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6 Trifluoromethylsulfur Trifluoride. An Improved Synthesis, New NMR Data and Stereochemistry.

by R. W. Braun, A. H. Cowley, M. C. Cushner

10 and R. J. Lagow*

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

An improved synthesis of CF_3SF_3 has been devised which involves the direct fluorination of CF_3SSCF_3 in a continuous flow reactor. ^{13}C and variable temperature ^{19}F NMR data have been acquired for CF_3SF_3. These data indicate that the CF_3 group occupies an equatorial site on an idealized trigonal bipyramidal structure. The barrier to intramolecular fluorine exchange in CF_3SF_3 is unusually high (> 17 kcal/mole).

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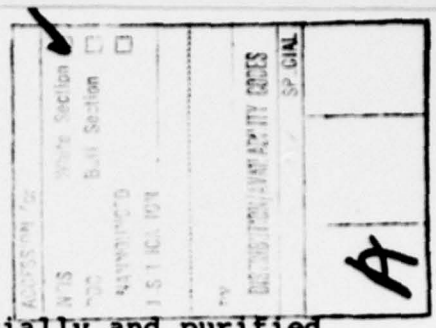
Trifluoromethylsulfur Trifluoride. An Improved Synthesis, New NMR Data and Stereochemistry

R. W. Braun, A. H. Cowley,* M. C. Cushner, and R. J. Lagow*

Received _____

Trifluoromethylsulfur trifluoride has been prepared by the action of F_2 or oxidative fluorinating agents on CS_2, CF_3SCl, or $(CF_3S)_2CS$.[1] However, the commercial availability of CF_3SSCF_3 renders this compound an ideal starting point for the one-step synthesis of CF_3SF_3. The conversion $CF_3SSCF_3 \rightarrow 2\ CF_3SF_3$ has, in fact, been accomplished previously by treatment with CF_3OF,[1c] ClF_3,[2] or F_2.[1c] However, the CF_3OF and ClF_3 reactions are difficult to control, and the direct fluorination involved a labor intensive batchwise method. The present paper describes a greatly improved procedure for direct fluorination of CF_3SSCF_3 which avoids handling molecular fluorine in Pyrex glass.

Trifluoromethylsulfur trifluoride is generally thought to possess an essentially trigonal bipyramidal geometry in which the CF_3 moiety adopts an equatorial location. However, in view of the controversy which has surrounded the delineation of the ground state geometry of the analogous phosphorane, CF_3PF_4,[3] it seemed appropriate to reinvestigate the stereochemical features of CF_3SF_3 by means of ^{19}F dynamical NMR (dnmr) spectroscopy.[4] Furthermore, since erroneous results had been obtained in dnmr studies of SF_4 in Pyrex glass NMR tubes[5] it was decided to employ quartz NMR tubes and an HF scavenger in the present study. Finally, we report the first ^{13}C NMR data for CF_3SF_3.



Experimental Section

The compound CF_3SSCF_3 was obtained commercially and purified by fractional vacuum condensation prior to use. The four-zone cold reactor fluorination system has been described previously.[6] A typical reaction involved the injection of 2.0 g of CF_3SSCF_3 into the reactor, the second zone of which was maintained at -120° by means of thermostatically controlled liquid nitrogen cooling. The helium flow was set at 60 ml/min and the fluorine flow at 1 ml/min. Various reaction times were investigated; the optimum time was discovered to be 38 h. Longer reaction times resulted in the production of CF_3SF_5. After 72 h fluorination CF_3SF_5 was the only major product. After 38 h the fluorine flow was terminated and the reactor was allowed to assume ambient temperature. The products which had collected in a glass trap were transferred to a standard glass high vacuum line and subjected to fractional distillation with U-traps held at -93, -110, and -196°. The -196° trap contained CF_3SOF plus traces of SF_6, SF_4, CF_4, and COF_2. The desired product condensed in the -110° trap. Based on the CF_3SSCF_3 consumed, the conversion to CF_3SF_3 was ~90%.

NMR samples were run both with and without $(C_6H_5)_3PNH$ present as HF scavenger. No spectral differences were discerned throughout the temperature ranges studied. In each experiment the CF_3SF_3 had been stored briefly over NaF prior to distillation into the quartz NMR cell. Preliminary ^{19}F NMR samples were run in 5 mm quartz tubes on a Varian 56/60 instrument. The variable temperature ^{19}F NMR experiments were conducted on a Varian HA 100 spectrometer. The ^{13}C NMR measurements were made on 10 mm quartz tubes on a Brucker WH 90

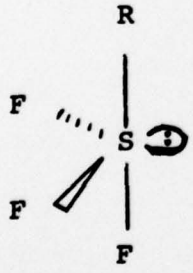
spectrometer operating in the FT mode.

