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Chemistry of 2-hydroxy-2-(dimethylaminomethyl)-1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane

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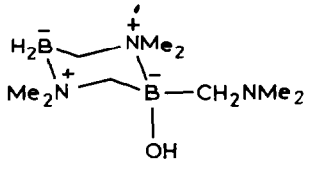
Abstract

Reactions at OH and NMe_2 functionalities of 2-hydroxy-2-(dimethylaminomethyl)-1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane produce acetyl, alkyl, and borane derivatives, some of which have a structural analogy to choline and acetylcholine. The BOH function generally is not hydrogen bonded when the amine is quadrivalent. Notable kinetic stability towards air and aqueous environments is observed for acetyl derivatives.

The novel heterocycle, 2-hydroxy-2-(dimethylaminomethyl)-1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane (**1**) [1] has three functional sites, BH,



(1)

CH_2NMe_2, and BOH. A study of reactivity of the latter two has led to the isolation and characterization of alkyl, acetyl, and borane derivatives. An important concern in the investigation was whether the structural integrity of the parent six-membered ring could be retained in substitutions since the ring is theoretically a multipolar acid–base dimer of a biphilic monomer, and one of the ring borons is labilized by hydroxyl. Formal charge which results from adduct formation is shown in the above structure by + and − symbols. Cleavage of the adduct bonds by a strongly acidic or basic reagent is possible, and, should it occur readily, could preclude efforts to develop an extended derivative chemistry.

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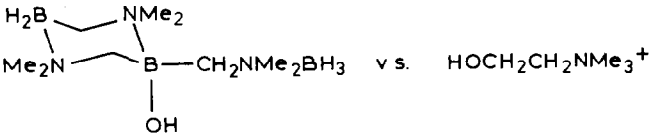
Borane and proton adducts

Reaction of **1** with THF-BH_3 in THF (tetrahydrofuran) solution is rapid, with no hydrogen evolution, producing a sublimable, air-stable adduct, **2**. An extremely sharp OH stretch absorption in the IR at 3550 cm^{-1} implies that there is little or no hydrogen bonding. Absence of the broad BO absorption near 1340 cm^{-1} characteristic of trigonal boron-bonded oxygen [2] confirms that the hydroxylated boron is still tetrahedral. The OH stretching frequency is comparable to that (3500 cm^{-1}) of a similar tetravalent BOH in the substituted-pyridine(py′)-boronic acid, py′-$B(OH)Ph_2$ [3]. The proposed structure is analogous to that of choline, at least in geometry and separation of the biologically active OH and NMe_3 functions by the equivalent of two tetrahedral carbon atoms, a known feature of choline-like neurotransmitters [4]. The BH_3 group is isomorphous to (but of different polarity than)



(**2**)

the methyl group of choline. This analogy recently has been illustrated in dimethylaminoethanolborane and related adduct models of choline and acetylcholine investigated by Spielvogel and co-workers [5].

A proton adduct cation, **3**, was obtained by ion exchange or competitive reactions (eq. 1 and 2, wherein **1** is abbreviated HOHA = hydroxylated heterocyclic amine).

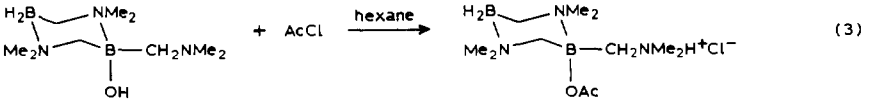
$$\mathrm{HOHA} + \mathrm{H_2O} \rightleftharpoons \mathrm{HOHAH^+OH^-} \xrightarrow{\mathrm{Q^+Cl^-}} \underset{(3)}{\mathrm{HOHAH^+Cl^-}} \qquad (1)$$

$$\mathrm{HOHA} + (\mathrm{Et_3NH^+})\mathrm{PF_6^-} \rightarrow \underset{(3)}{\mathrm{HOHAH^+PF_6^-}} + \mathrm{Et_3N} \qquad (2)$$

The salts are stable for extended periods of time in aqueous or chloroform solutions and in contact with air. There was no evidence for loss of water intermolecularly to produce spiro-ring systems, even under forcing conditions or in the presence of dehydrating agent (phosphorus pentoxide).

