2-Chloropentaborane(9).—The isomerization of 1-ClB_5H_8 to 2-ClB_5H_8 occurs cleanly in diethyl ether solution at room temperature. A number of isomerization experiments were carried out in nmr tubes in an attempt to obtain kinetic data. Owing to the nature of the ^{11}B nmr spectra, however, reliable data could not be obtained. It was found however that the equilibrium mixture in diethyl ether at room temperature contained about 80% 2-ClB_5H_8 and that 1–5 *M* solutions appeared to be near equilibrium after 1 day. The isolation of 1-ClB_5H_8 and 2-ClB_5H_8 was readily accomplished by repeated fractional condensations at -30 and $-63°$, respectively.

The 2-ClB_5H_8 was identified by comparison of its ^{11}B nmr, infrared, and mass spectra with those previously reported.[2]

1,2-Dichloropentaborane(9).—In a preparation similar to that used for 1-ClB_5H_8, 8.0 mmoles of 2-ClB_5H_8 was condensed into a 125-ml reaction flask that had previously been charged with about 0.5 g of $AlCl_3$. About 10 ml of BCl_3 and 9.3 mmoles of Cl_2 were then condensed into the flask. The flask was warmed, with stirring, from -75 to $-25°$ over a 9-hr period, and then stored at 0° for 12 hr. The product was separated from the yellow reaction solution and purified using procedures similar to those described for 1-ClB_5H_8. The 1,2-$Cl_2B_5H_7$ was condensed at $-30°$, melted over the range 18.2–19.5°, and exhibited a vapor pressure of considerably less than 1 mm at room temperature. The yield of 1,2-$Cl_2B_5H_7$ was 0.688 g (5.2 mmoles), or 65%. There was 1.9 mmoles of 2-ClB_5H_8 recovered from the reaction.

In similar reactions that were allowed to warm more rapidly the yields were 45 ± 5%.

The composition and structure of 1,2-$Cl_2B_5H_7$ were determined by nmr, infrared, and mass spectral studies. The mass spectrum cuts off at *m/e* 136, which corresponds to $^{11}B_5H_7{}^{37}Cl_2{}^+$. The most intense peaks in the parent group at *m/e* 131 and 132 correspond to the most probable combination of boron and chlorine isotopes in the parent skeleton. The ^{11}B nmr spectrum (Figure 1) of 1,2-$Cl_2B_5H_7$, obtained at 32.1 Mc, is tabulated in Table I. The ^1H nmr spectrum of 1,2-$Cl_2B_5H_7$, obtained at 100 Mc, is shown in Figure 1 along with tentative assignments of the resonances. The infrared spectrum of 1,2-$Cl_2B_5H_7$ was obtained in carbon disulfide solution and in the gas phase. Owing to the low volatility of the compound, the gas-phase spectrum contains only the most intense absorptions. The major bands (cm^{-1}) were found at 2620 (s), 1800 (w, br), 1530 (s, br), 1385 (s, br), 1190 (sh), 1165 (s), 1075 (w), 1050 (m), 1028 (s), 980 (sh), 970 (s), 875 (s), 825 (w), 775 (w), 660 (m), 630 (m).

Isomerization of 1,2-$Cl_2B_5H_7$.—In a flask similar to that used previously, 138 mg (1.1 mmoles) of $(CH_2)_6N_4$ and 624 mg (4.72 mmoles) of 1,2-$Cl_2B_5H_7$ were brought into contact for 6.5 hr at room temperature. Separation of the products was effected using a low-temperature fractional distillation column.[11] The material of slightly greater volatility than the 1,2-$Cl_2B_5H_7$ froze as a glass even after repeated fractionations. The mass spectrum was similar to that of 1,2-$Cl_2B_5H_7$ with a cutoff at *m/e* 136. The ^{11}B nmr spectrum was consistent with that expected for an approximately equimolar mixture of 2,3- and 2,4-$Cl_2B_5H_7$, though no appreciable separation of these isomers was ever obtained. The yield of the mixed isomers was 193 mg (1.46 mmoles), or 31%.

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[11] J. E. Dobson and R. Schaeffer, design to be published.

