

THE PREPARATION OF TRIALKYL VINYLBORATES AND THEIR REACTIONS WITH OXIRANES AND WITH IODINE. A FACILE SYNTHESIS OF 1,4-ALKANEDIOLS AND 1-ALKENES

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(Received in Japan 25 December 1976; Received in UK for publication 18 February 1977)

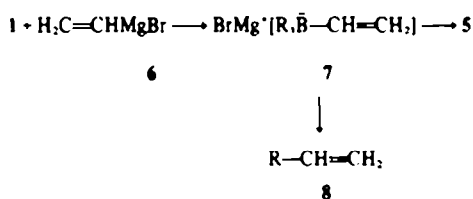
Abstract—Reaction of trialkylboranes with vinyl lithium gives non-isolable lithium trialkylvinylborates which react with oxirane and methyloxirane affording 1,4- and 2,5-alkanediols, respectively. Treatment of trialkylboranes with vinylmagnesium bromide produces bromomagnesium trialkylvinylborates which analogously afford alkanediols. Successive treatment of the borates with aqueous alkali and iodine provides 1-alkenes.

Recently lithium trialkyl-1-alkynylborates prepared from trialkylboranes and 1-lithio-1-alkynes have attracted much attention as versatile nucleophiles¹ leading to acetylenes,² olefins,³ ketones,⁴ alcohols,⁵ and many other organic compounds including γ -diketones⁶ and γ -hydroxy ketones.⁷ Branched chain γ -diketones were prepared in good yields,^{8,9} but more important straight chain representatives serving as useful intermediates for 2,3-disubstituted 2-cyclopentenones could not be obtained satisfactorily. This paper describes the preparation of trialkylvinylborates¹⁰ and the reaction with oxiranes affording 1,4- and 2,5-alkanediols which are useful precursors for straight chain γ -dicarbonyl compounds. Further studies will be devoted to the oxidation of the ate complexes leading to 1-alkenes.¹²

Treatment of tributylborane with ethereal vinyl lithium afforded a clear solution of lithium tributylvinylborates.¹¹ Reaction with oxirane or methyloxirane at room temperature¹⁵ followed by oxidative work-up gave 1,4-octanediol and 2,5-nonanediol, respectively as shown in Table 1. *cis*-1,2-Epoxycyclohexane, an example of 2,3-disubstituted oxirane, furnished only 30% yield¹⁶ of the expected diol **5d** under the same conditions but heating of the reaction mixture at 50°C improved the yield up to 77%.¹⁶

When tetrahydrofuran (THF) was employed as a solvent in the reaction of lithium tributylvinylborate with methyloxirane, the yield of 2,5-nonanediol decreased to only 38%. Furthermore, none of the desired diol was obtained in the presence of hexamethylphosphoric triamide (HMPT) or of *N,N,N',N'*-tetramethylethylenediamine added to promote strong solvation or chelation of Li⁺. These facts are explained by assuming that the important prerequisite of oxirane reaction is the coordination of Li⁺ on the oxygen atom and that the free borate ion is not sufficiently nucleophilic to attack the oxiranes.

Grignard reagents are usually more readily accessible than organolithium reagents, but they have rarely been utilized in the preparation of boron ate complexes.¹⁷ We have found that vinylmagnesium bromide **6** can be used much more conveniently than vinyl lithium for the preparation of boron ate complexes **7** and also of alkanediols **5**.



Treatment of vinylmagnesium bromide with tripropylborane¹⁸ and then with oxirane followed by usual oxidative work-up gave 1,4-heptanediol. The yields of the diols were dependent upon the reaction temperature: treatment with oxirane at -78°C gave 61%, -20°C 76%, 0°C 77%, room temperature 32% of the desired diol. Methyloxirane produced 2,5-octanediol in 85% yield. Although these yields are a little inferior to those with lithium intermediates, the easy accessibility would justify the use of the Grignard reagent **6**.

