Journal of Fluorine Chemistry, *31* (1986) 213–229

Received: November 19, 1985; accepted: December 30, 1985

DISTINCTIVE AND SOLVENT-DEPENDENT BEHAVIOUR OF SOME PER(CHLORO,FLUORO)ETHANES IN THEIR REACTIONS WITH PhSNa . COMPETING MECHANISTIC PATHWAYS IN HALOPHILIC REACTIONS [1]

LI Xing-ya*, PAN He-qi , FU Wei-min and JIANG Xi-kui

Shanghai Institute of Organic Chemistry, Academia Sinica.
345 Lingling Lu, Shanghai (China)

SUMMARY

Per(chloro,fluoro)ethanes CF_2XCCl_2Y (1) react spontaneously with PhSNa at room temperature or below to give $PhSCF_2CCl_2Y$ (2) in fair to good yield, which as well as the by-products $PhSCF_2CCl_3$ (3) and $PhSCF=CCl_2$ (4) (for 1b and 1c) are most probably produced by an anionic chain process initiated by the chlorophilic attack of PhS^- on C-Cl bonds. In case of 1c, the coexistence of two competitive reaction pathways is indicated by the two products 2b and $PhSCCl_2CF_3$ (10). The reaction rates and the product distribution have been found to be highly solvent-dependent. Products 2b, 4 and 10 all react further with PhSNa to afford multi-substituted ethylenes PhSCF=C(Cl)SPh (7) $(PhS)_2C=C(Cl)SPh$ (8) and $(PhS)_2C=C(SPh)_2$ (9).

INTRODUCTION

In the family of halogenoperfluoroalkanes, those containing only fluorine and chlorine are the least reactive in nucleophilic reactions. However, we recently reported [2] that 1,1,2-trifluoro-trichloroethane (1a), 1,1-difluorotetrachloroethane (1b) and 1,1,1-trifluoro-trichloroethane (1c) all have been found to react spontaneously at room temperature with sodium thiophenoxide

0022-1139/86/$3.50

to afford per(chloro,fluoro)alkyl phenyl sulfide 2 and 3, as well as considerable amounts of disulfide 5.

$$PhSNa + \underset{1}{CF_2XCCl_2Y} \longrightarrow \underset{2}{PhSCF_2CCl_2Y} + \underset{3}{PhSCF_2CClHY} +$$

a: X = Cl, Y = F
b: X = Cl, Y = Cl
c: X = F, Y = Cl

$$\underset{4}{PhSCF{=}CCl_2} + \underset{5}{PhSSPh}$$

Phenyl vinyl sulfide 4 was also formed from the reactions of 1b and 1c, but never from that of 1a. In this paper we wish to report not only these halophilic reactions in detail, but also the more interesting solvent dependency of the product distributions and the competing mechanistic pathways thus implicated.

RESULTS AND DISCUSSION

Reactions with $CF_2ClCFCl_2$ (1a)

Owing to its low reactivity, few reactions of 1a with nucleophiles were known. In diglyme, 1a reacts very slowly with PhSNa to give 2a and 3a in poor yields. Addition of catalytic amounts of dibenzo-18-crown-6 shorten the reaction time several-fold and increase the yield of 2a slightly. However, in polar aprotic solvents such as DMSO, HMPA and DMF, 1a reacts very smoothly with PhSNa to give excellent yield of the main product 2a (see Table 1). Formation of the by-product 3a actually becomes negligible, and the last few percentages of 5 might be derived from the oxidation of the thiophenoxide during experimental operations.

An anionic chain mechanism has been suggested (Scheme I). In comparison with other analogous mechanisms [3], Scheme I is characterized by the initial chlorophilic attack on C-Cl bonds by PhS^- and supported by the following facts: (1). The entering PhS group always ends up on CF_2, in accordance with the usual regiospecific nucleophilic additions to fluoro olefins [4]. (2). GC detection of small amounts of the intermediate olefin $CF_2{=}CFCl$.

