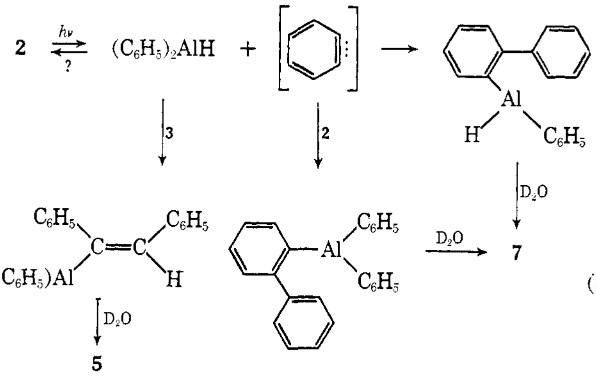
counterpart, hexaphenyl-1,4-dialumina-1,4-cyclohexadiene (**12**).[15]

Finally, the formation of significant amounts of 2-deuteriobiphenyl (**7**) and α-deuterio-*cis*-stilbene (**5**) can be jointly reconciled by a minor, alternative photodecomposition of **2** into benzyne and diphenylaluminum hydride (eq 4) (*cf.* ref 8b).



(4)

This technique of trapping lower valent organometallic intermediates currently is being extended to diverse photolyses and redox reactions. Also, the applicability of these findings to the development of new approaches to arynes and to organometallic heterocycles is being evaluated.

Acknowledgment. We are grateful to the National Science Foundation for support of this research under Grant GP-6679. Dr. Henry Fales of the National Institutes of Health was of great assistance in the measurement and interpretation of the mass spectral data reported herein.

(15) *Cf.* J. J. Eisch and L. J. Gonsior, *J. Organometal. Chem.* (Amsterdam), **8**, 53 (1967), for evidence in support of boron counterparts of 11 or 12.

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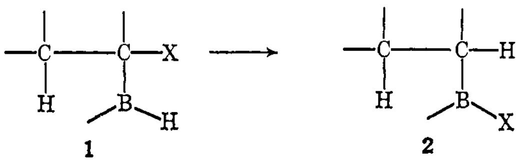
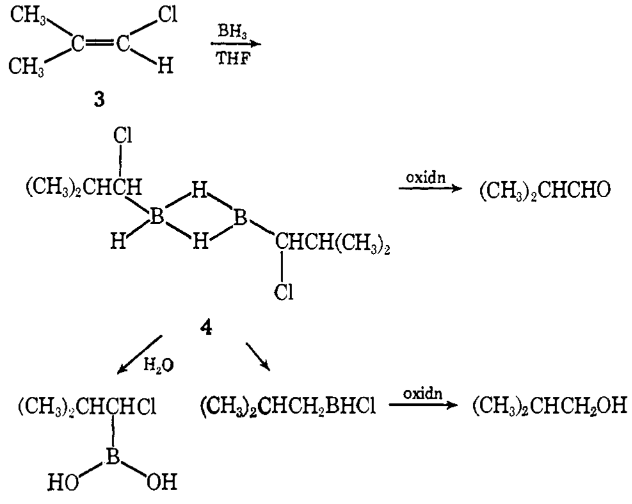
Transfer Reactions Involving Boron. XVII. On the Kinetics of the α-Transfer Reaction[1]

Sir:

Recent studies in our laboratories have been concerned with the chemistry of α- and β-heterosubstituted organoboranes which are formed in the hydroboration of heterosubstituted olefins.[2–6] These studies have indicated that the α-heterosubstituted organoboranes **1** undergo reaction to give derivatives having structure **2**. Previously we had pictured this rearrangement as proceeding *via* an intramolecular four-centered transition state. Brown[7] has suggested that the replacement of X by hydrogen could occur *via* a nucleophilic displacement, apparently employing a borohydride species in an intermolecular displacement.[7] All of the pertinent facts concerning the conversion of **1** → **2** will be cited later in this communication and incorporated into a consistent mechanistic description of the reaction. Unfortunately, the systems studied previously underwent reaction at a sufficiently fast rate that kinetic measurements were not possible. Recently, however, Brown and Sharp[7] have shown that the adduct formed in the hydroboration of 1-chloro-2-methylpropene (**3**) was reasonably stable to rearrangement. It is reported that immediate oxidation of the hydroboration product of **3** produces isobutyraldehyde.[6] We observed that if the hydroboration reaction mixture were allowed to stand in tetrahydrofuran at room temperature for several hours and then subjected to oxidation, only 2-methyl-1-propanol was isolated. We therefore investigated this system in greater detail.





