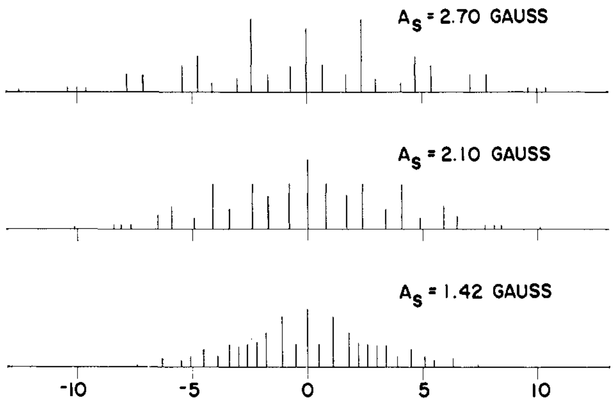

Figure 3.—Calculated proton hyperfine structure for $VO(H_2O)_5^{2+}$ in $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$ with H parallel to bisector of $V–O_8$ and $V–O_9$.

rotational relaxation[11] predicts that the residual width from this source should vary as T/η. The spin-rotational line width for $VO(H_2O)_5^{2+}$ given by the Kivelson theory is 1.8 gauss at 30° for $\tau_c = 2.5 \times 10^{-11}$ sec. McCain and Myers' residual width at 9070 Mc is 5.1 gauss. The greater observed residual width, particularly the temperature independent part of that width, is very likely due to isotropic proton hyperfine broadening, the dipolar part being averaged to zero by tumbling. By reconstructing the nine-line proton hyperfine spectrum, assuming each to have Lorentzian shape with a width of 9.4 gauss, it is found that the resulting line width is 12.7 gauss for $A_s = 2.2$ gauss, in fair agreement with the above interpretation of proton hyperfine splitting in vanadyl-doped $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$.

In view of the possibility that the VO^{2+} ion may be coordinated to five H_2O molecules in this Tutton salt, the spectrum for ten protons with the fifth H_2O molecule in the O_7 position and H parallel to the $V–O_9$ bond was also calculated, both with and without isotropic hyperfine coupling to the fifth H_2O molecule. The result was a severely broadened spectrum in both cases, which suggests that the fifth H_2O molecule is very likely absent. It is perhaps significant that Palma-Vittorelli, *et al.*,[12] have found that in $VOSO_4 \cdot 5H_2O$ there are only four H_2O molecules coordinated to the VO^{2+} ion, the sixth coordination position being filled by a sulfate oxygen atom.

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Photochemistry of Borazine. Preparation of B-Monoalkoxyborazines[1]

BY M. NADLER AND R. F. PORTER

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Recent studies[2] have shown that B-monohydroxyborazine is a product of the photochemical reaction of gaseous borazine and water vapor. This product was found to be unstable and could not be separated and isolated in macroscopic quantities. However, since it was shown that substitution of OH at a single boron atom could occur photochemically, further work was initiated to test the procedure for preparing monoalkoxyborazines by irradiating gaseous mixtures of borazine and alcohol. In this paper we describe results of the reaction using methanol, ethanol, and 2-propanol as reagents.

Experimental Section

The experimental apparatus has been described.[2] The reaction vessel holding a quartz immersion cell was modified by joining it to an infrared cell through a 2-in. opening of Pyrex. The optical path for the ultraviolet radiation extended from the quartz well into the infrared cell to a total length of about 84 mm. With this arrangement the reaction could be monitored by noting changes in the infrared spectrum with time. It was essential to terminate the reaction when the alcohol was completely consumed to prevent thermal reactions between borazine and alcohol from occurring when the mixture was condensed in the separation steps. The radiation source was a Hanovia medium-pressure Hg lamp, providing intense radiation at about 1850 A. Borazine absorbs strongly between about 1700 and 2000 A.[3] Methanol and ethanol absorb in this region[4] but not as strongly as borazine.

