

Received: June 7, 1986; accepted: July 10, 1986

PREPARATION AND SOME REACTIONS OF 2,3,5,6-TETRAFLUOROBENZENESULFENYL CHLORIDE

PAUL F. BUTLER and MICHAEL E. PEACH

Chemistry Department, Acadia University, Wolfville, N.S., BOP 1X0 (Canada)

## SUMMARY

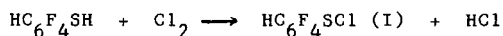
2,3,5,6-Tetrafluorobenzenesulfenyl chloride was prepared from the thiol and chlorine. Its reactions with olefins, ammonia, aromatic and heterocyclic compounds show that it acts as a typical sulfenyl chloride and several new compounds have been isolated. These were characterized by elemental analysis, as well as by NMR (H-1 and F-19), mass and infrared spectroscopy.

## INTRODUCTION

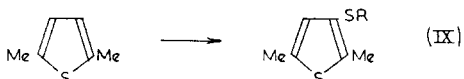
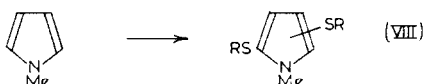
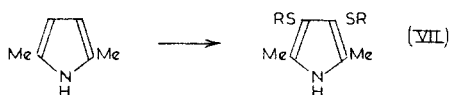
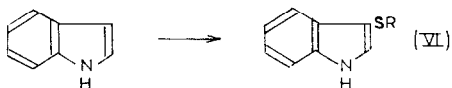
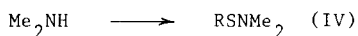
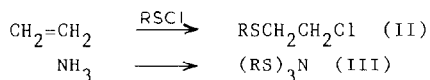
Some of the chemistry of 2,3,5,6-tetrafluorobenzenethiol has recently been reported [1]. The reactions described used the thiol or its metallic derivatives as a source of the 2,3,5,6-tetrafluorophenylthio group. In these compounds the polarity is  $\text{HC}_6\text{F}_4\overset{\delta-}{\text{S}}\overset{\delta+}{\text{X}}$  (X = H or metal) and the tetrafluorophenyl group acts as a nucleophile. 2,3,5,6-Tetrafluorobenzenesulfenyl chloride has been prepared. The polarity of the sulfenyl chloride is  $\text{HC}_6\text{F}_4\overset{\delta+}{\text{S}}\overset{\delta-}{\text{Cl}}$  and the tetrafluorophenylthio group acts as an electrophile. Several new compounds have been prepared using 2,3,5,6-tetrafluorobenzenesulfenyl chloride, involving addition and electrophilic substitution reactions.

## RESULTS AND DISCUSSION

2,3,5,6-Tetrafluorobenzenesulfenyl chloride, a high boiling yellow orange liquid, is readily prepared from tetrafluorobenzenethiol and chlorine in a sealed tube [2]. Various reactions of the sulfenyl chloride have been



studied, including addition to an olefinic bond and substitution at carbon and nitrogen. The reactions are shown below (RSCl =  $\text{p-HC}_6\text{F}_4\text{SCl}$ ).



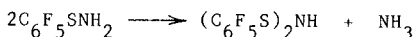
The reactions observed are similar to those reported for the somewhat analogous sulfonyl chlorides, pentafluorobenzene- and trifluoromethanesulfonyl chlorides [3-7]. Various addition reactions of pentafluorobenzene-sulfonyl chloride have been reported [3,5], including addition to alkenes and

$$\text{C}_6\text{F}_5\text{SCl} + \text{CH}_2=\text{CH}_2 \longrightarrow \text{C}_6\text{F}_5\text{SCH}_2\text{CH}_2\text{Cl} \quad (\text{ref. 3})$$

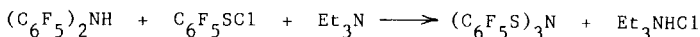
alkynes. These addition reactions are characteristic of sulfonyl chlorides.

Substitution reactions of pentafluorobenzene-sulfonyl chloride have been observed at carbon in aromatic and heterocyclic compounds and at nitrogen [3,4].