The hydroboration of 1-chloro-2-methylpropene (**3**), with 0.99 mol of borane in tetrahydrofuran per 1.00 mol of olefin, produced **4**. The ^1H nmr spectrum of **4** displayed a double doublet at δ 0.95 (6 H, $(C\mathit{H}_3)_2CH$), the remaining peaks being obscured by the solvent resonance peaks. The ^{11}B nmr spectrum displayed only a double triplet at -29.3 ppm (relative to boron trifluoride etherate internal capillary) with J_{BH} (terminal) = 130 Hz and J_{BH} (bridge) = 47 Hz, corresponding to a symmetrical dialkyldiborane.[8] Addition of water and careful removal of the solvent under reduced pressure gave 1-chloro-2-methylpropylboronic acid (**5**); mp 63–64°.[9]

The ^1H nmr spectrum of **5** in deuteriochloroform displayed two doublets at δ 1.00 and 1.06 (6H, $(C\mathit{H}_3)_2$-CH, J = 6.6 Hz), a multiplet at 2.22 (1 H, $(CH_3)_2C\mathit{H}$) overriding a broad absorption ($B(O\mathit{H})_2$), and a doublet at 3.62 (1 H, $C\mathit{H}ClB(OH)_2$, J = 3.3 Hz). The ^{11}B nmr spectrom of **5** displayed a broad singlet at -29.3 ppm characteristic of an alkylboronic acid.[10] During the course of several hours the ^1H nmr spectrum of **4** changed quite dramatically, eventually displaying an AB portion of an ABX system at δ 0.55 (2 H, $C\mathit{H}_2$-

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(1) Part XVI: D. J. Pasto and J. Hickman, *J. Amer. Chem. Soc.*, **89**, 4445 (1967). Taken from the Ph.D. Thesis of J. H., University of Notre Dame, 1967.

(2) D. J. Pasto and J. Miesel, *J. Amer. Chem. Soc.*, **85**, 2118 (1963).

(3) D. J. Pasto and C. C. Cumbo, *ibid.*, **86**, 4343 (1964).

(4) D. J. Pasto and R. Snyder, *J. Org. Chem.*, 31, 2773 (1966).

(5) D. J. Pasto and R. Snyder, *ibid.*, 31, 2777 (1966).

(6) D. J. Pasto and J. Hickman, *J. Amer. Chem. Soc.*, **89**, 5608 (1967).

(7) H. C. Brown and R. L. Sharp, *ibid.*, **90**, 2915 (1968).

(8) D. J. Pasto and V. Balasubramaniyan, unpublished results.

(9) See footnote 34 of ref 7.

(10) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, p 972.

BHCl) and a doublet at 0.90 (6 H, $(CH_3)_2CH$), the remaining peaks being obscured by the solvent. This nmr spectrum is consistent with a tetrahydrofuran complex of **6**, the diastereotopic nature of the methylene hydrogens being due to the asymmetry at the boron atom.[11] Oxidation of the reaction mixture at this time gave only isobutyl alcohol.

The rate of the rearrangement was followed in the following manner. The hydroboration of 1-chloro-2-methylpropene was carried out as described above in a thermostated vessel at 25°. Aliquots were removed periodically by means of a hypodermic syringe and hydrolyzed with water, the volume of hydrogen evolved being measured in a gas buret.

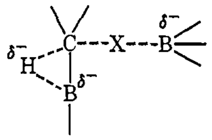
The initial consumption of available "hydride" for the transfer reaction was exceedingly fast, up to 20–35% within the first few minutes (see later discussion for an explanation of this phenomenon). The remaining consumption of hydride produced good first-order kinetic plots for the disappearance of "hydride" (one-half of the total available hydride). Half-order and second-order plots showed considerable curvature. The derived rate constants (see Table I) show some scatter; however, considering the experimental procedure employed the scatter of the first-order rate constants is not considered excessive. Of importance is the fact that there is no discernible trend in the rate constants with concentration of **4**.

