

the Co(NH₃)₅Cl²⁺ ion at 49.4°). By analogy to the hydrolysis of such cobalt(III) complexes and since an S_N1 classification may imply too limited a role for water in the transition state, it is suggested that haloborane-amine hydrolysis be designated mechanistically as an I_d process³² to underscore the dissociative character of the reaction with respect to the boron-halogen bond.

The trend in rate for the monohaloboranes, $k_{\text{BH}_2\text{I}} > k_{\text{BH}_2\text{Br}} > k_{\text{BH}_2\text{Cl}}$, presumably reflects the relative leaving-group tendencies of the respective halide ions. This is similar to the trend generally observed in nucleophilic substitution reactions of alkyl halides, wherein the ease of displacement of halide ion (I⁻ > Br⁻ > Cl⁻) correlates inversely with the basicity of the leaving group.^{33,34} Since the degree of solvation of halide ions by water lies in the order Cl⁻ > Br⁻ > I⁻,^{35,36} the relative degree of solvation of halide in the respective transition states may to a large extent account for the observed trend in ΔS^\ddagger values for the monohaloboranes.

The relative rates of reaction of the mono- and di-

(32) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 1.

(33) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp 258-263.

(34) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 81, 82.

(35) E. M. Arnett and D. R. McKelvey, *J. Am. Chem. Soc.*, **88**, 2598 (1966).

(36) R. F. Rodewald, K. Mahendran, J. L. Bear, and R. Fuchs, *ibid.*, **90**, 6698 (1968).

iodoboranes can be explained quite reasonably in terms of the substituent effect of X in I. Electronic inductive effects of iodide and hydride are such that stabilization of the incipient boronium ion should be greater when X = H as in the monoiodoborane adduct.

In considering possible pathways for haloborane-amine hydrolysis, it is worth noting that the monohaloborane adducts of trimethylamine are isoelectronic with neopentyl halides which exhibit severe steric inhibition to displacement *via* back-side attack but for which many examples of unimolecular dissociation have been cited.³⁷ Due to many factors including the highly polar character of the boron-nitrogen bond, analogies between amine-boranes and isoelectronic carbon-carbon compounds are necessarily limited. Nevertheless, a study of the comparative kinetics of selected reactions, such as the hydrolysis of progressively less hindered substrates as, for example, -BH₂X adducts of dimethyl- and monomethylamine, may provide a useful approach to further understanding of the route of nucleophilic displacement in such borane-donor addition compounds.

Acknowledgments.—The authors gratefully acknowledge the support of The Robert A. Welch Foundation and the T.C.U. Research Foundation. Proton and ¹¹B nmr spectra were obtained by Mr. Gary L. Smith.

(37) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 403-410, 511-515.

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Reaction of Boron-Hydrogen Compounds with Dimethylchloramine

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Dimethylchloramine has been shown to react with amine-boranes to give amine-chloroboranes as the first product. Thus, trimethylamine-borane gives trimethylamine-mono-chloroborane. In the reaction with dimethylamine-borane and pyridine-boranes, the chloroboranes react further to give boron cations. The reactions with sodium borohydride and diborane were also investigated.

Dimethylchloramine is usually thought of as an aminating agent. Thus, with tertiary phosphines or arsines,¹ it forms aminophosphonium or aminoarsonium compounds. It has also been used for amination of aromatic compounds.² We have allowed it to react with several boron-hydrogen-containing compounds and have found that it behaves as a chlorinating agent. Although this is unusual, it is not unknown. Thus, it has been found to chlorinate *n*-heptane in concentrated sulfuric acid.³ In the reaction with primary and secondary phosphines, dimethylchloramine has been postulated to form first the chlorophosphine.

