Structure and mechanism of hydrolysis of diaryl(acylamino)-(chloro)-λ⁴-sulfanes and diaryl(acylamino)sulfonium salts †

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Aryl (methylaminocarbonylaryl) sulfides were converted by *t*-BuOCl to diaryl(acylamino)(chloro)-λ^4-sulfanes or the corresponding diaryl(acylamino)sulfonium chlorides depending on the substituent of the *S*-aryl group. ^{1}H NMR data showed that chloro-λ^4-sulfanes exist only in $CDCl_3$ and DMSO-d_6 solvents, whereas in CD_3OD complete ionic dissociation takes place, leading to sulfonium chlorides. Both the chemical shifts of ^{1}H NMR signals and NOE data suggest that chloro-λ^4-sulfanes and sulfonium salts having an *o*-MeO, *o*-Cl or *o*-Me substituent on the phenyl ring assume a skew conformation, whereas the aryl ring in compounds without an *ortho*-substituent can rotate practically free about the S–C(1′) axis. In *o*-MeO-substituted derivatives there exists an equatorial 1,4 type S···O close contact. Sulfonium salts with axial 1,5 type S···O close contacts involving neighbouring COOMe, CONHMe, COMe or NO_2 groups occur in butterfly conformation, like spiro-λ^4-sulfanes. There is a correlation between the ^{15}N chemical shift of the amide-nitrogen and the elongation of the S–N covalent bond, by which the interdepending S–N, S–Cl and S···O bonds can be characterized. Effective intermolecular S···O interaction was detected between the sulfonium centre and solvent molecules having a negatively polarized oxygen atom. The hydrolysis of sulfonium salts yielding sulfoxides was investigated by a kinetic method in 98 : 2 (v/v) dioxane–water mixture and in water. On the basis of medium, substituent (ρ +1.03), steric, salt and kinetic isotope effects detailed mechanisms involving a hydroxy-λ^4-sulfane intermediate are proposed. The more reactive sulfonium salts with a five-membered hetero ring are hydrolyzed by water, whereas the sulfonium centre of the less reactive analogues with a six-membered ring is attacked only by OH^- ions.

Introduction

In the late 1970s cyclic diaryl(acyloxy)(chloro)-λ^4-sulfanes (*e.g.* **2i** with O instead of NMe; see Scheme 1) were described as possible reactive intermediates formed from the corresponding diaryl sulfides by treatment with chlorinating agents.[1] Later, several stable representatives of (alkoxy)(chloro)-λ^4-sulfanes[2–4] and diaryl(acylamino)(chloro)-λ^4-sulfanes[5] were prepared and their structures which exhibited trigonal bipyramidal geometry, were determined by X-ray diffraction. As is expected from earlier studies on "nonsymmetric" λ^4-sulfanes,[2–11] the axial bonds in chloro-λ^4-sulfanes proved to be of a different character. For example,[5] the S–N bonds are practically covalent single bonds in **2a** and **10a** (1.727 and 1.675 Å, respectively; see Schemes 1 and 3), whereas the S–Cl bonds correspond to weak and strongly polarized hypervalent bonds. The latter are significantly longer (2.690 and 3.101 Å) than the covalent S–Cl bonds (2.05–2.20 Å), but shorter than the sum of the van der Waals radii (3.65 Å). Data also indicate that the relative strengths of S–N and S–Cl bonds are influenced by steric factors, *e.g.* by the nature of the *S*-aryl substituents.

Owing to the polarized structure, chloro-λ^4-sulfanes may readily undergo ionic dissociation yielding sulfonium chlorides. ^{1}H NMR investigations showed that compounds exhibiting an (alkoxy)(chloro)-λ^4-sulfane structure in the solid state may dissociate in protic solvents (*e.g.* in CD_3OD) to give (alkoxy)-sulfonium chlorides.[2–4] A similar dissociation may also be expected for (acylamino)(chloro)-λ^4-sulfanes (*e.g.* **2a**⇌**3a**; see Scheme 1).

We found earlier[5] that *ortho*- (or *peri*-) methoxycarbonyl-substituted (acylaminoaryl) aryl sulfides were not converted to (acylamino)(chloro)-λ^4-sulfanes by chlorinating reagents, but to ionized (acylamino)sulfonium chlorides (*e.g.* **1f**→**3f**, **6**→**7**, **9f**→**11f**; see Schemes 1–3), in which the positive sulfonium centre is stabilized by S···O close contact involving the carbonyl-oxygen of the neighbouring substituent (*i.e.* the dissociation of chloride ion may be attributed to neighbouring-group participation).

In the first part of this paper we report on how electronic factors, *i.e.* the different *ortho*, *para* and *peri* substituents, and various solvents control the formation of cyclic diaryl-(acylamino)(chloro)-λ^4-sulfanes and corresponding diaryl-(acylamino)sulfonium chlorides from the precursor sulfides. Using ^{1}H and ^{15}N NMR spectroscopy data including DNOE we attempt to determine the constitution and the conformation of products formed in the chlorination reaction. In the second part we describe kinetic investigations on the hydrolysis of chloro-λ^4-sulfanes and sulfonium chlorides obtained, and propose a detailed mechanism for reactions yielding sulfoxides.

Results and discussion

Model compounds

Diaryl (acylamino)(chloro)-λ^4-sulfanes (**2**, **10**) and diaryl(acylamino)sulfonium chlorides (**3**, **7**, **11**) or perchlorates (**4**, **12**)

† ^{1}H and ^{13}C NMR data are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b008156f/

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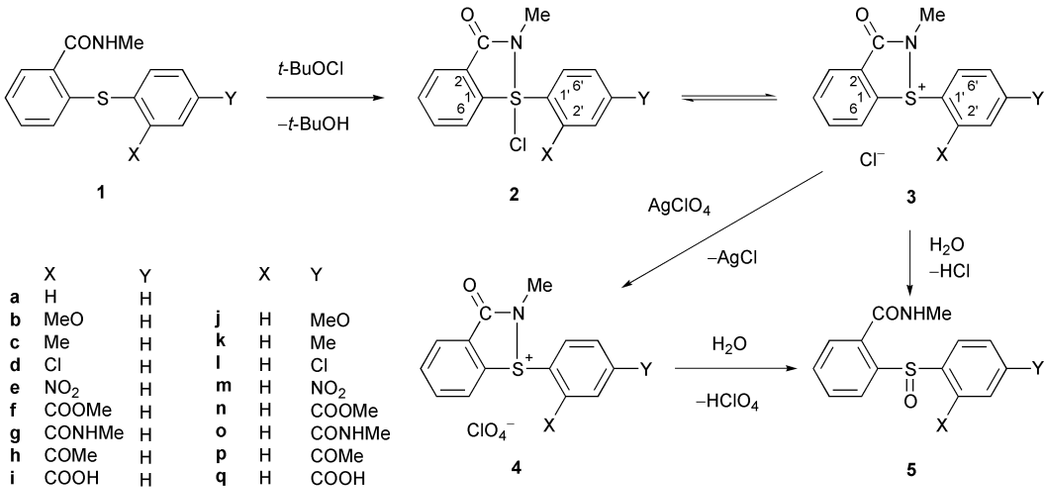
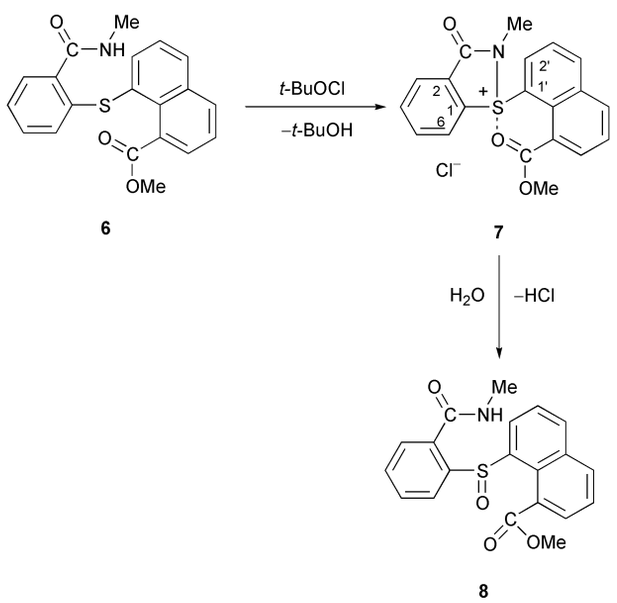


	X	Y		X	Y
a	H	H			
b	MeO	H	**j**	H	MeO
c	Me	H	**k**	H	Me
d	Cl	H	**l**	H	Cl
e	NO_2	H	**m**	H	NO_2
f	COOMe	H	**n**	H	COOMe
g	CONHMe	H	**o**	H	CONHMe
h	COMe	H	**p**	H	COMe
i	COOH	H	**q**	H	COOH

Scheme 1 Synthesis and hydrolysis of diaryl(acylamino)(chloro)-λ^4-sulfanes **2a**–**2h** and **2j**–**2q**, and diaryl(acylamino)sulfonium salts **3a**–**3h**, **3j**–**3q**, **4a** and **4b**.



Scheme 2 Synthesis and hydrolysis of diaryl(acylamino)sulfonium salts **7**.

were obtained from aryl (methylaminocarbonylaryl) sulfides substituted differently on the phenyl (**1**, **9**) or naphthyl ring (**6**), as shown in Schemes 1–3.

The following types of precursor sulfides were chosen: (i) derivatives of phenyl (2-methylaminocarbonylphenyl) sulfide (**1a**) carrying an "inert" (OMe, Me, Cl) or an "active" (NO_2, COOMe, CONHMe, COMe, COOH) *ortho*-substituent (**1b**–**1d** and **1e**–**1i**, respectively); the "active" groups may be involved in the formation of intramolecular S···O close contact with a five-membered "ring"; (ii) the *para*-isomers of the former compounds (**1j**–**1q**); (iii) compound **6** in which the COOMe substituent is in the *peri*-position of a naphthalene ring (possible formation of a six-membered "ring" with S···O close contact); (iv) phenyl (8-methylaminocarbonylnaphthyl) sulfide (**9a**) and its derivative carrying an *o*-COOMe group (**9f**). Compounds of (i)–(iii) and (iv) type were converted in a chlorination reaction to cyclic products (chloro-λ^4-sulfanes or sulfonium chlorides) having a five-membered 1,2-thiazoline or six-membered 1,2-thiazine ring, respectively. Under similar conditions sulfide **1i** yielded the spiro-λ^4-sulfane **14**[9] (see Fig. 1). Spiro-λ^4-sulfane **15** was prepared from **3g** by treatment with KH.[12] All λ^4-sulfanes and sulfonium salts gave sulfoxides (**5**, **8**, **13**) on hydrolysis.

