Reaction of trialkylboranes with alkylamines: synthesis of dialkylamines

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Organometallics, **1989**, 8 (4), 1093-1095• DOI: 10.1021/om00106a034 • Publication Date (Web): 01 May 2002

mol^{-1} and $D(Br–Mn(CO)_5)$[1b] = 276 kJ mol^{-1}, and we calculate the difference $D(ClC(O)CH_2–Br) - D(Br–Mn(CO)_5)$ to be 4 kJ mol^{-1}. This difference adds as a consequence little to ΔH_4. The difference between the electron affinities of $Mn(CO)_5$ and $ClC(O)CH_2$ was on the other hand calculated as $A[Mn(CO)_5] - A[ClC(O)CH_2] = -83$ kJ mol^{-1}. It is thus clear that the driving force behind the abstraction reaction is due to the strong stabilization of a negative charge by the enolate.

We have assumed that reaction 2a proceeds in a stepwise fashion (**4a** through **4d**). It is also possible that ketene and Cl^- is liberated directly from the adduct **5b** in a concerted mode. We expect in either case ketene and Cl^- to be produced readily once bromine has been abstracted in the step **5a** to **5b**.

Acknowledgment. Financial assistance from the Natural Sciences and Engineering Research Council, in the form of operating grants to T.S. and T.Z., made this research possible. We thank the University of Calgary for access to its Cyber-205 installations.

Registry No. $Mn(CO)_5^-$, 14971-26-7; 2-bromoacetyl chloride, 22118-09-8; 2-chloroacetyl chloride, 79-04-9; 2-iodoacetyl chloride, 38020-81-4.

Reaction of Trialkylboranes with Alkylamines: Synthesis of Dialkylamines

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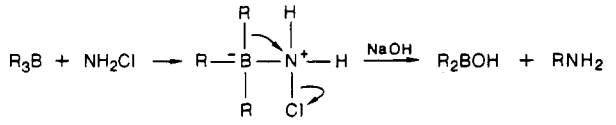
Received July 6, 1988

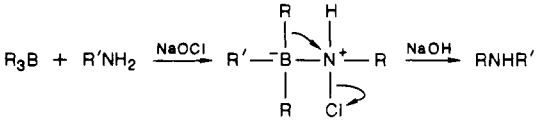
Trialkylboranes react with alkylamines, in the presence of sodium hypochlorite, to form dialkylamines. The reaction proceeds via an anionotropic rearrangement of the organoborate complex formed by the organoborane and the *N*-chloroalkylamine generated in situ.

Introduction

Organoboranes have proven to be valuable synthetic intermediates due to their ease of formation and facile reactivity.[1,2] Many of the borane rearrangements involve anionotropic rearrangements of appropriately substituted organoborate complexes; generally, an alkyl group migrates from an electron-rich boron atom to an electron-deficient neighboring atom.[3] The reaction has been used to prepare a wide variety of organic molecules including those in which the migration terminus is a nitrogen atom.[4–6]



The nature of the leaving group[7–11] and the groups attached to nitrogen have been varied extensively.[7–13] We wish to report a simple reaction sequence involving the in situ preparation of an *N*-chloroalkylamine which leads to dialkylamine products.



Results and Discussion

The rapid reaction of sodium hypochlorite with amines is well documented.[14] On the basis of our earlier studies, the reaction of organoboranes with *N*-chloroalkylamines formed in situ appeared likely.[15,16] Our investigations involved two different protocols for preparing the *N*-chloroalkylamines: route A in which the sodium hypochlorite was added dropwise to a mixture of organoborane and alkylamine and route B in which the sodium hypochlorite was first added to the alkylamine and this solution was then added to the organoborane. Both protocols were utilized throughout the study. In general, method B leads to slightly higher yields of the desired product.

The reactions were run at 0 °C utilizing equimolar quantities of organoborane, alkylamine, and sodium hypochlorite. Preliminary experiments using trihexylborane and *n*-hexylamine revealed that excess quantities (50% and 100%) of amine and hypochlorite did not increase the yield of product. Evaluation of reaction temperatures demonstrated that optimum yields were obtained when reactions were carried out at 0 °C and allowed to warm to room temperature.

