slope of ln a vs. t plots. Reactions were typically first order for several half lives, and the correlation coefficients were 0.995 or better. Second-order rate constants were obtained from the slope of the pseudo-first-order rate constant vs. the diene concentration. Three diene concentrations were used to obtain each second-order rate constant. The second-order rate constants were obtained in triplicate.

In a typical experiment 10 mL of diene solution was placed in a rubber capped reaction flask containing a stirring bar. The flask was put in a thermostated bath and stirred for 30–60 min. At the same time the bath water was circulated through a jacket especially designed to house the IR cell (Precision Cells, Inc., part no. 20710). The reaction flask was connected to the IR cell by Teflon tubing. With the IR instrument set at 2128 $\mathrm{cm^{-1}}$ and in the time drive mode about 0.1 mL of approximately 1 M Hfe in the reaction solvent was injected into the reaction flask. The reaction mixture was then forced through the IR cell by inert-gas pressure supplied by a nitrogen or argon tank while the absorbance vs. time data was obtained. Rate data was obtained for 60–300 s. Kinetics data were obtained at 20, 30, and 40 °C for activation energy studies. Carbon monoxide was used in place of the inert gas in each step of the experiment to test its retarding effect on the rate. Similarly rates were measured by using a solvent that was successively 0.1, 0.2, and 0.3 M in trichlorosilane.

Procedure b. For the slower reactions, reaction mixtures were made up in a constant temperature bath and aliquots were periodically transferred to the IR cell.

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Registry No. Hfe, 33361-70-5; Dfe, 91002-46-9; 1,3-butadiene, 106-99-0; 2-methyl-1,3-butadiene, 78-79-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; *trans*-1,3-pentadiene, 2004-70-8; *cis*-1,3-pentadiene, 504-60-9; 1,3-cyclohexadiene, 592-57-4; 3-methylenecyclohexene, 1888-90-0; (*E*,*E*)-2,4-hexadiene, 5194-51-4; deuterium, 7782-39-0.

Organometallic Chemistry. 21. Silyl Trifluoromethanesulfonate (Triflate)–Boron Trichloride (Tribromide) Complexes[1]

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Trimethyl- and triethylsilyl triflate form with $\mathrm{BCl_3}$ and $\mathrm{BBr_3}$ strongly polarized donor–acceptor complexes. The deshielding of the ^{29}Si NMR shifts [$\Delta\delta_{^{29}\mathrm{Si}}$ ($\mathrm{BCl_3}$) 28.81 and 32.26, respectively] and shielding of ^{11}B NMR shifts characteristic for tetracoordinated boron are consistent with the development of partial positive charge at silicon involving *O*-coordination of boron halide with the triflates. Data also show that no ionization to silicenium ions takes place. Similarly, dimethylisopropyl- and tri-*n*-butylsilyl triflate gave donor–acceptor complexes on reaction with $\mathrm{BCl_3}$ [$\Delta\delta_{^{29}\mathrm{Si}}$ 30.51 and 25.18, respectively]. In general $\mathrm{BCl_3}$ was found to interact more strongly than $\mathrm{BBr_3}$. The reaction of a number of other alkylarylsilyl triflates or dialkylsilyl ditriflates with $\mathrm{BX_3}$ was also investigated. The deshielding of ^{29}Si NMR shifts diminished when the steric bulkiness of the alkyl ligands on silicon was increased, such as in the case of $(i\text{-Pr})_3\mathrm{SiOTf}$ or $\mathrm{Me_2}(t\text{-Bu})\mathrm{SiOTf}$. Ligand exchange of the triflates with $\mathrm{BX_3}$ is a competing process in the reactions, the rate of which increases significantly by increasing the temperature or reaction time. The reaction of tris(alkylthio)silyl triflate with $\mathrm{BCl_3}$ at low temperature led only to ligand exchange. The reaction of $\mathrm{Me_3SiOR}$ (R = Me, Et, Ph) with $\mathrm{BBr_3}$ (−30 °C) or with $\mathrm{BCl_3}$ (−75 °C) gave $\mathrm{Me_3SiBr}$, $\mathrm{Me_3SiCl}$, and the corresponding $\mathrm{ROSiX_2}$ indicative of initial complexation followed by rapid Si–O cleavage. The initial complexation, however, could not be observed by NMR. The reaction of $\mathrm{AlCl_3}$ and $\mathrm{AlBr_3}$ with silyl triflates resulted only in ligand exchange. Attempts to utilize the $\mathrm{R_3SiOTf{-}BX_3}$ systems as electrophilic trialkylsilylating agents for aromatics were unsuccessful.