TABLE 1

The reactions of 1a with PhSNa at room temperature [a]

$PhSCF_2CFCl_2$ (2a) $PhSCF_2CFClH$ (3a) PhSSPh (5)

conditions			% yield [b]		
solvent	additive	time(h)	2a	3a	5
Diglyme		48	13	6	25
Diglyme		168	44	9	32
Triglyme		24	68	7	17
DMSO		0.5	93(86)	0.9	3
HMPA		0.5	95	<1	1
DMF		0.5	89	1	4
DMF	H_2O(20 mmol)	48	16	18	38
DMF	CH_3OH(20 mmol)	48	10	8	31
DMF	$C_6H_5NO_2$(2.8 mmol)	0.5	85	1	7
DMF	styrene(2.6 mmol)	0.5	88	<1	4

[a] 3.78 mmol of PhSNa, 20 mmol of 1a and 7 ml of the solvent were used for each run. [b] Determined by GC or HPLC based on PhSNa; The number in parentheses is isolated yield.

$$PhS^- + \underset{1}{CF_2XCCl_2Y} \longrightarrow PhSCl + [CF_2XCClY^-] \quad (1)$$

$$[CF_2XCClY^-] \longrightarrow CF_2{=}CClY + X^- \quad (2)$$

$$PhS^- + CF_2{=}CClY \longrightarrow \underset{6}{PhSCF_2CClY^-} \quad (3)$$

$$\underline{6} + \underline{1} \longrightarrow \underline{2} + [CF_2XCClY^-] \quad (4)$$

$$\underline{6} + H^+\text{-donor} \longrightarrow \underline{3} \quad (5)$$

$$PhS^- + PhSCl \longrightarrow \underline{5} + Cl^- \quad (6)$$

Scheme I

(3). The formation of the hydrogenated by-product 3a is incompatible with a S_N2 attack on carbon. (4). The fact that water and other proton-donating species retard the reaction and increase the yield of 3a serves also as good supporting evidence for the anionic pathways. (5). No inhibition was observed when nitrobenzene [5] or styrene [6] was added. That means a $S_{RN}1$-like mechanism is rather improbable.

Reactions with CF_2ClCCl_3 (1b)

1b is much more reactive than 1a in the reactions with thiophenoxide. In polar aprotic solvents DMSO, HMPA and DMF, the reactions at room temperature are too fast to be followed by the usual GC analysis. Although they appeared to be instantaneous, the yields of the main product 2b are not as high as that of 2a both in glymes or in polar aprotic solvents while considerable amounts of phenyl vinyl ether 4 as well as 5 were formed (Table 2). However, low temperature reactions gave good yields of 2b . Thus, when the reactions were carried out at $-20^{\circ}C$ and $-55^{\circ}C$, the yields of 2b increased respectively to 88% and 93% whereas the formations of 4 and 5 were suppressed.

Although the mechanism shown in Scheme I is also valid for the reactions of 1b, it is now necessary to consider the β-scission of the intermediate carbanion 6 (here Y = Cl) to give 4.

$$\underset{\text{6b, Y = Cl}}{PhSCF_2CCl_2^-} \xrightarrow{\beta\text{-scission}} \underset{4}{PhSCF{=}CCl_2} + F^- \qquad (7)$$

Similar to the case of 1a, the reactions of 1b with PhSNa are also retarded by water. Surprisingly, however, in this case it was the yield of the vinyl sulfide 4 which was notably increased, whereas the yield of the hydrogenated product 3b was only slightly enhanced, even though more than 10 molar equivalents of water were added (Table 2).

Side reaction (7) is the main cause of the low yields of 2b since, as one of the terminations steps , it will shorten the reaction chain and indirectly favor the formation of more disulfide 5. Thus, by forming one mole of 4, three moles of

TABLE 2

The reactions of 1b with PhSNa [a]

$PhSCF_2CCl_3$ (2b) $PhSCF_2CCl_2H$ (3b) $PhSCF{=}CCl_2$ (4)

conditions				% yield [b]			
solvent	additive	temp.(°C)	time	2b	3b	4	5
Diglyme		r.t.	24 h	28	4	17	46
Triglyme		r.t.	4 h	39	3	14	41
DMSO		r.t.	5 min	46	0.8	12	28
HMPA		r.t.	5 min	29	1	19	46
DMF		19	5 min	51	0.6	12	24
DMF		-20	15 min	88	0.2	3	8
DMF		-55	15 min	93(73)	0	1	6
DMF	$C_6H_5NO_2$ (2.8 mmol)	r.t.	5 min	52	0.8	11	26
DMF	styrene	r.t.	5 min	49	0.7	12	28
DMSO	H_2O (40 mmol)	r.t.	24 h	9	2	23	53
DMF	$PhSO_2Na$	r.t.	5 min	52	0.7	10	trace

[a] PhSNa (3.79 mmol), 1b (23 mmol) and 7 ml of the solvent were used for each run, except for the trap experiment (see footnote [c]).

[b] Yields were determined by GC or HPLC analyses and based on the starting PhSNa. The number in parentheses is isolated yield.

