hr. The mixture was filtered while hot and all components boiling below 160° were removed by distillation. Upon cooling, the residue formed a solid which was recrystallized from ethanol to mp 87-88°. The yield of product was 30.5 g (66%).

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41. Found: C, 72.77; H, 7.12.

3,3-Dimethylbutylamine was prepared by dissolving 84 g (0.36 mole) of N-(3,3-dimethylbutyl)phthalimide in 400 ml of hot ethanol and cooling the solution rapidly with stirring to form a fine suspension. To this suspension, 21 g (0.42 mole) of hydrazine hydrate and 200 ml of ethanol were added slowly. The addition of 300 ml of 6 *N* hydrochloric acid to the resulting slurry produced first a clear solution and then a granular precipitate. The precipitate was removed by filtration, and ethanol removed from the filtrate by distillation. The aqueous residue was adjusted to pH 12 with concentrated potassium hydroxide solution and extracted with two 400-ml portions of ether. The combined ether extracts were dried and distilled, yielding 10 g (22%) of amine, bp 115-116°.

Anal. Calcd for $C_6H_{15}N$: C, 71.22; H, 14.94; N, 13.84. Found: C, 71.25; H, 14.58; N, 13.89.

N-(3,3-Dimethylbutyl)formamide. A mixture of ethyl formate (7.8 g, 0.11 mole) and 3,3-dimethylbutylamine (9.5 g, 0.095 mole) was refluxed under a nitrogen atmosphere for 3 hr. The product, isolated as a viscous liquid in 80% yield by distillation directly from the reaction mixture, had bp 76-78° (0.4 mm) and was used without further purification.

3,3-Dimethylbutyldimethylamine. A mixture of 8.5 ml of 37% aqueous formaldehyde, 8.4 g of formic acid, and 3.8 g of 3,3-dimethylbutylamine was refluxed for 48 hr. The reaction mixture was cooled, treated with 14 ml of 4 *N* HCl, and evaporated to dryness under reduced pressure. The residue was dissolved in 30 ml of water, extracted once with ether, made strongly basic, and extracted twice with ether. The ether extracts from the basic solution were dried (KOH), concentrated, and distilled yielding ~1 g of product, bp 123-124°.

Anal. Calcd for $C_8H_{19}N$: C, 74.35; H, 14.82; N, 10.84. Found: C, 74.02; H, 14.53; N, 10.48.

3,3-Dimethylbutyl cyanide was prepared by refluxing a solution of 21.6 g of 3,3-dimethylbutyl chloride and 35.2 g of potassium cyanide in 400 ml of ethanol for 1 week. The reaction mixture was cooled, poured into 1 l. of water, and extracted with 500 ml of diethyl ether. The ether layer was extracted with three 500-ml portions of water, dried ($MgSO_4$), concentrated, and distilled, yielding 5.8 g (30%) of nitrile as a colorless liquid, bp 165-170°; infrared absorption (CCl_4) at 2250 cm^{-1} ($C\equiv N$).

Anal. Calcd. for $C_7H_{13}N$: C, 75.62; H, 11.78; N, 12.60. Found: C, 75.76; H, 12.00; N, 12.80.

3,3-Dimethylbutyl fluoride was prepared by heating a mixture of 30.1 g of 3,3-dimethylbutyl chloride, 100 g of anhydrous potassium fluoride, and 150 ml of ethylene glycol at 100° in a hood.[46] After 6 days, the components of the reaction mixture boiling below 100° were separated by distillation, dried ($CaSO_4$), and redistilled. The product (bp 75-77°, lit.[47] bp 75-77°) obtained using this procedure was 70% pure as estimated from its nmr spectrum; however, the spectra of the impurities did not interfere with the spectrum of the fluoride, and no further purification was attempted.

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[46] See F. L. M. Pattison and J. J. Norman, *J. Am. Chem. Soc.*, **79**, 231 (1957), for a discussion of the toxicity of monofluoroalkanes.

[47] C. B. Linn and L. Schmerling, U. S. Patent 2,451,843 (1948); *Chem. Abstr.*, **43**, 2628 (1949).