B-Monomethoxyborazine.—Borazine and methanol were added to the reaction vessel to provide initial pressures in the ranges 10–15 mm and 15–20 mm, respectively. A thermal reaction between borazine and methanol produces $B(OCH_3)_3$ and NH_3 in the gas phase. For this reason it was necessary to initiate the irradiation immediately after mixing the reagents. The irradiation time was usually between 20 and 25 min for the disappearance of methanol. The products were pumped through a series of traps at −35, −80, and −196° and hydrogen was removed. Unreacted borazine was recovered from the −80 and −196° traps. The −35° trap contained NH_3 and $B(OCH_3)_3$, identified from their infrared spectra,[5] and a new product which was not observed in the absence of irradiation. Ammonia and $B(OCH_3)_3$ could not readily be distilled from the mixture, since on liquefication they form an adduct[6] that has a volatility close to that of the unknown product. Separation was finally achieved by allowing the NH_3 to react with a small quantity of B_2H_6 to form a nonvolatile adduct and pumping off the $B(OCH_3)_3$ while the mixture was held at −35°. The product recovered from the −35° trap has a vapor pressure of about 6 mm at 25°. The best yield obtained was about 25% based on the amount of borazine reacted. A mass spectrum and infrared spectrum of the compound in the vapor phase are shown in Figures 1a and 2a. The high-mass cutoff in the mass spectrum is consistent with a molecular weight for $B_3N_3H_5OCH_3$. High-mass groupings corresponding to the hypothetical compounds $B_3N_3H_5(OCH_3)_2$ and $B_3N_3H_3(OCH_3)_3$ were not observed. A trace of $B(OCH_3)_3$ in the product was noted by the appearance of a small-ion intensity of $B(OCH_3)_2^+$. The infrared spectrum of the new compound shows frequencies expected for a borazine derivative, the B–H stretch (2520 cm^{-1}), the N–H stretch (3480 cm^{-1}), and ring stretching vibrations at 1490 and 1440 cm^{-1}. The presence of the latter two bands is probably a consequence of a splitting of an E′ ring stretching vibration in borazine by symmetry change due to substitution at one ring position. The strong band at about 1275 cm^{-1} may be assigned to a B–O stretch. Other bands

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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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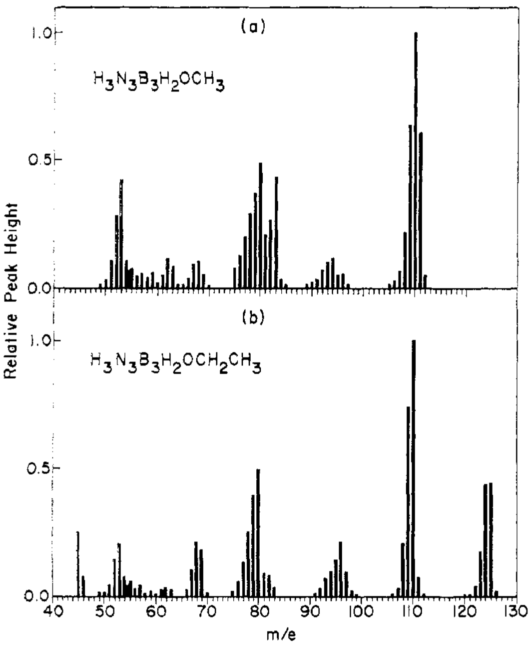

Figure 1.—(a) Portion of mass spectrum of B-monomethoxyborazine. (b) Portion of mass spectrum of B-monoethoxyborazine.

around 2900 and 1042 cm^{-1} are interpreted as C–H stretches in the CH_3 group and a C–O stretch, respectively.

