the brosylates with 1.24 (5.85 mmol) of $C_5H_5(CO)_2Fe^-K^+$ in 100 mL of THF. Pure **8a,b**, 1.32 g (61% yield), was obtained after separation by column chromatography. $^1H$ NMR of **8a,b** in $C_6D_6$ shows four broad peaks corresponding to $H_A$, $H_B$, $H_C$, and $H_D$ in equal intensity (**8a**:**8b** = 1:1). The $\{^1H,^1H\}$ COSY 2D NMR spectrum shown in Figure 2 demonstrated that **8a,b** were stereospecifically labeled as expected. $^{13}C$ NMR spectra of **8a,b** showed that $C_\alpha$ and $C_\beta$ were deuterium-labeled.[14] IR ($CH_2Cl_2$) $\nu_{CO}$ 2001 and 1943 cm$^{-1}$; $^1H$ NMR ($C_6D_6$, 25 °C, decoupling at 4.05 ppm) **8b**, $\delta$ 2.18 ppm (d, $J(H_AH_D)$ = 12.7 Hz, FeCHDC$H_A$D), 1.39 (d, $J(H_DH_A)$ = 12.6 Hz, FeC$H_D$–); **8a**, $\delta$ 1.99 ppm (d, $J(H_BH_C)$ = 12.9 Hz, FeCHDC$H_B$D), 1.76 (d, $J(H_CH_B)$ = 12.6 Hz, FeC$H_C$D–); $^{13}C$ NMR ($C_6D_6$, 25 °C) **8a,b**, $\delta$ −1.87 ppm (t, $J_{DC}$ = 20.5 Hz, Fe*C*HD–), −1.79 ppm (t, $J_{DC}$ = 20.5 Hz, Fe*C*HD–), 46.67 (t, $J_{DC}$ = 19.4 Hz, FeCHD*C*HD–), 46.71 (t, $J_{DC}$ = 19.2 Hz, FeCHD*C*HD–). Other signals are the same as those of **4**.

**Generation of Phenylcyclopropane from $C_5H_5(CO)_2FeCH_2CH_2CH(OCH_3)C_6H_5$, 4.** Trimethylsilyl triflate (0.12 mL, 0.67 mmol), was added to a methylene chloride solution (10 mL, −78 °C) containing 0.20 g (0.61 mmol) of compound **4** and 10 μl (0.07 mmol) of triethylamine. The solution was allowed to warm to 25 °C overnight. The deep red solution was extracted with 50 mL of a saturated aqueous sodium bicarbonate solution and 75 mL of isopentane. The isopentane layer was dried over anhydrous potassium carbonate, and most of the isopentane was distilled off. Nonane (20 μL) was added to the residue. Phenylcyclopropane was isolated by preparative GC, and the yield (75%) was determined by using nonane as an internal standard: $^1H$ NMR ($CDCl_3$, 25 °C) 1.88 ppm ($H_A$, tt, $J(H_AH_B) = J(H_AH_{B'})$ = 5.2 Hz, $J(H_AH_C) = J(H_AH_{C'})$ = 7.9 Hz), 0.68 ppm ($H_B$, $H_{B'}$ (cis to phenyl), ddd, $J(H_BH_C, H_{B'}H_{C'})$ = −4.6 Hz, $J(H_BH_{C'}, H_{B'}H_C)$ = 6.4 Hz, $J(H_AH_B, H_AH_{B'})$ = 5.2 Hz), 0.94 ppm ($H_C$, $H_{C'}$ (trans to phenyl), ddd, $J(H_CH_A, H_{C'}H_A)$ = 8.4z, $J(H_BH_{C'}, H_{B'}H_C)$ = 6.4 Hz, $J(H_BH_C, H_{B'}H_{C'})$ = 4.5 Hz), 7.24 ppm ($H_m$(−Ph), dd, $J(H_mH_p)$ = 7.2 Hz, $J(H_mH_o)$ = 7.6 Hz), 7.13 ppm ($H_p$(−Ph), t, $J(H_mH_p)$ = 7.2 Hz), 7.06 ppm ($H_o$(−Ph), d, $J(H_mH_o)$ = 7.6 Hz). Experimental $^1H$ NMR data were confirmed by simulation.[14]

**Generation of *cis*-2,*cis*-3-Dideutero and *trans*-2,*trans*-3-Dideuterio-*r*-1-Phenylcyclopropanes from *threo*-$d_2$-$C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$, 7a,b.** As in the ionization of unlabeled **4**, 0.15 mL (0.78 mmol) of trimethylsilyl triflate was added to 10 mL of a methylene chloride solution (−78 °C) containing 0.26 g (0.79 mmol) of **7a,b** and 11 mL (0.08 mmol) of triethylamine. Workup was carried out as previously described. Nonane (20 μL) was added to the residue. The dideuteriophenylcyclopropanes (75% yield) were separated by preparative GC: $^1H$ NMR ($CDCl_3$, 25 °C) *cis*-2,*cis*-3-dideuteriophenylcyclopropane, $\delta$ 0.90 ppm (d, $J_{HH}$ = 8.4 Hz, $H_C$ and $H_{C'}$), 1.88 (broad t, $J_{HH}$ = 8.4 Hz, overlapped with $H_A$ of *trans*-2,*trans*-3-$D_2$ isomer, $H_A$); *trans*-2,*trans*-3-dideuteriophenylcyclopropane, $\delta$ 0.64 ppm (d, $J_{HH}$ = 4.8 Hz, $H_B$ and $H_{B'}$), 1.88 (broad t, $J_{HH}$ = 4.8 Hz, overlapped with $H_A$ of *cis*-2,*cis*-3-$D_2$ isomer, $H_A$). $^1H$ NMR spectra together with decoupling experiments confirmed the structural assignments.[14]

**Generation of *cis*-2,*trans*-3-*r*-1-Phenylcyclopropane from *erythro*-$d_2$-$C_5H_5(CO)_2FeCHDCHD(OCH_3)C_6H_5$, 8a,b.** As in the ionization of unlabeled **4**, 0.15 mL (0.78 mmol) of TMSOTf was added to a 10 mL methylene chloride solution (−78 °C) containing 0.25 g (0.76 mmol) of **8a,b** and 10 μL (0.07 mmol) of triethylamine. Nonane (30 μL) was added to the residue. Dideuteriophenylcyclopropane (70% yield) was separated by preparative GC: $^1H$ NMR ($CDCl_3$, 25 °C) $\delta$ 1.88 ppm (broad d of d, $J_{HH}$ = 8.4 Hz, $J_{HH}$ = 4.4 Hz, $H_A$), 0.93 (broad d of d, $J_{HH}$ = 8.0 Hz, $J_{HH}$ = 6.4 Hz, $H_C$), 0.68 (broad d of d, $J_{HH}$ = 4.8 Hz, $J_{HH}$ = 6.4 Hz, $H_{B'}$). $^1H$ NMR spectra together with decoupling experiments confirmed the structural assignments.[14]

**Acknowledgment** is made to the National Institutes of Health (GM28938) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We thank E. L. Eliel for helpful discussions.

