2-butene[g]	10	2,3-Dimethyl-2-butanol	83

[a] To a 0.5 M solution of diborane in dichloromethane at −16°C, an olefin was added and the contents were stirred at the same temperature.

[b] Completion of reaction was checked by ^{11}B NMR.

[c] Product alcohols were obtained after standard oxidation using $NaOH/H_2O_2$. The ratio of the alcohols was established by GC analysis.

[d] Isolated yield.

[e] To a 0.5 M (5.0 mL, 2.5 mmol) solution of diborane in dichloromethane 15 mmol of olefin were added.

[f] To a 0.5 M (5 mL, 2.5 mmol) solution of diborane in dichloromethane 10 mmol of olefin were added.

[g] To a 0.5 M (5.0 mL, 2.5 mmol) solution of diborane in dichloromethane 5 mmol of olefin were added.

In order to understand this unusual reactivity more thoroughly, similar experiments were also conducted in a few other chlorohydrocarbons such as chloroform, 1,2-dichloroethane, and 1,1,2,2-tetrachloroethane. When diborane gas was passed into chloroform, in addition to dissolved diborane (+17.6, 62%) and $CHCl_3{:}BH_3$ (+2.2, 8%), considerable amounts of an impurity (+27.2, d, 30%) was noted by ^{11}B NMR examination,[7] due to a reaction between chloroform and diborane (with hydrogen evolution). However, such impurities are absent when diborane is passed into 1,2-dichloroethane and 1,1,2,2-tetrachloroethane. The results were summarized in Table 2. These solutions also hydroborated simple, unhindered olefins instantaneously at −16°C. These hydroborations also proceed at lower temperatures, as low as −78°C. However, the reaction time is longer at such temperatures.

Table 2
Various signals observed in ^{11}B NMR examination of diborane in chlorohydrocarbons[a]

Chlorohydrocarbon	Diborane (%[b], δ ppm)	Chlorocarbon:BH_3 (%[b], δ ppm)	Other signals (%, δ ppm)
Dichloromethane	92 (+17.4, m)	8 (+2.4, q)	–
Chloroform	62 (+17.6, m)	8 (+2.2, q)	30 (+27.2, d)[c]
1,2-Dichloroethane	85 (+17.2, m)	15 (+2.4, q)	–
1,1,2,2-Tetrachloroethane	91 (+17.4, m)	9 (+2.2, q)	–

[a] Into chlorohydrocarbon (5.0 mL), diborane (20 mmol, excess) was passed slowly at −16°C.

[b] Yield (%) was established by ^{11}B NMR.

[c] Amount increased with time when kept at 0°C.

Large-scale hydroboration reactions can be conveniently carried out by taking the olefin to be hydroborated in a chlorohydrocarbon solvent, such as dichloromethane, 1,2-dichloroethane or 1,1,2,2-tetrachloroethane, and passing in diborane gas at an ice–salt mixture temperature, providing instantaneous hydroboration. The regioselectivities of these hydroborations are similar to those observed for THF:BH_3 and Me_2S:BH_3 (Table 1). The organoboranes obtained after hydroboration can be converted into the corresponding alcohols by standard oxidation procedures (NaOH/H_2O_2), with the addition of THF, methanol or ethanol as co-solvents, as these chlorohydrocarbons are completely immiscible with the aqueous phase.

In conclusion, for the first time we have observed that instantaneous hydroborations can be carried out in chlorohydrocarbons with diborane. More interestingly, these hydroborations readily take place at lower temperatures (instantaneous at −16°C, with slower reactions at −78°C). This for the first time provides a temperature handle to hydroboration in such solvents and we are currently looking at applications for selective hydroborations.

Acknowledgements

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6. **Typical procedure for the preparation of diborane solutions in chlorohydrocarbon solvents with hydroboration of representative olefins.** The procedures followed for 1,2-dichloroethane and 1,1,2,2-tetrachoroethane are identical to that used for dichloromethane described below. An oven-dried RB flask provided with a septum inlet, stirring bar and gas bubbler was assembled hot and cooled to room temperature under a stream of nitrogen. The gas bubbler was connected to a diborane generation set-up, as described elsewhere.[5b] The flask was kept at −16°C (ice–salt temperature) and dichloromethane (5.0 mL) was introduced into the flask. Diborane gas (20 mmol, excess), generated as described elsewhere,[5b] was slowly passed into the reaction mixture. After the complete generation of diborane gas, the bubbler was disconnected. The ^{11}B NMR examination of the reaction mixture showed the signals corresponding to dissolved diborane (92%, δ +18.1) and the borane–dichloromethane complex (8%, +1.1(q)). The concentration of active hydride was established to be 0.5 M in B_2H_6, using hydride analysis. Another oven-dried RB flask, provided with a septum inlet and stirring bar, was cooled to −16°C under dry nitrogen. The flask was charged with 2.5 mL of a 0.5 M solution of diborane in dichloromethane at −16°C (ice–salt temperature). α-Pinene (5 mmol) was added slowly at that temperature and the contents were stirred for 10 min. The ^{11}B NMR of the methanolized reaction mixture showed signals due to $\mathrm{IpcB(OMe)_2}$ (65%, major) and $\mathrm{Ipc_2BOMe}$ (35%, minor). The active hydride in the reaction mixture was destroyed using careful addition of methanol (3.0 mL). Once the hydride evolution subsided, the hydrogen was flushed out and aqueous NaOH (3.0 M, 2.0 mL) was added, followed by H_2O_2 (6 mmol). The organic layer was separated and the aqueous layer was extracted with ether and the combined organic extract was washed with brine and dried over anhydrous $MgSO_4$. Evaporation of solvent gave essentially pure isopinocampheol (0.68 g, 88% yield), the analytical data of which matched with the authentic sample.
7. The ^{11}B NMR examination of diborane in chloroform showed signals corresponding to dissolved diborane (+17.6, 62%) and $CHCl_3{:}BH_3$, in addition to a signal at +27.2 (d, 30%). The amount of this product increased with time. However, when this mixture reacted with 1-octene, in addition to trialkylborane, the signal at +27.2 was also observed in ^{11}B NMR examination, indicating its non-reactivity towards 1-octene under the present conditions. We tentatively assign this signal due to the formation of $(Cl_3C)_2BH$. Further studies on the structure and reactivity of this species are in progress.