The reaction does not appear to be sensitive to the steric requirements of the organoborane. As illustrated in Table

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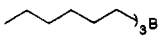
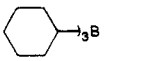
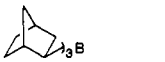
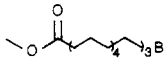
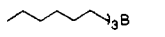
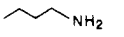
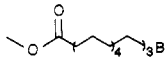
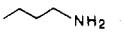
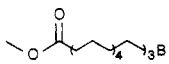
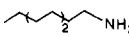
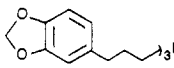
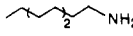
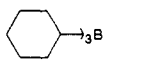
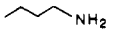
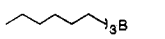
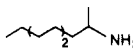
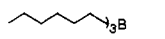
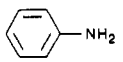
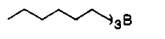
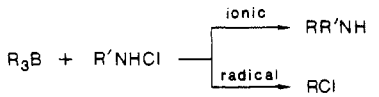
Table I. Reaction of Trialkylboranes (R_3B) with Alkylamines ($R'NH_2$) To Yield $RNHR'$[a]

entry	organoborane	amine	% yield[b] method A	% yield[b] method B
1		CH_3NH_2	59	78
2		CH_3NH_2	68	77
3		CH_3NH_2	65	67
4		CH_3NH_2	81[c]	57
5			56	72
6			59	48
7			48	39
8			56	35
9			65	83
10			0	0
11			0	0
12		$(CH_3)_2NH$	0	0

[a] Reactions were run utilizing equimolar quantities of borane, amine, and hypochlorite. [b] Isolated yields of pure products based on one alkyl group transfer. [c] GC yield.

I, tri-*exo*-norbornylbornane (entry 3) produces a good yield of 1-aminonorbornane. The reaction also tolerates functionality in the organoborane (entries 4, 6, 7, and 8), an important consideration in many syntheses. On the other hand, the reaction cannot be utilized with hindered amines (entry 10) and secondary amines (entry 12). These observations are consistent with the proposed formation of a complex between the organoborane and the *N*-chloroamine which would form more slowly, if at all, when the complexing chloramines are sterically crowded. Retardation of complex formation is presumably responsible for the dichotomy observed for reactions of trialkylboranes with chloramine reagents. Thus, it has been documented that *N*-chlorodialkylamines react with trialkylboranes to yield chloroalkanes rather than trialkylamines.[16,17] The chlorinated products arise via a free radical chain reaction; such chain reactions can be arrested through the use of free radical inhibitors such as galvinoxyl.[17,18]

The current investigation supports the postulation that competitive anionic and free radical pathways are involved in reactions of trialkylboranes with chloramine reagents. Gas chromatographic analyses of the various reaction mixtures summarized in Table I indicate that modest quantities of chloroalkanes (5–15%) are formed as byproducts in all reactions. Upon addition of galvinoxyl, the chloroalkane byproducts essentially disappear (<3%) and a concomitant increase in the yields of desired dialkylamine products is observed.



As anticipated, the reaction involving the sterically more demanding *N*-chlorodimethylamine produced only a trace of the desired trialkylamine (entry 12); 1-chlorohexane was the only product identified (75% yield).[17] Interestingly, the addition of galvinoxyl to this reaction mixture had no significant effect on the product distribution. Aromatic amines, such as aniline, do not lead to the desired secondary amines (entry 11); oxidized products were, however, detected in the reaction mixtures.

Experimental Section

Borane–tetrahydrofuran complex was obtained commercially (Aldrich) and was used without further purification. All alkenes were distilled prior to use. Galvinoxyl and the monoalkylamines were purchased (Aldrich) and were used without further purification. Commercial bleach was used as the oxidant after titration to determine the concentration of sodium hypochlorite. Gas chromatographic analyses were performed on a Varian Model 3700 gas chromatograph (10% SE 30 on Chromosorb W 80/100, 10 ft). Both PMR and carbon-13 NMR were recorded on a JEOL-FX90Q spectrometer. Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected.