This then reacts with more phosphine to give a phosphorus-phosphorus bond.⁴ A similar reaction has been observed for arsines.⁵ Another compound containing a nitrogen-chlorine bond, N-chlorosuccinimide, has also been reported to chlorinate amine-boranes.⁶

Experimental Section

Reaction of Dimethylchloramine with Trimethylamine.—A solution in CCl₄ of 2.08 g (28.5 mmol) of (CH₃)₃NBH₃ and 2.27 g (28.5 mmol) of (CH₃)₂NCl was heated at 35-40° for 40 hr. After filtering, the solution was evaporated to give a 75% yield (2.27 g) of (CH₃)₃NBH₂Cl, mp 80°. The identity was confirmed by the ir and nmr spectra and sublimation gave a sample melting at 84° (lit.⁷ mp 84-85°). The nmr spectra of other reaction mix-

(1) H. H. Sisler and S. R. Jain, *Inorg. Chem.*, **7**, 104 (1968).

(2) See, for example, V. L. Heasley, P. Kovacic, and R. M. Lange, *J. Org. Chem.*, **31**, 3050 (1966).

(3) R. Bernarde, T. Galli, and F. Minisci, *J. Chem. Soc.*, **B**, 324 (1968).

(4) R. E. Highsmith and H. H. Sisler, *Inorg. Chem.*, **7**, 1740 (1968).

(5) L. K. Krannish and H. H. Sisler, *ibid.*, **8**, 1032 (1969).

(6) J. E. Douglass, *J. Org. Chem.*, **31**, 962 (1966).

(7) H. Nöth and H. Beyer, *Chem. Ber.*, **93**, 2251 (1960).

tures showed that the major component was $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$, approximately 80%, and that some $(\text{CH}_3)_3\text{NBHCl}_2$ was produced before all the $(\text{CH}_3)_3\text{NBH}_3$ had reacted. The spectrum also showed $(\text{CH}_3)_2\text{NH}$ and an amount of chloroform that would correspond to approximately 10% of the $(\text{CH}_3)_3\text{NBH}_3$ reacting with the solvent.

Reaction of Dimethylchloramine with Dimethylamine-Borane.—To a solution of 1.00 g (17.0 mmol) of $(\text{CH}_3)_2\text{HNBH}_3$ in 25 ml of CCl_4 was added, with stirring, 1.34 g (16.9 mmol) of $(\text{CH}_3)_2\text{NCl}$ in 25 ml of CCl_4 dropwise over 10 min. At this time a white solid was present and the solution was warm from the reaction. Five hours later the solution was filtered to give 2.15 g of $[(\text{CH}_3)_2\text{HN}]_2\text{BH}_2+\text{Cl}^-$, mp 161–167°, 92% yield. An analytical sample, precipitated from CH_2Cl_2 with petroleum ether (bp 30–60°), melted at 165.5–167.0° (lit. mp 78°⁸ and 167–169°). *Anal.* Calcd for $[(\text{CH}_3)_2\text{HN}]_2\text{BH}_2\text{Cl}$: C, 34.70; H, 11.65; Cl, 25.61; N, 20.23. Found: C, 34.50; H, 11.59; Cl, 25.45; N, 20.23.

The nmr spectrum in CH_2Cl_2 contained a doublet at –2.58 ppm, $J = 5.2$ Hz, and a very broad band at –7.77 ppm.

The ir spectrum, KBr pellet, contained bands at 3025 (s), 3000 (sh), 2830 (m), 2685 (m), 2435 (s), 2340 (m), 2275 (w), 1461 (s), 1360 (m), 1340 (sh), 1188 (s), 1167 (m), 1156 (m), 1100 (w), 1034 (w), 1019 (m), 998 (m), 921 (m), 881 cm^{-1} (m).

The chloride salt was converted to the hexafluorophosphate salt with an 87% conversion by treatment with excess saturated aqueous NH_4PF_6 that was made acidic with HCl. After precipitation from CH_2Cl_2 with petroleum ether (bp 30–60°) the sample melted at 104–105° (lit.¹⁰ mp 102–104°).

The nmr spectrum in CH_2Cl_2 contained a doublet at –2.60 ppm, $J = 5.4$ Hz, and a very broad band at –4.63 ppm.

