REACTIONS OF SULPHURYL FLUORIDE, SULPHURYL CHLOROFLUORIDE AND SULPHURYL CHLORIDE WITH AMINES

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SUMMARY

The reactions of sulphuryl fluoride, sulphuryl chlorofluoride and sulphuryl chloride with the amines tert-butylamine, benzylamine, piperidine, pyridine and quinoline have been investigated. The primary and secondary amines react with the elimination of hydrogen halides and formation of S-N bonds whereas tertiary amines form 1:2 adducts.

INTRODUCTION

During the course of our investigation on the chemical behaviour of sulphuryl fluoride [1] and sulphuryl chloro-fluoride [2,3], it has been observed that they react with primary, secondary and tertiary amines. The primary amines studied are tertiary butylamine, $(CH_3)_3CNH_2$ and benzylamine, $C_6H_5CH_2NH_2$, the secondary amine is piperidine and pyridine and quinoline are the tertiary amines. Primary and secondary amines react with the elimination of hydrogen halides and formation of S-N bonds. Tertiary amines on the other hand form adducts. For purposes of comparison, these reactions have also been carried out with sulphuryl chloride. The products of the above reactions have been isolated and characterised.

EXPERIMENTAL

Reagents

Sulphuryl fluoride and sulphuryl chlorofluoride were prepared by the fluorination of sulphuryl chloride with potassium bifluoride [1] and lead fluoride [4] respectively in boiling acetonitrile. Similarly N-sulphonyl fluoride was prepared by fluorination of N-sulphonyl chloride with potassium bifluoride in acetonitrile in presence of pyridine [5]. The sample was purified by distillation under reduced pressure (83°C/5 mm).

Sulphuryl chloride and all the amines used in the present work were freshly distilled before use. Solvents were purified by standard methods, dried and distilled prior to use.

Reaction with amines

a) A known amount of (0.02 ml) of tertiary butyl amine or benzyl-amine in diethyl ether (25 ml) was taken in a suitable reaction vessel and cooled in liquid nitrogen bath. Calculated amounts of the oxyhalide (0.005 ml) was introduced. The frozen reaction mixture was allowed to attain the room temperature (25°C) and stand for 4 hours. The sulphamide was separated from the amine hydrochloride and purified by recrystallization from ethanol.

b) As the reaction product from piperdine was found to depend upon the relative amounts of the reactants, it became necessary to maintain different experimental conditions to obtain purified products. When the molar ratio of the reactants was 1:2, liquid products were formed which could be isolated by distillation under reduced pressure, when the relative ratio was maintained at 1:4, solid products were formed which could be isolated and purified by recrystallisation from ethanol.

c) A known amount (0.02 mol) of pyridine or quinoline in cooled
diethyl ether (25 ml) was allowed to react with a known quantity
of (0.01 mol) of sulphuryl chlorofluoride and a solid powder
separated when the reactants were allowed to attain room temperature
and kept for about 3 to 4 hours. The solid was filtered in dry
nitrogen atmosphere, washed with ether and dried in vacuum.
These complexes are highly hygroscopic and are handled in a
dry box. These preparations can be carried out in solvents
like ether, carbon tetrachloride, petroleum ether and also
in gas phase.

There is no observable reaction between sulphuryl
fluoride and pyridine or quinoline under the above conditions.

Characterisation of compounds

Table 1 forms a consolidated list of all the compounds
prepared with some physical properties.

The products of reactions were characterised by
chemical analysis, infrared and ^{1}H NMR spectral data. Sulphur,
nitrogen, chlorine and fluorine were estimated by standard
procedures. Carbon and hydrogen were determined using a
COLEMAN carbon–hydrogen analyser. Analytical data for all the
compounds prepared are given in Table 2.

The IR spectra were recorded on a UR-10 Carl-Zeiss
spectrophotometer in the range 400-4000 cm^{-1}. The ^{1}H NMR
spectra were recorded on a Varian T-60 MHz NMR spectrometer
with TMS as the internal standard. Table 3 summarises the IR
and ^{1}H NMR data. The major IR bands have been assigned [6]
and presented in Table 4.

