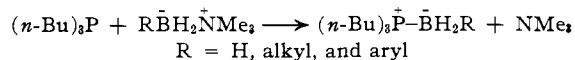


## Mechanism of Displacement Reactions at Tetrahedral Boron. Triethyl- and Trimethylamine-Borane Substrates

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 reported<sup>1</sup> 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-alkyl<sup>2</sup> and B-aryl<sup>3</sup> tertiary amine-boranes allowed the effect of substitution at boron to be examined<sup>4</sup> in terms of stereoelectronic effects.



In the displacement reactions reported here,<sup>5</sup> tri-*n*-butylphosphine (I) was employed as the nucleophile in *o*-dichlorobenzene solution with (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NBH<sub>3</sub> (II), (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NBD<sub>3</sub> (III), and (CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub> (IV) as substrates. Tri-*n*-butylphosphine-borane was established as the product of the displacement reactions by isolation and comparison with authentic material.<sup>1</sup> All kinetic experiments were conducted at 49.6°.

The reaction of I with II was examined using the colorimetric analytical method.<sup>5</sup> 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<sup>-4</sup> l. mole<sup>-1</sup> sec<sup>-1</sup>) 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.*<sup>6</sup> The III obtained was approximately 85% isotopically pure as determined from its infrared and <sup>11</sup>B 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  $\alpha$ -deuterium isotope effect was observed since a second-order rate constant of 2.58 × 10<sup>-4</sup> l. mole<sup>-1</sup> sec<sup>-1</sup> was observed. This observation is in agreement with the second-order nature of the reaction and the previously described<sup>7</sup> absence of  $\alpha$ -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<sup>-4</sup> l. mole<sup>-1</sup> sec<sup>-1</sup>) 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.

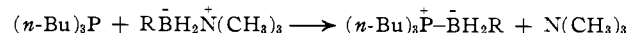
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## Displacement Reactions at Tetrahedral Boron. Trimethylamine-Alkyl- and Arylboranes

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-alkylboranes<sup>1</sup> and a series of trimethylamine-arylboranes.<sup>2</sup> 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 <sub>2</sub> N(CH <sub>3</sub> ) <sub>3</sub>	Temp., °C.	First-order rate constant, sec. <sup>-1</sup> × 10 <sup>6</sup>	Second-order rate constant, l. mole <sup>-1</sup> sec. <sup>-1</sup> × 10
<i>n</i> -Butyl	29.5	0.267	0.167 <sup>a</sup>
Isobutyl	29.5	0.697	0.070 <sup>a</sup>
<i>sec</i> -Butyl	29.5	1.90	0.361
<i>sec</i> -Butyl <sup>b</sup>	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

<sup>a</sup> Calculated from rate data determined at 40.1 and 49.8°.

<sup>b</sup> Substrate *sec*-C<sub>4</sub>H<sub>9</sub>BD<sub>2</sub>N(CH<sub>3</sub>)<sub>3</sub>. <sup>c</sup> 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 ( $\lambda_{\text{max}}$  484 m $\mu$  ( $\epsilon$  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).

scribed flow method<sup>1</sup> and low conversion to products.

**Alkylborane Systems.**—The four isomeric trimethylamine-butylboranes were examined in their reaction with I. The iso- and *n*-butyl systems were too slow to measure at 29.6° and rate data obtained at 49.8 and 40.1° were employed to estimate their rates<sup>3</sup> at 29.6° (see Table I). In all of these systems, with the single exception of *t*-butyl, the over-all rate expression was composed of first- and second-order kinetic terms. The *t*-butyl system gave only first-order kinetics at 29.6°. This is not surprising in view of the fact that the reaction site is analogous to that present in the neopentyl carbon system which does not enter into bimolecular nucleophilic displacement reactions.

The *sec*-butyl system presents the highest bimolecular reactivity in the butyl series. This probably reflects a large internal steric compression in a system which is not seriously encumbered toward bimolecular attack by a nucleophile. As in the case of triethylamine-borane,<sup>4</sup> the *sec*-butyl system was labeled at boron with deuterium<sup>5</sup> and the resulting substrate was examined kinetically. As previous work would suggest,<sup>6</sup> the second-order kinetic term remained unchanged while the first-order term gave rise to a  $k_H/k_D$  of 1.29. These data further support the idea that the first-order term represents a dissociative process and that the second-order term represents an S<sub>N</sub>2 process. Further work is in progress which will deal with possible  $\beta$ -deuterium isotope effects.

**Arylborane Systems.**—The reactions of phenyl, *p*-tolyl, *p*-bromophenyl, *p*-anisyl, *o*-tolyl, and mesityl (trimethylamine)boranes with I were studied at 30°. As seen in Table I, the mesityl and *p*-anisyl systems produced rate expressions which contained a predominant second-order term and a small first-order term. The other compounds studied in this series most probably have smaller first-order terms in their rate expressions which lie within the region of experimental error. The effect of *para* substituents upon the rates of the second-order reactions was surprisingly small and suggests transition states of low polarity. The most striking result pertained to the effect of *o*-methyl substituents upon rate. Thus, the *o*-tolyl and mesityl systems were approximately 4.2 and 47 times, respectively, as reactive as the phenyl system. Such substituent effects on bimolecular displacement reactions have been noted before<sup>7</sup> in similar benzyl systems and ascribed to the operation of London dispersion forces. The observation of first-order terms in the rate expressions of the *p*-anisyl and mesityl systems might be attributed to enhanced electronic stabilization of the borane intermediate and to steric acceleration of dissociation, respectively.