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Investigations of the Photochemistry of $H_2B_2O_3$[1]

By F. A. GRIMM and RICHARD F. PORTER

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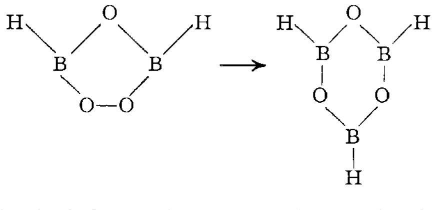
The ultraviolet spectrum of gaseous $H_2B_2O_3$ shows continuous absorption starting at about 2500 Å and extending to shorter wavelengths. The compound photochemically decomposes to yield B_2O_3(s) and H_2(g) and reacts with B_2H_6 to yield boroxine ($H_3B_3O_3$). Rates of the photochemical reactions are much higher than those observed for the thermal reactions and are accelerated by mercury photosensitization. Information on the mechanism of the B_2H_6–$H_2B_2O_3$ reaction was derived from studies with selectively prepared isotopic species of $H_2B_2O_3$.

Introduction

Gaseous $H_2B_2O_3$ was first observed as an intermediate in the slow oxidation of B_5H_9.[2] Later work has shown that $H_2B_2O_3$ is formed in the oxidation of BH_3CO, B_4H_{10} and $H_3B_3O_3$,[3,4] and by electrical discharge or photolysis of low-pressure mixtures of B_2H_6 and O_2.[5,6] One of the more interesting aspects of $H_2B_2O_3$ is its chemical behavior to regenerate $H_3B_3O_3$ by reaction with B_2H_6 under nonthermal conditions.[5] Microwave studies have shown that $H_2B_2O_3$ is a planar molecule with C_{2v} symmetry.[7] It was of interest, therefore, to examine the experimental conditions necessary for the conversion



and to obtain information about the mechanism. The procedure adopted was to investigate the reactions

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[1] Work supported by the Army Research Office, Durham, N. C., and the Advanced Research Projects Agency, Cornell University, Ithaca, N. Y.

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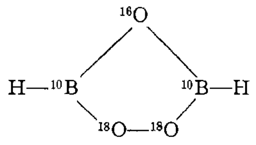
of $H_2B_2O_3$ under photochemical conditions, which are more easily controlled than those imposed by electrical discharge.

Experimental Section

Apparatus and Procedure.—The progress of the $H_2B_2O_3$ reactions was followed either with a mass spectrometer or an infrared spectrophotometer. For the mass spectrometric studies a very small sample of the gaseous reactants and products was continuously pumped from the reaction tube into the mass spectrometer through a "pinhole" leak. Details of themeth od and apparatus are the same as those for the study of the photochemical oxidation of diborane and have been reported elsewhere.[6] For the infrared studies the vessel shown in Figure 1 was constructed. The vessel consisted of two sections, one for the ultraviolet optics and the other for the infrared optics. The quartz immersion well was capable of transmitting the 1849-Å line of mercury and is available commercially from Engelhard Hanovia Inc. The infrared cell had a path length of 10 cm and was equipped with KBr windows. A modified Perkin-Elmer Model 337 grating Infracord was used for absorbance measurements. The modification made it possible to record absorbance continuously at a fixed wavelength *vs.* time. To reduce the effect of mercury all gases were transferred in an oil vacuum system. The one mercury manometer used in the vacuum line was covered with 2 cm of Dow Corning silicone fluid No. 704 before installation and the system was checked periodically for mercury by introducing a liquid nitrogen cold trap into the vacuum line. The presence of mercury will cause a black deposit to form in the cold trap. No black deposit was detected during the course of these experiments. While this test indicated that only a minimum amount of mercury (less than 10^{-5} mm) is present, the test does not guarantee the complete absence of mercury. Therefore, whenever the phase mercury "absent" is used below, it is understood that the system may still contain a very small amount of mercury. In other experiments the effect of mercury photosensitization was noted by adding a drop of mercury to the reaction vessel. When radiation below 2000 Å was removed with a Vycor-glass filter, the reaction proceeded in the presence of mercury. Thus, it could be concluded that the reactions are to some extent photosensitized by the 2537-Å line of mercury. No reaction was detected when a Pyrex-glass tube was used to remove the radiation below 3300 Å. Reactions were run in initially clean cells and in cells coated with B_2O_3, which was formed as a product in a preceding run. Clean cells were prepared by washing with nitric acid, water, methanol, and acetone, in that order.