NMR studies

Product analysis. NMR investigations of products obtained from sulfides **1a**–**1q**, **6**, **9a** and **9f** by chlorination were carried out in $CDCl_3$, DMSO-d_6 and CD_3OD solvents. The obtained NMR parameters were compared to those of the nonsymmetric and symmetric spiro-λ^4-sulfanes **14** and **15** (Fig. 1) to establish the solvent-dependent transformation between λ^4-sulfanes and sulfonium salts (**2**⟸⟹**3**, **10**⟸⟹**11**) and the conformation of these compounds. Detailed assignations for all novel compounds are provided as supplementary material.

Previous observations[2,4,5] showed that the characteristic downfield shift of the H-6 *ortho*-proton lying near to the hypervalent S–Cl bond may be an indicator of the existence of the chloro-λ^4-sulfane structure (see Fig. 1). Data in Table 1 suggest that chlorination products obtained from sulfides **1a**–**1d**, **1j**–**1q** and **9a** exhibit chloro-λ^4-sulfane structures **2a**–**2d**, **2j**–**2q** and **10a**, respectively, in dipolar aprotic DMSO-d_6 [δH-6 (or δH-2 for **10a**) = 8.9–9.2 ppm].

The H-6 signal was significantly upfield shifted in DMSO-d_6 for other products obtained from sulfides **1e**–**1h**, **6** and **9f** (δH-6 or δH-2 = 8.1–8.8 ppm), for spiro-λ^4-sulfane **14** (formed from **1i**) and its *N*-symmetric analogue **15** (prepared from **1g** through **3g**) (δH-6 = 8.3 and 7.5 ppm, respectively). Thus the former products were assigned as sulfonium chlorides **3e**–**3h**, **7** and **11f**, respectively, stabilized by axial S···O close contact. The upfield shift of H-6 signals can be explained by the fact that in sulfonium structures the H-6 atom (in contrast with the corresponding chloro-λ^4-sulfanes) is not deshielded by an axial S–Cl hypervalent bond (Fig. 1). A similar upfield shift was observed in DMSO-d_6 for sulfonium perchlorates **4a**–**4b** and hydroxysulfonium chloride **5b·HCl** (δH-6 = 8.4, 8.5 and 7.9 ppm, respectively), all having a positive sulfur atom but a somewhat different conformation (see later).

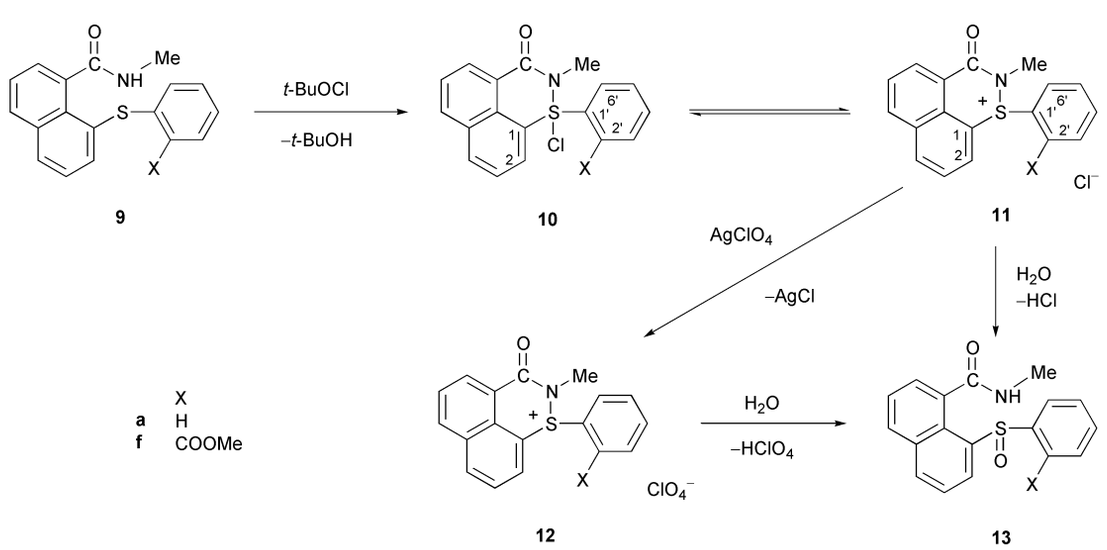
The same results were obtained when $CDCl_3$ as a less polar solvent was used (Table 1), with the exception that product formed from **1e** carrying an *ortho*-NO_2 substituent proved to be chloro-λ^4-sulfane **2e** (δH-6 = 9.6 ppm) instead of sulfonium chloride **3e**. That deviation may be ascribed to the *ortho*-NO_2 neighbouring group which is less effective at forming an S···O close contact than the carbonyl group. Products formed from **1m**–**1q** could not be investigated in $CDCl_3$ because instantaneous hydrolysis yielding sulfoxide took place, caused by the water impurity of the solvent.

In dipolar protic CD_3OD solvent only sulfonium chlorides **3a**–**3h**, **3j**–**3q** (δH-6 = 8.2–8.5 ppm) and **7**, **11a**, **11f** [δH-6 (or δH-2 for **11a** and **11f**) = 8.7–8.9 ppm] were detected, owing to the ionic dissociation of chloro-λ^4-sulfanes formed primarily (Table 1).

Table 1 Selected data obtained by ^{1}H NMR,[a,b] ^{15}N NMR [a,c] and X-ray analysis for products prepared from sulfides **1a**–**1q** by chlorination

		δH-6			δH-6′			δ^{15}N			
Sulfide	Product	(C)	(D)	(M)	(C)	(D)	(M)	(C)	(D)	(M)	S–N/Å
1a	**2a**	9.66	9.07		7.77	7.75		125.0	125.1		1.727[5]
1a	**3a**			8.50			7.82			109.9	
1a	**4a**	8.19	8.41	8.26	7.71	7.80	7.81	110.8	116.0	111.3	1.678[5]
1b	**2b**	9.56	8.87		7.12	7.39		121.0	118.8		
1b	**3b**			8.35			7.55			104.5	
1b	**4b**	8.33	8.46	8.24	7.75	7.42	7.54	100.8	113.3	104.5	
1b	**5b·HCl**		7.89	7.73		7.19	7.11				
1c	**2c**	9.71	9.13		6.39	6.63		130.0	126.4		
1c	**3c**			8.51			7.04			110.2	
1d	**2d**	9.68	9.21		6.47	6.70		127.8	125.7		
1d	**3d**			8.54			7.12			110.2	
1e	**2e**	9.63			6.69			128.8			
1e	**3e**		8.64	8.31		7.44	7.80		114.3	101.2	
1f	**3f**	9.06	8.41	8.33	6.78	7.56	7.68	116.2	109.5	101.5	
1g	**3g**	8.43	8.28	8.31	7.34	7.63	7.72	114.9	111.9	101.2	1.685[5]
1g	**15**	7.52	7.54	7.57	7.52	7.54	7.57	169.2	169.2	170.6	1.899[d]
1h	**3h**	8.74	8.12	8.51	6.97	7.65	7.69	115.7	108.0	101.9	
1i	**14**	8.39	8.29	8.38	7.22	7.47	7.48	131.7	129.3	122.7	1.734[9]
1j	**2j**	9.43	8.86		7.72	7.70		122.7	122.2		
1j	**3j**			8.28			7.77			110.2	
1k	**2k**	9.52	8.92		7.68	7.57		121.6	122.5		
1k	**3k**			8.32			7.75			110.4	
1l	**2l**	9.49	9.08		7.71	7.75		126.0	123.6		
1l	**3l**			8.35			7.82			110.1	
1m	**2m**		9.22			7.99			127.1		
1m	**3m**			8.43			8.08			110.9	
1n	**2n**		9.02			7.87			124.5		
1n	**3n**			8.35			8.27			110.6	
1o	**2o**		9.15			7.89			123.8		
1o	**3o**			8.36			8.29			110.9	
1p	**2p**		9.05			7.80			124.3		
1p	**3p**			8.33			8.18			110.6	
1q	**2q**		9.01			7.85			124.1		
1q	**3q**			8.35			8.26			109.6	
6	**7**[e]	8.74	8.51	8.72	7.10	7.74	7.72	122.5	116.1	114.5	1.685[5]
9a	**10a**[f]	9.91	9.03		7.98	7.71		92.8	92.5		1.675[5]
9a	**11a**[f]			8.67			7.67			88.8	
9f	**11f**[f]	9.23	8.81	8.95	7.41	7.62	7.70	88.1	89.8	86.7	1.662[5]

[a] Solvents for NMR measurements: (C) $CDCl_3$, (D) DMSO-d_6, (M) CD_3OD. [b] The H-6 and H-6′ signals are doublets with coupling constants of 7.9 ± 0.5 Hz. [c] For N(Me) in hetero ring. [d] For the *N*,*N*′-diisopropyl analogue of **15** from ref. 13. [e] The numbering of atoms is changed in **7** (from H-6′ to H-2′). [f] The numbering of atoms is changed in **10a**, **11a** and **11f** (from H-6 to H-2).



Scheme 3 Synthesis and hydrolysis of diaryl(acylamino)(chloro)-λ^4-sulfane **10a** and diaryl(acylamino)sulfonium salts **11a**, **11f** and **12a**.

Conformation. ^{1}H NMR data suggest that chloro-λ^4-sulfanes **2c** and **2d** with *o*-Me and *o*-Cl substituents, respectively have a *skew* conformation (Fig. 1), meaning that the phenyl ring is nearly coplanar with the C(1)–S–C(1′) plane, whereas the condensed aromatic ring is perpendicular to it. The *o*-Me and *o*-Cl substituents hinder the rotation about the S–C(1′) bond, therefore the anisotropic shielding effect of the aromatic ring condensed to the heteroring gives rise to a considerable upfield shift of the H-6′ signals as compared to those of the *p*-substituted counterparts **2k** and **2l** ($\Delta\delta$H-6′ = 1.24–1.29 ppm in $CDCl_3$ and

Table 2 NOE data obtained for diaryl(acylamino)(chloro)-λ^4-sulfanes (**2** and **10**), diaryl(acylamino)sulfonium salts (**3**, **4**, **5** and **11**) and spiro-λ^4-sulfanes (**14** and **15**)[a]