Synthesis of Silacyclobutane and Some Related Compounds

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Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received August 11, 1966*

Abstract: The first preparation of silacyclobutane, its 1,1-difluoro derivative, and several other silicon compounds is reported. Infrared spectra of several silacyclobutanes demonstrate that these four-membered rings can be characterized by three absorption peaks in the 950-850-cm^{-1} range and by two near 1130 and 1180 cm^{-1}. The nmr spectra of these ring compounds are compared to other four-membered ring species. A mass spectrum of silacyclobutane is compared to that of silacyclopentane.

For the purpose of continuing a study[2] of the ring-puckering vibration in four-membered ring compounds, the preparation of several silicon compounds, including silacyclobutane and its 1,1-d_2 and 1,1-difluoro derivatives, has been accomplished.

The reaction scheme employed is shown in Scheme I. Preparation of 1,1-dichloro-1-silacyclobutane,[3,4] 3-chloropropyltrichlorosilane,[5] and 3-bromopropyltrichlorosilane[3] has been previously described, but that of the other five compounds is reported for the first time. Improvements have been made in the procedures for the dichloro ring compound and the bromopropyl species. The former, which can be very useful for the preparation of other silacyclobutanes, can be made in 70% yield from the latter.

As described previously,[5] the 3-halopropyltrichlorosilanes were prepared by addition of trichlorosilane to an allyl halide with chloroplatinic acid as catalyst. The fluorosilanes were then prepared by means of antimony trifluoride reagent. Antimony trifluoride is known to be a good fluorinating agent for silyl chlorides.[6,7]

The 1,1-dichloro-1-silacyclobutane can be prepared from $Cl_3SiCH_2CH_2CH_2X$ where X = Cl but forms much more readily when X = Br. The cyclic difluoro compound could not be prepared from 3-chloropropyltrifluorosilane in diethyl ether but formed readily from the corresponding bromide in tetrahydrofuran (THF) or ether. The chloropropyl species does react with magnesium powder very slowly in THF, however. 1,1-Difluoro-1-silacyclobutane can also be prepared

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[1] National Science Foundation Graduate Fellow, 1964-1966.

[2] See, for example, A. Danti, W. J. Lafferty, and R. C. Lord, *J. Chem. Phys.*, 33, 294 (1960); J. R. Durig and R. C. Lord, *ibid.*, **45**, 61 (1966).

[3] P. G. Campbell, Ph.D. Thesis, Pennsylvania State University, 1957.

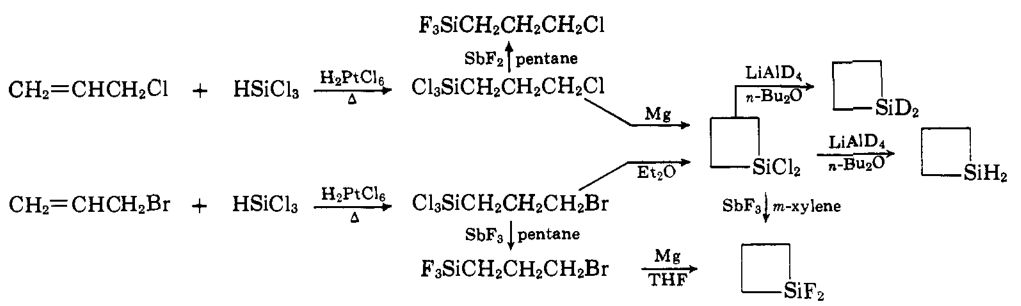
[4] V. M. Vdovin, N. S. Nametkin, and P. L. Grinberg, *Dokl. Akad. Nauk SSSR*, **150**, 799 (1963).

[5] J. W. Ryan, G. K. Menzie, and J. L. Speier, *J. Am. Chem. Soc.*, **82**, 3601 (1960).

[6] R. Müller, S. Reichel, and C. Dathe, *Ber.*, **97**, 1673 (1964).

[7] R. Müller and C. Dathe, *Z. Anorg. Allgem. Chem.*, 330, 195 (1964).

Scheme I



from the dichloro ring species, but the yield is lower (46%) because of the formation of side products resulting from ring cleavage by the antimony trifluoride.

