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ORGANOBORANES FOR SYNTHESIS. 7.
AN IMPROVED GENERAL SYNTHESIS OF PRIMARY AMINES FROM ALKENES *via* HYDROBORATION-ORGANOBORANE CHEMISTRY

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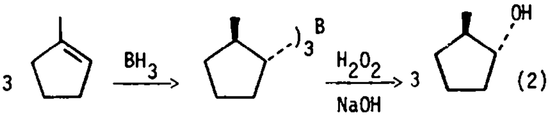
Abstract - Triorganylboranes, R_3B, and diorganylborinic esters, R_2BOR', react readily with preformed chloramine or hydroxylamine-*O*-sulfonic acid to produce the corresponding primary amines, RNH_2. However, the product of the reaction following hydrolysis is the boronic acid, $RB(OH)_2$, limiting the yield to 67% for R_3B and to 50% for R_2BOR'. This problem has now been overcome with the help of lithium dimethylborohydride, readily converted *in situ* to dimethylborane. The hydroboration of representative alkenes by dimethylborane provides the corresponding monoorganyldimethylborane, RMe_2B. Treatment of this intermediate with hydroxylamine-*O*-sulfonic acid provides the desired amines, RNH_2, in isolated yields of 73% to 95%. The reaction proceeds with complete retention, reproducing the precise structure of the organic group in the organoboranes, RMe_2B.

The oxidation of triorganylboranes by alkaline hydrogen peroxide is an ideal reaction, widely applicable to organoboranes with a wide range of structure (eq 1).[2] The reaction is essentially quantitative and proceeds with complete retention of configuration (eq 2).[3] The reaction can accommodate an exceptionally wide variety of substituents.[2]

$$R_3B + 3\ H_2O_2 + NaOH \longrightarrow 3\ ROH + NaB(OH)_4 \quad (1)$$



(2)

It appeared desirable to have available a comparable reaction to convert organoboranes into primary amines (eq 3). Initially we tried to use the nitrogen analogs of hydrogen peroxide, *i.e.*, hydroxylamine or hydrazine. But organoboranes merely formed simple addition compounds with these bases, with no further reaction evident (eqs 4 and 5). It was evident that we required a better leaving group.

$$R_3B \xrightarrow{?} 3\ RNH_2 \quad (3)$$

$$R_3B + H_2NOH \longrightarrow R_3B{\cdot}H_2NOH \quad (4)$$

$$R_3B + H_2NNH_2 \longrightarrow R_3B{\cdot}H_2NNH_2 \quad (5)$$

In this paper we report a detailed study of the reaction of organoboranes with chloramine and hydroxylamine-*O*-sulfonic acid (HSA) with special emphasis on establishing conditions for the quantitative utilization of the alkyl groups by employing a mixed organoborane, RR'_2B, in which the group R shows significantly greater migratory aptitude than R'.

RESULTS AND DISCUSSION

The reaction of trialkylboranes with freshly prepared chloramine proceeds in the presence of aqueous sodium hydroxide. However, we could utilize only two of the three groups in R_3B (eq 6).[4] Consequently, the maximum possible yield for R_3B is only 67%.

$$R_3B + 2\ NH_2Cl \xrightarrow{NaOH} 2\ RNH_2 + RB(OH)_2 \quad (6)$$

More hindered alkenes undergo hydroboration only to the dialkylborane stage.[5] These are readily converted into the corresponding dialkylborinic acids or esters. These derivatives also react with preformed chloramine to form the corresponding primary amines. But in this case, only one of the two groups could be made to react (eq 7).

Consequently, in such cases the maximum yield is only 50%. Moreover, the reaction of the more hindered dialkylborane derivatives is very sluggish, with decreased yields.

$$R_2BOR' + 2\ NH_2Cl \xrightarrow{NaOH} RNH_2 + RB(OH)_2 \qquad (7)$$

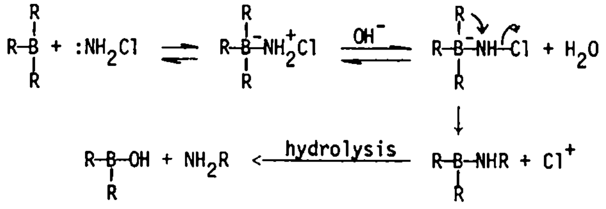
We also noticed that the yields of the amines in the reaction of organoboranes with chloramine are very low in the absence of sodium hydroxide, which indicates that the reaction is base-induced. In spite of the low yield (50-67%) of the product amine, the replacement of boron by the amino group occurs stereospecifically with retention of configuration similar to that realized for the oxidation of organoboranes by alkaline-hydrogen peroxide.[2] Representative results are summarized in Table 1.

