Journal of Organometallic Chemistry, 452 (1993) 13–18

JOM 23325

Allylboration of some ketones and aldehydes with 2-allyl-1,2-oxaborolane. Isolation of their intermediate adducts and synthesis of homoallylic alcohols

Weike Zhou, Shaofang Liang, Su Yu and Weiming Luo

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032 (China)

(Received September 18, 1992; in revised form October 31, 1992)

Abstract

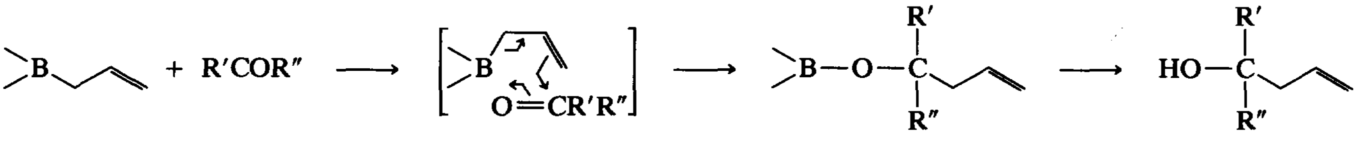
2-Allyl-1,2-oxaborolane (II), prepared by the reaction of 2-allyloxy-1,2-oxaborolane (I) with allylmagnesium bromide in ether, is an extremely reactive allylborane. This cyclic borinate ester II is a BCCO-type organoborane and can be used as a novel allylborating reagent. As is usual with allylboranes, II can also add smoothly to various ketones or aldehydes, and when followed by deboronation with diethanolamine gives the corresponding homoallylic alcohols IV. The adducts III, formed *via* a six-centre cyclic mechanism and allylic rearrangement, have been isolated and identified as a kind of 2-alkenoxy-1,2-oxaborolane.

1. Introduction

Mikhailov and Bubnov were the first to report that simple BCCC-type allylboranes, such as triallylborane [1], diallyl(alkyl)boranes and allyl(dialkyl)boranes, represent a class of highly reactive intermediates in organoboron chemistry [2,3]. In particular, such allylboranes can react with aldehydes and ketones, subsequent addition of the B-allyl fragment to the carbonyl group proceeding through allylic rearrangement [2–5]. Over two decades the allylboration of carbonyl compounds has been studied widely, however, up to now only a few organoborane adducts have been isolated as intermediates. A variety of allyl(alkyl) boranes (*e.g.* B-allyl-9-BBN *etc.*) have been utilized for the synthesis of homoallylic alcohols [2,6] (Scheme 1). Recently studies on many chiral allyl(dialkyl)boranes (allyl–BCC*) or allylboronate esters (allyl–BOO*) have made possible a fruitful approach to asymmetric synthesis [7].

In 1982 we reported that 2-allyl-1,2-oxaborolane (II, allyl–BCO) is another novel allylborane [8,9] which remains stable in an inert atmosphere for a long period. The cyclic borinate ester II is easily prepared by the heat exchange reaction of triallylborane with 2-allyloxy-1,2-oxaborolane (I) or by Grignard reaction of I with allylmagnesium bromide in ethyl ether [8–10].

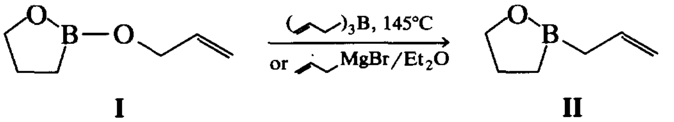
We have studied the physical and chemical properties of II in detail. B-Allylic rearrangement reactions of II include protolysis with water, alcohols or amines and allylboration of carbonyl compounds *via* C–C bond formation. A number of 2-alkoxy- and 2-amino-1,2-oxaborolanes has been synthesized in the former fashion, rupturing the B-allyl bond with the evolution of propene [10,11] (Scheme 3). In this paper we would like to report allylboration of 2-allyl-1,2-oxaborolane (II) with some aldehydes and ketones.



Scheme 1.

Correspondence to: Professor W. Zhou.

0022-328X/93/$6.00



Scheme 2.