**Supplementary Material Available:** Figures of $\{^1H,^1H\}$ COSY 2D NMR spectra for $C_6H_5CH(OCH_3)CH_2CH_2OH$, **3**, $C_5H_5(CO)_2FeCH_2CH_2CH(OCH_3)C_6H_5$, **4**, **5a,b**, and **6a,b**, $^{13}C$ NMR data for **7a,b** and **8a,b**, $^1H$ NMR and simulated $^1H$ NMR data for phenylcyclopropane, and $^1H$ NMR data and decoupling results for *cis*-2,*cis*-3-dideuterio-*r*-1-phenylcyclopropane, *trans*-2,*trans*-3-dideuterio-*r*-1-phenylcyclopropane, and *cis*-2,*trans*-3-dideuterio-*r*-1-phenylcyclopropane (9 pages). Ordering information is given on any current masthead page.

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# New Azasilatrane Cations: Quaternization of an Equatorial Nitrogen in Azasilatranes

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*Received June 13, 1990*

**Abstract:** Azasilatranes ($RSi(R'N_{eq}CH_2CH_2)_3N_{ax}$) possessing strong $SiN_{ax}$ transannular interactions are regioselectively quaternized by $Me^+$ or $Me_3Si^+$ at an equatorial nitrogen, giving stable isolable salts. For the reaction of $Me_3SiO_3SCF_3$ with the azasilatrane in which R = R′ = Me, mixtures of the triflate salts of the cations $MeSi[Me_3SiN^+(Me)CH_2CH_2](MeNCH_2CH_2)_2N$ and $MeSi(MeNCH_2CH_2)_3N^+SiMe_3$ are present in solution and in the solid state. The stability of the latter cation is suggested to arise from delocalization of electron density and the $N_{ax}$ positive charge in an elongated four-center four-electron MO system oriented along the molecular axis. The reaction of $MeSi(Me_3SiNCH_2CH_2)_3N$ with $Me_3SiO_3SCF_3$ is also unusual, giving the novel cation $MeSi(Me_3SiNCH_2CH_2)_2N^+CH_2CH_2N(SiMe_3)_2$, which may be in equilibrium with a dimer containing five-coordinate silicon. The $^1H$ $^{13}C$, $^{29}Si$, and $^{15}N$ NMR spectra of these compounds are discussed.

## Introduction

Despite the analogy with the extensively studied silatranes **1a**,[1] the interest in azasilatrnaes **1b** has grown steadily during the past decade. A reason for this development is the wider scope of azasilatrane chemistry, owing to the availability of the option to vary the substitution pattern at both the silicon and the equatorial nitrogen ligands in their compounds.[2] With the use of this approach, a systematic variation in the strength of the transannular $SiN_{ax}$ interaction to an extent unprecedented in silatrane chemistry has been achieved with azasilatranes.[2a,3] As a result of this

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[1] (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99. (b) Voronkov, M. G.; Dyakov, V. M.; Kirpichenko, S. V. *J. Organomet. Chem.* **1982**, *233*, 1.

[2] (a) Gudat, D.; Daniels, L. M.; Verkade, J. G. *Organometallics* **1989**, *8*, 2772. (b) Gudat, D.; Daniels, L. M.; Verkade, J. G. *Orgnometallics* **1990**, *9*, 1464.

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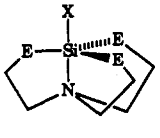
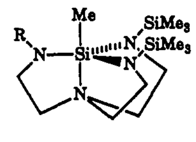
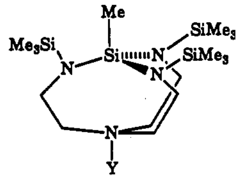


**1a**, E = O
**1b**, E = NH



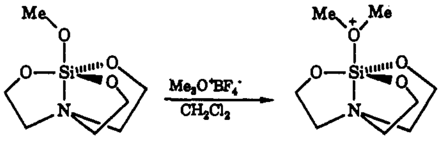
**2a**, R = SiMe$_3$
**2b**, R = Me
**2c**, R = H



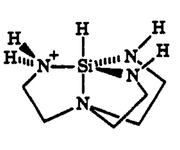
**3a** Y = CH$_3^+$
**3b** Y = BH$_3$

strategy, for example, compound **2a**, possessing an unusually weak SiN$_{ax}$ bond has been prepared.[3] The basicity of the N$_{ax}$ atom in this compound proved to be sufficient for quaternization by CF$_3$SO$_3$Me or BH$_3$·THF, yielding compounds **3a**[3] and **3b**,[4] respectively. From a comparison of their structural and spectroscopic properties, a detailed description of the bonding in these interesting compounds has been obtained.[4] Until now, efforts to induce reactions at the N$_{ax}$ atom of other silatranes and azasilatranes although considerable[5,6] have been without success.

Though the equatorial oxygen atoms in silatranes of type **1a** could in principle also be quaternized, no electrophile strong enough has heretofore been found. The relatively weak Lewis basicity of the equatorial O ligands in silatranes is illustrated by the conversion of **4** into an oxonium salt **5** in which the axial, rather than an equatorial, O ligands is alkylated.[6]



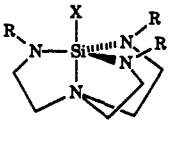
**4** **5**



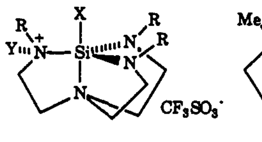
**6**

Because of the intrinsically higher basicity of an NH relative to an O functionality and because of the greater strength of the SiN$_{ax}$ bond in azasilatranes relative to that in the corresponding silatranes,[7] the basicity of the equatorial ligands in azasilatranes of type **1b** should be higher than in the corresponding silatranes of type **1a**. In accord with this prediction, we have been able to prepare and determine the structure of the equatorially protonated novel cation **6** of **1b** (X = H),[8] which has no stable, isolable silatrane analogue, though such a species has been postulated as an intermediate in the solvolysis of silatranes.[9] The structure of cation **6**[8] features a longer Si–NH$_2$ bond and a shorter Si–N$_{ax}$ bond than in its neutral precursor **1b** (X = H).[10] These structural differences must be of predominantly electronic origin, since there should be no appreciable steric crowding between the axial and equatorial hydrogens in either **6** or **1b** (X = H).

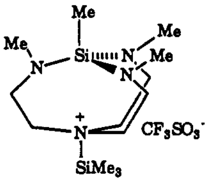
As part of our investigation of the influence of steric constraints on the physicochemical properties of and bonding in azasilatranes, it was of interest to explore the scope of quaternization reactions involving the equatorial nitrogen ligands in azasilatranes. Here we report the reactions of compounds **2a** and **7–9** with CF$_3$SO$_3$Me or CF$_3$SO$_3$SiMe$_3$, leading to the isolation of the azasilatrane



**7** X = H, R = Me
**8** X = Me, R = Me
**9** X = H, R = SiMe$_3$



**10** X = H, R = Y = Me
**11** X = H, R = Me, Y = SiMe$_3$
**12** X = H, R = SiMe$_3$, Y = Me
**13** X = Me, R = Y = Me
**14** X = Me, R = Me, Y = SiMe$_3$
**15** X = Me, R = SiMe$_3$, Y = SiMe$_3$



**16**

cations **10–16**. The IR and $^1$H, $^{13}$C, $^{29}$Si, and $^{15}$N NMR spectra of **7–9** and **10–16** are described and compared with those of **2a**, **3a**, and **3b**.[3,4] The implications of the results for the structure and bonding in **7–9** and **10–14** are also discussed.