The reactions of sulfonyl chlorides with nitrogen-hydrogen bonds are somewhat complicated. In the reaction of pentafluorobenzene-sulfonyl chloride with ammonia in ether both the mono- and di-substituted products,  $\text{C}_6\text{F}_5\text{SNH}_2$  and  $(\text{C}_6\text{F}_5\text{S})_2\text{NH}$ , can be obtained [8,9]. The monosubstituted product is not very stable and decomposes to the disubstituted compound [9]. The tri-



substituted product is obtained from the reaction of the disubstituted product and pentafluorobenzene-sulfonyl chloride in ether in the presence of triethylamine [9]. It decomposes at its melting point [9]. Vacuum sublimation of



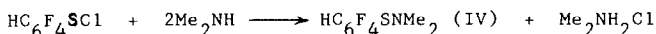
crude reaction products yields  $(\text{C}_6\text{F}_5\text{S})_2\text{NH}$  [10]. In the present study

the trisubstituted product was obtained from the reaction of 2.5 moles of ammonia with 1.0 moles of the sulfenyl chloride in a sealed tube in the presence of benzene. In an analogous reaction of pentafluorobenzenesulfenyl

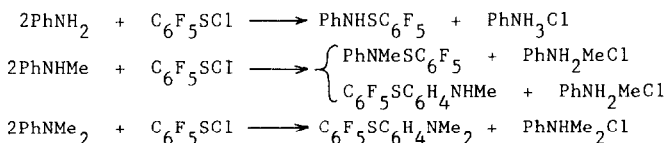
$$3\text{HC}_6\text{F}_4\text{SCl} + 4\text{NH}_3 \longrightarrow (\text{HC}_6\text{F}_4\text{S})_3\text{N} \text{ (III)} + 3\text{NH}_4\text{Cl}$$

chloride with ammonia in a sealed tube the disubstituted product,  $(\text{C}_6\text{F}_5\text{S})_2\text{NH}$ , was isolated [3].

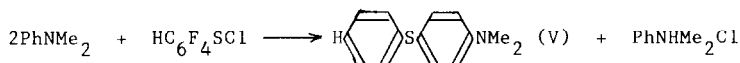
The reaction with dimethylamine was simple, there being only one possible product, formed by substitution of the N-H bond.



The reactions of the aniline derivatives,  $\text{C}_6\text{H}_5\text{NH}_x\text{Me}_{2-x}$  ( $x = 2, 1, 0$ ) with pentafluorobenzenesulfenyl chloride show substitution at the nitrogen or on the aromatic ring [4]. Electrophilic substitution of dimethylaniline was



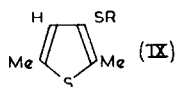
observed with 2,3,5,6-tetrafluorobenzenesulfenyl chloride.



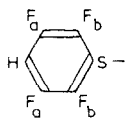
In reactions with the nitrogen containing heterocyclic compounds indole and 2,5-dimethylpyrrole substitution of the heterocyclic ring rather than the N-H bond occurred. This is in accord with reactions previously observed with sulfenyl chlorides [6,7]. With N-methylpyrrole a mixture of the products VIIa and VIIb was formed, as was the case with trifluoromethanesulfenyl chloride [7]. These could not be separated.



In the thiophene series substitution of the ring is the only possible reaction. Although pentafluorobenzenesulfenyl chloride reacts with thiophene giving the 2-substituted product [4], no reaction was observed between thiophene and 2,3,5,6-tetrafluorobenzenesulfenyl chloride under similar conditions. Monosubstitution of 2,5-dimethylthiophene occurs with sulfenyl chlorides and substitution occurred with 2,3,5,6-tetrafluorobenzenesulfenyl chloride, forming the 3-substituted product IX.



The NMR spectra, both H-1 and F-19, of the products have been examined. The proton NMR spectra, details of which are shown in Table 1, basically confirm the assigned structures. The coupling constants of the aromatic ring proton to the ortho and meta fluorines ( $J \approx 10$  and 7 Hz respectively) are



readily obtained from the aromatic region of the spectrum [1].