Diborane was prepared from the reaction of anhydrous stannous chloride with potassium borohydride *in vacuo* at 250°.[8] Matheson reagent grade oxygen was used without further purification.

Preparation of Isotopically Labeled $H_2B_2O_3$.—In the course of the experiments it was necessary to prepare pure isotopically labeled samples of $H_2B_2O_3$. As the method used in this preparation is new, it will be discussed in some detail. Boroxine was prepared by applying a Tesla coil discharge to a mixture of 10 mm of B_2H_6 and 10 mm of O_2 in a 2-l. bulb.[9] As soon as the boroxine was produced, O_2 equivalent to 10 mm in the reaction vessel was added from a reservoir containing sufficient backing pressure to prevent the back flow of boroxine. Gaseous $H_2B_2O_3$ is produced by a rapid thermal reaction of boroxine and oxygen.[4,5] After allowing the mixture to stand for 10 min it was pumped slowly through two cold traps in series, one at −130° and one at liquid nitrogen temperature. The liquid nitrogen trap contained small amounts of B_2H_6, BH_3CO, and $H_2B_2O_3$. When the $H_2B_2O_3$ in the −130° trap was warmed to room temperature the infrared spectrum showed no diborane and the mass spectrum showed no traces of O_2. Very small amounts of H_2 are sometimes found and are probably due to a small amount of decomposition. Yields as based upon complete conversion of B_2H_6 to $H_2B_2O_3$ are about 20%. *Caution should be exercised in the preparation and a shield placed between the operator and the reaction vessel. Diborane–oxygen mixtures and condensed $H_2B_2O_3$ are very unstable and may explode without warning.* With this method it is possible to prepare many different isotopic species of $H_2B_2O_3$. For example, if $^{16}O_2$ and $^{10}B_2H_6$ are used to prepare boroxine and then $^{18}O_2$ is added, $H_2{}^{10}B_2{}^{16}O^{18}O_2$ with the structure



is the major species produced. For preparing small quantities of $H_2B_2O_3$ this method has certain advantages since it utilizes the more easily handled diborane in place of higher boranes and avoids the difficulties encountered in separating $H_2B_2O_3$ from B_4H_{10}.[2]

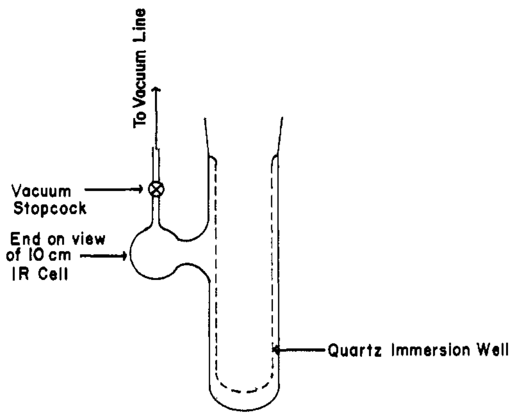


Figure 1.—Cell for studies of the photochemical reactions of $H_2B_2O_3(g)$.

Results and Discussion

Spectrum of $H_2B_2O_3$.—When this work was started, the ultraviolet absorption spectrum of $H_2B_2O_3$ was unknown. Before proceeding with the photochemical studies it was necessary to observe the spectrum. Samples of $H_2B_2O_3$, free of B_2H_6, were prepared by the method previously described and the absorption spectrum obtained. The spectrum down to 1800 Å (Figure 2) was obtained on a Cary 15 spectrophotometer,[10] purged to remove oxygen. The region between 1800 and 1200 Å was observed on the 35-ft vacuum grating spectrograph at the National Research Council in Ottawa.[11] The spectrum is continuous and appears structureless over the entire range. Diborane, oxygen, and the emission spectrum of the mercury lamp used in these experiments are also included in Figure 2. Our results for diborane agree with those recently published by Ogawa and Hirota.[12] The value of ϵ at 1850 Å is 73.4 l./mole cm for B_2H_6 and 70.5 l./mole cm for $H_2B_2O_3$ as obtained from $I = I_0 10^{-\epsilon c l}$.

Photochemical Decomposition of $H_2B_2O_3$.—Gaseous $H_2B_2O_3$ is known to decompose thermally with a lifetime at room temperature of approximately 2 or 3

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[8] W. Jeffers, *Chem. Ind.* (London), 431 (1961).

