ORGANOBORON COMPOUNDS

COMMUNICATION 197. REACTION OF TRIALLYLBORON

WITH α,β -UNSATURATED ALDEHYDES

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As is known, Grignard reagents are obtained from allyl halides with greater difficulty than are the organomagnesium compounds of the aliphatic and aromatic series, while their reactions with α,β -unsaturated aldehydes proceed successfully only if certain precautions are observed (strong dilution, simultaneous addition of the reactants to the Mg, etc.). As a continuation of our study of the reactions of allyl derivatives of boron with carbonyl compounds [1-3] we studied in the present paper the reaction between triallylboron and some α,β -unsaturated aldehydes, and specifically: with acrolein, crotonaldehyde, cinnamaldehyde, citral and β -cyclocitral, and also with α -cyclocitral. Triallylboron adds smoothly to α,β -unsaturated aldehydes by the organometallic synthesis scheme to the carbonyl group in the 1, 2 position. In those cases where the reaction was run using equimolar ratios of the aldehyde and triallylboron the intermediate organoboron compounds were not isolated, and instead were immediately hydrolyzed to the corresponding unsaturated alcohols, the yields of which in some cases exceeded the yields of the alcohols that were synthesized using allylmagnesium bromide:



1,5-Hexadien-3-ol (I), 1,5-heptadien-3-ol (II), and 1-phenyl-1,5-hexadien-3-ol (III) are obtained in yields of 75-78%, whereas the yield of (III) from cinnamaldehyde and allylmagnesium bromide is only 37.7% [4]. Alcohols (I) and (II) were obtained previously in high yields by the reaction of acrolein and crotonaldehyde with allylmagnesium bromide [4, 5] and diallylzine [6]. Citral reacts smoothly with triallylboron, forming 6,10-dimethyl-1,5,9-undecatrien-4-ol (IV), which was previously synthesized as the cis- and transisomers by the reaction of citral with allylmagnesium bromide [7]. It was especially interesting to study the reaction of triallylboron with the α - and β -cyclocitrals, a reaction that has hardly been studied with organometallic compounds. Only the reaction of β -cyclocitral with methylmagnesium bromide has been described [8], in which connection the yield of the obtained alcohol was indicated and its properties were not described. The reaction of equimolar amounts of β -cyclocitral and triallylboron gives, after hydrolysis, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1-buten-4-ol (V) in 73% yield. The reaction of triallylboron with α -cyclocitral also goes easily, but in this case, together with the alcohol 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-1-buten-4-ol (VIIa), the formation of which testifies to the cleavage of the three boron – carbon bonds in (C₃H₅)₃B.

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ated, %	н			I	1		11,41		11,41	
Calcul	D			l	1		80,35		80,35	
1, %	н	1		I	1		11,67		11,21	
Found	ت	-	. 1		1		80,60		80,13	
20	n_D^{20}		1.4533	1.5685	1,4810	100 <u>-</u> 61	I .		1	
Bp, °C (p, mm of Hg)		60.5-61.5 (40)	62 (15)	100 (0,1)	cis 80 (0,3) trans (80) (0.4)	(1(0) (00) 00000	I		I	
m troiv	Yield, %		82	37,7	84 79		1		1	 ······ .
From the	From the literature data		[5]	[4]	[7]		1		1	
120 120	n_D^{20}		1,4540	1,5650	1,4800		1,4950		1,4880	 U V T T
Bp, °C (p, mm	Bp, °C (p, mm of Hg)		6162, 5 (15)	85-87 (0,025)	102-103(0,4)		103—104 (4)		6264 (2)	
Yield of alcohol,	Yield of alcohol, γ_0 of theory		73,5	78,3	65,5		73		28,3 †	
Starting of aldehvda	Starting of aldehyde		CH3CH=CH-CHO	C,H,CH=CH-CHO	H _s C CH _s	CH.	HaC CH3 CH0	CH3	Hac GHa CHO	whether of (11) and (111)
Compound	Compound No.		п	III	N		*^		*IV	 * In the ID

TABLE 1, R-CH-CH₂-CH=CH₂ oH

* IN the LK spectra of (V) and (V1) were detected absorption bands at 1645 cm⁻¹ (allyl group) and 3400-3500 cm⁻¹ (OH group). † The low yield of (VI) is explained by the fact that borate (VIIa) hydrolyzes with greater difficulty under the adopted conditions. *