Compound	Solvent	NOE (%)		Torsion angle N–S–C(1′)–C(6′)/°	Proposed conformation
		H(6′)–NMe	H(6′)–H(6)		
2a	C/D	1.7/1.4	No effect	89 (ref. 5)	[b]
2b	C/D	1.1/0.8	2.5/1.7		Skew
2c	C/D	1.2/1.0	4.8/4.3		Skew
2d	C/D	1.0/0.8	5.4/5.0		Skew
2e	C	[c]			Skew[d]
2j–2q	D	0.8–1.5	No effect		[b]
3a	M	1.1	No effect		[b]
3b	M	0.8	1.4		Skew
3c	M	0.9	1.2		Skew
3d	M	0.8	1.3		Skew
3e	D/M	5.9/6.2	No effect		Butterfly
3f–3h	C/D/M	7.3–7.6/6.8–7.4/5.9–6.2	No effect	11 in **3g** (ref. 5)	Butterfly
3j–3q	M	0.7–1.0	No effect		[b]
4a	C/D/M	1.1/1.5/0.9	No effect	37 (ref. 5)	[b]
4b	C/D/M	1.2/0.8/0.9	2.5/2.0/1.6		Skew
5b·HCl	D/M	No effect	2.7/1.8	95.5[e]	Skew
7[f]	C/D/M	9.4/7.4/6.7	No effect	31 (ref. 5)	Butterfly-like
10a[g]	C/D	1.5/1.2	No effect	63 (ref. 5)	[b]
11a[g]	M	1.1	No effect		[b]
11f[g]	C/D/M	9.3/8.8/7.8	No effect	3 (ref. 5)	Butterfly
14	C/D/M	7.2/6.5/6.5	No effect	11 (ref. 9)	Butterfly
15	C/D/M	8.2/8.0/8.1	No effect	6.2 (ref. 13)[h]	Butterfly

[a] Solvents for measurements: (C) $CDCl_3$, (D) DMSO-d_6, (M) CD_3OD. [b] Practically free rotation about the S–C(1′) bond supported by the isotropy of H(2′) and H(6′) signals. [c] NOE cannot be measured because of decomposition. [d] Established only on the basis of the considerable upfield shift of H(6′) signal (6.69 ppm, see Table 1). [e] Torsion angle O(2)–S–C(1′)–C(6′). [f] The numbering of atoms is changed in **7** (from H-6′ to H-2′). [g] The numbering of atoms is changed in **10a**, **11a** and **11f** (from H-6 to H-2). [h] For the *N*,*N*-diisopropyl analogue of **15**.

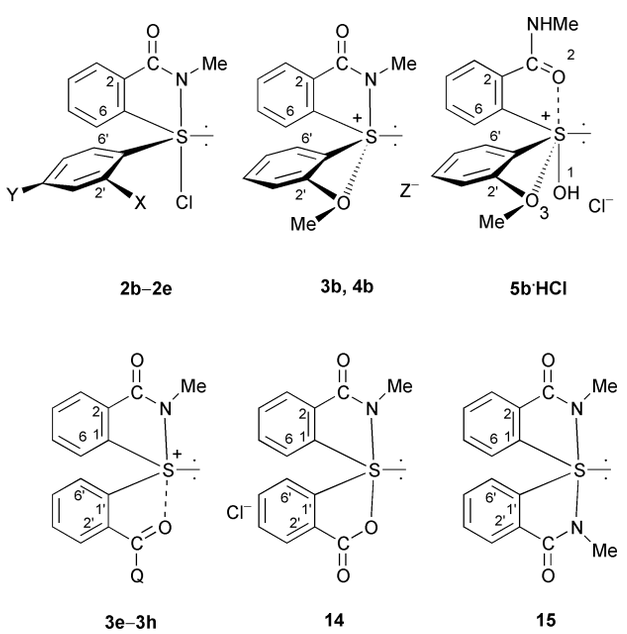


Fig. 1 The conformation of diaryl(acylamino)(chloro)-λ^4-sulfanes **2b**–**2e** (for X and Y, see Scheme 1), diaryl(acylamino)sulfonium salts **3b** ($Z^- = Cl^-$), **3e** (NO_2 instead of QCO), **3f** (Q = OMe), **3g** (Q = NHMe), **3h** (Q = Me), **4b** ($Z^- = ClO_4^-$), **5b·HCl**, and spiro-λ^4-sulfanes **14** and **15**.

1.04–1.05 ppm in DMSO-d_6). In the *para*-substituted compounds the rotation about the S–C(1) bond may be regarded as practically free. A much smaller effect was observed for the **2b**–**2j** pair carrying an MeO group in the *o*/*p* position ($\Delta\delta$H-6′ = 0.60 ppm in $CDCl_3$ and 0.31 ppm in DMSO-d_6; see explanation later).

The similarity of δH-6 and δH-6′ values found for spiro-λ^4-sulfane **14** and sulfonium salts **3e–3h** and **7** with S···O interaction (Table 1) reveals that the sulfur atom in the latter compounds should also exhibit trigonal bipyramidal geometry with N and O hetero atoms in axial positions, and they assume a *butterfly* conformation (Fig. 1). This means that both aromatic rings are nearly perpendicular to the C(1)–S–C(1′) plane.

Suggestions about the different conformations of chloro-λ^4-sulfanes and sulfonium chlorides, based on δ(H-6) and δ(H-6′) shifts, were confirmed by studies on NOE between H(6′)–NMe and H(6)–H(6′) protons (Table 2).

NOE was found between H-6′ and NMe for compounds with a butterfly conformation, whereas in the case of a skew conformation NOE was found between H-6 and H-6′. The observed NOE values vary according to the actual orientation of the non-condensed aromatic ring or the freedom of the rotation about the S–C(1′) bond. Data indicate that sulfonium salts **4a** and *o*-methoxy-substituted **3b**, **4b** and **5b·HCl** take up a skew shape as shown in Figs. 1 and 2. All these results are in agreement with those obtained by X-ray diffraction. The N–S–C(1′)–C(6′) torsion angle data indicative of H(6′)–N(Me) proton distance are listed in Table 2 for some compounds investigated also in the solid state.

NOE was not observed between H-6 and 2′-Me protons in **2c**, and very small NOEs could be detected between H-6′ and NMe protons in the case of **2c** and **2d**. These observations together with the upfield shielded H-6′ signals and the marked interaction of H-6 and H-6′ (Table 2) give further support for the rigid skew geometry of chloro-λ^4-sulfanes with *o*-Me and *o*-Cl substituents in the *exo* position, and suggest less hindered or practically free rotation about the S–C(1′) bond for compounds without *ortho*-substituents (*e.g.* **2a**, **2j**–**2q**, **4a**, **10a**).

In the case of chloro-λ^4-sulfane **2b** with an *o*-MeO group (similarly to the analogous sulfonium chloride **3b**, perchlorate **4b** and hydroxysulfonium chloride **5b·HCl**) a smaller NOE between H-6 and H-6′ protons (1.7–2.5%) was observed than for **2c** and **2d** (4.5–5.4%, Table 2), and the H-6′ protons in the former compounds (in contrast with **2c** and **2d**) do not experience a shielding effect from the condensed aromatic ring (see Table 1). These phenomena may be explained by the polarization of the S–Cl bond, *i.e.* the enhanced sulfonium character of **2b** (caused by an equatorially directed, 1,4 type S···O close contact between the positive sulfur atom and the methoxy-oxygen atom, see Figs. 1 and 2), associated with the widening of

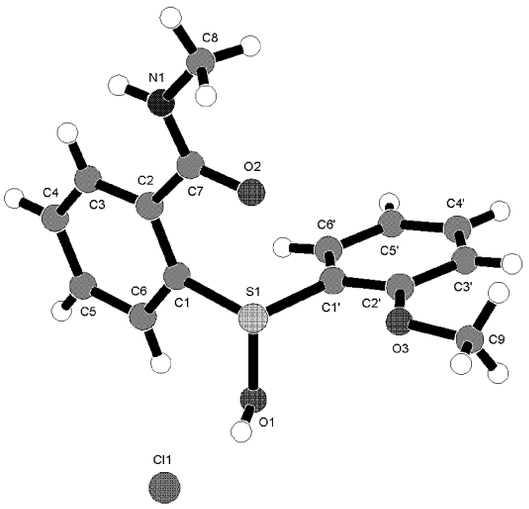


Fig. 2 Perspective representation of sulfoxide-hydrochloride **5b·HCl** molecule. Selected bond lengths (Å) and angles (°): S(1)–O(1) 1.587(4), S(1)···O(2) 2.411(4), S(1)···O(3) 2.764(4), S(1)–C(1) 1.770(6), S(1)–C(1′) 1.777(5), C(7)–O(2) 1.229(6), C(2′)–O(3) 1.357(7), θ(O1–S1···O2) 178.9(2), θ_1(O1–S1···O3) 97.9(2), θ_2(O1–S1···C1) 100.4(2), θ_3(O1–S1···C1′) 98.1(2), θ_4(C1–S1–C1′) 102.8(3), θ_5(S1–C1′–C2′) 115.2(4), θ_6(C1′–C2′–O3) 117.0(5), φ_1(S1–C1–C2–C7) 5.8(6), φ_2(C1–C2–C7–O2) 7.7(7), φ_3(C2–C7–O2···S1) −12.8(5), φ_4(C7–O2···S1–C1) 12.7(4), φ_5(O2···S1–C1–C2) −9.2(4), φ_6(O1–S1–C1–C2) 171.0(4), φ_7(O1–S1–C1′–C6′) 83.4(5), φ_8(C1′–S1–C1–C2) −88.1(4), φ_9(C1–S1–C1′–C6′) −19.2(5), φ_{10}(S1–C1′–C2′–O3) −177.5(5).

the C(1)–S–C(1′) bond angle characteristic of sulfonium structure (*cf*. data 82°, 102° and 104° in **2a**, **4a** and **5b·HCl**, respectively). Nevertheless, the small NOEs between H-6′ and NMe protons (Table 2) point to a skew conformation of **2b** and the other *o*-methoxy-substituted compounds (**4b** and **5b·HCl**).

S–N, S–Cl and S···O bonding. Further information about the axial NS–Cl and $NS^+\cdots O$ bond systems was gained from the comparison of the ^{15}N-chemical shifts of amide nitrogen in the investigated models with that of the reference spiro-λ^4-sulfanes **14** and **15**. Earlier X-ray diffraction studies revealed[5,9] that the strength of axial S–N bonds (reflected in different bond lengths) in spirocyclic (acylamino)-λ^4-sulfanes, monocyclic (acylamino)(chloro)-λ^4-sulfanes and in the corresponding (acylamino)sulfonium salts (stabilized by S···O close contact) depends on the relative electronegativities (nucleophilicities) of the axial heteroatoms. The weakest (longest) S–N (hypervalent) bond was found in the *N*,*N*-diisopropyl analog of symmetric bis(acylamino)spiro-λ^4-sulfane **15**[13] (1.898 Å) and the strongest (shortest) S–N (covalent) bond in the sulfonium salt **11f**[5] (1.662 Å). The S–N bond length data of compounds **14**,[9] **2a**,[5] **7**,[5] **3g**[9] and **10a**[5] lie between the former extreme values (1.734, 1.727, 1.685, 1.685, 1.675 Å, respectively). We may assume that the more pronounced is N(amide) lone pair delocalization toward the carbonyl oxygen ($O{=}CR{-}NR_2 \leftrightarrow {}^{-}O{-}CR{=}NR_2^{+}$) in these compounds the more the N–S bond is weakened. It is known, however, from NMR studies[14] that the shielding of the nitrogen attached to an unsaturated carbon is highly influenced by the degree of lone pair delocalization. Consequently, the increase in S–N bond lengths should be reflected in the downfield shift of ^{15}N signal, as compared to that of NH_3 ($\delta = 0$). δ^{15}N data in Table 1 (169.2, 129.3, 125.1, 116.1, 111.9, 92.5 and 89.8 ppm in DMSO-d_6 for **15**, **14**, **2a**, **7**, **3g**, **10a** and **11f**, respectively) support the correlation outlined above which may be recommended to characterize the S–N bonds in (acylamino)-λ^4-sulfanes and (acylamino)sulfonium salts. Here it should be mentioned that the observed ^{15}N chemical shifts represent a wide region (~90 ppm), whereas the measured ^{13}C resonances of the lactam carbonyls lie in a substantially narrower range (~4 ppm).

