Flash Thermolysis of Thioformanilides

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Abstract

Flash thermolysis of several thioformanilides at approximately 700° 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.^{1,2} 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

Com- pound	Wt (g)	Conditions (°C/mm)	t (min)	Starting mat. (%)	Product nitrile		
					Yield (%)	M.p.	v (cm ⁻¹)
4-MeC ₆ H₄NHCHS	0.20	700/0 · 1	45	trace	90	29°A	2250 ^в
and the second sec	0.49	500/0.08	25	61	36	as above	
4-ClC ₆ H ₄ NHCHS	0.49	700/0.03	30	24	75	, 96 ^c	D
4-MeOC ₆ H ₄ NHCHS	0.20	720/0.02	45	trace	62 ^E	61 ^{F}	G
2,6-Me ₂ C ₆ H ₃ NHCHS	0.066	720/0.01	25		100	90 ^н	2228 ^в
4-MeC ₆ H ₄ NCS	0.46	700/0.04	10	80	20	as above	

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

^A Lit. 29° (Sugden, S., and Wilkins, H., J. Chem. Soc., 1925, 127, 2522).

^B Identical with an authentic sample.

^c Lit. 96° (Metzger, J., and Plank, H., Bull. Soc. Chim. Fr., 1956, 684).

^D I.r. identical with published spectrum [Pouchert, C. J., 'The Aldrich Library of Infrared Spectra' p. 827 (Aldrich Chemical Company: Milwaukee 1970)].

^E Some starting material decomposed in the sublimation pot.

F Lit. 61-62° (Miller, J. A., Ber. Dtsch. Chem. Ges., 1889, 22, 2790).

^G I.r. identical with published spectrum [Pouchert, C. J., 'The Aldrich Library of Infrared Spectra' p. 828 (Aldrich Chemical Company: Milwaukee 1970)].

^H Lit. 90-91° (Scholl, R., and Kacer, F., Ber. Dtsch. Chem. Ges., 1903, 36, 322).

of these Ar-SH peaks were significantly reduced when the temperature of the inlet system of the mass spectrometer was reduced from 100° to 30° . Because this fragmentation appeared to be, at least in part, thermal, we investigated the flash thermolysis of some *N*-aryl thioamides. When subjected to flash thermolysis, *N*-aryl thioacet-

¹ Larsson, F. C. V., Lawesson, S.-O., Møller, J., and Schroll, G., Acta Chem. Scand., 1973, 27, 747. ² Walter, W., Becker, R. F., and Grützmacher, H. F., Tetrahedron Lett., 1968, 3515. 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 H₂S 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.



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 ¹³C 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

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