## Results and Discussion

**Reactivity of 2a and 7–9.** In view of the greater basicity of N$_{ax}$ relative to N$_{eq}$ in compound **2a**,[3,4] the regioselectivity of its reaction with CF$_3$SO$_3$SiMe$_3$ to yield equatorially trimethylsilylated **15** was quite unexpected. The difference in the regioselectivity of the reactions of **2a** with CF$_3$SO$_3$Me (which affords **3a**) and CF$_3$SO$_3$SiMe (which gives **15**) can, however, be rationalized by taking steric factors into account. Despite the relative weakness of the SiN$_{ax}$ bond in **2a**, the N$_{ax}$ atom displays a significant (0.16 Å) upward protrusion from the plane of the three adjacent carbon atoms, toward the silicon atom.[3] Consequently, the N$_{ax}$ atom in **2a** is accessible only to electrophiles of low steric demand, which can approach the N$_{ax}$ atom closely enough to form the transition state of the S$_N$2-type quaternization reaction being considered here. This satisfactorily accounts for the observation that the N$_{ax}$ atom in **2a** can be quaternized with a methyl but not with the bulky trimethylsilyl group. Though less basic than N$_{ax}$, the N$_{eq}$ atoms in **2a** are apparently sufficiently basic and sterically accessible to displace the CF$_3$SO$_3^-$ group from CF$_3$SO$_3$SiMe$_3$ in an S$_N$2 reaction to yield equatorially trimethylsilated **15**. In accord with the lower nucleophilicity of N$_{eq}$ relative to N$_{ax}$, this reaction was observed to be 10 times slower in CDCl$_3$ at 55 °C than the reaction of **2a** with CF$_3$SO$_3$Me leading to **3b**. Compound **15** would be the first reported example of a stable quaternary ammonium ion of the type (R$_3$Si)$_3$NR$^+$.

The difference in reactivity of **9** and **2a** can be rationalized similarly. Because of less steric congestion in **9**, this compound should possess a stronger SiN$_{ax}$ bond. This conclusion is in accord with the observed $^{29}$Si and $^{15}$N chemical shift data (vide infra). Hence, the N$_{ax}$ atom in **9** should be less basic and less sterically accessible than in **2a**. This rationalizes the observation that **9**, unlike **2a**, reacts with CF$_3$SO$_3$Me to give the equatorially methylated product **12**. Another consequence of the presence of a strong SiN$_{ax}$ bond in **9** is that, in this compound, the five-coordinate Si atom should be closer to an undistorted TBP geometry than in **2a**. This implies that the N$_{eq}$ ligands in **9** should be less sterically accessible than in **2a** in which the central silicon is distorted toward tetrahedral. Hence, **9** should react less readily with CF$_3$SO$_3$SiMe$_3$ than **2a**. In accord with this hypothesis, **9** and CF$_3$SO$_3$SiMe$_3$ do not react at all, even when stoichiometric quantities of these compounds are heated in CDCl$_3$ at 55 °C for 10 days. Under identical conditions, **2a** and CF$_3$SO$_3$SiMe$_3$ react to give **15** quantitatively in 48 h.

The regioselectivity of the quaternization reactions leading to compounds **10**, **11**, **13**, and **14** indicates a greater Lewis basicity of N$_{eq}$ relative to N$_{ax}$ in the starting azasilatranes **7** and **8**. The same regioselectivity has been reported for the indirect protonation of 1-H- or 1-methylazasilatrane **1b** (X = H or Me), which yield cations of type **6** rather than a species protonated at N$_{ax}$.[8] In **1b** (X = H or Me), **7**, and **8**, the greater basicity of N$_{eq}$ relative to N$_{ax}$ is consistent with the presence of strong SiN$_{ax}$ bonds in these compounds (vide infra).

The reaction of **8** with CF$_3$SO$_3$SiMe$_3$ is puzzling in that it yields a mixture of **14** and the axially trimethylsilylated isomer **16**, depending on the reaction temperature and solvent polarity. In

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(3) Gudat, D.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 8520.

(4) Woning, J.; Gudat, D.; Daniels, L. M.; Verkade, J. G. Manuscript in preparation.

(5) (a) Mazheika, I. B.; Libert, L. I.; Lukevics, E. J.; Voronkov, M. G. *Khim. Geterotsikl. Soedin.* **1968**, 561. (b) Pestunovich, V. A.; Shterenberg, B. Z.; Lippmaa, E. T.; Myaji, M. Y.; Alla, M. A.; Tandura, S. M.; Baryshok, V. P.; Petukhov, L. P.; Voronkov, M. G. *Dokl. Akad. Nauk. SSSR* **1981**, *258*, 1410.

(6) Garant, R.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.*, to be published.

(7) (a) Turley, J. W.; Boer, W. *J. Am. Chem. Soc.* **1968**, *90*, 4026. (b) Parkanyi, L.; Simon, K.; Nagy, Y. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2328. (c) Parkanyi, L.; Nagy, J.; Simon, K. *J. Organomet. Chem.* **1975**, *101*, 11. (d) Macharashvili, A. A.; Shklover, V. E.; Struchkov, Y. T.; Lapsina, A.; Zelchan, G.; Lukevics, E. *J. Organomet. Chem.* **1988**, *349*, 23.

(8) Woning, J.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1990**, *112*, 4601.

(9) Timms, R. E. *J. Chem. Soc. A* **1971**, 1969.

(10) Gudat, D.; Woning, J.; Verkade, J. G. Manuscript in preparation.

**Table I.** FT-IR Spectral Data of Azasilatranes **7**, **8**, **10**, **11**, and **15**$^{a}$

| | compound | | | | |
|---|---|---|---|---|---|
| assignment | **7** | **10** | **11** | **8** | **15**$^{b}$ |
| $CH_3$ str | 2969 s | 2956m, 2899 m | 2953 m, 2876 m | 2970 s | 2953 m, 2897 m |
| $CH_2$ str | 2947 s, 2927 s, 2849 s | 2931 m, 2816 m | 2812 m | 2955 s, 2926 s, 2865 s, 2827 s | |
| overtones | 2782 s, 2681 m, 1889 s, 1817 w | 1979 w | 1975 w | 2788 s, 2693 m, 2633 w | 2802 w |
| SiH str | 2000 vs | 2080 m | 2074 w | | |
| $CH_2$ scissor | 1482 w m, 1449 s | 1478 m, 1456 m | 1472 m, 1456 m | 1486 w, 1454 s | 1477 w, 1449 w |
| $CH_3$ def | 1415 w, 1376 w | not resolved | not resolved | 1402 w, 1381 w | 1405 w |
| $CH_2$ wag | 1357 m. 1348 m | 1357 w | 1354 w | 1361 s, 1351 s | 1358 w |
| $CH_2$ twist | 1283 s, 1240 s, 1213 s | 1275 s, 1256 s, 1196 w | 1260 s br$^{c}$ | 1281 s, 1245 s, 1209 s | 1254 s br$^{c}$ |
| SO str | | 1225 m | 1224 m | | 1244 m |
| $\nu_{10}(E)$ | 1168 s | 1158 s | 1142 s | 1146 s | 1154 s |
| $\nu_1(A_1)$ | 1116 m | 1111 m | absent | 1119 m | absent |
| $CH_3$ rock | | | 1092 w | | 1079 w |
| $\nu_{12}(E)$ | 1053 s | 1056 s | 1054 m | 1061 s | 1031 s |
| $H_3C$–N str | 1031 m, 949 s | 1029 s, 951 m | 1030 s, 945 m | 1037 s | |
| $\nu_2(A_1)$ | 963 s | 956 m | 956 m | 950 s | 957 w |
| $\nu_3(A_1)$ | 915 m | 923 sh, br, w | 906 w | 905 s | 917 m |
| $CH_2$ rock | 859 s, 818 w | 896 w, 871 w, 816 w | 868 w, 849 m, 822 w | | 896 w, 870 sh, 840 s br |
| $\nu_{13}(E)$ | 762 w | 788 m | 780 w | 785 s | 785 w |
| | 670 s | 762 w, 728 w, 679 w | 759 w, 725 w, 689 w$^{d}$ | 662 s, 637 s$^{d}$ | 754 m, 682 m,$^{d}$ 638 s$^{d}$ |
| $\nu_4(A_1)$ | 618 m | 623 s | absent | absent | absent |