Introduction

We have previously shown that trimethylsilyl halides form donor–acceptor complexes with Lewis acid halides such as $\mathrm{AlBr_3}$, $\mathrm{AlCl_3}$, and $\mathrm{BI_3}$ in solvents such as $\mathrm{CS_2}$, $\mathrm{CH_2Cl_2}$, and $\mathrm{CH_2Br_2}$.[2] Spectroscopic evidence for the formation of these polarized complexes is based on the observed deshielding of the ^{29}Si NMR shifts and a considerable sharpening of ^{27}Al NMR resonances, indicating a pseudotetrahedral environment around the aluminum atoms. However, the Si–halogen bonds are not ionized and no trivalent silicenium ions were formed in these systems (eq 1).

$$\mathrm{Me_3Si^{\delta+}Br \rightarrow {}^{\delta-}AlBr_3} \qquad (1)$$

Recently, the generation of a stable silicenium ion was reported by Lambert by hydride abstraction from tris(isopropylthio)silane with trityl perchlorate in $\mathrm{CH_2Cl_2}$ at room temperature. The poorly resolved ^{29}Si NMR signal was deshielded by only 17 ppm as compared to the silane precursor. This was attributed to "polymer formation", and it was suggested that the ^{29}Si NMR signal of the ion has a very slow relaxation time.[3] We feel this evidence is inadequate, and further studies are needed to substantiate whether a truly electron-deficient silicenium ion was obtained. The formation of silicenium ylides and their

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[1] For part 20 see: Olah, G. A.; Field, L. D.; Lammertsma, K.; Pacquin, D.; Suemmerman, K. *Nouv. J. Chim.* **1983**, *7*, 279.

[2] Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485.

[3] Lambert, J. B.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 1671.

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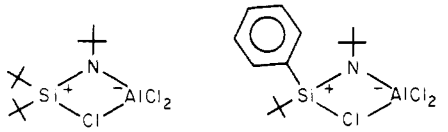
Table I. ^{29}Si and ^{11}B NMR Chemical Shifts of Silyl Triflate-BX_3 Complexes

		$\delta\ ^{29}Si$			$\delta\ ^{11}B$
compound[a]	Lewis acid	starting material	complex	exchange	complex
Me_3SiOTf		43.54			
Me_3SiOTf	BCl_3 (−35 °C)		72.35	29.02	−2.62
Me_3SiOTf	BBr_3 (rt)		61.52	25.74	−2.45
Me_3SiOTf	$AlBr_3/CS_2$ (rt)			25.24	
Me_3SiOTf	$AlCl_3/CS_2$ (rt)	41.85			
Me_3SiOTf	$AlCl_3/CS_2$ (−30 °C)	43.05		29.07	
Et_3SiOTf		44.46			
Et_3SiOTf	BCl_3 (−35 °C)		76.72	34.73	−2.75
$Et_2Si(OTf)_2$		13.35			
$Et_2Si(OTf)_2$	BCl_3 (−35 °C)		35.14	12.94	−2.55
$Et_2Si(OTf)_2$	BBr_3/CH_2Cl_2 (rt)		31.04		−2.45
i-Pr_3SiOTf		41.15			
i-Pr_3SiOTf	BCl_3 (−35 °C)			34.35	
n-Bu_3SiOTf		45.23			
n-Bu_3SiOTf	BCl_3 (−60 °C)		70.41	31.81	−3.09
Me_2(*i*-Pr)SiOTf		45.05			
Me_2(*i*-Pr)SiOTf	BCl_3 (−60 °C)		75.56	33.27	−2.82
Me_2(*t*-Bu)SiOTf		43.50			
Me_2(*t*-Bu)SiOTf	BCl_3 (−35 °C)	42.56			
Me_2(*t*-Bu)SiOTf	BBr_3 (rt)	43.79		34.16	
$Ph_2(Me)SiOTf$		11.54			
$Ph_2(Me)SiOTf$	BBr_3 (rt)		29.79	8.42	
$Ph_2(Me)SiOTf$	BCl_3 (−35 °C)	10.54	17.55		

[a] ^{29}Si NMR spectra of the starting triflates are recorded as neat solution at room temperature (rt).