The ir spectrum, KBr pellet, contained bands at 3280 (m), 3070 (s), 3010 (sh), 2825 (m), 2675 (m), 2440 (s), 2345 (m), 2285 (w), 1471 (s), 1415 (m), 1352 (m), 1191 (s), 1164 (m), 1038 (m), 1021 (m), 996 (m), 921 (m), 840 (vs), 560 cm^{-1} (s).

In a similar experiment in which the $(\text{CH}_3)_2\text{NCl}$ was added rapidly and precautions to exclude moisture were not observed, no reaction was observed for 17 min. Then the solution became warm and a solid precipitated. About 23 min after the addition of the chloramine the temperature of the solution reached the maximum.

Reaction of Dimethylchloramine with 4-Methylpyridine-Borane.—A solution of 18.3 mmol (1.45 g) of dimethylchloramine in 25 ml of CCl_4 was added dropwise over 80 min, with stirring, to a suspension of 1.96 g (18.3 mmol) of 4-methylpyridine-borane in 15 ml of CCl_4 . After another 3 hr the solvent was removed under vacuum to give a nonvolatile viscous liquid and a solution. The solution contained 0.6 mmol of $(\text{CH}_3)_2\text{NCl}$, determined by oxidizing strength and nmr integrals, and 0.5 mmol of CHCl_3 , determined by nmr integrals. The 4.14-g amount of viscous liquid was dissolved in dilute hydrochloric acid and saturated NH_4PF_6 was added. The nmr spectrum of the resulting precipitate (2.67 g) showed it to be better than 95% $(4\text{-CH}_3\text{C}_5\text{H}_4\text{N})_2\text{BH}_2+\text{PF}_6^-$. Recrystallization from hot water gave 1.71 g of pure compound, mp 130.5–132° (lit.¹¹ mp 132.5–133°). The NH_4PF_6 solution was evaporated to dryness under reduced pressure and the resulting solid extracted with CH_2Cl_2 to give 2.34 g of a viscous liquid. The nmr spectrum showed it to be about 85% $[(\text{CH}_3)_2\text{HN}]_2\text{BH}_2+\text{PF}_6^-$ and 15% $(4\text{-CH}_3\text{C}_5\text{H}_4\text{N})_2\text{BH}_2+\text{PF}_6^-$. This was shaken with a small amount of 1,2-dichloroethane and filtered to give 0.39 g of $[(\text{CH}_3)_2\text{HN}]_2\text{BH}_2+\text{PF}_6^-$, mp 99.5–102°. Of the starting boron 48% was found as $(4\text{-CH}_3\text{C}_5\text{H}_4\text{N})_2\text{BH}_2+\text{PF}_6^-$ and 44% as $[(\text{CH}_3)_2\text{HN}]_2\text{BH}_2+\text{PF}_6^-$. In a control experiment without $(\text{CH}_3)_2\text{NCl}$ there was no nmr evidence for CHCl_3 .

Reaction of Dimethylchloramine with Pyridine-Borane.—In a procedure similar to the above, 17.0 mmol (1.35 g) of $(\text{CH}_3)_2\text{NCl}$

was allowed to react with 16.6 mmol (1.55 g) of $\text{C}_5\text{H}_5\text{NBH}_3$. From this was isolated 1.04 g (mp 109–112°) plus 0.20 g (mp 97–107°) of $(\text{C}_5\text{H}_5\text{N})_2\text{BH}_2+\text{PF}_6^-$ (lit.¹² mp 116°), 1.02 g of a viscous liquid which the nmr spectrum showed to be mostly $[(\text{CH}_3)_2\text{HN}]_2\text{BH}_2+\text{PF}_6^-$, and 0.98 g of a mixture of both $(\text{C}_5\text{H}_5\text{N})_2\text{BH}_2+\text{PF}_6^-$ and $[(\text{CH}_3)_2\text{HN}]_2\text{BH}_2+\text{PF}_6^-$. Of the starting boron 75% was isolated as boron cations with approximately half present as each of the symmetrical cations. The presence of mixtures and the enhanced reactivities of these mixtures made the experimental work-up difficult. The nmr spectrum of the reaction mixture showed the presence of CHCl_3 , in an amount several times greater than in the picoline-borane reaction. That this was actually CHCl_3 was confirmed in this reaction by the increase in the height of the nmr peak upon the addition of a small amount of CHCl_3 , and in other reactions by the retention time in vapor-phase chromatography and the infrared spectrum.

