(CF2NC1)3, A NEW MILD FLUORINATING REAGENT Robert L. Kirchmeier, George H. Sprenger, and Jean'ne M. Shreeve Department of Chemistry University of Idaho Moscow, Idaho U.S.A. 83843 (Received 4 April 1975)

In its reactions with compounds which contain negative chlorine,  $(CF_2NC1)_3$  exhibits a chemistry similar to that of fluorinated acyclic chloramines, i.e., formation of chlorine with a concomitant fluoride shift. For example, compare the behavior of  $(CF_3)_2NC1$  and  $(CF_2NC1)_3$  with PF\_2C1

 $(CF_3)_2NC1 + PF_2C1 \rightarrow (CF_3)_2NPC1_2F_2 + PF_3 + C1_2 + CF_3N=CF_2$  (1)  $(CF_2NC1)_3 + PF_2C1 \rightarrow PF_3 + C1_2 + (FCN)_3$ 

Regardless of the conditions investigated and the chlorine-containing reactant (RCl) used, no substituted trimer  $(CF_2NR)_3$  was isolated. The invariable generation of chlorine and accompanying fluorination prompted an examination of  $(CF_2NCl)_3$  as a mild fluorinating agent.

#### Results and Discussion

Given in Table 1 are the series of reactions of  $(CF_2NC1)_3$  that we have examined as well as the amounts and conditions used, and the results obtained. The positive nature of the N-C1 chlorine in  $(CF_2NC1)_3$  is shown by its reaction with HC1 to give chlorine, HF  $(SiF_4)$  and  $(FCN)_3$ . The compound  $(CF_2NC1)_3$  has high thermal stability and is stable in Pyrex glass vessels at ambient temperature for at least three weeks. It is an involatile colorless liquid (~1 Torr at  $25^{\circ}$ ) and is most easily handled via syringes or pipettes. It can be transferred under dynamic vacuum, and, under conditions of low humidity, it can be exposed for short periods to the atmosphere with little or no decomposition.

Methylsulfinyl fluoride (CH<sub>3</sub>S(0)F) is obtained in good yields from the reaction of CH<sub>3</sub>S(0)Cl with either (CF<sub>2</sub>NCl)<sub>3</sub>, NaF, or CsF. Reaction times were 1 hr, 12 hr, and 1 hr, respectively. The compound is unstable and decomposes rapidly in glass to give CH<sub>3</sub>SO<sub>2</sub>SCH<sub>3</sub>, CH<sub>3</sub>SO<sub>2</sub>F, CH<sub>3</sub>SSCH<sub>3</sub>, SiF<sub>4</sub>, and a non-vola-tile liquid. The decomposition is similar to that observed for CH<sub>3</sub>S(0)Cl or CH<sub>3</sub>SCl. (2)

Reactant (mmol)	Conditions <sup>O</sup> C, hr	Product (% Yield)
H <sub>2</sub> O (excess) <sup>a</sup>	25, 36	$c-(CINCO)_3$ , $c-(HNCO)_3$ , $c(O)NCIC(O)NCIC(O)NH$ , $c(O)NHC(O)NCIC(O)NH$ , $siF_4$
CF <sub>3</sub> C(0)Br (3.0) <sup>a</sup>	25, 72	CF <sub>3</sub> C(0)Br(37), CF <sub>3</sub> C(0)F(55), SiF <sub>4</sub> , (FCN) <sub>3</sub> , Br <sub>2</sub> , Cl <sub>2</sub>
C1NO (3.0) <sup>a</sup>	25, 1	FNO, $(FCN)_3$ , $(NO)_2S1F_6$ , $C1_2$
PF2C1 (3.0) <sup>a</sup>	25, 1	(FCN) <sub>3</sub> (91), PF <sub>3</sub> , Cl <sub>2</sub>
SO <sub>2</sub> FC1 (3.0) <sup>a</sup>	25, 1	$SO_2F_2$ , (FCN) <sub>3</sub> , SiF <sub>4</sub> , Cl <sub>2</sub>
HC1 (3.0) <sup>a</sup>	-78, 1	$sif_4$ , (FCN) <sub>3</sub> , $cl_2$
CF <sub>3</sub> SC1 (1) <sup>c</sup>	25, 1	$CF_3SSCF_3$ , $C1_2$ , (FCN) <sub>3</sub> , $CF_3S(0)F$
CF3SSC1 (1) <sup>C</sup>	25, 12	No reaction
CF <sub>3</sub> C(0)SC1 (1.0) <sup>c</sup>	25, 3	$CF_{3}C(0)SF$ , (FCN) <sub>3</sub> , $Cl_{2}$
CF <sub>3</sub> S(0)C1 (1.0) <sup>c</sup>	25, 2	$CF_{3}S(0)F$ , (FCN) <sub>3</sub> , $Cl_{2}$
CF3CC12SC1 (1.0) <sup>c</sup>	25, 3	CF3CC12-nFnSC1, C12, (FCN)3
NaF (excess) <sup>a</sup>	140	No reaction
CsF (excess) <sup>a</sup>	140	N <sub>2</sub> O, COF <sub>2</sub> , (FCN) <sub>3</sub> , unidentified solid
(CF <sub>3</sub> ) <sub>2</sub> NO· (3) <sup>a</sup>	100, 0.25	(CF <sub>3</sub> ) <sub>2</sub> NO· (93%) recovered
(CF3)3COH (3) <sup>a</sup>	75, 12	No reaction
(CF <sub>2</sub> NC1) <sub>3</sub> <sup>a</sup>	120, 18	No decomposition
(CF <sub>2</sub> NC1) <sub>3</sub> <sup>a</sup>	350, 0.1	CF3Cl, CF3C(0)Cl, COF2, SiF4, CF3NCF2, (FCN)3, Non-condensables (10), unidentified solid <sup>d</sup>