B-Monoethoxyborazine.—Borazine–ethanol mixtures were studied by the same procedure described above. Initial pressure ratios of ethanol to borazine were between 1.5 and 2.0 with total pressure in the range 25–50 mm. Irradiation times for the disappearance of ethanol were about 25 min. Hydrogen, ammonia, and unreacted borazine were removed by pumping the products through a −45° trap. The contents of the trap, when warmed to room temperature, were $B(OC_2H_5)_3$ and a new product. Further separation was achieved by holding this mixture at −45° and pumping for about 50 min to remove the borate. Attempts to distil the mixture at higher temperatures led to incomplete separation. The purified product has a vapor pressure of about 5 mm at 25°. Mass and infrared spectra of the vapor are shown in Figures 1b and 2b, respectively. The high-mass cutoff indicates a molecular weight consistent with $B_3N_3H_5OC_2H_5$. Compounds of higher molecular weight were not observed in notable quantity. Comparison of the infrared spectrum for this compound with that for the monomethoxy derivative (Figure 2) shows the obvious relationship.

Discussion

Attempts were made to prepare pure B-monoisopropoxyborazine by irradiating mixtures of borazine and 2-propanol. Infrared spectra of the product clearly showed that a borazine derivative was present. However, attempts to separate the product from the borate by distillation were unsuccessful. It was noted that the relative concentration of borate obtained by repeated condensation and evaporation had increased. This indicated that the borazine derivative was undergoing decomposition in the liquid phase. The monomethoxy- and monoethoxyborazines appear to be relatively stable in the vapor phase but tend to decompose slowly if maintained in the liquid phase at ordinary temperatures. The appearance of large quantities of ammonia and alkyl borate in the photochemical reac-

