Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

The reaction of organoboranes with 2-methyl-2-nitrosopropane and with *cis*-azobenzene

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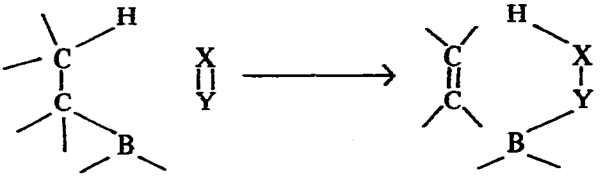
(Received June 26th, 1971)

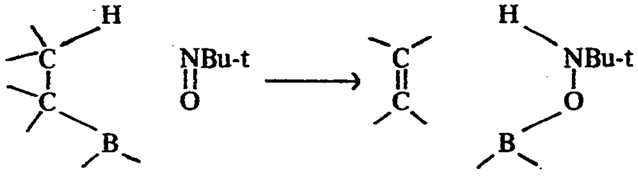
Two reactions of trialkylboranes are known which apparently involve the elimination of an olefin through a cyclic six transition state (Eq. 1).



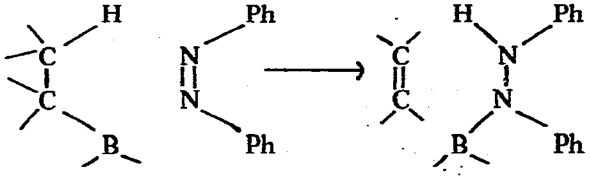
(1)

First, the reagent X═Y may be an aldehyde (X = RCH, Y = O); for example, benzaldehyde and tributylborane react to give 1-butene during 15 min at 100—150°[1] Second, X═Y may be an olefin; again, temperatures above 100° are usually needed to effect the reaction[2].

We wish to report that two further reagents will bring about a similar reaction under much milder conditions: both 2-methyl-2-nitrosopropane (Eq. 2) and *cis*- (but not *trans*-) azobenzene (Eq. 3) cause the elimination of one alkyl group rapidly at room temperature.



(2)



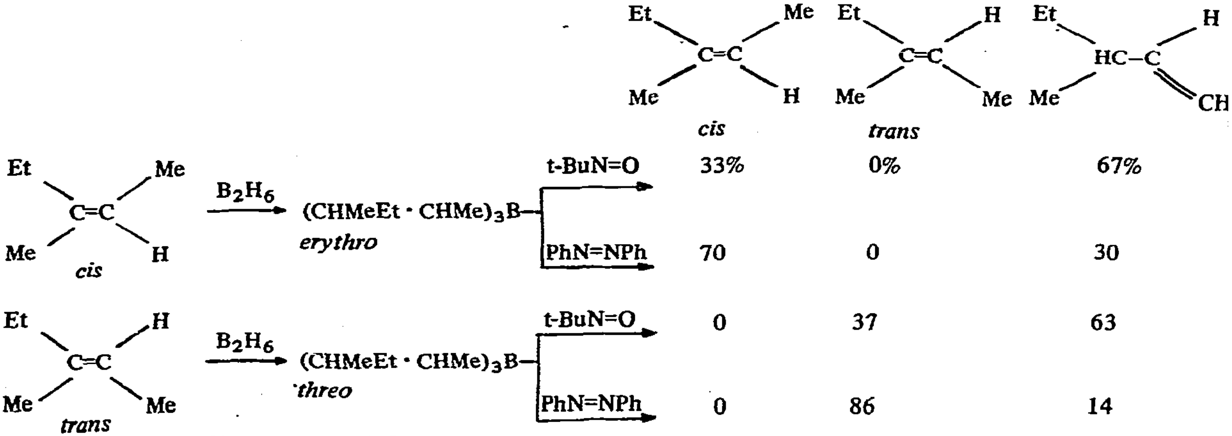
(3)

The blue colour of the nitroso compound, or the red colour of the azo compound, is immediately discharged when the reagent is mixed with tri-n-butyl-, tri-isobutyl-, tri-s-butyl-, or tri-n-hexyl-borane in an inert solvent, and the olefin and hydroborated reagent are formed in essentially quantitative yield (NMR)★. The olefins were further identified by GLC and the boron-containing products were hydrolysed and converted into characteristic derivatives.

If *trans*-azobenzene is irradiated with UV light in the presence of an organoborane, it gives the same product as does the dark reaction of *cis*-azobenzene, but it is not yet clear whether this involves photo-excited azobenzene (*cf.* the reaction of photo-excited ketones[3]), or *cis*-azobenzene produced by photo-isomerization.

Trineopentylborane, which has no hydrogen on the β-carbon atom, and triphenylborane, for which the six-centre transition state would be energetically inaccessible, do not react with either reagent even under much more severe conditions.

If *cis*- or *trans*-3-methyl-2-pentene is hydroborated, and then dehydroborated, the composition of the olefins which are formed are as shown in the following scheme.



The original olefin is regenerated with complete retention of configuration, as would be expected for the cyclic mechanism of Eq. 1; the variation in the ratio of terminal to medial olefins when azobenzene reacts with the isomeric boranes presumably reflects the different steric requirements in forming the transition states.

These reactions may be useful in organic synthesis through organoborane intermediates. They may also be useful analytically: by following the change in absorbance of a mixture of *cis*- and *trans*-azobenzene at 374 nm (where the extinction coefficients of the two isomers are equal), trialkylboranes can readily be estimated at concentrations of 10^{-3} to 10^{-4} *M*.

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2 *e.g.* B.M. Mikhailov, M.E. Kuimova and E.A. Shagova, *Dokl. Akad. Nauk SSSR*, 179 (1968) 1344.
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4 K. Torssell, *Tetrahedron*, 26 (1970) 2759.

★Reactions in which 2-methyl-2-nitrosopropane has been used as spin trapping reagent in the presence of organoboranes[4] therefore need to be re-evaluated.