The correlation works also in the case of (acylamino)-sulfonium salts without S···O interaction. δ^{15}N = 116.0 and 88.8 ppm were measured for **4a** and **11a** with S–N bond lengths 1.678[5] and 1.651 Å[5] (for **12a** perchlorate), respectively. It is also remarkable that the relatively low δ^{15}N shift in $CDCl_3$ (121.0 ppm) observed for *o*-MeO-substituted **2b**, as compared to those found for **2c**–**2e** with *o*-Me, *o*-Cl and *o*-NO_2 groups (130.0, 127.8 and 128.8 ppm, respectively), points to an enhanced sulfonium character of **2b**, as discussed above.

Data from X-ray diffraction and Table 1 also show that the shorter the axial S–N bond (*i.e.* the smaller the δ^{15}N shift) is, the longer the axial S–Cl hypervalent bond and axial S···O contact incorporated in a five-membered "ring" may appear; *e.g*. S–Cl is 2.690[5] and 3.101 Å[5] in **2a** and **10a** (with δ^{15}N = 125.1 and 92.5 ppm, respectively), and in a similar way S···O is 2.132[9] (weak hypervalent S–O bond), 2.373,[9] and 2.736 Å[5] in **14**, **3g** and **11f** (with δ^{15}N = 129.3, 111.9 and 89.8 ppm, respectively). The not quite regular behaviour of compound **7** (S···O 2.408 Å,[5] δ^{15}N = 116.1 ppm) may be attributed to the S···O contact built in a six-membered "ring".

We may conclude that axial hypervalent S–Cl bond and S···O close contact may also be characterized by using δ^{15}N data. Thus it seems very likely that *ortho*- or *para*-substitution in the aromatic ring of chloro-λ^4-sulfanes does not affect the S–Cl bond (except for the *o*-MeO group). It is also revealed that there is no significant difference in S···O contacts involving *o*-COOMe, *o*-CONHMe or *o*-COMe neighbouring groups (Table 1).

The neighbouring-group effect of the carbamoyl group may be better understood if we compare compounds **3g** and **3o** with a CONHMe substituent in *ortho* and *para* positions, respectively. The significant downfield shift of the ^{15}N(H) signal in **3g** as compared to that in **3o** (108.9 and 103.6 ppm, respectively, in DMSO-d_6) points to a more effective delocalization of the N(H) lone pair towards the carbonyl-oxygen in the former case, promoting the formation of S···O close contact.

Solvent effect. We discussed above that the actual structure of products formed from sulfides by chlorination depends on the solvent used. In addition, the solvent effect observed for ^{15}N signals gives further insight into the factors governing the N–S–Cl and $N{-}S^+\cdots O$ bonding systems.

δ^{15}N data in Table 1 show that $CDCl_3$ solvent is the most favourable for stabilizing both the S–Cl hypervalent bond in chloro-λ^4-sulfanes (**2a**–**2e** and **2j**–**2l**) and intramolecular S···O close contact in sulfonium chlorides having an *ortho* or *peri* neighbouring group (**3f**–**3h** and **7**). Thus S–N bonds in these compounds are somewhat weaker in apolar $CDCl_3$ than in polar DMSO-d_6. The latter solvent promotes the polarization of S–Cl and S···O bonding explaining *e.g*. that the chlorination product of *o*-NO_2-substituted sulfide **1e** occurs in DMSO-d_6 as a dissociated salt (**3e)** instead of a neutral chloro-λ^4-sulfane (**2e**). For the same reason, the *o*-CONHMe group in **3g** is less effective at forming an S···O close contact in DMSO-d_6 than in $CDCl_3$ [δ^{15}N(H) = 108.9/118.4 ppm, respectively].

The ^{15}N-resonances of perchlorates **4a** and **4b** in $CDCl_3$ (110.8 and 100.8 ppm, respectively) suggest that in apolar medium even the perchlorate anion can be involved in S···O contact, elongating the S–N bond in **4a**. As a consequence of the S···O interaction from the equatorial direction, the *o*-methoxy group in **4b** keeps the perchlorate anion away from the positive sulfur atom (see Fig. 1), and the enhanced sulfonium character pertains to the shortening of the S–N bond. On the other hand, the considerably downfield shifted ^{15}N-resonances of **4a** and **4b** measured in DMSO-d_6 (116.0 and 113.3 ppm, respectively) point to a marked interaction of the sulfonium centre with DMSO-d_6 molecules having a negatively polarized oxygen atom. In *o*-methoxy-substituted **4b** the equatorial S···O close contact may be responsible for the slightly weaker interaction with DMSO-d_6 molecules.

Owing to the dissociation of the S–Cl bond, chloro-λ^4-sulfanes **2a**–**2e** and **2j**–**2q** occur in the dipolar protic solvent CD_3OD as sulfonium chlorides **3a**–**3e** and **3j**–**3q**, respectively. The ^{15}N-resonances of the latter salts and **4a** in CD_3OD lie in a narrow region at about 110 ppm. In these compounds the sulfonium centre is not involved in intramolecular S···O interaction, so it is easily accessible to the solvent molecules with negatively polarized oxygen atoms. On the other hand, the comparison of ^{15}N-NMR shifts of *o*-methoxy-derivatives **3b** and **4b** having the same sulfonium cation (104.5 ppm) with that of *p*-methoxy-derivative **3j** (110.2 ppm) reveals that the 1,4 type intramolecular S···O contact in the equatorial position is preserved in CD_3OD, too, shielding the sulfonium centre from the solvent molecules.

Similar but larger differences in δ^{15}N shifts (about 101–110 ppm) were measured in CD_3OD for the *ortho–para* isomeric pairs with substituents forming an axial 1,5 type intramolecular S···O close contact in *ortho*-position (**3e**–**3m**, **3f**–**3n**, **3g**–**3o** and **3h**–**3p**) that may also be explained by the shielding of the sulfonium centre from the solvent molecules in the *ortho*-substituted derivatives. One may conclude that the interaction of the sulfonium centre with the nucleophilic solvent molecules weakens the S–N bond more effectively than intramolecular S···O close contact does in the axial position.

A much smaller solvent effect measured for naphthalene derivatives with a six-membered 1,2-thiazine ring (**10a** and **11f**) may be attributed to steric factors. It is remarkable that the nonsymmetric spiro-λ^4-sulfane **14** and sulfonium salt **7** with strong S···O close contacts are slightly affected by a solvent effect, whereas the structure of symmetric **15** is invariant to solvent change.

X-Ray diffraction studies

The molecular structure of diaryl(hydroxy)sulfonium chloride **5b·HCl** as determined by single-crystal X-ray diffraction is shown in Fig. 2 together with selected interatomic distances and angles. Some details can be found in the Experimental section. It is, however, noteworthy to mention here that the skew-like conformation of **5b·HCl** provides a means of forming both a remarkably short, 1,5 type axial S···O close contact [S···O 2.411 Å, θ(O–S···O) 179°] and an unusual 1,4 type equatorial S···O interaction [S···O 2.764 Å, θ(O–S···O) 98°]. The value of the $\theta(C_{ar}–S–C_{ar})$ bond angle (103°) resembles more a tetrahedral (sulfonium) geometry than a trigonal-bipyramidal (λ^4-sulfane) arrangement.

Kinetics and mechanism of hydrolysis reactions

NMR measurements showed that (acylamino)(chloro)-λ^4-sulfanes are converted immediately to (acylamino)sulfonium chlorides (*e.g.* **2a→3a)**, when dissolved in a protic solvent like methanol. As a continuation of our earlier work,[15–17] we investigated by a kinetic method the hydrolysis of (acylamino)-sulfonium chlorides (**3**, **7**, **11**) and perchlorates (**4**, **12**) leading to sulfoxides (**5**, **8**, **13**) in solvents containing water (*cf*. Schemes 1–3). The rates of hydrolysis were measured by a UV spectrophotometric method in dioxane–water mixtures or in water where water as nucleophile was always in a great excess compared to the reactants (for details see the Experimental section).

Diaryl(acylamino)sulfonium salts with five-membered 1,2-thiazoline ring. The hydrolyses of compounds **3a**–**3h**, **3j**–**3q**, **4a** and **7** proved to be so fast that their rates could be measured by conventional methods only at a low concentration of water [max. 2–4% (v/v)] in dioxane–water mixtures. The reactions followed first-order kinetics up to 50–70% conversion, but the rate constants increased significantly if the initial concentration of the reactants decreased by more than one order of magnitude (Table 3).

Table 3 Effects of the initial concentration of the reactant and that of the water content of the solvent on the rate constant of hydrolysis of diaryl(acylamino)sulfonium salts **3a**, **4a** and **7** at 25 °C

Dioxane–H_2O (v/v)	Initial reactant concentration/ mol dm^{-3}	$k/10^{-4}$ s^{-1}		
		3a	**4a**	**7**
98 : 2	7.5×10^{-4}	4.69	0.868	—
98 : 2	1.5×10^{-4}	7.77	1.41	1.02
98 : 2	3.0×10^{-5}	10.5	1.81	—
97 : 3	1.5×10^{-4}	20.2	9.67	4.04
96 : 4	1.5×10^{-4}	—	—	9.26

Table 4 Effects of TsOH and $LiClO_4$ on the rate constant of hydrolysis of diaryl(acylamino)sulfonium chloride **3f** in 98 : 2 (v/v) dioxane–water solvent at 25° C

[TsOH]/mol dm^{-3}	$k/10^{-4}$ s^{-1}
0	3.38[a]
10^{-4}	6.10
5×10^{-4}	8.90
10^{-3}	9.90
5×10^{-3}	12.1
10^{-2}	13.4

[a] Rate constants 1.61×10^{-4} and 1.52×10^{-4} s^{-1} were measured when solvent contained 5×10^{-5} and 10^{-4} mol dm^{-3} $LiClO_4$, respectively.

The rate of reaction of sulfonium chloride **3a** is faster than that of perchlorate **4a**. The difference in reactivities may be explained by the formation of ion aggregates in apolar solvents containing only a small amount of water. Ion pairs are known to have lower reactivity than free ions.[18] In the given media the ion-pairs of sulfonium chloride **3a** can dissociate more easily than those of **4a**, because chloride ions are solvated better with water than perchlorate ions in **4a**. Thus the concentration of free ions for **3a** is higher in the solution than that for **4a**. The separation of ion-pairs is also promoted by the increase in water content of the solvent. The rate constants for compound **4a** increase therefore much faster with the concentration of water than in the case of **3a** (Table 3).