Hydroboration. General Procedure. The alkene (30 mmol), in 10 mL of dry THF, was placed in a dry, 100-mL, nitrogen-flushed flask fitted with a septum inlet. The flask was cooled to 0 °C, and BH_3·THF (10 mmol, 10 mL of a 1 M solution) was added dropwise over a period of 3 min. The solution was allowed to warm to room temperature and stirred for 60 min.

Synthesis of Dialkylamines. General Procedure. Route A. The trialkylborane (10 mmol in 10 mL of THF) was cooled to 0 °C, while a nitrogen atmosphere was maintained; then the monoalkylamine (10 mmol) was slowly added to the flask. Sodium hypochlorite (10 mmol) was added slowly-with stirring. The solution was allowed to warm to room temperature and stirred at room temperature for 1.5 hours. **Route B.** Sodium hypochlorite (10 mmol) was added dropwise to a solution of alkylamine (10 mmol) contained in a 25-mL flask cooled to 0 °C. This mixture was added quickly, with stirring, to the flask containing the trialkylborane (10 mmol in 10 mL of THF) at 0 °C. The solution was allowed to warm to room temperature and stirred for 1.5 h. [In reactions involving free radical inhibitors, galvinoxyl (0.29 mmol, 0.84 g) was added to the trialkylborane solution prior to addition of the amine or chloramine.]

The reaction mixture (route A or route B) was then acidified to pH 1 (10% HCl) and washed with diethyl ether. The free amines were obtained via the addition of sodium hydroxide (6 N) to the aqueous layer (pH >13) and extraction of the product into ether. The ether layer was dried over potassium hydroxide and the product purified by chromatography (silica gel/chloroform/methanol/ammonia = 10:1:0.5).

1-(Methylamino)hexane. 1-Hexene (30 mmol, 2.53 g) was hydroborated with BH_3·THF (10 mmol) for 1 h. Methylamine (10 mmol, 0.78 g of 40% solution), and sodium hypochlorite (10 mmol) were then added as described in the general procedures to yield desired product: 0.68 g (59%) [procedure A] (0.90 g (78%) [procedure B]); bp 137 °C (lit[20] bp 138–140 °C); ^{13}CNMR ($CDCl_3$) (^{13}C NMR data are presented in two parts, the carbons in the original alkene are numbered 1, 2, 3, ···; the carbons in the original monoalkylamine are 1′, 2′, 3′, ···.) δ (ppm) 52.5 (C-1), 31.8 (C-2), 27.0 (C-3), 29.9 (C-4), 22.6 (C-5), 14.0 (C-6), 36.5 (C-1′); ^{1}H NMR ($CDCl_3$) δ 0.95 (3 H, CH_3), 1.17 (s, 1 H, NH, D_2O exchangeable), 1.26–1.60 (b, 8 H, $(CH_2)_4$), 2.43 (s, 3 H, CH_3N), 2.62 (t, 2 H, CH_2N).

(Methylamino)cyclohexane. Cyclohexene (33 mmol, 2.71 g) was hydroborated with BH_3·THF (10 mmol) for 3 h. Methylamine (10 mmol, 0.78 g of a 40% solution) and sodium hypochlorite were added to yield the desired product: 0.76 g (68%) [procedure A] (0.87 g (77%) [procedure B]); bp 148 °C (lit.[21] bp

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147–148 °C); ^{13}C NMR ($CDCl_3$) δ (ppm) 58.4 (C-1), 33.2 (C-2,6), 26.2 (C-4), 25.0 (C-3,5), 33.5 (C-1′); ^1H NMR ($CDCl_3$) δ 2.40 (s, 3 H, $>NCH_3$), 2.25 (s, 1 H, NH, D_2O exchangeable), 0.92–2.05 (9 H, d, b, H's of cyclohexane).