TABLE 1

List of sulphuryl halide-amine compounds prepared

Sl. No.	Reaction carried out	Compound obtained	Yield %	State	m.p. °C	b.p. °C
1	$(CH_3)_3CNH_2+SO_2F_2$, SO_2ClF or SO_2Cl_2	$[(CH_3)_3CNH]_2SO_2$	75-80	Colourless,needle shaped crystals	145	-
2	$C_6H_5CH_2NH_2+SO_2F_2$, SO_2ClF or SO_2Cl_2	$(C_6H_5CH_2NH)_2SO_2$	75-80	Colourless,flaky, shining crystals	180	-
3	$2C_5H_{10}NH+$ (i) SO_2F_2 or (ii) $C_5H_{10}NSO_2Cl+KHF_2$	$C_5H_{10}NSO_2F$	(i) 65-70 (ii) 45-50	Colourless liquid	-	83/5 torr
4	$2C_5H_{10}NH+$ (i) SO_2ClF or (ii) SO_2Cl_2	$C_5H_{10}NSO_2Cl$	(i) 45-50 (ii) 60-65	Colourless liquid	-	90/5 torr
5	$4C_5H_{10}NH+SO_2F_2$, SO_2ClF or SO_2Cl_2	$(C_5H_{10}N)_2SO_2$	70-75	Colourless, flaky crystals	93	-
6	$C_5H_{10}NSO_2F$ or $C_5H_{10}NSO_2Cl$ + $(C_2H_5)_2NH$	$C_5H_{10}NSO_2N(C_2H_5)_2^+$	90-95	Colourless liquid	-	132/1 torr
7	$C_5H_5N+SO_2ClF$	$2C_5H_5N.SO_2ClF^+$	99	White,hygroscopic solid	56	-
8	$C_9H_7N+SO_2ClF$	$2C_9H_7N.SO_2ClF^+$	99	White,hygroscopic solid	143	-

+ New compounds

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TABLE-2

Analytical data for the sulphuryl halide-amine compounds

Reaction carried out	Compound formed		Analysis (values in %)					
			C	H	N	S	Cl	F
$(CH_3)_3CNH_2+SO_2Cl_2$	$[(CH_3)_3CNH]_2SO_2$	c	46.15	9.61	13.46	15.38	-	-
		f	46.00	9.79	13.40	15.30	-	-
$C_6H_5CH_2NH_2+SO_2Cl_2$, SO_2ClF or SO_2F_2	$(C_6H_5CH_2NH)_2SO_2$	c	60.87	5.79	10.15	11.60	-	-
		f	60.79	5.82	10.01	11.54	-	-
$2C_5H_{10}NH+SO_2F_2$ or $C_5H_{10}NSO_2Cl+KHF_2$	$C_5H_{10}NSO_2F$	c	35.93	5.98	8.38	19.16	-	11.38
		f	35.85	6.00	8.11	19.00	-	10.88
$2C_5H_{10}NH+SO_2Cl_2$ or SO_2ClF	$C_5H_{10}NSO_2Cl$	c	32.70	5.45	7.63	17.44	19.34	-
		f	32.80	5.50	7.60	17.40	19.29	-
$4C_5H_{10}NH+SO_2Cl_2$, SO_2ClF or SO_2F_2	$(C_5H_{10}N)_2SO_2$	c	51.72	8.62	12.07	13.79	-	-
		f	51.41	8.60	11.97	13.50	-	-
$C_5H_{10}NSO_2Cl$ or $C_5H_{10}NSO_2F+(C_2H_5)_2NH$	$C_5H_{10}NSO_2N(C_2H_5)_2$	c	49.09	9.09	12.73	14.54	-	-
		f	49.00	9.11	12.61	14.49	-	-
$C_5H_5N+SO_2ClF$	$[2C_5H_5N]SO_2ClF$	c	43.40	3.61	10.13	11.57	12.83	6.87
		f	43.22	3.75	9.97	11.50	12.70	6.71
$C_9H_7N+SO_2ClF$	$[2C_9H_7N]SO_2ClF$	c	57.37	3.72	7.44	8.49	9.43	5.05
		f	57.12	3.90	7.41	8.42	9.42	4.96

