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A STEREOSELECTIVE SYNTHESIS OF 1,2-DIALKYLETHENYL BROMIDES VIA MONOHYDROBORATION OF 1-BROMO-1-ALKYNES WITH DIALKYLBORANES

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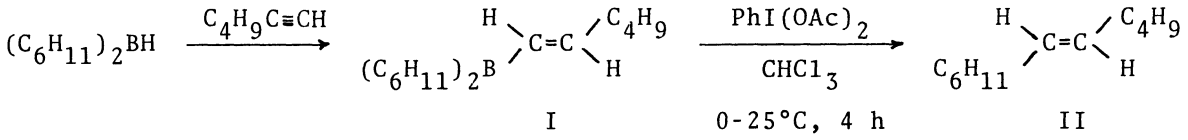
Treatment of 1-bromo-1-alkenyldialkylboranes with lead(IV) acetate or iodosobenzene diacetate afforded 1-bromo-1,2-dialkylethylenes in moderate yields. Furthermore, both E-isomers and Z-isomers could be independently obtained as the main products by the use of different reaction conditions.

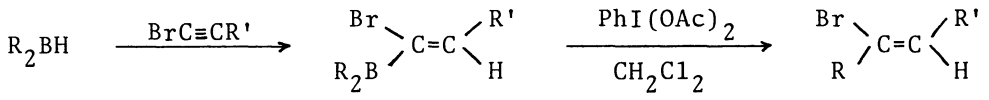
Recently, we have reported on the formation of alkyl acetate by oxidation of trialkylborane with lead(IV) acetate or iodosobenzene diacetate.[1] Our subsequent studies of the reaction of vinylboranes with the same reagents have revealed a formation of corresponding internal olefins by the migration of one alkyl group from boron to the adjacent carbon without formation of any alkyl or vinyl acetates. Thus, the addition of iodosobenzene diacetate in chloroform to the vinylborane (I) derived by hydroboration of 1-hexyne with dicyclohexylborane gives a 60% yield of (E)-1-cyclohexyl-1-hexene (II) with 92% isomeric purity (Scheme A).



Scheme A

Although Zweifel et al.[2] and Negishi et al.[3] have already reported the synthesis of internal olefins from vinylboranes, such reactions are carried out under strong basic conditions. Consequently, when organoboranes have alkyl groups which are sensitive to bases, those reactions are not used. In contrast, there are no problems even for such organoboranes in the present reaction, because the reaction proceeds under almost neutral conditions. Further, our findings suggest the possibility that a combination of alkyl group with halo alkenyl group occurs by the reaction of 1-halo-1-alkenylboranes (III) with iodosobenzene diacetate. Thus, we examined the reaction of 1-bromo-1-alkenyldialkylborane with iodosobenzene diacetate or lead(IV) acetate. As was expected, an addition of iodosobenzene diacetate to a dichloromethane solution of the vinylborane derived via hydroboration of 1-bromo-1-hexyne[4] (prepared from 1-hexyne) with dicyclohexylborane gives a 58% yield of (Z)-

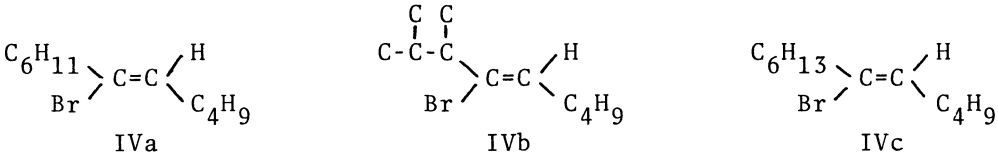
1-bromo-1-cyclohexyl-1-hexene (IVa) with an isomeric purity of 95% (Scheme B). We applied the Zweifel method to the same vinylborane, with the aid of both iodine only and iodine in alkaline medium, but could not obtain 1-bromo-1-cyclohexyl-1-hexene.



III IV

Scheme B

In this procedure, there is an apparent difficulty that requires dialkylboranes whose availability by the simple hydroboration is relatively limited.[5] A versatile method to obtain dialkylboranes has been reported.[6] In order to synthesize dialkylboranes, however, we employed another easier procedure in this experiment. Brown et al.[7] have reported that the reaction of two moles of 1-alkene with one mole of borane in THF at room temperature results in the formation of about 60% yield of dialkylborane. Consequently, the introduction of the solution of such a hydroboration stage to our reaction seemed to give corresponding enyl bromides. Thus, we tried the reaction on a hydroborated solution from 1-hexene. Finally, acceptablly pure 1-bromo-1-hexyl-1-hexene (IVc) was obtained in 50-60% yields without any by-products which obstructed isolation of the enyl bromide by column chromatography. The experimental results are summarized in Table 1.