All (acylamino)sulfonium salts with a five-membered ring (**3a**–**3h**, **3j**–**3q**, **4a** and **7**) are hydrolysed only by water molecules. The rate of the reaction of **3f** is not proportional to the concentration of the hydroxide ions, but increases slightly with the increase in the concentration of acid added to the solvent. On the other hand rate constants decrease when $LiClO_4$ is added to the reaction mixture (Table 4).

The solvation of lithium ions decreases the activity and the nucleophilicity of water, and the number of ion aggregates increases with increasing ionic strength, which may cause the decrease of the rate constants. Acids may have two opposing effects on the rate of the reactions. On the one hand the solvation of protons, like that of lithium ions, may decrease the activity of water and thus the rate of the reaction, on the other the protonation of the acylamino group in the substrate can increase the rate constants.

The *activation parameters* calculated from the temperature dependence of the rate constants for **3a**, **4a**, **3c**, **3f** and **7** suggest a bimolecular rate-determining step, especially as the entropies of activation have high negative values. Significant primary *kinetic isotope effects* were also observed in solvents containing D_2O, meaning that one of the O–H bonds in water molecules is broken in the slow step when the transition state is developed (Table 5).

The *substituent effect* was investigated by comparing the rate constant of **3a** with those of *para*-substituted derivatives **3j**–**3q**. Electron-withdrawing substituents (*e.g.* NO_2, Cl) increase the rate, whereas electron-releasing groups (*e.g.* MeO, Me) exert an opposite effect (Table 6).

Table 5 Temperature dependence of the rate constants, activation parameters and deuterium solvent isotope effect for the hydrolysis of diaryl(acylamino)sulfonium chlorides **3a**, **4a**, **3c**, **3f** and **7** in dioxane–water mixtures

	Temperature/°C	**3a** [a]	**4a** [b]	**3c** [a]	**3f** [a]	**7** [b]
$k/10^{-4}$ s^{-1}	20.0	6.15	8.52	3.89	2.42	2.88
	22.5	6.86	9.11	4.60	2.88	3.44
	25.0	7.77	9.67	5.38	3.38	4.04
	25.0	2.31 [c]	3.99 [c]	—	1.09 [c]	1.41 [c]
	27.5	8.56	10.2	6.35	4.07	4.79
	30.0	9.63	10.7	7.47	4.81	5.68
$\Delta H^{\ddagger}$/kJ mol^{-1}		30.5	14.3	45.5	48.3	47.3
$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}		−202	−255	−154	−149	−151
k_{H_2O}/k_{D_2O} [d]		3.4	2.4	—	3.1	2.9

[a] Measured in 98 : 2 (v/v) dioxane–H_2O. [b] Measured in 97 : 3 (v/v) dioxane–H_2O. [c] Measured in dioxane–D_2O mixtures of the same composition as in dioxane–H_2O. [d] Solvent isotope effects 3.0, 2.6, 2.8 and 2.6 were calculated from the rate constants given in Table 6 for compounds **3b**, **3h**, **3j** and **3q**, respectively.

Table 6 Substituent effect for the hydrolysis of *ortho*- and *para*-substituted diaryl(acylamino)sulfonium chlorides (**3a**–**q**) in 98 : 2 (v/v) dioxane–water mixture at 25 °C

	$k/10^{-4}$ s^{-1}				
Substituent	**3b**–**h** (*ortho*)		**3j**–**q** (*para*)		k_{ortho}/k_{para}
MeO	**3b**	3.30 [a]	**3j**	2.61 [a]	1.3
Me	**3c**	5.38	**3k**	4.97	1.1
Cl	**3d**	32.1	**3l**	13.3	2.4
NO_2	**3e**	31.3	**3m**	39.1	0.80
COOMe	**3f**	3.38	**3n**	20.3	0.17
CONHMe	**3g**	0.066 [b]	**3o**	13.8	0.005
$COCH_3$	**3h**	2.66 [a]	**3p**	18.3	0.15
COOH			**3q**	18.5 [a]	—
CO_2^-	**14**	0.0081 [c]	**3a** [d]	7.7	0.001 [d]

[a] Rate constants 1.11×10^{-4}, 1.02×10^{-4}, 9.22×10^{-5} and 7.08×10^{-4} s^{-1} were measured in 98 : 2 (v/v) dioxane–D_2O at 25 °C for **3b**, **3h**, **3j** and **3q**, respectively. [b] Calculated from the solvent dependence of the rate constants given in ref. 17. [c] Calculated from the solvent dependence of the rate constants given in ref. 16. [d] Rate constant for **3a** was used to calculate the k_{ortho}/k_{para} ratio. The σ_p Hammett constant of *p*-CO_2^- is zero; the rate constant should be equal to that of the unsubstituted compound **3a**.

The Hammett equation gave a good correlation with the σ constants taken from ref. 19 [eqn. (1)].

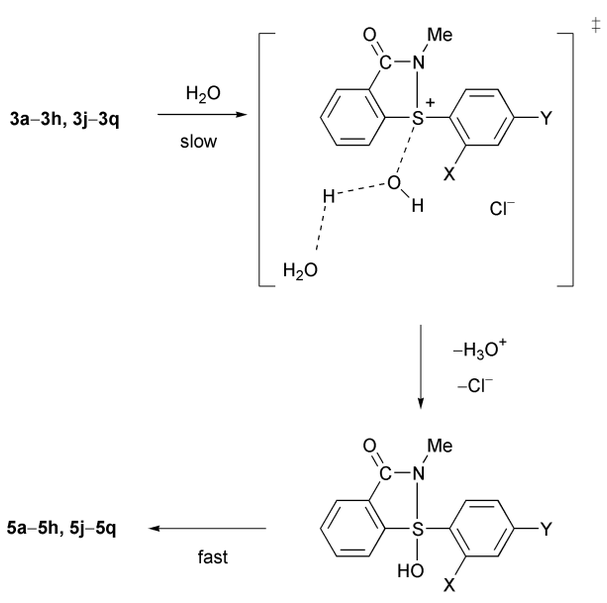
$$\log k = (1.03 \pm 0.07)\sigma - (3.19 \pm 0.03) \quad (r = 0.986) \quad (1)$$

The positive value of the reaction constant (ρ +1.03) is in accordance with the nucleophilic attack of water on the positively charged sulfur atom in the rate-determining step, which is promoted by electron-withdrawing substituents.

In order to study the *steric effect* of the neighbouring *ortho*-substituents, we compared the rate constants of the hydrolysis obtained for *ortho*- and *para*-substituted (acylamino)sulfonium salts listed in Table 6. Because the electronic effect of the *ortho*-substituents can be regarded as similar to that of the *para*-analogues, the ratio of the rate constants of *ortho*- and *para*-substituted compounds (k_{ortho}/k_{para}) should characterize the steric effect of the *ortho*-substituent. If the *ortho*-substituents do not interact effectively with the sulfonium centre (*e.g.* MeO, Me), the k_{ortho}/k_{para} ratio is near to one (**3b**/**3j**, **3c**/**3k**), showing that hydrolysis is not hindered sterically. (The equatorial S···O interaction in the skew-like conformation of **3b**, as shown in Fig. 1, does not influence the rate of the hydrolysis.) Surprisingly, compound **3d** with an *o*-Cl group is twice as reactive as the *para*-derivative **3l**. This observation may be interpreted by the strong electron-withdrawing effect of the *ortho*-chlorine atom. Although the *o*-NO_2 group in **3e** is also strongly electron-withdrawing, the k_{ortho}/k_{para} ratio is somewhat less than unity in this case. The contradiction may be explained by the weak axial S···O interaction developed between the sulfonium centre and the nitro-oxygen atom [20] (see the butterfly conformation of **3e** in Fig. 1) by which the nucleophilic attack of water molecules on the sulfonium centre is somewhat hindered.

As is known,[5,11,20] more effective sulfur–oxygen close contact can be formed in sulfur compounds having a carbonyl group in the *ortho*-position of an aromatic ring bonded to the sulfur atom. In the (acylamino)sulfonium salts studied the carbonyl-oxygen of the *o*-COQ group (Q = OMe, NHMe, Me, O^-) approaches the sulfonium centre from the axial direction (see the butterfly conformation of **3f**, **3g**, **3h** and **14** in Fig. 1; in the latter case the S···O close contact is regarded as a weak hypervalent bond). As a result, the positive sulfur atom is more or less hindered from the nucleophilic attack of water, depending on the relative nucleophilicity of the neighbouring group. The stronger the S···O close contact is, the smaller the value which may be expected for the k_{ortho}/k_{para} ratio. Indeed, data in Table 6 indicate that *o*-$COOCH_3$, *o*-$COCH_3$, *o*-$CONHCH_3$ and *o*-CO_2^- groups decrease the rate of the reaction to 1/6, 1/7, 1/200 and 1/1000 parts, respectively, of those measured for the the *para*-substituted compounds.

Starting from the above results we propose a detailed mechanism shown in Scheme 4 for the hydrolysis of (acylamino)-sulfonium salts containing a five-membered 1,2-thiazoline ring



Scheme 4 Mechanism of hydrolysis of diaryl(acylamino)sulfonium salts **3a**–**3h** and **3j**–**3q**.

Table 7 Rate constants for the hydrolysis of diaryl(acylamino)-sulfonium salts **11a**, **12a** and **11f** at different acid concentrations in water at 25 °C

	$k/10^{-4}$ s^{-1}		
[TsOH]/mol dm^{-3}	**11a**	**12a**	**11f**
5×10^{-4}	6.34	8.74	4.48[a]/0.746[a,b]
7.5×10^{-4}	4.81	5.28	—
10^{-3}	3.75	3.70	0.528
10^{-2}	0.384	0.348	—

[a] Solvent contained 10^{-4} mol dm^{-3} TsOH. [b] In D_2O.

(formed occasionally from the corresponding chloro-λ^4-sulfane by fast ionic dissociation in a protic solvent).

In the rate-determining first step the sulfonium centre is attacked by a water molecule from which a proton is split off to give an (acylamino)(hydroxy)-λ^4-sulfane intermediate (**16**). Sulfoxide is produced in subsequent fast steps by *O*-deprotonation, *N*-protonation and splitting of the S–N bond. The attack of the water molecule is obviously hindered by the *ortho*-carbonyl group, which occupies the axial position about the central sulfur atom of trigonal bipyramidal geometry.

Diaryl(acylamino)sulfonium salts with six-membered 1,2-thiazine ring. Sulfonium salts having an acylamino group incorporated in a six-membered hetero ring hydrolyze much more slowly than their analogues with a five-membered ring.[9] In the case of compounds **11a**, **12a** and **11f** rates can be measured with conventional methods only in water. The hydrolysis reactions, however, do not follow first-order kinetics in this solvent; the calculated rate constants decrease with the progress of the reaction.