Table 1. Synthesis of amines by the hydroboration-amination reaction using freshly prepared chloramine

Alkene[a]	Amines	Yield,[b] %	Bp, °C (torr)
1-decene	*n*-decylamine	51	90-93(15)
2-methyl-1-pentene	2-methylpentylamine	58[c]	
α-methylstyrene	2-phenylpropylamine	58	108-110(25)
cyclopentene	cyclopentylamine	50	109(760)
cyclohexene	cyclohexylamine	49	135-136(760)
norbornene	*exo*-norbornylamine	51	49(10)
β-pinene	*cis*-myrtanylamine	48	60-61(2)

[a] The alkenes were converted into the corresponding organoboranes by reaction with $BH_3 \cdot THF$. [b] Yields of pure distilled products, based on the olefins. [c] Yield determined by titration of the amine solution against perchloric acid in acetic acid using methyl red as indicator.

We previously mentioned that both hydroxylamine and hydrazine formed simple addition compounds with the organoborane, but the desired transfer of an alkyl groups from boron to nitrogen could not be achieved. We concluded that we required a better leaving group than -OH or $-NH_2$. In chloramine, -Cl provides such a leaving group. The experimental results suggest the following mechanism for the operation of this reaction (Scheme 1). Further reaction of dialkylborinic acid R_2BOH with chloramine proceeds by very much the same mechanism, producing the alkylboronic acid, $RB(OH)_2$, as the by-product. The low reactivity of the alkylboronic acids is presumably a result of the high electron density on boron arising from the mesomeric effect of the two hydroxyl groups.

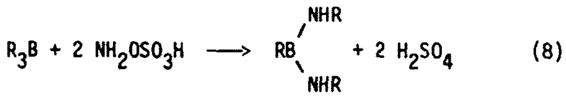


Scheme 1

This procedure possesses three major difficulties. First, the precise yield in the synthesis[6] of chloramine is erratic, averaging about 50%. Consequently, the chloramine solution requires analysis for its chloramine content before utilization in the reaction. Second, the chloramine is unstable and cannot be stored. This requires a fresh preparation each time the material is to be used. Finally, the reaction utilizes only two of the three groups in R_3B and one of the two groups in R_2BOR'. This limits the yield to a maximum of 67% for R_3B and a maximum of 50% for R_2BOR'.

More recently, Kabalka *et. al.* reported the reaction of trialkylboranes with chloramine generated *in situ*.[7] One organic group is transferred readily from boron to nitrogen, but there is no evidence that the reaction proceeds further than we had achieved with preformed chloramine. No results with hindered alkyl groups are reported.

The commercial availability of hydroxylamine-*O*-sulfonic acid suggested that it might have advantages. It proved more convenient and we realized similar or slightly better yields of primary amines as compared to the chloramine procedure.[8] However, this method did not solve the problem of the residual organic group on boron (eq 8). Nor did it improve results with highly hindered alkyl groups.



$$R_3B + 2\ NH_2OSO_3H \longrightarrow RB\begin{matrix}\diagup NHR\\ \diagdown NHR\end{matrix} + 2\ H_2SO_4 \qquad (8)$$

