TABLE I[a]

$$R^1SiOR^3 + (CF_3)_2CO \longrightarrow R^1SiOC(CF_3)_2OR^3$$

Compd	R	R^1	R^2	R^3	Yield, %	Bp, °C (mm)	$n^{25}D$	Formula	Calcd, % C	H	F	Si	Found, % C	H	F	Si
Va	CH_3	CH_3	OC_2H_5	C_2H_5	54.7	42 (0.35)	1.3483	$C_9H_{16}F_6O_3Si$	34.4	5.1	36.3	8.9	34.5	5.2	36.8	8.6
Vb	$CH=CH_2$	OC_2H_5	OC_2H_5	C_2H_5	57.9	100 (46.0)	1.3622	$C_{11}H_{18}F_6O_4Si$	37.1	5.1	32.0	7.9	37.3	5.2	32.0	7.8
Vc	C_6H_5	OC_2H_5	OC_2H_5	C_2H_5	88.3	92–93 (1.4)	1.4029	$C_{15}H_{20}F_6O_4Si$	44.3	5.0	28.1	6.9	44.3	5.1	28.1	7.2
Vd	OC_2H_5	OC_2H_5	OC_2H_5	C_2H_5	81.8	60 (2.0)	1.3520	$C_{11}H_{20}F_6O_5Si$	35.3	5.4	30.5	7.5	35.3	5.4	30.5	7.7
Ve	OC_2H_5	OC_2H_5	$(CH_2)_2COOC_2H_5$	C_2H_5	83.0	82–83 (0.35)	1.3872	$C_{14}H_{24}F_6O_6Si$			26.5	6.5			26.2	6.5
Vf	OCH_3	OCH_3	$(CH_2)_3OC(=O)C(CH_3)=CH_2$	CH_3	65.5	110–112 (1.5)	1.3933	$C_{13}H_{20}F_6O_6Si$			27.5	6.8			27.4	6.8
Vg	H	OC_2H_5	OC_2H_5	C_2H_5	73.2	27–28 (0.08)	1.3343	$C_9H_{16}F_6O_4Si$	32.7	4.9		8.5	33.0	5.1		8.5

[a] All products are colorless liquids. The infrared and proton nmr spectra of all compounds are in agreement with the proposed structures.

Compounds Va, Vb, and Ve are stable up to 170°, where the reaction is reversed and hexafluoroacetone is liberated. The new adducts are water insoluble and much less susceptible to hydrolysis than the parent alkoxysilanes.

The reaction of excess hexafluoroacetone with a monoalkoxysilane results in the insertion of only one molecular equivalent of hexafluoroacetone into the Si–O bond. This is different from the observed repeated insertion of many moles of chloral in the Sn–O bond of tributyltin methoxide.[5] As expected, hexafluoroacetone reacts with triethylsilane at 150° to give 1,1,1,3,3,3-hexafluoropropoxytriethylsilane (VI). With compounds such as triethoxysilane or methyl diethoxysilane, containing both an Si–H and $SiOC_2H_5$ group, we have found that the reaction occurs exclusively at the $SiOC_2H_5$ group, even when the second mole of hexafluoroacetone is introduced.

$$(C_2H_5)_3SiH + (CF_3)_2C{=}O \longrightarrow \underset{\text{VI}}{(C_2H_5)_3SiOC(CF_3)_2H}$$

$$(C_2H_5O)_3SiH + (CF_3)_2C{=}O \longrightarrow \underset{\text{Vg}}{(C_2H_5O)_2SiHOC(CF_3)_2OC_2H} \not\longrightarrow (C_2H_5O)_3SiOC(CF_3)_2H$$

$$2(CF_3)_2C{=}O \longrightarrow \underset{\text{VII}}{C_2H_5OSiH(OC(CF_3)_2OC_2H_5)_2}$$

The properties of these compounds are summarized in Table I and their structures have been established by their infrared, nmr, and mass spectra, which were completely consistent with the proposed structures.