The hydrolyses do not deviate from first-order kinetics if acid is added to the reaction mixture in great excess. In water the equilibrium between chloro-λ^4-sulfane **10a** and the corresponding sulfonium salt **11a** is obviously shifted completely to the latter, and both chloride **11a** and perchlorate **12a** are dissociated to free ions. As expected, **11a** and **12a** show practically the same reactivity; their rate constants are equal within experimental error (Table 7).

Both chloride and perchlorate anions are solvated well, and therefore the reversible formation of ion pairs need not to be taken into account. The rate constants of the hydrolysis of compounds **11a** and **12a** decrease when the concentration of acid is increased, *i.e.* when the concentration of hydroxide ions is decreased (Table 7). The log *k versus* pH plot is linear with a slope near to unity [eqn. (2)].

$$\log k = (0.96 \pm 0.03)\text{pH} - (6.32 \pm 0.09) \quad (r = 0.999) \quad (2)$$

The rate of the hydrolysis of *o*-COOMe-substituted **11f**, which reacts more slowly than **11a**, cannot be measured in acidic solutions. In solvent containing 10^{-2} mol dm^{-3} TsOH the reaction hardly shows any measurable progress. In acetate buffer, however, the rate constants can be determined, showing an increase with the concentration of hydroxide ions (Table 8); log *k* is a linear function of the pH [eqn. (3)].

$$\log k = (0.88 \pm 0.03)\text{pH} - (7.00 \pm 0.12) \quad (r = 0.998) \quad (3)$$

Data indicate that (acylamino)sulfonium salts with a six-membered hetero ring react only with hydroxide ions which are efficient enough to attack the sulfonium centre to cause the loosening of the strong S–N covalent bond (see Table 1 and ref. 9) in these compounds. (The *N*-methylacylamino group incorporated into a six-membered ring is a poorer leaving group than in a five-membered ring.) Acid formed as co-product during the reaction changes the concentration of the hydroxide ions, and this is the reason why the hydrolysis does not follow first-order kinetics in non-buffered media.

Table 8 pH dependence of the rate constant for the hydrolysis of diaryl(acylamino)sulfonium chloride **11f** in 0.2 mol dm^{-3} aqueous acetate buffer ($I = 0.074$) at 25 °C; NaCl was added to the solvent to maintain constant ionic strength

pH	$k/10^{-4}$ s^{-1}
3.60	1.39
3.80	2.15
4.00	3.42
4.20	4.72
4.40	7.06

Table 9 Effects of the buffer concentration and ionic strength on the rate constant of the hydrolysis of diaryl(acylamino)sulfonium chloride **11f** in aqueous acetate buffer (pH 4.00), at 25 °C; ionic strength was adjusted by the addition of NaCl to the solvent

	$k/10^{-4}$ s^{-1}		
[Buffer]/ mol dm^{-3}	$I = 0.074$	$I = 0.036$	$I = 0.009$
0.2	3.42	3.88	—
0.1	—	3.77	—
0.05	—	3.84	4.17

At constant ionic strength the rate constants obtained for the hydrolysis of **11f** are independent of the concentration of the acetate ions in buffered media (Table 9), meaning that the hydrolysis is not general base-catalysed.

If NaCl was added to the buffered reaction mixture the rate constant of the hydrolysis decreased with the increase of the ionic strength (Table 9). These data point to a reaction between two oppositely charged ions, *i.e.* to that of the sulfonium and hydroxide ions.

The values of the deuterium solvent isotope effect found for sulfonium salts **11a**, **11f** and **12a** with a six-membered hetero ring are higher than six (Table 10). The primary kinetic isotope effect observed suggests that proton-transfer is involved in the rate-determining step.

The activation parameters calculated from the temperature dependence of the rate constants (Table 10) are in accordance with an unimolecular rate-determining step for the hydrolysis of the above (acylamino)sulfonium salts. The values of both activation enthalpies and entropies are higher than those obtained for analogues with a five-membered hetero ring.

On the basis of experimental data we propose the detailed mechanism shown in Scheme 5 for the hydrolysis of acylamino-sulfonium salts containing a six-membered 1,2-thiazine ring. The first step is the fast nucleophilic addition of hydroxide ion to the sulfonium centre, *i.e.* the formation of an (acylamino)-(hydroxy)-λ^4-sulfane (**17**) intermediate. We surmise that the opening of the hetero ring is started by the rate-determining deprotonation of the *S*-hydroxy group in **17**. The electronic shift from the negatively charged oxygen in **18,** *i.e.* the formation of a sulfinyl group with a strong S–O bond in sulfoxides **13a** and **13f**, can displace the acylamino group from the sulfur atom, which is assisted by *N*-protonation.

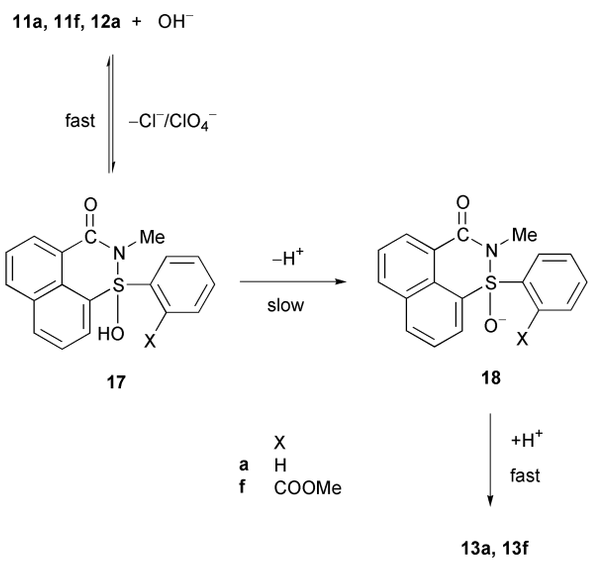
Experimental

The preparation of chloro-λ^4-sulfanes **2a** and **10a**, sulfonium perchlorates **4a** and **12a**, sulfonium chlorides **3g**, **7** and **11f**, and sulfides **1a**, **1g**, **1i**, **6**, **9a** and **9f** has been published previously.[5,9] The synthesis of spiro-λ^4-sulfanes **14** and **15** has also been described.[9,12] In the synthesis of diaryl sulfides **1b**–**1q** 2,2′-dithiobenzoic acid (**19**) was first converted into bis-*N*-methylcarbamoyl derivative **20** through the corresponding acid

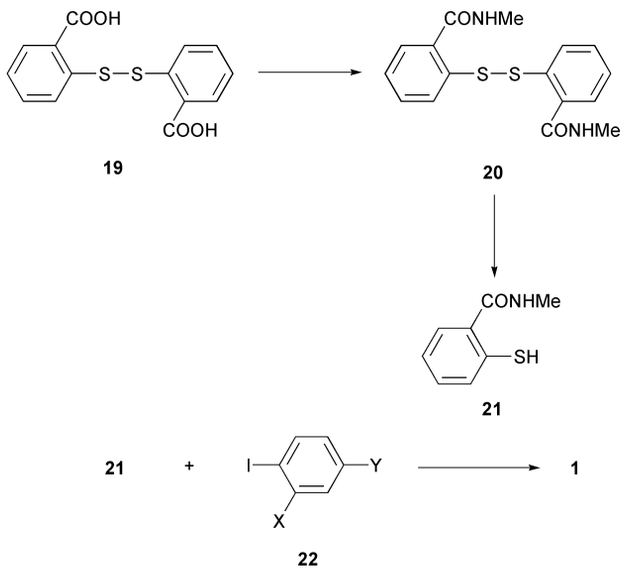
Table 10 Temperature dependence of the rate constants, activation parameters and kinetic isotope effects for the hydrolysis of diaryl(acylamino)-sulfonium salts **11a**, **12a** and **11f** in water

	Temperature/°C	**11a**[a]	**12a**[a]	**11f**[c]
$k/10^{-4}$ s^{-1}	20.0	2.79	3.05	2.21
	22.5	3.73	3.98	3.03
	25.0	4.81/0.746[b]	5.28/0.796[b]	3.88
	27.5	6.40	6.94	5.86
	30.0	8.35	8.90	7.88
$\Delta H^{\ddagger}$/kJ mol^{-1}		78.7	77.1	95.9
$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}		−45.9	−48.9	12.1
k_{H_2O}/k_{D_2O}[d]		6.5	6.6	6.0[e]

[a] Water contained 7.5×10^{-4} mol dm^{-3} TsOH. [b] In D_2O. [c] Measured in 0.2 mol dm^{-3} acetate buffer at pH 4.00. [d] Solvent contained 10^{-4} mol dm^{-3} TsOH. [e] Rate constants are given in Table 7.



Scheme 5 Mechanism of hydrolysis of diaryl(acylamino)sulfonium salts **11a**, **11f** and **12a**.



Scheme 6 Synthesis of substituted diphenyl sulfides **1b**–**1q** (for X and Y, see Scheme 1).

chloride, then disulfide **20** was reduced with zinc in AcOH to give thiol **21**. Compound **21** was coupled with the corresponding aryl iodide (**22b**–**22q**) yielding sulfides **1b**–**1q** (Scheme 6).

Diaryl(acylamino)(chloro)-λ^4-sulfanes and (acylamino)sulfonium chlorides

General procedure. To the mixture of an *N*-methylcarbamoyl-substituted diaryl sulfide (0.01 mol) in dry CH_2Cl_2 (30 cm^3) was added dropwise *tert*-butyl hypochlorite (0.12 cm^3, 0.01 mol) under stirring at 20 °C. After 1 h further stirring pentane (5–20 cm^3) was added and the mixture was allowed to stand overnight at 20 °C. The crystals were filtered off, washed with pentane and dried.