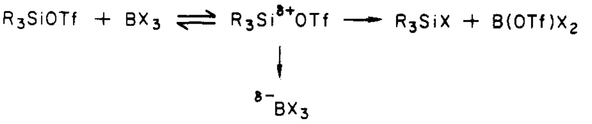
stabilization with AlX_3 were also reported. The partial zwitterion character of these species is based on ^{29}Si and ^{27}Al NMR data.[4]



The silylating ability of trimethylsilyl triflate Me_3SiOTf is well-known. We have ourselves previously developed an improved synthetic method for the in situ generation of this reagent for silylating carboxylic acids, alcohols, phenols, mercaptans, and ketones.[5] Our recent studies of R_FSO_2OH–BX_3 systems and the finding that tricoordinated boron has a high tendency to coordinate triflate ligands[6] led us to study the complexation of silyl trifluoromethanesulfonates (triflates) with BX_3 by NMR (^{29}Si, ^{11}B) and to search for suitable substituents on silicon to enhance the donor–acceptor complex formation. It was also attempted to use the trimethyl- and triethylsilyl triflate–BX_3 reagent for electrophilic silylation of alkylbenzenes.

Results and Discussion

When liquid BCl_3 was slowly added with efficient stirring to Me_3SiOTf at dry ice/acetone temperature, an oil layer was formed. The ^{29}Si NMR spectrum of the resulting oil recorded directly in BCl_3 at −35 °C consisted of two absorptions, a deshielded signal at $\delta_{^{29}Si}$ 72.35 for the complex ($\Delta\delta_{^{29}Si}$ 28.81) and a shielded absorption at $\delta_{^{29}Si}$ 29.02 for Me_3SiCl, formed by ligand exchange, in a 1:3 ratio. Upon standing at −75 °C the complex slowly precipitated from BCl_3 solvent. After removal of excess BCl_3, the complex was dissolved in SO_2ClF. The corresponding ^{11}B NMR spectrum of the complex was observed at −2.62 ppm, viz., in the region of tetracoordinated boron compounds. Similarly, BBr_3 forms a complex that at room temperature shows two signals in the ^{29}Si NMR spectrum ($\delta_{^{29}Si}$ 61.52, $\Delta\delta_{^{29}Si}$ 18) and the ligand exchange product Me_3SiBr ($\delta_{^{29}Si}$ 25.74). The corresponding ^{11}B NMR signal of the complex was observed at $\delta_{^{11}B}$ −2.45. A variable-temperature ^{29}Si NMR study (−60 to −20 °C) of Me_3SiOTf–BCl_3 system showed reversible exchange broadening of the ^{29}Si signal of the donor–acceptor complex with the solvent BCl_3. The ligand exchange process is, however, irreversible, and Me_3SiCl increases slowly by increasing temperature at the expense of donor–acceptor complex. It is also noted that the expected $B(OTf)X_2$ formed by ligand exchange does not show a separate signal from BCl_3 or BBr_3 solvent in the ^{11}B NMR spectra, suggesting that it undergoes exchange with the medium (eq 2). Whereas $AlCl_3$ and $AlBr_3$ were found to give donor–acceptor complexes with Me_3SiCl,[2] with trimethylsilyl triflate only ligand exchange of chlorotrimethylsilane was observed. This is in agreement with the finding that AlX_3 readily reacts with triflic acid with the evolution of HX to form triflates.[7]



$$R_3SiOTf + BX_3 \rightleftharpoons R_3\overset{\delta+}{Si}OTf \underset{\delta-}{\overset{}{\underset{BX_3}{\downarrow}}} \longrightarrow R_3SiX + B(OTf)X_2 \qquad (2)$$