TABLE 1. Physical data for adducts **IIIa–j**

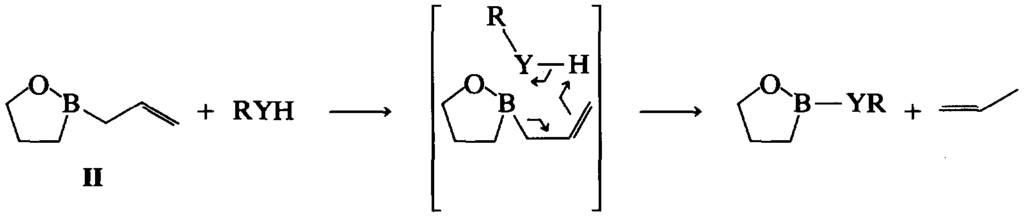
Formula **III**	Yield (%)	B.p. (°C/mbar)	n_D^{20}	d_4^{20}	MR (calcd. [13])
a $BC_9H_{17}O_2$	96	92–93/65	1.4381	0.9064	48.68 (48.61)
b $BC_{10}H_{19}O_2$	86	96–98/45	1.4447	0.9108	53.17 (53.26)
c $BC_{11}H_{21}O_2$	87	102–104/30	1.4459	0.9075	57.61 (57.91)
d $BC_{14}H_{19}O_2$	90	115–116/4.6	1.5132	1.0178	67.98 (68.28)
e $BC_{11}H_{19}O_2$	80	76–77/4.6	1.4681	0.9751	55.34 (55.67)
f $BC_{12}H_{21}O_2$	65	87–88/4	1.4721	0.9712	60.01 (60.50)
g $BC_9H_{17}O_2$	85	103–104/65	1.4473	0.9237	48.60 (48.61)
h $BC_{10}H_{17}O_2$	87	85–86/10	1.4633	0.9360	53.00 (52.78)
i $BC_{13}H_{17}O_2$	81	108–109/12	1.5173	1.0273	63.67 (63.69)
j $BC_9H_{14}O_2F_3$	70	62–63/20	1.4030	1.1180	48.46 (47.87)

2. Results and discussion

Allylboration of some ketones and aldehydes with 2-allyl-1,2-oxaborolane (**II**) proceeds smoothly without any solvent (Scheme 4). The conditions of reaction with aldehydes are milder (0°C–r.t.) than with ketones ($\geqslant$ 100°C). These adducts **III** can be isolated in good yields and have been identified by elemental analyses and IR, proton NMR and mass spectroscopies. The physical data of 2-alkenoxy-1,2-oxaborolanes **III** are listed in Table 1.

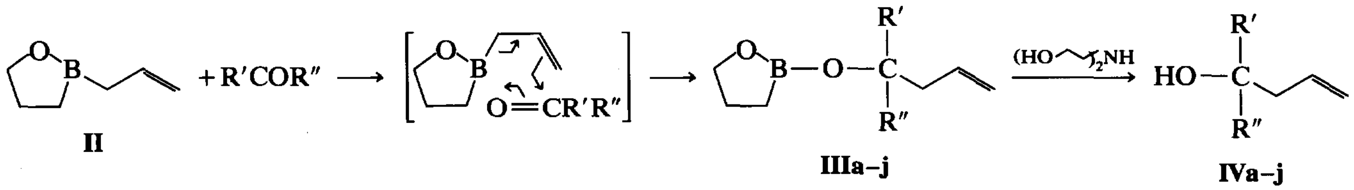
As with allyl(dialkyl)boranes (allyl–BCC), allylboration of α,β-unsaturated aldehydes, *e.g.* crotonaldehyde, with **II** (allyl–BCO) proceeds *via* 1,2-addition on the carbonyl group in order to satisfy the requirement of a six-membered transition state [14]. Only the 1,2-addition product **IIIh** was obtained. Allylborane **II** also reacts with fluoro-containing ketones, *e.g.* trifluoroacetone, to give the corresponding fluoro-containing derivatives. Spectroscopic data and elemental analyses of **III** confirmed the structures of 2-alkenoxy-1,2-oxaborolanes.

The intermediates **IIIa–j** can be hydrolyzed to yield the corresponding homoallyl alcohols **IVa–j** by re-esterification with diethanolamine. The products **IVa–j** are three-carbon atom enhanced β,γ-unsaturated carbinols. The alkenols **IV** can be converted into the corresponding **III** by treatment with **II**.



Y = O, R = Et [11];
Y = NH, R = Allyl, Pr, Bu, ^{t}Bu, ^{c}C$_6$H$_{11}$, NMe$_2$;
Y = NR, R = Allyl, ^{i}Pr, Bu, ^{c}C$_6$H$_{11}$;
or R$_2$ = -(CH$_2$)$_5$-, -CH$_2$CH$_2$OCH$_2$CH$_2$- [10].

