Four-Centre Skeletal Rearrangements in the Mass Spectra of Thioanilides

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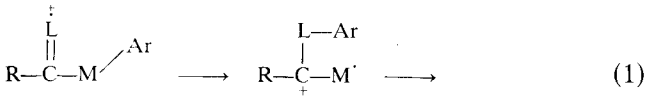
Abundant peaks in the mass spectra of thioanilides involve loss of a substituted thiophenoxy radical by a process involving aryl migration from nitrogen to sulfur (a four-centre skeletal rearrangement). The effects of substituents on this process have been studied. Substituents in the amide ring, in the acid part of the molecule and on the nitrogen atom were studied. Four-centre aryl migrations seem to be favoured if the aryl group migrates from one atom to either a more polarizable or a more electronegative atom, and in the case of thioanilides this migration is more important in tertiary compounds than in secondary compounds.

INTRODUCTION

A number of authors have reported four-centre skeletal rearrangements to explain the occurrence of certain ions in the mass spectra of various acid and thioacid derivatives. Such rearrangements have



(1)

$$R-\overset{+}{C}=M + ArL^{\cdot}$$

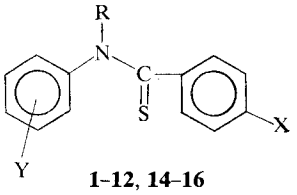
where L = O or S and M = NH, NMe or O.

been reported in the mass spectra of some acetanilides[1] and *N*-phenylmaleimide[2] (N—O aryl migration), the dithio derivative of *N*-phenylphthalimide[3] (N—S aryl migration) and thiobenzoates[4] (O—S aryl migration). A report from a recent conference[5] noted a rearrangement in the mass spectrum of thiobenzanilide and its *N*-methylderivative, and suggested that the tertiary *N*-methylthiobenzanilides may be suitable models for studying this process since the base peak in the spectrum of *N*-methylthiobenzanilide is derived from this process [Eqn (1), where R = Ph, L = S and M = NMe]. However, such rearrangements have not been reported in the mass spectra of thioformanilide[6] or thioacetanilides,[7] which are secondary compounds (i.e. M = NH).

In an effort to determine the scope of such aryl migrations in the mass spectra of thioanilides we prepared a series of secondary (M = NH) and tertiary (M = NCH_3) thiobenzanilides (**1–12**, **14–16**), thioacetanilides (**17–18**) and thioformanilides (**19–20**).

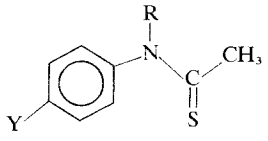
RESULTS AND DISCUSSION

The mass spectral abundance data for a series of thiobenzanilides (**1–12**, **14–16**), thioacetanilides (**17–18**) and thioformanilides (**19–20**) are given in Tables 1, 2 and 3, respectively.



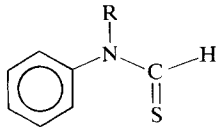
1–12, 14–16

Y = H; 2-NO_2; 3-NO_2; 4-NO_2; 2,6-Me_2; 2-Aza; 4-Me
X = Me; H; NO_2; MeO; Cl
R = H; Me



17–18

Y = 4-NO_2
R = H; Me



19–20

R = H, Me

The main fragmentation routes for tertiary thioanilides are shown in Scheme 1, using compound **2** as an example. The pathways marked (*) have been confirmed by the presence of metastable peaks.

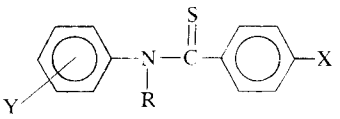
The $[M-1]^+$ peak

The mass spectrum of thioformanilide[6] (**20**) and some thioacetanilides[7] (R = H; Y = H, CH_3) contain abundant peaks corresponding to loss of hydrogen. By the use of isotopic labelling[6] it was shown that an *ortho* hydrogen on the aromatic ring was lost, presumably by intramolecular substitution.[7]

All of the thioanilides studied (**1–12**, **14–20**) had significant $[M-1]^+$ peaks, the intensity of which ranged from 8% (**3**) to 100% (**19**), while for the oxygen anilides (**13** and **21**) this peak was ≤2% of the base peak. This confirms the involvement of the sulfur atom in this process.

