

Figure 1. Temperature-viscosity ratios at coalescence of the low-field pair of lines of the eight-line esr pattern of 2, R = I.

construction of a specific empirical solvent scale of general utility for rotational correlation times.

Acknowledgment. We are indebted to Professor H. M. McConnell for helpful comments.

*Address correspondence to this author.

Edwin F. Ullman,* Ludwig Call

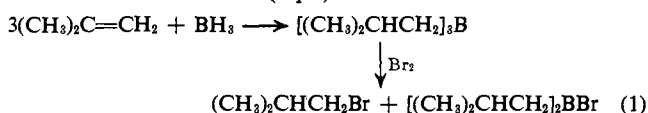
Contribution No. 21, Synvar Research Institute
Palo Alto, California 94304

Received August 15, 1970

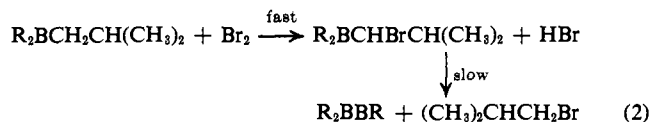
The Formation of Alkyl Bromides in the Dark Reaction of Bromine with Organoboranes. Evidence for an Unusual Pathway Involving the Prior Bromination of the Organoborane

Sir:

Tri-*n*-butylborane reacts readily with dry bromine in the absence of a solvent to yield *n*-butyl bromide, di-*n*-butylboron bromide, *n*-butane, and hydrogen bromide.^{1,2} The reaction is greatly facilitated by the use of methylene chloride as a solvent and provides a convenient procedure for the anti-Markovnikov hydrobromination of olefins (eq 1).³



Investigation revealed an unexpected feature—the reaction does not involve simple rupture of the carbon-boron bond by bromine. Instead, the reaction proceeds through the fast α bromination of the organoborane⁴ followed by a subsequent reaction of the intermediate with the hydrogen bromide (eq 2).



(1) J. R. Johnson, H. R. Snyder, and M. G. Van Campen, Jr., *J. Amer. Chem. Soc.*, **60**, 115 (1938).

(2) Similarly, tri-*n*-hexylborane reacts with excess bromine in the absence of a solvent to give equimolar amounts of 1-bromohexane and *n*-hexane, the total amount being equivalent to one *n*-hexyl group.

(3) For an alternative procedure involving hydroboration-mercuration-bromodemercuration, see J. J. Tufariello and M. M. Hovey, *Chem. Commun.*, 372 (1970).

(4) It has recently been reported that triethylborane and bromine react rapidly in the gas phase, with no detectable amount of ethyl bromide observed: J. Grotwald, E. A. Lissi, and J. C. Scaiano, *J. Organometal. Chem.*, **19**, 431 (1969).

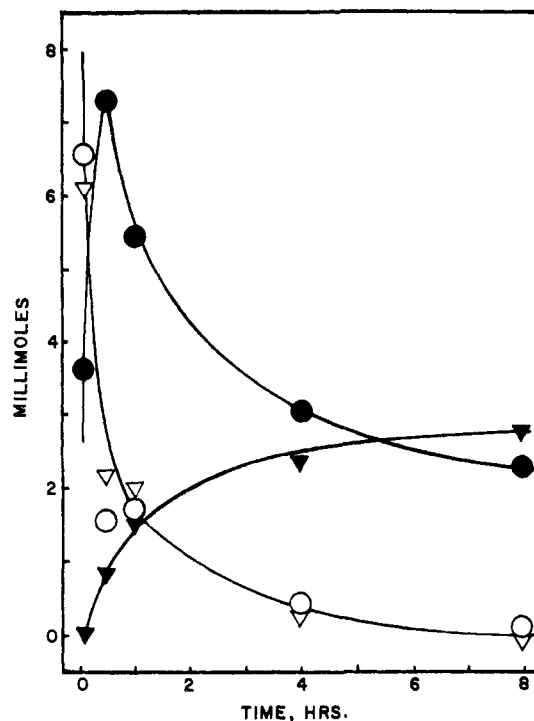


Figure 1. The dark reaction of tri-*sec*-butylborane (10 mmol) with bromine (10 mmol) in 20 ml of carbon tetrachloride solvent: O, Br₂; ▽, R₂B; ●, total HBr; ▼, 2-bromobutane.