The parent silacyclobutane, $(CH_2)_3SiH_2$, was prepared by reducing the dichloro derivative in *n*-butyl ether at 0°. The ring was not cleaved as might be expected from the work of Gilman and Atwell,[8] who find ring cleavage of silacyclobutanes by lithium aluminum hydride. 1-Silacyclobutane-1,1-d_2 is formed similarly by reduction with lithium aluminum deuteride.

Experimental Section

Materials. Commerically available pentane and *m*-xylene were dried over anhydrous magnesium perchlorate and distilled through a spinning-band column prior to use. *n*-Dibutyl ether was dried over lithium aluminum hydride and distilled. All other chemicals were used as obtained commercially.

Preparation of Compounds. All the halides and hydrides of silicon dealt with here are somewhat air sensitive as they are hydrolyzed by water. Thus a steady stream of dried nitrogen was used to flush the reaction apparatus in each experiment. In most cases, a three-necked flask equipped with a dropping funnel, reflux condenser, and a mechanical or magnetic stirrer was used. The compounds obtained are all clear liquids and stable enough to be stored in glass bottles for extended periods. Only $(CH_2)_3SiF_2$ and $F_3SiCH_2CH_2CH_2Br$ appear to undergo slow decomposition.

A. **3-Chloropropyltrichlorosilane.** This was prepared in the manner previously described.[5] Reaction of 432 g (3.2 moles) of trichlorosilane and 253 g (3.3 moles) of allyl chloride produced 447 g (2.1 moles) of product, bp 180–181°, yield 66%.

B. **3-Bromopropyltrichlorosilane.** Allyl bromide (340 g, 2.8 moles) to which had been added chloroplatinic acid (~10 mg) was heated to reflux in a flask equipped with a reflux condenser, dropping funnel, and thermometer. No stirring was used. To this was added trichlorosilane (390 g, 2.9 moles) at a rate slow enough that the temperature of the mixture did not fall below 65°. The addition took 24 hr, and the reaction mixture was refluxed for an additional 48 hr. A cold trap connected to the condenser collected propylene (a side product) and trichlorosilane which had escaped. The former was expelled by warming to room temperature, and the silane was added again through the dropping funnel. Distillation produced 430.7 g (1.7 moles) of product, bp 202–204°; 80° (14 mm), yield 60%.

Anal. Calcd for $C_3H_6BrCl_3Si$: C, 14.06, H, 2.34. Found: C, 14.20; H, 2.34.

Also recovered was 95 g of starting products; bromotrichlorosilane, bp 80–81°, 42 g; and propyltrichlorosilane, bp 121–124°, 15 g.

C. **1,1 Dichloro-1-silacyclobutane 1.** To 40 g (1.7 g-atoms) of magnesium powder in 500 ml of ethyl ether was added dropwise over a 3-hr period 3-chloropropyltrichlorosilane (200 g, 0.94 mole) in 300 ml of ether. Heating and rapid stirring of the mixture was maintained for 72 hr. At this point the flask was allowed to cool, and the white magnesium chloride and excess magnesium powder were filtered off through a large sintered glass filter. The residue was washed several times with more ether and the filtrate collected and distilled. After discarding the ether distillate, 80.0 g (0.57 mole) of product was obtained, bp 113–115°, yield 61%.

2. In like manner 443.5 g (1.7 moles) of 3-bromotrichlorosilane in 400 ml of ether was added to 75 g (3.1 g-atoms) of magnesium powder in 800 ml of ether over a 3-hr period. The total reaction was completed in 24 hr. After filtration and distillation, 170.2 g (1.2 moles) of product was obtained, yield 70%. In contrast to the reaction of $Cl_3SiCH_2CH_2CH_2Cl$ with magnesium in which no side products are observed, several grams of a yellow solid were produced when $Cl_3SiCH_2CH_2CH_2Br$ was reacted. This presumably resulted from intermolecular rather than intramolecular interaction and could be minimized by using dilute solutions.