O-Acylated derivatives

The hydroxyl function of **1** was acylated in a manner analogous to that of organic alcohols (eq. 3). The reaction is very rapid with the appearance of a reaction of a

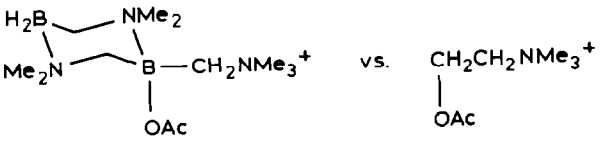


(3)

(**1**) (**4**)

Lewis acid with a Lewis base. The product is a crystalline, air- and water-stable, protonated amine salt. Subsequent quaternization of the parent amine was accom-

plished by a slow heterogeneous reaction in which a chloroform solution of the salt and methyl iodide is contacted with sodium carbonate. The resulting cationic derivative, **5**, is structurally related to acetylcholine.



(**5**)

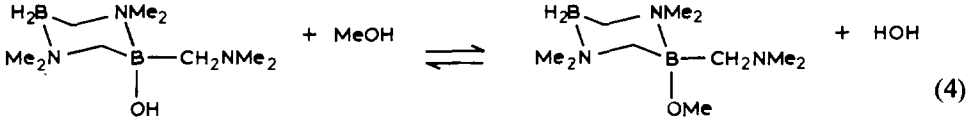
Because of the similarity of **2**, **5** (as the PF_6^- salt), and $HOHAMe^+PF_6^-$ with biologically active species, samples have been submitted for evaluation by means of in vitro screens of the Dupont Company. No significant anticancer, cardiovascular, central nervous system, or anti-infective activity, however, was found.

Generally, an aromatic or aromatically substituted boron is needed for sufficient stability of the BOH function to display the "normal" reactivity of OH. Stability of Ph_3BOH^- in various solvents [6], formation of $(2\text{-}CH_3C_6H_4)(Bu)BOLi$ [7], and various hydroxylated borazaro and boroxaro systems [8] may be cited. Thus the robust and at times "normally" functioning BOH of **1** is unusual.

Stereochemistry of the product has not been established; the quaternary amine is shown equatorial only because of its somewhat larger bulk compared to acetyl. Proton NMR signals of the *N*-methyl groups are four closely spaced singlets, compatible with a chair form of ring, inverting or not. Other monosubstituted derivatives of the parent ring similarly display four *N*-methyl resonances, including one in which no inversion occurs [9*]. That the parent heterocycle and some of its derivatives can invert has been unequivocally determined by study of the temperature dependence of the bis(neopentyl)-substituted derivative [10].

O-Alkyl derivatives

O-Alkylation was accomplished only with methyl. Simple dissolution of **1** in methanol leads to equilibration (eq. 4). A similar exchange with ethanol was not



(4)

(**6**)

observed. The methoxide derivative is a crystalline solid, whereas **1** is a liquid. Subsequent alkylation of the amine function of the methoxide derivative produced a cation, **7**, sensitive to hydrolysis. This lability of the *O*-alkyl is in sharp contrast to the aqueous stability of *O*-acetylated derivatives.