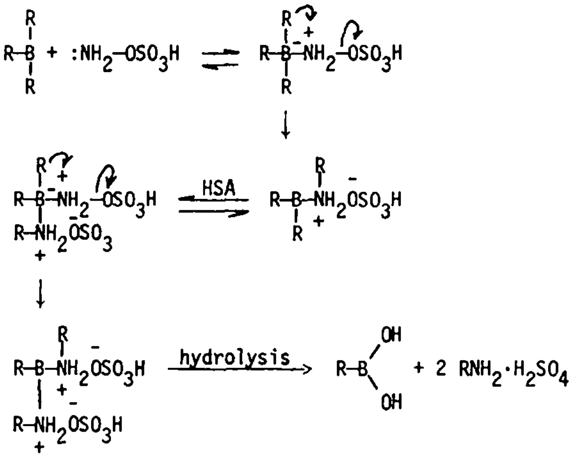
We later discovered that HSA was soluble in diglyme. This provided a simple means for purifying the reagent. This solvent also permitted extending the reaction to more hindered alkyl groups. Unfortunately, the total conversion of alkyl groups into amines was not improved, with the yields realized being in the range of 50-67%. Thus in both THF and DG, the reactions essentially stop following the migration of two (from R_3B) or one alkyl group (from R_2BOR'), leaving a residual alkyl group on boron. The inertness of the boronic acid derivative presumably arises because of the relatively high electron supply from the two oxygen and/or nitrogen atoms on boron, making it difficult for the last molecule of HSA to coordinate to achieve the transfer of the last group. The maximum yield of amine is 67% for R_3B and 50% for R_2BOR'. Representative primary amines have been prepared by this method (Table 2).

Table 2. Conversion of alicyclic and bicyclic alkenes into amines by hydroboration-amination using hydroxylamine-*O*-sulfonic acid

Alkene[a]	Amine	Yield,[b] % THF	Yield,[b] % DG	Bp, °C (torr)	Derivative[d] Mp, °C
1-octene	*n*-octylamine	64		119(13)	
α-methyl stryene	2-phenylpropylamine	58		108-110(25)	
cyclopentene	cyclopentylamine	59		109(760)	
cyclohexene	cyclohexylamine	55		135-136(760)	
norbornene	*exo*-norbornylamine	52	48	49(10)	143-144[e]
1-methylcyclopentene	*trans*-2-methylcyclopentylamine		45	121(740)	117-118[f]
1-methylcyclohexene	*trans*-2-methylcyclohexylamine		45	148(750)	151-152[g]
1-phenylcyclopentene	*trans*-2-phenylcyclopentylamine		43	85(1)	162-163[h]
1-phenylcyclohexene	*trans*-2-phenylcyclohexylamine		38	48-55[c]	181-182[i]
β-pinene	*cis*-myrtanylamine	55		60-61(2)	
α-pinene	isopinocampheylamine		45	83(10)	129-130[j]

[a]The alkenes were converted into the corresponding organoboranes by reaction with BH_3·THF. [b]Yields of pure distilled products based on the alkenes. [c]Melting point. [d]Benzamide derivatives, except where otherwise indicated. [e]Acetamide derivative. Mp: *exo* 144 and *endo* 132. See ref. 15. [f]Mp: *trans* 116 and *cis* 85. W. Hückel and R. Kupka, *Chem. Ber.*, 89, 1694 (1956). [g]Mp: *trans* 151-153 and *cis* 114-115. W. Hückel and K. D. Thomas, *Justus Liebigs Ann. Chem.*, 645, 177 (1961). [h]Mp: *cis* 154. T. R. Govindachai, K. Nagarajan, B. R. Pai and N. Arumygam, *J. Chem. Soc.*, 4280 (1956). [i]Mp: *trans* 180-181 and *cis* 125-127. D. Y. Curtin and S. Schmukler, *J. Am. Chem. Soc.*, 77, 1105 (1955). [j]Mp: pinocampheylamine derivative, 144. W. A. Tilden and F. G. Shepheard, *J. Chem. Soc.*, 89, 1560 (1906).

A plausible mechanism for the reaction of organoboranes with HSA is depicted in Scheme 2.



Scheme 2

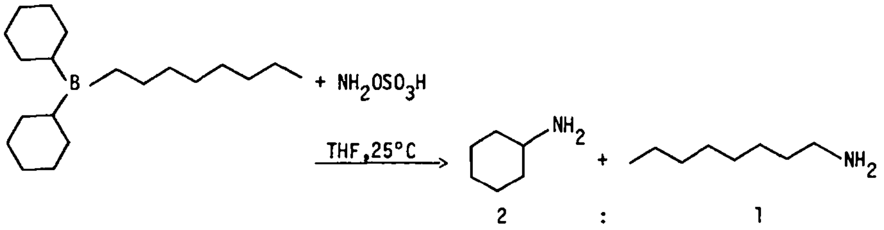
It is, of course, possible that the first intermediate undergoes hydrolysis to the borinic acid prior to reaction of the second alkyl group.

