Rearrangements in the Electron Impact Induced Fragmentations of Sulfonyl Chlorides

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The major fragmentation pattern observed in the mass spectra of simple alkane- and arylsulfonyl chlorides may be rationalized by loss of a chlorine atom from the molecular ion, followed by loss of SO₂ with concomitant carbocation formation. The mass spectra of α -mesyl sulfonyl chlorides and napthalenesulfonyl chlorides exhibit ions resulting from chlorine atom migration to the α -carbon atom with concomitant loss of SO₂. The mass spectra of α -mesyl sulfonyl chlorides also show ions which involve chlorine atom migration to the β -sulfonyl group.

Very little work has been reported on the mass spectrometry of sulfonyl chlorides.¹⁻³ Previously, we have described¹ a fragmentation pathway for alkanesulfonyl chlorides (Scheme 1, $a \rightarrow c \rightarrow d$). In addition, we have



reported a new rearrangement process involving chlorine atom migration in the fragmentation of the α -mesyl sulfonyl chlorides 1 and 2 (Scheme 2). A





rigorous structure proof of 2 has been published.⁴

$$1 2 3 4CH_3SO_2CX_2SO_2Cl1: X = H2: X = Cl$$

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The migration of chlorine from sulfur to carbon has been reported previously^{2,3} when arylsulfonyl chlorides were subjected to electron impact. However, in previously reported cases it was a minor process which received little comment. An analogous process is dominant in the fragmentation of benzenesulfonic acid³ and is also a major one in the fragmentation of *S*-alkyl and *S*-aryl sulfonamides.²

We report here an examination of the mass spectra of a series of alkane- and arylsulfonyl chlorides as well as four new α -sulfonyl sulfonyl chlorides, in order to assess the propensity for chlorine atom migrations as a function of structure.

RESULTS AND DISCUSSION

The synthesis of the sulfone-sulfonyl chloride (1) has been described by Opitz.⁵ The route to the dichloro-sulfone-sulfonyl chlorides (2-4) as well as a detailed discussion of the chlorination of sulfone-benzylic sulfides has been reported previously.⁴

The mass spectra of alkanesulfonyl chlorides are simple and can be rationalized in a straightforward manner (Scheme 1, $a \rightarrow c \rightarrow d$). Our initial report¹ delineates this proposal on the basis of the mass spectra of methane and ethanesulfonyl chlorides. In support of this proposal, the mass spectra of a number of alkanesulfonyl chlorides are presented in Table 1.

We have reported previously¹ the observation of ions arising from the migration of the chlorine atom, initially attached to sulfur, to the α -carbon atom with concomitant loss of SO₂ during the fragmentation of some sulfonyl chloride molecular ions. At that time we proposed that chlorine atom migration might be anticipated 'whenever a particularly labile group is attached to that carbon atom.' Since the π electrons of an aromatic ring may be regarded as a labile substituent, it appeared that initial ionization with the creation of radical character on the α -carbon atom might make a parallel process observable in the mass

Table 1. Major ions in the mass spectra of sulfonyl chlorides (30 eV)

Compound	m/e (Relative abundance)						
	[M] ⁺	[M-CI] ⁺	[M-CI-SO2]	$[M - SO_2]^{\dagger}$	[SO ₂] ¹	[SO] [†]	Other ions
CH ₃ SO ₂ CI		79(100)	15(55)		64(16.5)	48(31.6)	
CH ₃ CH ₂ SO ₂ CI		93(100)	29(99)		64(54.9)	48(55.6)	
CH ₃ (CH ₂) ₂ SO ₂ CI	_	107(7.0)	43(100)	_	64(18.0)	48(14.3)	
CH ₃ (CH ₂) ₃ SO ₂ Cl			57(100)	_	64(9.0)	_	41(82.3)
PhCH ₂ SO ₂ CI	192(1.5); 190(4.6)	_	91(100)				65(5.3)
PhSO ₂ Cl	178(4.5); 176(13.6)	141(41)	77(100)	114(1.5); 112(4.5)			
Naphthalene-1- sulfonyl chloride	228(7.6); 226(23.9)	191(11.3)	127(100)	164(9.0); 162(26.9)	—	_	115(8.4); 101(10.9); 77(17.8)
Naphthalene-2- sulfonyl chloride	228(22); 226(67)	191(37.8)	127(100)	164(12.5); 162(37.5)			115(11.3); 101(21.5); 77(38.0)



Figure 1.^a Mass spectrum of CH₃SO₂CH₂SO₂Cl (1) at 30 eV.

spectra of aromatic sulfonyl chlorides (i.e. Scheme 1, $a \rightarrow b$). The appearance of an ion pair at $m/e \ 112/114$ in the mass spectrum of benzenesulfonyl chloride and an ion pair at $m/e \ 162/164$ in the mass spectra of both naphthalene-1-sulfonyl chloride and naphthalene-2-sulfonyl chloride clearly indicate that such a process does, in fact, occur. (vide Table 1).