$^{a}$0.1–0.5% in KBr. The vibrations $\nu_1$–$\nu_4$, $\nu_{10}$, $\nu_{12}$, and $\nu_{13}$ are assigned according to ref 12. $^{b}$One absorption (978 m) unassigned. $^{c}$$(H_3C)_3Si$ def. $^{d}$SiC str.

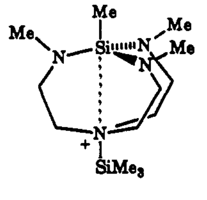
$CDCl_3$ solution at ambient temperature, the equatorial isomer **14** is formed almost quantitatively, with only a trace (<5% by $^1H$ NMR spectroscopy) of **16** present. Subsequent attempts to isolate **14** by the evaporation of the solvent, however, gave a waxy solid consisting of a 1:1 mixture of **14** and **16**, as indicated by the $^1H$ NMR spectrum taken immediately after dissolution in $CDCl_3$. After it stood for 48 h at room temperature, this solution had reverted nearly completely to **14**. In hexane at 70 °C, on the other hand, **16** is the favored product. When a boiling solution containing stoichiometric quantities of **8** and $CF_3SO_3SiMe_3$ in hexane is quickly cooled to room temperature, a crystalline material consisting of a 3:7 mixture of **14** and **16** separates. The same result is obtained when the 1:1 mixture of **14** and **16** (isolated from the reaction of **8** with $CF_3SO_3SiMe_3$ in $CDCl_3$) is crystallized from hot hexane. The overall stoichiometry of the crystalline product was verified by elemental analysis. Allowing a $CDCl_3$ solution of this material to stand at room temperature for 48 h again resulted in reversion to the equatorial isomer **14**.

From these results it is clear that **14** and **16** are in equilibrium with the starting materials **8** and $CF_3SO_3SiMe_3$. Formation of the equatorially trimethylsilylated isomer **14** is favored at low temperature and polar solvents. As a $CDCl_3$ solution of **14** is

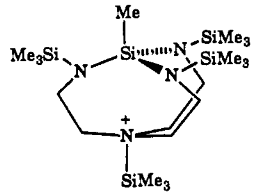
$$\mathbf{14} \rightleftarrows \mathbf{8} + CF_3SO_3SiMe_3 \rightleftarrows \mathbf{16}$$

evaporated, the equilibrium shifts toward **16**. This also provides a plausible explanation for the impossibility of isolating pure **14** from a solution in $CDCl_3$. Similarly, the isolation of pure, crystalline **16** is prevented by the fact that cooling a hot hexane solution containing mostly **16** causes the equilibrium to shift toward **14**. Since the crystalline material obtained from quenching a hot hexane solution contains more **16** than the solid isolated upon mixing stoichiometric quantities of **8** and $CF_3SO_3SiMe_3$ in either hexane or $CDCl_3$ at room temperature, **16** is concluded to be somewhat more stable thermodynamically than **14**.

In view of the fact that the more sterically congested **2a** gives only equatorially quaternized **15** in the presence of $CF_3SO_3SiMe_3$, the reasons underlying the formation and stability of **16** relative to **14** from sterically less congested **2a** are not clear. The observation that **8** reacts exothermally with $CF_3SO_3Me$ to yield exclusively the equatorially methylated compound **13** demonstrates that, in **8**, $N_{eq}$ is more basic than $N_{ax}$. To explain the formation of **16** from **8** it could then be argued that, in **8**, the steric accessibility of $N_{eq}$ relative to that of $N_{ax}$ would decrease when the incoming substituent is changed from a methyl into a bulky trimethylsilyl group, thereby favoring attack of the latter on $N_{ax}$. However, the $SiN_{ax}$ bond in **8** and hence the upward protrusion of $N_{ax}$ from the plane of the three adjacent carbon atoms should be stronger than in **2a**. Hence, the steric accessibility of the $N_{ax}$ atom in **8** should be less than in **2a** and thus insufficient for allowing the $N_{ax}$ atom in **8** to enter into an $S_N2$ reaction with $CF_3SO_3SiMe_3$, which contradicts the experimental results. The thermodynamic stability of **16** relative to **14** may be attributable to better electron and positive charge delocalization in **16** relative to **14**, an effect that may override the steric considerations given above for the lack of our observation of trimethylsilylation of the $N_{ax}$ position of **2a** (vide supra) depicted for comparison in structure **17**. Thus, the $SiN_{ax}$ distance in **16** is sterically permitted by the methyl groups to be less than in sterically more congested **17**. Consequently, the bridgehead silicon and nitrogen atoms in **16** could each possess a distorted trigonal-bipyramidal coordination geometry in which the axial CSi--NSi atoms engage in a four-center four-electron bonding MO system. That the $SiN_{ax}$ distance in **16** could be sufficiently short for such a bonding interaction is suggested by the 2.775 (7) Å for this distance observed for **2a**, which though ca. 0.7 Å longer than expected in a silatrane, is ca. 0.9 Å shorter than the sum of the van der Waals radii.[3] If the $SiN_{ax}$ distance in **16** is sufficiently short for a bonding interaction, this compound would represent the first example of hypercoordinate nitrogen in a discrete molecule. Efforts to grow crystals of **16** suitable for X-ray crystallography separable from **14** to which it readily reverts have so far been unsuccessful.



**16**



**17**

**IR Spectroscopy.** As pointed out previously,[4] the IR spectra of silatranes and azasilatranes possessing a strong $SiN_{ax}$ bond are very similar and can be interpreted consistently in terms of a vibrational analysis of the silatrane skeleton.[11] Three absorption bands at ca. 950, 910, and 620 $cm^{-1}$ could be assigned to skeletal modes of the atrane cage in which the internal $SiN_{ax}$ bond stretching coordinate contributes significantly to the overall vibration. In the IR spectra of azasilatranes **2a**,**b** and **3a**,**b** possessing

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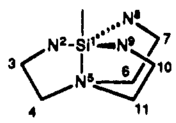
[11] Imbernotte, M.; Palavit, G.; Legrand, P.; Huvenne, J. P.; Fleury, G. *J. Mol. Spectrosc.* **1983**, *102*, 40.