Recently, a new reagent, *O*-mesitylenesulfonylhydroxylamine, has been developed for the conversion of organoboranes into primary amines. But this reagent has given far poorer yields (25-50%).[9]

We then attempted the reaction of thexylmonoalkylborane derivatives, ThxRBH, with HSA to explore the possibility of utilizing thexyl group as a nonmigratory blocking group. Unfortunately, the reaction proved very sluggish and difficult to complete. The yields achieved were not significantly better than those we had achieved with R_3B and R_2BH.[10]

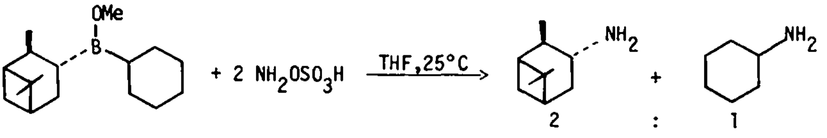
Evidently, these reactions are sensitive to both steric and electronic factors so that, at best, only two of the three alkyl groups can be utilized. This was confirmed by the isolation of boronic acid, $RB(OH)_2$, from the reaction mixture. We have also observed that $RB(OH)_2$ and boronic acid derivatives, such as $RBO_2(CH_2)_3$ and RBX_2 (X = H, Cl, OAc, $OCOCF_3$ and O_3SMe), fail to react with HSA. We were forced to seek another means of overcoming this limitation to quantitative utilization of alkyl residues by utilizing a mixed organoborane, RR'_2B, in which group R shows significantly greater migratory aptitude than R'.

Initially we explored the reaction of various mixed organoborane intermediates with HSA at 25°C in selected solvents, tetrahydrofuran (THF), diglyme (DG) and diethyl ether (EE). In EE the reaction is slow and isolation of amines from DG is rather difficult. Even though HSA is insoluble in THF, the reaction is mildly exothermic and results in clear solutions at the conclusion of the reaction. The reaction of dicyclohexyl-*n*-octylborane gives a mixture of amines, which indicates that the cyclohexyl group migrates more readily than the *n*-octyl group (eq 9). Preferential migration of the cyclooctyl group of *B*-cyclohexyl-9-borabicyclo[3.3.1]nonane is observed.



(9)

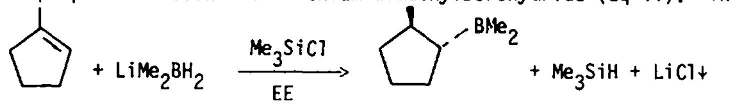
Isopropyl phenylcyclohexylborinate reacts with HSA to give a mixture of amines, which indicates that cyclohexyl group migrates twice as fast as the phenyl group. On the other hand, methyl isopinocampheylcyclohexylborinate gives a mixture of amines, which indicates that the isopinocampheyl group migrates twice as readily as the cyclohexyl group (eq 10).



(10)

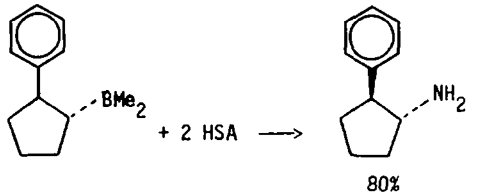
Since secondary groups migrate preferentially in the reaction of organoboranes with HSA, we checked the possibility of utilizing the methyl group as the nonmigratory blocking group. There are scattered references in the literature suggesting that the methyl group is particularly resistant to migration from boron to carbon.[11-13] We had recently developed a convenient synthesis for lithium dimethylborohydride[14] and for its ready conversion into dimethylborane in the presence of olefins.[13] This development made the organodimethylboranes, RMe_2B, readily available. Accordingly, we tested these derivatives with hydroxylamine-*O*-sulfonic acid. To our delight, these compounds reacted readily to afford essentially quantitative yields of the corresponding amine. In the procedure we finally adopted, we utilized two equivalents of HSA per mole of RMe_2B. That maximized the yield of the desired amine. Fortunately, the methylamine produced does not get extracted by diethyl ether under the experimental conditions.