The mass spectra of compounds 1-4, in which no metastable ions were observed (Figs. 1-4), all show



Figure 2.^a Mass spectrum of CH₃SO₂CCl₂SO₂Cl (2) at 30 eV.

^a All isotope peaks excepting those due to CI-37 have been omitted.



Figure 3.^a Mass spectrum of PhSO₂CCl₂SO₂Cl (3) at 30 eV.

ions indicating a chlorine atom migration from sulfur to carbon.

$$RSO_2CCl_2SO_2Cl$$

3: $R = Ph$
4: $R = ClCH_2$

The presence of ions at m/e 49 (compound 1, Fig. 1) and m/e 117 (compound 2, Fig. 2) is the basis for the original proposal¹ of chlorine atom migration from sulfur to carbon. The chloromethyl analogue (4) also



Figure 4.ª Mass spectrum of CICH₂SO₂CCl₂SO₂CI (4) at 30 eV.



shows the trichloromethyl cation as the most important ion in the spectrum (Fig. 4). The mass spectrum of the phenyl analogue (3, Fig. 3) shows a greatly reduced relative abundance for the trichloromethyl cation. This observation is attributable to the enhanced stability of the phenylsulfonyl cation over the methylsulfonyl cation, which results in the failure of the $-CCl_2SO_2Cl$ fragment to carry the positive charge upon fragmentation of the molecular ion.

The second type of chlorine atom migration observable in these compounds, results in the formation of an ion at m/e 98 in the mass spectrum of 1. The formation of this ion may be rationalized by assuming an initial migration of C-3 from S-2 to an oxygen atom on S-2. This rearrangement of sulfones, upon electron impact, is well documented.⁶⁻¹⁰ The resultant sulfinate ester could then rearrange with chlorine migrating from S-4 to S-2 with concomitant loss of CH₂SO₃ to produce the molecular ion of methanesulfinyl chloride as depicted in Scheme 3. The mass spectrum of methanesulfinyl chloride (Fig. 5) is consistent with this proposal. While it would clearly be advantageous to obtain 1 deuterated at C-1 or C-3, in order to find



Figure 5.° Mass spectrum of methanesulfinyl chloride at 30 eV.

^a All isotope peaks excepting those due to CI-37 have been omitted.

support for these fragmentation processes, selectively deuterated 1 cannot be prepared. The sulfone-sulfonyl chloride (1) is very sensitive to water and/or alcohols so that direct exchange experiments are precluded. Furthermore, 1 is prepared by the dimerization of sulfene (generated *in situ* from methanesulfonyl chloride) which thereby prevents selective labelling of the starting material.

CONCLUSIONS

The mass spectra of some α -mesyl sulfonyl chlorides exhibit two new fragmentation pathways involving migration of the chlorine atom of the chlorosulfonyl group to the α -carbon atom as well as to the β -sulfur atom. Migration of chlorine from sulfur to carbon is observable as a major process in the mass spectra of the two naphthalene sulfonyl chlorides and as a minor process in the mass spectra of some other arylsulfonyl chlorides.

EXPERIMENTAL

General

The mass spectra were recorded on a DuPont 21–490 instrument. The samples were directly introduced and the spectra run at 30 eV with a source temperature of 200 °C.

The n.m.r. spectra were obtained on samples in $CDCl_3$ solution with tetramethylsilane as the internal reference using a Varian T-60 instrument. The i.r. spectra were recorded on samples in $CHCl_3$ solution using a Beckman I.R.-10 grating spectrophotometer. All compounds were homogeneous on t.l.c.

Preparation of alkane and arylsulfonyl chlorides

Methanesulfonyl chloride, naphthalene-1-sulfonyl chloride and naphthalene-2-sulfonyl chloride were obtained commercially and were purified by distillation or recrystallization. Ethanesulfonyl, *n*-propanesulfonyl, *n*-butanesulfonyl and benzylsulfonyl chlorides were prepared from the corresponding thiols or symmetric sulfides as outlined below.

The appropriate thiol or symmetric sulfide (16 g) was dissolved in glacial acetic acid (50 ml) and water (6.6 ml) was added. Cl₂ was bubbled gently through the reaction mixture while the temperature was maintained between 25 and 30 °C. When the reaction was no longer exothermic the solvent was distilled off at reduced pressure. The residue was rectified at reduced pressure or recrystallized. Melting points and boiling points conformed to the values reported previously.^{12–14} All samples had the expected i.r., ¹H n.m.r. and ¹³C n.m.r. spectra.

