Tetrahedron Letters,Vol.28,No.23,pp 2599-2602,1987 0040-4039/87 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

REACTIONS OF 2-ALKYL-, 2-PHENYL- AND 2-ALKOXY-1,2-OXABOROLANES WITH (DICHLOROMETHYL)LITHIUM. A NOVEL SYNTHESIS OF 1,4-ALKANEDIOLS.

Ding Hongxun, Zhou Weike* and Bai Junchai

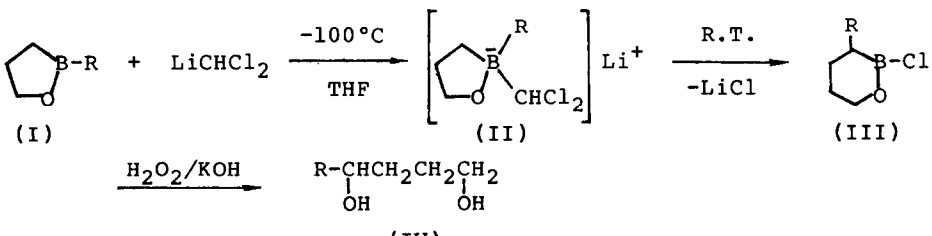
Shanghai Institute of Organic Chemistry, Academia Sinica
345 Lingling Lu, Shanghai, CHINA

Summary: Two novel alternative procedures for the synthesis of 1,4-alkanediols were described by involving the reactions of (dichloromethyl)lithium with some 1,2-oxaborolane derivatives readily obtainable from allyl alcohol.

A highly efficient homologation of cyclic boronic esters ($RBO_2C_2R_4$) to the corresponding α-chloroboronic esters ($R\text{-}CHCl\text{-}BO_2C_2R_4$) with (dichloromethyl)lithium has been found recently by Matteson and his co-workers.[1] Brown and his co-workers have also reported a systematic study of the reactions of $LiCHCl_2$ with various organoborane intermediates.[2] We wish to report here the reactions of some 1,2-oxaborolane derivatives with $LiCHCl_2$ which revealed two alternative syntheses of 1,4-alkanediols.

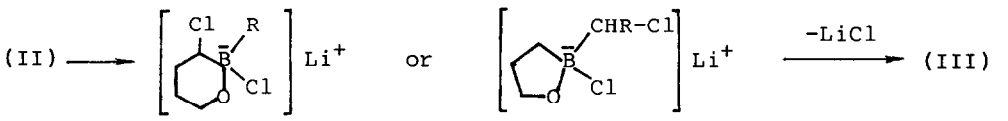
A series of 2-alkyl-, 2-phenyl- and 2-alkoxy-1,2-oxaborolanes were synthesized from allyl alcohol according to our previous methods.[3]

2-Alkyl- and 2-phenyl-1,2-oxaborolanes (I) reacted with $LiCHCl_2$[1] at -100 °C, to form the "borate" complexes (II), which were converted into the intermediates (III) on warming the reaction mixture to room temperature. The 1,2-oxaborinanes (III) without isolation were treated with alkaline hydrogen peroxide to give 1,4-alkanediols (IV) (Scheme 1).



Scheme 1

The formation of the intermediates (III) may be explained by the following scheme:



Thus, starting from allyl alcohol[3], 1,4-alkanediols (IV) were prepared in good yields, as shown in Table 1.

