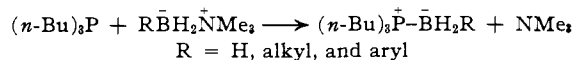


Mechanism of Displacement Reactions at Tetrahedral Boron. Triethyl- and Trimethylamine-Borane Substrates

Sir:

The tetrahedrally bonded boron atom is isoelectronic with the tetrahedral carbon atom and bears a formal negative charge. It was therefore of interest to examine the nucleophilic displacement reactions which occur at such boron atoms and to attempt a mechanistic correlation with similar displacement reactions which occur at carbon centers. If mechanistically similar paths were found, the effects of substrate charge type and related solvent effects, among others, could be elucidated. The previously reported¹ displacement of trimethylamine from trimethylamine-borane by tertiary phosphines suggested the use of similar reactions in a mechanism study. In addition, the ready availability of a variety of B-alkyl² and B-aryl³ tertiary amine-boranes allowed the effect of substitution at boron to be examined⁴ in terms of stereoelectronic effects.



In the displacement reactions reported here,⁵ tri-*n*-butylphosphine (I) was employed as the nucleophile in *o*-dichlorobenzene solution with (C₂H₅)₃NBH₃ (II), (C₂H₅)₃NBD₃ (III), and (CH₃)₃NBH₃ (IV) as substrates. Tri-*n*-butylphosphine-borane was established as the product of the displacement reactions by isolation and comparison with authentic material.¹ All kinetic experiments were conducted at 49.6°.

The reaction of I with II was examined using the colorimetric analytical method.⁵ The crude rate data obtained from runs pseudo-first-order in I obeyed the integrated first-order equation to about 80% completion. The calculated second-order rate constant (2.55 × 10⁻⁴ l. mole⁻¹ sec⁻¹) was not altered by the initial addition of triethylamine (0.2 *M*). Substitution of deuterium for hydrogen on the boron atom of II was accomplished using the exchange procedure of Davis, *et al.*⁶ The III obtained was approximately 85% isotopically pure as determined from its infrared and ¹¹B n.m.r. spectra. This material was employed as the substrate in reactions with I under conditions identical

with those employed with II. Within experimental error, no α -deuterium isotope effect was observed since a second-order rate constant of 2.58 × 10⁻⁴ l. mole⁻¹ sec⁻¹ was observed. This observation is in agreement with the second-order nature of the reaction and the previously described⁷ absence of α -deuterium kinetic isotope effects in bimolecular nucleophilic displacement reactions at tetrahedral carbon centers.

The reaction of IV with I was examined using the flow method and low conversions to product. The calculated second-order rate constant (1.34 × 10⁻⁴ l. mole⁻¹ sec⁻¹) was approximately one-half that observed in the case of II and suggests that the latter substrate is the more reactive due to greater internal steric repulsions which are partially relieved in the bimolecular transition state.

Further work is in progress and will be reported at a later date.

Acknowledgment.—The authors wish to acknowledge the generous support of this investigation by the National Science Foundation under Grant GP-69.

(7) See A. Streitwieser, Jr., "Solvolytic Displacement Reactions," Supplement, McGraw-Hill Book Company, Inc., New York, N. Y., 1962, for collected examples.

(8) Alfred P. Sloan Research Fellow.

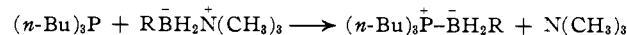
DEPARTMENT OF CHEMISTRY M. FREDERICK HAWTHORNE⁸
THE UNIVERSITY OF CALIFORNIA WILLIAM L. BUDDE
RIVERSIDE, CALIFORNIA

RECEIVED SEPTEMBER 10, 1964

Displacement Reactions at Tetrahedral Boron. Trimethylamine-Alkyl- and Arylboranes

Sir:

As a portion of our study of nucleophilic displacement reactions at tetrahedral boron, we have examined the kinetics of the reaction of tri-*n*-butylphosphine (I) with a series of trimethylamine-alkylboranes¹ and a series of trimethylamine-arylboranes.² All phosphine-



borane reaction products were prepared by the displacement of trimethylamine from the corresponding trimethylamine-borane with I and gave satisfactory elemental analyses. All kinetic data are presented in Table I and were obtained using the previously de-

TABLE I
COLLECTED KINETIC DATA

R in RBH ₂ N(CH ₃) ₃	Temp., °C.	First-order rate constant, sec. ⁻¹ × 10 ⁶	Second-order rate constant, l. mole ⁻¹ sec. ⁻¹ × 10
<i>n</i> -Butyl	29.5	0.267	0.167 ^a
Isobutyl	29.5	0.697	0.070 ^a
<i>sec</i> -Butyl	29.5	1.90	0.361
<i>sec</i> -Butyl ^b	29.5	1.48	0.351
<i>t</i> -Butyl	29.5	17.6	<i>c</i>
Phenyl	30.0	<i>c</i>	1.16
<i>p</i> -Anisyl	30.0	1.22	1.39
<i>p</i> -Bromophenyl	30.0	<i>c</i>	1.26
<i>p</i> -Tolyl	30.0	<i>c</i>	1.11
<i>o</i> -Tolyl	30.0	<i>c</i>	5.15
Mesityl	30.0	63.9	54.6

^a Calculated from rate data determined at 40.1 and 49.8°.

^b Substrate *sec*-C₄H₉BD₂N(CH₃)₃. ^c Kinetic term too small to detect if present.

(1) R. A. Baldwin and R. M. Washburn, *J. Org. Chem.*, **26**, 3549 (1961).

(2) M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 831 (1961).

(3) M. F. Hawthorne, *ibid.*, **80**, 4291 (1958).

(4) M. F. Hawthorne, W. L. Budde, and D. Walmsley, *ibid.*, **86**, 5337 (1964).

(5) Two methods were developed for monitoring the extent of reaction. The first method made use of the red complex (λ_{max} 484 m μ (ϵ 54)) formed from carbon disulfide and I in *o*-dichlorobenzene solution. The reaction was effectively quenched and remaining I determined spectrophotometrically upon the addition of aliquots of reaction mixture to carbon disulfide. The second analytical method made use of the rapid and quantitative volatilization of trimethylamine from the reaction mixture when reactions were conducted in the presence of a rapidly flowing stream of nitrogen. The effluent gas, carrying trimethylamine product, was passed through an aqueous solution of standard acid containing brom thymol blue indicator. The time at which neutralization of incremental amounts of acid was observed provided a means of rate determination. The second method was sufficiently sensitive to allow initial reaction rates to be determined (up to 10% conversion) with $\pm 5\%$ reproducibility. The use of initial reaction rate data was often required due to the slowness of the reaction observed. Reactant concentrations were chosen in such a manner as to provide a wide range of initial reactant concentration ratios. Raw kinetic data were treated by the usual integrated equations when the first method of analysis was employed and by the differential method when initial rates were determined.

(6) R. E. Davis, A. E. Brown, R. Hopman, and C. L. Kibby, *J. Am. Chem. Soc.*, **85**, 487 (1963).

(1) M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 831 (1961).

(2) M. F. Hawthorne, *ibid.*, **80**, 4291 (1958).