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Organic Derivatives of Boron.
Part I. Reactions of Alkanolamines with Ethyl Borate

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Reactions of alkanolamines [R_1R_2NXOH; $R_1 = H$, CH_3, C_2H_5, $C_4H_9^t$, C_6H_5; $R_2 = H$; CH_3, C_2H_5 *and* X = $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CHCH_3$, $-C_6H_4CH_2CH_2-$, $-CH_2CH_2SCH_2CH_2-$] *with ethyl borate in different molar ratios (1 to 3) yield the tris-product only. All the derivatives are distillable liquids, soluble in common organic solvents and susceptible to hydrolysis even by atmospheric moisture. The new derivatives are characterized by elemental analyses, I.R., ^1H NMR spectra, refractive indices and molecular weight measurements.*

Introduction

Alkoxy derivatives of boron have received extensive attention during the last three decades whereas little attention appears to have been paid to orthoborates containing nitrogen in the organic moiety [1–7]. These derivatives may be interesting due to the possibility of internal coordination from nitrogen to boron. A few interesting results obtained from the alcohol interchange reactions with various metals *e.g.*, organosilicon [8–9], organotin [10–12] and titanium [13] *etc.* have been reported from our laboratories. Keeping in view the encouraging results obtained, the alcohol interchange technique was utilized to synthesise such boron derivatives in order to investigate the probability of internal coordination because of the greater electron deficient nature of boron. Initial attempts in this regard were also carried out in our laboratories [3], but no systematic study, however, appears to have been made. Moreover, the two reactive sites of alkanolamines and the lower stability of unsymmetrical mono- and bis-alkanolamine orthoborates prompted us to carry out and study these reactions in detail.

Results and Discussion

The present paper deals with the reactions of ethyl borate with alkanolamines, *viz.* 2-methylamino, 2-ethylamino, 2-tert-butylamino, 2-phenylamino and 2-(2-aminoethyl)-thioethanol; 3-dimethylamino-1-propanol, 1-diethylamino-2-propanol and *p*-aminophenethyl alcohol.

The reactions may be summarised as follows:

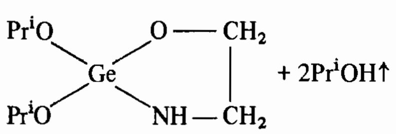
$$B(OEt)_3 + 3HOXNR_1R_2 \xrightarrow{\text{benzene}} B(OXNR_1R_2)_3 + 3EtOH\uparrow$$

(where R_1 = H, CH_3, C_2H_5, $C_4H_9^t$, C_6H_5; R_2 = H, CH_3, C_2H_5 and X = $-CH_2-CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2\underset{|}{C}HCH_3$, $-C_6H_4CH_2CH_2-$, $-CH_2CH_2SCH_2CH_2-$)

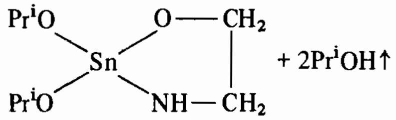
Ethyl borate was refluxed with alkanolamines in stoichiometric ratios using benzene as a solvent. The progress of the reaction was checked by the estimation of the azeotrope collected with the help of a fractionating column. It was observed that the liberation of the first two mol of ethanol was fast. However, the liberation of the third mol was rather slow, but it could be achieved by prolonging the refluxing time.

The reactions of germanium [14] and tin [15–16] alkoxides with alkanolamines are facile and in contrast to their reactions with alkyl borates, both the protons of OH and NH_2 get replaced.

$$Ge(OPr^i)_4 + HOCH_2CH_2NH_2 \xrightarrow{\text{benzene}}$$



$$Sn(OPr^i)_4 + HOCH_2CH_2NH_2 \xrightarrow{\text{benzene}}$$



$$3Bu_3SnOEt + HOCH_2CH_2NH_2 \xrightarrow{m\text{-dichlorobenzene}} Bu_3SnOCH_2CH_2N(SnBu_3)_2 + 3EtOH\uparrow$$

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The reaction of ethyl borate with N-methylethanolamine in 1:1 and 1:2 molar ratios (Table IV) gave ethanol equivalents in amounts to the N-methylethanolamine taken, indicating that probably only the hydroxy group is reactive. The lack of reactivity with NH_2 protons in the case of boron derivatives could be attributed to the strong (p–p) π interaction of the B–O bond. Absence of d-orbitals as well as smaller radius of the boron atom could be presumed as additional factors for the lack of this reactivity. This is further revealed by the M–O bond energies of these elements: B–O ~ 128 (B_2O_3) [17], Si–O ~ 112 (SiO_2) [18]; Ge–O ~ 85 (GeO_2) [19] and Sn–O ~ 82 (SnO_2) Kcal mol^{-1}.