Scheme 3.



a: R′ = Me, R″ = Me; **b**: R′ = Me, R″ = Et;
c: R′ = Me, R″ = Pr; **d**: R′ = Me, R″ = Ph;
e: R′, R″ = -(CH$_2$)$_5$-; **f**: R′, R″ = -(CH$_2$)$_6$-;
g: R′ = H, R″ = Et; **h**: R′ = H, R″ = -CH=CHCH$_3$;
i: R′ = H, R″ = Ph; **j**: R′ = Me, R″ = CF$_3$.

Scheme 4.

3. Experimental details

All operations with the organoboranes were carried out under purified nitrogen. We prepared 2-allyloxy-1,2-oxaborolane (I) by dehydrogenation-hydroboration of allyl alcohol with KBH_4-HOAc [10,12]. 2-Allyl-1,2-oxaborolane (II) was prepared in about 50% yield from I by the Grignard reaction [10]. IR spectra were recorded on a Specord 75 spectrophotometer. ^1H or ^{19}F NMR spectra were recorded on a Varian Model EM-360 (60 MHz) instrument relative to external TMS or trifluoroacetic acid respectively. ^{13}C NMR spectrum of **IIId** was recorded on an FX-90Q instrument. Mass spectra were determined with a Finnigan MS-4021 instrument. All reagents were purified before use.

Thermometers used were uncorrected.

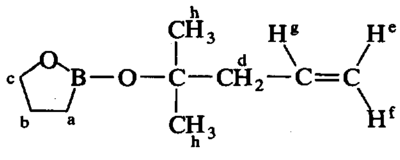
3.1. General procedure for allylboration of ketones with II

3.1.1. 2-(2-Methyl-4-penten-2-yloxy)-1,2-oxaborolane (IIIa)

A 25 ml dry, nitrogen-filled round bottomed flask equipped with a side arm capped with a rubber septum, a magnetic bar, a reflux condenser and a connecting tube attached to a bubbler, was charged with 7.70 g (70 mmol) of **II**. 4.07 g (70 mmol) of acetone was added dropwise during 10 min and then the reaction mixture was heated at 80–100°C for 3 h. Distillation under vacuum gave 11.3 g (96.1%) of **IIIa**, b.p. 97–98°C/80 mbar, n_D^{20} 1.4381.

Redistillation provided the analytical sample for determination of physical data (Table 1), spectroscopic and microanalytical data.

^1H NMR (CCl_4): δ 0.66 (t, 2H, $J = 7.8$, a); 1.10 (s, 6H, h); 1.66 (q, 2H, $J = 7.2$, b); 2.16 (d, 2H, $J = 3.5$, d); 3.79 (t, 2H, $J = 6.4$, c); 4.66, 4.86, 5.58 (m, 3H, e,f,g). IR (film): ν (cm^{-1}) 595w, 620w, 645w, 730w, 795w, 825w, 860w, 900s, 915s, 970m, 990s, 1030s, 1150s, 1170s, 1195s, 1225s, 1250s, 1275m, 1310m, 1360s, 1400s, 1445s, 1495s, 1640m, 2885s, 2980s, 3075m. MS (DEI): m/z (%) M + 1, 169 (13.3); M^+, 168 (4.1); M-allyl, 127 (11.0); M + 1 − $BC_3H_6O_2$, 84 (100.0).

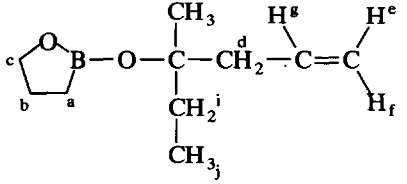


Anal. Found: B, 6.18; C, 64.00; H, 10.64. $BC_9H_{17}O_2$ calcd.: B, 6.43; C, 64.33; H, 10.20%.

3.1.2. 2-(3-Methyl-5-hexen-3-yloxy)-1,2-oxaborolane (IIIb)

As described above, the mixture of 7.70 g of **II** and 5.05 g (70 mmol) of 2-butanone was heated at 120°C for 3 h. 11.0 g (86.3%) of **IIIb** was obtained. B.p. 100–101°C/45 mbar, n_D^{20} 1.4445.