[9] L. Barton, F. A. Grimm, and R. F. Porter, *Inorg. Chem.*, **5**, 2076 (1966).

[10] We wish to thank Richard Castonguay for his help in obtaining these spectra.

[11] We are grateful to Dr. G. Herzberg and Dr. A. E. Douglas for the use of the facilities at NRC for these measurements.

[12] F. Ogawa and K. Hirota, *J. Mol. Spectry.*, **21**, 29 (1966).

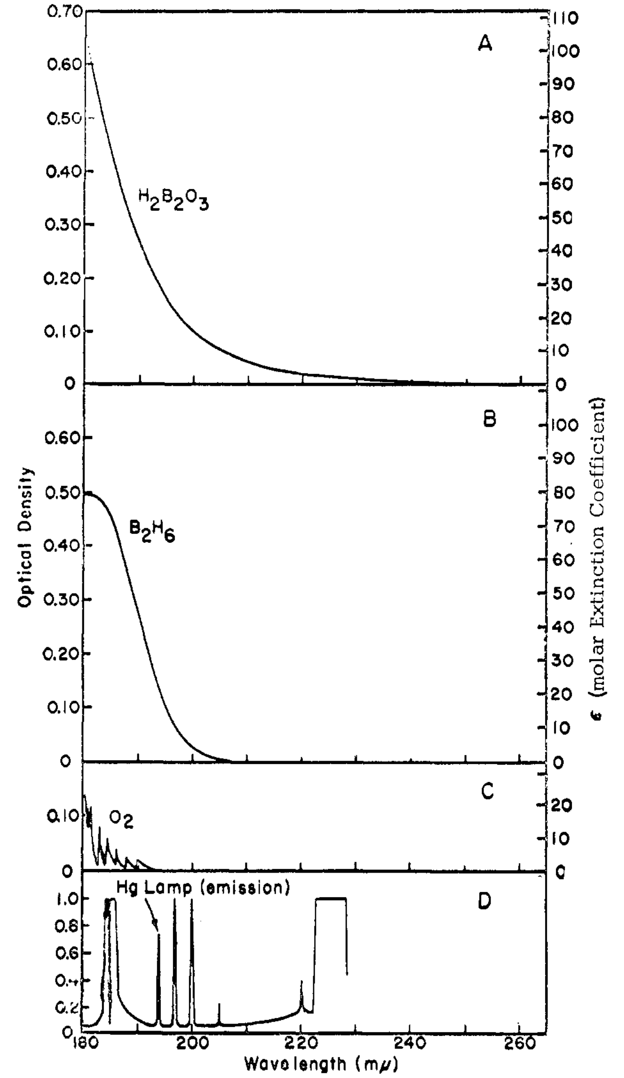

Figure 2.—A, B, C: ultraviolet absorption spectra of $H_2B_2O_3$, B_2H_6, and O_2. D: emission spectrum of medium-pressure mercury lamp used in these experiments.

days. Ditter and Shapiro found the decomposition products to be B_2O_3, a small amount of B_2H_6, and "probably H_2."[2] When low pressures of $H_2B_2O_3$ (2–5 mm) were exposed to a medium-pressure mercury lamp, the decomposition rate was greatly accelerated over that observed in the thermal decomposition. Figure 3 shows the results for typical runs with mercury "absent" and with mercury present. Within the limits of lamp intensity no change in rate was observed in runs in a clean cell and those having a coating of B_2O_3. The products of the decomposition were found to be B_2O_3 and hydrogen. The addition of mercury affected only the rate and not the products. If the decomposition is assumed to be

$$H_2B_2O_3(g) \xrightarrow{h\nu} H_2(g) + B_2O_3(s) \qquad (1)$$

then there should be no change in pressure during the reaction. To check this, several runs were made in which the initial and final pressures were recorded. The final pressure was obtained by allowing the gases to expand into a vacuum system equipped with an oil manometer. An average of five runs gave a 20% drop

