cyclization of diphenolic benzyltetrahydroisoquinoline derivatives.[4,5] Investigations are in progress to determine the possible implications of these observations for aporphine alkaloid biosynthesis and for intermolecular oxidative coupling.

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Alkyl and Aryl Difluorosulfuranes[1]

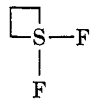
Sir:

There has been considerable interest in sulfuranes in the past few years. Several have been isolated and a number have been postulated as reaction intermediates.[2] Despite this interest little is known about simple aliphatic sulfuranes with α protons. In fact there is only one report of the preparation of such a material, $CH_3CH_2CH_2CHFSF_3$.[2h] It has now been found that reaction of trifluoromethyl hypofluorite (**1**) with sulfides at low temperatures yields difluorosulfuranes, **2**. ^{19}F nmr studies of these difluorosulfuranes have provided significant structural information and have indicated that they undergo ionization under some conditions. Ionization can be inhibited by neutralizing acid which is formed during the preparation of the sulfuranes.

$$\underset{\mathbf{1}}{CF_3OF} + R_2S \longrightarrow \underset{\mathbf{2}}{R_2SF_2}$$

Reaction of trimethylene sulfide with **1** in methylene chloride at −78° yielded a solution to which was added solid calcium hydride.[3] The sample was allowed to warm with agitation. Gas was evolved. The sample was cooled and then allowed to warm several times until no more gas was evolved. The ^{19}F nmr spectrum showed one major absorption at +5.76 ppm relative to fluorotrichloromethane. The ^1H nmr spectrum of another sample at −78° showed two broad absorptions at δ 3.85 and 3.58 in the ratio of *ca.* 2:1. A reaction mixture was hydrolyzed with aqueous bicarbonate solution to give trimethylene sulfoxide, *ca.* 60%, which was identified by glpc, ^1H nmr, and infrared spectroscopy. The results strongly suggest that the difluorosulfurane, **3**, is the species present in solution. The finding that the fluorines are equivalent on the nmr time scale is in accord with structure **3**; however, **4** can also account for the results if equatorial–apical switching "pseudorotation" is occurring. Finally fast ionization, **5**, could account for the equivalency. A choice was made between these possibilities by allowing 3-methylthiacyclobutane[4] to react with **1** at −78°. The ^{19}F nmr spectrum after calcium hydride treatment showed two doublets at δ −7.03 and +16.3, J_{F-S-F} = 167 Hz. Structure **6** uniquely meets the requirements of two nonequivalent fluorines coupled to each other. A "pseudorotating" structure, **4**, with the added methyl group would have given two singlets. There would have been two diastereoisomers if equatorial–apical switching of fluorines and the ring was occurring. Rapid ionization would have led to equivalent fluorines or two noncoupled nonequivalent fluorines. Finally it should be noted that **6** is not pseudorotating rapidly at −78°. The ^1H nmr spectrum of **6** was in agreement with the assigned structure; a doublet for the absorptions of the hydrogens of the methyl group was found at δ 1.46, J_{HCCH} = 5 Hz, and two other complex absorptions were found at δ 3.5 and 4.0. Hydrolysis afforded a mixture of the cis and trans sulfoxides in high yield.[5]

3



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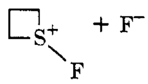

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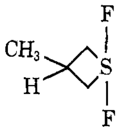

6

The ^{19}F nmr spectrum of **6** varied with solvent and reaction conditions. For example, in methylene chloride with no treatment to remove acid, there was found two broad absorptions at −80° centered at δ −2.6 and +19.1. When **6** was prepared in methylene chloride–trichlorofluoromethane (1:1), the ^{19}F nmr spectrum at −80° showed two poorly resolved doublets at δ 5.3 and +17.5. Addition of trimethyl-*N*,*N*-diethylaminosilane changed the spectrum to two well resolved doublets as was found with the calcium hydride treated reaction mixture. In another experiment **6** was prepared in a solvent mixture which was primarily trichlorofluoromethane. The ^{19}F nmr spectrum at −80° showed fairly well resolved doublets; on warming to higher temperatures, *ca.* −40 to −20°, the doublets collapsed into "mound-like" absorptions. These experiments suggest that ionization of **6** can occur. No evidence for pseudorotation has been found; however, it cannot be excluded. Other workers have not found pseudorotation in similar compounds.[2a,e,o,p]

Tetrahydrothiophene (**7**), di-*n*-propyl sulfide (**8**), diphenyl sulfide (**9**), and perfluorodiphenyl sulfide (**10**) have been allowed to react with **1** at −78°. Hydrolysis of the reaction mixtures from **7**, **8**, and **9** led to isolation of the corresponding sulfoxides, and in the case of **8** substantial amounts of sulfone was isolated which suggests that some $(CH_3CH_2CH_2)_2SF_4$ was formed. The ^{19}F nmr spectrum also suggested that this compound was present. The sulfuranes from **7** and **8** were much less thermally stable than **3** and **6** and they also underwent intermolecular fluorine exchange to much lower temperatures than did **3** and **6**. As might have been expected the sulfuranes from **9** and **10** were relatively stable. The product from **10**, *i.e.*, **11**, had absorptions

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[1] This research has been supported by the National Science Foundation and by a Public Health Service Research Grant No. CA-10737 from the National Cancer Institute.