**Table II.** Proton NMR Data for Azasilatranes[a]

| | chemical shifts, ppm | | | | | | |
|---|---|---|---|---|---|---|---|
| compound | $H_3$CSi(1) | $(H_3C)_3$SiN(2) | $(H_3C)_3$SiN(8,9) | C$H_3$N(2) | C$H_3$N(8,9) | $H$Si(1) | bridging C$H_2$ |
| **1b**, E = NH, X = H | | | | | | 3.92 | 2.98 t (6 H),[j,k] 2.73 t (6 H,)[l] |
| **8** | 0.09 | | | | | | 2.81 t (6 H),[k,m] 2.66 t (6 H)[l] |
| **9**[e] | | 0.03 (s, 27 H) | | 2.52 (s, 9 H) | | 4.62 | 2.69 t (6 H),[k,n] 2.40 t (6 H)[l] |
| **1b**, E = NH, X = Me | −0.38 | | | | | | 3.01 t (6 H),[k,m] 2.70 t (6 H)[l] |
| **12** | 0.13 | 0.47 (s, 18 H) | 0.13 (s, 18 H) | 2.65 (s, 3 H) | | 4.08 | 3.34 m (2 H),[j,o] 3.00 m (10 H)[p] |
| **11** | | 0.39 (s, 9 H) | | 2.46 (s, 3 H) | 2.50 (6 H)[i] | 3.83 | 3.48 m (1 H),[o,q] 3.23 m (1 H)[a] |
| **7e** | | | | 2.52 (s, 9 H) | | 3.70 | 2.77 t (6 H),[k,r] 2.70 t (6 H)[l] |
| **13** | 0.24 | | | 2.59 (s, 6 H) | 2.54 (s, 6 H) | | 3.26 m (2 H),[m,o] 2.95 m (10 H)[s] |
| **10** | | | | 2.58 (s, 6 H) | 2.54 (s, 6 H) | 3.60 | 3.33 t (2 H),[m,o] 3.03 m (10 H),[s] |
| **14** | 0.28 | 0.37 (s, 9 H) | | 2.54 (s, 3 H) | 2.50 (s, 6 H) | | 2.99 m (12 H)[t] |
| **2a** | 0.08 | | 0.09 (s, 18 H) | | | | 2.77 m (6 H),[k] 2.59 t (2 H)[u,v] |
| **2b** | 0.27 | 0.08 (s, 27 H) | | | | | 2.70 m (6 H),[v,w] 2.54 s (br, 6 H)[c,i] |
| **3a**[f] | 0.33 | 0.11 (s, 27 H) | | | | | 3.52 m, 3.01 m (12 H)[t] |
| **3b**[f,g] | 0.46 | 0.22 (s, 27 H) | | | | | 3.70 m, 3.28 m (12 H)[t] |
| **15** | 0.72 | 0.16 (s, 18 H) | 0.11 (s, 18 H) | | | | 3.94 m[g] (2 H),[o] 3.23 m (8 H)[d,x] |
| **16**[e] | 0.20 | 0.49 (s, 9 H) | | 2.52 (9 H) | | | 3.14 m, 3.06 m, 2.89 m, 2.75 m (12 H)[t] |

[a] In $CDCl_3$ unless otherwise specified. The numbering scheme of the atoms for this and subsequent tables is that of the structure



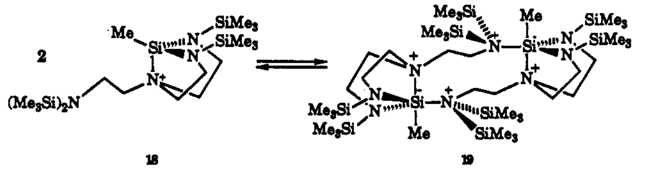
[b] H(3′), remaining cage protons at $\delta_H$ = 2.90 (10 H). [c] H(6) and H(11) at 2.38 t (4 H, $^3J_{HH}$ = 5.1). [d] H(4) at 2.72 m (2 H). [e] Data taken from ref 2a. [f] Data taken from ref 3. [g] In $CD_2Cl_2$. [h] Concentration sensitive $\delta$ = 4.11 in dilute $CDCl_3$. [i] Resolved into two equally intense peaks: $\Delta\delta$ = 0.04 ppm. [j] $J_{HH}$ = 6.0 Hz. [k] H(4,6,11). [l] H(3,7,10). [m] $^3J_{HH}$ = 5.9 Hz. [n] $^3J_{HH}$ = 5.6 Hz. [o] H(3). [p] H(4,6,10,11). [q] $^2J_{HH}$ = 12.9, $^3J_{HH}$ = 4.9 Hz. [r] $^3J_{HH}$ = 5.8 Hz. [s] H(4,6,7,10,11). [t] H(3,5,6,7,10,11). [u] $^3J_{HH}$ = 5.7 Hz. [v] H(4). [w] $J_{HH}$ = 5.1 Hz. [x] H(6,7,10,11).

$SiN_{ax}$ bonds that are weakened to varying degrees, these three modes are relatively weak or absent, demonstrating the usefulness of IR spectroscopy for qualitatively evaluating the $SiN_{ax}$ bond strength in azasilatranes.[4]

The IR spectral data of **7** and **8** (Table I) are very similar to those of **1a** (X = H, Me)[11] and **1b** (X = H, Me).[4,8] The IR spectrum of **7** displays the three absorption bands at 953, 915, and 618 $cm^{-1}$ characteristic of azasilatranes and silatranes possessing a strong $SiN_{ax}$ bond. Although the IR spectrum of **8** lacks an absorption band at ca. 620 $cm^{-1}$, those at 905 and 958 $cm^{-1}$ are stronger than the corresponding bands at 915 and 953 $cm^{-1}$ in the IR spectrum of **7**, suggesting that the more sterically encumbered **8** may possess a somewhat weaker $SiN_{ax}$ bond. The intensities of these absorption bands in the IR spectra of **10**, **11**, and **15** indicate that there is still substantial $SiN_{ax}$ bonding in these compounds, compared with **3a** or **3b**.[4] The trend in the observed frequencies of the SiH bond-stretching mode agrees well with this conclusion. According to the observed $\nu_{SiH}$ values, the $SiN_{ax}$ bond strength decreases in the order **1b** (X = H) ($\nu_{SiH}$ = 1975 $cm^{-1}$)[8] > **7** ($\nu_{SiH}$ = 2000 $cm^{-1}$) > **6** ($\nu_{SiH}$ = 2023 $cm^{-1}$)[8] > **10** ($\nu_{SiH}$ = 2074 $cm^{-1}$) ≈ **11** ($\nu_{SiH}$ = 2080 $cm^{-1}$). These $\nu_{SiH}$ values are nevertheless significantly below the value ($\nu_{SiH}$ = 2115 $cm^{-1}$) reported[12] for the tetrahedral model compound $(EtNH)_3SiH$, indicating that even in **10** and **11** significant $SiN_{ax}$ bonding exists. The decrease in bond strength in the above order parallels an increase in the extent of steric crowding among the substituents at the bridgehead Si and the $N_{eq}$ atoms in **1b** (X = H), **6**, **7**, **10**, and **11**.

**$^1$H NMR Spectroscopy.** $^1$H NMR spectroscopy is a particularly convenient and useful method for discriminating between axially quaternized compounds such as **3a**, **3b**, or **16** and the less symmetrical equatorially quaternized compounds **10**–**15**. As can be seen in Table II, the two types of regioisomers differ in the number and integration of the singlets attributable to the trimethylsilyl groups ($\delta_H$ = 0–0.5 ppm) and the MeN fragments ($\delta_H$ = 2.4–2.7 ppm).