Results and Discussion

We have found that CF_3SF_3 can be prepared in approximately 90% yields by the direct fluorination of CF_3SSCF_3 in a continuous flow reactor which features helium dilution and maintenance of the substrate at -120°. The reaction times were found to be critically important. Optimum yields of CF_3SF_3 are produced after a 38 h run; extension of reaction times beyond 38 h generates progressively larger quantities of CF_3SF_5. After 72 h essentially complete conversion to CF_3SF_5 occurs.

The ^{19}F NMR data for CF_3SF_3 are displayed in Figure 1, and the F axial (F_a) and F equatorial (F_e) chemical shift and $J_{F_aSF_e}$ coupling constant data have been assembled in Table I, along with those for analogous RSF_3 sulfuranes which feature sulfur-carbon bonds, viz. alkyl, perfluoroalkyl, C_6H_5 or C_6F_5 substituents.

Two trigonal bipyramidal models can be considered for RSF_3 molecules,



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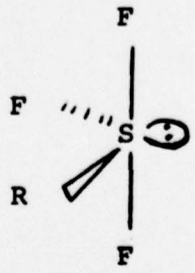

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It is clear that both the axially substituted model, 1, and the equatorially substituted model, 2, will yield AX_2 (or AB_2) ^{19}F

NMR spectral patterns under the condition of slow ligand permutation. The differentiation of the structures must, consequently, rely on ^{19}F chemical shift data. The F_a and F_e chemical shift assignments in Table I exhibit a very consistent pattern. The premise upon which these assignments are based is that CH_3SF_3 must adopt structure 2 because of the very small apicophilicity of the CH_3 group.[7] It may, therefore, be concluded that CF_3SF_3, like the other C-S bonded compounds prefers structure 2.

The ^{19}F NMR spectra of CF_3SF_3 are unchanged up to 75°C, thus implying a barrier to intramolecular fluorine exchange in excess of 17 kcal/mole. The conformational stability of CF_3SF_3 is remarkable in view of the fact that fluorine exchange in the phosphorane analogs, CF_3PF_4 and $(CF_3)_2PF_3$, persists down to -150°.[3]

The ambient temperature ^{13}C NMR spectrum of CF_3SF_3 consists of the anticipated 24 line spectrum centered at 122 ppm relative to external $(CH_3)_4Si$ (Figure 2) with J_{CF} = 323.6, J_{F_aSC} = 11.8, and J_{F_eSC} = 19.1 Hz. These data confirm the stereochemical rigidity of CF_3SF_3 at ambient temperature. The fact that J_{F_eSC} is slightly larger than J_{F_aSC} may be a reflection of the fact that the equatorial plane of a trigonal bipyramid features more sulfur 3s character than the axes. The differences in the axial and equatorial F-S-C couplings may be useful for the stereochemical assay of fluorosulfuranes.

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Table I. Nmr Data for CF_3SF_3 and Related Compounds[a]

Compound	F_a	F_e	$J_{F_aSF_e}$ (Hz)	Reference
CF_3SF_3	-52	+48	67	b
CH_3SF_3	-60	+51	72	c
$(CF_3)_2CFSF_3$	-61	+54	4.8	d
$C_6H_5SF_3$	-72	+26	53	e
$C_6F_5SF_3$	-73	+50	70	f

[a] ^{19}F chemical shifts in ppm relative to CCl_3F. Upfield shifts from CCl_3F are considered to be positive.

[b] This work. These data are in essential agreement with earlier work.

[c] Reference 4b

[d] R. M. Rosenberg and E. L. Muetterties, Inorg. Chem., 1, 756 (1962).

[e] Reference 1b

[f] P. Meakin, D. W. Ovenall, W. A. Sheppard, and J. P. Jesson, J. Am. Chem. Soc., 97, 522 (1975).

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(1) (a) E. A. Tyczkowski and L. A. Bigelow, J. Am. Chem. Soc., 75, 3523 (1953); (b) W. A. Sheppard, ibid., 84, 3058 (1962); (c) C. T. Ratcliffe and J. M. Shreeve, ibid., 90, 5403 (1968).

(2) G. H. Sprenger and A. H. Cowley, J. Fluorine Chem., 7, 333 (1976).

(3) For a summary of this controversy, see R. C. Cavell, J. A. Gibson, and K. I. The, J. Am. Chem. Soc., 99, 7841 (1977).

(4) For previous ^{19}F nmr data on CF_3SF_3 at ambient temperature or below, see (a) reference 1c and (b) W. Gombler and R. Budenz, J. Fluorine Chem., 7, 115 (1976), and references therein.

(5) W. G. Klemperer, J. K. Krieger, M. D. McCreary, E. L. Muetterties, D. D. Traficante, and G. M. Whitesides, J. Am. Chem. Soc., 97, 7023 (1975), and references therein.