When triethylsilyl triflate was reacted with BCl_3 in a similar fashion in an NMR tube, the ^{29}Si NMR spectrum recorded at −35 °C showed two absorptions at $\delta_{^{29}Si}$ 76.72 and 34.73 for the donor–acceptor complex ($\Delta\delta_{^{29}Si}$ 32.26) and Et_3SiCl, respectively, in a 1:2 ratio. Since the complex slowly precipitated out of solution at low temperature, in order to observe the ^{11}B NMR spectrum of the complex ($\delta_{^{11}B}$ −2.75) it was necessary to remove excess BCl_3 and to dissolve the precipitate in SO_2ClF. Diethylsilyl ditriflate similarly formed a complex with BCl_3 at low temperature. The ^{29}Si NMR spectrum of the mixture again showed two absorptions at $\delta_{^{29}Si}$ 35.14 and 12.94 for the donor–acceptor complex ($\Delta\delta_{^{29}Si}$ 21.79) and the unchanged starting material, respectively, in a 1:4 ratio. Surprisingly, no ligand ex-

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(4) Clegg, W.; Klingebeil, U.; Neemann, J.; Sheldrick, G. M. *J. Organomet. Chem.* **1983**, *249*, 23.

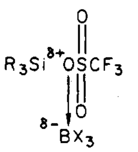
(5) Olah, G. A.; Husain, A.; Gupta, B. G. B.; Sales, G. F.; Narang, S. C. *J. Org. Chem.* **1981**, *46*, 5212.

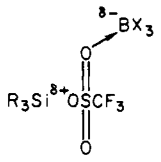
(6) Olah, G. A.; Laali, K.; Farooq, O., submitted for publication in *J. Org. Chem.*

(7) Olah, G. A.; Laali, K., unpublished results.

change product was formed. The corresponding ^{11}B NMR signal of the complex was at $\delta_{^{11}B}$ −2.55. Treatment of $Et_2Si(OTf)_2$ with a dilute solution of BBr_3 in dry CH_2Cl_2 also resulted in a donor–acceptor complex with the absorption in the ^{29}Si NMR at $\delta_{^{29}Si}$ 31.04 ($\Delta\delta_{^{29}Si}$ 17.69) and the corresponding boron signal at $\delta_{^{11}B}$ −2.45. *t*-Bu_2SiF_2 with triflic acid does not form *t*-$Bu_2Si(OTf)_2$. Similarly, *t*-$Bu_2Si(OTf)_2$ could not be obtained from its chloride and triflic acid.

i-Pr_3SiOTf on treatment with BCl_3 at low temperature did not give an observable complex. Only ligand exchange of triflate for Cl was observed, giving chlorotriisopropylsilane indicative of ionization followed by immediate quenching of the silicenium ion by chloride. *n*-Bu_3SiOTf formed a donor–acceptor complex with BCl_3 ($\Delta\delta_{^{29}Si}$ 25.18) together with *n*-Bu_3SiCl in a 1:3 ratio at −60 °C. The corresponding ^{11}B NMR signal of the complex was at $\delta_{^{11}B}$ −3.09 (SO_2ClF). Me_2(*i*-Pr)SiOTf similarly formed a donor–acceptor complex on addition of BCl_3 at dry ice/acetone temperature ($\Delta\delta_{^{29}Si}$ 30.51) and Me_2(*i*-Pr)SiCl in a 0.8:1 ratio at −60 °C. ^{11}B NMR spectrum of the complex dissolved in SO_2ClF was observed at $\delta_{^{11}B}$ −2.82. Me_2(*t*-Bu)SiOTf did not react with BCl_3. However, with BBr_3 ligand exchange was observed at ambient temperature. Bulkiness of the ligands on silicon therefore affects the stability of the donor–acceptor complexes. NMR data, however, cannot differentiate complexation on the sulfonyl or ether oxygen. Analogy with protonation (or complexation) of carboxylic acid esters, however, suggests that it is the ether oxygen complexation which results in Si–O bond cleavage with subsequent formation of the corresponding halosilane ligand exchange product.