Alkanediols obtained by the above described procedures are useful intermediates for the synthesis of γ -diketones and 4-oxoalkanoic acids, which are well known precursors of furans,¹⁹ pyrroles,²⁰ cyclopentenones,²¹ γ -lactones²² and cyclopentane-1,3-diones.²¹ The reaction of trialkylvinylborates with ox-

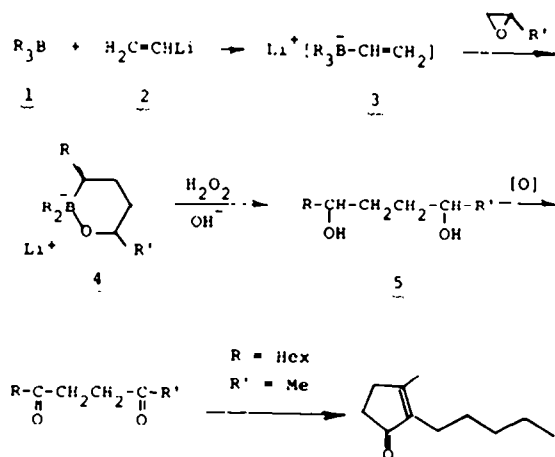


Table 1. Alkanediols prepared from R₃B, H₂C=CHLi and oxiranes

R in R ₃ B ^a	Oxirane	Alkanediol	Yield (%) ^d
n-Bu	Oxirane	1,4-Octanediol 5a	quant.
n-Bu	Methyloxirane	2,5-Nonanediol 5b ^b	93
i-Pr	Methyloxirane	6-Methyl-2,5-heptanediol 5c ^b	quant.
n-Bu	cis-1,2-Epoxy-cyclohexane	2-(2-Hydroxyhexyl)-cyclohexanol 5d ^c	77 ^e
Hex	Oxirane	1,4-Decanediol 5e	89
Hex	Methyloxirane	2,5-Undecanediol 5f ^b	93 (85) ^f

^aPrepared from RMgBr and BF₃ etherate. ^bBis(trimethylsilyl) ether of the diol was gas-chromatographically homogeneous (Silicon HVSG and PEG 20M). Whether the diol is one of the possible two diastereomers or a mixture is still uncertain. ^cThe stereochemistry was assumed to be trans. ^dYields are based on trialkylboranes. ^eReaction at 50°C. ^fTrihexylborane was prepared by hydroboration of 1-hexene in tetrahydrofuran (THF). The reaction of the borate with methyloxirane was performed in THF and ether mixture. The resulting diol consisted of 2,5-undecanediol and 6-methyl-2,5-decanediol (89:11).

iranes, therefore, opens up a novel approach to a variety of compounds. Following examples are illustrative.

Chromic acid oxidation (Jones procedure)²⁴ of 2,5-undecanediol 5f gave 2,5-undecanedione (94% yield) which afforded dihydrojasnone in 94% yield upon alkaline treatment.²⁵ Overall yield of dihydrojasnone based on trihexylborane was 82%. Analogous oxidation of 1,4-decanediol 5e afforded 4-oxodecanoic acid in 76% yield (overall yield from trihexylborane being 68%).

Finally, it should be noted that the oxidation of 7 with iodine furnished 1-alkenes 8 in good yields (R=CH=CH₂; R=Hex 82%, R=Decyl 67%).¹² As tri-n-alkylboranes can be prepared from 1-alkenes, this procedure opens a method for two carbon homologation of 1-alkenes using vinylmagnesium bromide.

EXPERIMENTAL

Gas chromatography was performed on a Shimadzu GC-4BPT with 3 m × 3 mm glass column packed with 20% Silicon HVSG and 20% PEG 20M on Chromosorb W-AW (80-100 mesh). ¹H NMR spectra were obtained on a JEOL JNM-PMX-60 and a Varian Associates EM-360 using tetramethylsilane as an internal standard, mass spectra on a Hitachi RMC-6L with a chamber voltage of 70 eV, and IR on a Shimadzu IR-27G grating spectrometer. Elemental analyses were performed by the Elemental Analyses Centre of Kyoto University.