Furthermore, $^1$H NMR spectra also provide important information on the structure and bonding in the compounds listed in Table II. Comparing, for example, the $\delta_H$ values of the protons of the $Me_3Si$ substituents located at the quaternized nitrogen atoms in **11**, **12**, and **14**–**16** indicates that the net positive charge of the quaternary $N_{eq}$ atom in **11**, **12**, and **14** and the $N_{ax}$ atom in **16** is higher than that of the quaternary $N_{eq}$ atom in **15**. Since all these quaternary N atoms bear a formal +1 charge, it can be concluded that in **15** the positive charge is removed effectively from the quaternized N atom, which suggests that **15** could have a structure different from that of **11**, **12**, **14**, and **16**. This suggestion is supported by the unusually large downfield shift ($\Delta\delta_H$ = 0.45 ppm) of the methyl protons associated with the bridgehead silicon in **15** relative to that of the parent silatrane **2a**. Trimethylsilylation or methylation of an $N_{eq}$ atom in **8** results in downfield movements smaller than 0.2 ppm for the $^1$H chemical shifts of the $H_3CSi$(bridgehead) group (see Table II). The unusual $\delta_H$ values of the $Me_3SiN_{eq}$ and the $H_3CSi$(bridgehead) protons in **15** can be rationalized by assuming **15** to have the open structure **18** containing four-coordinate silicon, instead of a normal tricyclic atrane structure. The formation of dimer **19** in concentrated solution would then rationalize the considerable concentration dependence of the $\delta_H$ value for the protons of the methylene group adjacent to $N_{eq}$ in **15**. Structure **18** represents an extreme example of Si(bridgehead)–$N_{eq}$ bond elongation of the type observed in cation **6**,[8] enforced by steric repulsion between the methyl group at the bridgehead Si and the two $Me_3Si$ groups at $N_{eq}$ in **15**. Structures **18** and **19** would also rationalize the observed stability of **15** toward nucleophiles in the solid state as well as in solution, compared with the equatorially trimethylsilylated analogues **11** and **14**. Thus, the latter compounds are moisture-sensitive in the solid state and decompose in MeCN solutions.



**18** **19**

**$^{13}$C NMR Spectroscopy.** For space considerations, the $^{13}$C NMR data of azasilatrane **1b** (X = H, Me), **2a**,**b**, **3a**,**b**, and **7**–**15** are presented as supplementary material. In contrast with those of compounds **2b**, **3a**,**b**, and their hydrocarbon analogues,[4] the $^{13}$C chemical shifts and coupling constants $^1J_{CH}$ of the cage carbons in compounds **7**–**15** do not vary systematically with changes in the $SiN_{ax}$ bond strength. On the other hand, the coupling constants $^1J_{CH}$ of the $H_3CSi$(bridgehead) group appear to do so in an approximate manner. Thus, the $^1J_{CH}$ values increase in the order **1b** (X = Me) (113.9 Hz)[4,12] > **8** (115.4 Hz) ≈ **2a** (115.6 Hz) >

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(12) Kupce, E.; Lapsina, A.; Zelchan, G.; Lukevics, E. *J. Organomet. Chem.* **1987**, *333*, 1.

**Table III.** $^{29}$Si and $^{15}$N NMR Data for Azasilatranes[a]

| | Si(1) | | | | | | |
|---|---|---|---|---|---|---|---|
| compound | $\delta_{Si}$ | $^1J_{SiH}$ | $^2J_{SiH}$ | SiMe$_3$, $\delta_{Si}$ | N(5), $\delta_N$ | N(2), $\delta_N$ | N(8), N(9), $\delta_N$ |
| **1b**, E = NH, X = H[b] | −82.3 | 177 | | | −346.8 | | −350.1 |
| **8** | −70.8 | | 5.9 | | −353.9 | | −366.6 |
| **9** | −70.1 | 198 | | 3.20 | −363.5 | | −358.0 |
| **1b**, E = NH, X = H[b] | −68.3 | | 5.8 | | −354.5 | | −352.8 |
| **12** | −66.3 | 227 | | 3.06, 8.56 | −351.3[f] | −350.8[f] | −351.1[f] |
| **11** | −64.2 | 225 | | 35.3 | −356.0[c] | −347.5[c] | −353.6[c] |
| **7** | −62.2 | 194 | | | −362.7[c] | | −349.4[c] |
| **13** | −60.5 | | 6.0 | | −356.7[c] | −342.7[c] | −343.4[c] |
| **10** | −56.2 | 224 | | | −357.5[c] | −345.4[c] | −346.3[c] |
| **14** | −55.9 | | 6.6 | 31.6 | −361.4 | −347.4 | −360.0 |
| **2a**[e] | −36.2 | | 6.5 | 3.20 | −372.8 | −359.8 | −360.8 |
| **2b**[e] | −25.7 | | 6.9 | 3.16 | −379.4 | | −360.8 |
| **3a**[e] | −11.6 | | 7.3 | 4.93 | −342.9 | | −359.9 |
| **3b**[e] | −10.3 | | 6.9 | 6.80 | −321.3[d] | | −355.8[d] |
| **15** | 19.0 | | 7.8 | 7.71, 8.90 | −371.8 | −335.3 | −351.8 |

[a] In $CDCl_3$ unless indicated otherwise. The numbering scheme for the atoms is given in footnote *a* of Table II. [b] $^{29}$Si and $^{15}$N chemical shifts taken from ref 13. [c] In $CDC_3CN$. [d] In $CD_3CN/CDCl_3$ (1:1, v/v). [e] $^{29}$Si and $^{15}$N NMR data taken from refs 3 and 4. [f] Tentative assignment.

**2b** (116.4 Hz) ≈ **15** (116.6 Hz) > **13** (117.2 Hz) ≈ **14** (117.8 Hz) > **3a** (118.7 Hz) ≈ **3b** (119.4 Hz). This trend coincides roughly with an increase in steric crowding between the substituents at the $N_{eq}$ atoms and the methyl group at the bridgehead Si and hence with an increase in the tetrahedrality of the Si(bridgehead) atom.

The observed $^1J_{CH}$ value (116.6 Hz) for the $H_3CSi$(bridgehead) group in **15** is unexpectedly low to account for the anticipated degree of steric crowding among the four equatorial $Me_3Si$ groups and the methyl group at the Si(bridghead) atom, which is consistent with the suggestion made earlier that **15** is an equilibrium mixture of **18** and **19**. Also consistent with this suggestion is the observation that the 116.6-Hz $^1J_{CH}$ coupling is somewhat less than that in the tetrahedral model compound $(Me_2N)_3SiCH_3$ (117.2 Hz).[13]

The $^{13}$C NMR spectra of **3a** and **10–15** convincingly demonstrate their ionic nature. The $^{13}$C chemical shifts ($\delta_C$ = 119.98–120.62 ppm) and the carbon-fluorine coupling constants ($^1J_{CF}$ = 319.8 ± 0.2) of the $CF_3SO_3^-$ ions of these compounds were observed to vary within a very narrow range. These $\delta_C$ values are consistently below those found for the covalent compounds $CF_3SO_3Me$ ($\delta_C$ = 118.60 ppm, $^1J_{CF}$ = 319.8 Hz) and $CF_3SO_3SiMe_3$ ($\delta_C$ = 118.19 ppm, $^1J_{CH}$ = 317.4 Hz), indicating that the $CF_3SO_3$ groups in **3a** and **10–16** are ionic.