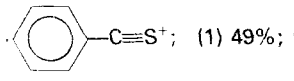
The intensity of the $[M-1]^+$ peak for secondary compounds (R = H) appears to be equal to or greater than the intensity for tertiary compounds (R = Me),

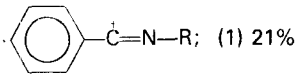
Table 1. Mass spectral data[a] for the thiobenzanilides (1–16)



	Compound X	Y	R	$[M]^+$	$[M-1]^+$	$X-C_6H_4-C\equiv\overset{+}{S}$	$X-C_6H_4-\overset{+}{C}=N-R$	$[Y-C_6H_4-S]^+$	$[Y-C_6H_4SH]$	$[X-C_6H_4]^+$	$[Y-C_6H_4]^+$
1	H	H	CH_3	227(28)	226(23)	121(59)	118(100)[h]	109(2)	110(<1)	.....77(34).....	
2	H	4-NO_2	CH_3	272(31)	271(16)	121(100)	118(95)	154(<1)	155(<1)	77(20)	[b]
3	CH_3	4-NO_2	CH_3	286(16)	285(8)	135(100)	132(97)	154(<1)	155(<1)	91(54)	122(2)
4	NO_2	4-NO_2	CH_3	317(31)	316(17)	166(34)[c,1]	163(100)[d,1]	154(<1)	155(<1)	.....122(<1).....	
5	NO_2	3-NO_2	CH_3	317(52)	316(46)	166(52)[c,2]	163(100)[d,2]	154(<1)	155(<1)	.....122(4).....	
6	NO_2	H	CH_3	272(31)	271(20)	166(16)[c,3]	163(100)[d,3]	109(4)	110(1)	122(3)	77(25)
7	NO_2	2,6-Me_2	CH_3	300(10)	285(14)[e]	166(3)[c,4]	163(100)[d,4]	123(<1)	138(<1)	122(<1)	105(6)
8	H	2-AZA[i]	CH_3	228(55)	227(30)	121(100)	118(19)	110(2)	111(1)	77(47)	78(40)
9	MeO	4-NO_2	CH_3	302(28)	301(8)	151(100)	148(52)	154(<1)	155(<1)	107(1)	122(<1)
10	H	2-NO_2	CH_3	272(11)	226(100)[j]	121(53)	118(9)	154(<1)	155(<1)	77(6)	[b]
11	NO_2	4-CH_3	CH_3	286(17)	285(6)	166(6)[c,7]	163(100)[d,5]	183(<1)	124(<1)	122(<1)	91(11)
12	Cl	4-NO_2	CH_3	306[k](25)	305[k](11)	155[k](100)	152[k](85)	154(<1)	155(<1)	111[k](15)	122(<1)
13	NO_2[f]	4-NO_2	CH_3	301(13)	300(<1)	150(100)[f;c,5]	163(2)	138(<1)[f]	139(<1)	.....122(3).....	
14	H	H	H	213(43)[g,1]	212(43)	121(100)	104(14)	109(10)	110(21)	.....77(40).....	
15	H	4-NO_2	H	258(36)[g,2]	257(17)	121(100)	104(15)	154(<1)	155(<1)	77(29)	[b]
16	NO_2	H	H	258(86)[g,3]	257(94)	166(77)[c,6]	149(21)	109(13)	110(100)	[b]	77(81)

[a] *m/e* (% of base peak).
[b] Increased by isotope contribution of a large peak either 1 or 2 a.m.u. lower.

[c] *m/e* 120;  (1) 49%; (2) 59%; (3) 35%; (4) 8%; (5) 29%; (6) 94%; (7) 20%.

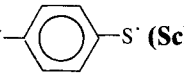
[d] *m/e* 117;  (1) 21%; (2) 27%; (3) 29%; (4) 23%; (5) 20%.

[e] Since this is the 2',6'-dimethyl compound this is in fact $[M-15]^+$.
[f] Oxygen anilide.
[g] [M−33] (for the R = H compounds); (1) 180(14); (2) 225(8); (3) 225(32).
[h] Accurate mass: calculated for C_8H_8N, 118.06571; measured, 118.06611.
[i] $[M-CS]^+$ and $[M-CHS]^+$ are <1%.
[j] Since this is a 2'-nitro compound this is in fact $[M-46]^+$.
[k] For chlorine-containing ions the entry includes both isotopes.

i.e. cyclization is not hindered in secondary thioanilides relative to tertiary thioanilides.