A borane adduct of the methoxide can be made in hexane solution from diborane(6) directly. It is an oil (in contrast to the crystalline borane adduct of HOHA), soluble in this solvent. Like the *N*-methyl cation **7** it rapidly is hydrolyzed

* A reference number with an asterisk indicates a note in the list of references.

irreversibly, even by traces of moisture in air, to the borane adduct of HOHA. This lability to water of methoxide derivatives cannot derive merely from cationic charge since the borane adduct is neutral. Irreversible hydrolysis of alkylated or borane adduct derivatives of MeOHA, on the one hand, and the reversible equilibration of HOHA with methanol, on the other, is curious. Since methyl/hydrogen exchange is unlikely, the mechanism for equilibration probably involves methoxide attack with ring opening or formation of a 5-coordinate transition state. A highly restricted transition can be inferred by the failure of ethanol to undergo reaction. The hydrolyses of the methyl and borane derivatives unlikely do not involve basic species like methoxide, since both are neutral in solution. A possible site for attack would be the boron-bonded oxygen acting as a Lewis base toward water, followed in a concerted fashion with OMe/OH group exchange. The less basic oxygen of the acetyl derivatives **4** and **5**, a consequence of resonance effects, would explain their greater hydrolytic stability. Hydroxylic deuterium exchange in D_2O for $HOHAMe^+$ was found to be dependent on basic catalysis, presumably via exchange of OD^- for OH^-.

N-Alkylated derivatives

Alkylation typical of organic amines proceeds with **1** and alkyl halides. The methyl derivative $HOHAMe^+$ has been reported previously [1], but longer chain derivatives more suited as surfactants were sought, using lauryl and cetyl bromides. Solvent choice is crucial to reasonable yields. With DMF (dimethylformamide), using a work-up developed previously [11], alkylated cations, **8** and **9**, as crystalline bromide salts were obtained. Metathesis to hexafluorophosphate salts was surprisingly slow, requiring in one case 2 h standing. This remarkable aqueous solubility, unusual for long chain quaternary salts, must be related to the BOH function since the unhydroxylated analogues [11] are essentially water-insoluble even as the bromides. The OH infrared absorption is much broader than that in the methylated analog $HOHAMe^+$. Crystalline packing effects of the bulkier alkyl may be responsible.

Conclusion

Substitutions at the BOH and amine functions of **1** lead to good yields of derivatives without cleavage of the parent ring adduct bonds. Except for the methoxides, kinetic stability of the derivatives is sufficient for water work-up. The robust nature of the acetyl derivatives relative to methoxide derivatives may be the consequence of resonance effects making the boron-bonded oxygen less basic.

Experimental details

Reagent grade solvents were employed; DMF was dried by distillation from phosphorus pentoxide; $CHCl_3$ was freed from ethanol by washing with water and drying over sodium sulfate, followed by distillation from phosphorus pentoxide. Lauryl and cetyl bromides were prepared from the corresponding alcohols by a standard procedure [12]. Acetyl chloride and THF-borane were used as received. Diborane(6) (Callery Chemical Co.) was essentially free of higher boron hydrides.

Vacuum transfers and sublimations were carried out on a vacuum line equipped with o-ring joints and needle valves, capable of evacuating to pressures of 10^{-5} mmHg. Infrared and low field proton NMR spectral data were obtained on Beckman 4240 and Hitachi/Perkin–Elmer R24B instruments. Microanalytical data are from MicAnal, Tuscon, AZ, and Schwarzkopf Microanalytical Laboratory, Woodside, NY; mass spectral data are from the Midwest Center for Mass Spectrometry, Lincoln, NE; high field proton NMR are from NMR Regional Center, Colorado State University, Fort Collins, CO. Proton chemical shifts are reported in ppm downfield from internal tetramethylsilane with relative proton areas in parentheses. IR data are reported in cm^{-1}, and are for mineral oil mulls, so absorptions masked by the mulling agent are not reported.

2-Hydroxy-2-dimethylaminomethyl-1,1,4,4-tetramethyl-1,1-diazonia-2,5-diboratacyclohexane (1: HOHA)

A total of 3.9 g of the title compound was prepared in seven batches from the controlled hydrolysis of $Li^+Me_2CH_2BH_2CH_2NMe_2BH_2CH_2NMe_2^-$ according to published procedures [1] in overall yields averaging 43%. Stock solutions in hexane solvent were prepared from weighed samples, and portions were used for the reactions described, evaporating the hexane solvent if necessary.