Table I. First-Order Rate Constants for the Rearrangement of **4**

Run no.	**4**, M	$k_1 \times 10_3$, min^{-1}
1	0.525	9.1
2	0.442	8.7
3	0.441	10.8
4	0.401	10.5
5	0.250	10.0
6	0.075	13.9

Before interpreting the rate data in terms of a mechanistic description of the reaction, several other known facts concerning the transfer reactions should be made apparent. The rearrangement of **4** is strongly catalyzed by Lewis acids. Rearrangement of **4** in the presence of 4 mol % excess of borane in tetrahydrofuran results in complete reaction within 30 min. This borane-catalyzed rearrangement undoubtedly causes the very fast disappearance of **4** during the kinetic runs at very early times, the rate of hydroboration of **3** being competitive with the catalyzed rearrangement of **4**. Only after complete utilization of borane is accomplished is the nonborane-catalyzed reaction apparent. The addition of 1 mol % of boron trifluoride etherate results in the complete rearrangement of **4** in less than 5 min. Other pertinent facts are: (1) the α- and β-transfer reactions occur with complete inversion of configuration at carbon;[1,6] (2) the α-transfer reaction occurs very rapidly at quaternary carbon[2-4] which is not consistent with an intermolecular SN2 displacement of X^-; and (3) alkyl transfer reactions have also been characterized.[2]

The transition state most consistent with all of the observations is represented as **7** in which an intramolecular hydride displacement of complexed X occurs. The catalytic action by borane could conceivably involve an intermolecular hydride transfer; however, the similar catalytic effect by boron trifluoride would not be consistent with this viewpoint. The intramolecular nature of this rearrangement is favored sterically over an intermolecular transfer, and alkyl transfer would be feasible *via* **7** (H = alkyl) but not by an intermolecular transfer. A similar intramolecular displacement transition state has been proposed by Matteson and Mah for the enhanced rate of nucleophilic displacement of chloride in α-chloroalkaneboronic esters.[12]



7

The kinetics of the reaction, however, demands that the rearrangement of **4** be first order in dimer. It is not obvious how the hydrogen-bridged dimer **4** in the absence of other acidic catalysts can directly produce the rearranged product. We believe that the dimer **4** must dissociate to monomer **4**, one molecule of **4** acting as the catalyst to affect the rearrangement of the other molecule of **4** *via* transition state **7**. This process requires the kinetics to be first order in dimer **4**. Although monomeric **4** cannot be detected by ^{11}B nmr, this does not preclude its existence as a reaction intermediate. Nmr data[8] from other similar systems indicate that the rate constants in monomer–dimer equilibria (k_1 and k_{-1}) are large compared to the nmr time scale, indicating that the rearrangement step is rate controlling (see eq 1 and 2).

$$M_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2M \tag{1}$$

$$M + M \xrightarrow{k_{rd}} \mathbf{7} \longrightarrow \text{products} \tag{2}$$

The synthetic utility of such intramolecular transfer reactions has been recently demonstrated by Brown and coworkers in the elegant syntheses of ethyl alkyl- and dialkylacetates by treatment of trialkylboranes and ethyl chloro- and dichloroacetates with base.[13]

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(11) Monoalkylboron chlorides are strongly complexed with tetrahydrofuran, the exchange of solvent being very slow compared to the nmr time scale of observation (D. J. Pasto and P. Balasubramaniyan, *J. Amer. Chem. Soc.*, **89**, 295 (1967).

(12) D. S. Matteson and R. W. H. Mah, *ibid.*, **85**, 2684 (1963).

(13) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818, 1911 (1968).

(14) Alfred P. Sloan Foundation Research Fellow, 1967–1969.

(15) Reilly Research Fellow, 1965–1966; National Institutes of Health Predoctoral Fellow (1-Fl-GM-31, 055-01Al), 1966–1967.

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Ether Cleavage and Boron Cation Formation with Amine–Iodoboranes

Sir:

We wish to report a novel reaction of amine adducts of monoiodoborane with diethyl ether, which leads to cleavage of the ether under surprisingly mild conditions and to the formation of a bis(amine)dihydroboron(1+) cation. Cleavage of ethers to alkyl iodide normally requires temperatures of around 150° and is carried