The fluorine NMR spectra have not been analysed in detail. The presence of two distinct multiplets of equal intensity corresponding to  $F_a$  and  $F_b$  ( $\delta$  approximately 137 and 134 ppm with reference to  $CFCl_3$  as internal standard) confirm the presence of the 2,3,5,6-tetrafluorophenyl group.

Comparison of the chemical shifts and coupling constants derived for VI, VII and IX with spectra of the  $CF_3S$  analogs confirm the assigned structures [6,7]. Similarly in the spectrum of VIII it is possible to detect the two isomers VIIIa and VIIIb, in a ratio of approximately 2:1 [7].

The mass spectra confirm the molecular weights and the infrared spectra the presence of the various functional groups.

The reactions described here show that 2,3,5,6-tetrafluorobenzenesulfonyl chloride exhibits properties that are typical of a sulfonyl chloride. The sulfonyl chloride is readily prepared and is a useful reagent for the introduction of the 2,3,5,6-tetrafluorophenylthio group into various compounds.

## EXPERIMENTAL

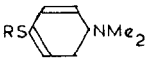
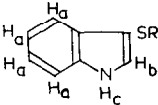
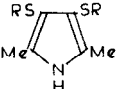
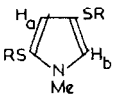
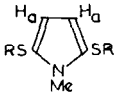
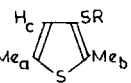
All reagents were available commercially. Microanalyses were performed by Canadian Microanalytical Services Ltd., Vancouver, B.C.. The analytical data, physical properties of the new compounds and reaction conditions are shown in Table 2. Mass spectra (70 eV) were recorded on a DuPont Model 21-451 Mass Spectrometer, using a direct introduction technique. The NMR spectra of  $CDCl_3$  solutions were recorded on a Varian EM360 L NMR Spectrometer, using TMS (H-1) and  $C_6F_6$  (F-19) as internal standards.


All reactions, except the preparation of the sulfonyl chloride, were studied on the 5-10 mmol scale.

### Method A

The thiol and an approximately 10% excess of chlorine were reacted in a sealed evacuated tube and the products were separated by low temperature distillation [2].

TABLE 1  
 Proton NMR spectra

Compound*	Chemical Shift (ppm)†	Coupling Constants (Hz)
RSCl	7.49 (ArH) TT	$J(\text{H-F}_{\text{ortho}})$ 9.7: $J(\text{H-F}_{\text{meta}})$ 7.4
RSCH <sub>2</sub> CH <sub>2</sub> Cl	3.53 (CH <sub>2</sub> ) A <sub>2</sub> B <sub>2</sub> 7.07 (ArH) TT	$J(\text{H-F}_{\text{ortho}})$ 10.0: $J(\text{H-F}_{\text{meta}})$ 6.8
(RS) <sub>3</sub> N	7.92 (ArH) TT	$J(\text{H-F}_{\text{ortho}})$ 10.4: $J(\text{H-F}_{\text{meta}})$ 7.6
RSNMe <sub>2</sub>	2.65 (Me) S 7.14 (ArH) TT	$J(\text{H-F}_{\text{ortho}})$ 10.4: $J(\text{H-F}_{\text{meta}})$ 7.2
	2.92 (Me) S 6.97 (C <sub>6</sub> H <sub>4</sub> )AA'BB' 7.03 (ArH) TT	$J(\text{H-F}_{\text{ortho}})$ 9.6: $J(\text{H-F}_{\text{meta}})$ 7.0
	6.87 (ArH) TT 7.27 (H <sub>a</sub> ) M 7.53 (H <sub>b</sub> ) D 8.26 (H <sub>c</sub> ) S broad	$J(\text{H-F}_{\text{ortho}})$ 10.0: $J(\text{H-F}_{\text{meta}})$ 7.0 J 2.8
	2.36 (Me) S 6.83 (ArH) TT 7.25 (NH) S	$J(\text{H-F}_{\text{ortho}})$ 10.0: $J(\text{H-F}_{\text{meta}})$ 7.2
	3.73 (Me) S 6.73 (H <sub>a</sub> ) D 7.01 (H <sub>b</sub> ) D 7.04 (ArH) TT	$J_{3,5} \sim 1.5$ $J(\text{H-F}_{\text{ortho}})$ 10.0: $J(\text{H-F}_{\text{meta}})$ 7.6
	3.83 (Me) S 6.59 (H <sub>a</sub> ) S 7.04 (ArH) TT	$J(\text{H-F}_{\text{ortho}})$ 10.0: $J(\text{H-F}_{\text{meta}})$ 7.6
	2.37 (Me <sub>a</sub> ) S 2.54 (Me <sub>b</sub> ) S 6.58 (H <sub>c</sub> ) S 6.98 (ArH) TT	$J(\text{H-F}_{\text{ortho}})$ 9.6: $J(\text{H-F}_{\text{meta}})$ 7.4