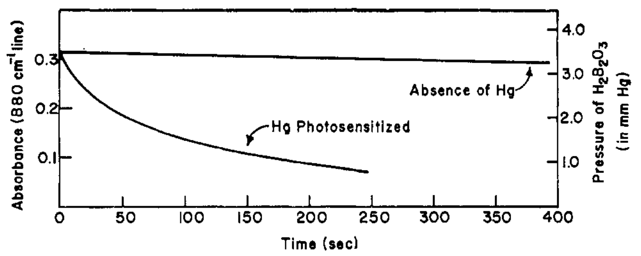

Figure 3.—Time dependence of decomposition of $H_2B_2O_3$; B_2O_3 coating not present initially.

in pressure. If a positive pressure of hydrogen was added to the system before decomposition was started, no pressure change was observed. Therefore, it seems reasonable to attribute the slight pressure decrease in the absence of hydrogen to the absorption of hydrogen in the vacuum system.

Photochemical Reaction with Diborane.—In the presence of diborane the major product other than hydrogen is boroxine ($H_3B_3O_3$). As can be seen from a comparison of Figures 3 and 4 the reaction rate is much slower than in the photochemical decomposition of $H_2B_2O_3$. As in the case of the straight decomposition, the addition of mercury did not change the products, but only the rate of reaction. The greatest yield of boroxine was obtained when the ratio of B_2H_6 to $H_2B_2O_3$ was greater than 2. The simplest net equation we can write for the major reaction is

$$H_2B_2O_3 + 0.5B_2H_6 \xrightarrow{h\nu} H_3B_3O_3 + H_2 \qquad (2)$$

It was difficult to obtain an accurate check on the stoichiometry because of the competing photochemical decomposition of $H_2B_2O_3$ and the rapid thermal decomposition of the product ($H_3B_3O_3$). In all cases more $H_2B_2O_3$ than expected from eq 2 was consumed. A correction for the $H_2B_2O_3$ decomposition could not be applied, because the rate of decomposition was diminished in the presence of B_2H_6.

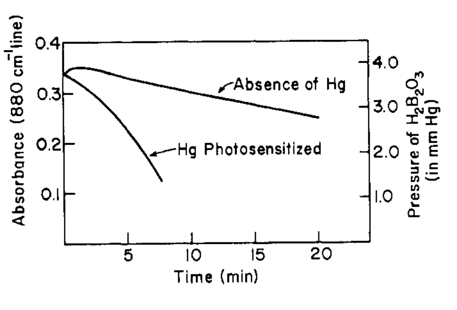

Figure 4.—Time dependence of the reaction of $H_2B_2O_3$ and B_2H_6.

A slight maximum is shown at the onset of the reaction in the absence of mercury (Figure 4). This effect can be attributed to the presence of a small quantity of oxygen which reacts with B_2H_6 to form $H_2B_2O_3$ preceding the reaction between $H_2B_2O_3$ and B_2H_6. That portion of the curve after the maximum is typical of the B_2H_6–$H_2B_2O_3$ reaction with mercury "absent" and when no oxygen is present in the reaction vessel. It was found that even in the presence of trace amounts of oxygen all of the oxygen must react before any evidence of a reaction between $H_2B_2O_3$ and diborane is found. This effect was also found when diborane and $H_2B_2O_3$ were allowed to react under electrical discharge conditions.[5] In the absence of B_2H_6, oxygen was found to react photochemically with $H_2B_2O_3$ to produce boric acid type products. This reaction accounts for the observation that in the photochemical reaction of B_2H_6 and O_2 the ratio of O_2 to B_2H_6 used is greater than the stoichiometric value of 2.[6]

As the concentration of B_2H_6 was increased relative to the concentration of $H_2B_2O_3$, the rate of the reaction was decreased. This suggests that B_2H_6 acts as a light filter and, therefore, the primary photochemical step is the excitation of $H_2B_2O_3$. This is also supported by subsequent experiments (discussed below) that show that the $H_2B_2O_3$ ring is fragmented in the reaction.