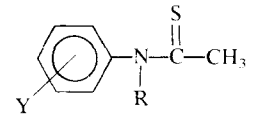
For **7**, a 2',6'-dimethyl compound cyclization resulted in loss of methyl (i.e. $[M-15]^+$).

Fate of the $[M-1]^+$ ion. In the mass spectrum of thioacetanilide Larsson *et al.*[7] report the loss of CH_3CN from the $[M-1]^+$ fragment giving *m/e* 109; $[C_6H_5S]^+$ (17%) (metastable peak at *m/e* 79.2). In our studies such a fragmentation of the $[M-1]^+$ ion is negligible for all the *N*-methyl thioanilides except *N*-methylthioformanilide (30%), but is present for all the secondary thioanilides except compound **15** (Y = 4-NO_2) where the destabilizing effect of the 4-nitro group would be prohibitive.

The loss of  **(Scheme 1)**

Origin of the ion. All of the compounds studied (**1–12, 14–20**) had peaks corresponding to the loss of a substituted thiophenoxy radical from the molecular ion.

Table 2. Mass spectral data[a] for the thioacetanilides (17–18)

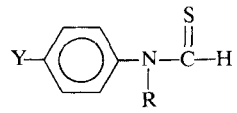


	Compound Y	R	$[M]^+$	$[M-1]^+$	$[Y-C_6H_4-NHR]^+$	$[CH_3-C\equiv S]^+$	$CH_3-\overset{+}{C}=N-R$
17	4-NO_2	Me	210(43)	209(17)	152(3)	59(60)	56(100)
18	4-NO_2	H	196(34)	195(21)	138(19)	59(100)	42(26)

		$[Y-C_6H_4-S]^+$	$[Y-C_6H_4SH]^+$	$[Y-C_6H_4]^+$
4-NO_2	Me	154(<1)	155(<1)	122(4)
4-NO_2	H	154(<1)	155(6)	122(3)

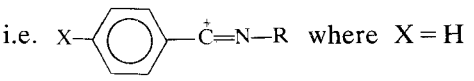
[a] *m/e* (% of base peak).

Table 3. Mass spectral data[a] for the thioformanilides (19–21)



	Compound									
	Y	R	$[M]^{\ddagger}$	$[M-1]^{+}$	$[Y-C_6H_4NHR]^{\ddagger}$	$[Y-C_6H_4NR]^{+}$	$[Y-C_6H_4SH]^{\ddagger}$	$[YC_6H_4S]^{+}$	$H-\overset{+}{C}=N-R$	$[HC\equiv S]^{+}$
19	H	CH_3	151(98)	150(100)	107(8)	106(30)	110(81)	109(30)	42(98)	45(25)
20	H	H	137(100)	136(100)	93(27)	92(7)	110(37)	109(23)	28(10)	45(24)
21	H	CH_3[b]	135(62)	134(2)	107(16)	106(100)	94(20)[b]	93(10)[b]	42(20)	29(10)[b]
			$[Y-C_6H_4]^{+}$							
	H	CH_3	77(63)							
	H	H	77(71)							
	H	CH_3[b]	77(47)							

[a] *m/e* (% of base peak)
[b] Oxygen anilide.

The composition of the fragment ion was confirmed by accurate mass measurement for compound **1** (X = Y = H, R = CH_3), i.e.  where X = H and R = CH_3.

However, while the $[M-YC_6H_4S^{\cdot}]^{+}$ peak was the base peak for most of the tertiary anilides, i.e. where R = Me, it was substantially less (14–26%) than the base peak for the secondary anilides, i.e. where R = H (**14**, **15** and **16**). Since the intensity of the $[M-1]^{+}$ peak is not reduced greatly in the secondary thioanilides relative to the tertiary thioanilides, this suggests that the $[M-YC_6H_4S^{\cdot}]^{+}$ peak is probably formed from the molecular ion rather than from the $[M-1]^{+}$ ion.

