Flash Thermolysis of Thioformanilides

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Abstract
Flash thermolysis of several thioformanilides at approximately 700°C gives good yields of aromatic nitriles.

The mass spectra of N-aryl thioamides Ar—NH—C(=S)—R show peaks arising from cleavage of the molecule or its molecular ion into Ar—SH and R—CN fragments. We also observed these peaks and confirmed the formulae of the Ar—SH species by accurate mass measurements. We further noted, however, that the relative abundances of these Ar—SH peaks were significantly reduced when the temperature of the inlet system of the mass spectrometer was reduced from 100°C to 30°C. Because this fragmentation appeared to be, at least in part, thermal, we investigated the flash thermolysis of some N-aryl thiaoacet-

Table 1. Results of pyrolyses of thioformanilides and 4-tolyl isothiocyanate

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wt (g)</th>
<th>Conditions (°C/min)</th>
<th>t (min)</th>
<th>Starting mat. (%)</th>
<th>Product nitrile</th>
<th>Yield (%)</th>
<th>M.p. (°)</th>
<th>ν (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-MeC₆H₄NHCS</td>
<td>0·20</td>
<td>700/0·1</td>
<td>45</td>
<td>trace</td>
<td>90</td>
<td>29父 2250父</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0·49</td>
<td>500/0·08</td>
<td>25</td>
<td>61</td>
<td>36</td>
<td>as above</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-ClC₆H₄NHCS</td>
<td>0·49</td>
<td>700/0·03</td>
<td>30</td>
<td>24</td>
<td>75</td>
<td>96父 96父</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-MeOC₆H₄NHCS</td>
<td>0·20</td>
<td>720/0·02</td>
<td>45</td>
<td>trace</td>
<td>62父 61父 61父</td>
<td>6父</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,6-Me₂C₆H₄NHCS</td>
<td>0·066</td>
<td>720/0·01</td>
<td>25</td>
<td>—</td>
<td>100</td>
<td>90父 90父</td>
<td>2228父</td>
<td></td>
</tr>
<tr>
<td>4-MeC₆H₄NCS</td>
<td>0·46</td>
<td>700/0·04</td>
<td>10</td>
<td>80</td>
<td>20</td>
<td>as above</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B Identical with an authentic sample.
E Some starting material decomposed in the sublimation pot.

amides and thiobenzamides were converted into mixtures of products which did not contain more than traces of the aryl thiols. Several thioformanilides, however, lost hydrogen sulphide at 700°/0.1 mm and were smoothly converted into aromatic nitriles (Table 1).

The conversion of a thioformanilide into a nitrile might proceed by $\alpha$-elimination of $\text{H}_2\text{S}$ from a thioimidate tautomer (1a) to give an intermediate isonitrile, or by dehydrogenation of (1) to give an intermediate isothiocyanate followed by loss of sulphur. At these temperatures an isonitrile would rapidly rearrange to a nitrile$^3$ (Scheme 1). We consider the former the more probable route because 4-tolyl isothiocyanate gave only 20% conversion into 4-tolunitrile on thermolysis at 700°. This suggests that if an isothiocyanate were an important intermediate then it should have appeared in the products, and this was not the case.

Thus under our conditions the thermal reaction does not parallel the mass spectral fragmentation. The conversion of an aromatic amine into a nitrile by this route seems to offer no preparative advantage over conventional routes.

**Experimental**

The thioanilide was sublimed at low pressure from a silica flask into a silica pyrolysis tube (30 by 2.6 cm i.d.) packed with 5-mm lengths of silica tubing (5 mm i.d./7 mm o.d.) and heated to approx. 700° by means of an external electric furnace. The pressure was measured with a Vacustat gauge near the exit elbow. Unchanged starting material collected in the exit elbow within 5 cm of the heated zone. The aromatic nitrile formed was recovered from a trap cooled with liquid nitrogen and was identified after recrystallization. The results of these experiments are summarized in Table 1.

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**Corrigendum**

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Page 152, l. 11: *Omit last four words on l. 10*. Replace lines 11 and 12 by shown to be (9) from spectral data. The $^{13}$C n.m.r. spectrum showed only ten resonances, which is consistent with the plane of symmetry in the meso compound or with the $C_2$ axis in the ($\pm$) compound.

*and omit linkage on line 13*