A marked tendency of higher boiling points observed in case of NH_2 derivatives can be presumed to be due to enhanced hydrogen bonding; the lower boiling points observed in the reported derivatives containing NHR and NRR_1 are in good correlation with the observation.

All the derivatives of boron are found to be monomeric in boiling benzene, whereas those of germanium and tin are polymeric. This may be due to the smaller radius of boron atom, which hinders intermolecular association through nitrogen and/or oxygen.

All the new derivatives reported in Table I are monomeric, colourless liquids (except a few), soluble in common organic solvents and hygroscopic in nature.

I.R. Spectra

The I.R. spectra of these derivatives have been recorded in the region 400–4000 cm^{-1}. The presence of bands in the region 1300–1380 cm^{-1} is in agreement with the reported values [20] of ν_{as} (B–O) stretching modes. The disappearance of O–H stretching modes, usually served in the region 3590–3650 cm^{-1}, in case of the derivatives obtained from dialkylaminoalkanols is a pretty good indication for complex formation taking place through the OH group. The retention of N–H stretching frequency at ~3360 cm^{-1} in case of derivatives obtained from the rest of aminoalkanols again emphasizes the non-reactivity of the hydrogen present on nitrogen in these ligands. Cragg *et al.* [21–22] interpreted the appearance of a shoulder on the ν(N–H) stretching mode as being due to some association in the case of 2-phenyl-1,3,2-oxazaborolans and 2-phenyl-1,3,2-azathiaborolidine. However, no such shoulder is present in the spectra of the derivatives reported in this communication. This further supports the monomeric nature of newly synthesized derivatives. Absorption bands characteristic of δ(N–H) are also observed in the region 1590–1620 cm^{-1} in primary aminoalkoxy derivatives.

Two bands appearing in the region 1070 ± 20 cm^{-1} and 1000 ± 20 cm^{-1} may be assigned to the ν_{as}(C–O) and ν_s(C–O) stretching modes, respectively, of the alkanolamine system. Absorption bands at 1460–1485 cm^{-1} and 2780–2825 cm^{-1} characteristic of $\delta(CH_3–N)$ and $\nu(CH_3–N)$ respectively [23] are present in the spectra of substituted aminoalkoxides as well as in the corresponding alkanolamines. In case of derivatives synthesized from 2-phenylaminoethanol and *p*-aminophenethyl alcohol, characteristic bands of phenyl ring, with peaks at 1410–1435 cm^{-1}, 1465–1480 cm^{-1} and 1590–1620 cm^{-1} are observed, which are due to CH, C=C vibrations and ring deformations. The bands appearing in the region 750–760 cm^{-1} and 675–705 cm^{-1} may be due to 'X-sensitive' planar ring vibrations and out-of-plane hydrogen deformation modes. Similar assignments were made by Kriegsmann *et al.* [24]. Several other bands with weak to strong intensities appearing in the region 500–900 cm^{-1} are due to rocking of CH_3 or CH_2 groups attached to nitrogen and skeletal vibrations of the complexes.

The smaller size of boron atom has no appreciable effect on the I.R. spectra of the aminoalkoxy part of the complexes, as the assignments for this part are quite in agreement with such complexes of titanium [13] and tin [16].

The assignments are summarized in the Table II.