[c] $PhSO_2SPh$ (3.8 mmol, 25% towards PhSNa) was isolated from the reaction mixture of PhSNa (15.2 mmol), 1b (31 mmol) and $PhSO_2Na$ (35 mmol) in 40 ml of DMF.

PhSNa will be exhausted. The fact that lowering the reaction temperature increases the yields of 2b and depresses the formation of 4 is intelligible based on the competition between reactions (4) and (7), because lowering temperature often favours bimolecular rather than unimolecular reactions.

Further reactions of the product 2b

Another complication of the reactions of 1b arises from the high reactivity of the main product 2b towards PhSNa. If 1b is not in great excess, bis-, tris- and tetra -(phenylthio)ethylenes 7, 8 and 9 are also formed. When PhSNa is in great excess, 9 and disulfide 5 will be the only products. Scheme II can rationalize the formation of 7, 8 and 9. This mechanism is supported by the experiments using 2b as the

$$\underset{\underline{2b}}{PhSCF_2CCl_3} + PhS^- \longrightarrow PhSCl + \underset{\underline{6b}}{PhSCF_2CCl_2^-} \quad (8)$$

$$\underline{6b} \longrightarrow \underset{\underline{4}}{PhSCF{=}CCl_2} + F^- \quad (7)$$

$$\underline{4} + PhS^- \longrightarrow PhS\bar{C}F\text{-}C(Cl)_2SPh$$

$$PhS\bar{C}F\text{-}C(Cl)_2SPh \xrightarrow{-Cl^-,\beta\text{-scission}} \underset{\underline{7}}{PhSCF{=}C(Cl)SPh} \quad (9)$$

$$\underline{7} + PhS^- \longrightarrow (PhS)_2CF\text{-}\bar{C}(Cl)SPh$$

$$(PhS)_2CF\text{-}\bar{C}(Cl)SPh \xrightarrow{-F^-} \underset{\underline{8}}{(PhS)_2C{=}C(Cl)SPh} \quad (10)$$

$$\underline{8} + PhS^- \longrightarrow (PhS)_2\bar{C}\text{-}C(Cl)(SPh)_2$$

$$(PhS)_2\bar{C}\text{-}C(Cl)(SPh)_2 \xrightarrow{-Cl^-} \underset{\underline{9}}{(PhS)_2C{=}C(SPh)_2} \quad (11)$$

Scheme II

substrate. Thus, by adding PhSNa to the DMF solutions of 2b, all the intermediate products 4, 7 and 8 were formed at beginning. When more PhSNa were added, 7 and 8 disappeared rapidly and were all converted to 9 eventually. The formation of disulfide 5 provides an evidence for the chlorophilic attack of PhS^- on 2b (eqn. 8). The stoichiometry is in good agreement with Scheme II. Furthermore, when the vinyl sulfide 4 was

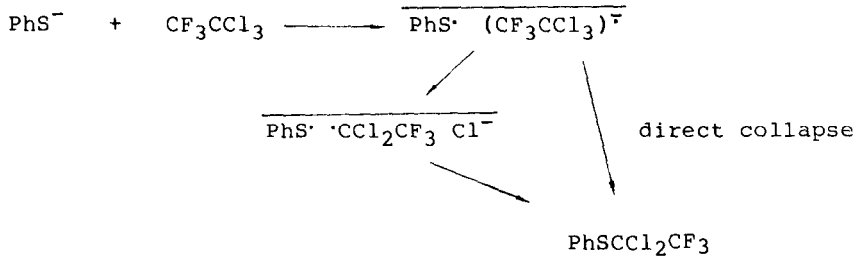
allowed to react with PhSNa, we got the same products 7, 8 and 9 as expected by Scheme II.

Reactions with CF_3CCl_3 (1c). Two competitive pathways.

If the reactions of 1c with PhSNa are also through an anionic chain mechanism as shown in Scheme I, one would expect that the products should be the same as those from reactions of 1b, i.e. main product $PhSCF_2CCl_3$ (2c = 2b) and by-products $PhSCF_2CCl_2H$ (3c = 3b), $PhSCF{=}CCl_2$ (4) and 5. This proved to be the case when the reactions were carried out in diglyme. However, surprising results were obtained when the reactions were carried out in polar aprotic solvents like DMSO, HMPA and DMF. In these cases, the main products were $PhSCCl_2CF_3$ (10) and PhSCF=CClSPh (7) while 2b and 4 were found only in trace amounts (less than 1%). As proved later, 7 is derived from 10 (vide infra).