Borane adduct of 1: HOHABH$_3$ (2)

In a standard o-ring-equipped 50-ml reactor, 156 mg (0.726 mmol) **1** was dissolved in 2.0 ml THF (from sodium ketyl) transferred in vacuum. Nitrogen was introduced, and 1.0 mole-equivalent of 1 molar THF-BH_3 was added via syringe dropwise. No gas was evolved. Solvent evaporation under vacuum left a white solid which was subsequently sublimed (80 °C/high vacuum) to give $HOHABH_3$, m.p. 100–102 °C/dec. (sealed cap), 151 mg, 90%. Anal. Found: C, 47.59; H, 14.14; N, 18.69. $C_9H_{30}N_3OB_3$ calcd.: C, 47.25; H, 13.22; N, 18.37%. IR: 3550s, 2360s, 2400 and 2340w shoulders, 2305m, 2275m, 1405w, 1380w, 1370 shoulder, 1355w, 1335w, 1320w, 1300w, 1295 shoulder, 1215m bd, 1205m shoulder, 1230 and 1245w shoulders, 1195m, 1170s, 1160s, 1135w, 1110m, 1085m, 1095w shoulder, 1035w, 1010m, 1020w shoulder, 975m, 945vw, 920w, 905w, 880m, 845m, 805m, 750m, 735w, 685w cm^{-1}.

Proton adduct of 1: HOHAH$^+$Cl$^-$(3 Cl$^-$)

A 36.3 mg sample (0.169 mmol) of **1** was dissolved in deoxygenated water and passed through a Rexyn® 201 chloride ion exchange resin bed. Effluent was collected until neutral. Solvent was removed under vacuum to leave a white solid, $HOHAH^+Cl^-$, m.p. 172–175 °C. Anal. Found: C, 43.11; H, 11.34; N, 16.32. $C_9H_{28}N_3OB_2Cl$ calcd.: C, 43.00; H, 11.23; N, 16.71%. IR: 3495m bd, 2710s, 2390w, 2315m, 2345w shoulder, 2255w, 2235vw, 1350w, 1345 and 1320w shoulders, 1310w, 1292w, 1232w, 1185m shoulder, 1170s, 1155w shoulder, 1135w, 1115m, 1080m, 1030w, 1008–1015m doublet, 980m, 925 shoulder, 940vw, 925w, 855s, 840w, 800m, 755w, 745m, 680w cm^{-1}.

The corresponding PF_6^- salt was prepared by metathesis in a mixture of 72.6 mg (0.338 mmol) **1**, 74.5 mg (0.301 mmol) $NEt_3H^+PF_6^-$, and 2 ml of chloroform. After stirring 2 days, the crystalline solid was filtered and dried under vacuum, 56.5 mg $HOHAH^+PF_6^-$, m.p. 146–148 °C, 52% yield. Anal. Found: C, 29.84; H, 8.00; N,

11.40. $C_9H_{28}N_3OB_2PF_6$ calcd.: C, 29.95; H, 7.81; N, 11.64%. Proton NMR ($CDCl_3$ 300 MHz): NMe 2.799 doublet (3) (J(HNCH) 4.8 Hz); NMe 2.685 doublet (3) (J(HNCH) 3.9 Hz); ring N-methyl 2.643 (3), 2.501 (3), 2.440 (3), 2.389 (3). IR: 3650m, 3670w shoulder, 3250m, 3180w, 2410w, 2330m, 2275w, 1350w, 1340w, 1325w, 1300w, 1205w, 1175m, 1185w shoulder, 1155w, 1130w, 1110w, 1065m, 1085w shoulder, 1075m, 1010m, 1020 shoulder, 980–970m, 930w, 840s doublet cm^{-1}.

