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 $700^{\circ}/0.1$ mm and were smoothly converted into aromatic nitriles (Table 1).

The conversion of a thioformanilide into a nitrile might proceed by α -elimination of H_2S 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 nitrile³ (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.

$$Ar-N=C$$

$$(1a)$$

$$Ar-N=C=S$$

$$Ar-N=C$$

$$Ar$$

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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³ Casanova, J., Werner, N. D., and Schuster, R. E., J. Org. Chem., 1966, 31, 3473.

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