Table 1. Synthesis of 1,4-Alkanediols (IV) from Alkyloxaborolanes (I)

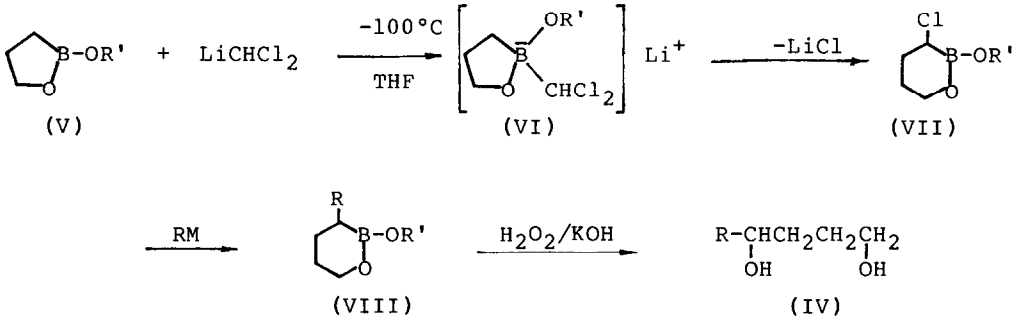
Entry	R of (I)	Product$^{\alpha}$ (IV)	Yield$^{\beta}$(%)
a	n-Butyl	1,4-Octanediol	81
b	n-Hexyl	1,4-Decanediol	77
c	n-Heptyl	1,4-Undecanediol	71
d	Cyclohexyl	1-Cyclohexyl-1,4-butanediol$^{\gamma}$	77
e	Allyl	6-Heptene-1,4-diol	65
f	Phenyl	1-Phenyl-1,4-butanediol	86

α. All products were identified by ^{1}H NMR, IR and MS spectra.
β. Isolated yield. γ. This compound was reported as a liquid,[4] but it is a solid in our work, m.p. 44°C.

The typical procedure is as follows. A solution of 2.0 mL (30 mmol) of dichloromethane in 20 mL of THF was cooled with a liquid nitrogen/ethanol bath. 7.8 mL (11 mmol) of 1.4M n-BuLi in hexane was added dropwise under stirring at the temperature below -80°C.[1] To the well-stirred solution, 2-alkyl- or 2-phenyl-1,2-oxaborolane (I) (10 mmol) was added in one portion at -100°C. The reaction mixture was stirred and kept overnight at room temperature. Then 9 mL of 3N KOH and 1.5 mL of 33% H_2O_2 were added at 0°C. After stirring for 1 h at room temperature, the product was extracted with ethyl ether three times and the combined organic layers were dried over $MgSO_4$. The residue concentrated under vacuum was purified by column chromatography (silica gel, ethyl acetate and petroleum ether) to give pure 1,4-alkanediol (IV).

Alternatively, 2-alkoxy-1,2-oxaborolanes (V) reacted with $LiCHCl_2$ at -100°C to give the similar "ate" complexes (VI) which gave the corresponding ring expansion products (VII) with elimination of LiCl at about 50°C. In this case, 2-alkoxy-3-chloro-1,2-oxaborinanes (VII)[5] were isolated in 85% yields by distillation. The homologated products (VII) were treated with organometal-

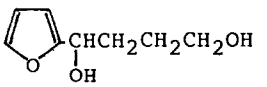
lic reagents (RM = RLi or RMgX), followed by oxidation with alkaline H_2O_2, to give the corresponding 1,4-alkanediols (IV). By this sequence (Scheme 2) some more 1,4-diols were prepared in moderate yields (Table 2).



(a) R'= Butyl; (b) R'= Cyclohexyl

Scheme 2

Table 2. Synthesis of 1,4-Alkanediols (IV) from Alkoxyoxaborolane (Va)

Entry	RM	Product (IV)	Yield (isolated)
a	CH_3Li	$CH_3CH(OH)CH_2CH_2CH_2OH$	66%
b	$CH_3CH_2CH_2CH_2Li$	$CH_3(CH_2)_3CH(OH)CH_2CH_2CH_2OH$	80%
c	$CH_3CH_2CH(CH_3)MgBr$	$CH_3CH_2CH(CH_3)-CH(OH)CH_2CH_2CH_2OH$	61%
d	$(CH_3)_3CMgBr$	$(CH_3)_3C-CH(OH)CH_2CH_2CH_2OH$	25%
e	$CH_2=CHCH_2MgBr$	$CH_2=CHCH_2CH(OH)CH_2CH_2CH_2OH$	77%
f	PhMgBr	$Ph-CH(OH)CH_2CH_2CH_2OH$	67%
g			56%