1,4-Octanediol 5a. Tributylborane (1.82 g, 10.0 mmol) was added to a stirred solution of vinylolithium²⁶ (10.0 mmol, 20.0 ml of 0.5 M ether solution) maintained at 0°C under argon atmosphere. Yellow colour of vinylolithium was discharged to colourless. After being stirred at room temp. for 30 min, the mixture was treated with oxirane (1 ml, 20 mmol) during 10 min at 0°C. The mixture was stirred overnight at room temp. The resulting pale yellow viscous mixture was oxidized with 3N NaOH (3 ml) and 30%

H₂O₂ (5 ml) at 0°C for 5 min and room temp. for 1 h. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with brine, dried (Na₂SO₄), and concentrated under reduced pressure. Distillation of the residue in a Kugelrohr gave 1,4-octanediol as a colourless viscous oil (1.47 g, quantitative), bp 125°C (bath temp.)/4 mm (lit.²⁶ bp 139°C/10 mm). IR (neat): 3400, 1118, 1060 cm⁻¹; ¹H NMR (CDCl₃): δ 0.90 (t, J = 6 Hz, 3H), 1.0–2.0 (m, 10H), 2.80 (broad s, 2H), 3.3–3.9 (m, 3H); MS of bistrimethylsilyl ether: *m/e* (rel. %) 275 (M-15, 14), 233 (3), 159 (66), 147 (10), 143 (69), 103 (23), 75 (61), 73 (100).

2,5-Nonanediol 5b. A solution of lithium tributylvinylborate (5.0 mmol) in ether prepared as described above was treated with methyloxirane (0.67 ml, 10.0 mmol) at 0°C and the whole was stirred overnight at room temp. Oxidation followed by distillation gave 2,5-nonanediol (757 mg, 93% yield), b.p. 130°C (bath temp.)/4 mm. IR (neat): 3320, 1190, 1023 cm⁻¹; ¹H NMR (CDCl₃): δ 0.89 (t, J = 6 Hz, 3H), 1.23 (d, J = 7 Hz, 3H), 1.1–1.6 (m, 10H), 2.84 (s, 2H), 3.3–4.0 (m, 2H); MS of bistrimethylsilyl ether: *m/e* (rel. %) 289 (M-15, 0.1), 247 (3), 159 (82), 157 (87), 117 (45), 75 (35), 73 (100). The diol 5b was converted to the corresponding diacetate (acetic anhydride-pyridine) which was submitted for elemental analysis (Found: C, 63.94; H, 10.06. Calc. for C₁₁H₂₂O₄: C, 63.90; H, 9.90%).

Before oxidative work-up a small aliquot of the reaction mixture was subjected to GLC, which revealed that two products (92:8) were formed upon injection. Mass spectral data of the major eluent was ascribed to 9: *m/e* (rel. %) 210 (M⁺ of 9, 4), 169 (5), 126 (57), 84 (90), 70 (40), 69 (52), 56 (100), 55 (78). The minor one remains undetermined.

To the borate solution (3 mmol) in ether HMPT (3 ml) was added at room temp. and the resulting solution was treated with methyloxirane (4.5 mmol) at 0°C and stirred overnight at room temp. GLC analysis of the oxidized product showed that the no desired diol was obtained.

One equivalent of *N,N,N',N'*-tetramethylethylenediamine

(0.45 ml, 3.0 mmol) was added to the borate solution (3.0 mmol) at room temp. The same treatment as described above gave no desired diol.

2,5-Nonanediol 5b. Preparation in THF. Tributylborane (0.91 g, 5.0 mmol) was added to a stirred solution of vinyl lithium in THF (5.0 mmol, 3.6 ml of 1.38 M solution, obtained from Alfa Products) at 0°C. The resulting solution was stirred at 0°C for 30 min, treated with methyloxirane (0.67 ml, 10.0 mmol) at 0°C, and stirred overnight at room temp. After dilution with ether, the mixture was oxidized with 3N NaOH (2 ml) and 30% H₂O₂ (3 ml). Concentration, chromatography (silica gel, hexane-ethyl acetate, gradient elution) and distillation in a Kugelrohr of the ethereal solution gave **5b** (0.30 g, 38% yield).

