CHEMISTRY LETTERS, pp. 1493-1496, 1974. Published by the Chemical Society of Japan

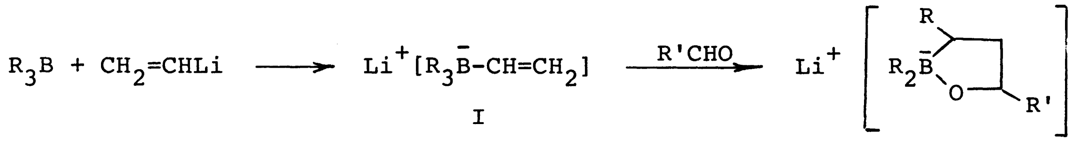
THE REACTION OF LITHIUM TRIALKYLVINYLBORATES AND ALDEHYDES AS APPLIED TO THE SYNTHESIS OF 1,3-DIOLS, γ-CHLOROALCOHOL, AND CYCLOPROPANE

Kiitiro UTIMOTO, Keiichiro UCHIDA, and Hitosi NOZAKI
Department of Industrial Chemistry, Kyoto University
Yoshida, Kyoto 606

Reaction of lithium trialkylvinylborates with aldehydes gives non-isolable boron compounds, 1,2-oxaborolane-bases borates (II) whose oxidative work-up furnishes 1,3-diols (III) smoothly. Successive treatment of a cyclic borate with phosphorus pentachloride and aqueous alkali provides a cyclopropane.

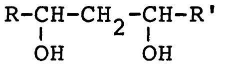
The discovery of hydroboration[1] and trialkylborane-carbon monoxide reaction[2] has motivated an extensive investigation of the novel syntheses with organoboranes.[3] More recently, reactions of lithium trialkylalkynylborates with electrophilic reagents attracted much attention in a sense of alkylative reduction of acetylenic bond.[4] In continuation of our interest in the reaction of lithium trialkylvinylborates (I) with oxiranes,[5] this paper describes the reaction of the borates I with aldehydes[6] affording cyclic borates (II), which have proved to be useful reaction intermediates.

To a stirred solution of vinyllithium (5.0 mmol in 7 ml of ether) maintained under argon atmosphere at 0°C, tributylborane (5.0 mmol) was added. The resulting solution of the borate I (R = Bu) was stirred for 30 min at 25°C, added with 0.4 g (5.5 mmol) of isobutyraldehyde at 0°C, and the whole mixture was stirred at 45°C for 13 h. The reaction product at this stage is believed to be a non-isolable cyclic borate II on the analogy to the reaction of I with oxiranes.[7] The cyclic borates II have been easily converted into the 1,3-diols III. In addition, the successful preparation of 1-chloro-3-heptanol (IV) and 1-ethyl-2-phenylcyclopropane (V) from the appropriate borates II illustrates the versatile character of the intermediates in γ-chloroalcohol and cyclopropane syntheses.



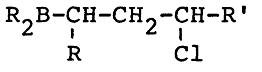
I

II



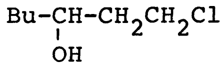
$R\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}R'$

III



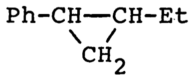
$R_2B\text{-}\underset{R}{CH}\text{-}CH_2\text{-}\underset{Cl}{CH}\text{-}R'$

VI



$Bu\text{-}\underset{OH}{CH}\text{-}CH_2CH_2Cl$

IV



V

1,3-Diols

Work-up of the above-described reaction mixture containing the borate II (R = Bu, R' = i-Pr) with alkaline hydrogen peroxide afforded 2-methyl-3,5-nonanediol [III, R = Bu, R' = i-Pr, ir (liquid film) 3380, 1049 cm^{-1}, nmr ($CDCl_3$) δ 0.8∿1.1 (m, 9H), 1.2∿2.0 (m, 9H), 3.36 (s, 2H), 3.4∿4.0 (m, 2H), ms of trimethylsilyl ether m/e (rel. intensity %) 303 (0.1, M-15), 275 (2), 159 (100), 145 (40), 75 (18), 73 (63)] in 74% overall yield. This product was found to be a mixture of two diastereomers (nearly 1:1) upon glc of its trimethylsilyl ether. 1,3-Diols prepared in this way are listed in Table 1.