We synthesized all of the RMe_2B used in this study by hydroboration of the corresponding olefins with dimethylborane prepared *in situ* from lithium dimethylborohydride (eq 11). The EE solution of trialkylboranes thus obtained was diluted with THF so as to give a 0.5 *M* solution. It was then reacted with two equivalents of HSA at 25°C. The initial exothermic reaction is controlled by the rate of addition of HSA and by the controlled cooling of the reaction flask with a water bath. Hydroxylamine-*O*-sulfonic acid slowly dissolved to give a clear solution. The reaction mixture was stirred at 25°C for 12 h to ensure completion of reaction. Water was added and the amines were then isolated from the acidic aqueous solutions by standard methods.



(11)

Using this general procedure, 1-octene was converted into *n*-octylamine and 2-methyl-1-pentene into 2-methylpentylamine. Similarly, phenylcyclopentene was converted into *trans*-2-phenylcyclopentylamine (cypenamine) and norbornene into *exo*-norbornylamine (eqs 12 and 13). The results are summarized in Table 3.



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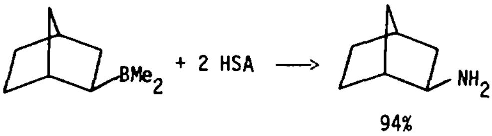


(13)

The reaction of HSA with RMe_2B proceeds with retention of configuration at the migrating carbon atom, as observed in other related 1,2-migration reactions of organoboranes.[5] Thus, the *trans*-geometry obtained by hydroboration of 1-methylcyclopentene is retained in the product, *trans*-2-methylcyclopentylamine. The isomeric purity of all of the cyclic amines was confirmed by gas chromatographic analysis on a 50-*M* methyl silicone capillary column or on a 20-*M* Supelcowax capillary column. In the case of *exo*-norbornylamine, the isomeric purity was determined by ^1H NMR analysis of the *N*-acetyl derivative. Authentic *N*-acetyl-*endo*-norbornylamine[15] shows a sharp peak assigned to the methyl protons in the amide grouping at δ 2.00 while the *N*-acetylnorbornylamine prepared by the hydroboration-amination reaction shows a peak at δ 1.92 with no peak at δ 2.00. Additionally, the isomeric purity of all of the products is also indicated by the ready preparation of solid derivatives with sharp melting points.

APPLICATIONS

Some recent applications of this synthesis of amines *via* organoborane chemistry may be pointed out. Kabalka and his coworkers utilized preformed monochloroalkylamines to achieve the synthesis of secondary amines (eq 14).[16] Pelter *et. al.* utilized chloramine-*T* to achieve a transfer of alkyl group from boron to nitrogen (eq 15).[17] Presumably, hydrolysis of the product would provide the corresponding amine.

$$R_3B + R'NHCl \longrightarrow RR'NH \qquad (14)$$

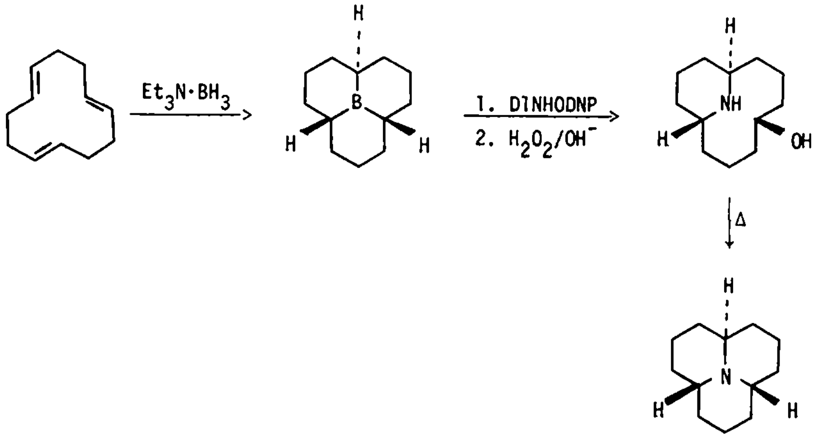
$$R_3B + \overset{-}{N}ClTs\overset{+}{N}a \longrightarrow R_2BNRTs \xrightarrow{OH^-} RNHTs \qquad (15)$$