D. **3-Chloropropyltrifluorosilane.** 3-Chloropropyltrichlorosilane (154 g, 0.73 mole) in 150 ml of pentane was added dropwise to 132 g (0.74 mole) of antimony trifluoride in 100 ml of pentane over a 3-hr period. Rapid stirring and cooling with an ice–water bath were used. After the addition was complete, cooling was discontinued but the mixture was stirred for 15 hr more. The resulting reddish liquid was then decanted off from the remaining solid and distilled. After removal of the pentane, 77 g (0.47 mole) of product was obtained, bp 94–96°, yield 65%.

Anal. Calcd for $C_3H_6ClF_3Si$: C, 22.15; H, 3.72; F, 35.05. Found: C, 22.41; H, 3.85; F, 34.70.

E. **3-Bromopropyltrifluorosilane.** As in the previous reaction, 321 g (1.25 moles) of 3-bromopropyltrichlorosilane and 224 g (1.25 moles of antimony trifluoride were reacted using a total of 400 ml of pentane. The product (182.8 g, 0.88 mole) obtained had bp 112.5–114°, yield 71%.

Anal. Calcd for $C_3H_6BrF_3Si$: C, 17.40; H, 2.92; F, 27.52. Found: C, 17.84; H, 3.31; F, 28.05.

F. **1,1-Difluoro-1-silacyclobutane. 1.** To 17 g (1.1 g-atoms) of magnesium powder in 150 ml of THF was added dropwise 148 g (0.7 mole) of 3-bromopropyltrifluorosilane which had been mixed with 150 ml of THF. Magnetic stirring was used, and the mixture was cooled with an ice–water bath. The addition was complete after 2.5 hr but stirring was continued for 20 hr more. The mixture was initially distilled through an 18-in. length fritted glass column and the fraction, bp 35–54°, was collected. This portion was then distilled over a platinum–gold spinning-band column and the product collected, bp 36.5–37.5°, 54 g (0.5 mole), yield 70%.

Anal. Calcd for $C_3H_6F_2Si$: C, 33.31; H, 5.59; F, 35.13. Found: C, 33.42; H, 5.44; F, 34.95.

2. 1,1 Dichloro-1-silacyclobutane (70.7 g, 0.5 mole) in 50 ml of *m*-xylene was added dropwise to antimony trifluoride (90.8 g, 0.5 mole) in 50 ml of *m*-xylene. Magnetic stirring and cooling with an ice–water bath were used. After 20 hr the reddish mixture was distilled to obtain 25.1 g (0.23 mole) of product, bp 36–38°, yield 46%. Both lower and higher boiling side products were also collected but were not identified.

3. Reaction of 3-chloropropyltrifluorosilane in ethyl ether with magnesium powder did not proceed despite addition of iodine and heating. When THF was used as solvent, the reaction proceeded very slowly, the mixture taking on a black color. An infrared spectrum of the distillate (bp 30–60°) obtained after 4 days indicated that a very small amount of 1,1-difluoro-1-silacyclobutane had been formed.

G. **Silacyclobutane.** 1,1-Dichloro-1-silacyclobutane (50.8 g, 0.36 mole) in 30 ml of *n*-butyl ether was added dropwise to 7.0 g (0.185 mole) of lithium aluminum hydride in 100 ml of the ether. A magnetic stirrer and a Dry Ice–acetone condenser were used. The addition was completed over a 5-hr period and the reaction flask maintained between −5 and +5° with a salt–ice–water bath. The addition was sufficiently slow that the exothermic reaction did not cause a significant temperature increase in the flask. After 10 hr the reaction was allowed to proceed at room temperature and after 24 hr the mixture was distilled. The pot was heated to only 120° to avoid decomposition of lithium aluminum hydride. The product (15.5 g, 0.215 mole) obtained had bp 45–46°, yield 60%.

Anal. Calcd for C_3H_8Si: C, 49.91; H, 11.17. Found: C, 49.87; H, 11.24.

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(8) H. Gilman and W. H. Atwell, *J. Am. Chem. Soc.*, **86**, 2687 (1964).