To rule out the possibility that the salt was a dimeric dication produced by loss of water, N-methylation was carried out on a 14 mg sample in acetonitrile with excess methyl iodide and sodium carbonate. After stirring overnight, solvent was removed to give a nearly quantitative yield of a mixture of iodide and PF_6^- salts of $HOHAMe^+$. Recrystallization from hot water gave the pure PF_6^- salt with an identical infrared spectrum as a known, sample made by methylation of HOHA directly. It is unlikely that weakly nucleophilic carbonate, insoluble in acetonitrile, would have cleaved an oligomeric cation had it been present. Reaction in the absence of methyl iodide gave HOHA by deprotonation.

O-Acetylation of ***1****: AcOHAMe*$^+$ *PF*$_6^-$ *(****5*** *PF*$_6^-$*)*

Acylation of **1** was carried out with acetyl chloride or acetic anhydride in hexane or chloroform solutions. In 2 ml hexane, 145 mg **1** (0.658 mmol) was treated with 50 μl acetyl chloride, whereupon a white solid immediately precipitated. After solvent removal in vacuum, the solid was dissolved in 4 ml anhydrous chloroform and treated with 0.5 ml methyl iodide and a small portion of sodium carbonate. The mixture was stirred for 12 h in an o-ring-equipped reaction flask. Filtration of solid and evaporation of solvent gave a solid product that was then metathesized with aqueous ammonium hexafluorophosphate. The PF_6^- salt was recrystallized from methylene chloride/hexane to give crystalline, white $AcOHAMe^+PF_6^-$; 96 mg, 36%, m.p. 155–157°C. Anal. Found: C, 34.50; H, 7.92; N, 9.80. $C_{12}H_{32}N_3O_2B_2PF_6$ calcd.: C, 34.56; H, 7.74; N, 10.08%. Proton NMR ($CDCl_3$, 360 MHz): NMe_3 3.033 (9), ring N-methyl 2.582, 2.576, 2.553 (2.550 shoulder) (15), CH_3CO 2.045 (3). IR: 2410w, 2370m, 2340m, 2290w bd, 1692s, 1415–1422w doublet, 1350w bd, 1306s, 1315 and 1280vw shoulders, 1240w, 1225w, 1198m, 1205w shoulder, 1185w, 1172m, 1175w shoulder, 1152m, 1130w, 1110–1100w doublet, 1055m bd, 1040m, 1030m, 1002–998m doublet, 970m, 955m, 925–930w doublet, 900m, 880w shoulder, 840s bd, 770w, 742–748w doublet, 725w cm^{-1}.

The product obtained from reaction of **1** with acetic anhydride had identical m.p. and infrared spectrum, except for a small additional peak at 1655 cm^{-1} in the carbonyl region, perhaps due to coprecipitating acetate anion.

$AcOHAH^+PF_6^-$ (**4** PF_6^-) was prepared as a product in a failed attempt to quaternize the nitrogen using lithium bis(trimethylsilyl)amide and methyl iodide, m.p. 172–173°C. Anal. Found: C, 32.52; H, 7.40; N, 10.21. $C_{11}H_{30}N_3O_2B_2PF_6$ calcd.: C, 32.79; H, 7.50; N, 10.42%. IR: 3090w, 2405w shoulder, 2350m bd, 2280w, 2260w shoulder, 1660m, 1340m, 1330m, 1320m, 1310m, 1290m, 1235w, 1195m, 1190 and 1205vw shoulders, 1170m, 1155vw shoulder, 1135–1125w doublet, 1120w, 1105w, 1055m, 1035m, 1000m, 965m, 950vw, 930w, 895m, 880m, 940s, 780w, 750w, 735w cm^{-1}. Proton NMR (360 MHz, $CDCl_3$): substituent NMe_2 2.920, 2.871 (6); NMe_2 ring 2.681, 2.659, 2.620, 2.592 (12.3); CH_3CO_2 2.174 (2.3).