In view of the known electrophilic nature of the carbonyl carbon atom of hexafluoroacetone, the most likely reaction sequence for the reaction between an alkoxysilane and hexafluoroacetone is

$$R_3SiOR^1 + (CF_3)_2C{=}O \longrightarrow R_3Si^{\oplus}{-}OR^1 \;\; {}^{\ominus}O{-}C(CF_3)_2 \longrightarrow R_3SiOC(CF_3)_2OR^1$$

Experimental Section[6]

Diethoxy 2-Ethoxy-1,1,1,3,3,3-hexafluoropropoxysilane (Vg) and Ethoxybis(2-ethoxy-1,1,1,3,3,3-hexafluoropropyl)silane (VII).—Triethoxysilane (65.5 g, 0.4 mole) and hexafluoroacetone (133.0 g, 0.8 mole) were heated in a stainless steel bomb at 150° for 6 hr at autogenous pressure. The crude product (173.0 g) fractionated to give 76.8 g (58.7%) of IIIg (see Table I) and 65.0 g (32.7%) of IV; bp 45° (0.5 mm), $n^{25}D$ 1.3418. The infrared spectra of both compounds contained a strong Si–H band at 2221 cm^{-1} and no OH peaks.

Anal. Calcd for $C_{12}H_{16}F_{12}O_5Si$: C, 29.0; H, 3.3; F, 45.9; Si, 5.7. Found: C, 29.4; H, 3.6; F, 45.7; Si, 5.7.

The mass spectrum was consistent with the proposed structure for IIIg and contained m/e = 450 and 427 (parent ion minus $C_2H_5^+$ and CF_3^+, respectively).

In another reaction, triethoxysilane (24.9 g, 0.15 mole) and hexafluoroacetone (100.0 g, 0.6 mole) were heated at 175° for 6 hr in a bomb. The only product isolated was VII, 58.8 g (73.2%). Both Vb and VII have a singlet in their nmr spectra at τ 5.55 which is attributed to the silane hydrogen atom.

Related reactions were conducted under similar conditions and are summarized in Table I.

(6) Boiling points are uncorrected. The silanes were obtained from Peninsular Chemical Research, Inc.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTH DAKOTA, VERMILLION, SOUTH DAKOTA

Thermal Properties of Dimethylaminomethylborane Cyclic Dimer

BY N. E. MILLER, M. D. MURPHY, AND D. L. REZNICEK

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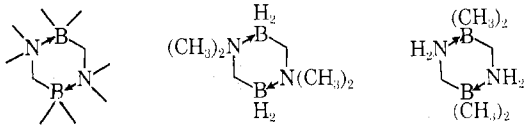
Two isomeric derivatives of the heterocyclic ring[1] system I (aminomethylborane dimer) have been reported recently.[2,3] Compound II, in which the nitrogen atoms are methylated (dimethylaminomethylborane dimer), apparently exists only as a dimer,[2] whereas compound III, in which the boron atoms are methylated (aminomethyldimethylborane) exists as an equilibrium mixture of monomer and polymers.[3] This difference in properties of the methylated derivatives is not unexpected and is readily explained by simple Lewis acid–base interactions. It is well-established that increasing methyl substitution increases base strength of amines (in the absence of steric hindrance) and conversely decreases acid strength of

(1) The ring system could be named 1,4-bisazonia-2,5-bisborylacyclohexane.

(2) N. E. Miller and E. L. Muetterties, *Inorg. Chem.*, **3**, 1196 (1964).

(3) R. Schaeffer and L. J. Todd, *J. Am. Chem. Soc.*, **87**, 488 (1965).

boranes.[4,5] Because boron and nitrogen atoms are of similar size, the steric effects of methyl substitution upon the stabilities of the boron–nitrogen bonds should not be very different for III than for II. Thus, the change of methyl groups from nitrogen to boron ought to cause the dative bonds in III to be considerably weaker than those in II.



I II III

As any dissociation of II might give rise to monomers that could exist as three-membered rings, it seemed desirable to study the vapor density of II as a function of temperature. It should be noted that aminomethyldimethylborane (monomer of III) is the only monomeric, potentially cyclic compound with a BCN sequence. The compound $t\text{-}C_4H_9N{=}C(CH_3)B(CH_3)_2$, earlier reported to be a monomer,[6] has subsequently been found to be a cyclic dimer.[7]

A better synthetic route to II was first sought because the yields from the reaction of sodium hydride and dihydrobis(trimethylamine)boron(1+) chloride were less than 5%. The mechanism for this reported reaction would appear to involve abstraction of a proton from the borane cation followed by a one- or two-step loss of trimethylamine from an intermediate ylide to produce the dimeric product.

$$[(CH_3)_3N]_2BH_2^+ \xrightarrow{-H^+} (CH_3)_3NBH_2N(CH_3)_2 \xrightarrow{-N(CH_3)_3} {}^1/_2\text{II}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad :CH_2$$

The poor yield probably results from the fact that both reactants are solids and there is limited contact between them. Attempts to increase the contact by better stirring or grinding were not successful.