H. **Silacyclobutane-1,1-d_2.** This was prepared by the same method as the dihydride. Reaction of 43.5 g (0.31 mole) of 1,1-dichloro-1-silacyclobutane, mixed with 30 ml of *n*-butyl ether, with 6.0 g (0.15 mole) of lithium aluminum deuteride in 80 ml of the ether gave 12.8 g (0.173 mole) of $(CH_2)_3SiD_2$, bp 45.5–46.5°, yield 58%. Intensity measurements in the Raman spectrum indicated that the compound had less than 1 atom % impurity of the ^1H species.

Analyses. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.; by Stephen Nagy, Massachusetts Institute of Technology Microanalytical Laboratory; and at the Central Research Department, E. I. du Pont de Nemours & Co., through the courtesy of Dr. W. E. Mochel.

Instrumental Measurements. Infrared spectra of the compounds were obtained in the gas phase in 10-cm cells equipped with KBr windows. A Perkin-Elmer 521 spectrophotometer was used.

Raman spectra of the pure liquids in 7-mm tubes were recorded on a Cary 81 instrument.

The nmr spectra of the compounds as pure liquids or in carbon disulfide solution were recorded on a Varian A-60 analytic spectrometer, using tetramethylsilane (TMS) as an internal standard.

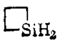
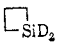
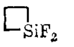
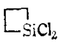
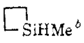
Mass spectra of silacyclobutane and silacyclobutane-1,1-d_2 were obtained using either a single focusing mass spectrometer (CEC 21-103C) through the courtesy of Mr. W. R. Wasdyke and Professor K. Biemann or on a Hitachi Perkin-Elmer RMU-6D instrument through the courtesy of Mr. Lee Mitchell. Ionizing voltages of 70, 15, 10, and 8.2 v were used.

Results and Discussion

There is no doubt that the structures of the compounds prepared are those that have been suggested. 1,1-Difluoro-1-silacyclobutane was prepared by two routes, both of which should give the ring structure. Preparation of silacyclobutane-1,1-d_2 from the 1,1-dichloro compound confirmed the ring structure for the parent silane. That only Si–D and no C–D bonds were formed in the reaction, and thus that no ring cleavage occurred, was demonstrated by infrared spectra. Moreover, the spectrum of *n*-propylsilane, which would result from ring cleavage, has been reported[9] and differs greatly from that of silacyclobutane. Nmr spectra of the 1,1-d_2 ring showed the expected triplet and quintuplet with an intensity ratio 2:1. In addition, the analyses of all compounds are in general agreement with the theoretical compositions.

Vibrational Spectra. A study of the infrared and Raman spectra of several silacyclobutanes indicated that many of the peaks are found consistently in all spectra and can be considered as characteristic of the ring species. Table I lists some of the infrared absorption peaks of the silacyclobutanes prepared in this work and also of 1-methyl-1-silacyclobutane.[10] The low-resolution spectra of the silacyclobutanes prepared by Campbell show no inconsistencies with these characteristic bands.[3]

Table I. Characteristic Absorption Peaks[a] in Silacyclobutanes

 SiH_2	 SiD_2	 SiF_2	 $SiCl_2$	 SiHMe[b]	Raman polariz[c]	Approx vibration type
927 s	925 m	913 m	914 m	920 s	D	Ring mode
910 s	902 m	934 vs	893 m	~910 s	P	Ring mode
877 s	867 m	873 s	857 s	870 s	P	Ring mode
1127 s	1128 ms	1135 vs	1130 ms	1118 ms	P	CH_2 mode
1191 w	1193 w	1185 mw	1183 w	1183 w	D	CH_2 mode

[a] Reported as infrared gas-phase values in cm^{-1}: s, strong; m, medium; w, weak; v, very. [b] Solid spectrum at 77°K; Raman spectrum not recorded. [c] D, depolarized; P, polarized.

Absorption bands near 1130, 1180, and 920 cm^{-1} have been observed previously in a series of such ring compounds.[11] The first of these peaks especially is quite strong and in a region where there is generally little interference from other absorption bands.

There are six ring vibrations expected for a four-membered ring, one of which, the ring puckering, has a frequency below 200 cm^{-1}.[2] Three of the ring modes in these silicon compounds are strong in the infrared and occur between 950 and 850 cm^{-1}. The other two are more variable from compound to compound and thus not as useful for characterizing the silacyclobutanes.

