Arabian Journal of Chemistry (2014) 7, 518–521

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Synthesis of C–B–O five membered ring by hydroboration of allylalcohols in standard conditions

Samia Amirat, Ahmed Djellal *

Laboratory of Organic Synthesis, Department of Chemistry, Faculty of Sciences, University of Annaba, B.P. 12 Annaba (23000), Algeria

Received 2 October 2010; accepted 25 November 2010
Available online 28 November 2010

KEYWORDS

Hydroboration;
Allylalcohol;
Trimethylsilyloxy;
Oxaborolanes

Abstract The hydroboration of protected allylalcohols by two different groups gives no linear structures of siloxypropylboranyls as predicted but gives the C–B–O five membered ring 1,2-H-oxaborolanes with good yield. A mechanism is also proposed to explain this cyclisation.

1. Introduction

The organoboron compounds are known for their great interest in chemical synthesis (Steinberg and Brotherton, 1966; Brown and Unni, 1968; Brown, 1975), in asymmetric synthesis (Corey et al., 1997; Corey and Rodhes, 1997; Abiko et al., 1997; Niatteson and Majumdar, 1980), in cancer therapy as "cluster of boron" (Hatanaka and Nakagawa, 1994), Barth et al., 1992) in biology (Dugger, 1983; Hu and Brown, 1994), in transport of sugars as catalyst transfer agent (Dicko et al., 2001). Certain organoboron compounds have an interest in the formulation of some lubricants because of their anti-oxidize properties (Guanqui et al., 2000). The 1,2-oxaloborolanes and related compounds are novel cyclic organoboron involving a simple C–B–O five-membered ring. Their synthesis in two steps with moderate yield (35%) is reported (Zhou et al., 1990). Herein we would like to report the synthesis of oxaborolanes by hydroboration of allylalcohols in standard conditions with good yield and propose a mechanism to explain this cyclic elimination.

2. Results and discussion

2.1. Synthesis of sillyled allylalcohol 3, 4

One of synthetic methods of organoboron compounds consists in an ethylenic bond reduction by the boron hydrides (Brown, 1975). To avoid any competitive reaction allylalcohols **1**, 2 must be protected. Among protective groups proposed by the literature (Greene, 1987) we have chosen trimethylsilyl group because it is little sensible to hydroboration agent BH_3 (borane–methyl sulfide complex BMS) because its introduction and its cleavage are easy (Scheme 1).

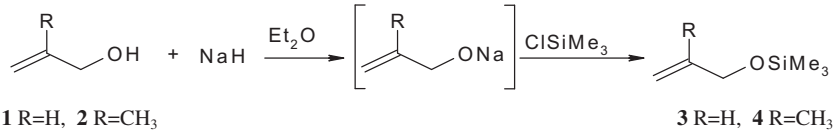
IR spectrum shows the band corresponding to the trimethylsilyl group at 1250 cm^{-1} and the disappearance of alcohol

* Corresponding author. Tel.: +213 797252451.
E-mail address: adjellaldz@yahoo.fr (A. Djellal).

Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

1878-5352 © 2010 Production and hosting by Elsevier B.V. on behalf of King Saud University.
http://dx.doi.org/10.1016/j.arabjc.2010.11.012



1 R=H, **2** R=CH_3 **3** R=H, **4** R=CH_3

Scheme 1 Synthesis of sillyled allylalcohols.

band at 3600 cm^{-1} ^1H NMR exhibits a centered singlet at 0.15 ppm which on integration gives 9 protons and the absence of exchangeable peak corresponding to alcohol function.