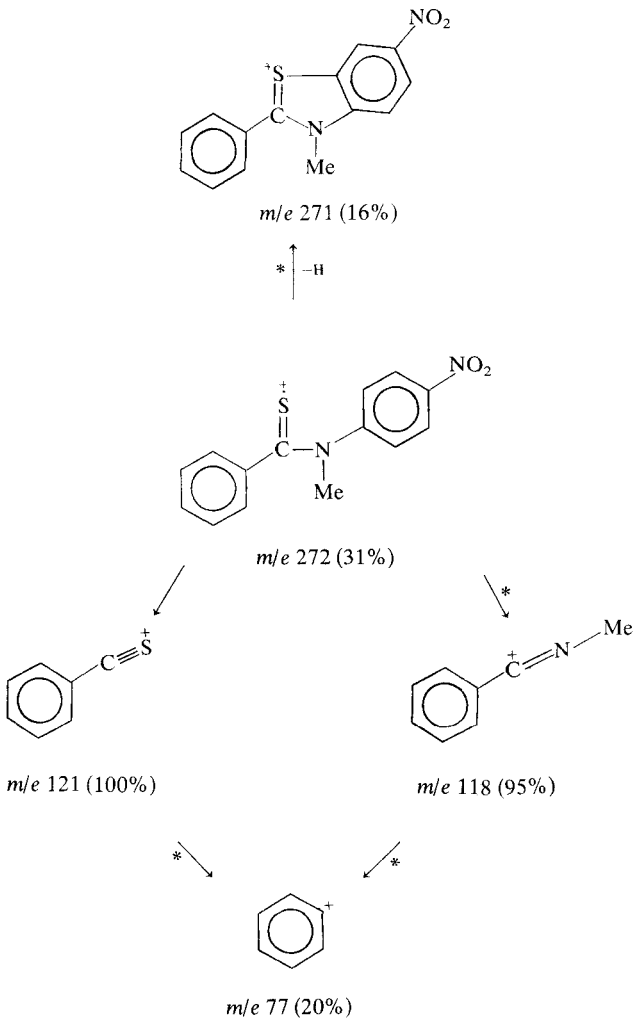
In most compounds, e.g. **6** and **7**, the presence of a prominent diffuse peak corresponding to the metastable ion decomposition $[M]^{\ddagger} \rightarrow [M-YC_6H_4S^{\cdot}]^{+}$ indicated that the fragment ion was formed either from the molecular ion or from some rearrangement product of the molecular ion.

Utilizing the accelerating voltage scan technique (Barber-Elliott) for **11** and **12** showed that the precursor of the $[M-YC_6H_4S^{\cdot}]^{+}$ ion was the molecular ion $[M]^{\ddagger}$ in both cases.

The kinetic energy release (T)[8] accompanying the metastable decomposition $[M]^{\ddagger} \rightarrow [M-YC_6H_4S^{\cdot}]^{+}$ for a number of compounds is given in Table 4. The metastable decompositions were observed in the first field free region using the accelerating voltage scan technique (Barber-Elliott) and the energy release values were calculated [Eqn (2)] from metastable peak widths at half height.

$$T = \frac{X^2 m_2^2 eV}{16 m_1 m_3 Y}\left(\frac{\Delta V}{V}\right)^2 \qquad (2)$$

It can be seen that for substituents (Y) in the amide



Scheme 1. Major fragmentation routes for tertiary thioanilides using compound **2** as an example.

Table 4. Kinetic energy released (T) in the metastable decomposition $[M]^{\ddagger} \rightarrow [M-YC_6H_4S^{\cdot}]^{+}$ from *N*-methyl thiobenzanilides

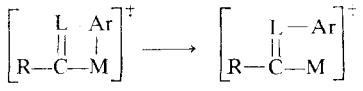
	Compound		
	X	Y	T(MeV)
1	H	H	99
6	4-NO_2	H	38
11	4-NO_2	4′-Me	69
5	4-NO_2	3′-NO_2	57
9	4-OMe	4′-NO_2	96
12	4-Cl	4′-NO_2	106
3	4-Me	4′-NO_2	134

ring, T is at a minimum for the unsubstituted compound, increasing for compounds containing either electron donating (Me) or electron accepting (NO_2) substituents; while for substituents (X) in the acid ring, T is at a maximum for the unsubstituted compound, decreasing for compounds containing either electron donating (MeO, Me) or electron accepting (NO_2) substituents.