(6) N. J. Maraschin, B. D. Catsikis, L. H. Davis, G. Jarvinen, and R. J. Lagow, J. Am. Chem. Soc., 97, 513 (1975).

(7) For phosphoranes the order of apicophilicity is (in part) F > Cl > Br > CF_3 > alkyl. See reference 3.

Figure Captions

Figure 1. 94.1 MHz ^{19}F nmr spectra of CF_3SF_3 at 29° C (a) axial (F_a) region, (b) equatorial (F_e) region, and (c) CF_3 region (+ 69.9 ppm relative to internal CCl_3F)

Figure 2. 22.6 MHz ^{13}C nmr spectrum of CF_3SF_3 at 30°C.

Fig. 1

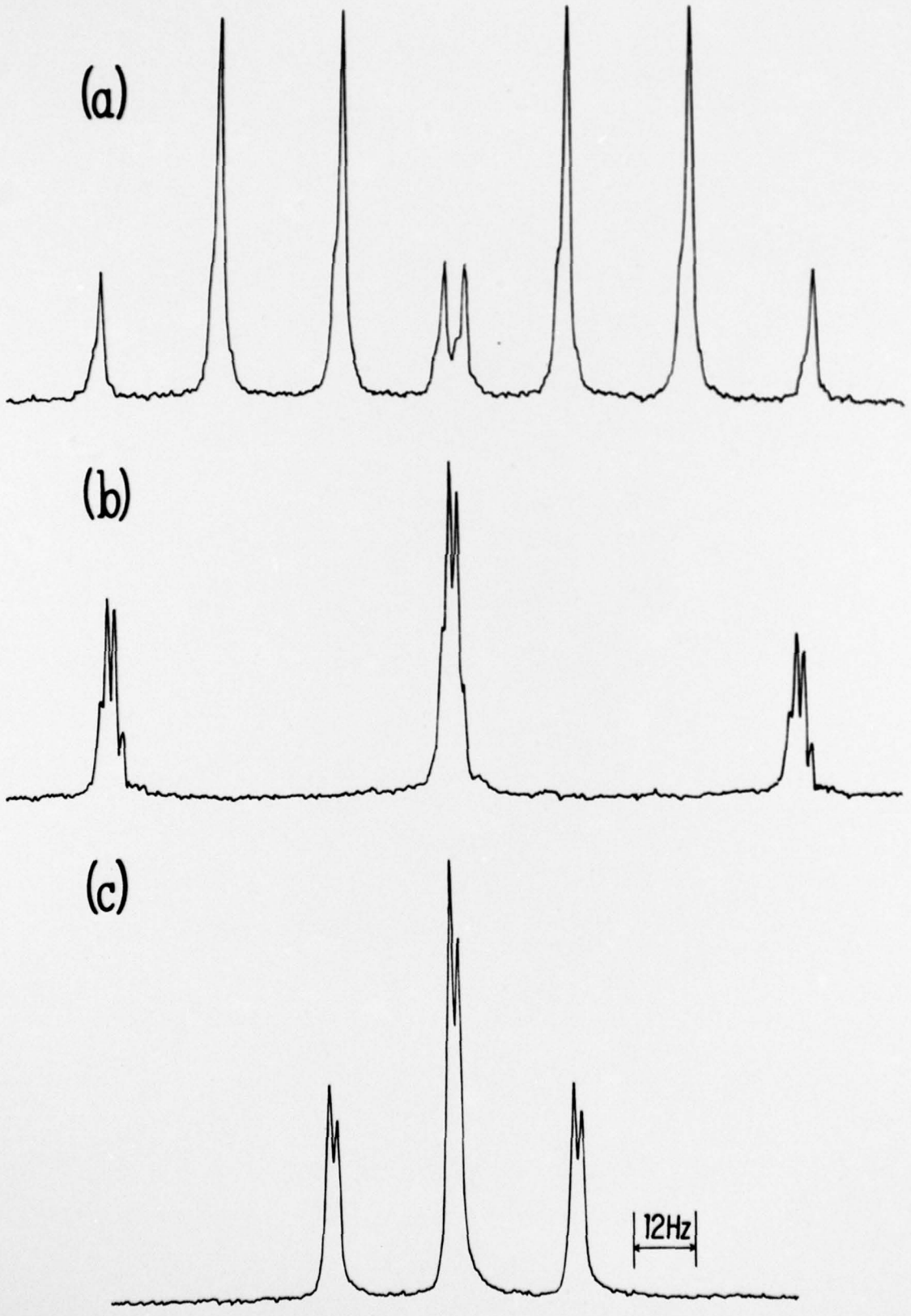

Fig. 2