Reaction of Dimethylchloramine with Sodium Borohydride.—Although the reaction between $(\text{CH}_3)_2\text{NCl}$ and NaBH_4 was run several times in acetonitrile and 1,2-dimethoxyethane it was not possible to get clean separation of the products. In one experiment the nmr spectrum showed a very broad band at 466 Hz and a doublet at 156, 151 Hz, which were assigned to $[(\text{CH}_3)_2\text{HN}]_2\text{BH}_2+\text{Cl}^-$. In another reaction after conversion to the hexafluorophosphate salt in aqueous medium, a solid melting at 100–103° was obtained. The ir spectrum confirmed the identity as $[(\text{CH}_3)_2\text{HN}]_2\text{BH}_2+\text{PF}_6^-$. In one reaction the nmr spectrum showed a very broad band at 30 Hz above TMS, assigned to part of a partially collapsed B–H quartet and a doublet (149 and 144 Hz downfield). Dimethylamine-borane has the corresponding bands at 54 Hz above TMS and at 153.5 and 148 Hz. (The chemical shifts of these compounds are sensitive to the concentration and the presence of other solutes.) In another reaction a sample melting at 31–34° was separated by vacuum sublimation (lit.¹³ mp 37° for $(\text{CH}_3)_2\text{HNBH}_3$). The order of addition made very little difference in the amounts of products formed.

Reagents.—Trimethylamine- and dimethylamine-borane, obtained from Callery Chemical Co., were purified by vacuum sublimation. 4-Picoline-borane was prepared by transamination from trimethylamine-borane and purified by vacuum sublimation, mp 74.5–75.5° (lit.¹⁴ mp 72–73°). Pyridine-borane, also from Callery Chemical Co., was used as received. Dimethylchloramine was prepared from “Chlorox” and dimethylammonium chloride,³ distilled into carbon tetrachloride or diethyl ether, and stored below 15° over molecular sieves. The concentration was determined by iodometric titration with $\text{Na}_2\text{S}_2\text{O}_3$. The nmr spectrum and another titration after several months gave no evidence for decomposition of these solutions. Solvents were reagent grade and stored over molecular sieves.

Measurements.—The ^1H nmr spectra were recorded on a Varian A-60A instrument using tetramethylsilane (TMS) as an internal standard. The infrared spectra were recorded on a Beckman IR-10. Elemental analyses were performed by Peninsular ChemResearch Inc., Gainesville, Fla. Melting points are uncorrected.

Results

Dimethylchloramine reacts with trimethylamine-borane over several days at 25° or several hours at slightly elevated temperatures to produce $(\text{CH}_3)_3\text{NBH}_2\text{Cl}$ in 75% yield. The nmr spectrum showed the presence of $(\text{CH}_3)_2\text{NH}$ and small amounts of $(\text{CH}_3)_3\text{NBHCl}_2$ and other unidentified products. The reaction of $(\text{CH}_3)_2\text{NCl}$ with $(\text{CH}_3)_2\text{HNBH}_3$ gives $[(\text{CH}_3)_2\text{HN}]_2\text{BH}_2+\text{Cl}^-$ in 92% yield. Pyridine- and 4-picoline-borane react at about the same rate as does dimethyl-

(8) H. Nöth, H. Beyer, and H. Vetter, *Chem. Ber.*, **97**, 110 (1964).