c - calculated   f - found

TABLE 3

IR and NMR data for the sulphuryl halide-amine compounds

Sl. No.	Compound	IR data		NMR data	
		Phase	Frequency in cm^{-1}	Solvent	δ ppm
1.	$[(CH_3)_3CNH]_2SO_2$	KBr	3320vs, 2990s, 2950m, 2875 m, 1485w, 1440w, 1420w, 1390vs, 1375 vs, 1315s, 1240m, 1205m, 1145vs, 1055w, 1010vs, 940w, 890w, 630s, 595m, 520m, 490w	CDCl$_3$	1.23 [s, $(CH_3)_3C-$] 6.03 [s, N-H]
2.	$(C_6H_5CH_2NH)_2SO_2$	KBr	3280-3300vs(b), 3090s, 3075s, 3040s, 2975s, 2935s, 2875s, 1605m, 1500s, 1460s, 1440s, 1390s, 1355s, 1320vs, 1265w, 1220w, 1210w, 1150vs, 1095s, 1070s, 1050s, 1030s, 1020s, 935s, 910s, 900s, 860s, 760s, 735vs, 700vs, 595m, 545s, 525s, 455m .	CDCl$_3$	7.23 [s, $-C_6H_5$] 4.02 [s, $-CH_2-$] 3.90 [s, $-CH_2-$] 3.20 [b, N-H]
3.	$C_5H_{10}NSO_2F$	Neat	3000m, 2960vs(b), 2930vs(b), 2875vs, 1480s, 1450-70vs(b), 1410-45vs(b), 1370s, 1350s, 1320s, 1290s, 1215vs, 1170m, 1120vs, 1080vs, 1030vs, 960vs, 915vw, 870s, 860m, 840m, 750-80vs (b), 705vs, 600vs, 530vs, 500-520vs	CDCl$_3$	1.7 [s, γ and β -H] 3.63 [m, α-H]

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			IR	NMR
4.	$C_5H_{10}NSO_2Cl$	Neat	3000m, 2960vs, 2930vs, 2875vs, 1480s, 1470vs, 1460vs, 1390–1410vs(b), 1365s, 1350m, 1320vs, 1290vs, 1220vs, 1190vs(b), 1160vs, 1100vs, 1070s, 1065s, 975s, 950vs, 920s, 870s, 850s, 710vs,540–80vs(b), 490vs	CDCl$_3$: 1.7 [m, γ and β-H]; 3.3 [m, α-H]
5.	$(C_5H_{10}N)_2SO_2$	KBr	3010m, 2930–50vs(b), 2860s, 1480w, 1475m, 1460m, 1398w, 1365s, 1350s, 1335s, 1300s, 1275vw, 1225s, 1175vs, 1150vs, 1120s, 1070s, 1040s, 975w, 940vs, 870m, 750vs,595s, 580s, 500s.	CDCl$_3$: 1.6 [s, γ and β-H]; 3.17 [s, α-H]
6.	$C_5H_{10}NSO_2N(C_2H_5)_2$	Neat	2980s, 2950vs, 2865s, 1480m, 1460s, 1375s, 1340vs, 1305s, 1280v, 1215m, 1205s, 1175s, 1150vs, 1115m, 1065s, 1025s, 940vs, 870m, 850m, 795s, 740vs, 690s, 670m, 595s, 575m, 545m, 500m	CDCl$_3$: 1.175 [t, -CH$_3$; J=7 Hz]; 1.59 [m, γ and β-H of C$_5$H$_{10}$N-]; 3.12 [t, α-H on C$_5$H$_{10}$N] J=5 Hz; 3.25 [q, -CH$_2$; J=7 Hz]
7.	$2C_5H_5N.SO_2ClF$	KCl	1645s, 1615s, 1545s, 1495s, 1400m(b), 1290–1310vs(b), 1265m, 1175m, 1120vs(b), 1085s, 1075m, 1010w, 760vs, 685vs, 620m, 580s, 480w.	CD$_3$CN: 8.47 [m, C$_5$H$_5$N]
8.	$2C_9H_7N.SO_2ClF$	KCl	1650vs, 1602s, 1570s, 1500m, 1415s, 1400s, 1390vs, 1280–1310vs(b),1170m, 1150s, 1135m, 1075s, 1070w, 1020w, 945s, 925w, 880vs, 820vs, 785s, 750vs, 615s, 580s, 525w, 475–485s(b)	CD$_3$CN: 9.0 [m, complex]

TABLE 4

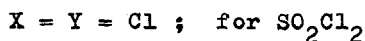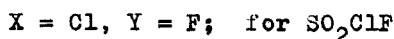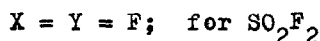Some important IR bands of sulphuryl halide–amine compounds