For the initial exploration of the reaction of bromine with organoboranes, simple conditions were selected. Three isomeric tributylboranes (10 mmol) (*n*-butyl, *sec*-butyl, and isobutyl) were treated in the dark at 25° with 10 mmol of bromine in 20 ml of several representative solvents (cyclohexane, carbon tetrachloride, chloroform, and methylene chloride). At the end of appropriate intervals of time, 20 mmol of cyclohexane was added to convert the residual bromine to 1,2-dibromocyclohexane and residual hydrogen bromide to bromocyclohexane. An internal standard was added and the reaction mixture was analyzed directly by glpc. Hydrogen bromide which escaped from the reaction mixture was trapped in sodium hydroxide and determined by titration.

The rate of reaction was fastest with tri-*sec*-butylborane, slower with tri-*n*-butylborane, and slowest with triisobutylborane. The yields appeared to be most favorable in methylene chloride, so this solvent was selected for the preparative studies. The results of these studies are summarized in Table I.⁵

In methylene chloride the organoborane and bromine disappeared at approximately the rate at which the alkyl bromide appeared. This corresponds to the expected mechanism involving formation of the product by direct reaction of bromine with the alkyl-boron bond (eq 3). However, in cyclohexane, carbon tetra-



chloride, and chloroform, it was observed that bromine and the tributylborane disappear at essentially the same rate, *but the corresponding butyl bromide makes its*

(5) The reaction of bromine with organoboranes in the presence of base provides for a higher utilization of alkyl groups: H. C. Brown and C. F. Lane, *J. Amer. Chem. Soc.*, **92**, 6660 (1970).

Table I. Dark Reaction of Bromine with Trialkylboranes in Methylene Chloride Solvent^a

Organoborane from olefin	Product	Yield, % ^b
1-Butene	1-Bromobutane	80
	2-Bromobutane	11
2-Butene	2-Bromobutane	88
Isobutylene ^c	Isobutyl bromide	85
2,4,4-Trimethyl-1-pentene	1-Bromo-2,4,4-trimethylpentane	82
Cyclopentene	Bromocyclopentane	84
Cyclohexene	Bromocyclohexane	99
Norbornene	<i>exo</i> -Bromonorbornane ^d	88

^a Reactions were allowed to proceed for 24 hr at ~25° in a closed system using a 10% excess of bromine. ^b By glpc analysis. The yield is based on a maximum production of 1 mol of RBr from 1 mol of R₃B (eq 1). ^c After 48 hr at ~25°. ^d The absence of the endo isomer was indicated by glpc analysis (<1%).

appearance at a much slower rate. Typical results for the reaction of bromine with tri-*sec*-butylborane in carbon tetrachloride are shown graphically in Figure 1.

These results are clearly incompatible with a mechanism involving the direct rupture of the carbon-boron bond by bromine. It requires that the bromine react with the organoborane in an initial fast reaction to produce an intermediate of relatively low volatility which is converted in a subsequent slow stage to the product.

Further support for this interpretation is provided by the observation that when the reaction is carried out under reduced pressure to facilitate escape of hydrogen bromide, the amount of alkyl bromide present in the reaction mixture decreases with a corresponding increase in the amount of hydrogen bromide present in the trap.

The following observations are significant in indicating that the first intermediate must be the α -bromo-organoborane. The reaction of bromine with organoboranes containing one alkyl branch at the α position, as in tri-*sec*-butylborane, proceeds more readily than corresponding organoboranes without this feature, such as tri-*n*-butyl- and triisobutylborane. Moreover, bromination of the xethyl di-*n*-octylborane yields only *n*-octyl bromide and no detectable amount of the xethyl bromide. α bromination of the xethyl group is of course not possible. Finally, confirmation of the structure of the intermediate was achieved through study of the transfer reaction.⁶