Preparation of $CH_3SO_2CH_2SO_2Cl$ (1), $CH_3SO_2CCl_2-SO_2Cl$ (2) and CH_3SOCl

The preparation of the sulfone-sulfonyl chloride (1) has been detailed elsewhere.⁵

A detailed discussion of the preparation and structure of 2 has been reported previously.⁴

The synthesis of methanesulfinyl chloride has been presented in a previous publication.¹¹

Preparation of phenyl chloromethyl sulfone

Phenyl chloromethyl sulfide (2.969 g)¹⁵ was dissolved in glacial acetic acid (10 ml). The sulfide/acetic acid solution was then added dropwise, over a 10 min period, to a cooled mixture of CrO_3 (4.705 g) in glacial acetic acid (100 ml). The reaction mixture was then heated to 90-100 °C for 0.5 h. Iced water (75 ml) was added and the solution extracted with chloroform $(4 \times 100 \text{ ml})$. The chloroform layers were combined and washed with 2.5% NaOH (100 ml aliquots) until the pH of the aqueous layer remained basic. The last aqueous wash was acidified with 10% HCl and backextracted with chloroform (100 ml). The combined chloroform layers were dried (MgSO₄), filtered and rotary evaporated. The residue (3.637 g) was recrystallized from 95% ethanol. The recrystallized product had m.p. 47-49 °C: i.r. (CHCl₃) 1330 and 1160 cm⁻¹ n.m.r. (CDCl₃) 72.26 (5H, m) and 5.36 (2H, s).

Preparation of PhSO₂CH₂SCH₂Ph

Sodium metal (0.676 g) was dissolved in absolute ethanol (100 ml), followed by the addition of benzyl thiol (3.6 ml). Phenyl chloromethyl sulfone (5.003 g) was added and the reaction mixture refluxed for 1 h. Water (100 ml) was added and the solution extracted with chloroform (3×100 ml). The chloroform layers were combined, dried (MgSO₄), filtered and the chloroform rotary evaporated. The residue was crystallized from 95% ethanol furnishing the sulfonesulfide (1.610 g; m.p. 107–109 °C): i.r. (CHCl₃) 1320 and 1145 cm⁻¹: n.m.r. (CDCl₃) τ 2.36 (10H, m), 6.06 (2H, s) and 6.26 (2H, s).

Preparation of PhSO₂CCl₂SO₂Cl (3)

 $PhSO_2CH_2SCH_2Ph$ (4.518 g) was added to a solution of glacial acetic acid (25 ml) and water (3.3 ml).

Chlorine (c. 200 ml min⁻¹) was bubbled through the reaction mixture for 0.5 h. Water (50 ml) was added and the resultant mixture extracted with chloroform (3×100 ml). The combined chloroform layers were washed with 2.5% w/v NaOH (2×50 ml). The chloroform was dried (MgSO₄), filtered and rotary evaporated. Upon cooling, crystals (2.898 g) formed in the crude residue. The crystals were filtered off and recrystallized from carbon tetrachloride. The recrystallized product had m.p. 86–87 °C: i.r. (CHCl₃) 1400, 1365, 1180 and 1160 cm⁻¹: n.m.r. (CDCl₃) τ 2.20 (multiplet). The mass spectrum is presented as Fig. 3. Anal. Calc. for C₇H₅Cl₃S₂O₄: C, 25.98; H, 1.56. Found C, 26.05; H, 1.42.

Preparation of ClCH₂SO₂CCl₂SO₂Cl (4)

 $ClCH_2SO_2CH_2SCH_2Ph$ (0.690 g)¹⁶ was added to a solution of glacial acetic acid (25 ml) and water (3.3 ml). Chlorine (c. 200 ml min^{-1}) was bubbled through the reaction mixture for 35 min. Water (50 ml) was added and the resultant mixture was extracted with chloroform $(3 \times 50 \text{ ml})$. The combined chloroform layers were washed with 2.5% w/v NaOH $(2 \times 50 \text{ ml})$. The chloroform was dried (MgSO₄), filtered and rotary evaporated. Upon cooling, crystals (0.429 g) formed, were filtered off and recrystallized from carbon tetrachloride. The recrystallized product had m.p. 62-63 °C: i.r. (CHCl₃) 1400, 1380, 1170 and 1160 cm⁻¹: n.m.r. (CDCl₃) τ 4.86 (s). The mass spectrum is presented as Fig. 4. Anal. Calc. for C₂H₂Cl₄S₂O₄: C, 8.12; H, 0.68. Found C, 8.24; H, 0.60

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