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Preparation of 2-oxygen derivatives of 1,2-oxaborolane from 2-allyloxy-1,2-oxaborolane

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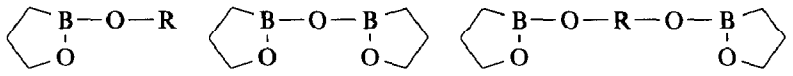
Abstract

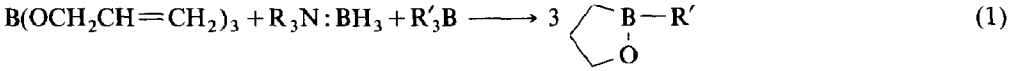
2-Allyloxy-1,2-oxaborolane (V), readily obtained by hydroboration of allyl alcohol with borane reagents such as KBH_4–HOAc, was used as a key reactant in the synthesis of a series of 2-oxygen derivatives of 1,2-oxaborolane. 2-Allyl-1,2-oxaborolane (XXIII) and 2-hydro-1,2-oxaborolane dimethylsulfide complex (XXIV), prepared from the reaction of V with allylmagnesium bromide and dimethylsulfide-borane complex (BMS) respectively, were also used as the reactive intermediates for some of the lower 2-alkyloxy-1,2-oxaborolanes. Five procedures and other probable routes from V to 2-oxygen derivatives of 1,2-oxaborolane are described.

Introduction

The 2-oxygen derivatives of 1,2-oxaborolane, possessing a boron–carbon ring bond and a boron–oxygen ring bond, in addition to an exocyclic boron–oxygen bond, share some of the features of alkyl boranes (R_3B) and borate esters ($(RO)_3B$). The structural form of this class of cyclic boronate esters and related bis-(1,2-oxaborolane)s are shown below:



In 1960 Koester briefly described the first preparation of 1,2-oxaborolane derivatives (eq. 1) [1]. In 1965 Mikhailov and Dorokhov reported the preparation of some 2-alkoxy-1,2-oxaborolanes (I–IV) from triallyl borate (eqs. 2, 3) [2].



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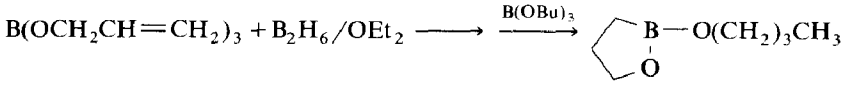
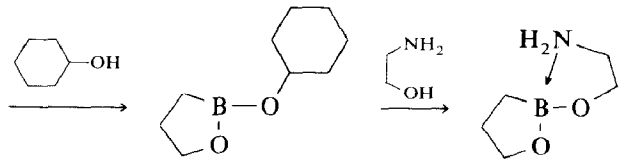
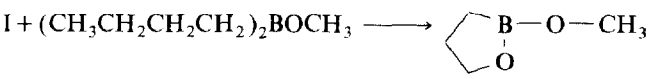


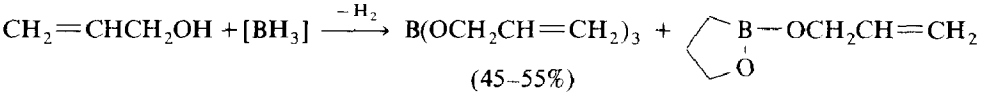
(I, 52%)



(II) (III) (2)



(IV, 97%) (3)



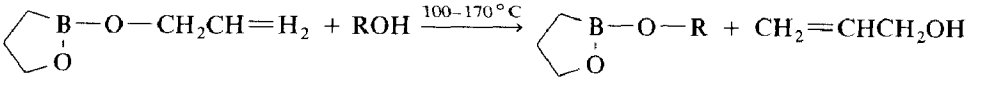
(45–55%) (V, 40–50%) (4)

$[BH_3] = Et_3N : BH_3$ (> 100 °C)
or $[BH_3] = NaBH_4$ or KBH_4 with HOAc (R.T. to 100 °C)

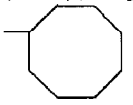
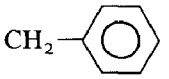
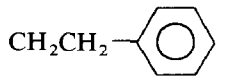
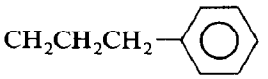
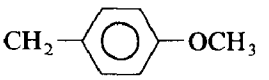
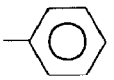
During 1981–1982 we published similar results on the hydroboration of allyl alcohol (eq. 4) and triallyl borate [3,4]. The reaction of allyl alcohol with hydroborating agents, such as triethylamineborane, sodium or potassium borohydride-acetic acid, gives 2-allyloxy-1,2-oxaborolane (V) in addition to triallyl borate in moderate yield. We decided to investigate the general procedure for preparation of 2-substituted derivatives of 1,2-oxaborolane, and herein we report some of the results on the preparation of 2-oxygen derivatives starting from V.

Results and discussion

Dehydrogenation–hydroboration of allyl alcohol with KBH_4–HOAc at room temperature without other solvent directly gives the cyclic product V in 40–50% yield [3]. In turn, the 1,2-oxaborolane V can be used as a convenient starting material for preparing some interesting 2-alkyloxy- and 2-aryloxy-1,2-oxaborolanes by transesterification [4,5] (Procedure A).

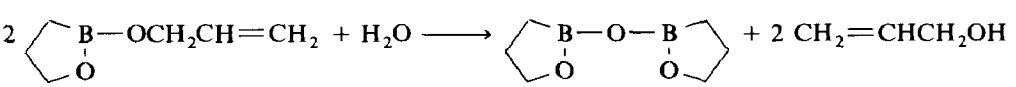


(V) (73–95%) (5)

	R		R
VI	$(CH_2)_4CH_3$	VII	$(CH_2)_7CH_3$
II		VIII	
IX	$CH_2C{\equiv}CH$		
III	$CH_2CH_2NH_2$		
X	$CH_2CH_2OCH_3$	XI	$CH_2CH_2OC_2H_5$
XII	$(CH_2CH_2O)_2C_2H_5$	XIII	$(CH_2CH_2O)_3OC_2H_5$
XIV	CH_2CH_2Cl	XV	CH_2CH_2Br
XVI		XVII	
XVIII			
XIX			
XX			

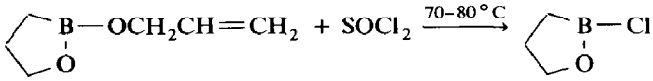
Owing to the greater stability of the 1,2-oxaborolane ring the heat exchange reaction of 2-allyloxy-1,2-oxaborolane (V) with alcohols (or phenols) becomes facile if a slight excess of higher boiling point ($> 100\,°C$) alcohols is used. A variety of products (II, III and VI–XX) having various functional groups can be readily obtained in 73–95% yields (eq. 5). The mass spectra of some of the compounds have been determined and the mass spectrometric fragmentation pattern has been discussed [6].

A 2 : 1 molar ratio reaction of V with water gave a glassy partial-hydrolysis product XXI (eq. 6). The structure of XXI was determined by elemental analysis, IR, ^1H NMR and mass spectroscopy. 2,2′-Oxy-bis-(1,2-oxaborolane) (XXI) is a reactive intermediate and may be considered as a cyclic boronic anhydride.