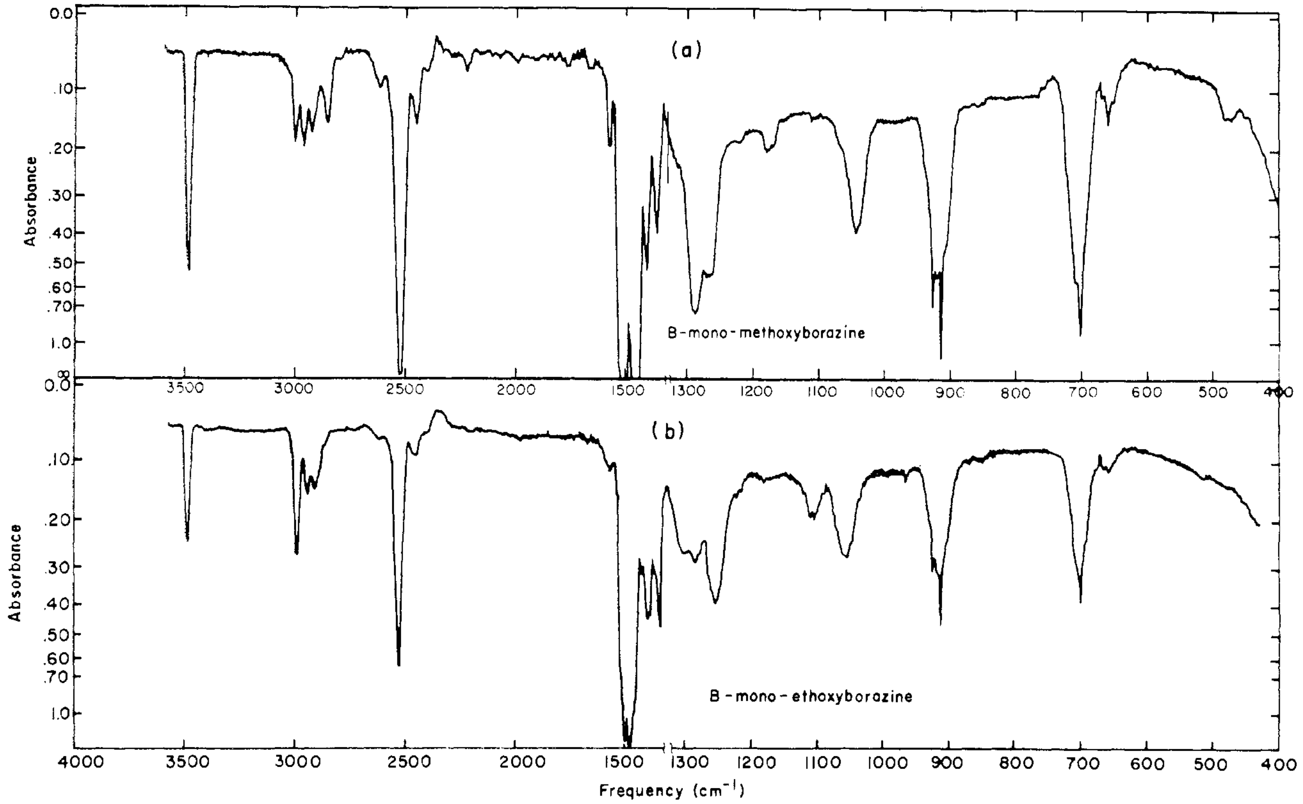

Figure 2.—(a) Infrared spectrum of B-monomethoxyborazine. Note: Part of the band at 1360 cm^{-1} could be due to an impurity of $B(OCH_3)_3$. (b) Infrared spectrum of B-monoethoxyborazine. Note: part of the band at 1350 cm^{-1} could be due to an impurity of $B(OC_2H_5)_3$.

tion is probably due to the formation of di- and trisubstituted borazines which decompose more readily than the monosubstituted derivative. The formation of polysubstituted borazines is indicated from the observation that alcohol was always consumed faster than borazine even when the initial alcohol to borazine ratio was greater than unity.

The most abundant ions produced by fragmentation in the mass spectrum of borazine are $B_3N_3H_5^+$, $B_3N_2H_2^+$, $B_2N_2H_3^+$, $B_2NH_2^+$, and BNH_3^+.[7] In the mass spectrum of B-monomethoxy- and B-monoethoxyborazine major ion fragments occur in positions corresponding to the base groups in borazine shifted to higher masses due to the substitution of an alkoxy group for an H atom. Ion fragments in the alkoxy derivatives also arise by splitting off segments of the side chain.

(7) American Petroleum Institute Research Project 44, Mass Spectral Data, Serial No. 1346.

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The Preparation of Methylsilyl Methyl Ether and a Base Strength Study of the Monomethoxy Derivatives of Methylsilane

BY J. T. WANG AND C. H. VAN DYKE

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There have been very few investigations reported in the literature which compare the carbon functional and silicon functional isomers of CH_3SiH_3.[1-3] In a recent report, Varma has described the preparation and properties of the first carbon-substituted methoxy derivative of CH_3SiH_3, *i.e.*, $CH_3OCH_2SiH_3$.[4] The present investigation was undertaken to prepare and characterize the silicon-substituted isomer, $CH_3OSiH_2CH_3$, and to investigate the Lewis basicities of the two compounds.

Experimental Section

General Methods.—A conventional Pyrex-glass high-vacuum system was used to manipulate all volatile materials. Mass spectra (at 70 v) were obtained by means of a Consolidated Electrodynamics mass spectrometer, Model 21-103C. Infrared absorption spectra were recorded with a Perkin-Elmer 137B infracord spectrophotometer on the gaseous phase at room temperature with the sample confined in a 10-cm cell fitted with KBr windows. Proton nuclear magnetic resonance data were obtained on a Varian Associates A-60 spectrometer operating at room temperature. The spectra were calibrated by the standard audiofrequency side-band interpolation technique. Gas chromatographic separations were performed on a slightly modified Varian-Aerograph Model A-90-P3 gas chromatograph equipped with a 20 ft × $^3/_8$ in aluminum column packed with 25% Carbowax 400 on Chromosorb W support (60–80 mesh). The unit was operated at a flow rate of 100 ml of He/min and at a column temperature of 30°. Infrared data on the hydrogen-bonding systems were obtained on a Beckman IR-9 spectrophotometer. Techniques employed for these measurements were identical with those previously reported.[5] Infrared spectra of the carbon tetrachloride–methanol (or phenol)–ether solutions (in an 0.08-mm cell) were taken for the silicon compounds studied after each base strength measurement in order to confirm their purity.