^1H NMR (CCl_4): δ 0.66 (t, 5H, $J = 6.8$, a,j); 1.05 (s, 3H, h); 1.52, 1.65 (q, 4H, $J = 7.0$, i,b); 2.20 (d, 2H, $J = 6.4$, d); 3.78 (t, 2H, $J = 6.5$, c); 4.68, 4.90, 5.58 (m, 3H, e,f,g). IR (film): ν (cm^{-1}) 910m, 990m, 1030m, 1125m, 1195s, 1250m, 1310m, 1360s, 1405s, 1415s, 1460s, 1490m, 1640m, 2880m, 2970s, 3075w. MS (DEI): m/z (%) M + 1, 183 (10.9); M^+, 182 (3.1); M − allyl, 141 (21.3); M − $BC_3H_6O_2$, 99 (100.0).

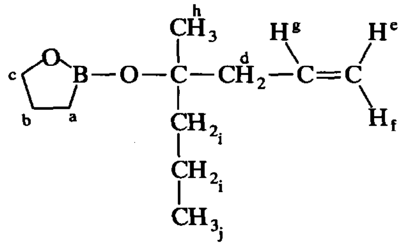


Anal. Found: B, 5.74; C, 65.86; H, 10.91. $BC_{10}H_{19}O_2$ calcd.: B, 5.94; C, 65.97; H, 10.52%.

3.1.3. 2-(4-Methyl-1-hepten-4-yloxy)-1,2-oxaborolane (IIIc)

The mixture of 7.70 g of **II** and 6.03 g (70 mmol) of 2-pentanone was heated at 140°C for 3 h. 11.8 g (86.0%) of **IIIc** was obtained. B.p. 106–107°C/ 35 mbar, n_D^{20} 1.4457.

^1H NMR (CCl_4): δ 0.64, 0.76 (m, 5H, a,j); 1.11 (s, 3H, h); 1.33, 1.64 (m, 6H, i,b); 2.20 (d, 2H, $J = 6.4$, d); 3.80 (t, 2H, $J = 6.8$, c); 4.73, 4.93, 5.63 (m, 3H, e,f,g). IR (film): ν (cm^{-1}) 740w, 795w, 825w, 855w, 880w, 915s, 950m, 970m, 990s, 1025s, 1150m, 1170m, 1195s, 1250s, 1310m, 1360s, 1400s, 1450s, 1490s, 1640m, 2875s, 2960s, 3070m.

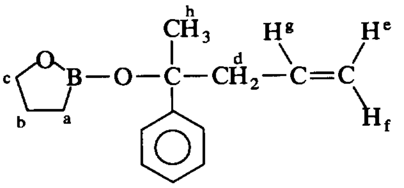


Anal. Found: B, 5.38; C, 67.00; H, 11.24. $BC_{11}H_{21}O_2$ calcd.: B, 5.51; C, 67.37; H, 10.79%.

3.1.4. 2-(2-Phenyl-4-penten-2-yloxy)-1,2-oxaborolane (IIId)

As above, starting from 7.70 g of **II** and 8.41 g (70 mmol) of acetophenone, 20.7 g (90.0%) of **IIId** was prepared. B.p. 115–116°C/4.6 mbar, n_D^{20} 1.5132.

^{1}H NMR (CCl_4): δ 0.73 (t, 2H, $J = 8$, a); 1.63 (s, 3H, h); 1.73 (q, 2H, $J = 7.5$, b); 2.77 (d, 2H, $J = 6.2$, d); 3.87 (t, 2H, $J = 7$, c); 4.7–6.1 (m, 3H, e,f,g); 7.0–7.6 (m, 5H, Ph). IR (film): ν (cm^{-1}) 665s, 700s, 760m, 910m, 990m, 1015s, 1070w, 1160w, 1200m, 1250m, 1275m, 1290m, 1310m, 1360s, 1400s, 1450s, 1495s, 1640m, 2885m, 2985s, 3080m. ^{13}C NMR ($CDCl_3$/TMS): 78.6 (C-1); 24.3 (C-2); 68.8 (C-4); 27.3 (C-5); 48.3 (C-6); 117.6 (C-7); 134.0 (C-8); 147.0 (C-9); 124.9 (C-10, C-14); 127.9 (C-11, C-13); 126.4 (C-12). MS (DEI): m/z (%) M + 1, 231 (7.2); M$^+$, 230 (1.4); M − allyl, 189 (27.7); M + 1 − $BC_3H_6O_2$, 145 (100.0).