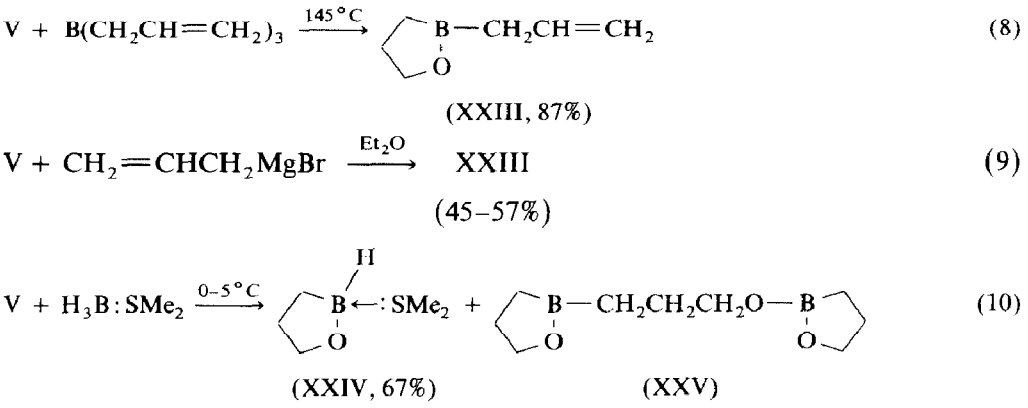


(V) (XXI, 50–78%) (6)

Up to now considerable work has been directed at finding a more reactive derivative having a versatile exocyclic substituent in the 1,2-oxaborolane system. Our efforts have been successful. The reaction of V with thionyl chloride gives 2-chloro-1,2-oxaborolane (XXII) [4]; the reaction of V with triallylborane or allylmagnisum bromide gives 2-allyl-1,2-oxaborolane (XXIII) [4,5]; 2-hydro-1,2-oxaborolane dimethylsulfide (XXIV) can be isolated from the reaction of V with dimethylsulfide-borane (BMS) in good yield [7], eqs 7; 8; 9; 10, respectively.

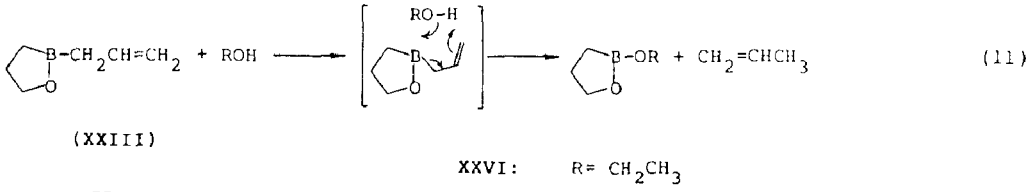


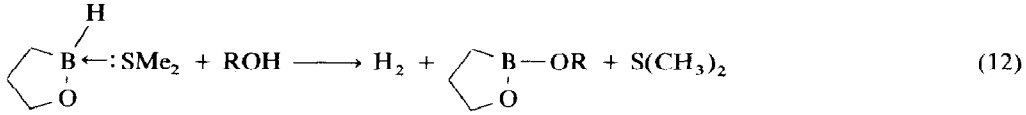
(V) (XXII, 70%) (7)

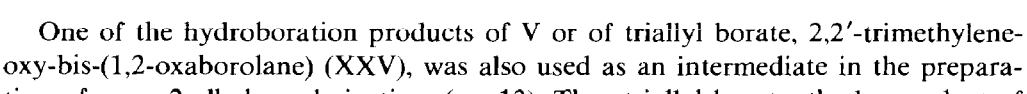


Thus a variety of 2-alkyloxy-1,2-oxaborolanes can be prepared by the interaction of the reactive compounds XXI, XXII, XXIII or XXIV with alcohols.

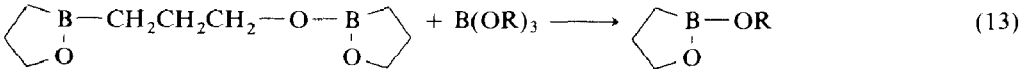
Particularly the lower derivatives, which cannot be prepared from V by Procedure A, were obtained by Procedure B (eq. 11) or Procedure C (eq. 12) in satisfactory yield. Compounds XXIV and XXIII possess high reactivities because XXIV is a specific hydroborating agent and XXIII is a specific allylborane.



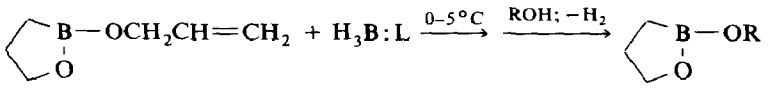




One of the hydroboration products of V or of triallyl borate, 2,2′-trimethyleneoxy-bis-(1,2-oxaborolane) (XXV), was also used as an intermediate in the preparation of some 2-alkyloxy derivatives (eq. 13). Thus triallyl borate, the by-product of the hydroboration of allyl alcohol, can be transformed into the cyclic compound V by this procedure. In Procedure C the small amount of $B(OR)_3$ present as an impurity can be removed by this heat exchange reaction, so that the facile one-pot Procedure D is recommended. A number of 2-alkyloxy-1,2-oxaborolanes (XXIX–XXXI) were conveniently prepared from the reaction of V with dimethylsulfide-borane or triethylamineborane complex, in situ, followed by reaction with an alcohol (eq. 14).



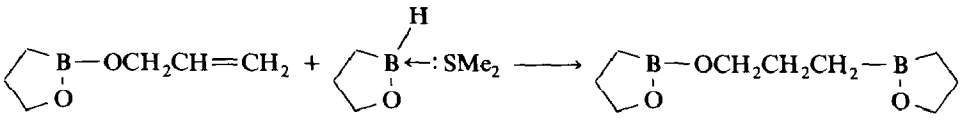
	R
I	$CH_2CH_2CH_2CH_3$
V	$CH_2CH{=}CH_2$



(V) (82–90%) (14)

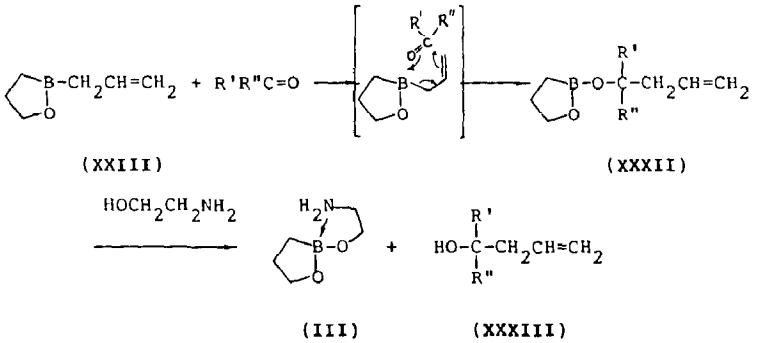
	R
L = SMe_2	
XXIX	$CH(CH_3)CH_2CH_3$
L = SMe_2	
XXX	$C(CH_3)_3$
L = NEt_3	
XXXI	$CH_2CH(CH_3)_2$

The hydroboration of V with XXIV gives bis-1,2-oxaborolane XXV (eq. 15) [7].

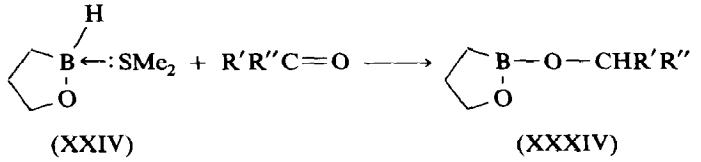


(V) (XXIV) (XXV, 92%) (15)

Of course the key reactants XXIII and XXIV were also used in alternative synthetic reactions in which 2-oxygen derivatives of 1,2-oxaborolane are formed as intermediates. The reaction of allylborane XXIII with ketones or aldehydes proceeds smoothly to give the intermediates XXXII; subsequent heat exchange reaction with ethanolamine or triethanolamine gives the corresponding allylic carbinols XXXII (eq. 16) [8]. In the reduction of ketones and aldehydes with the borane reagent XXIV, an intermediate XXXIV were isolated (eq. 17). For example, 2-cyclohexyloxy-1,2-oxaborolane II was obtained from the reduction of cyclohexone [7].