**$^{29}$Si and $^{15}$N NMR Spectroscopy.** The $^{29}$Si chemical shifts of compounds **7–14** (Table III) indicate that there should be appreciable $SiN_{ax}$ bonding in these compounds. The $\delta_{Si}$ values, ranging from −70.8 ppm for **8** to −55.9 ppm for **14**, also demonstrate the presence of essentially five-coordinate silicon in these compounds, as indicated by the high shielding of the silicon atoms in **7–14** with respect to those in the analogous tetrahedral model compounds $(EtNH)_3SiH$ ($\delta_{Si}$ = −32.3 ppm),[13] $(PrNH)_3SiH$ ($\delta_{Si}$ = −34.8 ppm),[13] $(PrNH)_3SiMe$ ($\delta_{Si}$ = −23.3 ppm)[13] or $(Me_2N)_3SiMe$ ($\delta_{Si}$ = −16.3 ppm).[12,13] Relatively extreme deshielding of the Si(bridgehead) atom is seen in compound **15** (Table III), suggesting (in accordance with the conclusions drawn from the $^1$H and $^{13}$C NMR data) an unusual structure for this compound (vide supra).

Whereas the $\delta_{Si}$ values of the Si(1) atom in compounds **10–12** clearly rank them in the category of five-coordinate silicon compounds, the coupling constants $^1J_{SiH}$ of **10–12** (Table III) are equal to those reported[12] for the analogous tetrahedral compounds $(EtNH)_3SiH$ ($^1J_{SH}$ = 226.9 Hz) and $(PrNH)_3SiH$ ($^1J_{CH}$ = 227.0 Hz). It could be argued that the exceptionally large $^1J_{SiH}$ coupling constants in **10–12** arise from partial transfer of positive charge from the quaternized $N_{eq}$ to the Si(bridgehead) atom. However, the marginal differences in the $\delta_{Si}$ values within the sets **7**, **10**, **11** and **9**, **12** ($\Delta\delta_{Si}$ < 6 ppm) weaken this argument. The origin of this effect is currently under investigation.

**Conclusions.** In azasilatranes possessing a strong $SiN_{ax}$ bond, the Lewis basicity of the $N_{eq}$ atoms is higher than that of the $N_{ax}$ atom. Accordingly, the reactions of compounds **7–9** with $CF_3SO_3Me$ or $CF_3SO_3SiMe_3$ give rise to the formation of the products **10–14**, in which the $N_{eq}$ atom is regioselectively quaternized. The formation of the axially quaternized **16**, along with **14** in the reaction of **8** with $CF_3SO_3SiMe_3$, is an interesting exception to this reactivity pattern. Compounds **14** and **16** appear to be in thermodynamic equilibrium with the reactants **8** and $CF_3SO_3SiMe_3$, **14** being the favored product in polar media. The temperature dependence of the equilibrium in hexane suggests that **16** is thermodynamically slightly more stable than **14**. The formation of a delocalized four-center four-electron bonding MO system may be largely responsible for stabilizing **16** relative to **14**.

Steric restraints in both reactants are responsible for the observed regioselectivity of the reaction between **2a** and $CF_3SO_3SiMe_3$. The regioselective formation of equatorially trimethylsilylated **15** (which appears subsequently to engage in an equilibrium with **18** and **19**) is inconsistent with the relative basicities of the $N_{eq}$ and the $N_{ax}$ atoms in **2a**. The observed regioselectivity of the reaction between **9** and $CF_3SO_3Me$ to yield **12** and the failure of **9** to react with $CF_3SO_3SiMe_3$ can be rationalized on steric grounds.

## Experimental Section

The equipment used to acquire the FT-IR and the $^1$H, $^{13}$C, $^{29}$Si, and $^{15}$N NMR spectra is described in a previous paper.[4] TMS was used as an internal NMR standard for $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopy. The $^{15}$N NMR spectra were recorded with $CD_3CN$ as an external standard. A conversion constant $\delta_N$ = −140.73 ppm for the chemical shift of $CH_3CN$ relative to $CH_3NO_2$[14] was used to rescale the $^{15}$N chemical shifts with respect to neat $CH_3NO_2$.

All chemical reactions and manipulations of IR and NMR samples were carried out under strict exclusion of moisture. Solvents used were dried according to standard procedures and distilled under nitrogen.

The preparations of **7** and **9** have been described earlier.[2a] The crude materials were purified by three vacuum sublimations at 1 × $10^{-3}$ Torr.

**1-Methyl-*N*,*N*′,*N*″-trimethylazasilatrane (8).** The crude compound was prepared by heating a stirred mixture of 6.020 g (34.33 mmol) of tris(dimethylamino)methylsilane, 6.166 g (32.74 mmol) of $(MeNHCH_2CH_2)_3N$,[2a] and 50 μL of chlorotrimethylsilane for 1$^1/_2$ h at 125 °C and then for an additional 1$^1/_2$ h at 133 °C. The reaction mixture was cooled and the crude product purified twice by vacuum sublimation at 60 °C and 2 × $10^{-3}$ Torr, affording pure crystalline **8**: 46% yield; mp 67–67.5 °C; MS (EI, 70 eV) for $C_{10}H_{24}N_4Si$ 228.1767, calcd 228.1770 ($M^+$), for $C_9H_{21}N_4Si$ 213.1535, calcd 213.1535 ($M^+ - CH_3$). See Tables I–III for IR and NMR data.

**Compound 10.** A 10-mL round bottom flask, equipped with a septum, was charged with 290.0 mg (1.353 mmol) of **7** and 4 mL of dry hexane. Then 160 μL (1.41 mmol) of $CF_3SO_3$ was added slowly (ca. 15 min)

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(13) Tandura, S. N.; Pestunovich, V. A.; Voronkov, M. G.; Zelchan, G. I.; Solomennikova, I. I.; Lukevichs, E. *Khim. Geterotsikl. Soedin.* **1977**, 1063.

(14) Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; Wiley: New York, 1983; pp 33, 72.

while the solution was agitated ultrasonically, affording **10** as a white precipitate in quantitative yield. After removal of the solvent via a syringe, the precipitate was washed with dry hexane (2 × 4 mL), dried under high vacuum, and stored under $N_2$. According to the $^1H$ and $^{13}C$ NMR spectra, **10** prepared in this way is NMR pure. Without ultrasonic agitation, **10** separates from the reaction mixture as a viscous syrup, which can be solidified to a waxy mass only with great difficulty. According to the $^1H$ and $^{13}C$ NMR spectra, the waxy solid consisted of >98% pure **10**. See Tables I–III for spectroscopic data of **10**.

**Compound 11.** Compound **11** was prepared in quantitative yield from 331.6 mg (1.547 mmol) of **7** and 310 μL (1.60 mmol) of $CF_3SO_3SiMe_3$ in 4.4 mL of hexane/benzene (10:1, v/v), according to the procedure outlined for **10**. The only difference in the procedure was that the precipitate of crude **11** was removed by filtration. The purity of the product isolated in this way was 90–95%; mp 50 °C dec. Anal. Calcd for $C_{13}H_{31}N_4F_3O_3Si_2S$ (found): C, 35.76 (34.43); H, 7.16 (7.00); N, 12.83 (13.51). Attempts to purify **11** by recrystallization from $CHCl_3$, $C_6H_6$, $CH_3CN$, hexane, or their mixtures yielded only a viscous, polymeric oil when the warm solutions of **11** were cooled in these solvents. Solutions of pure **11** in $CDCl_3$ suitable for NMR spectroscopy were, however, conveniently prepared by reacting stoichiometric quantities of **7** and $CF_3SO_3SiMe_3$ in an NMR tube. The high sensitivity of **11** to nucleophiles is illustrated by the observation that solutions of **11** in $CDCl_3/CD_3CN$ (1:1) decompose at a rate of ca. 5%/h. The NMR data on pure **11** are given in Tables II and III.

