

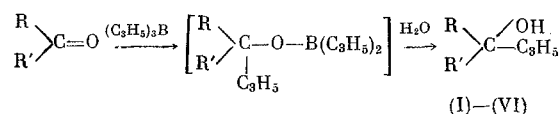
## ORGANOBORON COMPOUNDS

COMMUNICATION 189. REACTION OF TRIALLYLBORON WITH  $\alpha,\beta$ -UNSATURATED KETONESG. S. Ter-Sarkisyan, N. A. Nikolaeva,  
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Triallylboron adds smoothly to the two carbonyl groups of 1,4-benzoquinone or 1,4-naphthoquinone in the 1,2-position to form the corresponding 1,4-diallyl-1,4-dihydroxy derivatives [1]. It was of interest to ascertain how the reaction of triallylboron with other  $\alpha,\beta$ -unsaturated ketones proceeds. As is known, the reaction of organomagnesium compounds with  $\alpha,\beta$ -unsaturated ketones often leads to formation of saturated ketones (1,4-addition) along with preparation of tertiary unsaturated alcohols (1,2-addition).

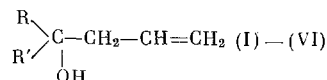
In the present work we have studied the reactions of triallylboron with benzalacetone, benzalacetophenone, cinnamylideneacetone, mesityl oxide, and  $\alpha$ - and  $\beta$ -ionones. The reactions were carried out at equimolar ratios of the starting materials, and the esters of allyl- and diallylboric acids formed thereby, as well as borates, were not isolated but were at once subjected to hydrolysis. To remove saturated ketones which could have been formed as a result of addition of triallylboron to the  $\alpha,\beta$ -unsaturated ketones in the 1,4-position from the reaction products, the compounds isolated after hydrolysis were treated with a methanol solution of semicarbazide acetate. Attempts to isolate saturated ketones in the form of their semicarbazones or 2,4-dinitrophenylhydrazones did not give positive results. All the  $\alpha,\beta$ -unsaturated ketones which we studied reacted with triallylboron in the 1,2-position, forming tertiary unsaturated alcohols in high yield, according to the scheme



Thus, benzalacetone reacts with triallylboron forming 1-phenyl-3-methyl-1,5-hexadiene-3-ol (I) in 77.5% yield, while allylmagnesium bromide [2] gives alcohol (I) with this ketone in 31% yield. It must be noted that diallylzinc [3] adds to benzalacetone in the 1,2-position just as easily as triallylboron, forming 1-phenyl-3-methyl-1,5-hexadiene-3-ol in almost quantitative yield.

Benzalacetophenone, which is more prone to 1,4-addition of organomagnesium compounds, reacts smoothly with triallylboron and (after hydrolysis) gives 1,3-diphenyl-1,5-hexadiene-3-ol (II) in 77% yield, while with allylmagnesium bromide [2] the yield of this alcohol is considerably less (34%).

As an example of an  $\alpha,\beta$ -unsaturated ketone with two double bonds we selected cinnamylideneacetone, where addition of organometallic compounds is theoretically possible in the 1,2-, 1,4-, or 1,6-positions. It turned out that triallylboron reacts with cinnamylideneacetone only in the 1,2-position, to form (after hydrolysis) 1-phenyl-5-methyl-1,3,7-octatriene-5-ol (III). The residue after fractionation of alcohol (III)



luminesces strongly in benzene solution, which indicates the presence of an unsaturated hydrocarbon in it, obtained on dehydration of the alcohol. The representatives of aliphatic and terpene  $\alpha,\beta$ -unsaturated ketones which we studied also react easily with triallylboron. With mesityl oxide, triallylboron smoothly forms 2,4-dimethyl-2,6-heptadiene-4-ol (IV); with  $\alpha$ - and  $\beta$ -ionones it gives the corresponding tertiary

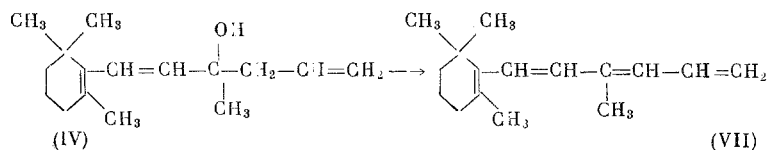
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TABLE 1

Compound No.	Starting ketone	Yield of tertiary alcohol, %		Boiling point, °C (p in mm Hg)	$n_D^{20}$	Literature data		
		crude	pure			Boiling point, °C (p in mm Hg)	$n_D^{20}$	Lit. reference
I	Benzalacetone	94.5	77.5	89-80(0.08)	1.5530	122-123(2) 90-92(0.1)	1.5512 1.5525	[2] [3]
II	Benzalacetophenone	90.4	77.1	140-142(0.02)	1.5975	170-170.5(2)	—	[2]
III	Cinnamylideneacetone	91.2	79.5	124-126(0.01)	1.6020	—	—	
IV	Mesityl oxide	90.5	77.9	53-54(10)	1.4600	58(2) 47-48(4)	1.4610 1.4598	[2] [4]
V	$\alpha$ -Ionone	91.0	82.8	110-112(2.5)	1.4950	137-140(9)	—	[5]
VI	$\beta$ -Ionone	89.2	78.5	85-87(0.1)	1.5020	83-85(0.2)	1.5019	[6]

alcohols, 3-methyl-1-(2,6,6-trimethyl-2-cyclohexene-1-yl)hexadiene-1,5-ol-3 (V) and 3-methyl-1-(2,6,6-trimethyl-1-cyclohexen-1-yl)hexadiene-1,5-ol-3 (VI) in almost quantitative yields. It must be noted that allylmagnesium bromide reacts mainly with mesityl oxide [2, 4],  $\alpha$ -ionone [5] and  $\beta$ -ionone [6] in the 1,2-position also.