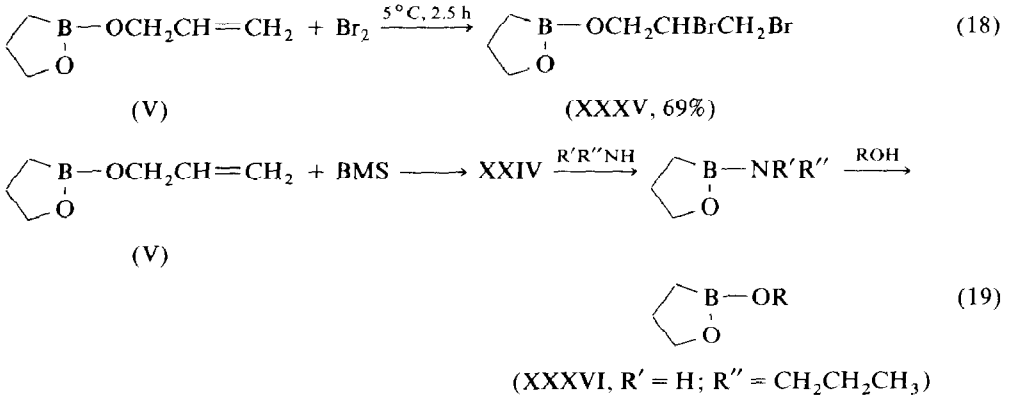
(XXIII) (XXXII) (III) (XXXIII) (16)



(XXIV) (XXXIV) (17)

Bromination of V gives 2-(2,3-dibormopropoxy)-1,2-oxaborolane (XXXV) (eq. 18), which can also be obtained by Procedure A from V and 2,3-dibromopropanol. It has been found that 2-amino-1,2-oxaborolanes (XXXVI), obtained from one-pot

reaction of V with XXIV and followed with amine, can also be converted into 2-alkyloxy derivatives without difficulty (eq. 19) [9].



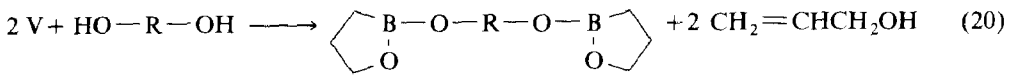
(18)

(V) (XXXV, 69%)

(19)

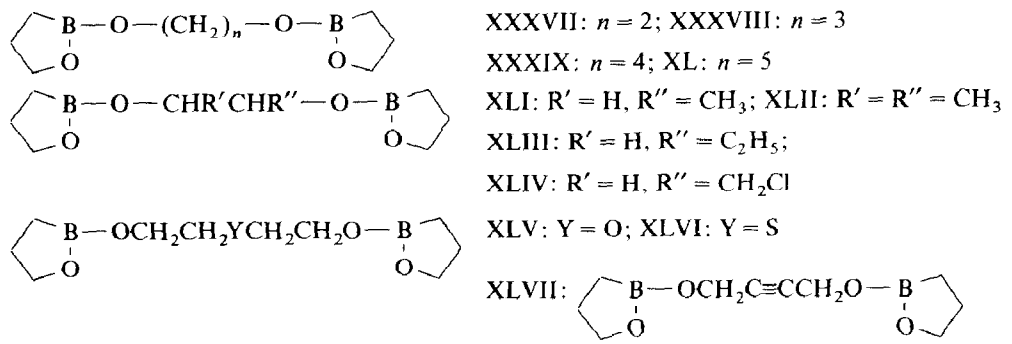
(XXXVI, R′ = H; R″ = $CH_2CH_2CH_3$)

A number of related bis-(1,2-oxaborolane) derivatives (XXXVII–L) were prepared by the heat exchange reaction of V with diols, such as catechol, resorcinol, hydroquinone, in 2 : 1 molar ratio (Procedure E, eq. 20). The formulas are shown below:



(20)

(XXXVII–L, 70–90%)



XXXVII: $n = 2$; XXXVIII: $n = 3$

XXXIX: $n = 4$; XL: $n = 5$

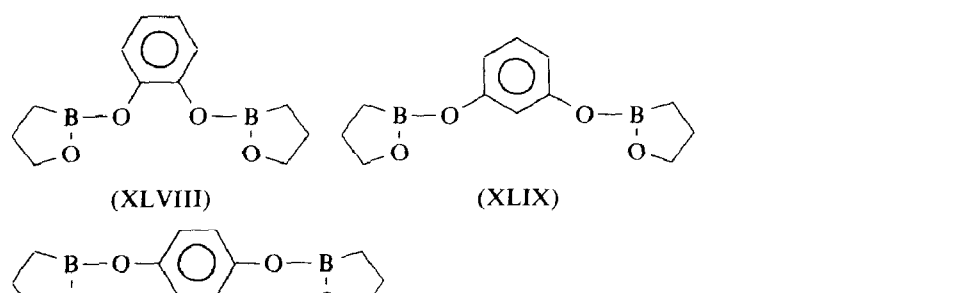
XLI: R′ = H, R″ = CH_3; XLII: R′ = R″ = CH_3

XLIII: R′ = H, R″ = C_2H_5;

XLIV: R′ = H, R″ = CH_2Cl

XLV: Y = O; XLVI: Y = S

XLVII:



(XLVIII) (XLIX)

(L)

Some bis-(1,2-oxborolane) derivatives have been shown to possess bicyclic and network-like structures according to their Raman spectra [10,11].

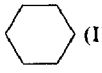
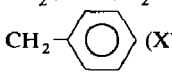
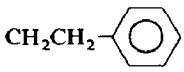
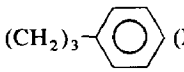
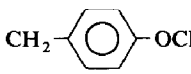
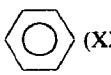
These 2-oxygen derivatives of 1,2-oxoborolane were usually isolated pure; most are colourless liquids. Their physical data and molar refractions are listed in Tables

1 and 2. The especially reactive compounds XXI, XXII, XXIII, XXIV and XXXVI as well as starting material V are listed in Table 3. Their analytical and spectral data are given in the experimental section.

The reactions of V as a typical example are summarized as depicted in Scheme 1. We are presently investigating their potential in organic synthesis, e.g. for the

Table 1

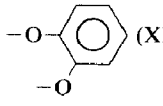
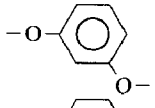
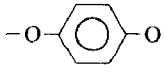
2-Alkoxy- and 2-aryloxy-1,2-oxaborolanes

Compound R (No.)	Yield (%) [Procedure or ref.]	B.p. (°C/mmHg)	n_D^{20}	d_4^{20}	Molar refraction	
					Calcd.	Found
CH_3 (IV)	97 [2]	104–106 °C	1.4327	0.996	25.83	26.06
CH_2CH_3 (XXVI)	80 [B]	118–120 °C	1.4208	0.9323	30.48	30.98
$CH_2CH_2CH_3$ (XXVII)	83 [C]	134–136 °C	1.4133	0.9011	35.13	35.44
$CH(CH_3)_2$ (XXVIII)	87 [C]	123–124 °C	1.3978	0.8629	35.13	35.78
$CH_2CH_2CH_2CH_3$ (I)	52 [2]	70–73/25	1.4345	0.931	39.78	39.76
$CH_2CH(CH_3)_2$ (XXXI)	76 [D]	68–71/37	1.4311	0.9254	39.78	39.73
$CH(CH_3)CH_2CH_3$ (XXIX)	85 [D]	67–69/42	1.4240	0.9080	39.78	39.91
$C(CH_3)_3$ (XXX)	71 [D]	48–50/42	1.4149	0.8883	39.78	40.02
$CH_2(CH_2)_3CH_3$ (VI)	83 [3]	76–77/15	1.4298	0.9109	44.43	44.23
$CH_2(CH_2)_6CH_3$ (VII)	73 [A]	115–117/12	1.4413	0.9030	58.37	57.98
 (II)	82 [2]	90–92/12	1.4668	0.993	46.86	46.94
	76 [4]	94–95/15	1.4663	0.9949	46.86	46.81
 (VIII)	90 [4]	118–120/20	1.4813	1.002	56.31	55.73
$CH_2CH{=}CH_2$ (V)	[a] [3]	55–56/15	1.4489	0.9729	34.65	34.72
$CH_2C{\equiv}CH$ (IX)	92 [A]	49–52/15	1.4658	1.042	33.00	32.93
$CH_2CH_2OCH_3$ (X)	67 [A]	59–62/10	1.4420	1.030	36.91	36.99
$CH_2CH_2OCH_2CH_3$ (XI)	75 [A]	49–50/1.5	1.4390	0.9970	41.56	41.68
$(CH_2CH_2O)_2C_2H_5$ (XII)	81 [A]	92–93/1.2	1.4470	1.0387	52.64	51.98
$(CH_2CH_2O)_3C_2H_5$ (XIII)	87 [A]	130–131/1.6	1.4499	1.0406	63.72	63.55
$CH_2CH_2NH_2$ (III)	95 [2,4]	Mp. 161–162 °C				
CH_2CH_2Cl (XIV)	83 [A]	66–67/15	1.4647	1.163	35.32	35.25
CH_2CH_2Br (XV)	78 [A]	83–84/15	1.4910	1.4687	38.20	38.03
$CH_2CHBrCH_2Br$ (XXXV)	69 [b]	96–98/1	1.5322	1.7424	50.56	50.84
 (XVI)	75 [A]	76–77/0.3	1.5242	1.076	50.28	50.07
 (XVII)	88 [A]	101–104/3	1.5181	1.0519	54.93	54.76
 (XVIII)	86 [A]	115–117/3	1.5129	1.0285	59.57	59.63
 (XIX)	73 [A]	151–152/10	1.5303	1.118	57.16	56.96
 (XX)	81 [A]	94–95/10	1.5326	1.113	45.78	45.14