This sort of substituent effect on T is similar to that observed by Beynon *et al.*[9] for the elimination of HCN from the molecular ions of substituted benzaldoxime *O*-methyl ethers. In that case T was at a minimum for the unsubstituted compound but increased for compounds containing either electron withdrawing or electron donating substituents.

Mechanism of the fragmentation (Scheme 2). The $[M]^+ \rightarrow [M-YC_6H_4S^{\cdot}]^+$ decomposition must involve a rearrangement—an aryl migration from nitrogen to sulfur—followed by decomposition of the product of rearrangement $a \leftrightarrow b$. Such electron impact induced aryl migrations are well documented[2] and occur for trifluoroacetanilides[1] (N to O) and thioesters[4] (O to S). There is no evidence for migration in carbonyl oxygen labelled ethyl benzoate[4] (O to O) or thiolesters[1] (S to O).

This led to the following orders of reactivity for the migration of Ar in the general scheme below:

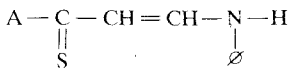


The tendency of Ar to migrate increases as M is changed from S to O to N and increases as L is changed from O to S, that is, migration of Ar is favoured by transfer from an atom (M) to another atom (L) to the right or below (M) in the periodic table, i.e. to a more electronegative or polarizable atom. Thus migration from N can occur to O[1] (more electronegative) or S (more polarizable) and migration from O can occur to S[4] (more polarizable). However, migration from O to N (less electronegative) has not been reported, while migrations from S to O (less polarizable) and from O to O have been excluded.[1,4] It would be interesting to extend the work to more polarizable atoms such as selenium and tellurium.

For trifluoro-*N*-methylacetanilide, Johnstone *et al.*[1] consider the aryl migration as an interaction between the oxygen atom and the 1-carbon in the aromatic ring, although Bentley and Johnstone[2] later stress that 'the scheme is only a pictorial representation without mechanistic implications in the absence of a known ion structure'. Unfortunately, it seems unlikely that information on the structure of the rearrangement product will be forthcoming since the fragment of most interest (i.e. $YC_6H_4S^{\cdot}$) is lost as a neutral fragment. However, we suggest looking on the aryl migration as a form of α-cleavage as shown in Scheme 2.

Interaction of the sulfur atom with the 2-carbon on the aromatic ring seems to be precluded since that gives rise to the $[M-1]^+$ fragment by hydrogen atom loss. Although the aryl migration above is viewed as a 4-membered ring transition state, molecular models show that the distance between the 1-carbon and the sulfur is only about 1.5 °A when the planes of the thioamide and the aromatic ring are orthogonal.

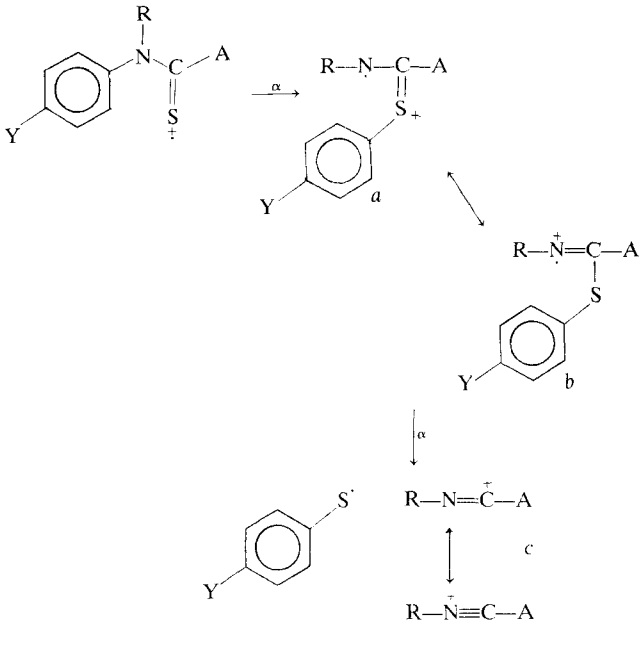
It may be of interest to see if this process is more favourable via a 6-membered ring transition state, i.e. for thioanilide vinylogues, but the only compounds studied to date[10] are secondary compounds **22–23** for which only a small $[M-YC_6H_4S^{\cdot}]^+$ ion is observed. The process should be more favourable in the tertiary (*N*-methyl) compounds.