Mass spectral patterns obtained from the photochemical reaction of ^{16}O–^{18}O isotopically labeled samples of $H_2B_2O_3$ with B_2H_6 are shown in Figure 5. The ratios of $^{16}O_3$, $^{16}O_2{}^{18}O$, $^{16}O^{18}O_2$, and $^{18}O_3$ in the $H_2B_2O_3$ ring were calculated using the known mass spectrum of $H_2B_2O_3$ with the natural isotopic abundances.[2] The nonstatistical calculation for $H_2B_2O_3$ was obtained from the "normal" mass spectral pattern assuming the ^{16}O–^{18}O ratios given in Figure 5. This would be the expected pattern if there were no fragmentation of the $H_2B_2O_3$ ring. The statistical calculation was obtained from the ratio $^{16}O:{}^{18}O$ = 0.459:0.541. By comparison of the observed and calculated mass spectral patterns for $H_3B_3O_3$, it is evident that the $H_2B_2O_3$ ring must be fragmented in the reaction. Thus, the photochemical reaction between $H_2B_2O_3$ and B_2H_6 cannot be viewed as a simple insertion of a BH group into the $H_2B_2O_3$ ring at the O–O bond, but must involve fragmentation of the ring and subsequent reaction with B_2H_6. In order to obtain the complete statistical scrambling found in boroxine, it is necessary that intermediates containing single oxygen atoms be formed. The complexity of the reaction suggests that it proceeds by a surface mechanism with possible intermediates like HBO.

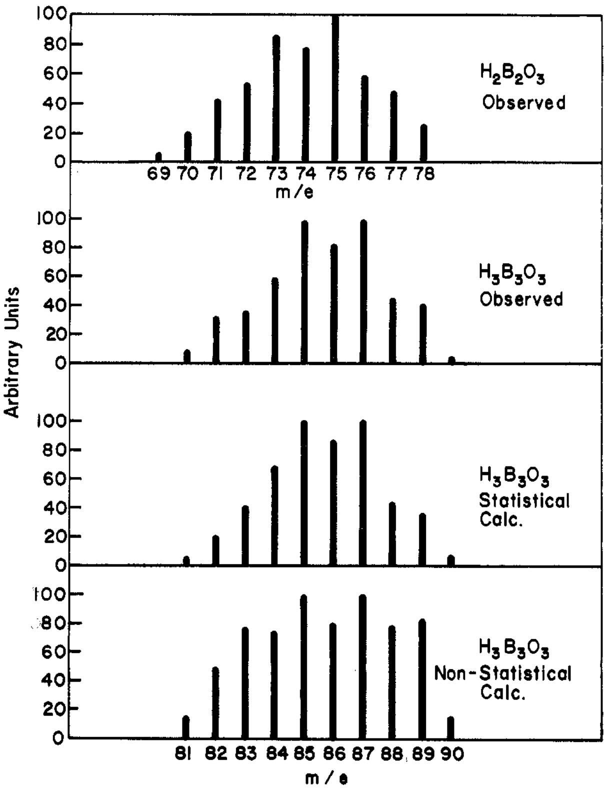

Figure 5.—Observed and calculated mass spectral patterns from the isotopic labeling experiments in the $H_2B_2O_3$–B_2H_6 reaction. Starting ratios of $H_2B_2O_3$ were $H_2B_2{}^{16}O_3$:$H_2B_2{}^{16}O_2{}^{18}O$:$H_2B_2{}^{16}O$-$^{18}O_2$:$H_2B_2{}^{18}O_3$ = 0.195:0.261:0.270:0.274.

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Chemistry of Trimethylsilyl Ylides. Reactions of Trimethylsilylmethylenetrimethylphosphorane with Halogen Compounds

BY D. R. MATHIASON[1a] AND N. E. MILLER[1b]

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A study of the reactions of trimethylsilylmethylenetrimethylphosphorane with a broad scope of halogen compounds was made. Nucleophilic substitution of alkyl halides was examined and found to proceed only with *n*-alkyl halides. New stable ylides have been uncovered, one of which is the dibasic ylide $(CH_3)_3SiC\ddot{P}(CH_3)_2P(CH_3)_3$.

Of the known isolable ylides with trimethylsilyl substitution,[2] trimethylsilylmethylenetrimethylphosphorane, $(CH_3)_3SiCHP(CH_3)_3$ (**1**), was chosen for initial investigation because of its good thermal stability and relatively convenient synthesis. It is believed that a detailed study of this class of ylides will contribute to the understanding of substituent effects upon structure and chemistry of ylides. Such a study would have the further practical value of determining

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[1] (a) National Defense and Education Act Fellow, 1963–1966; (b) author to whom inquiries should be addressed at the University of South Dakota.

[2] N. E. Miller, *Inorg. Chem.*, **4**, 1458 (1965).