Finally, a fascinating synthesis of perhydro-9*b*-azaphenalene from perhydrohydroboraphenalene[18] has been described (eq 16).[19]

Table 3. Stereospecific synthesis of amines from RMe_2B using hydroxylamine-*O*-sulfonic acid

			$RNH_2 \cdot HCl$	
Olefin[a]	Amine	GC Yield,[b] %	Mp,[c] °C	Isolated Yield,[b] %
1-octene	*n*-octylamine	91	204-206	85
2-methyl-1-pentene	2-methylpentylamine		140-142	95
cis-2-butene	2-butylamine		138-140	95
cis-3-hexene	3-hexylamine	97	228-230	92
norbornene	*exo*-2-norbornylamine		208(decomp)	94
cyclohexene	cyclohexylamine	94		
2-methyl-2-butene	3-methyl-2-butylamine		206-208	87
1-methylcyclopentene	*trans*-2-methylcyclopentylamine	84	182-186	81
1-methylcyclohexene	*trans*-2-methylcyclohexylamine	80	284(decomp)	78
1-phenylcyclopentene	*trans*-2-phenylcyclopentylamine	80	134-136	73

[a] The olefins were converted to the corresponding RMe_2B derivative by reaction with $LiMe_2BH_2$-Me_3SiCl. [b] Yields based on the olefins. [c] Determined in sealed capillary tubes.



(16)

CONCLUSION

The present study reports a simple procedure for the conversion of alkenes into the corresponding primary amines. Incidentally, *trans*-2-phenylcyclopentylamine (cypenamine) is an antidepressant without significant monoamine oxidase inhibitory activity.[20] This primary amine synthesis from organoborane intermediates provides a novel method of introducing an amine functionality into olefins in a regio- and stereoselective manner.

EXPERIMENTAL SECTION

All operations were carried out under a nitrogen atmosphere with oven-dried glassware.[5] The ^{11}B NMR spectra were recorded on a Varian FT-80A spectrometer and the chemical shifts are in δ relative to $EE \cdot BF_3$ with chemical shifts downfield from $EE \cdot BF_3$ assigned as positive. The ^1H NMR spectra were scanned on a Varian T-60 spectrometer and ^{13}C NMR spectra were obtained on a Varian FT-80A instrument. Chemical shifts, all in D_2O, are in δ relative to external Me_4Si for ^1H and ^{13}C NMR spectra. Gas chromatographic analyses were carried out with a Varian 1400 FID instrument equipped with a Hewlett-Packard 3390A integrator/plotter using a 6 ft x 0.125 in column of 10% Carbowax 20M-2% KOH on Chromosorb W and an internal standard. Capillary gas chromatographic analyses were carried out with a Hewlett-Packard 5890 chromatograph.

Materials. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Anhydrous diethyl ether (EE) was purchased from Mallinckrodt, Inc. and was used directly. Chloramine was prepared freshly prior to use following literature procedure.[6] Hydroxylamine-*O*-sulfonic acid (HSA) obtained from Aldrich Chemical Company was used as such. Chlorotrimethylsilane was purchased from Aldrich Chemical Company and was used as received. Lithium dimethylborohydride was prepared as described before.[13,14]

Reaction of Organoboranes with Freshly Prepared Chloramine. The following procedure for the preparation of 2-phenylpropylamine is representative. In a 500-ml flask was placed 11.8 g (100 mmol) of α-methylstyrene and 30 ml of tetrahydrofuran. The flask was flushed with nitrogen and 33.3 ml of a 1.0-*M* solution of borane in tetrahydrofuran was injected with a hypodermic syringe (exothermic reaction). After 1 h, 3 ml of water was added to destroy residual hydride, followed by 50 ml of 3 *M* aqueous sodium hydroxide. The amination was accomplished by adding 215 ml of 0.31 *M* freshly prepared chloramine solution (66.7 mmol).[21] After 1 h at room temperature, the reaction mixture was acidified with hydrochloric acid and the acidified solution extracted with ether. The solution was made strongly alkaline with sodium hydroxide and the amine extracted with ether. There was obtained 6.94 g (51.5% yield) of 2-phenylpropylamine, bp 106-110°C (25 torr).