22–23

where A = CH_3, [M − 109] (20%)
where A = *p*-$MeOC_6H_4$, [M − 109] (5%)

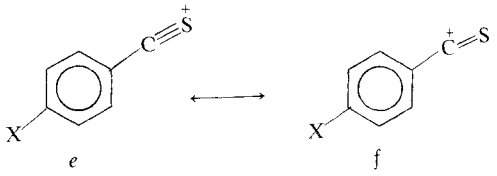
The decomposition of the rearranged molecular ion $a \leftrightarrow b$ to the $[M-YC_6H_4S]^+$ ion $c \leftrightarrow d$ is visualized as an α-cleavage reaction as shown in Scheme 2.



A = aryl (**1–12**, **14–16**), methyl (**17–18**) and hydrogen (**19–20**).

Scheme 2. Mechanism of conversion of $[M]^+ \rightarrow [M-YC_6H_4S^{\cdot}]^+$

Substituent effects. Substituent effects on the abundance of the $[M-YC_6H_4S^{\cdot}]^+$ ion can be explained by considering the major competing pathways available for decomposition of the molecular ion (Scheme 1), i.e. production of the $[M-YC_6H_4S^{\cdot}]^+$ ion $c \leftrightarrow d$ versus production of the thioacylium ion $e \leftrightarrow f$.

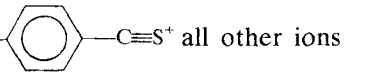


(a) **Secondary vs tertiary thioanilides (R = H or CH_3).** Secondary thioanilides (e.g. **14**, **18**, **20**) show

much less of ion $c \leftrightarrow d$ than do the corresponding tertiary thioanilides (**1**, **17**, **19**). This is explained by stabilization of product ion $c \leftrightarrow d$ by the electron donating methyl group in the tertiary compounds relative to hydrogen in the secondary compounds. For the secondary compounds the base peak is the competing ion $e \leftrightarrow f$.

(b) **Variation of the acid fragment (A) in Me—$\overset{+}{N}$=C—A.** If we express intensities as percent of total ionization rather than as a percentage of the base peak we see that ion $c \leftrightarrow d$ is less prominent in the mass spectrum of thioformanilides (**19**, $c \leftrightarrow d = 17\%$ of $\sum 10$ most intense peaks) than for thioacetanilides (**17**, 39%) or for thiobenzanilides (**1**, 35%).

This result also, can be explained by electron donation by the alkyl or aryl group (A) relative to hydrogen in product ion $c \leftrightarrow d$. We can now see why no evidence of this process was present in the published spectra of thioformanilide[6] (effects a and b) and thioacetanilide[7] (effect a).

For most tertiary thiobenzanilides and thioacetanilides there are only two intense ions in the mass spectra, viz. $[M-YC_6H_4S^{\cdot}]^+$ and  all other ions being <50% of the base peak. Thus, it is sufficient to consider the percentage of the base peak when discussing the intensity of the $[M-YC_6H_4S^{\cdot}]^+$ peak. However, for thioformanilide (**19**) there are other important ions of high intensity, e.g. $[M]^{\ddagger}$ (98%); $[M-1]^+$ (100%) and $[YC_6H_4SH]^{\ddagger}$ (81%), and it becomes necessary to express intensities as $\%\sum$.