[a] Starting material: 2-allyloxy-1,2-oxaborolane. [b] By bromination of V.

Table 2

Some bis-(1,2-oxaborolane)s obtained from the reaction of V with diols or phenols

Compound –ORO– (No.)	Yield (%) [Procedure or ref.]	B.p. (°C/mmHg)	n_D^{20}	d_4^{20}	Molar Refraction	
					Calcd.	Found
–O– (XXI)	50–78 [a]	115–116/15	glassy			
$-OCH_2CH_2O-$ (XXXVII)	87 [4]	98–100/0.2	1.4602	1.098	49.61	49.37
$-O\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_2O-$ (XLI)	86 [4]	92–95/0.3	1.4520	1.056	54.26	54.12
$-O\underset{\displaystyle CH_3}{\underset{\vert}{C}}H-\underset{\displaystyle CH_3}{\underset{\vert}{C}}HO-$ (XLII)	90 [4]	110–112/0.4	1.4513	1.038	58.91	58.63
$-O\underset{\displaystyle CH_2CH_3}{\underset{\vert}{C}}H-CH_2O-$ (XLIII)	82 [E]	105–108/2	1.4536	1.041	58.91	58.72
$-O\underset{\displaystyle CH_2Cl}{\underset{\vert}{C}}H-CH_2O-$ (XLIV)	84 [E]	106–107/0.1	1.4722	1.180	59.09	58.47
$-O(CH_2)_3O-$ (XXXVIII)	83 [E]	89–91/0.3	1.4622	1.085	54.26	53.70
$-O(CH_2)_4O-$ (XXXIX)	87 [E]	107–108/3.5	highly viscous fluid			
$-O(CH_2)_5O-$ (XL)	85 [E]	116–118/0.3	highly viscous fluid			
$-OCH_2CH_2OCH_2CH_2O-$ (XLV)	84 [E]	113–118/2	highly viscous fluid			
$-OCH_2CH_2SCH_2CH_2O-$ (XLVI)	80 [E]	118–128/2	highly viscous fluid			
$-OCH_2C{\equiv}CCH_2O-$ (XLVII)	70 [E]	120–125/0.3	highly viscous fluid			
 (XLVIII)	76 [E]	109–111/0.3	1.5155	1.149	64.35	64.50
 (XLIX)	[b] [E]	151–155/0.4	white solid			
 (L)	[b] [E]	145–150/0.4	white solid			

[a] By partial hydrolysis of V. [b] Not the exact isolated yield.

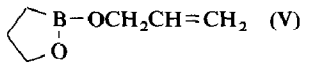
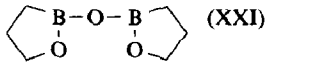
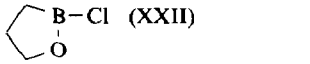
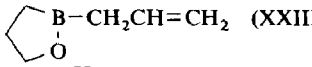
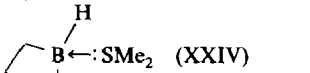
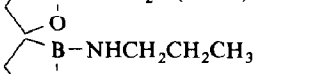
synthesis of 1,4-alkanediols from allyl alcohol by hydroboration and homologation of the 1,2-oxaborolane intermediate [12].

Experimental

All operations with the organoboranes were carried out under purified nitrogen. IR were recorded on a Specord 75 spectrophotometer. ^1H NMR spectra were recorded on a Varian Model EM-360 (60 MHz) or a JEOL 90 MHz instrument relative to internal TMS. ^{11}B NMR spectra were recorded on a Varian XL-200 spectrometer relative to external $F_3B:OEt_2$.

Table 3

The more reactive 1,2-oxaborolane derivatives

Compound (No.)	B.p. (°C/mmHg)	n_D^{20}	d_4^{20}	Ref.
 (V)	55–56/15	1.4489	0.9729	[3]
 (XXI)	115–116/15		glassy	this work
 (XXII)	Mp. 94.5–96 °C	white needle-like crystals		[4]
 (XXIII)	48–50/50	1.4308	0.8616	[4,5] this work
 (XXIV)	40–41/60	1.4472	0.824	[7]
 (XXXVI)	58–61/20	1.4382	0.8976	[9]

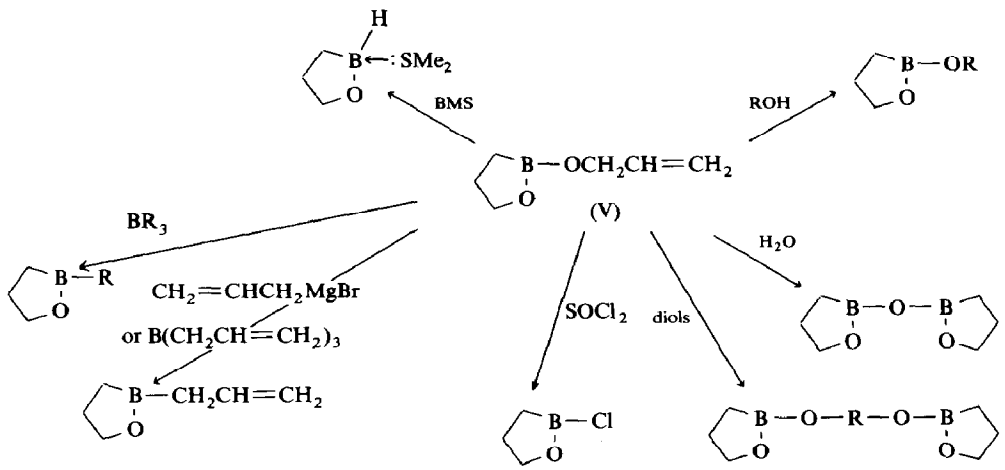
Starting material V was prepared by the reaction of allyl alcohol with KBH_4–HOAc as described previously [3]. 2-Allyl-1,2-oxaborolane (XXIII) and 2-hydro-1,2-oxaborolane dimethylsulfide complex (XXIV) were obtained from the reaction of V with allylmagnesium bromide in ether and from the reaction of V with the dimethylsulfide-borane complex (BMS) in methyl sulfide, respectively (Table 3). BMS was purchased from the Aldrich Company.

Boiling points are uncorrected.