*2.2. Synthesis of oxaborolanes **5**, **6***

The sillyled allylalcohols **3**, **4** obtained react with BH_3 in standard conditions to afford no linear structures such as trimethylsiloxypropanylboranyl but the unexpected ring forms such as 1,2-oxaborolanes **5**, **6** (Scheme 2). In fact we have been surprised by a look at ^1H NMR spectra of products which appears at 0.85 ppm and at 3.8 ppm as two dedoubled doublets (dd) characteristic of no symmetrical cyclic structures. The peak at 0.15 ppm due to trimethylsillyl is absent. IR spectrum gives 2300 cm^{-1} band vibration of B–H bond and the disappearance of intensive band at 1250 cm^{-1} corresponding to silyl group.

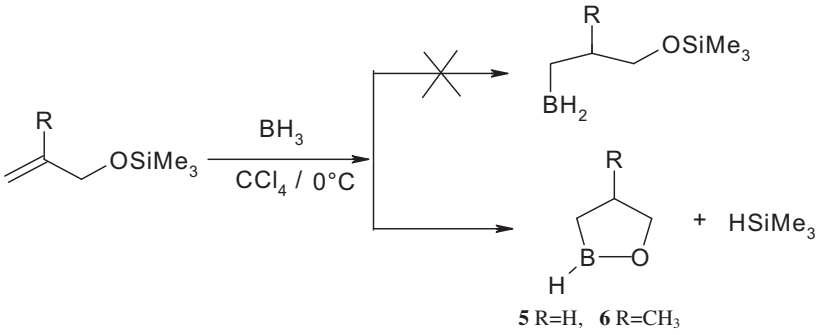
*2.3. Synthesis and hydroboration of triallyloxylborates 7, **8***

In order to know the behavior of reaction when protector group is modified, the allylalcohols are transformed into triallyloxyborates **7**, **8** which are easily obtained by reaction of 1 equivalent of BH_3 with 3 equivalents of allylalcohols accompanied by emission of 3 equivalent. Hydrogen (step of Scheme 3). Surprisingly we observe a formation of oxaborolanes (step 2 of Scheme 3) and we can say that the reaction has the same behavior like the first case. The collected gaseous emission and spectroscopic analysis IR, and ^1H NMR are the two methods of investigation used to explain results. Effectively 3 equivalents of hydrogen are collected and IR spectrum gives band at 2300 cm^{-1} of B–H bond. ^1H NMR gives two dd at 0.85 ppm and at 3.8 ppm characteristic of no symmetric ring structures. (See Scheme 4).

2.4. Direct synthesis of oxaborolanes

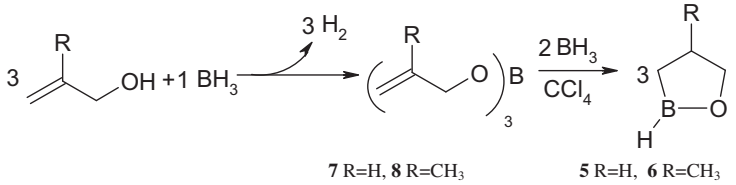
Because the reaction is not affected by the type of protect group we can say that the oxaborolanes can be synthesized directly by the action of BH_3 on allylalcohols via the formation of no isolated triallyloxyborates (Scheme 5).

A mechanism is proposed to explain this cyclisation–elimination. The protective group is rapidly cleaved by an



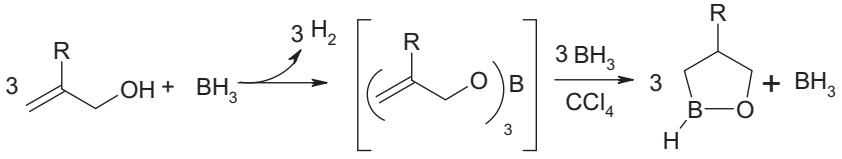
5 R=H, **6** R=CH_3

Scheme 2 Hydroboration of sillyled allylalcohol.