Borate (VIIb) can be isolated by the reaction of 3 moles of β -cyclocitral with 1 mole of triallylboron. The intermediate organoboron compound, as the 1,5-dihexadien-3-yl ester of allylboronic acid (VIII), was isolated from the reaction of 2 moles of acrolein with 1 mole of triallylboron:

$$2 \operatorname{CH}_{2} = \operatorname{CH} - \operatorname{CHO} + (\operatorname{C}_{3}\operatorname{H}_{5})_{3} \operatorname{B} \leftrightarrow \begin{bmatrix} \operatorname{O} \\ 1 \\ \operatorname{CH}_{2} = \operatorname{CH} - \operatorname{CH} \\ 1 \\ \operatorname{C}_{3}\operatorname{H}_{5} \end{bmatrix}_{2} \operatorname{BC}_{3}\operatorname{H}_{5} \xrightarrow{\operatorname{H}_{2}\operatorname{O}} (I)$$
(VIII)

EXPERIMENTAL

Preparation of Unsaturated Alcohols from α,β -Unsaturated Aldehydes. To an ether solution of the aldehyde was added an equimolar amount of triallylboron in 20-30 min. The reaction mass was kept at room temperature: for acrolein and crotonaldehyde 1.5 h, cinnamaldehyde 0.5 h, and citral 1.5 h (35°). In the case of α - and β -cyclocitral an equimolar amount of triallylboron was added to a benzene solution of the aldehyde in 35 min and the mixture was heated at 80-86° for 3 h. In all cases the reaction mass was decomposed with aqueous ethanolamine solution, after which the organic layer was washed with water, then with aqueous bicarbonate solution, and dried over Na₂SO₄. Removal of the solvent, followed by fractional distillation of the residue, gave the corresponding secondary unsaturated alcohols, the yields and properties of which are given in Table 1.

[Tri-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-1-butenyl]borate (VIIa). To a benzene solution of 41.2 g of α -cyclocitral was added 36.3 g of triallylboron in 30 min. The mixture was refluxed for 3 h and, after cooling to 20°, was decomposed with aqueous ethanolamine solution. The benzene solution was washed with water, then with aqueous NaHCO₃ solution, and dried over MgSO₄. After removal of the benzene and fractional distillation of the residue we obtained 15 g (28.3%) of (VI) with bp 62-64° (2 mm); nD²⁰ 1.4880; IR spectrum (ν , cm⁻¹): 1642 (-CH = CH₂), 3440-3480 (OH group), and 10.5 g (19.7%) of borate (VIIa); bp 222-224° (0.02 mm); nD²⁰ 1.5020. Found: C 79.05; H 10.56; B 1.75%. C₃₉H₆₃O₃B. Calculated: C 79.27; H 10.75; B 1.86%. IR spectrum (ν , cm⁻¹): 1645 (-CH = CH₂), 1330 (B - O).

[Tri-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1-butenyl]borate (VIIb). To an ether solution of 10.26 g of triallylboron was added 35.4 g of β -cyclocitral in 1 h. The reaction mass was kept at 20° for 24 h, the ether was distilled off, and the residual viscous mass was decomposed with aqueous diethanolamine solution, after which ether was added and the mixture was worked up in the usual manner. After removal of the solvent and fractional distillation of the residue we obtained 8.2 g (17.6%) of (V); IR spectrum (ν , cm⁻¹): 1645 (-CH = CH₂), 3440-3480 (OH group), and 20.1 g of borate (VIIb), which after distillation represented a viscous liquid with bp 235-236° (0.03 mm); nD²⁰ 1.5030. IR spectrum (ν , cm⁻¹): 1642 (-CH = CH₂); 1430-1455 (B-O). Found: C 79.56; H 10.70; B 1.66%. C₃₉H₆₃O₃B. Calculated: C 79.27; H 10.75; B 1.86%.

1,5-Dihexadien-3-yl Ester of Allylboronic Acid (VIII). To an ether solution of 13.3 g of triallylboron was added in 30 min, at 15-20°, a solution of 9.9 g of acrolein in 20 ml of absolute ether, and the mixture was kept at 20° for 24 h. After removal of the solvent and fractional distillation of the residue we obtained 15.8 g (83%) of (VIII), bp 87-89° (4 mm); nD^{20} 1.4530. IR spectrum (ν , cm⁻¹): 1645 (CH=CH₂); 1300-1400 (B-O). Found: C 73.27; H 9.51; B 4.46%. C₁₅H₂₃O₂B. Calculated: C 73.13; H 9.41; B 4.46%.

CONCLUSIONS

Triallylboron adds smoothly to the carbonyl group of acrolein, citral, α - and β -cyclocitral, crotonaldehyde and cinnamaldehyde with the formation (after hydrolysis) of the corresponding secondary unsaturated alcohols.

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