Procedure A: The reaction of V with alcohols and phenol

2-n-Octoxy-1,2-oxaborolane (VII)

A dry, nitrogen-filled, 30-ml distillation flask equipped with a side arm capped with a rubber septum, a magnetic stirring bar, a Claisen head attached to an oil



Scheme 1

bubbler, was charged with 7.56 g (60 mmol) of 2-allyloxy-1,2-oxabororane (V) and 9.5 ml of n-octanol. The mixture was stirred and heated on an oil-bath at 160–180 °C for 2 h, the allyl alcohol was slowly distilled off under atmospheric pressure. Distillation of the residue under vacuum gave 8.63 g (85.1%) of VII, b.p. 115–117 °C/12 mmHg, n_D^{20} 1.4413. Anal. Found: B, 5.52; C, 66.38; H, 12.04. $B_{11}H_{23}O_2$ calcd: B, 5.46; C, 66.69; H, 11.94%.

IR(film): $\nu(cm^{-1})$ 724w, 825w, 861w, 900m, 995s, 1025m, 1063m, 1139m, 1201s, 1255s, 1355s, 1409sh, 1428s, 1457s, 1493s, 2850sh, 2950vs. ^1H NMR(CCl_4): δ (ppm) 0.87 (m, 5H, BCH_2, CH_3); 1.28, 1.97 (m, 14H, $(CH_2)_6$, CCH_2C); 3.82, 3.95 (tt, 4H, J 7 Hz, $(OCH_2)_2$).

2-(2-Propynyloxy)-1,2-oxaborolane (IX)

Starting from 12.6 g (100 mmol) of V and 8.0 g (142 mmol) of propargyl alcohol, the procedure as described above gave 11.4 g (92.0%) of IX, b.p. 48.5–51.5 °C/15 mmHg, n_D^{20} 1.4658. Anal. Found: B, 8.62; C, 58.19; H, 7.45. $BC_6H_9O_2$ calcd: B, 8.72; C, 58.14; H, 7.32%.

IR(film): $\nu(cm^{-1})$ 639sh, 667m, 825w, 863w, 900m, 929m, 992s, 1005s, 1043m, 1059m, 1140m, 1212s, 1252s, 1315sh, 1349s, 1408sh, 1427s, 1465s, 1495s, 2121w, 2892s, 2952s, 3299s. ^1H NMR ($CDCl_3$) δ (ppm) 0.75 (t, 2H, J 7.5 Hz, BCH_2); 1.63 (q, 2H, J 7 Hz, CCH_2C); 2.40 (s, 1H, C≡CH); 3.60, 3.72 (tt, 2H, J 6.5 Hz, OCH_2); 4.26 (d, 2H, J 3 Hz, $OCH_2C{\equiv}C$). ^{11}B NMR ($CDCl_3$): δ (ppm) 37.04.

2-(2-Methoxyethoxy)-1,2-oxaborolane (X)

Starting from V and 2-methoxyethanol (1 : 1, 100 mmol), 9.6 g (66.7%) of X was prepared as described above, b.p. 59–62 °C/10 mmHg, n_D^{20} 1.4420. Anal. Found: B, 7.43; C, 50.25; H, 8.76. $BC_6H_{13}O_3$ Calcd: B, 7.51; C, 50.05; H, 9.10%.

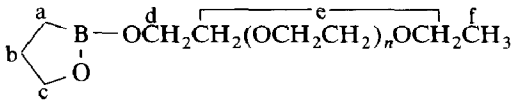
IR(film): $\nu(cm^{-1})$ 745w, 843m, 865w, 900m, 993m, 1025m, 1076m, 1101m, 1136s, 1203s, 1255m, 1325s, 1357s, 1428s, 1459s, 1495s, 2887s, 2943s. ^1H NMR($CDCl_3$): δ (ppm) 0.68 (tt, 2H, J 7.5 Hz, BCH_2); 1.57 (qq, 2H, J 7 Hz, CCH_2C); 3.11 (s, 3H, OCH_3); 3.26 (t, 2H, J 6 Hz, $COCH_2$); 3.65, 3.76 (tt, 4H. J 6.5 Hz, $BOCH_2$). ^{11}B NMR ($CDCl_3$): δ (ppm) 36.40.

2-(2-Ethoxyethoxy) (XI), 2-(2-ethoxy-2-ethoxyethoxy)- (XII) and 2-(2-ethoxy-2-ethoxy-2-ethoxyethoxy)-1,2-oxaborolanes (XIII)

XI, XII and XIII were prepared as described above, starting from V, in 74.6, 81.2 and 86.7% yields, respectively. The IR and ^1H NMR spectra of these compounds are very similar. XI: Anal. Found: B, 6.80, 7.03. $BC_7H_{15}O_3$ calcd: B, 6.84%. XII: Anal. Found: 5.61, 5.88. $BC_9H_{19}O_4$ calcd:, B, 5.35%. XIII: Anal. Found: 4.51, 4.53. $BC_{11}H_{23}O_5$ calcd. B, 4.39%.

IR(film) XI: $\nu(cm^{-1})$ 746w, 825w, 900w, 939w, 991m, 1022m, 1064m, 1121s, 1202s, 1251s, 1317s, 1346s, 1425s, 1491s, 2886s, 2973s. XII: $\nu(cm^{-1})$ 740vw, 823w, 900w, 946w, 989m, 1020m, 1071m, 1113s, 1203m, 1248m, 1316s, 1347s, 1425s, 1492m, 2886s, 2966s. XIII: $\nu(cm^{-1})$ 900w, 937w, 989m, 1020m, 1110m, 1124s, 1205m, 1250m, 1290m, 1313s, 1348s, 1424s, 1493m, 2883s, 2961s. ^1H NMR(CCl_4) XI: δ (ppm) 0.79 (t, 2H, J 7.5 Hz, a), 1.07 (t, 3H, J 7 Hz, f); 1.82 (q, 2H, J 8 Hz, b); 3.30, 3.43 (m, 4H, e); 3.76, 3.88 (tt, 4H, J 6.5 Hz, c, d). XII: δ (ppm) 0.79 (t, 2H, J 7 Hz, a), 1.07 (t, 3H, J 7 Hz, f); 1.81 (q, 2H, J 7 Hz, b); 3.32, 3.43 (m, 8H, e); 3.76, 3.88 (tt, 4H, J 6.5 Hz, c, d). XIII: δ (ppm) 0.79 (t, 2H, J 7 Hz, a); 1.07 (t, 3H,

J 7 Hz, f); 1.81 (q, 2H, *J* 7 Hz, b); 3.28, 3.43 (m, 12H, e); 3.76, 3.88 (tt, 4H, *J* 6.5 Hz, c, d).

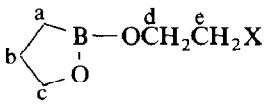


$n = 0, 1, 2$

2-(2-Chloroethoxy)- (XIV) and 2-(2-bromoethoxy)-1,2-oxaborolane (XV)

XIV or XV was readily obtained in good yield from procedure A as described above, but starting from V and 2-chloroethanol or 2-bromoethanol (1 : 1.2). XIV: Yield, 82.9%; b.p. 66–67 °C/15 mmHg; n_D^{20} 1.4647. Anal. Found: B, 7.13; C, 40.34; H, 6.76; Cl, 23.36. $BC_5H_{10}O_2Cl$, calcd.: B, 7.29; C, 40.47; H, 6.79; Cl, 23.89%. XV: Yield, 78.3%; b.p. 82.5–84 °C/15 mmHg; n_D^{20} 1.4910. Anal. Found: C, 31.33; H, 5.15; Br, 41.46. $BC_5H_{10}O_2Br$ calcd: C, 31.14; H, 5.23; Br, 41.43%.