Product 10 is mechanistically meaningful because it contains a CF_3 group, which apparently remains unchanged during the reaction course and, in contrast to all other products, the entering PhS group ends up on CCl_2 instead of CF_2. Evidently, Scheme I is not fit to explain the formation of 10.

A radical chain mechanism like $S_{RN}1$ is unlikely since no notable effects were observed when the reactions were carried out in the dark, by exposure to air or in the presence of 20 mol % of nitrobenzene or styrene, which has recently been prover to be a good inhibitor for the reactions of PhSNa with R_FI [6]. However, a non-chain mechanism involving SET process (Scheme III) could not be ruled out. The difficulty of accepting



Scheme III

TABLE 3

The reactions of 1c with PhSNa at room temperature [a]

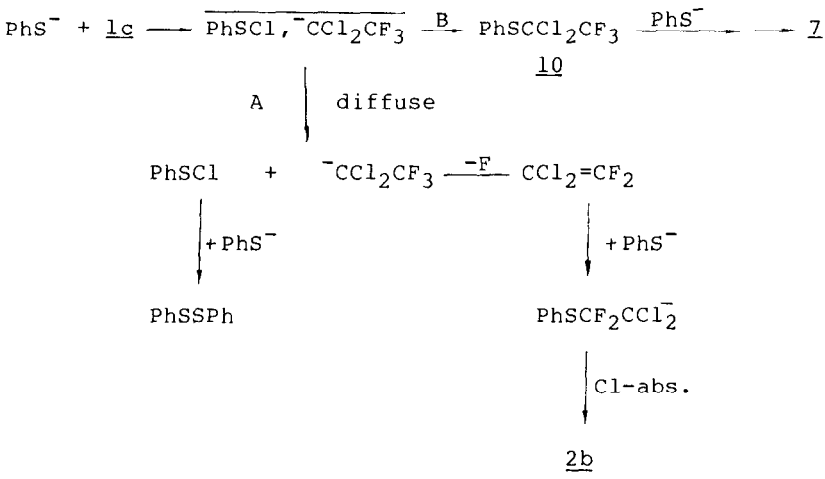
$PhSCF_2CCl_3$ 2c (= 2b) | $PhSCF_2CCl_2H$ 3c (= 3b) | $PhSCCl_2CF_3$ 10 | PhSCF=CClSPh 7

conditions			% yield [b]						
solvent	additive	time	2b	3b	4	5	7	10	7+10
Diglyme		48 h	45	0.1	4	32	13	5	18
Tetraglyme		4 h	27	0.1	4	30	21	9	30
DMF		5 min	0.3	0.1	0.8	38	34	19	53
HMPA		5 min	0.5	0.1	0.4	28	22	32	54
DMSO		5 min	0.6	0.1	1.5	40	30	13	43
DMF	H_2O(20 mmol)	1 h	0.5	0.1	0.1	54	30	13	43
DMF	CH_3OH(20 mmol)	1 h	0.2	0.1	0.1	69	4	7	11
DMF	styrene(2.6 mmol)	5 min	0.3	0.1	0.2	38	30	17	47
DMF	$C_6H_5NO_2$(2.8 mmol)	5 min	0.3	0.1	0.2	39	30	17	47

[a] See footnote [a] of Table 1.

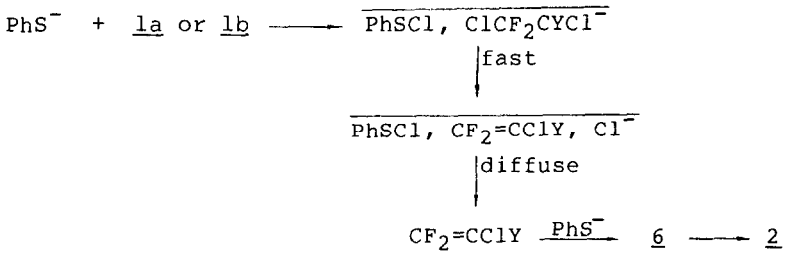
[b] See footnote [b] of Table 1.

this mechanism is to explain why the reactions of 1a and 1b do not seem to follow this pathway. Instead, a somewhat better rationalization could be given based on the competition of the reaction of carbanion $CF_3CCl_2^-$ with PhSCl (the attack on S of $CF_3CCl_2^-$ probably occurs mostly in cage) and the β-elimination of F^- from $CF_3CCl_2^-$ (which most likely occurs in the bulk of the solution.).