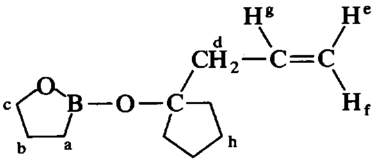


Anal. Found: B, 4.87; C, 72.60; H, 8.75. $BC_{14}H_{19}O_2$ calcd.: B, 4.70; C, 73.08; H, 8.32%.

3.1.5. *2-[1-(2-Propenyl)cyclopentyloxy]- (IIIe) and 2-[1-(2-propenyl)cyclohexyloxy]-1,2-oxaborolane (IIIf)*

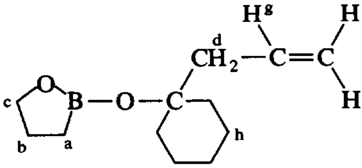
Starting from cyclopentanone or cyclohexanone and heating at 160°C for 3 h, **IIIe** or **IIIf** was obtained in an analogous way.

IIIe: Yield, 86.8%; b.p. 75–76°C/4.6 mbar, n_D^{20} 1.4681. ^{1}H NMR (CCl_4): δ 0.62 (t, 2H, $J = 7.2$, a); 1.51, 1.61 (m, 10H, h,b); 2.31 (d, 2H, $J = 6.3$, d); 3.77 (t, 2H, $J = 6.8$, c); 4.67, 4.86, 5.58 (m, 3H, e,f,g). IR (film): ν (cm^{-1}) 665m, 860w, 885w, 915s, 985s, 1030s, 1130m, 1190s, 1250s, 1305s, 1315s, 1360s, 1400s, 1450s, 1490s, 1640m, 2865s, 2945s, 3070m.



Anal. Found: B, 5.65; C, 67.39; H, 10.18. $BC_{11}H_{19}O_2$ calcd.: B, 5.57; C, 68.08; H, 9.87%.

IIIf: Yield, 65.4%; b.p. 87–88°C/4 mbar, n_D^{20} 1.4721. ^{1}H NMR (CCl_4): δ 0.72 (t, 2H, $J = 7.2$, a); 1.27 (m, 10H, h); 1.69 (q, 2H, $J = 7.6$, b); 2.27 (d, 2H, $J = 6.3$, d); 3.84 (t, 2H, $J = 6.8$, c); 4.74, 4.95, 5.63 (m, 3H, e,f,g). IR (film): ν (cm^{-1}) 670m, 680m, 730w, 780w, 825w, 865w, 880w, 915s, 970s, 995s, 1030m, 1145m, 1165m, 1195s, 1250s, 1300s, 1310m, 1365s, 1405s, 1460s, 1495s, 1645m, 2865s, 2930s, 3085m. MS (DEI): m/z (%) M-allyl, 167 (2.2); M + 1 − $BC_3H_6O_2$, 124 (66.3); 44 (100.0).



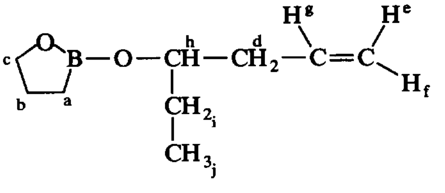
Anal. Found: B, 5.12; C, 68.85; H, 10.60. $BC_{12}H_{21}O_2$ calcd.: B, 5.19; C, 69.26; H, 10.17%.

3.2. *General procedure for allylboration of aldehydes with II*

Aldehyde (70 mmol) was added slowly to **II** (7.70 g, 70 mmol) over 30 min at 0°C. After addition, stirring was continued for another 2 h at room temperature. Then distillation under vacuum gave the product (**IIIg–i**). Redistillation provided the analytical sample for determination of physical, microanalytical and spectroscopic data.

3.2.1. *2-(5-Hexen-3-yloxy)-1,2-oxaborolane (IIIg)*

Yield, 84.5%; b.p. 105–106°C/76 mbar, n_D^{20} 1.4473. ^{1}H NMR (CCl_4): δ 0.69, 0.72 (m, 5H, a,j); 1.33 (q, 2H, $J = 6.6$, i); 1.73 (q, 2H, $J = 7.8$, b); 2.06 (t, 2H, $J = 6.3$, d); 3.80 (t, 2H, $J = 6.8$, c); 3.93 (q, 1H, $J = 6.5$, h); 4.03, 4.94, 5.64 (m, 3H, e,f,g). IR (film): ν (cm^{-1}) 665m, 825w, 860w, 910s, 970s, 990s, 1015s, 1085m, 1110m, 1135m, 1165m, 1195s, 1250s, 1305s, 1345s, 1405–1420s, 1450–1460s, 1490s, 1645m, 2875s, 2930s, 2960s, 3080m. MS (DEI): m/z (%) M + 1, 169 (2.2); M$^+$, 168 (0.8); M − allyl, 127 (24.3); M + 1 − $BC_3H_6O_2$, 84 (51.9); $C_3H_7{}^+$, 43 (100.0).