(c) **Substituents (Y) in the amide ring.** The production of the ion $e \leftrightarrow f$ is less for compounds containing electron donating Y groups (**6**, **7**) than for those with electron withdrawing Y groups (**4**, **5**). Since group Y would have no effect on the stability of the ion $e \leftrightarrow f$ we conclude that the competing production of ion $c \leftrightarrow d$ is favoured by electron donating Y groups, probably as a result of stabilization of the product of aryl migration $a \leftrightarrow b$. The mass spectrum of the 2'-aza compound (**8**), which was prepared in connection with other research,[11] was interesting since the ion $c \leftrightarrow d$ was of low intensity (*m/e* 118, 19%). To determine whether this was characteristic of a strong electron withdrawing *ortho* substituent or a specific effect of the heterocyclic nitrogen atom the 2'-nitro compound (**10**) was prepared. The ion $c \leftrightarrow d$ for compound **10** was of low intensity (*m/e* 118, 9%) suggesting that the production of ion $c \leftrightarrow d$ is more sensitive to strong electron withdrawing substituents in the *ortho* position than in the *para* position (cf. compound **2**).

(d) **Substituents (X) in the acid ring of thiobenzanilides.** Electron withdrawing X groups enhance production of the ion $c \leftrightarrow d$ (**9**, X = MeO, 52% and **4**, X = NO_2, 100%) in direct contrast to their effect in the amide ring. This is probably a result of hindering the competing production of the ion $e \leftrightarrow f$ (**9**, 100%, **4**, 34%), i.e. it is not a direct effect on the production of ion $c \leftrightarrow d$.

(e) **Importance of the sulfur atom.** The corresponding oxygen anilides **13** and **21** show negligible production of the ion $c \leftrightarrow d$ compared with thioanilides **4** and **19**.

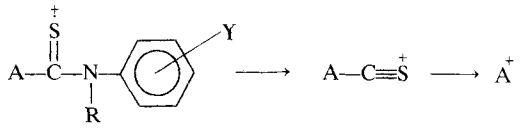
Related reactions $[M]^{\ddagger} \rightarrow [PhSH]^+$

The mass spectra of secondary amides, e.g. benzanilide, are reported[2] to give odd electron fragment ions $[PhOH]^+$, which must involve migration of both hydrogen and the phenyl ring. We measured the mass spectrum of benzanilide in connection with other work[11] and found that the intensity of the peak *m/e* 94, i.e. $[PhOH]^+$ was only 0.4%. The mass spectra of secondary thioanilides (**14**, **16**, **18** and **20**) do have significant peaks corresponding to this type of process but the tertiary thioanilides did not. For compound **14** a metastable peak confirmed the reaction $[M]^{\ddagger} \rightarrow [YC_6H_4SH]^{\ddagger}$.

Walter[6] detected this type of reaction in the spectrum of thioformanilide and explained it as aryl migration in a tautomer of the molecular ion followed by α-cleavage. Horvath,[5] however, prefers aryl migration before hydrogen rearrangement. For tertiary thioanilides neither tautomerism of the molecular ion nor subsequent hydrogen migration is possible and thus we do not observe the $[YC_6H_4SH]^{\ddagger}$ ion for these compounds.

Competing processes

The major process competing with aryl migration in the mass spectra of thioanilides is the normal α-cleavage reaction producing the thioacylium ion which can undergo further cleavage producing $[A]^+$ where



A = aryl, methyl or hydrogen. This process is very important in the mass spectra of thiobenzanilides (Table 1), producing the $[X—C_6H_4—C{\equiv}S]^+$ and $[XC_6H_4]^+$ fragment ions especially in the case of secondary anilides and also in the thioacetanilides (Table 2) producing $[CH_3C{\equiv}S]^+$. It is less important in the spectra of thioformanilides (Table 3) as expected on electronic grounds. For compound **14**, a metastable ion confirms the reaction $[ØC{\equiv}S]^+ \rightarrow [Ø]^+$.

EXPERIMENTAL

Benzanilides and acetanilides were prepared from the appropriate anilines by reaction with benzoyl chloride and acetic acid/acetic anhydride, respectively. Formanilide was prepared by condensation of aniline with formic acid in benzene solution[12] and *N*-methylformanilide was prepared by the method of Roberts and Vogt.[13]

The anilides were thiolated[14] with phosphorus pentasulfide using either pyridine or benzene as a solvent and were purified by dry column chromatography (alumina/chloroform). Satisfactory elemental analyses or accurate molecular weights were obtained for all new compounds.

Mass spectral, metastable ion and exact mass measurements were carried out on a JEOL JMS D-100 double focusing mass spectrometer, source temperatures 100–170 °C and electron energy 75 eV.

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