Table 1 Reactions of (CEaNC1)a

<sup>a</sup>1 mmol of (CF2NC1)3; <sup>b</sup>the compounds were identified by mass spectra only; <sup>C</sup>0.5 mmol of (CF2NC1)3; <sup>d</sup>the solid gave rise to mass spectral peaks corresponding to CF2NCF2C1<sup>+</sup>, CFNCF2C1<sup>+</sup>, CF2NC1<sup>+</sup> and CF2C1<sup>+</sup>.

 $\begin{array}{rcl} \mathrm{CH}_3\mathrm{S}(\mathrm{O})\mathrm{F} & \xrightarrow{250} & \mathrm{CH}_3\mathrm{SO}_2\mathrm{F} + \mathrm{CH}_3\mathrm{SF} & (99\% - 10 \text{ minutes}) \\ \\ \mathrm{CH}_3\mathrm{SF} & \longrightarrow & \mathrm{CH}_3\mathrm{SSCH}_3 + \mathrm{CH}_3\mathrm{F} + \mathrm{CH}_3\mathrm{SF}_3 \text{ (spontaneous)} \\ \\ \mathrm{3 \ CH}_3\mathrm{S}(\mathrm{O})\mathrm{F} + \mathrm{H}_2\mathrm{O} & \longrightarrow & \mathrm{CH}_3\mathrm{SO}_2\mathrm{SCH}_3 + \mathrm{CH}_3\mathrm{SO}_2\mathrm{F} + 2\mathrm{HF} \end{array}$ 

The stability of  $CH_3S(0)F$  in glass is increased from minutes at  $25^{\circ}$  to three or four weeks at  $25^{\circ}$  in the presence of CsF or NaF which will complex any HF formed.

Methylsulfinyl chloride was reacted with trimethylamine in an attempt to obtain  $(CH_2S(0))$ ; however, the only product found, in addition to trimethylammonium chloride, was  $CH_3S(0)CH_2S(0)C1$ . The latter was identified by its mass spectrum only which contained major fragments at m/e 160  $(CH_3S(0)CH_2S(0)C1^+)$ , 125  $(P^+ - 35)$ , and 63  $(CH_3S(0)^+)$ . When a similar reaction was run with methylsulfinyl fluoride,  $CH_3SSCH_3$ ,  $CH_3SO_2SCH_3$ , and an unidentified non-volatile liquid were obtained.

The reaction of  $CF_3C(0)SC1$  with  $(CF_2NC1)_3$  in a Ke1-F nuclear magnetic resonance tube gave rise to a resonance at + 288 ppm relative to Freon 11. Such a large positive chemical shift is in the region associated with sulfenyl fluorides, and indicates the presence of  $CF_3C(0)SF$ . Subsequent attempts to characterize this sulfenyl fluoride further led only to decomposition. When

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the synthesis of this sulfenyl fluoride was also attempted with CsF, no S-F resonance was observed in the nuclear magnetic resonance spectrum, and only  $CF_2C(0)F$  (by infrared spectra) and elemental sulfur were identified.

The fluorination of  $CF_3CCl_2SCl$  is of particular interest. It is reported in the literature that the fluorination of  $CCl_3SCl$  with KF gives rise to a series of isomeric sulfinyl chlorides. (3) The compounds  $CCl_{3-n}F_nSF$  were reported to be sufficiently stable at  $-50^\circ$  to be observed using nuclear magnetic resonance. At room temperature, however, (in the gas phase at pressures greater than 10 Torr or in the liquid phase) they rapidly rearrange to give  $CCl_{3-n}F_nSCl$ . The compound  $NF_2CCl_2SCl$  (4) is reported to give the stable sulfenyl fluoride  $NF_2CCl_2SF$  upon fluorination with  $HgF_2$ . This sulfenyl fluoride shows no tendency to undergo rearrangement to  $NF_2CClFSCl$ . On the other hand, when  $NF_2CCl_2SCl$  is fluorinated with activated KF, 70% of the product is  $CF_3NSF_2$ . We find with  $CF_3CCl_2SCl$ , that fluorination with  $(CF_2NCl)_3$  or KF gives rise to new C-F resonance peaks in the  $^{19}F$  nmr spectrum at  $25^\circ$  but shows no sulfur-fluorine resonance. The stability of these sulfenyl fluorides may be related to the susceptibility of the carbon alpha to the sulfur to nucleophilic attack by the fluorine bonded to the sulfur.