Subsequently the reaction of the borane cation with a variety of proton-abstracting bases was surveyed. It was found that the reaction of butyllithium in hydrocarbon solvent gave yields of better than 30% (of recrystallized dimer), a substantial improvement over previous yields. A further advantage of this synthetic method is that the product is not contaminated with trimethylamine borane as is the product prepared using sodium hydride. This impurity is difficult to remove because its solubilities in organic solvents are similar to those of II.

A study of the vapor density of II showed that there was *no significant dissociation* into monomer at temperatures below 170°. Above 160° a slow, irreversible decomposition which produced noncondensable gas (less than 1% at 177° for 1 hr) became noticeable. This decomposition reaction precluded accurate measurements much above 170°. The vapor pressure and dissociation data are collected in Table I.

TABLE I
VAPOR PRESSURES AND DISSOCIATION MEASUREMENTS OF $[H_2BCH_2N(CH_3)_2]_2$

Temp, °C	Vapor pressure (gas pressure)[a]	Calcd[b] vapor pressure	Mol wt[e]
37.6	0.52	0.35	
50.5	1.13	1.06	
54.1	1.48	1.43	
60.3	2.31	2.34	
61.6	2.56	2.59	
66.5	3.38	3.93	
	3.72[c]		
72.5	5.44	5.89	
	5.78[c]		
78.4	8.44	8.97	
	9.18[c]		
84.5	13.20	13.80	
	14.11[c]		
91.6	(15.73)		141.6
100.8	(16.40)		141.8
121.2	(17.09)		141.6
126.5	(17.34)		141.6
135.0	(17.74)		141.5
144.9	(18.24)		141.2
160.1	(19.07)		140.4
177.2	(20.09)		138.9 (141.0)[d]

[a] Corrected for thermal expansion of mercury. [b] Calculated from the equation $\log p(\text{mm}) = -3780/T + 11.707$. [c] Second run after sample was heated to 109°. [d] Corrected for presence of 0.19 mm of noncondensable gas. [e] Calcd for $[H_2BCH_2N(CH_3)_2]_2$: 141.9.

Experimental Section

Molecular weight and vapor pressure measurements were carried out in a 311.5-ml glass tensimeter with attached 16-mm diameter mercury manometer.[8] The tensimeter was closed with a Delmar Urry needle stopcock[9] so that the sample in the tensimeter was in contact only with glass, mercury, Teflon,[10] and trace amounts of Viton A.[10] The tensimeter was heated in a thermostatic mineral oil bath of about 3-gal capacity. Temperature control and uniformity were within ±0.1°. The mercury manometer was viewed through plate glass ports connected to the bath with large O rings. A Gaertner traveling microscope was used to read the pressure. Reproducibility and accuracy of the measuring system were between 0.01 and 0.05 mm, the latter figure applying to measurements at very high temperature where visibility was somewhat impaired by temperature gradient swirls in the bath.

Dimethylaminomethylborane Cyclic Dimer.—Dihydrobis(trimethylamine)boron(1+) chloride was dried under vacuum for 5 hr at 60° before use. A slurry of 0.389 g (2.35 mmoles) of the dry salt in 1.0 ml of dry hexane was mixed with 1.0 ml of 2.35 *M* butyllithium in hexane and allowed to stir 8 hr at 60°. During the first half-hour the mixture changed appearance, going from a gummy semisolid to an easily-stirred slurry of light solid. The reaction vessel was cooled to room temperature, and hexane was removed under vacuum. The residue left after evaporation was heated slowly to about 120°, and the volatile material evolved was

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(9) Product of Delmar Scientific Laboratories, Inc., Maywood, Ill.