(9) B. M. Mikhailov, N. S. Fedotov, T. A. Shegoleva, and V. D. Sheludyakov, *Dokl. Akad. Nauk SSSR*, **145**, 340 (1962); *Proc. Acad. Sci. USSR, Chem. Sect.*, **145**, 605 (1962).

(10) V. R. Miller and G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **92**, 1558 (1970).

(11) K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Chem.*, **7**, 1316 (1968).

(12) G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **89**, 3145 (1967).

(13) H. Nöth and H. Beyer, *Chem. Ber.*, **93**, 928 (1960).

(14) J. A. Bigot, T. J. DeBoar, and F. L. J. Sixma, *Rec. Trav. Chim.*, **76**, 996 (1957).

amine-borane. The products are [(CH₃)₂HN]₂BH₂⁺Cl⁻ and (C₅H₅N)₂BH₂⁺Cl⁻ or (4-CH₃C₅H₄N)₂BH₂⁺Cl⁻ in about equal yields.

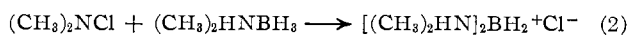
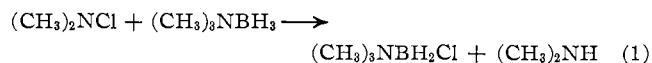
In most cases a small amount, less than 10%, of CHCl₃ was also produced from the solvent CCl₄. Trimethylamine-borane produced the most while pyridine-borane and 4-picoline-borane produced only a small amount. Part but not all of the CHCl₃ produced in the (CH₃)₃NBH₃-(CH₃)₂NCl system could be accounted for by an uncatalyzed reaction of the amine-borane with CCl₄.¹⁵ In the pyridine- and 4-picoline-borane systems none of the CHCl₃ could be attributed to a reaction with the solvent. The nmr spectrum of the dimethylamine-borane reaction did not show a chloroform peak.

The reaction of dimethylchloramine with trimethylamine-borane proceeds at the same rate with a less than 5-min exposure to the laboratory light as with almost continuous exposure. The reaction can be initiated by a free-radical source as shown by the fact that the reaction in the presence of di-*t*-butyl peroxyoxalate proceeds to about the same extent in 3 hr as the reaction without initiation does in 24 hr.

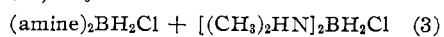
In the reaction between dimethylchloramine and sodium borohydride it was possible to isolate and identify (CH₃)₂HNBH₃ by melting point and [(CH₃)₂HN]₂BH₂⁺Cl⁻ by melting point and ir spectrum. When the reactants were present in the ratio 1:1, the proton nmr spectrum showed that roughly half the material was the amine-borane, and the other half was unidentified. When the chloramine to borohydride ratio was 2:1, the nmr spectrum of the reaction mixture indicated that the percentages of the methyl groups present as the amine-borane, the boron cation, and unidentified material were approximately equal.

Discussion

The reactions of dimethylchloramine with various amine-boranes at first glance appear to follow different reaction paths depending on the nature of the coordinated amine. Chlorination is observed with trimethylamine-borane according to eq 1. On the other hand, dimethylamine-borane is aminated according to eq 2,



whereas pyridine-borane and 4-methylpyridine-borane, according to eq 3, are aminated but give disproportionation products, *i.e.*, two symmetrically substituted bis-



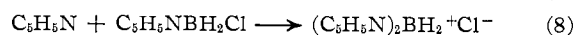
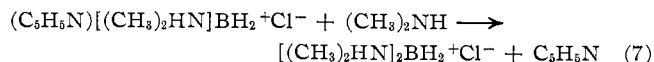
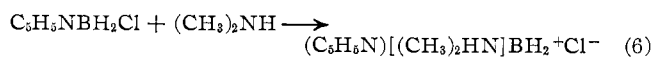
(amine)boronium salts instead of the unsymmetrical dimethylamine-pyridine cation. This surprising disparity in the nature of the final products can be explained by a single sequence of reaction steps where the differences in products are not determined by the be-

havior of dimethylchloramine but by the chemical properties of intermediate compounds.