Scheme IV

As shown in Scheme IV, there are two competitive pathways, path A finally gives 2b and path B leads to the formation of 10 When the solvent is changed from diglyme to tetraglyme to DMF, DMSO and HMPA, path B might be favoured owing to the growing importance of the cage reaction.



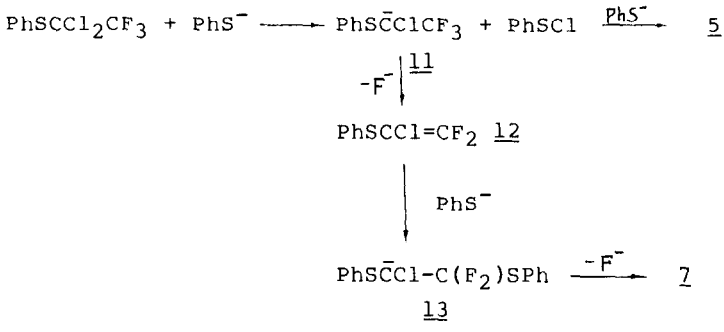
Scheme V

In the cases of 1a and 1b (Scheme V), the related carbanion $CF_2ClCFCl^-$ and $CF_2ClCCl_2^-$ are much less stable than $CF_3CCl_2^-$ [7] because they both have a chlorine, a much better leaving group compared to fluorine, on the β-carbon and could immediately undergo β-elimination after their formation. Therefore, all the products are derived from the intermediate olefins $CF_2=CClY$.

To support the rationalization given above, efforts have been made to detect the expected volatile products, i.e. $CF_2=CYCl$ and $CF_2XCYClH$. GC analysis actually showed the existence of $CF_2=CFCl$ and $CF_2=CCl_2$ in the reaction systems of 1a and 1b, respectively, but never of the protonation products of the carbanions 6, namely $CF_2ClCFClH$ and CF_2ClCCl_2H, even when the reactions were carried out at -65°C or in the presence of water or t-butanol. This fact indicates that the chlorophilic attack by PhS^- on 1a or 1b might lead to concerted formation of the olefin $CF_2=CYCl$ or that the carbanions formed must be extremely short-lived. In contrast, it is not $CF_2=CCl_2$ but CF_3CCl_2H that was found in the reaction solutions of 1c. Only in diglyme/crown ether system, trace amounts of $CF_2=CCl_2$ were detected besides considerable amounts of CF_3CCl_2H. These results are in accordance with the expectation that $CF_3CCl_2^-$ is really an intermediate of the reactions of 1c.

Further Reactions of 10 with PhS^-Na^+

Product 10 has been found to react very fast with PhSNa at room temperature forming 7 and disulfide 5. Scheme VI shows a possible mechanism for the reactions.



Scheme VI

We do find considerable amounts of 7 in the reaction system of 1c with PhSNa. As described in above section, 7 could also be derived from the reaction of 2b with PhSNa. In order to establish whether the product 7 found in the reaction systems of 1c is derived from 2b or from 10 or from both, a competition experiment was conducted by adding a mixture of 2b and 10 into the DMF solution of PhSNa (molar ratio of 2b:10:PhSNa = 1:1:1). The GC analysis showed that 74% of 10 had disappeared within 1 min while 2b did not change at all. That means if there is an excess of 10 in the system, 2b will not be able to react with PhSNa and, therefore, all the product 7 found in the reaction system of 1c and PhSNa must be produced only by the further reactions of 10 with PhSNa.

Trapping of $PhSCl$ by $PhSO_2^-$

By Scheme I we have suggested that the formation of PhSSPh is a consequence of the reaction of PhS^- with PhSCl. If this is true it might be possible to trap the PhSCl with phenylsulfinate ion [8]. Indeed, this could be accomplished if the reaction of 1b with PhSNa was conducted in the presence of 2.3 molar equivalents of $PhSO_2Na$. Data in TABLE 2 showed that $PhSO_2SPh$ (11) formed in a yield of 25% relative to the starting PhSNa while the formation of PhSSPh is cut out. This result may represent the highest efficiency observed so far among such kind of trappings [8,9].

However, the trapping experiments in the reaction systems of 1a and 1c failed to give unambiguous results as only small or trace amounts of 11 were detected. Actually, further experiments have demonstrated that the amounts of 11 detectable in the system depend on the competitiveness of the other species, e.g. 1a 1b or 1c, in their reactions with PhS^-. For the least reactive 1a, even when it exists in large excess, PhS^- will almost exclusively attack on 11 and annihilate it from the system. In the case of 1c, when 10:1 molar ratio of 1c and 11 was allowed to

$$\underset{11}{PhSO_2SPh} + PhS^- \xrightarrow[DMF]{\text{very fast}} PhSSPh + PhSO_2^-$$

react with 1.1 molar equivalent of PhSNa, 98% of the 11 disappeared within one minute. Only the most reactive 1b can win the competition, as indicated by the fact that only 37% of 11 disappeared after reaction under the same conditions.