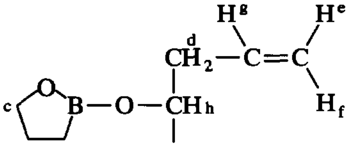


Anal. Found: B, 6.36; C, 63.68; H, 10.54. $BC_9H_{17}O_2$ calcd.: B, 6.43; C, 64.33; H, 10.20%.

3.2.2. *2-(1,6-Heptadien-4-yloxy)-1,2-oxaborolane (IIIh)*

Yield, 86.5%; b.p. 86–87°C/10 mbar, n_D^{20} 1.4633. ^{1}H NMR (CCl_4): δ 0.65 (t, 2H, $J = 7.8$, a); 1.47 (d, 3H, $J = 6.4$, k); 1.66 (q, 2H, $J = 7.8$, b); 2.04 (t, 2H, $J = 7.8$, d); 3.74 (t, 2H, $J = 6.8$, c); 4.35 (m, 1H, h); 4.67, 4.88, 5.28, 5.33, 5.60 (m, 5H, e,f,i,j,g). IR (film): ν (cm^{-1}) 665m, 910s, 965s, 990s, 1020s, 1135m, 1200s, 1250s, 1310s, 1350s, 1415s, 1450s, 1490s, 1640m, 1675w, 2935s, 3075m. MS (DEI): m/z (%) M + 1, 181 (4.0);

M^+, 180 (2.1); M − allyl, 139 (30.3); M − $BC_3H_6O_2$, 95 (100.0).

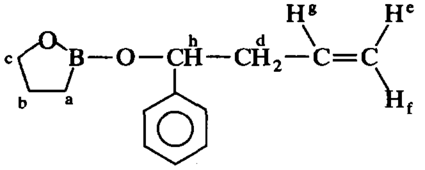


Anal. Found: B, 5.93; C, 66.44; H, 10.09. $BC_{10}H_{17}O_2$ calcd.: B, 6.00; C, 66.71; H, 9.52%.

3.2.3. 2-(1-Phenyl-3-buten-1-yloxy)-1,2-oxaborolane (IIIi)

Yield: 90.0%; b.p. 114–116°C/5 mbar, n_D^{20} 1.5167.

^1H NMR (CCl_4): δ 0.76 (t, 2H, $J = 7.8$, a); 1.75 (q, 2H, $J = 7.4$, b); 2.37 (t, 2H, $J = 6.6$, d); 3.86 (t, 2H, $J = 6.8$, c); 4.77, 4.98, 5.05, 5.57 (m, 4H, e,h,f,g); 7.13 (m, 5H, Ph). IR (film): ν (cm^{-1}) 657w, 692s, 748m, 904m, 980s, 1012m, 1045m, 1125m, 1190s, 1242s, 1343s, 1400s, 1483s, 1595m, 1632m, 1700w, 1810w, 1862w, 1940w, 2845s, 2900s, 2985m, 3030m.

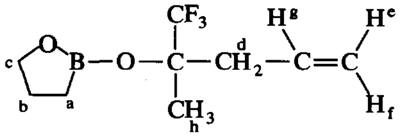


Anal. Found: B, 5.09. $BC_{13}H_{17}O_2$ calcd.: B, 5.00%.

3.3. 2-(1,1,1-Trifluoro-2-methyl-4-penten-2-yloxy)-1,2-oxaborolane (IIIj)

A 25 ml dry, nitrogen-filled round bottomed flask equipped with a side arm capped with a rubber septum, a magnetic stirring bar, a condenser with a dry-ice head and a connecting tube attached to a bubbler, was charged with 6.7 g (60 mmol) of **II**. The flask was immersed in a dry ice-alcohol cooling bath. Then 9.16 g (80 mmol) of trifluoroacetone was added dropwise slowly at low temperature with the aid of a cooling syringe. Stirring was continued for 2 h at room temperature after removing from the cooling bath. Then the mixture was heated at 100°C for a further hour. Distillation under vacuum gave 9.35 g (70.2%) of **IIIj**, b.p. 63–65°C/20 mbar, n_D^{20} 1.4030, d_4^{20} 1.1180.