An attempt to acetylate $HOHAMe^+PF_6^-$ with acetic anhydride in chloroform solution stirred with sodium carbonate gave only recovered starting material (75%).

O-Methylation. MeOHA (6) and derivatives

A solution of 89.8 mg **1** in 3 ml methanol was allowed to stand 2 h and the solvent removed to leave a somewhat soft solid. Another treatment with a new quantity of methanol gave a hard crystalline product subliming at 40–50 °C, 46 mg, m.p. 38–43 °C, IR: 2710s, 2385m, 2330s, 2275w, 1335w, 1320m, 1325vw shoulder, 1300m, 1270w, 1250w, 1240w shoulder, 1195–1185m doublet, 1165s, 1150m, 1125m, 1100s bd, 1110 and 1095w shoulders, 1045m, 1155w shoulder, 1035m, 1025m, 1005s, 970s, 960m, 920m, 935w shoulder, 885s, 875w shoulder, 840w, 820w, 800vw bd, 780m, 745m, 735m, 675w cm^{-1}. Proton NMR (60 MHz, CD_3CN): OMe 3.07; NMe_2 ring 2.72, 2.66, 2.58, 2.40, 2.38; NMe_2 substituent 2.12. Proton NMR of **1** in $CDCl_3$, for comparison has NMe_2 ring (12) 2.80, 2.55, 2.45, 2.40; NMe_2 substituent (6),

Table 1

Mass spectral data [a]. MeOHA (6), $C_{10}H_{29}N_3OB_2$

Composition	*m/e*	Δ, mmass	Int		Assignment
			Obs.	Calcd. [b]	
$C_{10}H_{29}N_3O^{11}B_2$	229.2503	0.6	0.2		Parent
$C_{10}H_{28}N_3O^{11}B_2$	228.2411	−0.7	2.9		*P* − 1,
$C_{10}H_{28}N_3O^{11}B^{10}B$	227.2468	1.3	1.9	1.4	
$C_{10}H_{28}N_3O^{10}B_2$	226.2516	2.5	0.1	0.2	
$C_9H_{24}N_3O^{11}B_2$ [c]	212.2118	1.3	0.5		
$C_9H_{24}N_3O^{11}B^{10}B$ [c]	211.2126	3.6	0.3	0.2	
	199.2367		3.6		
$C_9H_{26}N_3{}^{11}B_2$ [c]	198.2322	0.9	13.0		
$C_9H_{26}N_3{}^{11}B^{10}B$ [c]	197.2335	−1.4	6.5	6.4	
$C_7H_{21}N_2O^{11}B_2$	171.1843	0.3	39.9		
$C_7H_{21}N_2O^{11}B^{10}B$	170.1875	−0.1	18.6	19.7	
$C_6H_{19}N_2O^{11}B_2$	157.1679	−0.4	6.6		
$C_6H_{19}N_2O^{11}B^{10}B$	156.1725	0.5	3.0	3.2	
$C_6H_{17}N_2O^{11}B_2$	155.1566	4.0	5.5		
$C_6H_{17}N_2O^{11}B^{10}B$	154.1587	2.4	1.5	2.7	
$C_6H_{19}N_2{}^{11}B_2$	141.1722	−1.2	7.0		
$C_6H_{19}N_2{}^{11}B^{10}B$	140.1779	4.5	1.6	1.8	
	140.1690		1.0		
	140.1496		0.6		
	140.1447		1.2		
	112.1194		19.9		
	111.1150		12.9		
	100.0928		15.0		
	99.1053		29.3		
	98.1107		10.8		
	97.1008		16.7		
	84.0966		72.6		
	83.0966		33.0		
	81.0723		11.8		
	71.0870		24.4		
$C_3H_9N^{11}B$	70.0824	−0.4	59.1		
$C_3H_9N^{10}B$	69.0867	0.3	12.1	14.6	
C_3H_8N	58.0680	2.2	100		Me_2NCH_2

[a] Electron ionization data from Midwest Center for Mass Spectrometry. [b] Intensity calculated from isotope abundance, based on most intense peak of a cluster. [c] High mass cluster found in HOHA [1].