In general, when the alkyl groups on silicon were replaced by phenyl, the extent of positive charge on silicon is reduced. This is in accord that diphenylmethylsilyl triflate gave an observable donor–acceptor complex on reaction with BBr_3 at room temperature, the ^{29}Si NMR absorption of which was $\delta_{^{29}Si}$ 29.79 ($\Delta\delta_{^{29}Si}$ 18.25). Subsequent ligand exchange was also observed, giving diphenylmethylsilyl bromide. On standing in BBr_3, side reactions occurred and the solution gradually darkened. With BCl_3 at low temperature the ^{29}Si NMR indicated only complex formation ($\delta_{^{29}Si}$ 17.55, $\Delta\delta_{^{29}Si}$ 6) and no ligand exchange was found. On the basis of the NMR data no apparent correlation between the magnitude of the positive charge on silicon, reflected in $\Delta\delta_{^{29}Si}$ values, and the extent of cleavage vs. complex formation could be found.

The behavior of tris(isopropylthio)silyl triflate was also studied with BCl_3 in order to examine the influence of the alkylthio ligands on donor–acceptor complex formation. The product observed was chlorotris(isopropylthio)silane ($\delta_{^{29}Si}$ 20.67) indicative of ligand exchange, and no intermediate donor–acceptor complex was observed.

Whereas the cleavage of trimethylsilyl ethers to trimethylsilyl halides by reaction with BBr_3 or BCl_3 is known,[8] to our knowledge direct observation of the intial step, i.e., the formation of a donor–acceptor complex, has not been reported. We therefore examined the reaction of Me_3SiOR (R = Me, Et, Ph) with BBr_3 at ambient temperature and at −30 °C as well as with BCl_3 at −75 °C. ^{29}Si NMR spectrum of a neat sample of Me_3SiOMe at room temperature gave a single absorption at $\delta_{^{29}Si}$ 16.98 with the corresponding $\delta_{^{13}C}$ shifts at −1.74 and 49.02 ppm at −20 °C. Slow addition of excess BBr_3 to this sample at −55 °C gave a colorless solution, the ^{29}Si spectrum of which showed only Me_3SiBr ($\delta_{^{29}Si}$ 26.36). The ^{13}C NMR spectrum of this sample showed two absorptions at $\delta_{^{13}C}$ 4.12 (Me_3SiBr) and $\delta_{^{13}C}$ 59.38. The latter is in close agreement with the reported values for methoxy attached to tricoordinated boron[9] and is therefore assigned to $MeOBBr_2$ ($\delta_{^{11}B}$ 26.27 at −30 °C). Similarly, low-temperature addition (−50 °C) of BBr_3 to Me_3SiOEt ($\delta_{^{29}Si}$ 14.36) and Me_3SiOPh ($\delta_{^{29}Si}$ 20.07) gave Me_3SiBr ($\delta_{^{29}Si}$ 26.11 and 26.37). Excess BCl_3 reacted rather violently with Me_3SiOMe and Me_3SiOEt cooled to dry ice/acetone temperature. The ^{29}Si NMR spectra of both samples were consistent with Me_3SiCl ($\delta_{^{29}Si}$ 30.91 and 30.70), and a donor–acceptor complex was not observed.

Attempted Silylation of Aromatics. Electrophilic silylation of aromatics under Friedel–Crafts condition has not so far been achieved. We felt of interest to study the reaction of the presently studied R_3SiOTf–BCl_3 (R = Me, Et) complexes with reactive aromatic compounds. When cumene was allowed to react with Me_3SiOTf–BCl_3 whereas GC analysis of the reaction mixture after removal of BCl_3 indicated the presence of higher boiling isomeric products, they were found to be disproportionation products (diisopropylbenzene isomers based on GC–MS analysis). The only silicon-containing compound identified was Me_3SiCl formed by ligand exchange with the Lewis acid, i.e., the same processes observed in our NMR studies of the complex. Control experiments showed that under the reaction condition, neither BCl_3 nor Me_3SiOTf itself were able to disproportionate cumene. The catalyst for disproportionation is therefore the conjugate acid formed by the reaction between BCl_3 and triflic acid impurity.[6] Similarly, no silylated aromatics were found in reaction with toluene or anisole. The latter gave a 10% yield of isomeric methylphenols. In subsequent experiments 2,4,6-tri-*tert*-butylpyridine was used as a proton trap in order to suppress acid-catalyzed desilylation that would have taken place. Once again, however, silylated aromatics were not detected.