^1H NMR (CCl_4): δ 0.77 (t, 2H, $J = 8$, a); 1.33 (s, 3H, h); 1.73 (q, 2H, $J = 7.6$, b); 2.50 (d, 2H, $J = 6.4$, d); 3.93 (t, 2H, $J = 6.8$, c); 4.90, 5.06, 5.60 (m, 3H, e,f,g). ^{19}F NMR (CCl_4): δ 2.4 (upfield from TFA). IR (film): ν (cm^{-1}) 657w, 692s, 748m, 904m, 980s, 1012m, 1045m, 1125m, 1190s, 1242s, 1343s, 1400s, 1483s, 1595m, 1632m, 1700w, 1810w, 1862w, 1940w, 2845s, 2900s, 2985m, 3030m. MS (DEI): m/z (%) M + 1, 223 (4.2); M^+, 222 (1.7); M − allyl, 181 (0.8); M − $BC_3H_6O_2$, 137 (3.4), 43 (100.0).



Anal. Found: B, 4.65; C, 48.73; H, 6.40. $BC_9H_{14}O_2F_3$ calcd.: B, 4.87; C, 48.69; H. 6.36%.

3.4. Deboronation of III with diethanolamine. General procedure

Into a dry, nitrogen-filled micro-distillation flask equipped with a side arm capped with a rubber septum, a magnetic stirring bar, and a Claisen head attached to an oil-bubbler was placed 10 mmol of **III** and 0.64 g (about 6 mmol) of diethanolamine. The mixture was stirred and heated at 120–160°C for 1–2 h to give the product (**IVa** and **IVj**) or distillation under vacuum gave the product (**IVb**–**IVi**). Redistillation or column chromatography provided the analytical samples.

4. Conclusion

2-Allyl-1,2-oxaborolane (**II**) is a novel allylborane (allyl-BCO, a cyclic borinate ester) and can react with ketones or aldehydes to give the adducts **III** under mild conditions. 2-Alkenoxy-1,2-oxaborolanes (**III**) can be isolated in the pure state and then converted into the corresponding homoallylic alcohols **IV**.

Acknowledgment

This project was supported by the National Natural Science Foundation of China (287107).

References

1 B. M. Mikhailov, *Izv. Akad. Nauk SSSR., Ser. Khim.*, (1964) 1874.
2 B. M. Mikhailov and Yu. N. Bubnov, *Organoboron Compounds in Organic Synthesis*, pp. 571–598. Harwood Academic Publishers, GmbH, Chur, 1984.
3 Yu. N. Bubnov, *Pure Appl. Chem.*, *59* (1988) 895.
4 B. M. Mikhailov, Yu. N. Bubnov, A. V. Tsyban and M. Sh. Grigoryan, *J. Organomet. Chem.*, *154* (1978) 131.
5 Yu. N. Bubnov, M. E. Gurskii, I. D. Gridnev, A. V. Ignaterko, Yu. A. Ustynyuk and V. I. Mistislavsky, *J. Organomet. Chem.*, *424* (1992) 127.
6 A. Pelter, K. Smith and H. C. Brown, *Boron Reagents*, pp. 310–317. Academic Press, London, 1988.
7 H. C. Brown, *Pure Appl. Chem.*, *63* (1991) 307.
8 W. Zhou, G. Zhang and H. Ding, *Youji Huaxue*, (1982) 19; *Chem. Abstr.*, *96* (1982) 181336.
9 W. Zhou, G. Zhang and H. Ding, in B. K. Teo (ed.), *New Frontiers in Organometallic and Inorganic Chemistry*, Science Press, Beijing, China, 1984 p-139.

10 W. Zhou, Sh. Liang and W. Luo, *Synthesis*, (1990) 685.
11 W. Zhou, W. Luo, G. Zhang, H. Ding and Sh. Liang, *J. Organomet. Chem., 387* (1990) 131.
12 H. Ding and W. Zhou, *Youji Huaxue*, (1981) 178. *Chem. Abstr., 95* (1981) 204021.
13 R. Sayre, *J. Chem. Eng. Data, 8* (1963) 244.
14 G. S. Ter-Sarkisyan, N. A. Nikolaeva and B. M. Mikhailov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1970) 876.