2.19, CH_2 1.4–2 broad multiplet. Mass spectral data are collected in Table 1. Crystals revert to liquid **1** on exposure to air for a day.

Treatment of the 46 mg MeOHA with methyl iodide in methanol for a day gave a clear film residue after solvent evaporation. Metathesis to the PF_6^- salt in water only slowly deposited crystals of $HOHAMe^+PF_6^-$, identified by its IR spectrum. Hydroxylic deuterium exchange experiments with this latter salt showed exchange merely by contact with (since most was not in solution) a D_2O sample that was contaminated with silicate. The OH infrared absorption at 3680, shoulder at 3660 changed to OD absorption at 2715 cm^{-1} and remained without change in air overnight. Exchange appears to require liquid contact and presence of base. Contact with water in absence of the silicate contaminant did not lead to exchange. With the silicate, slow exchange was observed.

A 62 mg sample (0.27 mmol) of MeOHA was dissolved in hexane and treated with 0.136 mmol of diborane(6). The mixture turned opalescent but did not deposit a solid. Evaporation of solvent under vacuum, followed by attempted sublimation led to a clear liquid distillate on the cold finger. The product infrared spectrum rapidly changed to that of $HOHABH_3$ in the air. An attempt to reverse the transformation by addition of methanol to $HOHABH_3$, warming and standing 2 h gave unreacted material.

In attempts to use ethanol in place of methanol for *O*-alkylation, no ethyl proton NMR resonance appeared in the residue after repeated treatments with ethanol over a period of days.

N-Alkylation. HOHA-cetyl$^+$*Br*$^-$ *(9 Br*$^-$*), HOHA-lauryl*$^+$*Br*$^-$ *(8 Br*$^-$*)*

A solution of 54.8 mg (0.255 mmol) **1**, 160 μl (0.53 mmol) cetyl bromide, and 2 ml DMF contained in an o-ring-equipped reactor was mixed and allowed to stand 12 h at room temperature. Addition of dry ether precipitated a crystalline solid which was collected and vacuum dried to give HOHA-cetyl$^+$Br$^-$, 61.2 mg, 46%, m.p. 103–104°C. Anal. Found: C, 57.97; H, 11.87; N, 7.58. $C_{25}H_{60}N_3OB_2Br$ calcd.: C, 57.71; H, 11.62; N, 8.08%. IR (PF_6^- salt) 3330v bd w, 2390vw, 2320w, 1340w, 1310w, 1180w shoulder, 1170m, 1160w shoulder, 1135w, 1100m, 1060m bd, 1030m, 1000m bd, 970m, 840s bd, 855 shoulder cm^{-1}.

By a similar procedure but with heating at 40°C for 7 days in an ampoule, HOHA-lauryl$^+$Br$^-$ was prepared in 40% yield, m.p. 138–141°C. Anal. Found: C, 54.50; H, 11.63; N, 8.86. $C_{21}H_{52}N_3OB_2Br$ calcd.: C, 54.34; H, 11.29; N, 9.05%. IR: 3450m bd, 2390w, 2325m, 2280 and 2300w shoulders, 2250w, 1335w, 1315w, 1235w, 1190w, 1165s, 1170 and 1155w shoulders, 1130w, 1140w shoulder, 1105m, 1005m, 970m, 940w, 930w, 910w, 900m, 845m, 820m, 760w, 720w cm^{-1}.

Neither the *N*-lauryl nor the *N*-cetyl salt has the sharp OH stretch characteristic of the *N*-methyl derivative.

Acknowledgement

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