1,4-Alkanediols are useful intermediates for synthesis of γ-diketones, γ-lactones or cyclopentenones, for example, used as precursors for synthesis of cis-jasmone and prostaglandin B_2.[6] Although 1,4-alkanediols may be also obtained by alternative approach via organoboranes, i.e. treatment of vinyl

lithium with trialkylboranes and then with oxanes, followed by oxidation,[7] only one of the three alkyl groups of R_3B was utilized in this sequence. However, the present procedure (Scheme 1) permitted complete utilization of the alkyl group resulting from olefin if the intermediates (I) were prepared by hydroboration with 2-hydro-1,2-oxaborolane dimethyl sulfide complex.[3c]

We are actively exploring the potentialities of some cyclic organoboron compounds in organic synthesis.

References and Notes

1. Matteson, D.S.; Majumdar, D., Organometallics, **1983**, 2, 1529.
2. (a) Brown, H.C.; Imai, T.; Perumal, P.T.; Singaram, B., J. Org. Chem.,**1985**, 50, 4032. (b) Brown, H.C.; Naik, R.G.; Singaram, B.; Pyun, C., Organometallics, **1985**, 4, 1925.
3. (a) Compounds V and Ia were prepared by heat exchage reaction of 2-allyloxy-1,2-oxaborolane (IX) easily obtainable from allyl alcohol via hydroboraton. Zhou Weike; Zhang Gaoyi; Ding Hongxun, Youji Huaxue, **1982**, 19. C.A. 96, 181336q and C.A. 95, 204021d. (b) Compounds Ie and If were prepared by Grignard reaction of (IX) with RMgX. See: Zhou Weike; Zhang Gaoyi; Ding Hongxun, New Front. Organometal. Inorg. Chem., Proc. China-Japan-U.S.A. Trilateral Semin., 2nd 1982 (pub. **1984**), P-139. Edited by Boon-Keng, Teo. Sci. Press. (c) Compounds Ib, Ic and Id were prepared by hydroboration of the corresponding alkenes with 2-hydro-1,2-oxaborolane dimethyl sulfide (X) , which was easily prepared from the hydroboration of (IX). Zhou Weike; Lo Weiming; Liang Shaofang. To be published.
4. Kazlauskas, D.; Liet. TSR Mosla Akad. Darb. Ser. B, **1967**, 35.
5. 2-Alkoxy-3-chloro-1,2-oxaborinanes (VII) were identified by ^1H NMR, IR, MS spectra. a) 2-Butoxy-3-chloro-1,2-oxaborinane, b.p. 101°C/9mmHg, n_D^{20} 1.4552, ^1H NMR (CCl_4) δ 0.92(t,J=7Hz,3H), 1.2-2.1(m,8H), 3.49(t,J=5Hz,1H), 3.7-4.2 (m,4H); Calcd. from $BC_8H_{16}O_2Cl$, C% 50.45, H% 8.47, B% 5.68, Cl% 18.61; Found C% 50.25, H% 8.52, B% 5.68%, Cl% 18.67. b) 2-Cyclohexyloxy-3-chloro-1,2-oxaborinane, b.p. 134°C/9mmHg, n_D^{20} 1.4836, ^1H NMR (CCl_4) δ 1.2-2.2(m, 14H), 3.48(t,J=5Hz,1H), 3.9-4.2(m,3H), Calcd. from $BC_{10}H_{18}O_2Cl$, C% 55.47, H% 8.38, B% 4.99, Cl% 16.37%, Found C% 55.19, H% 8.23, B% 4.92, Cl% 16.25%.
6. Ellison, R.A., Synthesis, **1973**, 397.
7. Utimoto, K.; Uchida, K.; Yamaya, M.; Nozaki, H., Tetrahedron, **1977**,33,1945.

(Received in Japan 11 November 1986)