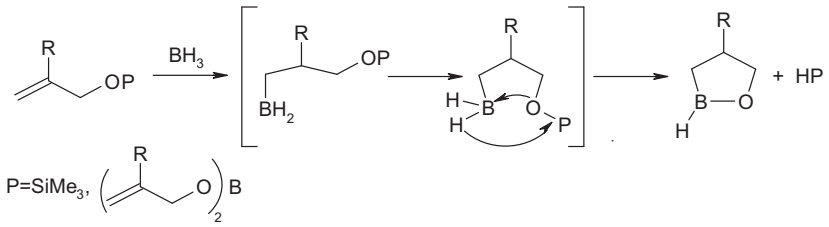


7 R=H, **8** R=CH_3 **5** R=H, **6** R=CH_3

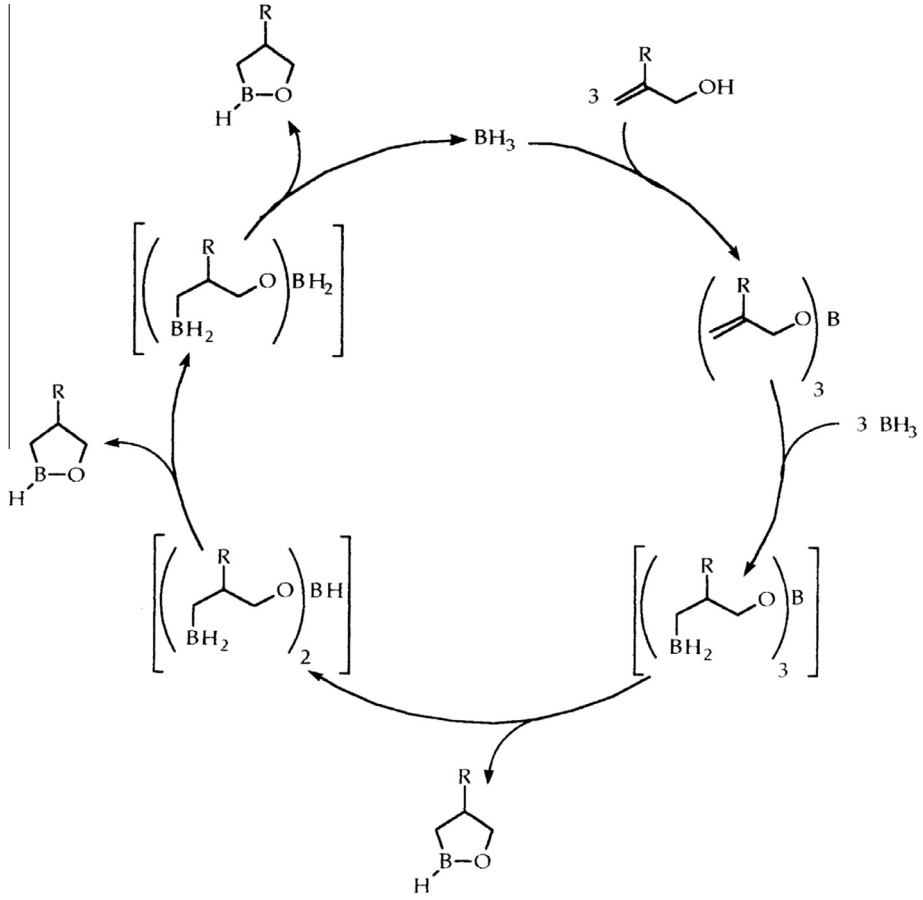
Scheme 3 Synthesis and hydroboration of triallyoxylborates.



Scheme 4 Direct formation of oxaborolanes.



Scheme 5 Mechanism of cyclisation proposed.



Scheme 6 Mechanism of reaction.

intramolecular interaction oxygen–boron bond going through a four-membered cyclic elimination to lead 1,2-oxaborolanes (Scheme 5).