Methyl 11-(Methylamino)undecanoate. Methyl 10-undecenoate (30 mmol, 5.95 g) was hydroborated with BH_3·THF (10 mmol) for 80 min. Methylamine (10 mmol, 0.78 g of a 40% solution) and sodium hypochlorite were added to yield the desired product: 2.09 g (91%, GC 89%) [procedure A] (1.3 g (57%) [procedure B]); mp (hydrochloride) 139.5–141 °C (acetone); ^{13}C NMR ($CDCl_3$) δ (ppm) 52 (C-1), 30.0 (C-2), 27.1 (C-3), 29.3 (C-4), 29.0 (C-5), 29.1 (C-6), 29.7 (C-7), 29.0 (C-8), 25.0 (C-9), 33.7 (C-10), 173.6 (C-11), 51 (C-12), 36.6 (C-1′); ^1H NMR ($CDCl_3$) 3.66 (s, 3 H, CH_3O), 2.6–2.2 (m, 8 H, $COCH_3$, CH_2NHCH_3), 1.7–1.15 (envelope, 16 H, aliphatic). The methyl ester was characterized by conversion[22] to the known acid: mp 103–106 °C (lit.[23] mp 105–105.5 °C).

1-(1-Butylamino)hexane. 1-Hexene (30 mmol, 2.53 g) was hydroborated with BH_3·THF (10 mmol) for 1 h. *n*-Butylamine (10 mmol, 0.73 g) and sodium hypochlorite (10 mmol) were then added to yield the product: 0.87 g (56%) [procedure A] (1.12 g (72%) [procedure B]; bp 202 °C (740 mmHg) (lit.[24] bp 201 °C (738 mmHg)); ^{13}C NMR ($CDCl_3$) δ (ppm) 50.3 (C-1), 30.3 (C-2), 27.2 (C-3), 32.5 (C-4), 22.7 (C-5), 14.1 (C-6), 49.9 (C-1′), 32.8 (C-2′), 20.2 (C-3′), 14.1 (C-4′); ^1H-NMR ($CDCl_3$) δ 2.62 (2 H, CH_2N), 2.55 (2 H, NCH_2), 1.9–1.1 (13 H, b, aliphatic), 1.0 (3 H, CH_3), 0.92 (3 H, CH_3).

(*n*-Butylamino)cyclohexane. Cyclohexene (33 mmol, 2.71 g) was hydroborated with BH_3·THF (10 mmol) for 3.5 h. *n*-Butylamine (10 mmol, 0.73 g) and sodium hypochlorite (10 mmol) were added to yield the desired product: 1.0 g (65%) [procedure A] (1.3 g (83%) [Procedure B]); bp 207 °C (740 mmHg) (lit.[25] mp 207 °C (740 mmHg)); ^{13}C NMR ($CDCl_3$) δ 57.1 (C-1), 33.7 (C-2, C-6), 25.3 (C-3, C-5), 26.4 (C-4), 46.8 (C-1′), 32.7 (C-2′), 20.8 (C-3′), 14.1 (C-4′); ^1H NMR ($CDCl_3$) δ 2.75 (m, 4 H, NH, $CHNCH_2$, D_2O exchange, one H less), 2.0–0.9 (m, 17 H, aliphatic).

Methyl 11-(1-Butylamino)undecanoate. Methyl 10-undecenoate (30 mmol, 5.95 g) was hydroborated with BH_3·THF (10 mmol) for 70 min. *n*-Butylamine (10 mmol, 0.73 g) and sodium hypochlorite (10 mmol) were added to yield the product: 1.79 g (59%) [procedure A] (1.31 g (48%) [Procedure B]); mp (hydrochloride) 182 °C dec; ^{13}C NMR ($CDCl_3$) 47.9 (C-1), 26.0 (C-2), 27.0 (C-3), 29.4 (C-4), 29.1 (C-5), 29.7 (C-6), 29.4 (C-7), 29.1 (C-8), 21.5 (C-9), 34.1 (C-10), 174.2 (C-11), 51.4 (C-12), 47.6 (C-1′), 27.9 (C-2′), 20.2 (C-3′), 13.6 (C-4′); ^1H NMR ($CDCl_3$) δ 9.56 (b, 1 H, NH(HCl), D_2O exchangeable), 3.65 (s, 3 H, CH_3O), 2.92 (m, 4 H, CH_2NCH_2), 2.30 (m, 2 H, $COCH_2$), 1.9–1.2 (envelop, 20 H, aliphatic), 0.84 (t, 3 H, CH_3). The methyl ester was characterized by conversion[22] to the known acid: mp 136–137 °C (lit.[26] mp 138–39 °C).