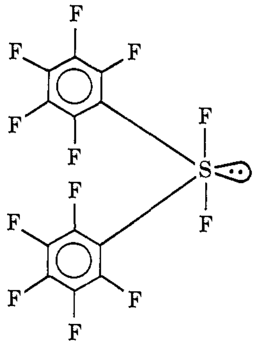
[2] (a) R. J. Arhart and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 4997 (1972). (b) R. J. Arhart and J. C. Martin, *ibid.*, **94**, 5003 (1972). (c) I. C. Paul, J. C. Martin, and E. F. Perozzi, *ibid.*, **94**, 5010 (1972). (d) J. I. Musher, *Advan. Chem. Ser.*, No. 110, 44 (1972). (e) D. T. Sauer and J. M. Shreeve, *J. Fluorine Chem.*, 1, 1, 1971. (f) R. W. La Rochelle and B. M. Trost, *J. Amer. Chem. Soc.*, **93**, 6077 (1971). (g) C. R. Johnson and J. J. Rigan, *ibid.*, **91**, 5398 (1969). (h) W. A. Sheppard, *ibid.*, **84**, 3058 (1962). (i) W. A. Shepard, *ibid.*, 5597 (1971). (j) I. Kapovitz and A. Kalman, *Chem. Commun.*, 649 (1971). (k) D. Harrington, J. Weston, J. Jacobus and K. Mislow, *J. Chem. Soc., Chem. Commun.*, 1079 (1972). (l) D. C. Owskey, G. K. Helmkamp, and R. F. Rettig, *J. Amer. Chem. Soc.*, **91**, 5239 (1969). (m) G. E. Wilson, Jr., and M. M. Yang Chang, *Tetrahedron Lett.*, 875 (1971). (n) D. Swern, I. Ikeda, and G. F. Whitfield, *ibid.*, 2635 (1972). (o) W. A. Sheppard and D. W. Ovenall, *Org. Magn. Resonance*, **4**, 695 (1972). (p) D. G. Ibbott and A. F. Janzen, *Can. J. Chem.*, **50**, 2428 (1972).

[3] The use of calcium hydride and the alternate warming and cooling procedure resulted from variations in a number of experimental variables. In subsequent experiments trimethyl-*N*,*N*-diethylaminosilane has been used to remove acid.[2p]

[4] F. G. Bordwell and W. A. Hewett, *J. Org. Chem.*, **23**, 636 (1958).

[5] R. Tang and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 5644 (1969).

at −80° in its ^{19}F nmr spectrum at −19.4, +130, +133, +142, and +155 in the ratio 2:2:2:2:4. Such a spectrum could arise from **11** if the ortho fluorines



11

are nonequivalent, which is not unreasonable.[6] Further work on these compounds and related materials is in progress and details will be reported in a subsequent publication.

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(6) The difluorosulfurane 11 has also been prepared by W. A. Sheppard, Du Pont Central Research Department, from reaction of pentafluorophenyllithium and sulfur tetrafluoride. A detailed ^{19}F nmr study of compound 11 will be published by Sheppard, Ovenall, Meakin, Jesson, and Read of Du Pont. By private communication with Dr. Sheppard, our preliminary observations agree with their detailed studies.

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Consecutive 1,2- and 1,4-Trimethylsilyl Shifts in the Anionic Rearrangement of 1,1-Bis(trimethylsilyl)-1,2-diphenylethane[1]

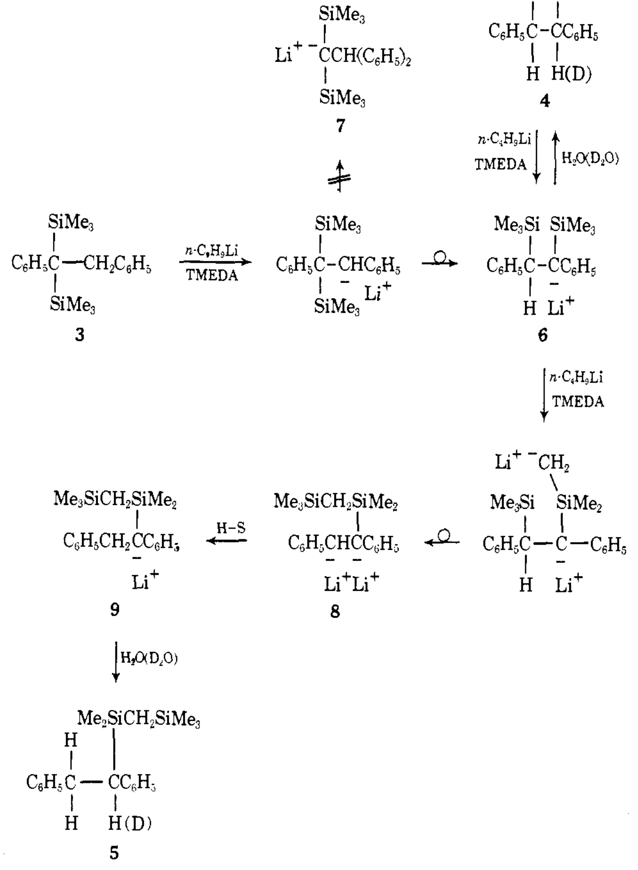
Sir:

Although 1,2 shifts of trialkylsilyl groups between anionic nitrogen centers have been amply established by the excellent studies of West and coworkers,[2] little is known about such shifts between carbanionic sites.[3] Even though treatment of $(Cl_3Si)_2CHCH_3$ with either methyllithium or methyl Grignard reagents leads to a mixture of $[(CH_3)_3Si]_2CHCH_3$ (**1**) and $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$ (**2**), it was shown that **1** and **2** are not interconverted by the action of the methyl organometallic reagents.[4] Consequently, a cationic 1,2 silyl shift, induced by metallic halides, seems to be a more reasonable cause of this rearrangement,[3] rather than a 1,2 shift involving carbanions.

As part of our interest in 1,2-carbanionic shifts,[5] therefore, we undertook a search for a genuine carbanionic 1,2-trialkylsilyl rearrangement. Investigation of the behavior of 1,1-bis(trimethylsilyl)-1,2-diphenylethane (**3**) toward butyllithium not only uncovered a genuine carbanionic 1,2-trialkylsilyl shift but a subsequent 1,4-trialkylsilyl shift as well. Thus, treatment of a solution of **3** in *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA) with a fourfold excess of butyllithium in hexane gave, after 4 days at 25°, 5% of 1,2-bis(trimethylsilyl)-1,2-diphenylethane (**4**) and, unexpectedly, 90% of 1-[dimethyl(trimethylsilylmethyl)silyl]-1,2-diphenylethane (**5**). Work-up of a similar reaction mixture with deuterium oxide and nmr spectral examination showed that both **4** and **5** were deuterated only at the benzylic position. The structural assignment of **5** follows from (a) elemental and mass spectral analysis (prominent *m/e* peaks at 70 eV, 326 parent, 180 ($C_6H_5CH{=}CHC_6H_5$) and 145 ($Me_3SiCH_2SiMe_2$)), (b) cleavage with alcoholic KOH solution[6] to yield bibenzyl, and (c) nmr spectral data (δ relative to Me_3Si of **5** as 0, neat) −0.29, 2 H (Si-CH_2-Si); 0, 15 H (Me_3Si,Me_2Si); 2.30, 1 H (t) (1-CH-$SiMe_3$); 3.30, 2 H (d) (2-CH_2); and 7.00, 10 H (s) (2-C_6H_5). The identity of **4** was established by comparison with an authentic sample prepared in a well-established manner.[7]

The mechanism of formation of **4** from **3** can be readily depicted in an anionic fashion, as shown in Scheme I: metalation of **3** at the benzylic position and the 1,2 shift of the trimethyl group to yield the anion **6** of **4**. The absence of any sign of **7** shows, as a bonus,

Scheme I



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(1) Part IX of a series devoted to "Rearrangements of Organometallic Compounds"; the following reports are considered as predecessors: J. J. Eisch and G. R. Husk, *J. Organometal. Chem.*, **4**, 415 (1965); **14**, P13 (1968); **25**, C33 (1970); **26**, C1 (1971); **30**, C97 (1971); **30**, 167 (1971); **38**, 209 (1972); **43**, C17 (1972).

(2) *Cf.* R. West and B. Bichlmeir, *J. Amer. Chem. Soc.*, **94**, 1649 (1972), and references cited therein.

(3) The 1,2 shifts of trichlorosilyl groups between carbon centers have been described previously; *cf.* V. F. Mironov and V. V. Nepomnina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1795 (1961); *Chem. Abstr.*, **56**, 8735 (1962). However, such shifts are effected by $AlCl_3$ and HCl and thus presumably involve carbenium ionic intermediates.

(4) (a) S. Nozakura, *Bull. Chem. Soc. Jap.*, **29**, 660 (1956), and (b) G. Fritz and G. Sonntag, *Z. Anorg. Allg. Chem.*, **332**, 41 (1963).

(5) J. J. Eisch and C. A. Kovacs, *J. Organometal. Chem.*, **25**, C33 (1970); **30**, C97 (1971).

(6) M. C. Musolf and J. L. Speier, *J. Org. Chem.*, **29**, 2519 (1964).

(7) C. R. Hauser and C. R. Hance, *J. Amer. Chem. Soc.*, 74, 5091 (1952).