In summary as shown by ^{29}Si and ^{11}B NMR data we have obtained polarized donor–acceptor complexes from a series of silyl triflates with boron trihalides. No observable silicenium ions were formed in the systems, although triflate to halide ligand exchange indicates intermediate S_Ni-like ionization or S_N2-like exchange through five coordinated silicon species.

Experimental Section

Trimethylsilyl triflate (Petrach) and dimethyl-*tert*-butylsilyl triflate (Aldrich) were commercial samples of sufficient purity and were used as received. Diethylsilyl ditriflate was prepared from Et_2SiHCl and triflic acid using the method recently described by Corey[10] for the preparation of *i*-$Pr_2Si(OTf)_2$.

Triethylsilyl triflate was prepared in ca. 90% yield (^{29}Si NMR) by an overnight reaction of Et_3SiCl and triflic acid (1 equiv) under dry nitrogen, followed by the removal of any dissolved HCl in solution under vacuum.

Tri-*n*-butylsilyl triflate and dimethylisopropylsilyl triflate were prepared from their corresponding chlorides and triflic acid (1 equiv) by room temperature mixing under argon for 18 h. ^{29}Si NMR spectrum of the reaction mixture showed a complete reaction, and no unreacted chloride could be detected.

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[9] Wrachmeyer, B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *12*, 227.

[10] Corey, E. J.; Hopkins, P. B. *Tetrahedron Lett.* **1982**, *23*, 4871.

Triisopropylsilyl triflate and diphenylmethylsilyl triflate were similarly prepared from their corresponding chlorides.

Tris(alkylthio)silyl chloride was prepared in ca. 95% yield (estimated by ^{29}Si NMR) from $SiCl_4$ and *i*-PrSH (3 equiv) using the method described in the literature for the preparation of tris(alkylthio)silane from trichlorosilane.[11] The reaction of the chloride with 1 equiv of triflic acid gave a ca. 65% yield of the triflate (estimated by ^{29}Si NMR). Unreacted triflic acid in the reaction mixture was removed by addition of the required amount of 2,4,6-tri-*tert*-butylpyridine. An aliquot of the solution was used for NMR studies (transferred to an NMR tube under nitrogen).

BBr_3 was doubly distilled, followed by distillation from aluminum powder, in an all glass distillation apparatus, until it was completely colorless. It was then stored in a drybox. BCl_3 (Matheson) was used as received. All aromatic compounds were commercial samples of highest purity and were used as received.

The ^{29}Si and ^{11}B NMR spectra were recorded an a Varian FT-80A instrument. The silicon chemical shifts were referenced to Me_4Si, whereas the boron shifts were referenced to $BF_3{\cdot}Et_2O$. GC analyses were performed on a Varian Model 3700 gas chromatography using a capillary as well as a short packed column (OV 101).

Complexation of Silyl Triflates with BX_3. The triflate (1 mL) was placed in an NMR tube and was cooled in dry ice/acetone under dry nitrogen with exclusion of moisture. After slow addition of BCl_3 (ca. 2 mL) and vortex mixing, the sample was first studied by ^{29}Si NMR directly in BCl_3 solvent, followed by ^{11}B NMR analysis usually after removal of excess BCl_3 and SO_2ClF as solvent. With BBr_3, whereas the addition was initially done at low temperature, the NMR tube was allowed to warm up slowly to room temperature prior to NMR studies. Same procedure was followed for the reaction of Me_3SiOR with BCl_3 and BBr_3.