Reaction of Organoboranes with Hydroxylamine-*O*-sulfonic Acid. The following procedure for the synthesis of *cis*-myrtanylamine is representative. In a 100-ml flask was placed 6.8 g (50 mmol) of β-pinene, $[\alpha]^{25}D$ -20.4° (neat, ℓ 1) (90% ee), in 8 ml of tetrahydrofuran. After flushing with nitrogen, the hydroboration was accomplished by injecting 16.7 ml of a 1.0-*M* solution of borane in tetrahydrofuran. To the solution was added 4.16 g (36 mmol) of solid hydroxylamine-*O*-sulfonic acid and the reaction mixture was heated under reflux for 3 h. The solution was acidified with dilute hydrochloric acid and worked up as in the chloramine procedure. There was obtained 4.05 g (53% yield) of *cis*-myrtanylamine: bp 60-61° (2 torr); $[\alpha]^{25}D$ -27.85° (neat, ℓ 1). Anal. Calcd. for $C_{10}H_{19}N$: C, 78.4; H, 12.42; N, 9.14. Found: C, 78.8; H, 12.33; N, 9.19. The *N*-benzoyl derivative exhibited mp 105-106°C (from petroleum ether). Anal. Calcd. for $C_{17}H_{23}NO$: C, 79.3; H, 8.94; N, 5.45. Found: C, 79.4; H, 8.82; N, 5.92.

Preparation of *trans*-2-Methylcyclohexylamine Using Hydroxylamine-*O*-sulfonic Acid in Diglyme. A dry 250-ml flask equipped with a dropping funnel, condenser and magnetic stirrer was flushed with nitrogen. A solution of 0.78 g (20.6 mmol) of sodium borohydride in 25 ml of diglyme was introduced, followed by 4.8 g (50 mmol) of 1-methylcyclohexene. The flask was immersed in an ice water bath and hydroboration was achieved by the dropwise addition of 3.90 g (27.5 mmol) of boron trifluoride etherate. The solution was then stirred at room temperature for 3 h. Hydroxylamine-*O*-sulfonic acid, 6.22 g (55 mmol) in 25 ml of diglyme, was added and the solution heated to 100°C for 3 h. The solution was cooled, treated with 20 ml of concentrated hydrochloric acid and then poured into 200 ml of water. The acidic aqueous phase was extracted with ether to remove diglyme and residual boronic acid. The solution was then made strongly alkaline with sodium hydroxide and the amine was extracted with ether. Titration of the ether extract indicated a 58% yield of amine. Distillation yielded 5.0 g (45%) of *trans*-2-methylcyclohexylamine: bp 148°C (750 torr). GC analysis showed > 99% isomeric purity.

Reaction of Dimethylalkylboranes with Hydroxylamine-*O*-sulfonic Acid. General Procedure. The following procedure for the preparation of *trans*-2-methylcyclopentylamine is typical. A 50-ml centrifuge vial fitted with a rubber septum and magnetic stirring bar was charged with 5.6 ml of a 1.8-*M* EE solution of lithium dimethylborohydride (10 mmol) and 1.1 ml of 1-methylcyclopentene (10.4 mmol) and cooled to 0°C. Neat chlorotrimethylsilane (1.3 ml, 10.2 mmol) was added with stirring. The reaction mixture was then stirred at 25°C for 4 h. The ^{11}B NMR spectrum of the reaction mixture showed a signal at δ +86 due to the clean formation of the trialkylborane. The reaction mixture was centrifuged and the clear supernatant liquid was transferred *via* a double-ended needle to a 50-ml flask. The LiCl was washed with 2 ml of EE and the washing was combined with the supernatant solution. The trialkylborane solution was diluted with 10 ml of THF and hydroxylamine-*O*-sulfonic acid (2.26 g, 20 mmol) was added using a solid addition tube. Initial exothermic reaction was controlled by the rate of addition of HSA and by water-bath cooling. The reaction mixture was stirred at 25°C for 12 h and water (10 ml) was added. The ^{11}B NMR spectrum of the organic layer showed a peak at δ +31 due to the formation of boronic acid derivative. The reaction mixture was extracted with EE (20 ml) and the acidic aqueous layer was separated. The aqueous phase was cooled to 0°C, EE (20 ml) and *n*-dodecane (1.022 g, 6 mmol) was added and the reaction mixture was made strongly alkaline by adding aqueous NaOH (17 *M*, 4 ml) with stirring. The organic phase was separated and the aqueous phase was extracted again with EE (20 ml). The combined organic phase was dried over anhydrous $MgSO_4$ and an aliquot was withdrawn for GC analysis. The EE solution of the amine was reacted with ethereal HCl (2 *M*, 6 ml) to precipitate the amine as its hydrochloride. The solid thus obtained was isolated, washed with EE (5 x 2 ml) and dried (25°C, 12 torr), 1.1 g (81%): mp 182-186°C; ^{1}H NMR δ 1.05 (*d*, *J* = 7 Hz, 3H), 1.1-2.33 (*m*, 7H), 3.0-3.3 (*m*, 1H), 4.70 (broad *s*, 3H); ^{13}C NMR δ 20.14, 24.72, 32.90, 35.04, 41.71, 61.37.