**Compound 12.** A solution of pure **12** in $CDCl_3$ was prepared by adding 113 μL (0.998 mmol) of $CF_3SO_3Me$ to a solution of 380 mg (0.977 mmol) of **9** in 2.3 mL of dry $CDCl_3$ in a 10-mm NMR tube. The reaction mixture was heated to 55 °C for 15 min to ensure completion of the reaction. No attempts were made to isolate **12**. Its NMR data are given in Tables II and III. An attempt to react **9** with $CF_3SO_3SiMe_3$ in $CDCl_3$ failed. When a solution of 27 mg (0.070 mmol) and 27 μL (0.14 mmol) of $CF_3SO_3SiMe_3$ was heated for 10 days at 55 °C, only the reactants plus a small amount (<5%) of polymeric reaction product could be detected by $^1H$ NMR spectroscopy in the reaction mixture.

**Compound 13.** Repeated attempts to prepare **13** from **8** and $CF_3SO_3Me$, according to the procedure described for **10** and **11**, resulted in the isolation of an intractable, moisture-sensitive, waxy semisolid, which according to $^1H$ and $^{13}C$ NMR was pure. Attempts to recrystallize the semisolid from a variety of solvent mixtures failed. Solutions of pure **13** in $CDCl_3$ for NMR spectroscopy were prepared as described for **11** and **12**. For NMR data on **13**, see Tables II and III. Cation **13** was generated independently by the reaction of equimolar quantities of **8** and a suspension of $Me_3O^+BF_4^-$ in $CDCl_3$. About 70% conversion to **13** was achieved after 3 days at room temperature. The cations in the $CF_3SO_3^-$ and $BF_4^-$ salts of **13** in the reaction products of **8** with $CF_3SO_3Me$ and with $Me_3O^+BF_4^-$ gave identical $^1H$ and $^{13}C$ NMR spectra.

**Compounds 14 and 16.** A 1:1 mixture of **14** and **16** was precipitated by the slow addition of 287 μL (1.485 mmol) of $CF_3SO_3SiMe_3$ to a solution of 332.5 mg (1.456 mmol) of **8** in 5 mL of hexane. The reaction mixture was then heated to the boiling point, which caused virtually complete dissolution of the precipitate, leaving a small amount of a gumlike residue. The solution was then quickly cooled to room temperature, causing the precipitation of fine, needle-shaped, colorless crystals. Following the removal of the solvent by syringe, the crystals were dried under vacuum, transferred into a drybox, and removed carefully from the gumlike residue. According to the $^1H$ NMR spectrum, taken immediately after dissolution of the crystalline material in $CDCl_3$, the composition of the product was a 7:3 mixture of **16** and **14**, mp 70–73 °C dec. Anal. Calcd for $C_{14}H_{33}N_4F_3O_3SiS$ (found): C, 37.31 (37.17); H, 7.38 (7.55); N, 12.43 (12.59); Si, 12.46 (12.33). For NMR data, see Tables II and III.

**Compound 15.** To a solution of 665.5 mg (1.652 mmol) of **2a** in 2.3 mL of $CDCl_3$ were added eight 40-μL portions of $CF_3SO_3Me$ (1.656 mmol). The reaction was monitored by NMR spectroscopy and was found to be complete in 12–16 h. Following the acquisition of the $^1H$, $^{13}C$, $^{29}Si$, and $^{15}N$ NMR spectra, the solvent was evaporated, leaving a sticky, light brown solid. The solid was washed with diethyl ether (2 × 5 mL) to remove the brown, polymeric side products. Then 8 mL of diethyl ether and the amount (ca. 1 mL) of $CHCl_3$ necessary to effect complete dissolution of the solid were added. The resulting solution was filtered and cooled slowly to ca. −20 °C, affording colorless, feathery crystals of **15**. The yield of pure, crystalline **15** was 50–70%; mp 138–140 °C. Anal. Calcd (found) for $C_{20}H_{51}N_4F_3O_3Si_5S$: C, 38.43 (37.94); H, 8.22 (8.45); N, 8.96 (8.97); F, 9.12 (13.80); Si, 17.70 (22.46); Si + F, 31.59 (31.46).

**Acknowledgment.** This research was supported by the Air Force Office for Scientific Research through a research grant to J.G.V. We thank Dr. Dietrich Gudat for helpful discussions and the W. R. Grace Co. for research samples of tren.

**Supplementary Material Available:** $^{13}C$ NMR data (1 page). Ordering information is given on any current masthead page.

# Ring Opening and Hydrogen Atom Transfer Trapping of the Bicyclo[2.1.0]pent-2-yl Radical

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**Abstract:** Relative rate constants ($k_r/k_H$) for ring opening of the bicyclo[2.1.0]pent-2-yl radical (**1**) to the cyclopent-3-enyl radical and trapping of radical **1** with *t*-BuSH, PhSH, and PhSeH in solvent THF were measured at temperatures between −78 and 50 °C. The hydrogen atom donors reacted more rapidly with radical **1** than with the cyclopropylcarbinyl radical (**6**). Rate constants for ring opening of **1** ($k_r$) could be obtained by estimating the values of $k_H$ via Marcus theory. From initial $k_H$ values for reactions with radical **6**, new $k_H$ values were calculated for increasingly exergonic reactions until the derived $k_r$ values from the three trapping agents agreed with one another and an extrapolated value of $k_r$ from Tempo trapping of **1**. The results suggest that hydrogen atom transfer reactions with **1** were about 3 kcal/mol more exergonic than reactions with **6**. Arrhenius functions for ring opening of **1** averaged $\log (k_s/s^{-1}) = 13.0 - 5.2/2.3RT$; the value of $k_r$ at 25 °C is $1.5 \times 10^9$ $s^{-1}$. Trapping studies of **1** and **6** with 2,6-dimethylthiophenol indicated that no special steric effects were present in hydrogen atom transfers to **1**. However, highly stereoselective trapping of **1** was observed in reactions with ArSD with *endo*-bicyclo[2.1.0]pentane-*2-d* predominating, and the rate constant for decarboxylation of the *endo*-bicyclo[2.1.0]pentane-2-carboxy radical (*endo*-**3**) at −78 °C apparently was greater than that for decarboxylation of *exo*-**3**. The stereochemical results are ascribed to a stereoelectronic effect between the C1–C4 bond and *endo*-C2–X bonds of bicyclo[2.1.0]pentanes that weakens *endo*-C2–X bonds.

The ring opening of the bicyclo[2.1.0]pent-2-yl radical (**1**) to the cyclopent-3-enyl radical (**2**)[1] was shown to be exceptionally fast by Jamieson et al.,[1] who were unable to observe an ESR spectrum for radical **1** at temperatures as low as −160 °C. On

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