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

(3) Approximate activation parameters for these two systems are: *n*-butyl, first-order term,  $\Delta H^*_1 = 30$  kcal./mole,  $\Delta S^*_1 = 38$  e.u.; second-order term,  $\Delta H^*_2 = 22$  kcal./mole,  $\Delta S^*_2 = 0$  e.u.; isobutyl, first-order term,  $H_1 = 32$  kcal./mole,  $\Delta S^*_1 = 18$  e.u., second-order term,  $\Delta H^*_2 = 26$  kcal./mole,  $\Delta S^*_2 = 2$  e.u.

(4) M. F. Hawthorne and W. L. Budde, *J. Am. Chem. Soc.*, **86**, 5337 (1964).

(5) The deuterium compound was prepared by lithium aluminum deuteride reduction of the corresponding boroxine. See ref. 1.

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

(7) J. F. Bunnett and J. D. Reinheimer, *J. Am. Chem. Soc.*, **84**, 3284 (1962).

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

(8) Alfred P. Sloan Research Fellow.

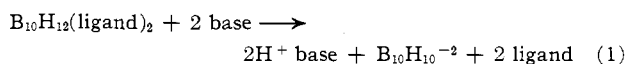
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## A Mechanism Study of B<sub>10</sub>H<sub>10</sub><sup>-2</sup> Formation

Sir:

The preferred synthetic route to B<sub>10</sub>H<sub>10</sub><sup>-2</sup> involves the reaction of B<sub>10</sub>H<sub>12</sub>(ligand)<sub>2</sub> compounds with bases such as triethylamine,<sup>1</sup> triphenylphosphorane,<sup>2</sup> and



ammonia.<sup>3</sup> Yields of B<sub>10</sub>H<sub>10</sub><sup>-2</sup> as high as 90% may be obtained on a large preparative scale accompanied by variable amounts of displacement products, B<sub>10</sub>H<sub>12</sub>(base)<sub>2</sub>, and less well-defined materials.

We have initiated a kinetic study aimed at elucidating the mechanism of B<sub>10</sub>H<sub>10</sub><sup>-2</sup> formation. Previous deuterium tracer work<sup>4</sup> indicated the course of the over-all geometrical change which accompanies the reaction.

A reliable and very sensitive spectrophotometric method was devised<sup>5</sup> for the determination of B<sub>10</sub>H<sub>10</sub><sup>-2</sup>. With this method, and where necessary by the use of initial reaction rates, it was possible to study the kinetics of B<sub>10</sub>H<sub>10</sub><sup>-2</sup> formation essentially uncomplicated by competitive reactions.

The reaction of B<sub>10</sub>H<sub>12</sub>(NEt<sub>3</sub>)<sub>2</sub> (I) with triethylamine (II) was examined in acetonitrile solution at 100°. This system employed an amine base identical with the attached ligand. Thus, with reference to eq. 1, the amine concentration remained constant throughout each kinetic run. Reactions were followed to at least 80% completion. The observed kinetics were first order in I and zero order in II over a wide range of initial concentration ratios and with a first-order rate constant of  $5.4 \times 10^{-5}$  sec.<sup>-1</sup>. These results indicated that the external base molecule was not incorporated in the rate-determining transition state.

The reaction of B<sub>10</sub>H<sub>12</sub>(SMe<sub>2</sub>)<sub>2</sub> (III) with II was examined at 20.0° in toluene solution. A preparative-scale experiment carried out under these conditions for 4.5 days with 0.02 *M* III and 0.15 *M* II produced 70% B<sub>10</sub>H<sub>10</sub><sup>-2</sup>, 15% I, and 15% unidentified oil. In another series of experiments, the infinite time yields of B<sub>10</sub>H<sub>10</sub><sup>-2</sup> were determined under kinetic conditions with 0.01 *M* III and varied initial concentrations of II. Maximum yields (80%) of B<sub>10</sub>H<sub>10</sub><sup>-2</sup> were obtained at 0.05 *M*, or higher, initial [II]. Below 0.05 *M*

(1) A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 5519 (1959).

(2) Unpublished results.

(3) E. L. Muettterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

(4) J. A. Dupont, M. F. Hawthorne, A. R. Pitochelli, and R. Ettinger, *J. Am. Chem. Soc.*, **84**, 1037 (1962).

(5) This method makes use of the quantitative formation of a red azo coupling product ( $\epsilon$  19,400,  $\lambda_{\text{max}}$  520 m $\mu$ ) which is formed from a large excess of phenyldiazonium ion and B<sub>10</sub>H<sub>10</sub><sup>-2</sup> in acetonitrile acidified with trifluoroacetic acid. The nature of this coupling product is presented elsewhere: M. F. Hawthorne and F. P. Olsen, *J. Am. Chem. Soc.*, **86**, 4219 (1964).