6-Methyl-2,5-heptanediol 5c. To a stirred solution of vinyl lithium (5.0 mmol, 8.1 ml of 0.62 M ether solution) was added triisopropylborane (0.70 g, 5.0 mmol) at 0°C. Immediately, a white precipitate was formed. After being stirred at room temp. for 30 min, the mixture was treated with methyloxirane (0.67 ml, 10.0 mmol) at 0°C and stirred overnight at room temp. A milky turbid slurry resulted and gave, after oxidative work-up and distillation, the diol **5c** (0.74 g, quantitative), b.p. 110°C (bath temp.)/4 mm. IR (neat): 3380, 1066 cm⁻¹; ¹H NMR (CDCl₃): δ 0.92 (d, J = 6 Hz, 6H) 1.18 (d, J = 6 Hz, 3H), 1.3–2.0 (m, 4H), 2.0–2.6 (m, 1H), 3.00 (broad s, 2H), 3.2–3.5 (m, 1H), 3.5–4.0 (m, 1H); MS of bistrimethylsilyl ether: *m/e* (rel. %) 275 (M⁺, 0.2), 247 (7), 157 (100), 147 (13), 145 (31), 117 (22), 75 (29), 73 (88). (Found: C, 66.00; H, 12.65. Calc. for C₈H₁₈O₂: C, 65.71; H, 12.41%).

2-(2-Hydroxyhexyl)-cyclohexanol 5d. To a stirred solution of lithium tributylvinylborate (5.0 mmol) in ether was added *cis*-1,2-epoxycyclohexane (540 mg, 5.5 mmol) at 0°C. The mixture was heated at reflux for 12 h. Oxidative work-up followed by distillation²⁸ gave the diol **5d** (1.54 g, 77% yield), b.p. 135–140°C/0.3 mm. IR (neat): 3340, 1038, 1060 cm⁻¹; ¹H NMR (CDCl₃): δ 0.90 (t, J = 6 Hz, 3H), 1.0–2.2 (m, 17H), 2.9–3.4 (m, 1H), 3.4–4.0 (m, 1H), 4.33 (s, 2H); MS of bistrimethylsilyl ether: *m/e* (rel. %) 344 (M⁺, 0.3), 287 (15), 197 (89), 170 (28), 159 (100), 147 (17), 130 (22), 75 (24), 73 (63). (Found: C, 71.72; H, 11.94. Calc. for C₁₇H₃₂O₂: C, 71.95; H, 12.08%).

When the reaction was performed overnight at room temp., the yield of the diol decreased as low as 30%.

1,4-Decanediol 5e. Tributylborane was replaced with trihexylborane in the procedure for the preparation of 1,4-octanediol. After oxidative work-up, distillation gave 1,4-decanediol (89% yield), b.p. 135–140°C (bath temp.)/3 mm (lit.²⁹ 131–132°C/2 mm). IR (neat): 3310, 1054 cm⁻¹; ¹H NMR (CDCl₃): δ 0.88 (t, J = 6 Hz, 3H), 1.1–1.9 (m, 14H), 3.3–4.0 (m, 5H), C(1)H₂, C(4)H and 2 OH; MS of bistrimethylsilyl ether: *m/e* (rel. %) 303 (M⁺, 0.2), 233 (8), 187 (63), 147 (29), 143 (98), 103 (17), 97 (17), 75 (39), 73 (100), 71 (27).

2,5-Undecanediol 5f. The diol was obtained from trihexylborane (1.33 g, 5.0 mmol), vinyl lithium (5.0 mmol, 10.0 ml of 0.5 M ether solution) and methyloxirane (0.67 ml, 10.0 mmol) in 93% yield by the procedure described in the preparation of 2,5-nonanediol. B.p. 123–126°C/3 mm (lit.³⁰ 129°C/1.5 mm). IR (neat): 3300, 1123, 1038 cm⁻¹; ¹H NMR (CDCl₃): δ 0.89 (t, J = 6 Hz, 3H), 1.16 (d, J = 6 Hz, 3H), 1.1–1.8 (m, 14H), 3.28 (broad s, 2H), 3.4–4.0 (m, 2H); MS of bistrimethylsilyl ether: *m/e* (rel. %) 247 (M⁺, 85, 9), 187 (65), 157 (100), 147 (18), 117 (40), 75 (37), 73 (91).