^1H NMR Spectra

Fenske and Becher [25] reported the ^1H NMR spectrum of triptych-boroxazolidine and assigned the peaks at 3.94 and 3.13 (δ values) to OCH_2 and NCH_2 protons respectively. The triplets obtained in case of reported derivatives at 4.15 ± 0.18 and 3.02 ± 0.45 (δ values) for OCH_2 and NCH_2 protons respectively are in good agreement with the above values and thus lend support to the purity of the derivatives reported in this communication. The δ values of 2.60, 2.50 for Me; 3.97, 4.09 for OCH_2 and 2.90, 2.70 for NCH_2 for the complexes $B(OCH_2CH_2NHMe)_3$ and $B(OCH_2CH_2CH_2NMe_2)_3$ closely resemble the values observed in such type of derivatives of titanium [13]. The other δ values of some complexes are summarized in Table III.

Experimental

Glass apparatus with interchangeable glass joints was employed. Precautions were taken to exclude the moisture. Solvents were dried by established methods. Alkanolamines were distilled before use. Ethyl borate (Fluka) was used as such.

Ethanol collected in the azeotrope was estimated by oxidimetric method [26]. Boron was estimated by the method reported by Thomas [1] and nitrogen by Kjeldahl method.

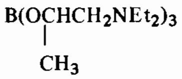
Molecular weights were determined in a semimicro ebulliometer (Gallenkamp) in boiling benzene.

TABLE I. Reactions of Ethyl Borate with Aminoalcohols. Analytical Data.

S. No.	Reactants	Mol ratio	Products and Nature	B.P. °C/mm	Yield % of distilled product	EtOH Liberated found (calc.) (in g)	Analysis		Mol. Wt. found (calcd.)	n_D^{30}
							% B found (calcd.)	% N found (calcd.)		
1	$B(OEt)_3$ $MeNHCH_2CH_2OH$	1:3	$B(OCH_2CH_2NHMe)_3$ colourless liquid	65/0.5	88	5.03 (5.07)	4.61 (4.64)	18.01 (18.00)	222 (233)	1.4570
2	$B(OEt)_3$ $EtNHCH_2CH_2OH$	1:3	$B(OCH_2CH_2NHEt)_3$ colourless liquid	68/0.6	89	3.03 (3.07)	3.82 (3.92)	15.06 (15.25)	261 (275)	1.4520
3	$B(OEt)_3$ $Me_3CNHCH_2CH_2OH$	1:3	$B(OCH_2CH_2NHCMe_3)_3$ colourless liquid	74/1.0	94	2.23 (2.25)	2.94 (3.01)	11.45 (11.68)	365 (360)	1.4265
4	$B(OEt)_3$ $C_6H_5NHCH_2CH_2OH$	1:3	$B(OCH_2CH_2NHC_6H_5)_3$ yellow liquid	210/0.6	95	2.33 (2.47)	2.57 (2.58)	9.82 (10.01)	410 (420)	1.5590
5	$B(OEt)_3$ $Et_2NCH_2CH_2OH$	1:3	$B(OCH_2CH_2NEt_2)_3$ Brownish liquid	152/0.8	90	1.76 (1.77)	3.05 (3.01)	11.61 (11.68)	340 (359)	1.4290
6	$B(OEt)_3$ $Me_2NCH_2CH_2CH_2OH$	1:3	$B(OCH_2CH_2CH_2NMe_2)_3$ colourless liquid	205/0.6	86	1.27 (1.29)	3.31 (3.40)	12.93 (13.22)	317 (318)	1.4350
7	$B(OEt)_3$ $Et_2NCH_2CH(OH)CH_3$	1:3	$B(O\overset{\overset{CH_3}{\vert}}{C}HCH_2NEt_2)_3$ colourless liquid	160- 162/0.6	78	1.68 (1.72)	2.67 (2.69)	10.21 (10.46)	380 (402)	1.4210
8	$B(OEt)_3$ p-$H_2NC_6H_4CH_2CH_2OH$	1:3	$B(OCH_2CH_2C_6H_4NH_2\ p)_3$-[a] dark brown viscous liquid	–	100	2.03 (2.09)	2.57 (2.58)	9.94 (10.01)	412 (420)	–
9	$B(OEt)_3$ $H_2NCH_2CH_2S{\cdot}CH_2CH_2OH$	1:3	$B(OCH_2CH_2SCH_2CH_2NH_2)_3$ [a] yellow viscous liquid	–	99	2.36 (2.45)	2.88 (2.91)	11.21 (11.32)	350 (371)	–

[a] Could not be distilled even at bath temperature of 290 °C at 0.6 mm pressure.