n-Octylamine Hydrochloride. ^{1}H NMR δ 0.97 (unresolved *t*, 3H), 1.45 (broad *s*, 12H), 3.1 (*t*, *J* = 6 Hz, 2H), 4.73 (*s*, 3H); ^{13}C NMR δ 16.30, 25.09, 28.99, 29.73, 31.57, 31.67, 34.30, 42.29.

2-Methyl-1-pentylamine Hydrochloride. ^{1}H NMR δ 0.87-1.87 (*m*, 6H), 1.90-2.27 (*m*, 5H), 2.93 (*m*, 2H), 4.70 (*s*, 3H); ^{13}C NMR δ 16.30, 19.16, 21.86, 33.39, 38.27, 47.98.

2-Butylamine Hydrochloride. ^{1}H NMR δ 1.0 (*t*, *J* = 7 Hz, 3H), 1.32 (*d*, *J* = 7 Hz, 3H), 1.62 (quintet, *J* = 7 Hz, 2H), 3.37 (unresolved sextet, *J* = 7 Hz, 1H), 4.70 (*s*, 3H); ^{13}C NMR δ 11.80, 20.07, 29.91, 52.07.

3-Hexylamine Hydrochloride. ^{1}H NMR δ 0.95-1.30 (*m*, 6H), 1.40-2.2 (*m*, 6H), 3.38 (unresolved *q*, 1H), 4.73 (*s*, 3H); ^{13}C NMR δ 11.52, 15.93, 20.58, 27.72, 36.32, 55.80.

exo-2-Norbornylamine Hydrochloride. ^{1}H NMR δ 1.13-2.13 (*m*, 8H), 2.43 (broad *s*, 3H), 3.27 (*m*, 1H), 4.73 (*s*, 3H); ^{13}C NMR δ 28.85, 29.85, 37.08, 38.69, 39.49, 43.11, 56.79.

3-Methyl-2-butylamine Hydrochloride. ^{1}H NMR δ 1.04 (*d*, J = 7 Hz, 6H), 1.31 (*d*, J = 7 Hz, 3H), 2.01 (*m*, 1H), 3.30 (*m*, 1H), 4.73 (*s*, 3H); ^{13}C NMR δ 17.37, 19.48, 20.64, 33.77, 55.90.

trans-2-Methylcyclohexylamine Hydrochloride. ^{1}H NMR δ 1.05 (*d*, J = 6 Hz, 3H), 1.2-2.2 (*m*, 9H), 2.7-3.1 (*m*, 1H), 4.70 (*s*, 3H); ^{13}C NMR δ 20.56, 27.04, 27.47, 33.40, 36.02, 38.55, 59.39.

trans-2-Phenylcyclopentylamine Hydrochloride. ^{1}H NMR δ 1.65-2.55 (*m*, 6H). 2.95-3.95 (*m*, 2H), 4.73 (*s*, 5H); ^{13}C NMR δ 24.91, 32.78, 36.08, 53.10, 61.29, 130.01, 130.25, 131.72, 143.62.

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