For reactions with aromatics, the donor–acceptor complexes formed upon reaction of Me_3SiOTf or Et_3SiOTf with BCl_3 at low temperature were added to an excess of the aromatic compound precooled to ca. −40 °C with efficient magnetic stirring under dry nitrogen. The temperature was then allowed to warm up slowly to room temperature, followed by an additional 30 min of mixing at room temperature. The remaining BCl_3 was then removed by passing a fast flow of nitrogen through the reaction mixture, and the mixture was analyzed by GLC. In some cases, the reaction mixtures were also subjected to aqueous workup and ether extraction prior to GLC analysis.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No. $Me_3SiOTf{\cdot}BCl_3$, 91158-42-8; $Me_3SiOTf{\cdot}BBr_3$, 91158-43-9; $Et_3SiOTf{\cdot}BCl_3$, 91158-44-0; *n*-$Bu_3SiOTf{\cdot}BCl_3$, 91158-45-1; Me_2(*i*-Pr)$SiOTf{\cdot}BCl_3$, 91158-46-2; Ph_2(Me)$SiOTf{\cdot}BBr_3$, 91158-47-3; Ph_2(Me)$SiOTf{\cdot}BCl_3$, 91158-48-4; Me_3SiCl, 75-77-4; Me_3SiBr, 2857-97-8; Et_3SiCl, 994-30-9; *i*-Pr_3SiCl, 13154-24-0; *n*-Bu_3SiCl, 995-45-9; Me_2(*i*-Pr)SiCl, 3634-56-8; Me_2(*t*-Bu)SiBr, 76358-45-7; Ph_2(Me)SiBr, 17571-61-8; B(OTf)Cl_2, 91158-32-6; B(OTf)Br_2, 91158-33-7; Me_3SiOTf, 27607-77-8; Et_3SiOTf, 79271-56-0; $Et_2Si(OTf)_2$, 91158-34-8; *i*-Pr_3SiOTf, 80522-42-5; *n*-Bu_3SiOTf, 91158-35-9; Me_2(*i*-Pr)SiOTf, 91158-36-0; Me_2(*t*-Bu)SiOTf, 69739-34-0; Ph_2(Me)SiOTf, 91158-37-1; BCl_3, 10294-34-5; BBr_3, 10294-33-4; $AlBr_3$, 7727-15-3; $AlCl_3$, 7446-70-0; Me_3SiOMe, 1825-61-2; Me_3SiOEt, 1825-62-3; Me_3SiOPh, 1529-17-5; $MeOBBr_2$, 29877-99-4; $EtOBBr_2$, 91158-38-2; $PhOBBr_2$, 91158-39-3; $MeOBCl_2$, 867-46-9; $EtOBCl_2$, 16339-28-9; $PhOBCl_2$, 75088-70-9; cumene, 98-82-8; tris(isopropylthio)silyl triflate, 91158-40-6; chlorotris(isopropylthio)silane, 91158-41-7.

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Thermolysis of 6-Oxa-3-silabicyclo[3.1.0]hexanes: A New Convenient Route to Silicon–Oxygen π-Bonded Species

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Received December 21, 1983

The direct generation of silanones and germanones from easily prepared 6-oxa-3-metallabicyclo[3.1.0]hexanes is reported. Application of this method to the transient formation of an [O═Si═O] species is given. This silicon analogue of carbon dioxide was trapped by hexamethylcyclotrisiloxane to yield 2,2,4,4,6,6,10,10,12,12,14,14-dodecamethyl-2,4,6,8,10,12,14-heptasila-1,3,5,7,9,11,13,15-octaoxaspiro[7.7]pentadecane, the expected spiro adduct, in 60% yield.

Silanones, compounds containing a silicon–oxygen double bond, have been postulated as transient intermediates in a variety of reactions.[1] Most of these reactions involve the conversion of other unsaturated silicon intermediates into silanones. For example, reaction of nonenolizable aldehydes or ketones with silenes,[2–6] silaimines,[7,8] or disilenes[9–11] yield silanones. Likewise, reaction of silylenes with sulfoxides give silanones.[12–17] On the other

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[1] For a general review of π-bonded silicon see: L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.*, **79**, 529 (1979).

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