CONCLUSIONS

Sodium thiophenoxide reacts spontaneously with per(chloro, fluoro)ethanes 1 to give per(chloro,fluoro)alkyl phenyl sulfides 2 and 3. 2a and 2b can be prepared in good yield by using some polar aprotic solvent as the reaction media. An anionic chain mechanism involving the chlorophilic attack on C-Cl bonds by $PhS^{\cdot}$ (Scheme I) is favored for these reactions although for the reaction of CF_2Cl_2 with PhSNa under similar conditions a $S_{RN}1$-like mechanism has recently been proposed by Wakselman and Tordeux [5]. The coexistence of two competing reaction pathways in the reactions of 1c is indicated by the two products 2b and 10, which differ from each other by the orientation of the entering PhS group. The product 2b is most likely formed from an anionic chain mechanism, but 10 might be formed in a competitive pathway in which the much longer-lived $CF_3CCl_2^-$ attacks a PhSCl molecule instead of losing its β-fluorine.

EXPERIMENTAL

^{1}H-NMR (60 MHz) and ^{19}F-NMR (56.4MHz) spectra were recorded on a Varian EM-360L NMR Spectrometer with TMS and $CFCl_3$ as internal and external references, respectively. Mass spectra were obtained with a Finnigan 4021 GC-MS apparatus. Quantitative GC analyses of the products were achieved with a Varian-3700 Gas Chromatograph calibrated by authentic sample. The HPLC analyses were accomplished on a Waters Model 244 HPLC apparatus using a 10 cm C18 column with Methanol or Ethanol/H_2O mixture as the eluant. All the melting and boiling points are uncorrected.

Material

1a, commercial, was purified by washing with conc. H_2SO_4 followed by fractional distillation. 1b and 1c were prepared from 1a by a literature method [10] . The solvents were purified by usual procedures [11] and stored over molecular sieves under argon. PhSNa was prepared by the reaction of Thio-

phenol with sodium in ether/diglyme (10:1). The precipitated PhSNa was filtered out, washed with ether, and finally dried under vacuum (1 torr) at 80 to 100°C for 8 h.

General procedure for the reactions of PhSNa with 1

The reaction flask was flamed and cooled to room temperature under argon before loading PhSNa in a dry box. The solvent was then injected into the flask through the serum cap. After 10 min stirring, the substrate 1 was added by syringe. The reactions were followed by GC or HPLC, and the GC or HPLC yields were determined before work-up. The resultant material was poured into water and then extracted with carbon tetrachloride. Pure products were separated by either distillation or centrifugal TLC.

Preparation of 2a

A mixture of 1a (14.2 g, 75.1 mmol), PhSNa (5.0 g, 37.9 mmol) in DMSO (40 ml), was stirred at room temperature for 30 min. Work-up and distillation (61-3°C/1 torr) gave 2a (8.5 g, 32.4 mmol 86%). Analysis: Found: C, 37.13; H, 1.88; Cl, 26.96; F, 21.74; S, 12.70%. $C_8H_5Cl_2F_3S$ requires: C, 36.80; H, 1.93; Cl, 27.16; F, 21.83; S, 12.28%.

Preparation of 2b

A mixture of PhSNa (20.0 g, 0.15 mol) in 150 ml DMF and 1b (100.0 g, 0.485 mol) were allowed to react at -55°C for 15 min. Work-up and distillation gave pure product 2b 30.5 g (0.110 mol, 73%), b.p. 64-6°C/0.2 torr, m.p. 22.5-23.5°C. Analysis: Found: C, 34.62; H, 1.76; F, 14.11; Cl, 38.31; S, 11.55%. $C_8H_5F_2Cl_3S$ requires: C, 34.62; H, 1.82; F, 13.69; Cl, 38.32; S, 11.55%.

