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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^1 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.

$$(C_{2}H_{5})_{2}BSC_{6}H_{13} \xrightarrow{(CH_{2}=CHCH_{2})_{2}B} (C_{2}H_{5})_{2}BCH_{2}CH = CH_{2} \xrightarrow{(C_{2}H_{5}OC \cong CH)} C_{2}H_{5}OC \cong CH$$

$$(Ia) \qquad H \qquad B$$

$$C_{2}H_{5} \qquad C_{2}H_{5} \qquad C_{2}H_{5}$$

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).

$$R^{2} \longrightarrow B - CH_{2}CH = CH_{2} \xrightarrow{R_{2}BSR^{1}} R_{2}BCH_{2}CH = CH_{2} + R^{2} \longrightarrow B - SR^{1}$$

$$(II) \qquad \qquad (I)$$

$$CH_{3}OH \longrightarrow C_{3}H_{6} \qquad C_{2}H_{5}CHO \longrightarrow 63\% \qquad (CH_{3})_{5}CO \longrightarrow 85\%$$

$$R_{2}BOCH_{3} \qquad R_{2}BOCHCH_{2}CH = CH_{2} \qquad CH_{3}$$

$$80\% \qquad C_{2}H_{5} \qquad (IV) \qquad R_{6}BOCCH_{2}CH = CH_{2}$$

$$CH_{3} \qquad (V)$$

$$R = C_{2}H_{5}, \ n\text{-}C_{4}H_{6}; \ R^{1} = C_{5}H_{11}; \ C_{6}H_{18}, \ R^{2} = C_{5}H_{11}$$

For all practical purposes the (I) compounds are not symmetrized when heated up to 115°; instead they undergo permanent intramolecular allylic rearrangement ($E_{act} = 11.8 \pm 0.2 \, kcal/mole$). 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) (I) (R=n-C ₄ H ₉) | 114—115 (756) 44—45 (40) 51—52 (2.5) | 1,4152 1,4380 | $ \begin{pmatrix} (II) \\ (IV) (R=C_2H_5) \\ (V) (R=C_2H_5) \end{pmatrix} $ | 49—50 (2) 68—70 (20) 77—78 (30) | 1,4658 1,4165 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).