### Experimental

Cyanuric fluoride (Cationics Inc.) and CIF (Ozark-Mahoning) were obtained commercially.  $CF_3SC1$  (5),  $CF_3SSC1$  (6),  $CF_3C(0)SC1$  (7), and  $CF_3S(0)C1$  (8) were synthesized by literature methods.  $CF_3CC1_2SC1$  was synthesized as described below. All reactions were carried out in either a 75 ml stainless steel Hoke vessel or a 25 ml Pyrex vessel equipped with a Rotaflo TF 2/13 Teflon stopcock. Compounds with the exception of  $(CF_2NC1)_3$  were handled by conventional vacuum line techniques.

Varian A-60 and HA-100 nuclear magnetic resonance spectrometers were used for proton and fluorine spectra, respectively, with tetramethylsilane and Freon 11 as internal standards. A 7 cm Pyrex cell equipped with KBr or NaCl windows was used for gas-phase infrared spectra. Gas chromatographic separations were accomplished by using columns constructed of 0.25 in. copper tubing packed with 20% Kel-F No. 3 polymer oil on Chromosorb P. The Kellogg-Cady method was used for vapor pressure determinations. (9) Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E mass spectrometer at ionizing potentials of 17 and 70 eV. Elemental analyses were performed by Beller Laboratories, Göttingen, Germany.

# (CF<sub>2</sub>NC1)<sub>3</sub>

When a three-fold molar excess of C1F was reacted with  $(FCN)_3$ ,  $(CF_2NC1)_3$ was synthesized. Typically, 32 mmol of C1F were combined with 10 mmol of  $(FCN)_3$ in a 75 ml stainless steel Hoke vessel. Yields ranged from 10 to 90% and were apparently dependent on the quality of C1F (Ozark Mahoning) used. The boiling point  $(425^{\circ}K)$ , molar heat of vaporization (9.65 kcal/mol), and Trouton constant (22.8 eu), were determined from a plot of log  $P_{Torr}$  versus  $1/T^{\circ}K$ . The mass spectrum shows fragments at m/e values assigned to  $(CF_2NC1)_2^+$ ,  $(FCN)_3^+$ , and many smaller fragments. The fluorine nuclear magnetic resonance spectrum contains a singlet resonance at + 72.7 ppm relative to Freon 11. The infrared spectrum has absorption bands at 1295 m sh, 1277 s, 1260 s, 1210 m, 1170 w, 1130 s, 1010 w, 967 m, 840 m, 778 m, 734 w, 590 w, 490 w, and 443 cm<sup>-1</sup>w.

Anal. Calcd: C, 12.12; N, 14.14; F, 38.38, Cl, 35.35. Found: C, 12.17; N, 14.10; F, 37.5; Cl, 35.17.

# CH2S(0)F

The reaction between  $CH_3S(0)C1$  and  $(CF_2NC1)_3$  at  $25^\circ$  for 1 hr gave good yields of  $CH_3S(0)F$ . Methylsulfinyl fluoride was also synthesized by the reaction between  $CH_3S(0)C1$  and NaF (12 hr at  $25^\circ$ ) or CsF (1 hr at  $25^\circ$ ). The infrared spectrum shows strong absorption bands at 1220 brd, and 702, cm<sup>-1</sup>. The mass spectrum contains a parent ion at m/e 82, P<sup>+</sup>-19, and others indicative of the molecule  $CH_3S(0)F$ . The proton nuclear magnetic resonance spectrum consists of a doublet (J=16.5 Hz) at  $\delta 2.69$ . The fluorine spectrum has a peak at about + 3 ppm relative to Freon 11. The compound was too unstable to obtain either vapor pressure data or an elemental analysis.

CF3CC12SC1

 $CF_3CCl_2SCl$  was synthesized in 50 to 75% yields via the reaction of  $CF_3C(0)SCl$  and  $PCl_5$  at 55° for 36 hr. It was purified by reaction with  $Al_2Cl_6$  (to remove POCl\_3), followed by low temperature trap-to-trap distillation. A plot of log P versus  $1/T^{O}K$  gives an extrapolated boiling point of  $349^{O}K$ . Decomposition began to occur above  $330^{O}K$ . The fluorine nuclear magnetic resonance spectrum has a resonance band at + 77.2 ppm relative to Freon 11. A vapor phase molecular weight determination gave a value of 219. The mass spectrum has parent ion at m/e 218, P<sup>+</sup>-35 at m/e 183, and other fragments characteristic of the compound  $CF_3CCl_2SCl$ . The infrared spectrum has absorption bands at: 1242 s, 1217 vs, 1160 w, 908 w, 868 m, 837 w, and 717 cm<sup>-1</sup>w.

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