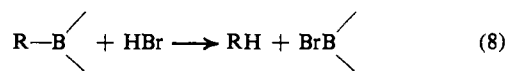
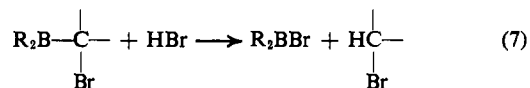
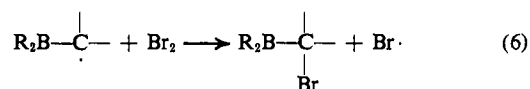
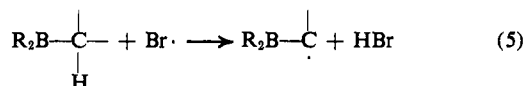
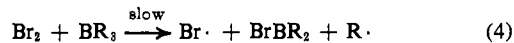
The mechanism we wish to propose involves free-radical chain bromination of the α position of the organoborane, a free-radical bromination that proceeds rapidly even in the dark⁷ (eq 5 and 6). The remarkably high reactivity of the organoborane toward attack by bromine atoms is indicated by the observation that even the use of cyclohexane as a solvent results in insignificant diversion of bromine atoms to this possible reactant. The precise nature of the initiation stage is uncertain, but may involve an attack of bromine on the organoborane⁸ (eq 4). The hydrogen bromide

(6) Addition of water to the reaction mixture from tri-*sec*-butylborane at 0.5 hr (Figure 1), followed by oxidation with alkaline hydrogen peroxide, yields 32% 3,4-dimethyl-3-hexanol, the product anticipated for transfer of an alkyl group from boron to the α -carbon position; D. J. Pasto and J. L. Meisel, *J. Amer. Chem. Soc.*, **85**, 2118 (1963).

(7) The reaction with bromine is greatly facilitated by light.

(8) For related reactions see A. G. Davies and B. P. Roberts, *Chem. Commun.*, 699 (1969).

produced in the substitution stage can then react preferentially to give the alkyl bromide⁹ (eq 7) or competitively either with the intermediate or unreacted organoborane to give alkane (eq 8). This mechanism readily accounts for the available experimental observations.



Although the dark reaction of organoboranes in methylene chloride does provide a convenient route to certain organic bromides (Table I), the observation that it is possible to achieve a facile α bromination of organoboranes in solution at room temperatures has enormous implication for the formation of carbon-carbon bonds and the synthesis of carbon structures.⁶ We are exploring these implications.

(9) Methylene chloride evidently favors this step. The reaction course in this solvent is otherwise quite similar.

(10) Graduate research assistant on Grant No. GM 10937 from the National Institutes of Health.

* Address correspondence to this author.

Clinton F. Lane,¹⁰ Herbert C. Brown*

Richard B. Wetherill Laboratory, Purdue University
Lafayette, Indiana 47907

Received June 26, 1970

Formation of a Novel Cobalt-Carborane Complex Involving the C₂B₆H₈⁴⁻ Ligand Produced by Reduction of 1,7-C₂B₆H₈

Sir:

The first bimetallic carborane complex formulated as [(B₅C₂H₁₁)Co]₂(B₈C₂H₁₀)²⁻ has been reported¹ in which two formal cobalt(III) atoms together with the apparent C₂B₈H₁₀⁴⁻ ion complete a closed 12-atom polyhedron.

We wish to report the preparation of the first bimetallic 10-atom polyhedral carborane complex which we formulate as (C₅H₅)₂Co₂C₂B₆H₈ (I). Treatment of 1,7-dicarba-*closo*-octaborane(8), 1,7-C₂B₆H₈, with 2 equiv of sodium naphthalide in tetrahydrofuran followed by the addition of a fivefold excess of Na⁺-C₅H₅⁻ and excess CoCl₂ produced a mixture which included the complex C₅H₅CoC₂B₆H₈²⁻ in addition to I. The green I was separated by column chromatography and recrystallized from hexane in 7.3% yield, mp 236–238°. *Anal.* Calcd for (C₅H₅)₂Co₂C₂B₆H₈: C, 41.76; B, 18.83; H, 5.22; Co, 34.17. Found: C,

(1) J. N. Francis and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 1663 (1968).

(2) G. B. Dunks, Ph.D. Dissertation, University of California, Riverside, Calif., 1970.