IR(film) XIV: $\nu(cm^{-1})$ 663s, 740m, 815m, 895m, 984s, 1013s, 1065sh, 1076s, 1136m, 1201s, 1249s, 1355s, 1421s, 1492s, 2885s, 2953s. XV: $\nu(cm^{-1})$ 565w, 668w, 741w, 816w, 859vw, 900m, 940w, 988s, 1028s, 1067s, 1139m, 1209s, 1285s, 1336sh, 1363s, 1428s, 2892s, 2965s. ^1H NMR ($CDCl_3$) XIV: δ (ppm) 0.83 (m, 2H, a); 1.68 (q, 2H, *J* 7 Hz, b); 3.50 (t, 2H, *J* 6 Hz, e); 3.89 (tt, 4H, *J* 5.5 Hz, c, d). XV: δ (ppm) 0.98 (m, 2H, a); 1.83 (q, 2H, *J* 7 Hz, b); 3.52, 3.85 (m, 4H, d, c); 4.15 (t, 2H, *J* 6 Hz, e) ^{11}B NMR ($CDCl_3$) XIV: δ (ppm) 37.37 ppm; XV: δ (ppm) 37.64.



X = Cl, Br

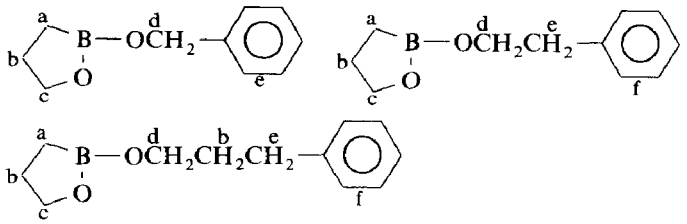
2-Benzyloxy- (XVI), 2-(2-phenylethoxy)- (XVII) and 2-(2-phenypropoxy)-1,2-oxaborolane (XVIII)

Starting from V and benzyl alcohol, XVI was prepared as described above in 75.0% yield, b.p. 76 °C/0.3 mmHg, n_D^{20} 1.5242. Anal. Found: B, 5.88; C, 68.39; H, 7.29. $BC_{10}H_{13}O_2$ calcd: B, 6.14; C, 68.24; H, 7.44%.

IR(film): $\nu(cm^{-1})$ 699s, 731s, 824m, 856w, 900m, 983s, 1027s, 1055m, 1080m, 1136m, 1207s, 1252s, 1325sh, 1353s, 1425s, 1453s, 1496s, 1583w, 1607w, 1713w, 1800w, 1868w, 1943w, 2883s, 2952s, 3028m, 3061m, 3085w. ^1H NMR($CDCl_3$): δ (ppm) 0.57 (t, 2H, *J* 7.5 Hz, a); 1.60 (q, 2H, *J* 7 Hz, b); 4.13 (t, 2H, *J* 6.5 Hz, c); 5.36 (s, 2H, d); 8.13 (m, 5H, e).

XVII and XVIII were obtained in good yields from the reactions of V with the relevant alcohols. XVII: Yield, 87.8%; B.p. 101–104 °C/3 mmHg; n_D^{20} 1.5181. Anal. Found: B, 5.61, 5.62. $B_{11}H_{15}O_2$ calcd: B, 5.69%. XVIII: Yield, 85.6%; B.p. 115–117 °C/3 mmHg; n_D^{20} 1.5129. Anal. Found: B. 5.21, 5.34. $B_{12}H_{17}O_2$ calcd: B. 5.30%.

IR(film) XVII: $\nu(cm^{-1})$ 671m, 703s, 753s, 834w, 909m, 993s, 1031s, 1060s, 1140m, 1200s, 1252s, 1352s, 1422s, 1455s, 1481sh, 1497s, 1586w, 1635m, 1752vw, 1826w, 1871w, 1946, 2887sh, 2943s, 3013s, 3057m. ^1H NMR($CDCl_3$) XVII: δ (ppm) 0.77 (t, 2H, *J* 7.5 Hz, a); 1.81 (q, 2H, *J* 7 Hz, b); 2.82 (t, 2H, *J* 6.5 Hz, e); 3.91, 4.02 (tt, 4H, c, d); 7.16 (m, 5H, f). XVIII: δ (ppm) 0.73 (t, 2H, *J* 8 Hz, a); 1.74 (q, 4H, *J* 7.5 Hz, b); 2.56 (t, 2H, *J* 7.5 Hz, e); 3.71, 3.81 (tt, 4H, *J* 6 Hz, c, d); 7.03 (m, 5H, f). ^{11}B NMR($CDCl_3$) XVII: δ (ppm) 35.71.



2-p-Methoxybenzyloxy-1,2-oxaborolane (XIX)

As described above, but starting from V and anisyl alcohol, XIX was prepared in 72.8% yield, b.p. 151–152 °C/10 mmHg, n_D^{20} 1.5303. Anal. Found: B, 5.11; C, 64.33; H, 7.09. $BC_{11}H_{15}O_3$ calcd: B, 5.25; C, 64.12; H, 7.34%.

IR(film) $\nu(cm^{-1})$ 705w, 750sh, 763m, 824s, 853s, 903m, 937w, 985s, 1040s, 1115m, 1140m, 1179s, 1211s, 1211s, 1252s, 1355s, 1431s, 1515s, 1617s, 1764w, 1880w, 1996w, 2055w, 2839s, 2895sh, 2956s. ^1H NMR($CDCl_3$): δ (ppm) 0.62 (t, 2H, J 7.5 Hz, BCH_2); 1.69 (q, 2H, J 7 Hz); 3.85 (s, 3H, OCH_3); 4.24 (t, 2H, J 6.5 Hz, OCH_2); 5.38 (s, 2H, OCH_2Ar); 7.63, 8.18 (m, 4H, Ar).

2-Phenoxy-1,2-oxaborolane (XX)

Starting from 12.6 g (100 mmol) of V and 9.4 g (100 mmol) of phenol, by the procedure described above 13.1 g (80.9%) of XX was prepared b.p. 94–95 °C/10 mmHg, n_D^{20} 1.5326. Anal. Found: B, 6.76; C, 67.25; H, 6.58. $BC_9H_{11}O_2$ calcd. B, 6.67; C, 66.73; H, 6.84%.

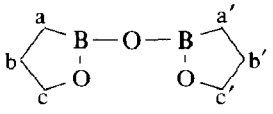
IR(film) $\nu(cm^{-1})$ 505w, 615vw, 692s, 765s, 808m, 840m, 898m, 968sh, 988m, 1021m, 1069m, 1167m, 1219s, 1263s, 1312s, 1355s, 1395s, 1427s, 1492s, 1597vs, 1712vw, 1765vw, 1849vw, 1925vw, 2885s, 2952s, 3033m. ^1H NMR($CDCl_3$): δ (ppm) 0.64 (t, 2H, J 7 Hz, BCH_2); 1.58 (q, 2H, J 7 Hz, CCH_2C); 4.18 (t, 2H, J 6.5 Hz, OCH_2); 7.76, 7.94 (m, 5H, Ph).

Partial hydrolysis of V

2,2′-Oxy-bis-1,2-oxaborolane (XXI)

The partial-hydrolysis product XXI was obtained in good yield from V and water (near 2 : 1 molar ratio) at 150–160 °C for 2 h. Allyl alcohol was distilled off under atmospheric pressure, and the residue was distilled under vacuum to give a glassy product, b.p. 115–116 °C/15 mmHg, in 50–78% yield. XXI is more sensitive to moisture in air. Anal. Found: 13.60–14.41. $B_2C_6H_{12}O_3$ calcd: 14.06%. MS: m/z M^+, 154(w); $M-15$(s), $M-42$, cleavage of the ring; 87(s), 69(s); cleavage of exocyclic B–O bond, i.e. the ring $BC_3H_8O_2$ cation and BC_3H_6O cation [6].

IR(film): $\nu(cm^{-1})$ 656w, 732w, 815w, 852w, 871w, 927w, 1017w, 1052m, 1132w, 1183m, 1229m, 1271s, 1345s, 1417s, 1479m, 1631vw, 2885sh, 2941s, 3393s. ^1H NMR($CDCl_3$) δ (ppm) a,a′ 0.87, 0.90 (tt, 4H, J 7 Hz); b,b′ 1.77, 1.91 (qq, 4H, J 7 Hz); c,c′ 3.88, 4.02 (tt, 4H, J 7 Hz).