TABLE II. I.R. Assignments (in cm^{-1}).[a]

Compound	ν_{as}(N–H)	ν_{as}(B–O)	Other characteristic bands
$B(OCH_2CH_2NHMe)_3$	3320s	1330m	2875mb, 2800m, 1470m, 1070m, 1000sh, 920mb, 800s, 660s
$B(OCH_2CH_2NHEt)_3$	3280m 3320m	1340s	2900s, 2800w, 1470s, 1020–40mb, 950m, 780m, 710m, 660s
$B(OCH_2CH_2NHCMe_3)_3$	3300–3340mb	1340b	2900sh, 2780w, 1480w, 1070s, 1025vs, 980vs, 840mb, 790s, 720vs, 670vs
$B(OCH_2CH_2NHC_6H_5)_3$	3400s	1320s	2950s, 2880s, 2790w, 1605vs, 1465s, 1435s, 1120s, 1055s, 990vs, 900mb, 870s, 750vs, 695vs, 660s, 505s
$B(OCH_2CH_2NEt_2)_3$	–	1300m 1325–1340mb	3000s, 2840s, 1480w, 1080m, 1060ms, 1000sh, 920vs, 800mb, 850vs, 805s, 785s, 730s, 710s, 690w, 670vs, 540mb
$B(OCH_2CH_2CH_2NMe_2)_3$	–	1325sh, 1355sh, 1380s	2895s, 2850s, 2800s, 1470m, 1085s, 1060s, 1010s, 925s, 895s, 845s, 780s, 705s, 660s, 525ms
 $B(O\underset{CH_3}{C}HCH_2NEt_2)_3$	–	1335m	2900s, 2830mb, 1485m, 1090s, 1040ms, 920vs, 890mb, 850s, 810s, 795s, 740s, 715s, 675s, 535mb
$B(OCH_2CH_2C_6H_4NH_2\text{-}p)_3$	3350s, 3420ms	1325s 1345sh	2950s, 2900sh, 1620s, 1590ms, 1480vs, 1410s, 1120s, 1050mb, 1020s, 820s, 750w, 690m, 655s, 545s, 520s

[a]Abbreviations: vs = very strong, s = strong, m = medium, ms = medium strong, sh = shoulder, mb = medium broad, w = weak, vw = very weak.

TABLE III. ^{1}H NMR Data (δ values).

S. No.	Compound	R	OCH$_2$	NCH$_2$	^{2}CH$_2$	N–H
1	$B(OCH_2CH_2NHMe)_3$	2.60s	3.97t[c]	2.90t	–	3.23s
2	$B(OCH_2CH_2NHEt)_3$	1.33t[a] 3.00q	4.31t	3.11t	–	3.28s
3	$B(OCH_2CH_2NHCMe_3)_3$	1.22t	4.13t	3.02t	–	3.38s
4	$B(OCH_2CH_2NHC_6H_5)_3$	7.22–8.06m	4.07t	3.47t	–	3.83s
5	$B(OCH_2CH_2C_6H_4NH_2\text{-}p)_3$	–[b]	4.31t	2.94t	–	3.80s
6	$B(OCH_2^2CH_2CH_2NMe_2)_3$	2.50s	4.09t	2.70t	1.86p	–

[a]Values represent CH$_3$ and CH$_2$ of Et respectively. [b]Multiplet due to ring obtained at 7.20–7.92 m. [c]s = Singlet, t = triplet, q = quartet, p = pentet, m = multiplet.

Refractive indices were measured by an Abbe refractometer (Toshniwal). I.R. spectra were recorded on a Perkin-Elmer 735 B spectorphotometer (4000–400 cm^{-1}) as neat liquid films and ^{1}H NMR spectra on a Perkin-Elmer R32 spectrometer (MHz 90) in CDCl$_3$ using tetramethylsilane as internal standard.

Reactions between Ethyl Borate and 2-Methylaminoethanol

Reactions between ethyl borate and 2-methylaminoethanol in different molar ratios were carried out in refluxing benzene. The liberated ethanol was removed azeotropically. The removal of excess

TABLE IV. Reactions of Ethyl Borate with N-methyl Ethanolamine in Different Molar Ratios.