IVa IVb IVc

In the case of R= hexyl, the E-isomer is obtained exclusively under the conditions (LTA in benzene-hexane, at 0°C), and the Z-isomer exclusively under the conditions (LTA in dichloromethane, at -50°C) respectively. The composition of the reaction products seemed to be influenced mainly by the reaction temperature and solvents. We are continuing to explore the synthetic possibility and the reaction mechanism.

The following procedure for the preparation of (Z)-1-bromo-1-hexyl-1-hexene (IVc) is representative. To 1-bromo-1-hexyne[4] (1.61 g, 10 mmol) in a 100-ml flask equipped with a septum inlet and a magnetic stirring bar and flushed with argon gas was added dropwise the hexylborane solution[7] (derived from 10 mmol of BH_3 in THF and 20 mmol of 1-hexene under 0°C for 24 h) at -25°C for 30 min, and the reaction mixture was stirred at -10 to -5°C for 1.5 h. Lead(IV) acetate (4.50 g, 10 mmol in 50 ml of dichloromethane) was added at -65°C for 5 min, and then the solution was kept at -50°C for 4 h. After addition of 3 ml of water in 5 ml of THF at -50°C for 5 min and then 7 ml of water at 20°C for 30 min, the mixture was extracted three times with hexane. The combined organic layer was washed twice with saturated aqueous sodium chloride solution, and dried over anhydrous sodium sulfate. After evaporation of the

solvents, the reaction product was isolated by column chromatography (silica gel, 100 g). On elution with hexane, 1.38 g (5.6 mmol, 56%) of 1-bromo-1-hexyl-1-hexene (Z, 96%; E, 4%) was obtained. Analytically pure materials were obtained by preparative VPC (10% FFAP on Diasolid M, 1m). (Z)-1-Bromo-1-hexyl-1-hexene: n_D^{20} 1.4682. MS; m/e=248(M^+). IR(neat); $\nu_{C=C}$ 1660 cm^{-1}. PMR(CCl_4, TMS); δ, 0.65-1.05 (m, 6H), 1.05-1.68 (m, 12H), 1.92-2.54 (m, 4H), 5.51 (t, 1H).[8, 10c] (E)-1-Bromo-1-hexyl-1-hexene: n_D^{20} 1.4718. MS; m/e=248(M^+). IR(neat); $\nu_{C=C}$ 1645 cm^{-1}. PMR(CCl_4, TMS); δ, 0.65-1.05 (m, 6H), 1.05-1.68 (m, 12H), 1.78-2.50 (m, 4H), 5.71 (t, 1H).[8, 10c]

Table 1. Reaction[a] of 1-Bromo-1-alkenyldialkylboranes with Lead(IV) Acetate (LTA) or Iodosobenzene Diacetate (IBA)

R	R'	Reagent	Solvent	Temp., °C	Time, h	Product (Z:E)	Yield,[b] %
Cyclohexyl	Butyl	IBA	CH_2Cl_2	-25	4	IVa (98: 2)	58 (54)[c]
3-Methyl-2-butyl	Butyl	LTA	CH_2Cl_2	-50	8	IVb (98: 2)	56 (50)[c]
Hexyl[d]	Butyl	IBA	CH_2Cl_2	0	4	IVc (48:52)	40
		LTA	CH_2Cl_2	0	4	IVc (21:79)	36
		LTA	CH_2Cl_2	-50	4	IVc (96: 4)	65 (56)[c]
		LTA	Benzene-hexane	0	4	IVc (5:95)	55 (52)[c]
Octyl	Butyl	LTA	CH_2Cl_2	-50	4	IV (97: 3)	(54)
		LTA	Benzene-hexane	0	4	IV (4:96)	(45)
2-Methylpentyl	Butyl	LTA	CH_2CCl_2	-50	4	IV (97: 3)	54 (51)
		LTA	Benzene-hexane	0	4	IV (10:90)	42 (35)

a) Mol ratio; III/reagent=1.

b) Determined by glpc based on BH_3 employed.

c) Isolated by elution with hexane on silica gel column.

d) Carried out by using the following solution; 2 × 1-hexene + BH_3·THF $\xrightarrow[24\ h]{25°C}$ $(hexyl)_2BH$ (63%).

Although a few instances of convenient syntheses of enyl halides from organoboranes[9] and other methods[10] have been reported, the present reaction for the first time provides a stereoselective synthetic procedure for 1,2-dialkylethenyl bromides via the reaction of organoboranes.

References and Notes

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3) The vinylborane from dicyclohexylborane and 1-bromo-1-hexyne gave (E)-1-cyclohexyl-1-hexene by the reaction with sodium methoxide and acetic acid; E. Negishi, J. -J. Katz, and H. C. Brown, Synthesis, 1972, 555.
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