Reaction of 2-chloro-1,2-oxaborolane (XXII) with alcohol

The reaction of 3.5 g of XXII and 10.3 g n-butanol by distillation gave 2.4 g of I (51% yield).

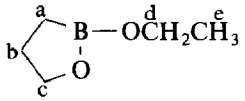
As above, the reaction of XXII with ethylene glycol gave 2,2′-ethylenedioxy-bis-1,2-oxaborolane (XXXVII) in 75% yield.

Procedure B: Reaction of allylborane XXIII with alcohols

2-Ethoxy-1,2-oxaborolane (XXVI)

A 25-ml dry, nitrogen-filled round flask equipped with a side arm capped with a rubber septum, a magnetic stirring bar, a reflux condenser and a connecting tube attached to a bubbler was charged with 1.72 g (16 mmol) of XXIII. 10 ml (17 mmol) ethanol was added dropwise during 10 min, and the reaction mixture was heatted at 100 °C for 30 min. After the evolution of about 200 ml gas, distillation under vacuum gave 1.45 g (80%) of XXVI, b.p. 47–49 °C/54 mmHg, n_D^{20} 1.4228. Anal. Found: B, 9.26, 9.23. $BC_5H_{11}O_2$ calcd: 9.49%.

IR(film): $\nu(cm^{-1})$ 471w, 617w, 661m, 738w, 818m, 858m, 883m, 988s, 1015s, 1044s, 1097s, 1132s, 1196s, 1271s, 1320s, 1367s, 1425s, 1487s, 2943s. ^1H NMR (CCl_4) δ (ppm) 0.83 (t, 2H, a); 1.18 (t, 3H, e); 1.86 (q, 2H, b); 3.93 (tt, 4H, c, d).



Procedure C: Reaction of borane agent XXIV with alcohols

2-n-Propoxy- (XXVII) and 2-iso-propoxy-1,2-oxaborolane (XXVIII)

A dry, nitrogen-filled 25-ml flask, equipped with a side arm capped with a rubber septum, a magnetic stirring bar, a reflux condenser and a connecting tube attached to a bubbler, was charged with 6.6 g (50 mmol) of XXIV. The flask was immersed in an ice-bath, 3.0 g (50 mmol) n-propanol was added dropwise at 0–5 °C during 1 h, and evolution of hydrogen took place immediately. After complete addition, the methyl sulfide was distilled off under atmospheric pressure. Then 1 ml of XXV was added and the mixture was heated at 140 °C for 2.5 h. Distillation under vacuum gave 5.3 g (82.8%) of XXVII, b.p. 133–135 °C, n_D^{20} 1.4175.

Starting from XXIV and 2-propanol, XXVII was prepared as described above in 80% yield. B.p. 123–125 °C, n_D^{20} 1.3978. XXVII: Anal. Found: B, 8.57. $BC_6H_{13}O_3$ calcd: B, 8.45% XXVIII: Anal. Found: B, 8.11. $BC_6H_{13}O_3$ calcd: B, 8.45%.

IR(film) XXVII: $\nu(cm^{-1})$ 667m, 740w, 760w, 825w, 863w. 900m, 960m, 992m, 1028m, 1070m, 1102w, 1140w, 1204s, 1253s, 1330s, 1360s, 1380sh, 1435s, 1485m, 2800sh, 2965s. XXVIII: $\nu(cm^{-1})$ 670m, 818w, 840w, 900w, 954s, 998w, 1032m, 1123s, 1174m, 1200m, 1252w, 1330s, 1380s, 1424s, 1470sh, 2855sh, 2950s.

^1H NMR(CCl_4) XXVII: δ (ppm) 0.82 (m, 2H, BCH_2); 0.92 (s, 3H, CCH_3); 1.36 (qq, 4H, $(CCH_2C)_2$); 3.59 (tt, 4H, $(OCH_2)_2$). XXVII: δ (ppm) 0.76 (t, 2H, J 7 Hz, BCH_2); 1.10 (d, 6H, $C(CH_3)_2$); 1.82 (m, 2H, CCH_2C); 3.91, 4.34 (m, 3H, OCH_2, $OCHC_2$).

The reaction of bis-1,2-oxaborolane XXV with trialkoxyboranes

With tributyl borate. In a 100-ml distillation flask was placed 20.0 g (102 mmol) of XXV and 23.0 g (100 mmol) of tirbutyl borate. The mixture was heated with stirring at 160–170 °C for 2 h. Distillation under vacuum gave I, 25.4 g (179%), b.p. 76–78 °C/40 mmHg, n_D^{20} 1.4366 (Lit. 70–73 °C/25 mmHg, n_D^{20} 1.4345 [2]).

With triallyl borate. Starting from 36.0 g (184 mmol) of XXV and 33.4 g (184 mmol) of triallyl borate, 32.8 g (142%) of V was prepared as described above, b.p. 53–55 °C/15 mmHg, n_D^{20} 1.4485 (Lit. 56 °C/mmHg, n_D^{20} 1.4498[3]).

Procedure D: One-pot reaction of V with boranes and alcohols

A dry, two-necked, 50-ml flask fitted with a magnetic stirring bar, a rubber septum, and a reflux condenser leading to a bubbler, was flushed with nitrogen and immersed in an ice-bath. 12.6 g (50 mmol) of V and 5 ml of methyl sulfide were injected into the flask by hypodermic syringe. 10 ml (50 mmol) of BMS was injected slwoly into the well-stirred solution over a period of 2 h. Then 50 mmol of the alcohol was added slowly with another syringe through the inlet tube to the well-stirred mixture. The ice-water bath was removed and the stirring was continued for 1 h until evolution of gas has ceased. Then the solvent was evaporated off by aaspiration and the residue was heated at 160 °C for 2 h, and distilled to give the 2-alkyloxy-1,2-oxaborolane. The examples, XXIX and XXX, were prepared in 85% and 71% yields, respectively.

2-sec-Butoxy- (XXIX) and 2-tert-butoxy-1,2-oxaborolane (XXX)

XXIX: Anal. Found: B, 7.37. $BC_7H_{15}O_3$ calcd: B, 7.61%. Anal. Found: B, 7.69. $BC_7H_{15}O_3$ XXX calcd: B, 7.61%.

IR(film) XXIX: $\nu(cm^{-1})$ 657m, 728vw, 818w, 853w, 902m, 963sh, 983s, 1015s, 1104m, 1118s, 1162m, 1193s, 1245s, 1313s, 1414s, 1486s, 2339vw, 2852sh, 2891sh, 2944s, 3413w. XXX: $\nu(cm^{-1})$ 668m, 904m, 973w, 1023m, 1038m, 1184s, 1241m, 1257m, 1345s, 1360s, 1405s, 1439m, 1457m, 1490m, 2882sh, 1955s. ^1H NMR (CCl_4) XXIX: δ 0.80 (t, 2H, J 7.5 Hz, BCH_2); 0.90, 1.06 (m, 6H, $(CH_3)_2$); 1.10–1.60, 1.82 (m, 4H, $(CCH_2C)_2$); 3.94 (t, 2H, J 6.5 Hz, OCH_2); 4.15 (m, 1H, $OCHC_2$). XXIX: δ (ppm) 0.79 (t, 2H, J 8 Hz, BCH_2); 1.30 (s, 9H, $C(CH_3)_3$); 1.82 (q, 2H, J 7 Hz, CCH_2C); 3.96 (t, 2H, J 6.5 Hz, OCH_2).

2-iso-Butoxy-1,2-oxaborolane (XXXI)

XXXI was obtained in 76% yield by the procedure described above, but triethylamino-borane and an oil-bath (140 °C) were used in place of BMS and the ice-bath, respectively.

XXXI: Anal: Found: B, 7.24. $BC_7H_{15}O_3$ calcd: B, 7.61%.