\* R =  (H designated as ArH in table)

† Solvent CDCl<sub>3</sub>; TMS internal standard

TABLE 2

Physical properties, yields and chemical analyses of new compounds

Compound, Color	m.p. (°C)	Method <sup>†</sup>	Yield (%)	Found (%)			Calculated (%)		
				C	H	N	C	H	N
I, orange	27/2.5*	A, 1:1	95	33.2	0.5	-	33.3	0.47	-
II, white	38-9	B, 1:1	38	39.2	1.95	-	39.3	2.06	-
III, off white	72-4	B, 1:2.5	10	38.5	0.54	2.76	38.8	0.54	2.51
IV, beige	50-2	B, 1:2	19	42.4	3.12	6.15	42.7	3.13	6.22
V, white	107-10	C, 1:1	13	55.5	3.56	4.49	55.8	3.68	4.65
VI, white	114-18	C, 1:1	23	56.3	2.61	4.36	56.6	2.37	4.71
VII, light brown	179-81	C, 1:1	26	47.2	1.91	3.07	47.4	1.99	3.07
VIII, yellow	76-8	D, 1:0.7	18	46.2	1.66	3.18	46.3	1.60	3.17
IX, yellow	48-9	D, 1:0.7	21	49.0	2.76	22.1 <sup>‡</sup>	49.3	2.76	22.0 <sup>*</sup>

\* b.p. °C/mm Hg

<sup>†</sup> Method and reactant stoichiometry RSCl:X (or for I RSH:Cl<sub>2</sub>)<sup>‡</sup>SulfurMethod B

Reactions were studied in an evacuated sealed tube, using 5 mL of benzene as a solvent. The desired product was isolated from the benzene.

Method C

The sulfenyl chloride was added dropwise to a solution of the other reactant in benzene and the mixture stirred until the loss of color of the sulfenyl chloride indicated completion of the reaction. Sometimes the mixture was refluxed for 1-2 h.

Method D

As method C except that Et<sub>2</sub>O was used as the solvent and anhydrous SnCl<sub>4</sub> as catalyst.

All products, except the sulfenyl chloride, were isolated from the organic solvent and purified by recrystallization from methanol or by vacuum sublimation.

## ACKNOWLEDGEMENTS

This work was supported by the Natural Sciences and Engineering Research Council (Canada) and the SEED '85 program. Mass spectra were recorded at the Atlantic Regional Laboratory, Halifax, N.S..

## REFERENCES

- 1 R.C. Hynes and M.E. Peach, *J. Fluorine Chem.*, 31 (1986) 129.
- 2 R.J. Neil, M.E. Peach and H.G. Spinney, *Inorg. Nucl. Chem. Letters*, 6 (1970) 509.
- 3 R.J. Neil and M.E. Peach, *J. Fluorine Chem.*, 1 (1971/2) 257.
- 4 T.S. Leong and M.E. Peach, *J. Fluorine Chem.*, 5 (1975) 545.
- 5 T.S. Leong and M.E. Peach, *J. Fluorine Chem.*, 6 (1975) 145.
- 6 A. Haas and V. Hellwig, *Chem. Ber.*, 109 (1976) 2475.
- 7 A. Haas and U. Niemann, *Chem. Ber.*, 110 (1977) 67.
- 8 P. Sartori and A. Golloch, *Chem. Ber.*, 103 (1970) 3936.
- 9 P. Sartori and A. Golloch, *Chem. Ber.*, 104 (1971) 967.
- 10 M.E. Peach *Can. J. Chem.*, 45 (1967) 429.