

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**

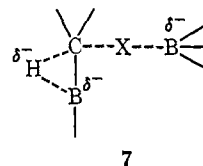
Run no.	4 , M	$k_1 \times 10^3$, min ⁻¹
1	0.525	9.1
2	0.442	8.7
3	0.441	10.8
4	0.401	10.5
5	0.250	10.0
6	0.075	13.9

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 carbon²⁻⁴ 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

(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. Balasubramanian, *J. Amer. Chem. Soc.*, **89**, 295 (1967).

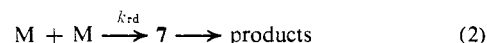
observations is represented as **7** in which an intramolecular hydride displacement of complexed X occurs. The catalytic action by borane could conceivably involve an intermolecular hydride transfer; however, the similar catalytic effect by boron trifluoride would not be consistent with this viewpoint. The intramolecular nature of this rearrangement is favored sterically over an



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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

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 ¹¹B nmr, this does not preclude its existence as a reaction intermediate. Nmr data⁸ 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).



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

(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-FI-GM-31, 055-01A1), 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

out in strongly acidic medium.¹ The present reaction occurs at 40° and without use of strong Brønsted or Lewis acids.

When pyridine-iodoborane³ (41.0 mmol) was refluxed at ~40° in 140 ml of benzene-ether (1:1 v/v), a precipitate gradually formed. The consumption of the iodoborane adduct was monitored by observing the precipitation of bis(pyridine)boronium iodide^{3a} on addition of pyridine to 1-ml aliquots withdrawn periodically from the solution. After 5 hr, the precipitate (4.12 g) was filtered and converted into the hexafluorophosphate salt of bis(pyridine)boronium ion. The yield was 13.75 mmol and corresponded to 95% of the weight expected if the crude precipitate had been pure bis(pyridine)boronium iodide. The product was identical with an authentic sample^{3b} and was free of N-ethylpyridinium ion. The filtrate yielded another 2.06 mmol of the boron cation on addition of excess pyridine. This quantity represented the amount of pyridine-iodoborane still unreacted at this point. Therefore 95% of the iodoborane had reacted.

The proton nmr spectrum of the remaining solution showed a quartet and a triplet which exactly corresponded in chemical shifts, coupling constants, and relative intensities to the properties of ethyl iodide in the same solvent mixture. Comparison of the integrated intensities with the ones obtained from a solution with a known concentration of ethyl iodide gave the amount of ethyl iodide produced (25 mmol). Distillation of the pyridine-containing solution left a water-soluble salt, N-ethylpyridinium iodide, which was identified by precipitation with HgI₂-KI solution and by comparison of the proton nmr and infrared spectra and the melting point of the water-insoluble product with that of the identical material derived from pyridine and ethyl iodide, mp 98–100°. The total moles of iodine-containing products, C₂H₅I and (C₅H₅N)₂BH₂⁺I⁻ (isolated as PF₆⁻ salt), amounted thus to 38.8 mmol, in excellent agreement with the moles of pyridine-iodoborane used (38.9 mmol). Of the total reacted, 64% produced ether cleavage as measured by the ethyl iodide produced, while 35% produced boron cation. These data were reproducible in separate experiments under identical conditions.⁴

In addition to the absorption for ethyl iodide, the filtrate from the reaction mixture showed a 1:3:3:1 quartet in the 60-Mc nmr spectrum centered at 32 cps downfield from the center of the quartet arising from

(1) (a) K. Ziegler, H. Weber, and H. G. Gellert, *Chem. Ber.*, **75**, 1715 (1942); (b) H. Stone and H. Shechter, *J. Org. Chem.*, **15**, 491 (1950); (c) Houben-Weyl, "Methoden der Organischen Chemie," Vol. VI, Part 3, 4th ed, Georg Thieme Verlag, Stuttgart, 1965, p 147.

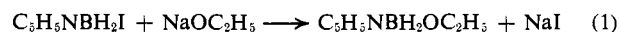
(2) K. C. Nainan and G. E. Ryschkewitsch, submitted for publication.

(3) (a) The term "boronium" is used to describe a tetracoordinated ion of BH₂⁺; (b) G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **89**, 3145 (1967).

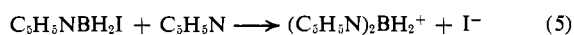
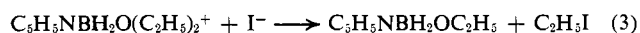
(4) We observed the same general reaction with trimethylamine-iodoborane: see K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Chem.*, **7**, 1316 (1968).

the ether CH₂ group, which was well separated from the latter peaks and the side bands. This quartet had the same integrated intensity as the quartet arising from the ethyl iodide.

The reaction of sodium ethoxide with pyridine-iodoborane yielded a solution showing the same nmr quartet as that found with the ether cleavage reaction. Product analysis and other spectral evidence from the solution are consistent with eq 1.



The evidence is in excellent support of the reaction scheme



Equations 2 and 3 represent the most probable path of ether cleavage, with eq 3 involving attack of the iodide species on the α-carbon of the ethyl group. The net equation (2 plus 3), (6), is amply supported by



product analysis, by the material balance for ethyl groups (equal proportions of ethoxy groups and ethyl iodide), and by the over-all iodine material balance. Equation 4 produces pyridine for subsequent reaction with pyridine-iodoborane in competition with ether cleavage. Alkoxyborane adducts of tertiary amines are almost unknown, but the fact that borate esters are very poor acceptors⁵ and the fact that trimethylamine-diisopropoxyborane has a very high dissociation pressure⁶ give strong plausibility to the contention that the dissociation step represented by eq 4 is a kinetically suitable precursor to eq 5. It is noteworthy in this context that evaporating the reaction mixture under fore-pump vacuum, at room temperature or below, moves into the cold traps a volatile boron compound associated with reducing power toward silver ion, an expected consequence of eq 4. The final step, iodide displacement from iodoborane, has been demonstrated to be an extremely facile process with amines^{3b,4,7} and proceeds easily under the conditions of the ether cleavage reaction.

Acknowledgment. Support of this work by the National Institutes of Health, Grant GM-13650, is gratefully acknowledged.

(5) S. V. Urs and E. S. Gould, *J. Am. Chem. Soc.*, **74**, 2948 (1952).

(6) H. C. Brown, H. I. Schlesinger, and A. B. Burg, *ibid.*, **61**, 673 (1939).

(7) G. E. Ryschkewitsch and J. M. Garrett, *ibid.*, **89**, 4240 (1967).

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