The other two absorptions listed in Table I result from vibrations involving methylene groups in the ring. Although peaks at other frequencies due to the CH_2 wag or twist have been observed to be remarkably consistent from one silacyclobutane to another, they are generally too weak to be useful for characterization of these compounds.

In 1,1-dichloro-1-silacyclobutane, the symmetric $SiCl_2$ stretching frequency falls at the unusually low value of 375 cm^{-1}. This may be due to the fact that the other two bonds to silicon are part of a highly strained ring. In silacyclobutane, however, the SiH_2 stretching frequencies have values in the expected range near 2140 cm^{-1}.

Infrared spectra of $F_3SiCH_2CH_2CH_2Cl$ and $F_3SiCH_2CH_2CH_2Br$ are almost identical, as expected, except for the difference in C–Cl and C–Br absorption peaks which occur at 775 and 580 cm^{-1}, respectively.

Nmr Spectra. The nmr data of the silicon ring compounds are compared to some other four-membered rings in Table II. The effect of the electropositive silicon in the ring is immediately evident from the small

Table II. Nmr Spectra[a] of Four-Membered Rings

Compound	δH_α	δH_β	$J_{H\alpha H\beta}$, cps	Comment
$(CH_2)_3SiH_2$	−1.1	−2.3	8	$\delta H_{Si} = -4.7$; $J_{H\alpha HSi} = 3.5$
$(CH_2)_3SiF_2$	−1.7	~−1.7	4	Overlapping resonance peaks
$(CH_2)_3SiCl_2$	−2.1	~−2.1	3	Overlapping resonance peaks
$(CH_2)_3CH_2$	−1.96		. . .	*c*
$(CH_2)_3CF_2$	−2.2	−1.4	7	*d*
$(CH_2)_3C{=}CH_2$	−2.7	−1.9	8	*e*
$(CH_2)_3C{=}O$	−3.0	−2.0	8	*c*
$(CH_2)_3NH$	−2.9	−3.6	Na[b]	*f*
$(CH_2)_3S$	−3.3	−3.3	Na[b]	*f*
$(CH_2)_3O$	−4.7	−2.7	8	*g*

[a] Chemical shift in ppm relative to TMS. [b] Na = not available. [c] K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961). [d] C. A. Tolman and R. C. Lord, unpublished results. [e] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "Nmr Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectrum 109. [f] H. S. Gutowsky, R. L. Rutledge, M. Tamres, and S. Searles, *J. Am. Chem. Soc.*, **76**, 4242 (1954). [g] Footnote *e*, this table, spectrum 33.

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(9) H. E. Opitz, J. S. Peake, and W. H. Nebergall, *J. Am. Chem. Soc.*, **78**, 292 (1956).

(10) Courtesy of Mr. R. Damrauer and Professor D. Seyferth.

(11) N. S. Nametkin, V. D. Oppengeim, V. I. Zav'yalov, K. S. Puschchevaya, and V. M. Vdovin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1547 (1965).

negative shift of the α protons in $(CH_2)_3SiH_2$. This effect is reduced when the silicon hydrogens are replaced by halogens; in this sense, the $SiCl_2$ group appears less electropositive than SiF_2.

Table III. Mass Spectra[a] of Cyclic Silanes

Ion	$(CH_2)_4$-SiH_2[b]	$(CH_2)_3$-SiH_2[d]
$M + 1$	...	1.3
M	9.4	12.3
$M - 1$	3.0	7.1
$M - 2$	1.5	8.1
$M - CH_2 + 1$	...	2.1
$M - CH_3$	0.9	4.3
$M - CH_2 - 2$	...	1.4[e]
$M - CH_2 - 3$	...	4.1[e]
$M - CH_2 - 5$	...	2.6[e]
$M - 2CH_2 + 1$	...	7.0
$M - 28$	48.3	13.6
$M - 29$	4.8	10.8
$M - 30$	~3[c]	6.9
$M - 31$	4.4	3.3
$M - 33$	~2[c]	4.0[e]
SiH_3^+	...	5.1
SiH_2^+	...	0.6
SiH^+	4.5	4.3
Si^+	3.1	14.5
$M - CH_2SiH_2$	1.4	

[a] Spectra at 70-v ionizing voltage; intensities given as per cent of total intensity above m/e 40. [b] Reference 12. [c] Estimated from given spectra. [d] Corrected to spectra expected for ^{28}Si, ^{12}C, ^{1}H. [e] Peaks that have essentially vanished in spectra at 8.2-v ionization potential.