2,3-Dihydro-1-chloro-1-(2-methoxyphenyl)-2-methyl-3-oxo-1,2-benzisothiazole **2b**, yield: 40%; mp 177–188 °C; IR (KBr): 1703vs (C=O) cm^{-1}; *2,3-Dihydro-1-chloro-1-(2-methylphenyl)-2-methyl-3-oxo-1,2-benzisothiazole* **2c**, yield: 50%; mp 200–218 °C; IR (KBr): 1710vs (C=O) cm^{-1}; *2,3-Dihydro-1-chloro-1-(2-chlorophenyl)-2-methyl-3-oxo-1,2-benzisothiazole* **2d**, yield: 42%; mp 178–189 °C; IR (KBr): 1702vs (C=O) cm^{-1}; *2,3-Dihydro-1-chloro-1-(4-methoxyphenyl)-2-methyl-3-oxo-1,2-benzisothiazole* **2j**, yield: 60%; mp 124–128 °C; IR (KBr): 1705vs (C=O) cm^{-1}; *2,3-Dihydro-1-chloro-1-(4-methylphenyl)-2-methyl-3-oxo-1,2-benzisothiazole* **2k**, yield: 59%; mp 119–124 °C; IR (KBr): 1710vs (C=O) cm^{-1}; *2,3-Dihydro-1-chloro-1-(4-chlorophenyl)-2-methyl-3-oxo-1,2-benzisothiazole* **2l**, yield: 40%; mp 145–149 °C; IR (KBr): 1700 cm^{-1}; *2,3-Dihydro-1-chloro-1-(4-nitrophenyl)-2-methyl-3-oxo-1,2-benzisothiazole* **2m**, yield: 66%; mp 182–183 °C; IR (KBr): 1700vs (C=O) cm^{-1}. *2,3-Dihydro-1-chloro-1-[4-(methoxycarbonyl)phenyl]-2-methyl-3-oxo-1,2-benzisothiazole* **2n**, yield: 51%; IR (KBr): 1715vs (C=O) cm^{-1}; *2,3-Dihydro-1-chloro-1-[4-(N-methylcarbamoyl)-phenyl]-2-methyl-3-oxo-1,2-benzisothiazole* **2o**, yield: 57%; mp 245–255 °C; IR (KBr): 3300m (N–H), 1700vs, 1630vs (C=O) cm^{-1}; *2,3-Dihydro-1-chloro-1-(4-acetylphenyl)-2-methyl-3-oxo-1,2-benzisothiazole* **2p**, yield: 39%; mp 155–159 °C; IR (KBr): 1695vs, 1660vs (C=O) cm^{-1}; *2,3-Dihydro-1-chloro-1-(4-carboxyphenyl)-2-methyl-3-oxo-1,2-benzisothiazole* **2q**, yield: 57%; mp 238–243 °C; IR (KBr): 3600–2300br (O–H), 1720vs, 1710sh (C=O) cm^{-1}; *2,3-Dihydro-1-(2-nitrophenyl)-2-methyl-3-oxo-1,2-benzisothiazol-1-ium chloride* **3e**, yield: 50%; mp 153–159 °C; IR (KBr): 1710vs (C=O), 1528vs (NO_2) cm^{-1}; *2,3-Dihydro-1-(2-methoxycarbonylphenyl)-2-methyl-3-oxo-1,2-benzisothiazol-1-ium chloride* **3f**, yield: 57%, mp 317–320 °C; IR (KBr): 1713vs, 1688vs (C=O) cm^{-1}; *2,3-Dihydro-1-(2-acetylphenyl)-2-methyl-3-oxo-1,2-benzisothiazol-1-ium chloride* **3h**, yield: 64%; mp 149–152 °C; IR (KBr): 1728vs, 1650vs (C=O) cm^{-1}.

Diaryl sulfides

General procedure. The mixture of an aryl iodide (**22b**–**22q**, 0.1 mol), thiol **21** (16.7 g, 0.1 mol) and Cu_2O (7.15 g, 0.05 mol) in dry pyridine (150 cm^3) was refluxed under nitrogen for 2 h and after cooling to room temperature was poured into a mixture of ice (600 g) and c. HCl (600 cm^3). The precipitate was filtered off, washed with water and dried then boiled with EtOH (200 cm^3) for 15 min. The insoluble part was filtered off then the filtrate was saturated with H_2S. The precipitate was removed by filtration, then the filtrate was evaporated and the solid crude product was recrystallized from a suitable solvent.

***N*-Methyl-2-sulfanylbenzamide (21).** To boiling thionyl chloride (330 cm^3, 4.55 mol) 2,2′-dithiobenzoic acid **19** (180 g, 0.587 mol) was added in small portions, then the reaction mixture was refluxed for 1 h. After evaporation of the excess thionyl chloride *in vacuo*, the residue was dissolved in dry benzene (800 cm^3) and added dropwise to the stirred solution of methylamine (109 g, 3.52 mol) in dry THF (900 cm^3) at 0 °C. The reaction mixture was allowed to stand overnight, then the solvent was removed *in vacuo*, the residue triturated with water (2000 cm^3), filtered and dried. The crude product was washed thoroughly with acetone (500 cm^3) to give *N*,*N*′-dimethyl-2,2′-dithiobenzamide (**20**) (147 g, 75%); mp 208–216 °C; IR (KBr): 3285vs (N–H), 1632vs, 1550vs (amide I, II) cm^{-1}. The mixture of disulfide **20** (100 g, 0.301 mol), zinc dust (79 g, 1.21 mol) and AcOH (900 cm^3) was refluxed for 6 h, then the solvent was removed *in vacuo*. After adding water (180 cm^3) and c. HCl (600 cm^3) to the residue, the mixture was filtered into water (1800 cm^3), the crystals were filtered off, washed with water, then dried to yield thiol **21** (40 g, 40%); mp 90–92 °C; IR (KBr) 3305s (N–H), 1618vs, 1540vs (amide I, II) cm^{-1}.

2-(N-Methylcarbamoyl)phenyl 2-methoxyphenyl sulfide **1b**, yield: 70%; mp 132–133 °C (109–110 °C in ref. 21); IR (KBr): 3260s (N–H), 1632vs, 1550s (amide I, II) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 2-methylphenyl sulfide* **1c**, yield: 67%; mp 95–96 °C; IR (KBr): 3280s (N–H), 1628vs, 1540vs (amide I, II) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 2-chlorophenyl sulfide* **1d,** yield: 66%; mp 125–127 °C; IR (KBr): 3270s (N–H), 1642vs, 1550s (amide I, II) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 2-nitrophenyl sulfide* **1e**, yield: 80%; mp 82–83 °C; IR (KBr): 3225s (N–H), 1632vs (amide I), 1510vs (NO_2) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 2-(methoxycarbonyl)phenyl sulfide* **1f**, yield: 70%; mp 125–128 °C; IR (KBr): 3265m (N–H), 1715vs (C=O), 1640vs, 1565s (amide I, II) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 2-acetylphenyl sulfide* **1h**, yield: 56%; mp 133–135 °C; IR (KBr): 3260s (N–H), 1668vs (C=O), 1630vs, 1552vs (amide I, II) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 4-methoxyphenyl sulfide* **1j**, yield: 74%; mp 140–141°C (140–140.5 °C in ref. 21); IR (KBr): 3300s (N–H), 1640vs, 1550vs (amide I, II) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 4-methylphenyl sulfide* **1k**, yield: 74%; mp 158–159 °C; IR (KBr): 3370s (N–H), 1645vs, 1534vs (amide I, II) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 4-chlorophenyl sulfide* **1l**, yield: 74%; mp 140–141°C; IR (KBr): 3300s (N–H), 1640vs, 1550vs (amide I, II) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 4-nitrophenyl sulfide* **1m**, yield: 77%; mp 189–192 °C; IR (KBr): 3260s (N–H), 1632vs, 1570vs (amide I, II) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 4-(methoxycarbonyl)-phenyl sulfide* **1n**, yield: 61%; mp 133–135 °C; IR (KBr): 3295s (N–H), 1722vs (C=O), 1640vs, 1550s (amide I, II) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 4-(N-methylcarbamoyl)phenyl sulfide* **1o**, yield: 70%; mp 197–201 °C; IR (KBr): 3330s, 3265s (N–H), 1632 vs, 1550vs (amide I, II) cm^{-1}; *2-(N-methylcarbamoyl)-phenyl 4-acetylphenyl sulfide* **1p**, yield: 54%; mp 151–153 °C; IR (KBr): 3325vs (N–H), 1680vs (C=O), 1632vs, 1548s (amide I, II) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 4-carboxyphenyl sulfide* **1q**, yield: 70%; mp 167–168 °C; IR (KBr): 3300s (N–H), 3450–2300br (O–H), 1695vs (C=O), 1640vs, 1548s (amide I, II) cm^{-1}.

Diaryl sulfoxides

General procedure. To the solution of a diaryl(acylamino)-(chloro)-λ^4-sulfane or a diaryl(acylamino)sulfonium chloride (0.01 mol) in dichloromethane (10 cm^3) was added water (10 cm^3) and the mixture was stirred for 6 h at room temperature. The organic phase was separated, dried with $MgSO_4$, then the solvent was removed *in vacuo*.

2-(N-Methylcarbamoyl)phenyl phenyl sulfoxide **5a**, yield: 88%; mp 63–65 °C; IR (KBr): 3310vs, 3560s (N–H), 1632vs, 1552s (amide I, II), 1030s (S=O) cm^{-1}; *2-(N-methylcarbamoyl)-phenyl 2-methoxyphenyl sulfoxide* **5b**, yield: 80%; mp 165–167 °C; IR (KBr): 3265s (N–H), 1650vs, 1560s (amide I, II), 1015vs (S=O) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 2-methylphenyl sulfoxide* **5c**, yield: 80%; mp 159–161 °C; IR (KBr): 3290s (N–H), 1640vs, 1545s (amide I, II), 987vs (S=O) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 2-chlorophenyl sulfoxide* **5d**, yield: 78%; mp 175–179 °C; IR (KBr): 3320s (N–H), 1635vs, 1548s (amide I, II), 990vs (S=O) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 2-nitrophenyl sulfoxide* **5e**, yield: 69%; mp 198–199 °C; IR (KBr): 3150–3400br (N–H), 1630vs, 1550vs (amide I, II), 990vs (S=O) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 2-(methoxycarbonyl)phenyl sulfoxide* **5f**, yield: 87%; mp 190–204 °C; IR (KBr): 3280w (N–H), 1712vs (C=O), 1665vs, 1550s (amide I, II), 1014vs (S=O) cm^{-1}; *bis[2-(N-methylcarbamoyl)-phenyl]sulfoxide* **5g**, yield: 78%; mp 212–214 °C (212–214 °C in ref. 11); IR (KBr): 3290m (N–H), 1646vs, 1532 (amide I, II), 1022vs, 1000s (S=O) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 2-acetylphenyl sulfoxide* **5h**: yield: 76%; mp 192–194 °C; IR (KBr): 3220s (N–H), 1668vs (C=O), 1645vs, 1560s (amide I, II), 1000vs (S=O) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 2-carboxyphenyl sulfoxide* **5i**, yield: 77%; mp 186–193 °C (182–193 °C in ref. 9); IR (KBr): 3480–2300br (O–H), 1682vs (C=O), 1648vs, 1560s (amide I, II), 1028vs (S=O) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 4-methoxyphenyl sulfoxide* **5j**, yield: 86%; mp 147–149 °C; IR (KBr): 3300s (N–H), 1640vs, 1555s (amide I, II), 1015vs (S=O) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 4-methylphenyl sulfoxide* **5k**, yield: 70%; mp 137–139 °C; IR (KBr): 3320s (N–H), 1628vs, 1545vs (amide I, II), 1035vs (S=O) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 4-chlorophenyl sulfoxide* **5l**, yield: 82%; mp 164–167 °C; IR (KBr): 3380s (N–H), 1635vs, 1535vs (amide I, II), 990vs (S=O) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 4-nitrophenyl sulfoxide* **5m**, yield: 77%; mp 210–216 °C; IR (KBr): 3290vs (N–H), 1650vs, 1562vs (amide I, II), 1017vs (S=O) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 4-(methoxycarbonyl)phenyl sulfoxide* **5n**, yield: 73%; mp 160–168 °C; IR (KBr): 3250s (N–H), 1725vs (C=O), 1650vs, 1548s (amide I, II), 1010s (S=O) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 4-(N-methylcarbamoyl)phenyl sulfoxide* **5o**, yield: 80%; mp 239–241 °C; IR (KBr): 3320vs (N–H), 1665vs, 1635vs, 1545vs (amide I, II), 990vs (S=O) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 4-acetylphenyl sulfoxide* **5p**, yield: 77%; mp 122–130 °C; IR (KBr): 3290s (N–H), 1685vs (C=O), 1638vs, 1550s (amide I, II), 988s (S=O) cm^{-1}; *2-(N-methylcarbamoyl)phenyl 4-carboxyphenyl sulfoxide* **5q**, yield: 66%; mp 244–247 °C; IR (KBr): 3350–2300br (O–H), 3250s (N–H), 1715vs (C=O), 1620vs, 1580vs (amide I, II), 993vs (S=O) cm^{-1}; *8-methoxycarbonyl-1-naphthyl 2-(N-methylcarbamoyl)-phenyl sulfoxide* **8**, yield: 66%; mp 211–214 °C; IR (KBr): 3372s (N–H), 1710vs (C=O), 1650vs, 1538s (amide I, II), 1032s (S=O) cm^{-1}; *8-(N-methylcarbamoyl)-1-naphthyl phenyl sulfoxide* **13a**, yield: 70%; mp 204–206 °C; IR (KBr): 3310s (N–H), 1650vs, 1555vs (amide I, II), 1021vs, 1015vs (S=O) cm^{-1}; *8-(N-methylcarbamoyl)-1-naphthyl 2-(methoxycarbonyl)phenyl sulfoxide* **13f**, yield: 70%, mp 208–237 °C; IR (KBr) 3300s (N–H), 1713vs (C=O), 1630s, 1570s (amide I, II), 1030vs (S=O) cm^{-1}.