When trihexylborane was obtained by hydroboration of 1-hexene, the following procedure was employed.

The borate solution was obtained by hydroboration of 1-hexene (1.26 g, 15.0 mmol) with borane (5.0 mmol, 3.8 ml of 1.33 M THF solution) at 0°C for 1 h and treatment with vinyl lithium (5.0 mmol, 10.0 ml of 0.5 M ether solution) for 30 min at room temp. The reaction of the borate with methyloxirane (0.67 ml, 10.0 mmol) overnight at room temp. afforded the diol **5f** (0.80 g, 85% yield). GLC analysis of the bistrimethylsilyl ether of the product showed that the diol contained 2,5-undecanediol and 6-methyl-2,5-decanediol (89:11).

2,5-Nonanediol. To a solution of 2,5-nonanediol (374 mg, 2.34 mmol) in 40 ml of acetone was added dropwise Jones reagent³⁴ at room temp. until the orange colour persisted. The excess reagent was quenched with 2-propanol. The solvent was removed *in vacuo*,

and the residue was extracted with hexane. The combined organic extracts were washed, dried (Na₂SO₄) and concentrated. Column chromatography (silica gel, hexane-ether 3:1) of the crude product gave 2,5-nonanediol³¹ (334 mg, 91% yield). IR (neat): 1711 cm⁻¹; ¹H NMR (CCl₄): δ 0.90 (t, J = 6 Hz, 3H), 1.1–1.7 (m, 4H), 2.11 (s, 3H), 2.37 (t, J = 7 Hz, 2H), 2.57 (s, 4H); MS: *m/e* (rel. %) 156 (M⁺, 0.7), 114 (57), 99 (70), 85 (48), 71 (67), 57 (86), 43 (100).

2-Propyl-3-methyl-2-cyclopentenone. 2,5-Nonanediol (293 mg, 1.88 mmol) was converted by published procedure³² to 2-propyl-3-methyl-2-cyclopentenone (227 mg, 89% yield). IR (neat): 1693, 1643 cm⁻¹; ¹H NMR (CCl₄): δ 0.88 (t, J = 6 Hz, 3H), 1.1–1.6 (m, 2H), 2.03 (s, 3H), 2.0–2.6 (m, 6H); MS: *m/e* (rel. %) 138 (M⁺, 82), 123 (88), 110 (100), 95 (38), (81) (54), 67 (59).

2,5-Undecanediol. Oxidation of the diol **5e** (403 mg, 2.14 mmol) was performed as described in preparation of 2,5-nonanediol. Column chromatography (silica gel, benzene) of the crude product afforded the diol (370 mg, 94% yield). IR (neat): 1709 cm⁻¹; ¹H NMR (CCl₄): δ 0.89 (t, J = 6 Hz, 3H), 1.1–1.8 (m, 8H), 2.10 (s, 3H), 2.36 (t, J = 7 Hz, 2H), 2.55 (s, 4H); MS: *m/e* (rel. %) 184 (M⁺, 3), 110 (62), 99 (40), 71 (54), 43 (100).

Dihydrojasmane. The diketone (356 mg, 1.93 mmol) was cyclized according to the Hunsdiecker procedure.³³ Extractive work-up followed by preparative TLC (silica gel, benzene) afforded dihydrojasmane (333 mg, 94% yield).