No.	$B(OC_2H_5)_3$	Weight of $MeNHCH_2CH_2OH$	C_2H_5OH in azeotrope	Yield of triborate	Found (%)[a] Boron	Found (%)[a] Nitrogen
1	5.50 g (37.67 mmol)	8.28 g (110.4 mmol)	5.03 g (109.3 mmol)	7.56 g (88%)	4.61	18.01
2	2.92 g (20.00 mmol)	3.00 g (39.96 mmol)	1.82 g (39.57 mmol)	2.89 g (93%)	4.62	17.99
3	6.88 g (47.12 mmol)	3.54 g (47.17 mmol)	2.18 g (47.40 mmol)	2.77 g (77%)	4.64	18.03

[a] Calcd for $B(OCH_2CH_2NHMe)_3$: B, 4.64; N, 18.00%.

solvent gave a colourless liquid which was purified by distillation (b.p. 65°/0.5 mm) in every experiment. The other essential details are given in Table IV.

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References

1 L. H. Thomas, *J. Chem. Soc.*, 820 (1946).
2 H. C. Brown and E. A. Fletcher, *J. Amer. Chem. Soc.*, *73*, 2808 (1951).
3 R. C. Mehrotra and G. Srivastava, *J. Ind. Chem. Soc.*, *39*, 521 (1962).
4 R. L. Letsinger and I. Skoog, *J. Amer. Chem. Soc.*, *77*, 2491 (1955).
5 H. Steinberg, *135th Meeting American Chemical Society*, Boston, April, 1959, Abstracts of papers, p. 34-M.
6 R. C. Mehrotra and G. Srivastava, *J. Chem. Soc.*, 4045 (1961).
7 R. C. Mehrotra and G. Srivastava, *J. Chem. Soc.*, 3819 (1962).
8 R. C. Mehrotra and P. Bajaj, *J. Organometal. Chem.*, *24*, 611 (1970).
9 R. C. Mehrotra and P. Bajaj, *J. Organometal. Chem.*, *25*, 359 (1970).
10 R. C. Mehrotra and B. P. Bachlas, *J. Organometal. Chem.*, *22*, 121 (1970).
11 D. P. Gaur, G. Srivastava and R. C. Mehrotra, *Z. Anorg. Allg. Chem.*, *398*, 72 (1973).
12 D. P. Gaur, G. Srivastava and R. C. Mehrotra, *J. Organometal. Chem.*, *63*, 213 (1973).
13 P. C. Bharara, V. D. Gupta and R. C. Mehrotra, *Z. Anorg. Allg. Chem.*, *403*, 337 (1974).
14 R. C. Mehrotra and G. Chandra, *Indian J. Chem.*, *3*, 497 (1965).
15 R. C. Mehrotra and S. Mathur, *J. Organometal. Chem.*, *6*, 11 (1966).
16 D. P. Gaur, G. Srivastava and R. C. Mehrotra, *J. Organometal. Chem.*, *65*, 195 (1974).
17 N. A. Lange, Lange's Hand Book of Chemistry, McGraw–Hill, 11th edition, 1973.
18 T. L. Cottrell, 'Strengths of Chemical Bonds', Butterworth, London, 1958, p. 157.
19 J. L. Bills and F. A. Cotton, *J. Phys. Chem.*, *68*, 802 (1964).
20 T. Tanaka, *Organometal. Chem. Revs.*, *A 5*, 1 (1970).
21 R. H. Cragg and A. F. Weston, *J. Chem. Soc. Dalton*, 1054 (1973).
22 R. H. Cragg and A. F. Weston, *J. Chem. Soc. Dalton*, 93 (1975).
23 L. J. Bellamy, 'The Infrared Spectra of Complex Molecules', Methuen, London, 2nd ed., 1966.
24 H. Kriegsmann and K. H. Schowtka, *Z. Phys. Chem. (Leipzig)*, *209*, 261 (1958).
25 D. Fenske and H. J. Becher, *Chem. Ber.*, *105*, 2085 (1972).
26 D. C. Bradley, F. M. A. Halim and W. Wardlaw, *J. Chem. Soc.*, 3450 (1950).