Table 1. 1,3-Diols (III)[8]

R	R'	Yield %	Diastereomer[a] ratio	bp °C (mmHg)[b]	Ref. bp °C (mmHg)
Et	Ph	78	51:49	170-80 (4)	--- - - -
Bu	H [$(CH_2O)_n$]	80		135-45 (18)	ref.[12] 140-4 (25)
Bu	H (formalin)[c]	49		"	" "
Bu	i-Pr	74	49:51	100-10 (2)	--- - - -
Bu	Ph	72	49:51	105-15 (0.08)	--- - - -
Bu	MeCH=CH-	48[d]	36:64	120-30 (3)	--- - - -
i-Pr	H [$(CH_2O)_n$]	74		160-70 (26)	ref.[13] 130 (10)[b]
i-Pr	Me	52	50:50	105-15 (10)	ref.[14] 75 (1)
i-Pr	i-Pr	73	56:44	95-105 (5)	ref.[14] [mp 68°C]
i-Pr	Ph	65	50:50	90-100 (0.06)	--- - - -
i-Pr	MeCH=CH-	28[d]	59:41	105-15 (5)	--- - - -

a) Diastereomer ratio was calculated by glc but diastereomers were not assigned.
b) Kugelrohr was used for distillation and bp means bath temperature.
c) Commercial material, 37% formaldehyde in water.
d) As a side reaction, Michael type addition is conceivable. Efforts to clarify this point were fruitless.

As shown in Table 1, formalin reacted with the borate I to give 1,3-diol in a similar procedure. This result indicates that the above described reaction of the borate I with aldehydes does not require the anhydrous condition.

1-Chloro-3-heptanol.

The reaction mixture containing the borate II (R = Bu, R' = H) was cooled to -15°C and was added with 10 ml of ether and 1.56 g (7.5 mmol) of phosphorus pentachloride.[9] The resulting mixture was stirred at 0°C for 4 h and the at 40°C for 1.5 h. Usual oxidative work up, extraction, and purification gave 1-chloro-3-heptanol (IV)[10] in 53% over-all yield probably via the chloroalkylborane VI (R = Bu, R' = H). Attempted treatment with phosphorus trichloride, thionyl chloride, or with sulfuryl chloride gave dissatisfactory results.

The procedure is simple and efficient in the preparation of γ-chloroalcohol from easily available reagents: trialkylborane, vinyllithium, paraformaldehyde and phosphorus pentachloride.

1-Ethyl-2-phenylcyclopropane.

The intermediate VI has proved to be a useful intermediate for cyclopropane synthesis. The reaction mixture containing the chloroalkylborane VI (R = Et, R' = Ph) was added with 10 ml of 3N-NaOH at room temperature and was stirred for 1 h to give 1-ethyl-2-phenylcyclopropane (V, 50:50 mixture of cis and trans isomers)[11] in 35% over-all yield.

The cyclopropane formation schematically consists in alkylative cyclopropanation of vinyllithium with trialkylborane and benzaldehyde.

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6. Ketones did not react with the borate I under a similar condition.
7. In contrast with the reported case,[5] glc and ms analyses of the reaction mixture did not give any definite proof about the formation of the cyclic borate II.
8. New compounds were determined by ir, nmr and ms.
9. Analogous chlorination with phosphorus pentachloride was reported: L. S. Vasil"ev, M. M. Vartanyan, V. S. Bogdanov, V. G. Kiselev, and B. M. Mikhailov, Zhur. Obshch. Khim., 42, 1540 (1972).
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11. (a) Isomer ratio was determined by glc and nmr; see also G. L. Closs and R. A. Moss, J. Amer. Chem. Soc., 86, 4042 (1964).

    (b) The analogous cyclization step was reported for the cyclopropane synthesis by hydroboration of propargyl chloride or allyl chloride and by successive treatment with bases; H. C. Brown and S. P. Rhodes, J. Amer. Chem. Soc., 91, 2149, 4306 (1969) and references cited therein.
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(Received September 26, 1974)