ALLYLDIALKYLBORANES

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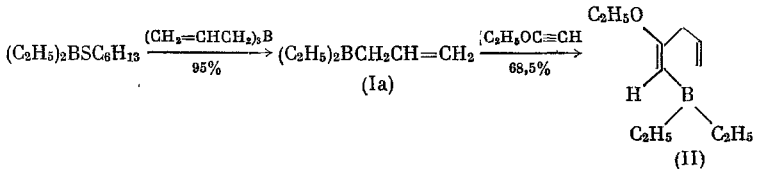
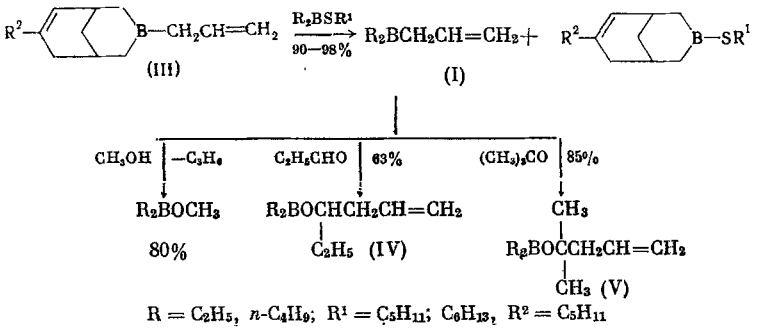
Previously the allyldialkylboranes were obtained by reacting tetraalkyldiboranes with allenic hydrocarbons [1]. We found a general method for synthesizing compounds of this type, which consists in reacting the esters of thioboric acids R_2BSR' with allylboranes.

Triallylborane and the derivatives of 3-allyl-3-borabicyclo[3.3.1]-6-nonene were used as the source of the allyl groups. Thus, from the n-hexyl ester of diethylthioboric acid and triallylborane we obtained allyldiethylborane (Ia) in 95% yield by distilling it from the reaction mixture.



The allyldialkylboranes (I) were also synthesized by the reaction of R_2BSR' with 3-allyl-3-borabicyclo[3.3.1]-6-nonene or its 7-substituted derivatives (III).



R = C_2H_5, n-C_4H_9; R^1 = C_5H_{11}; C_6H_{13}; R^2 = C_5H_{11}

For all practical purposes the (I) compounds are not symmetrized when heated up to 115°; instead they undergo permanent intramolecular allylic rearrangement (E_{act} = 11.8 ± 0.2 kcal/mole). The reactions of (I) with alcohols, aldehydes, ketones, and ethoxyacetylene are given in the schemes.

TABLE 1

Compound	Bp, °C (p, mm of Hg)	n_D^{20}	Compound	Bp, °C (p, mm of Hg)	$n_D^{23,5}$
(Ia)	114—115 (756)	1,4152	(II)	49—50 (2)	1,4658
	44—45 (40)		(IV) (R=C_2H_5)	68—70 (20)	1,4165
(I) (R=n-C_4H_9)	51—52 (2.5)	1,4380	(V) (R=C_2H_5)	77—78 (30)	1,4193

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The structure of all of the compounds was confirmed by the IR and NMR spectral data; the analyses are satisfactory; the constants are given in Table 1.

LITERATURE CITED

1. B. M. Mikhailov, V. N. Smirnov, and O. D. Ryazanova, Dokl. Akad. Nauk SSSR, 204, 612 (1972).