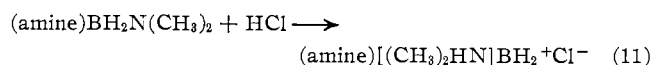
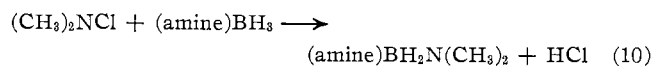
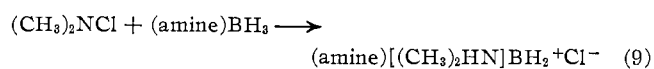
The first and relatively slow reaction, common to all systems studied here, is the chlorination of one of the B-H bonds in the coordinated BH₃ group to yield an adduct of BH₂Cl along with dimethylamine. When trimethylamine is coordinated to BH₃, the resulting chloroborane adduct is stable in the reaction mixture and can be isolated. The adducts of BH₂Cl with dimethylamine or pyridines, however, are quite reactive (amine)BH₃ + (CH₃)₂NCl → (amine)BH₂Cl + (CH₃)₂NH (4) toward displacement of halide ion by amine, as has been demonstrated by Nöth,⁸ and should react with the dimethylamine which is present in equivalent quantity (eq 5). The formation of an equimolar mixture of (amine)BH₂Cl + (CH₃)₂NH →



[(CH₃)₂NH]₂BH₂⁺ and (C₅H₅N)₂BH₂⁺ from pyridine-borane and dimethylchloramine can now be explained as the consequence of the rapid base-catalyzed reaction of the unsymmetrical cation expected from eq 5. This reaction has recently been reported¹⁰ and was shown to involve a pyridine-aminoborane intermediate which can lose pyridine for the further reactions

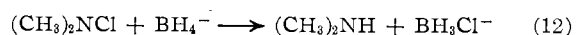


Alternate, not unreasonable stoichiometric mechanisms involving amination rather than chlorination on boron as a primary step can be ruled out. These are a concerted reaction, eq 9, or the related stepwise process, eq 10 and 11. Either path would lead to an



unsymmetrical cation which has been shown not to disproportionate in the absence of base.

Although the reactions of dimethylchloramine with sodium borohydride and diborane were not completely unraveled, some conclusions can be drawn. The production of dimethylamine-borane from the reaction with borohydride shows that hydrogen is transferred from boron to nitrogen. In analogy to the reaction with trimethylamine-borane the first step would be

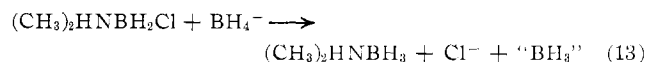


These products could then form the amine-borane either by loss of chloride from boron followed by addition of the amine or by displacement of the chloride by the amine. In the presence of excess chloramine the dimethylamine-borane would react further, eventually to give the boron cation. The presence of an

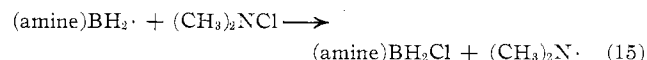
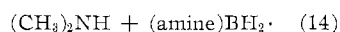
(15) Amine-boranes have been found to react with carbon tetrachloride to produce the amine-chloroborane and chloroform: V. R. Miller and G. E. Ryschkeiwitsch, to be submitted for publication.

approximately equal amount of other products shows that other reactions are occurring.