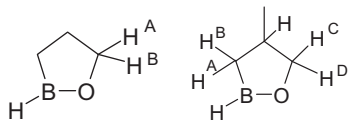
Another cyclic mechanism is proposed concerning the look at the reaction (Scheme 6). The reaction is initiated through the attack of one equivalent of boron hydrur on three equivalents of allylalcohols leading to one equivalent of triallyloxyborane, which reacts with three equivalents of boron hydrur. The last results are the formation of three equivalents of oxaborolanes and one equivalent of BH_3 is restored to continue the cycle.

3. Experimental

Melting points were recorded on Stuart SMP3 Melting point Apparatus. IR spectra were recorded on a Perkin–Elmer spectrophotometer 881. ^{1}H NMR spectra were recorded on Bruker AC-250 (25 MHz) spectrophotometer in $CDCl_3$ solution with TMS as internal standard (chemical shifts are given as δ in ppm). Reactions were carried out under dry argon.

*3.1. Representative procedure for the preparation of sillyled compounds **3**, **4***

A dry 100 ml, three-necked, round-bottomed flask equipped with a rubber septum and a magnetic stirrer is charged with 50 ml of anhydride ether and 10 mmol of sodium hydrur is added slowly. The reaction is controlled in measuring gaseous emission and when this is stopped we add 10 mmol of chlortrimethylsilane drop wise. After stirring two hours the mixture is washed with water. The product is extracted with ethylic ether and purified by distillation under reduced pressure.



5 6

Figure 1 Oxaborolanes synthesized.

*3.1.1. O-triméthylsilyloxy 2-propen **3***
Colorless liquid; b.p. 72 °C/5 mmHg; yield (80%). IR (film, cm^{-1}) 3080 (CH═CH); 1640 C═C); 1250 (Si–Me_3). ^1H NMR ($CDCl_3$, δ): 0.15 (s, 9H, Si(CH_3)$_3$; 4.1 (m, 2H, CH_2O); 5–6 (m, CH_2═CH).

*3.1.2. O-triméthylsilyloxy 2-méthyl 2-propen **4***
Colorless liquid; b.p. 84 °C/5 mmHg; yield (77%). IR (film, cm^{-1}) 3080 (CH═CH); 1650 (C═C); 1250 (Si–Me_3). ^1H NMR ($CDCl_3$, δ): 0.15 (s, 9H, Si (CH_3)$_3$; 1.8 (s, 3H, CH_3); 4 (s, 2H, CH_2–O); 4.8 (s; 1H; CH_A═C); 5 (s, 1H, CH_B═C).

*3.2. Hydroboration of sillyled alcohols to lead oxaborolanes **5**, **6***

(Fig. 1) To 30 mmol of allylalcohol dissolved in 50 ml of CCl_4 we add 10 mmol of borane methyl sulfur complex BH_3 (10 M) dropwise under dry argon and stirring 1 h at room temperature. The mixture was concentrated and the product was obtained by distillation under reduced pressure.

A dry 100 ml, three-necked, round-bottomed flask placed in ice-bath equipped with a rubber septum and a magnetic stirrer is charged with 50 ml of CCl_4 and 10 mmol of sillyled allylalcohols are dissolved in. To the mixture we add 10 mmol of BH_3 Borane Methyl Sulfur complex BMS (10 M). After 15 min the reaction is restored at room temperature and stirred for 1 h. After evaporation of solvent the product is purified by distillation under reduced pressure.

*3.2.1. 1,2 H-oxaborolane **5***
Colorless liquid; b.p. 68 °C/5 mmHg; yield (86%). IR (film, cm^{-1}): 2640 (B–H), 1360 (B–O). ^1H NMR ($CDCl_3$): 0.75 (t, 2H, CH_2–B); 1.6 (qn, 2H, CH_2–CH_2–CH_2); 3.85 (t, 1H, CH^A–O); 3.9 (t, 1H, CH^B–O).