IR(film): $\nu(cm^{-1})$ 659m, 817w, 856vw, 897m, 939w, 982s, 1129m, 1159m, 1191s, 1242s, 1310sh, 1345s, 1377s, 1404sh, 1421s, 2819sh, 2913s. ^1H NMR(CCl_4): δ (ppm) 0.82 (t, 2H, J 7.5 Hz, BCH_2); 0.90 (d, 6H, $C(CH_3)_2$); 1.10–1.16 (m, 1H, $CCHO_2$); 1.87 (q, 2H, J 7 Hz, CCH_2C); 3.55, 3.95 (m, 4H, $(OCH_2)_2$).

Bromination of V

2-(2,3-Dibromopropoxy)-1,2-oxaborolane (XXXIV)

A dry, nitrogen-filled 50-ml three-necked flask, equipped with a magnetic stirring bar, a thermometer, an addition funnel, a reflux condenser and a connecting tube attached to a bubbler, was charged with 12.6 g (100 mmol) of V and 10 ml of CH_2Cl_2. The flask was immersed in an ice-bath. 16.9 g (100 mmol) of bromine was added dropwise to the solution at 0–5 °C with stirring during 2.5 h. Stirring was then continued at room temperature for an additional hour. After removal of the solvent, the residue was heated at 120 °C for 1 h and was then distilled under vacuum to give 19.7 g (69.0%) of XXXV. b.p. 96–98 °C/1 mmHg, n_D^{20} 1.7424. Anal. Found: 3.79, 3.86. B, $BC_6H_{11}O_2Br_2$ calcd: 3.78%. IR(film): ν(cm^{-1}) 570m, 750w, 825w, 898w, 986s, 1020s, 1058m, 1110w, 1140m, 1204s, 1254s, 1323sh, 1358vs, 1420s, 1455w, 1493m, 2880s, 2952s. ^{1}H NMR(CCl_4): δ 0.99 (t, 2H, J 7.5 Hz, BCH_2); 2.01 (q, 2H, J 7.5 Hz, CCH_2C); 3.87 (m, 4H, $(OCH_2)_2$); 4.08, 4.30 (m, 3H, $CHBrCH_2Br$).

Procedure E: Reaction of V with diols

This procedure is similar to Procedure A. Representative examples (XXXVII, XLI and XLII) have been described previoously [4].

2,2′-Polymethylenedioxy-bis-1,2-oxaborolanes (XXXVIII–XL)

The method for the preparation of XXXVII [4] was used: a dry 50 ml flask was charged with 6.29 g (50 mmol) of V and 25 mmol of polymethylenediol. The mixture was heated at 160–180 °C with stirring for 2h. Distillation under vacuum gives the highly viscous product (XXXVIII, XXXIX or XL) in about 85% yield.

XXXV: Anal. Found: B, 9.85; C, 51.09; H, 8.27. $B_2C_9H_{18}O_4$ calcd: C, 10.21; C, 51.03; H, 8.56%. XXXVII: Anal. Found: B, 9.27; C, 53.39; H, 8.61. $B_2C_{10}H_{20}O_4$ calcd: B, 9.57; C, 53.17; H, 8.92%. XXXVII: Found: B, 8.73; C, 54.95; H, 9.27. $B_2C_{11}H_{22}O_4$ calcd: B, 9.01; C, 55.07; H, 9.24%.

XXXVIII: IR(film): ν(cm^{-1}) 735m, 816w, 840w, 899w, 932m, 982m, 1028m, 1067m, 1096m, 1133m, 1186s, 1235s, 1275s, 1316sh, 1347s, 1429s, 1482s, 2885s, 2941s. ^{1}H NMR($CDCl_3$): δ(ppm) 0.60 (tt, 4H, J 7.5 Hz, $(BCH_2)_2$); 1.43, 1.75 (m, 6H, $(CCH_2C)_3$); 3.62, 3.76 (m, 8H, $(OCH_2)_4$). ^{11}B NMR ($CDCl_3$): δ (ppm) 37.23.

2,2′-[(1-Ethyl-1,2-ethanediyl)bis(oxy)]- (XLIII) and 2,2′-[1-chloromethyl-1,2-ethanediyl)bis(oxy)]-bis-1,2-oxaborolane (XLIV)

Starting from 6.29 g (50 mmol) of V and 2.25 g (25 mmol) of 1,2-butanediol, 4.61 g (81.6%) of XLIII was prepared as described above, b.p. 111–113 °C/3 mmHg, n_D^{20} 1.4531. Anal. Found: B, 9.48. $B_2C_{10}H_{20}O_4$ calcd: B, 9.57%.

Starting from 10 g (80 mmol) of V and 4.40 g (40 mmol) of 3-chloropropylenediol 8.30 g (84.3%) of XLIV was prepared as described above, b.p. 106–107 °C/0.1 mmHg, n_D^{20} 1.4722. Anal. Found: B, 8.64, 8.75. $B_2C_9H_{17}O_4Cl$ calcd: B, 8.78%.

IR(film): ν(cm^{-1}) 656w, 752m, 821m, 860w, 902m, 988m, 1026s, 1069sh, 1110w, 1139sh, 1180sh, 1235s, 1291w, 1320sh, 1355s, 1382s, 1424s, 1485s, 1587w, 2880sh, 2950s. ^{1}H NMR($CDCl_3$): δ (ppm) 0.81 (tt, 4H, J 7 Hz, BCH_2); 1.64, 1.76 (qq, 4H, J 7 Hz, CCH_2C); 3.63, 4.07 (m, 9H, $(OCH_2)_3$, $OCHCH_2Cl$).

2,2′-(2,2′-Oxydiethoxy)- (XLV), 2.2′-(2,2′-thiodiethoxy)- (XLVI) and 2,2′-[2-butyne-1,4-diylbis(oxy)]-bis-1,2-oxaborolanes (XLVII).

Starting from V and diethylene glycol, di-β-hydroxyethyl sulfide and 2-butyne-1,4-diol, the bis-1,2-borolane derivatives XLV, XLVI and XLVII were prepared as described above in 84, 80 and 70% yields, respectively. XLV: Anal. Found: B, 8.77, 8.83. $B_2H_{10}H_{20}O_5$ calcd: B, 8.94%. XLVI: Anal. Found:, B, 8.01, 7.91. $B_2C_{10}H_{20}O_4S$ calcd: B, 8.38%. XLVII: Anal. Found: B, 8.81, 8.93. $B_2C_{10}H_{16}O_4$ calcd: B, 9.09%.

2,2′-(1,2-Phenylenedioxy)- (XLVIII), 2,2′-(1,3-phenylenedioxy)- (XLIX) and 2,2′-(1,4-phenylenedioxy)-bis-1,2-oxaborolanes (L)

The corresponding bis-1,2-oxaborolane derivative XLVIII, XLIX or L was prepared by treatment of V with catechol, resorcinol or hydroquinone in 2 : 1 molar ratio followed by distillation under vacuum. Their mass spectra have been reported and described in ref. 6. XLVIII: IR(film): $\nu(cm^{-1})$ 740s, 811m, 864w, 899w, 917w, 931m, 1010sh, 1026w, 1069w, 1131m, 1186m, 1208m, 1241s, 1260sh, 1355s, 1385s, 1432s, 1471s, 1611w, 1757w, 1873w, 2032w, 2890sh, 2949s, 3061w. ^{1}H NMR($CDCl_3$): δ (ppm) 0.33, 0.97 (tt, 4H, $(BCH_2)_2$); 1.51 (q, 4H, J 6.5 Hz, $(CCH_2C)_2$); 3.55 (tt, 4H, J 6 Hz, OCH_2); 6.66, 6.72 (m, 4H, Ph).

Anal. Found: B, 8.76; C, 58.68; H, 6.38. $B_2C_{12}H_{16}O_4$ calcd: B, 8.79; C, 58.62; H, 6.56%.

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