Since a possible side reaction could be attributed to the presence of "BH₃," the reaction between (CH₃)₂NCl and B₂H₆ was investigated. The nmr spectra of the reaction mixtures showed that the reaction is complicated and that products similar to those in the borohydride reaction are produced. The fact that the order of addition of the reagents in the dimethylchloramine-borohydride reaction made little difference in the products produced shows that if "BH₃" is responsible for the side reactions, it is produced from eq 12 and not by the reduction of amine-chloroborane

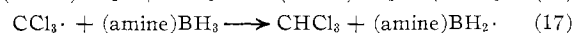
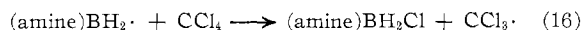


There is some evidence which supports a free-radical chain mechanism for the chlorination step of the amineboranes, eq 14 and 15. The reaction with (CH₃)₃-(CH₃)₂N· + (amine)BH₃ →



NBH₃ is accelerated by a free-radical initiator, di-*t*-butyl peroxyoxalate, while the reaction with (CH₃)₂-HNBH₃ shows an induction period. Another obser-

vation which supports a free-radical chain mechanism is the production of CHCl₃. The production of chloroform can be explained by a branching in the free-radical chain, *e.g.*



Based on bond-dissociation energies,¹⁶ both reactions are energetically favorable. It is difficult to conceive of any other mechanism which accounts for the concurrent production of CHCl₃.

As yet an unresolved difficulty in this mechanism is the nature of the initiation process. There is no evidence for low-energy homolysis of a B-H bond and (CH₃)₂NCl is usually assumed to proceed with heterolytic cleavage. The fact that the reaction with (CH₃)₂NCl proceeds more slowly when both oxygen and moisture are excluded shows that the initiation step is rather complicated. A confirmation of the free-radical nature of these reactions and the initiation step must await further study.

Acknowledgment.—Partial support of this work under NIH Grant GM 13650 is gratefully acknowledged.

(16) (a) T. L. Cottrell, "The Strength of Chemical Bonds," 2nd ed. Butterworth and Co. Ltd., London, 1958, Table 11.5.1; (b) E. L. Muetterties, "The Chemistry of Boron and Its Compounds," John Wiley and Sons, Inc., New York, N. Y., 1967, p 13.

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Pentaborane(9) Derivatives. II.¹ Synthesis of Di- and Trisubstituted Methyl-, Methylchloro-, and Methylbromopentaboranes. Detailed Nuclear Magnetic Resonance Studies

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Several new polysubstituted pentaborane derivatives are reported. These include 2-Br-3-CH₃B₅H₇, 1-Cl-2-CH₃B₅H₇, 2-Cl-1-CH₃B₅H₇, 2-Cl-3-CH₃B₅H₇, 2-Cl-4-CH₃B₅H₇, 1,2,3-(CH₃)₃B₅H₆, 2,3,4-(CH₃)₃B₅H₆, 2-Cl-1,3-(CH₃)₂B₅H₆, 2-Cl-1,4-(CH₃)₂B₅H₆, 2-Cl-3,4-(CH₃)₂B₅H₆, 3-Cl-2,4-(CH₃)₂B₅H₆, and 1-Cl-2,3-(CH₃)₂B₅H₆. The ¹H and ¹¹B nmr spectra of these and of some previously reported pentaborane derivatives are totally assigned. Substituent effects on the chemical shifts of contiguous, neighboring, and *trans* borons have been determined and are found to be additive for polysubstituted pentaboranes. An additivity relationship has also been found for the chemical shifts of bridge hydrogens in differing environments. Long-range coupling (*ca.* 6–7 Hz) between the apex boron and the attached methyl hydrogen of 1-methyl derivatives appears to be a general occurrence. A Friedel-Crafts alkylation of 2-methylpentaborane produces chlorinated derivatives of pentaborane in addition to the expected 1,2-dimethylpentaborane. Base-catalyzed rearrangement studies on polysubstituted pentaboranes lend experimental support to a "minimum atomic motion" mechanism.

Introduction

In an earlier report¹ the preparation of some pentaborane(9) derivatives was described and ¹H and ¹¹B nmr spectra were recorded in as much detail as was possible at that time. More recently several new pentaborane derivatives have been described; among

these are μ -trimethylsilyl-pentaborane(9),² group IV derivatives of pentaborane(9),³ chloro derivatives of pentaborane(9),⁴ iodo- and fluoropentaboranes,⁵ phosphinopentaboranes,⁶ and metal carbonyl derivatives of

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