Preparation of 4, 8 and 9

50.0 g PhSH (0.455 mol) and 60 g (1.07 mol) KOH were stirred in 155 ml DMSO at room temperature for 15 min. When 93 g (0.455 mol) 1b were added the temperature of the mixture went up to about 90°C. The mixture was stirred at room temperature for 4 h, and then saturated with 250 ml water followed by extraction

with $CF_2ClCFCl_2$ (2x25 ml). The crude 9 precipitate was filtered out. The organic layer was washed by water and stood at -20°C over night. After removal of the precipitate (PhSSPh mainly), the filtrate was dried over anhydrous $MgSO_4$ and distilled to afford 4 (8.0 g, 0.036 mol 7.9%), b.p. 76-9°C/1 torr. Pure 8 (0.14 g, 0.36 mmol) was separated from the distillation residue by centrifugal TLC with petroleum ether/$CHCL_3$ (10:1) as the eluant. Analysis: Found: C, 62.31; H, 3.85; Cl, 8.95; S, 25.16%. $C_{20}H_{15}ClS_3$ requires: C, 62.07; H, 3.91; Cl, 9.16; S, 24.86%. The crude 9 (21 g), washed with warm petroleum ether, was recrystallized from $CHCl_3$ to give pure sample (14.1 g, 30.6 mmol, 27%), m.p. 154-155°C Analysis: Found: C, 67.69; H, 4.20; S, 27.66%. $C_{26}H_{20}S_4$ requires: C, 67.79; H, 4.38; S, 27.84%.

Preparation of 10 and 7

1c (128.0 g, 0.677 mol) was added to a mixture of PhSH (25.0 g, 0.227 mol) and KOH (19.0 g, 0.34 mol) in 200 ml DMF cooled with an ice bath. The mixture was stirred at room temperature for 3 h and then poured into water (250 ml). The aqueous layer was extracted with $CF_2ClCFCl_2$ (2x25 ml). The combined organic phase was washed with water (3x100 ml), stood at -20°C over night and filtered. The filtrate was distilled to give 10 (6.6 g, mol, 11%), b.p. 69-70°C/2.5 torr.

The precipitate was shown by HPLC to contain mainly 5 and 7, as well as small amounts of 8 and 9. By a cycle of recrystallization -- centrifugal TLC -- recrystallization, crude 7 (4 g, 0.013 mol, 6%) was isolated as a mixture of cis- and trans- isomers which were further separated by fractional crystallization from pentane into isomer A (m.p. 47.5-48.5°C, ^{19}F δ= -68 ppm. Analysis: Found: C, 56.75; H, 3.23; Cl, 12.01; F, 6.73; S, 21.28%. $C_{14}H_{10}ClFS_2$ requires: C, 56.65; H, 3.40; Cl, 11.94; F, 6.40; S, 21.60%.) and isomer B (m.p. 33.0-33.5°C, ^{19}F δ= -77 ppm. Analysis: Found: C, 57.35; H, 3.43; Cl, 10.90; F, 7.02; S, 21.78%. $C_{14}H_{10}ClFS_2$ requires: see above.). The isomer A is tentatively designated as trans while isomer B as cis in consideration of the facts that (a) isomer A has a higher melting point and (b) isomer B is thermodynamically less stable and can be transformed into isomer A by heating as indicated by ^{19}F-nmr study.

TABLE 4

The NMR Spectral Data of the Products

	^{1}H-nmr	^{19}F-nmr [a]
$PhSCF_2CFCl_2$ **2a**	6.9-7.5(m)	-84(d, J = 13 Hz, 2F) -71(t, J = 13 Hz, 1F)
$PhSC(F^1)(F^2)-C(F^3)(H)-Cl$ **3a**	5.70(ddd, J = 47 Hz, 7.2 Hz, 4.7 Hz, 1H) 6.9-7.5(m, 5H)	ABMX system: $\delta_F 1$= -86, $\delta_F 2$= -90(J_{12} = 224 Hz, $J_{13} = J_{23}$ = 18.8 Hz, J_{F^1H} = 4.7 Hz, J_{F^2H} = 7.2 Hz), $\delta_F 3$= -148(dt, J_{F^3H} = 47 Hz, $J_{13} = J_{23}$ = 18.8 Hz)
$PhSCF_2CCl_3$ **2b**	6.9-7.5(m)	-80(s)
$PhSCF_2CCl_2H$ **3b**	5.47(t, J = 7.2 Hz, 1H) 6.9-7.5(m, 5H)	-82(d, J = 7.2 Hz)
$PhSCCl_2CF_3$ **10**	6.7-7.3(m)	-76(s)
$PhSCF{=}CCl_2$ **4**	6.9-7.5(m)	-85 (s)
PhSCF=C(Cl)SPh **7** cis-:	7.4(broad s)	-77(s)
trans-:	7.4(broad s)	-68(s)
$(PhS)_2C{=}CClSPh$ **8**	7.0-7.3(m)	
$(PhS)_2C{=}C(SPh)_2$ **9**	7.06(s)	

[a] Using CCl_3F as external standard (negative upfield).