Results of experiments on the reaction of triallylboron with the indicated ketones are given in Table 1. The presence of an allyl group and a hydroxyl group in the synthesized unsaturated alcohols was confirmed by the presence in their infrared spectra of characteristic absorption bands at 1642-1645  $\text{cm}^{-1}$  (allyl group) and wide absorption bands for hydroxyl groups in the 3200-3600  $\text{cm}^{-1}$  range. The tertiary alcohols (V) and (VI) which were obtained from  $\alpha$ - and  $\beta$ -ionones, were subjected to dehydration. By heating alcohol (VI) with glacial acetic acid and sodium acetate we obtained 3-methyl-1(2,6,6-trimethyl-1-cyclohexen-1-yl)hexatriene-1,3,5 (VII) in the form of a mixture of cis- and trans-isomers which had previously been synthesized by another method [7].



The dehydration of alcohol (V) with the same reagents takes place more difficultly. After a considerably longer heating period, 3-methyl-1-(2,6,6-trimethyl-2-cyclohexen-1-yl)hexatriene-1,3,5 (VIII) was obtained in lower yield, and, judging from analysis, it contained the starting alcohol as an impurity.

## EXPERIMENTAL

### Preparation of Unsaturated Tertiary Alcohols from $\alpha,\beta$ -Unsaturated Ketones.

All reactions were carried out in a nitrogen atmosphere. The ketone was dissolved in ether and an equimolar amount of triallylboron was added over a 15-30 min period. The reaction mixture was stirred at room temperature for 4 h in the case of benzalacetone, for 1.5 h in the case of  $\alpha$ -ionone,  $\beta$ -ionone, or mesityl oxide, and for 3 or 4 h, respectively, in the case of benzalacetophenone or cinnamylideneacetone. The reaction mixture was decomposed with an aqueous ethanolamine solution, the ether layer was washed with water and with aqueous  $\text{NaHCO}_3$  solution, and it was dried over  $\text{Na}_2\text{SO}_4$ . After removal of the ether, the residue was poured into a solution of semicarbazide acetate prepared from equimolar amounts of semicarbazide hydrochloride and sodium acetate (calculated on starting ketone) in 100 ml of methanol and the mixture was allowed to stand 24 h. The methanol solution was evaporated under vacuum, the residue was mixed with water, and the oil which separated was extracted with petroleum ether. The organic layer was separated, washed with water, and dried with  $\text{Na}_2\text{SO}_4$ . The solvent was removed (thereby giving the yield of crude alcohol), and after fractionation of the residue under vacuum the corresponding unsaturated alcohols

were isolated, whose yields and properties are given in Table 1. For the previously unknown 1-phenyl-5-methyl-1,3,7-octatriene-5-ol (III) the following analysis was obtained. Found %: C 83.82; H 8.55.  $C_{15}H_{18}O$ . Calculated %: C 84.07; H 8.47.

3-Methyl-1-(2,6,6-trimethyl-1-cyclohexen-1-yl)hexatriene-1,3,5 (VII). A mixture of 6.2 g of (VI), 22 ml of glacial acetic acid, and 1.1 g of  $CH_3COONa$  was boiled for 15 min in a nitrogen atmosphere. The cooled reaction mixture was poured into water and the mixture was extracted with ether. The ether solution was washed with water and with  $NaHCO_3$  solution, and was dried over  $MgSO_4$ ; after removal of the ether the residue was distilled under vacuum over Na. There was obtained 3.5 g (61.2%) of (VII), bp 111–113° (2.5 mm),  $n_D^{20}$  1.5560. Found %: C 88.65; H 11.10.  $C_{16}H_{24}$ . Calculated %: C 88.82; H 11.18. Ultraviolet spectrum:  $\lambda_{max}$  284 nm ( $\epsilon$  29,600). Literature [7]: trans-isomer, bp 70.80° (0.001 mm);  $n_D^{20}$  1.5560,  $\lambda_{max}$  284 nm ( $\epsilon$  20,500); cis-isomer,  $n_D^{20}$  1.5575,  $\lambda_{max}$  284 nm ( $\epsilon$  20,000).

3-Methyl-1-(2,6,6-trimethyl-2-cyclohexen-1-yl)hexatriene-1,3,5 (VIII). A mixture of 3.82 g of (V), 14 ml of glacial acetic acid, and 0.7 g of dry  $CH_3COONa$  was boiled for 2 h in a nitrogen atmosphere. The mixture was worked up similarly to the case above. There was obtained 1.65 g (43%) of (VIII), bp 120–123° (3 mm),  $n_D^{20}$  1.5341. Found %: C 87.20; H 11.25.  $C_{16}H_{24}$ . Calculated %: C 88.82; H 11.18. Literature [5]: bp 127–130° (10 mm).

## CONCLUSIONS

Triallylboron reacts with the  $\alpha,\beta$ -unsaturated ketones benzalacetone, benzalacetophenone, cinnamylideneacetone, mesityl oxide, and  $\alpha$ - and  $\beta$ -ionones in the 1,2-position to form (after hydrolysis) the corresponding unsaturated tertiary alcohols.

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