*3.2.2. 4-Méthyl-1,2 H-oxaborolane **6***
Colorless liquid; b.p. 71 °C/5 mmHg; yield (80%). IR (film, cm^{-1}): 2640 (B–H), 1360 (B–O). ^1H NMR ($CDCl_3$): 0.54 (dd, 1H, CH^A–BH); 0.99 (d, 3H, CH_3); 1.12 (dd, 1H, CH^B–BH); 2.3 (m, 1H, CH–CH_3); 3.5 ppm (dd, 1H, CH^C–O); 4.9 (dd, 1H, CH^D–O).

*3.3. Synthesis of triallyl borates **7**, **8***

*3.3.1. Triallyloxyborate **7***
Colorless liquid; b.p. 95 °C/5 mmHg; yield (80%). IR (film, cm^{-1}): 3080 (CH═CH); 1640 (C═C); 1360 (B–O). ^1H NMR ($CDCl_3$): 4.1 (m, 6H, 3CH_2O); 5–6 (m, 9H, 3CH_2═CH).

*3.3.2. Tri(2-méthylallyloxy)borate **8***
Colorless liquid; b.p. 104 °C/5 mmHg; yield (90%). IR (film, cm^{-1}): ν = 3080 (CH═C); 1650 (C═C); 1360 (B–O). ^1H NMR ($CDCl_3$): 1.8 (s, 9H, 3CH_3); 4 (s, 6H, 3CH_2–O); 5 (s, 6H, 3CH_2═C).

3.4. Hydroboration of triallyl borates

Hydroboration of triallyl borates is done according to the same procedure (Section 3.2).

3.5. Direct synthesis of oxaborolanes

In a 100 ml three-necked flask were placed 50 ml of CCl_4 and 30 mmol of allylalcohol; then 30 mmol of BH_3 was added dropwise under dry argon at 0 °C. The reaction mixture is stirred for 1–2 h at room temperature. After evaporation of the solvents, the residue was distilled at reduced pressure.

4. Conclusion

1,2 H-oxaborolanes can be synthesized directly by standard hydroboration of allylalcohols in soft conditions with a good yield. The change of nature of protector group of alcohol function does not affect the behavior of hydroboration reaction. The cyclisation results from great complexation of boron with electron-donating elements like oxygen.

References

Abiko, A., Liu, J.F., Wang, G.Q., Masamune, S., 1997. Tetrahedron Lett. 38 (18), 3261.

Barth, R.F., Soloway, A.H., Fairchild, R.G., Brugger, R.M., 1992. Cancer 70, 2995.

Brown, H.C. (Eds), 1975. Organic Syntheses via Boranes, John Wiley & Sons Inc., New York.

Brown, H.C., Unni, M.K., 1968. J. Am. Chem. Soc. 90, 2902.

Corey, E.J., Rodhes, J.J., 1997. Tetrahedron Lett. 38 (1), 34.

Corey, E.J., Barnes-Seeman, D., Lee, T.W., 1997. Tetrahedron Lett. 38 (25), 4351.

Dicko, A., Bui-Van, T., Baboulène, M., Dousset, B., 2001. Main Group Met. Chem. 24, 15.

Dugger, W.M. (Eds.), 1983. Encyclopedia of Plant Physiology. Inorganic Plant Nutrition. Springer-Verlag, New York.

Greene, T.W. (Eds.), 1987. Protective Groups in Organic Synthesis. John Wiley & Sons Inc., New York.

Guanqui, S., Zhi, Z., Yong, W., Xiangdong, X., Lili, C., Qixia, Y., Tianjan, S., Airou, L., 2000. Wear 246, 55.

Hatanaka, H., Nakagawa, Y., 1994. J. Radiat. Oncol. Biol. Phys. 28, 1061.

Hu, H., Brown, P.H., 1994. Plant Physiol. 105, 681.

Niatteson, D.S., Majumdar, D., 1980. J. Am. Chem. Soc. 102, 7590.

Steinberg, H., Brotherton, R.J. (Eds.), 1966. Wiley Interscience, New York.

Zhou, W., Liang, S., Lo, W., 1990. Synthesis 8, 685.