Tetrahedron Letters No. 17, pp.16-18, 1959. Pergamon Press Ltd. Printed in
Great Britain.

REACTION OF ISOTHIOCYANATES AND IODINE PENTAFLUORIDE

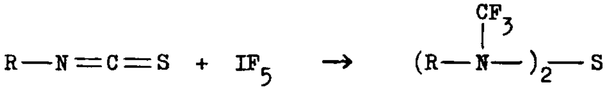
Travis E. Stevens

Rohm & Haas Co., Redstone Arsenal Research Division

Huntsville, Alabama

(Received 29 September 1959)

A UNIQUE fluorination has been observed in the reaction of iodine pentafluoride and some alkyl and aryl isothiocyanates. This fluorination, when conducted in pyridine solution at 75-90°, has been found to produce a new class of compounds, the bis-(N-substituted-N-trifluoromethyl)-aminosulfides (I).



$$\mathrm{R{-}N{=}C{=}S} + \mathrm{IF_5} \longrightarrow (\mathrm{R{-}}\overset{\overset{\displaystyle CF_3}{|}}{\mathrm{N}}\mathrm{{-}})_2\mathrm{{-}S}$$

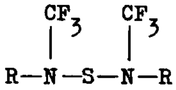
I

Table 1 lists the aminosulfides prepared in this way. The aromatic isothiocyanates were converted to the crude aminosulfides in almost quantitative yield,[1] however, recrystallization from ethanol or petroleum ether was necessary to obtain sharp-melting samples. Formulation

---

[1] No aminosulfide could be obtained from p-nitrophenyl, p-acetylphenyl, or p-dimethylaminophenyl isothiocyanates.

TABLE 1. *bis*-(N-Substituted-N-trifluoromethyl)-aminosulfides



$$R{-}\overset{CF_3}{\overset{|}{N}}{-}S{-}\overset{CF_3}{\overset{|}{N}}{-}R$$

R	M.P. (b.p.) (°C)	Yields (%)
Phenyl	53-54	19[a]
p-Fluorophenyl	32-33	34
p-Chlorophenyl	55-56	59
p-Bromophenyl	70-71	69
p-Iodophenyl	103-104	47[b]
m-Bromophenyl	(125°/0.5 mm)	90
p-Tolyl	58-59	40
Ethyl	(44°/30 mm)	33
Butyl	(80°/12 mm)	32

[a] The reaction product was a mixture of this and the *p*-iodo compound and the mixture was not separated completely.

[b] Also isolated from the phenyl isothiocyanate-iodine pentafluoride reaction.

---

of these compounds as aminosulfides is based on the analytical data, n.m.r. spectra and hydrolytic experiments outlined below.

All compounds listed in Table 1 gave satisfactory analytical values,[2]

---

[2] Data obtained by Dr. Keith S. McCallum.

for example, for bis-[N-(p-bromophenyl)-N-trifluoromethyl]-amino-sulfide was found C, 32.68; H, 1.76; N, 5.46; S, 6.59; F, 22.0; MW, 471.

The ^{19}F n.m.r. spectra of several of the aminosulfides were obtained using a Varian Associates model No. V-4300 B spectrometer with a 40 Mc probe.[2] Only a single peak, attributable to the CF_3 group, was observed; in compound I, R = p-bromophenyl, this fluorine resonance occurred at 927 c.p.s. lower field than trifluoroacetic acid, while when R = p-fluorophenyl resonance occurred at -892 c.p.s.,[3] and when R = n-butyl resonance at -760 c.p.s. was observed.

Hydrolysis of the aminosulfides I with aqueous ethanolic sodium hydroxide at room temperature for four hours resulted in the quantitative liberation of fluoride ion. The organic products of this hydrolysis in 75 per cent ethanol, in the case of I, R = p-bromophenyl, were p-bromoaniline (53 per cent) and p-bromophenylurethan (33 per cent). Similarly, I, R = p-chlorophenyl, yielded p-chloroaniline (51 per cent) and p-chlorophenylurethan (23 per cent). Hydrolysis with an ethanol-water-hydrochloric acid mixture gave the same products.

The aminosulfide I, R = p-bromophenyl, also was obtained (18 per cent yield) from the iodine pentafluoride-p-bromophenyl isonitrile-sulfur reaction. From the reaction of iodine pentafluoride, sulfur and N-n-butylformamide was obtained I, R = n-butyl (21 per cent).

Further details of this work will be reported later.

---

[3] Resonance observed at + 1412 c.p.s. was due to the aromatic fluorine.