[2-(*N*-Methylcarbamoyl)phenyl](2-methoxyphenyl)(hydroxy)-sulfonium chloride 5b·HCl. The product obtained from **1b** by chlorination was crystallized from dichloromethane–ether and the solid product separated was filtered off. After standing a week at room temperature, **5b·HCl** could be isolated from the mother liquor, owing to the hydrolysis of sulfonium salt **3b** brought about by a trace of water in the solvent. Mp 156–161 °C, IR (KBr) 3240s (N–H), 1625vs, 1565vs (amide I, II), 2550–1730br (O–H).

NMR Measurements

The ^1H, ^{13}C and ^{15}N NMR spectra were recorded in $CDCl_3$, DMSO-d_6 and CD_3OD in 5 mm tubes at RT on a Bruker DRX 500 spectrometer at 500.13 (^1H), 125.76 (^{13}C) and 50.58 (^{15}N) MHz, with the deuterium signal of the solvent as the lock and TMS as internal reference for ^1H and ^{13}C NMR. The standard

Bruker microprogram NOEMULT.AU to generate NOE was used with a selective preirradiation time. The 2D COSY, HSQC and HMBC (^{1}H–^{13}C and ^{1}H–^{15}N) spectra were obtained by using the standard Bruker gradient pulse programs COSYGS, INV4GSTP and INV4GSLRNDSW, respectively. In the 2D ^{1}H–^{15}N HMBC spectra the resolution in the ^{15}N dimension was 4.9 Hz/point (SW = 50 ppm and TD = 512) to give ^{15}N-resonances (downfield from the signal of liquid ammonia as external reference) with the accuracy of one decimal number.

X-Ray diffraction study of 5b·HCl

A single crystal of **5b·HCl** was mounted on a glass fiber and transferred to the diffractometer. Data were collected on a Rigaku RAXIS-II imaging plate detector using graphite-monochromated Mo-Kα radiation at 293 K. Data processing was carried out by using the software supplied with the diffractometer. Structure solutions with direct methods were carried out with the teXsan package.[22] The refinements were carried out by using the SHELXL-93 program[23] with the full matrix least squares method on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated based upon geometric evidence and their positions were refined by the riding model. The crystal data are as follows: $C_{15}H_{16}ClNO_3S$, M 325.80, triclinic, space group $P\bar{1}$, a = 10.162(4), b = 10.872(4), c = 8.234(2) Å, α = 104.94(3), β = 93.172(13), γ = 63.989(11)°, V = 788.2(4) Å^3, Z = 2, D_c = 1.373 Mg m^{-3}, 1688 independent reflections. At the end of the refinement R = 0.0676, $wR2$ = 0.1931 for the reflections with $I > 2\sigma I$ and R = 0.0948, $wR2$ = 0.2578 for all data. An extinction coefficient was refined to the value of 0.21(4). The maximal residual peak and hole in the final difference electron density map are 0.287 and −0.327 e Å^{-3}.

Fractional atomic coordinates, bond lengths and angles as well as thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.‡

Kinetics

Kinetic measurements were performed with a Cary 3E (Varian) UV–VIS spectrophotometer in tempered quartz cells of 1 cm path length, in the wavelength range 286–340 nm, where the absorption of the reactants and products differed significantly. Dioxane–water mixtures [2–4% (v/v) of water] were used as solvents for compounds **2a**–**2h, 2j**–**2q**, **4a** and **7**, and water for **11a**, **11f** and **12a**. The starting concentration of the reactants was 1.5×10^{-4} mol dm^{-3} if not otherwise stated. The measuring temperature and the concentrations of added acid, salt and buffer are given in Tables 3–10. The reaction was started by dissolving the reactants quickly in the solvent containing H_2O, D_2O, acid, salt and/or buffer as required. The rate of dissolution was fast; measurements were started immediately as the solution became homogenous. First order rate constants were calculated by using the kinetic computer programs of the Cary 3E spectrophotometer. Standard deviations of the rate constants are ±5%.

‡ CCDC reference number 188/283. See http://www.rsc.org/suppdata/p2/b0/b008156f/ for crystallographic files in .cif format.

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References

1 I. Kapovits, J. Rábai, F. Ruff and Á. Kucsman, *Tetrahedron*, 1979, **35**, 1869.
2 M. Balthazor and J. C. Martin, *J. Am. Chem. Soc.*, 1975, **97**, 5634; J. C. Martin and M. Balthazor, *J. Am. Chem. Soc.*, 1977, **99**, 152.
3 P. D. Livant, *J. Org. Chem.*, 1986, **51**, 5384.
4 K. Onogi, M. Kido, M. Hori, T. Katakao and H. Shimizu, *Tetrahedron Lett.*, 1983, 4337; J. Zhang, S. Saito and T. Koizumi, *J. Org. Chem.*, 1998, **63**, 5265.
5 D. Szabó, I. Kapovits, Á. Kucsman, P. Nagy, Gy. Argay and A. Kálmán, *J. Mol. Struct.*, 1999, **476**, 157.
6 Á. Kucsman and I. Kapovits, in *Organic Sulfur Chemistry: Theoretical and Experimental Advances*, ed. F. Bernardi, I. G. Csizmadia and A. Mangini, Elsevier, Amsterdam, 1985, pp. 191–245, and references therein.
7 R. A. Hayes and J. C. Martin, in *Organic Sulfur Chemistry: Theoretical and Experimental Advances*, ed. F. Bernardi, I. G. Csizmadia and A. Mangini, Elsevier, Amsterdam, 1985, pp. 408–483, and references therein.
8 P. Livant and J. C. Martin, *J. Am. Chem. Soc.*, 1977, **99**, 5761.
9 D. Szabó, I. Kapovits, Á. Kucsman, P. Huszthy, Gy. Argay, M. Czugler, V. Fülöp, A. Kálmán, T. Koritsánszky and L. Párkányi, *J. Mol. Struct.*, 1993, **300**, 23.
10 I. Kapovits, J. Rábai, D. Szabó, K. Czakó, Á. Kucsman, Gy. Argay, V. Fülöp, A. Kálmán, T. Koritsánszky and L. Párkányi, *J. Chem. Soc., Perkin Trans. 2*, 1993, 847.
11 D. Szabó, I. Kapovits, Á. Kucsman, V. Fülöp, M. Czugler and A. Kálmán, *Struct. Chem.*, 1990, **1**, 305; D. Szabó, I. Kapovits, Á. Kucsman, M. Czugler, V. Fülöp and A. Kálmán, *Struct. Chem.*, 1990, **2**, 529; D. Szabó, I. Kapovits, Gy. Argay, M. Czugler, A. Kálmán and T. Koritsánszky, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1045.
12 D. Szabó, T. Ádám and I. Kapovits, *Sulfur Lett.*, 1997, **21**, 21 and refs. therein.
13 L. J. Adzima, C. C. Chiang, I. C. Paul and J. C. Martin, *J. Am. Chem. Soc.*, 1978, **100**, 953.
14 G. J. Martin, J. P. Gouesnard, J. Dorie, C. Rabiller and M. L. Martin, *J. Am. Chem. Soc.*, 1977, **99**, 1381; W. Schwotzer and W. v. Philipsborn, *Helv. Chim. Acta*, 1977, **60**, 1501; M. I. Burgar, T. E. St. Amour and D. Fiat, *J. Phys. Chem.*, 1981, **85**, 502; B. Thomas, W. Bieger and G. Grossmann, *Z. Chem.*, 1981, **21**, 292.
15 E. Vass, F. Ruff, I. Kapovits, J. Rábai and D. Szabó, *J. Chem. Soc., Perkin Trans. 2*, 1993, 855.
16 E. Vass, F. Ruff, I. Kapovits, D. Szabó and Á. Kucsman, *J. Chem. Soc., Perkin Trans. 2*, 1997, 2061.
17 T. Ádám, F. Ruff, I. Kapovits, D. Szabó and Á. Kucsman, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1269.
18 F. Ruff and I. G. Csizmadia, *Organic Reactions*, *Equilibria*, *Kinetics and Mechanism*, Elsevier, Amsterdam, 1994, pp. 283–289.
19 C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
20 Á. Kucsman, I. Kapovits, I. Kövesdi, A. Kálmán and L. Párkányi, *J. Mol. Struct.*, 1985, **127**, 135; Á. Kucsman, I. Kapovits, L. Párkányi and A. Kálmán, *J. Mol. Struct.*, 1986, **140**, 141.
21 J. Jilek, K. Sindelar, J. Pomykacek, V. Kmonicek and Z. Sedivy, *Collect. Czech. Chem. Commun.*, 1989, **12**, 3294.
22 teXsan Crystal Structure Analysis Package, Molecular Structure Co., Houston, TX, 1985, 1992.
23 G. M. Sheldrick, SHELXL-93 Program for the refinement of crystal structures, University of Göttingen, 1993.