Mass Spectra. Mass spectra of both $(CH_2)_3SiH_2$ and $(CH_2)_3SiD_2$ were obtained. The important ions observed at an ionizing potential of 70 v for the nondeuterated species are compared in Table III to those found for $(CH_2)_4SiH_2$ as reported by Duffield and coworkers.[12] Spectra were also obtained at lower voltages. The percentage contribution of the molecular ion to the spectrum above m/e of 40 increased from 12.3% at 70 v to 20.9 (15), 29.5 (10), and 36.0% (8.2 v). In the spectrum at 70 v, over one-half of all intensity is distributed between 31 and 25 m/e; at 8.2 v this is only about 10%.

In general, the spectrum of the four-membered ring silane is richer in the number of peaks observed than that of silacyclopentane. However, some of these additional ions in the silacyclobutane spectrum were not observed at lower ionizing potentials. Both spectra have strong molecular ion peaks; both have a large intensity at $M - 28$, implying a loss of ethylene. Both spectra have $M - 1$ and $M - 2$ ions resulting primarily from Si–H bond cleavage. The 1,1-d_2 analogs of each give spectra with peaks corresponding to loss of one or two deuterium atoms.

A significant difference in the spectra of the two silanes is that in silacyclobutane peaks were observed at $M - nCH_2 + 1$ ($n = 1$–3). Thus, in the four-membered ring, Si–C bond cleavage seems to be accompanied by hydrogen transfer; this process appears unimportant in silacyclopentane fragmentation.

Acknowledgments. Advice from Professors R. C. Lord and D. Seyferth is greatly appreciated. This work has been supported in part by National Science Foundation Grant GP-2111.

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[12] A. M. Duffield, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, 87, 2920 (1965).

Nitrosative Cleavage of Tertiary Amines[1]

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Abstract: Tertiary amines react with aqueous nitrous acid, contrary to common belief, and undergo dealkylation to form a carbonyl compound, a secondary nitrosamine, and nitrous oxide. The ratios of products from *meta*- or *para*-monosubstituted tribenzylamines are affected but little by the electronic influence of the substituents, and obey the Hammett equation with a small negative value of the reaction constant. Susceptibility of an amine to nitrosative cleavage is markedly reduced by base-weakening effects, and is prevented altogether by quaternization. Quinuclidine, in which the tertiary nitrogen is at a bridgehead, is inert. α substituents in tribenzylamines and benzyldiethylamines strongly shift dealkylation to the unsubstituted groups, regardless of the electronic character of the α substituent (*e.g.*, alkyl or carboethoxy). Tribenzylamine-α,α-d_2 shows a deuterium isotope effect $k_H/k_D = 3.78$. The facts are correlated by a mechanism (eq 4–6) involving formation of an N-nitrosoammonium ion and *cis* elimination of nitroxyl to form a ternary immonium ion, $R_2N^+{=}CR_2$, which then undergoes hydrolysis and further nitrosation. Nitrosyl fluoroborate and tribenzylamine form an unstable 1:1 addition compound at −45°; above −20°, this substance decomposes to form tribenzylammonium and N,N-dibenzylbenzaldimmonium fluoroborates.

The belief that tertiary amines do not react with aqueous nitrous acid is probably the most persistent myth in organic chemistry, notwithstanding a veritable parade of experimental refutations extending over an even century. Scarcely a textbook currently in print suggests that aught beyond salt formation occurs, and the assumed inertness of tertiary amines has been made the basis of a test for distinguishing them from primary and secondary amines.

In actual fact, Guether[2] reported correctly in 1864

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[1] Presented at the XIXth I.U.P.A.C. Congress, London, 1963; from the doctoral dissertation of R. N. L.

[2] B. Guether, *Arch. Pharm.*, [2] 123, 200 (1864).