Materials.—$(CH_3SiH_2)_2S$ was prepared by passing CH_3SiH_2I over red HgS.[6] Analytical grade CH_3OH was dried over BaO and distilled in the vacuum line. $CH_3OCH_2SiH_3$ was prepared by allowing $ClCH_2OCH_3$ to react with solid $KSiH_3$.[4] The $CH_3OCH_2SiH_3$ could not be completely purified in the vacuum line and was purified by gas chromatographic techniques (retention time was 12.5 min; vapor pressure at −47.8° was found to be 16.8 mm; lit.,[4] 16.1 mm; confirmed by infrared spectrum[4]). $CH_3OCH_2CH_3$ was prepared by allowing $NaOCH_3$ to react with CH_3CH_2Br. The product was purified by vapor-phase chromatography (retention time, 9.5 min; identity and purity confirmed by its infrared spectrum[7]). Phenol was purified by sublimation *in vacuo*.

Synthesis of $CH_3OSiH_2CH_3$.—$(CH_3SiH_2)_2S$ (4.88 mmoles) and CH_3OH (9.28 mmoles) were combined and allowed to react at room temperature for approximately 5 min. No noncondensable material (at −196°) was produced in the reaction. Distillation of the products through a series of traps held at −112, −134, and −196° yielded pure $CH_3OSiH_2CH_3$ (*ca.* 8.7 mmoles, 94% yield; mol wt found 76.3, calcd 76.18) as a condensate in the −134° trap. H_2S (4.34 mmoles; mol wt found 33.8, calcd 34.08) collected in the −196° trap.

Anal.[8] Calcd for C_2H_8SiO: C, 31.54; H, 10.59; Si, 36.87. Found: C, 31.83; H, 10.57; Si, 36.78.

Infrared, Nmr, and Mass Spectra.—The absorption maxima in the infrared spectrum of $CH_3OSiH_2CH_3$ (pressure ~10 mm) are (in cm^{-1}): 2941 (w), 2809 (w), 2123 (s), {1261, 1245 (w)} d, 1188 (w), 1100 (s), 966 (sh), {942, 932 (vs)} d, 927 (sh), 864 (w), 758 (m).

The proton nuclear magnetic resonance spectrum (τ) of $CH_3OSiH_2CH_3$ (20% by volume in cyclohexane, τ(cyclohexane) 8.56) consisted of an unresolvable singlet at 6.58 (±0.01) (CH_3O protons), a 1:2:1 triplet at 9.77 (±0.01) (CH_3Si protons), and a 1:3:3:1 quartet at 5.44 (±0.01) (SiH_2 protons). Other data obtained from the spectrum: $J_{H-H'} = 3.0$ cps and $J_{^{29}Si-H} =$ 207.6 cps.

The mass spectrum of $CH_3OSiH_2CH_3$ is consistent with its proposed structure. Possible assignments of the major fragments observed are (*m/e*, ion, relative intensity): 76, C_2H_8SiO, 10.3; 75, C_2H_7SiO, 100.0; 61, CH_5SiO, 43.8; 59, CH_3SiO, 26.7; 45, CH_5Si and $HSiO$, 56.4; 31, CH_3O, 13.3; 15, CH_3, 13.4.

Vapor Pressure and Melting Point.—The vapor pressures of a freshly purified sample of $CH_3OSiH_2CH_3$ at a number of temperatures are listed in Table I. The inner surface of the manometer was pretreated with a separate sample of $CH_3OSiH_2CH_3$. Vapor pressures in the range −74.3 to −32.4° are given by

$$\log P_{\mathrm{mm}} = \frac{-1487.7}{t + 273.16} + 8.1956$$

which gives an extrapolated boiling point of +6.8°, a molar heat of vaporization of 6807.6 cal, and a Trouton constant of 24.3 cal deg^{-1} $mole^{-1}$.

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