4-Oxodecanoic acid. Jones oxidation³⁴ of 1,4-decanediol (**5e**, 470 mg, 2.70 mmol) at 0°C gave 4-oxodecanoic acid (380 mg, 76% yield) after column chromatography (silica gel, hexane-ethyl acetate 1:1). Recrystallization from hexane afforded colourless plates, m.p. 66–67°C (lit.³² 66°C). IR (Nujol): 3600–2300, 1700, 1237, 939 cm⁻¹; ¹H NMR (CDCl₃): δ 0.88 (t, J = 6 Hz, 3H), 1.1–2.0 (m, 8H), 2.44 (t, J = 7 Hz, 2H), 2.68 (s, 4H), 9.65 (broad s, 1H); MS of trimethylsilyl ester: *m/e* (rel. %) 258 (M⁺, 0.3), 243 (25), 188 (26), 173 (29), 147 (40), 113 (29), 98 (100), 85 (26), 75 (74), 73 (100).

1,4-Heptanediol. To a stirred solution of vinylmagnesium bromide (6.0 mmol in 5.5 ml of THF solution) maintained under argon atmosphere at 0°C, tripropylborane (5.0 mmol) was added and the resulting solution was stirred for 1 h at 0°C and for 1 h at room temp. Oxirane (0.40 ml, 8.0 mmol) was added at 0°C and the whole was stirred for 2 h at 0°C then 13 h at room temp. Usual work-up with alkaline hydrogen peroxide gave 1,4-heptanediol (506 mg, 77% yield), b.p. 100°C (bath temp.)/3 mm (lit.³¹ 112–115°C/3 mm). IR (neat): 3330, 1125, 1055 cm⁻¹; ¹H NMR (CCl₄): δ 0.92 (t, J = 6 Hz, 3H), 1.2–1.7 (m, 8H), 3.3–3.7 (m, 3H), 4.67 (s, 2H); MS of bistrimethylsilyl ether: *m/e* (rel. %) 276 (M⁺, 0.4), 261 (1), 233 (6), 147 (34), 145 (77), 143 (64), 103 (13), 75 (33), 73 (100), 71 (22), 55 (38).

2,5-Octanediol. Reaction of tripropylborane (700 mg, 5.0 mmol) with vinylmagnesium bromide (6.0 mmol) and methyloxirane (0.44 ml, 6.5 mmol) gave 2,5-octanediol (581 mg, 80% yield), b.p. 115°C (bath temp.)/3 mm (lit.³⁴ 144–146°C/20 mm). IR (neat): 3320, 1125, 1055 cm⁻¹; ¹H NMR (CCl₄): δ 0.92 (t, J = 6 Hz, 3H), 1.15 (d, J = 6 Hz, 3H), 1.3–1.6 (m, 8H), 3.2–4.0 (m, 2H), 4.4–4.8 (m, 2H); MS of bistrimethylsilyl ether: *m/e* (rel. %) 290 (M⁺, 0.1), 275 (0.1), 247 (3), 157 (55), 147 (21), 145 (56), 117 (41), 75 (40), 73 (100).

2,5-Nonanediol 5b. Reaction of tributylborane (910 mg, 5.0 mmol) with vinylmagnesium bromide (6.0 mmol in 8.6 ml of THF solution) and methyloxirane (0.44 ml, 6.5 mmol) gave the diol (680 mg, 85% yield).

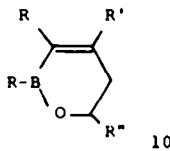
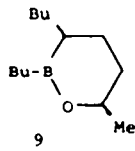
1-Octene. To a stirred solution of vinylmagnesium bromide (6.0 mmol in 8.6 ml of THF solution) under argon atmosphere, trihexylborane (700 mg, 5.0 mmol) was added at 0°C. The reaction mixture was stirred at room temp. for 2 h and was added with 15 ml of 1N sodium hydroxide at 0°C and 1.27 g of iodine (solution in 15 ml of THF) successively. GLC analysis of the reaction mixture indicated the yield of 1-octene was 82%.

1-Dodecene. Reaction of tridecylborane prepared from 1-decene (9.0 mmol) and borane (3.0 mmol of BH₃ in 2.9 ml of THF solution) with vinylmagnesium bromide (3.6 mmol in 5.1 ml of THF solution) and aq.-NaOH-I₂ gave a 67% yield of the olefin.

Acknowledgment—The authors wish to thank the Ministry of Education, Japan, for a Grant-in-Aid (911506).

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