Sl. No.	Compound	IR data (frequencies in cm^{-1})				
		$\nu_{S=O}$ asym.	$\nu_{S=O}$ sym.	ν_{S-Cl}	ν_{S-F}	ν_{S-N}
1.	$[(CH_3)_3CNH]_2SO_2$	1315	1145	–	–	940
2.	$(C_6H_5CH_2NH)_2SO_2$	1320	1150	–	–	935
3.	$C_5H_{10}NSO_2Cl$	1390	1190	560	–	950
4.	$C_5H_{10}NSO_2F$	1425	1215	–	770	960
5.	$(C_5H_{10}N)_2SO_2$	1350	1150	–	–	940
6.	$C_5H_{10}NSO_2N(C_2H_5)_2$	1340	1150	–	–	940
7.	$2C_5H_5N \cdot SO_2ClF$	1300	1120	580	760	–
8	$2C_9H_7N \cdot SO_2ClF$	1310	1150	615	750	–

RESULTS AND DISCUSSION

Reaction with primary amines

All the sulphuryl halides (SO_2F_2, SO_2ClF and SO_2Cl_2) react with primary amines forming symmetrically substituted sulphamides. These reactions may be represented by the general equation,

$$4RNH_2 + SO_2XY \longrightarrow (RNH)_2SO_2 + RNH_2 \cdot HX + RNH_2 \cdot HY$$

$$X = Y = F; \quad for \ SO_2F_2$$

$$X = Cl, \ Y = F; \quad for \ SO_2ClF$$

$$X = Y = Cl \ ; \quad for \ SO_2Cl_2$$

The change of solvent or the relative amounts of the reactants do not alter the course of the reactions. Tert-butylamine, $(CH_3)_3CNH_2$, reacts with the sulphuryl halides to give NN' di-tert-butyl sulphamide $[(CH_3)_3CNH]_2SO_2$. The IR absorption bands arising due to S=O and S-N stretching modes have been assigned [6] and are presented in Table 4. The N-H stretching which appears at 3200-3225 cm^{-1} as a broad band for tert-butylamine is shifted considerably to higher frequency. It occurs at 3320 cm^{-1} for the compound and the peak is sharp.

The ^1H NMR for the compounds showed resonances at $\delta = 1.23$ ppm ($-CH_3$) and $\delta = 6.03$ ppm ($-NH$) in the ratio 9:1. The weak signal at $\delta = 6.03$ disappears on deuteration.

In the case of benzylamine, NN' dibenzyl sulphamide is obtained. The interpretation of IR and NMR data is straight forward.

It is of interest to point out that both the halogen atoms of sulphuryl halides arereplaced in these reactions. Attempts to replace only one halogen atom and to prepare sulphanoyl halide $RNHSO_2X$ (X = Cl or F) have not been successful.

Reaction with secondary amines

In the case of secondary amines, the reaction is somewhat different. The products of reactions are decided by the relative amounts of the reactants. When excess of piperidine (molar ratio of sulphuryl halide to piperidine being 1:4 or more) is used, the final product is sulphopiperidide $(C_5H_{10}N)_2SO_2$, and if the molar ratio is 1:2, the product is predominantly piperidine N-sulphonyl halide $C_5H_{10}NSO_2X$. This indicates that it is possible to carry out step-wise substitution. Also when partial substitution occurs, fluorine is preferentially replaced as exemplified by sulphuryl chlorofluoride. Thus, when two moles of piperidine react with a mole of sulphuryl chloride or sulphuryl chlorofluoride, piperidine N-sulphonyl chloride is formed. However, in the case of the chlorofluoride, additional side reaction takes place forming piperidine N-sulphonyl fluoride, although the yield is considerably low compared to the chloride. The fluorinated derivative, piperidine N-sulphonyl fluoride can also be prepared by the fluorination of the chloride with potassium bifluoride. Pyridine functions as a scavenger for the hydrogen halide and promotes this exchange reaction.

It is evident from Table 4 that the S=O and S-N stretching frequencies for piperidine N-sulphonyl fluoride are higher compared to those in piperidine N-sulphonyl chloride. This is attributed to the higher electron withdrawing power of the fluorine atom and hence stronger S=O and S-N bonds.