TABLE 5

The Mass Spectral Data of the Products

2a	262(10), 260(16,M^+), 159(100,$PhSCF_2^+$), 109(40,PhS^+)
3a	228(12), 226(39,M^+), 159(100,$PhSCF_2^+$), 109(53,PhS^+)
2b	280(5.6), 278(18), 276(17,M^+), 159(100,$PhSCF_2^+$), 109(34,PhS^+)
3b	244(23), 242(34,M^+), 159(100,$PhSCF_2^+$), 110(10), 109(48,PhS^+)
10	264(6.4), 262(31), 260(49,M^+), 227(24), 225(68,M^+-Cl), 109(100,PhS^+)
4	226(6.6), 224(32), 222(50,M^+), 189(5.3), 187(13, M^+-Cl), 152(100,M^+-2Cl), 109(14.4)
7	cis-: 298(43), 296(100,M^+), 187(5.7), 152(12), 121(15), 109(7.4)
	trans-: 298(20), 296(50,M^+), 187(18,M^+-PhS), 186(22), 152(100,$PhSCFC^+$), 121(65,$PhSC^+$), 109(24,PhS^+)
8	388(4), 386(8.3,M^+), 201(10.5), 199(15), 170(9), 168(24), 123(100), 109(24)
9	460(100,M^+), 273(30), 242(75,M^+-2PhS), 165(13), 121(21), 110(8), 109(50)

Trapping of PhSCl by $PhSO_2Na$

6.4 g 1b (31 mmol) were added to a mixture of PhSNa (2.0 g, 15.2 mmol) and $PhSO_2Na$ (5.8 g, 35 mmol) in 40 ml DMF. After stirring at room temperature for 30 min., the GC and HPLC analyses showed the formation of 2b (7.9 mmol, 52%), 4 (1.5 mmol, 10%), trace amounts of 5 and large amounts of $PhSO_2SPh$. After work-up to remove the DMF, the resultant mixture was evaporated then dissolved in petroleum ether/$CHCl_3$ (10:1), stood at -20°C over night, to afford the crude $PhSO_2SPh$ which was recrystallized from MeOH/petroleum ether/$CHCl_3$ (1:3:2) to give the pure sample (0.95 g, 3.8 mmol, 25%) m.p. 44.0-44.5°C (lit. 45°C). Analysis: Found: C, 57.34; H, 3.95; S, 25.81%. $C_{12}H_{10}O_2S_2$ requires: C, 57.57; H, 4.03; S, 25.62%.

ACKNOWLEDGEMENT

We thank Professor C. J. M. Stirling (North Wales) for advice on trapping of the sulfenyl halide by Benzenesulfinate ion.

REFERENCES

1 Part 5 of 'Halophilic Reactions', Part 4, X.-Y. Li, H.-Q. Pan, X.-K. Jiang and Z.-Y. Zhan, Angew. Chem. Int. Ed. Engl., (1985), in press;
2 X.-Y. Li, H.-Q. Pan, and X.-K. Jiang, Acta Chemica Sinica, 42 (1984) 297;
3 P. Bey, J. P. Vevert, V. V. Dorsselaer and M. Kolb, J. Org. Chem., 44 (1979) 2732; I. Rico and C. Wakselman, J. Fluorine Chem., 20 (1982) 759;
4 R. D. Chambers, 'Fluorine in Organic Chemistry', N.Y., Wiley, 1973, p. 150;
5 C. Wakselman and M. Tordeux, J. Chem. Soc., Chem. Comm. (1984) 793;
6 A. E. Feiring, J. Fluorine Chem., 24 (1984) 191;
7 J. Hine, R. Wiesboeck and O. B. Ramsay, J. Am. Chem. Soc., 83 (1961) 1222; J. Hine and P. B. Langford, J. Org. Chem. 27 (1962) 4149;
8 B. R. Fishwick, D. K. Rowles and C. J. M. Stirling, J. Chem. Soc. Chem. Comm., (1983) 834;
9 C. D. Beadle, W. R. Bowman and J. Prousek, Tetrahedron Lett. 25 (1984) 4979;
10 K. Okuhara, J. Org. Chem., 43 (1978) 2745;
11 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, 'Purification of Laboratory Chemicals', 2nd ed., Pergamon, Oxford, 1980.