(10) Trademarks of the Du Pont Company for its fluorocarbon polymers.

passed through a U trap cooled to −50°. The crude product collected in the trap (130 mg, 79%) was recrystallized from ethanol to give 51 mg (31%) of II.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also supported in part by a grant from the research fund of the University of South Dakota. A gift of $H_2B[N(CH_3)_3]_2^+Cl^-$ from the Du Pont Company is also gratefully acknowledged.

Correspondence

The So-Called *cis–trans* Isomerism of Bis(isothiocyanato)tetra(pyridine)iron(II)[1]

Sir:

There is currently considerable interest in the preparation and properties of mixed-ligand complexes formed between transition metal ions, pyridine, and various anions.[2−5] This communication is concerned with the compound $Fe(py)_4(NCS)_2$. It was reported more than 50 years ago that this compound exists in two forms: a yellow form, prepared by Grossmann and Hunseler,[6] and a violet form, prepared by Spacu.[7,8] Both forms give violet solutions in chloroform, benzene, or toluene and yellow solutions in polar solvents such as pyridine, methanol, or ethanol.[7−9] The composition and structure of the violet form have been the subject of controversy for many years.[9−12] Recently, however, Spacu, *et al.*,[9] concluded from a series of physical measurements (dipole moments[13] and infrared and visible spectra) and chemical measurements (the reactions of the two forms with 2,2′-bipyridine and 1,10-phenanthroline) that the colors were due to *cis–trans* isomerism and that the yellow form was the *cis* isomer.

Our interest in these compounds arose from a desire to study *cis–trans* isomerism in high-spin iron(II) compounds *via* the Mössbauer technique in order to determine what influence this type of isomerism may have on the Mössbauer spectra. The only previous examples of true *cis–trans* isomers studied *via* the Mössbauer effect were several pairs of low-spin iron(II) compounds.[14] In these compounds the change in configuration results in a rather large and predictable change in the quadrupole splittings and in the chemical shifts of the Mössbauer patterns.

The yellow form was prepared by gradually adding 250 ml of a solution containing 9 g of hydrated ferrous perchlorate and a pinch of ascorbic acid to 400 ml of a solution containing 4 g of ammonium thiocyanate and 10 ml of pyridine. The yellow precipitate was filtered off and washed with a mixture consisting of 85% ethanol, 5% water, and 10% pyridine. The complex was recrystallized from a mixture consisting of 65% ethanol, 25% water, and 10% pyridine and dried *in vacuo* for 30 min. *Anal.* Calcd for $Fe(py)_4(NCS)_2$: Fe, 11.4; SCN^-, 23.8. Found: Fe, 11.4; SCN^-, 24.1.

The violet form was prepared by recrystallizing the yellow form from chloroform. According to Spacu, *et al.*,[9] this procedure is supposed to convert the *cis* isomer to the *trans* isomer. It was found instead that solutions prepared by dissolving the yellow form in air-free chloroform (or in air-free benzene) did not turn violet. The solutions did, however, turn violet gradually upon exposure to air, and very rapidly upon the addition of a few drops of a dilute solution of bromine in chloroform. Moreover, the violet color disappears upon the addition of ascorbic acid or upon bubbling hydrogen through the solution in the presence of a palladium catalyst and returns upon exposure to air. This suggests that the color change from yellow to violet results from the oxidation of the iron(II) complex and is not due to isomerization, a conclusion is substantial agreement with that previously reached by Rosenheim.[12] The iron(III) in the two forms was determined by dissolving the crystals in air-free 1 *M* $HClO_4$ and estimating the iron(III) in the resulting solutions polarographically. The yellow form contained 0.02% of iron(III) while the violet form contained 0.40% of iron(III). Violet crystals containing up to 1.6% of iron(III) have been obtained by dissolving the yellow form in oxygen-saturated chloroform containing a few drops of pyridine and allowing the excess solvent to evaporate over several hours. The color change produced by the addition of excess alcohol or pyridine to chloroform solutions of the violet form can be explained by the dissociation of the iron(III) complex in alcohol and by a combination of dissociation and reduction of the iron(III) complex in pyridine.

The conclusion that the yellow and violet forms are not geometrical or linkage isomers was confirmed by Mössbauer and X-ray studies. The Mössbauer spectra of the two forms are identical within the experimental

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.
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