1-(1-Octylamino)hexane. 1-Hexene (30 mmol, 2.53 g) was hydroborated with BH_3·THF for 1 h. *n*-Octylamine (10 mmol, 1.29 g) and sodium hypochlorite (10 mmol) were added to yield desired product: 1.22 g (57%, GC 93%) [procedure A] (1.32 g (62%, GC 90%) [procedure B]); bp 251–253 °C (740 mmHg) (lit.[27] bp 255–257 °C (760 mmHg)); ^{13}C NMR ($CDCl_3$) δ 50.1 or 52.3 (C-1), 30.2 (C-2), 26.8 (C-3), 29.2 (C-4), 22.0 (C-5), 13.9 (C-6), 52.3 or 50.1 (C-1′), 30.2 (C-2′), 26.8 (C-3′), 29.2 (C-4′), 29.5 (C-5′); 31.8 (C-6′), 22.6 (C-7′), 13.9 (C-8′); ^1H NMR ($CDCl_3$) δ 2.73 (2t, 4 H, CH_2NCH_2), 1.12–1.27 (b, 21 H, , aliphatic H's and N-H, after D_2O exchanges, 20 Hs) 0.88(t, 6 H, $2\times CH_3$).

(*n*-Octylamino)cyclohexane. Cyclohexene (33 mmol, 2.71 g) was hydroborated with BH_3·THF for 3.5 h. *n*-Octylamine (10 mmol, 1.29 g) and sodium hypochlorite (10 mmol) were added to yield the hydrochloride: 1.06 g (43%) [procedure A] (1.36 g (55%) [procedure B]); mp 210–212 °C (lit.[15] mp 212 °C); ^{13}C NMR ($CDCl_3$) δ 57.1 (C-1), 29.0 (C-2, C-6), 24.5 (C-3, C-5), 24.8 (C-4), 44.5 (C-1′), 27.0 (C-2′), 26.0 (C-3′) 29.0 (C-4′, C-5′), 31.6 (C-6′), 22.5 (C-7′), 14.0 (C-8′); ^1H NMR ($CDCl_3$) δ 2.9–2.6 (b, 4 H, CH_2NHCH), 2.2–1.1 (m b, 22 H, aliphatic H), 0.8 (t, 3 H, CH_3).

Methyl 11-(1-Octylamino)undecanoate. Methyl 10-undecenoate (30 mmol, 5.95 g) was hydroborated with BH_3·THF (10 mmol) for 80 min. 1-Octylamine (10 mmol, 1.29 g) and sodium hypochlorite (10 mmol) were added to yield the hydrochloride: 1.75 g (48%) [procedure A] (1.28 g (39.2%) [procedure B]); mp 178–180 °C (lit.[15] mp 181–183 °C); ^{13}C NMR ($CDCl_3$) δ 47.8 (C-1), 26.0 (C-2), 27.1 (C-3), 29.5 (C-4), 29.2 (C-5,6,7,8), 25.2 (C-9), 34.3 (C-10), 174.2 (C-11), 51.4 (C-12), 47.8 (C-1′), 27.1 (C-2′), 26.0 (C-3′), 29.2 (C-4′), 29.5 (C-5′), 32.0 (C-6′), 22.8 (C-7′), 14.1 (C-8′); ^1H NMR ($CDCl_3$) δ 3.66 (s, 3 H, CH_3O), 2.6–2.9 (m, 5 H, CH_2NHCH_2), 2.31 (m, 2 H, $C(=O)CH_2$), 1.9–1.2 (envelope, 28 H, aliphatic) 0.87 (t, 3 H, CH_3).

