1,1-BIS(DIPROPYLBORYLMETHYL)ETHYLENE AS A NEW ALLYLBORATION REAGENT

Yu. N. Bubnov, M. E. Gurskii, and
D. G. Pershin

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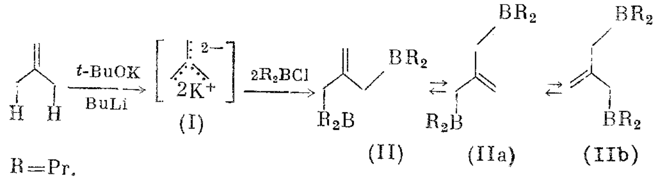
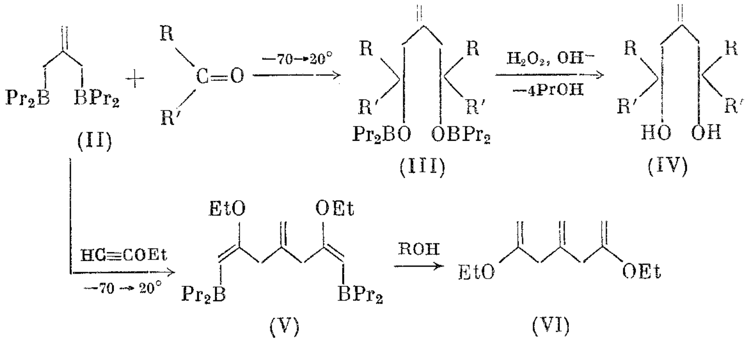
The reaction of the dipotassium derivative of isobutylene, "the dianion of 2-methyleneallyl" (I) [1] with two equivalents of Pr_2BCl gives 1,1-bis(dipropylborylmethyl)ethylene (II), which is the first representative of a new type of allylboranes.



R=Pr.

^{1}H and ^{13}C NMR spectroscopy indicates that (I) at about 20°C undergoes continuous allylic rearrangement: both the Pr_2B groups shift continuously from C^1 to C^3 of the allyl system (and back) with simultaneous displacement of the double bond ((II) $\rightleftarrows$ (IIa) $\rightleftarrows$ (IIb)).

Reagent (II) displays properties typical for classical allylboranes [2] and may be used for the synthesis of 1,5-bifunctional organic compounds. Thus, the reaction of (II) with aldehydes and ketones proceeds by addition to the C=O group and leads to diborate esters (III), whose oxidative deborylation gives gives bis-homoallyl alcohols (IV).



Borane (II) readily adds to ethoxyacetylene (by cis-bis-allylborylation) with the formation of adduct (V). The protolytic cleavage of (V) led to triene (VI).

The structures of the compounds obtained were confirmed by elemental analysis and spectral methods. The yield of (II) was 40%, bp 97-99°C (1 mm), n_D^{20} 1.4495. $\delta^{11}B = 85.75$ ppm. IR spectrum: 1634, 3075 cm^{-1}. The yield of (IV) ($R = H$, $R' = Me$) was 80%, bp 88-90 (2 mm), n_D^{20} 1.4678. The yield of (IV) ($R = R' = Me$) was 75%, mp 76-77°C [1]. The yield of (IV) ($R = H$, $R' = Ph$) was 71% (oil), n_D^{20} 1.5738. The yield of (IV) ($R + R' = (CH_2)_6$) was 78%, mp 97-99°C. The yield of (VI) was 68%, bp 57-59°C (1 mm), n_D^{20} 1.4549.

LITERATURE CITED

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