Similarly, the downfield shift (δ = 0.3 ppm) of the resonance signal of α-protons in the ^{1}H NMR spectrum of the fluorine compound compared to the one due to the α-protons in the chlorine compound is evident for reasons already mentioned.
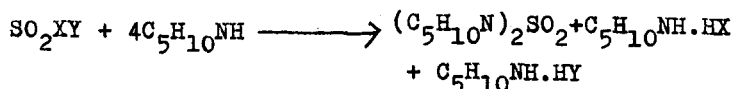
The sulphonyl halides react with excess of piperidine forming sulphopiperidide [7].

The reactions of sulphuryl halides with piperidine may be represented by the following equations:

(i) When the molar ratio is 1:2

$$SO_2XY + 2C_5H_{10}NH \longrightarrow C_5H_{10}NSO_2X + C_5H_{10}NH.HY$$

(ii) When piperidine is in excess

$$SO_2XY + 4C_5H_{10}NH \longrightarrow (C_5H_{10}N)_2SO_2 + C_5H_{10}NH.HX$$
$$+ C_5H_{10}NH.HY$$

$X = Y = F$; for SO_2F_2 ; $X = Cl$, $Y = F$; for SO_2ClF ;

$X = Y = Cl$; for SO_2Cl_2.

In these reactions one [Eqn. (i)] or two [Eqn. (ii)] moles of piperidine are used up for the formation of the hydrofluoride. The hydrogen halide could be removed from the sphere of reactivity by a suitable tertiary amine like pyridine.

Although change of solvent does not alter the course of these reactions, the yield of N-sulphonyl halide is found to be better in carbon tetrachloride medium.

Piperidine N-sulphonyl halide can react with a primary or a secondary amine with elimination of hydrogen halide. Diethylamine, a secondary amine, reacts in the following way:

$$C_5H_{10}NSO_2X + 2(C_2H_5)_2NH \longrightarrow C_5H_{10}NSO_2N(C_2H_5)_2 +$$
$$+ (C_2H_5)_2NH.HX$$
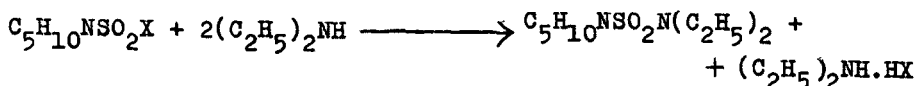
($X = Cl$ or F)

The ^{1}H NMR spectrum recorded on Varian T-60 MHz NMR spectrometer gives three signals: one triplet, a singlet and a quartet overlapping a singlet. The signals are resolved in the spectrum recorded on a Bruker 270 MHz F-T NMR spectrometer. They have been assigned and presented in Table 3.

Reaction with tertiary amines

Sulphuryl chlorofluoride reacts with tertiary amines giving rise to 1:2 adducts.

$$SO_2ClF + 2B \longrightarrow SO_2ClF.2B$$
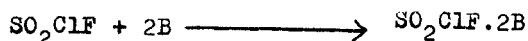
B = a tertiary amine (pyridine and quinoline)

Sulphuryl chlorofluoride acts as a Lewis acid and pyridine and quinoline as Lewis bases. The bonding occurs between sulphur and nitrogen by the donation of the non-bonding pair of electrons on nitrogen by the tertiary amine into the vacant 'd' orbitals of sulphur. This is supported by spectral data which shows a shift of the stretching modes. Considerable shifts of the bands (S-F, S-Cl) due to sulphuryl chlorofluoride and pyridine or quinoline are observed in the IR spectra of the complex. ν_{S-O} and ν_{S-F} of sulphuryl chlorofluoride [8] gets shifted on complex formation [ν_{S-O} : 1467 cm^{-1} (asym) and 1228 cm^{-1} (sym) to 1300 cm^{-1} and 1120 cm^{-1}. ν_{S-F}; 824 cm^{-1} to 760 cm^{-1}; ν_{S-Cl}; 629 cm^{-1} to 580 cm^{-1}]. The ^{1}H NMR spectrum of the adduct shows considerable deshielding of the protons in the pyridine ring. The complex multiplet signal at δ = 8.02 ppm for pyridine occurs at a lower field δ = 8.47 ppm in the adduct. The deshielding is due to the draining of electrons from the ring on adduct formation.

Sulphuryl fluoride reacts with tertiary amines very slowly. This is attributed to the closely surrounded fluorine and oxygen atoms around sulphur atom in SO_2F_2 which hinders nucleuphillic attack on the sulphur atom. In SO_2ClF considerable distortion of the structure occurs which facilitates reaction.

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