1-(1-Octylamino)-3-[3,4-(methylenedioxy)phenyl]propane. Safrole (30 mmol, 4.86 g) was hydroborated with BH_3·THF (10 mmol) for 80 min. *n*-Octylamine (10 mmol) and sodium hypochlorite (10 mmol) were added as described general procedures to yield the product as the hydrochloride: 1.82 g (56%) [procedure A] (1.14 g (35%) [procedure B]); mp 220–222 °C (lit.[15] mp 221–223 °C); ^{13}C NMR ($CDCl_3$) δ 47.1 (C-1), 27.7 (C-2), 32.5 (C-3), 133.6 (C-4), 108.5 (C-5), 147.8 (C-6), 146.1 (C-7), 108.8 (C-8), 121.2 (C-9), 100.8 (C-10), 48.0 (C-1′), 27.0 (C-2′), 26.0 (C-3′), 29.1 (C-4′, C-5′), 31.7 (C-6′), 22.6 (C-7′), 14.0 (C-8′); ^1H NMR ($CDCl_3$) δ 6.67 (s, 3 H, ArH), 5.90 (s, 2 H, OCH_2O), 2.8–2.4 (m, 6 H, CH_2NCH_2, $ArCH_2$), 2.3–1.5 (b, 3 H, CH_2CH_2NH), 1.5–1.0 (b, 12 H, aliphatic), 0.87–1.1 (t, 3 H, CH_3).

***exo*-2-(Methylamino)norbornane.** Norbornylene (33 mmol, 3.1 g) was hydroborated with BH_3·THF (10 mmol) for 2.5 h. Methylamine (10 mmol, 0.78 g of 40% solution) and sodium hypochlorite (10 mmol) were added to yield the desired product: 0.81 g (65%) [procedure A] (0.84 g (67%) [procedure B]); hydrochloride mp 198–202 °C (lit.[28] mp 199–201 °C); ^{13}C NMR ($CDCl_3$) δ 63.7 (C-1), 40.0 (C-2), 39.6 (C-3), 34.5 (C-4), 34.2 (C-7), 28.3 (C-5), 26.6 (C-6), 35.3 (C-1′); ^1H NMR ($CDCl_3$) δ 2.8–2.46 (m, 1 H, CHN), 2.37 (s, 3 H, NCH_3), 2.2 (b, 2 H, bridgehead H's), 0.90–1.9 (m, 8 H, aliphatic), 0.85 (s, 1 H, NH, D_2O exchangeable).

Acknowledgment. This research was supported by the Department of Energy, Grant DE-FG05-86ER-60434.

Registry No. CH_3CH_2, 74-89-5; $(CH_3)_2NH$, 124-40-3; 1-(methylamino)hexane, 35161-70-7; 1-hexene, 592-41-6; (methylamino)cyclohexane, 100-60-7; cyclohexene, 110-83-8; methyl 11-(methylamino)undecanoate, 24255-66-1; methyl 10-undecenoate, 111-81-9; 1-(1-butylamino)hexane, 30278-08-1; (*n*-butylamino)cyclohexane, 10108-56-2; methyl 11-(1-butylamino)undecanoate hydrochloride, 119392-93-7; 1-(1-octylamino)cyclohexane hydrochloride, 4922-19-4; methyl 11-(1-octylamino)undecanoate hydrochloride, 89231-71-0; 1-(1-octylamino)-3-[3,4-(methylenedioxy)phenyl]propane, 119392-94-8; safrole, 94-59-7; *exo*-2-(methylamino)norbornane hydrochloride, 119392-92-6; norbornylene, 498-66-8; trihexylborane, 1188-92-7; tricyclohexylborane, 1088-01-3; tris(bicyclo[2.2.1]heptyl)borane, 22801-27-0; tris(10-methoxycarboxyldodecyl)borane, 63399-92-8; tris[3-(1,3-benzodioxol-5-yl)propyl]borane, 78498-54-1; 1-methyloctylamine, 13205-58-8; aniline, 62-53-3; *n*-butylamine, 109-73-9; octylamine, 111-86-4.

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