Tetrahedron Letters No. 3, pp 211 - 214, 1973. Pergamon Press. Printed in Great Britain.

AROMATIC N-FORMYLSULPHENAMIDES, SYNTHESES AND REACTIONS
SULPHENYL ISOCYANIDES AND THIOCYANATES

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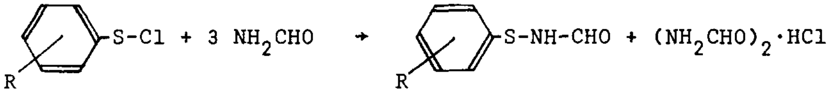
(Received in UK 1 December 1972; accepted for publication 14 December 1972)

Apparently only one N-formylsulphenamide has been reported in the literature hitherto, namely N-formyltrichloromethanesulphenamide.$^{1)}$ The present work describes the synthesis of aromatic N-formylsulphenamides. Two different synthetic pathways have been explored. As representatives of this class of compounds, N-formyl-o-nitrobenzenesulphenamide (Ia) and N-formyl-p-toluenesulphenamide (Ib) have been prepared.

These compounds are obtained in fair yields by the reaction:



I

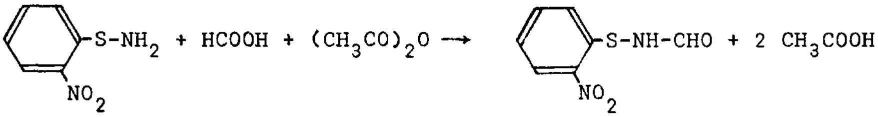
Ia: $R = 2\text{-}NO_2\text{-}$ Ib: $R = 4\text{-}CH_3\text{-}$

The compounds were obtained from solutions of the sulphenyl chlorides and excess formamide in dioxane. Stirring at room temperature (5-6 hours) followed by filtration and evaporation of the solvent left a solid. A few recrystallizations afforded the analytically pure substance.

The results are summarized in the following scheme:

	Compound.	m.p. °C	Yield after recryst. (solvent)
Ia:	$2\text{-}NO_2\text{-}C_6H_4\text{-}S\text{-}NH\text{-}CHO$	196-197 (decomp.)	61% (diglyme.)
Ib:	$4\text{-}CH_3\text{-}C_6H_4\text{-}S\text{-}NH\text{-}CHO$	92-92,5 (decomp.)	78% (cyclohexane)

The nitro compound (Ia) could be obtained directly from the sulphenamide and formic acid in acetic anhydride. The yield was 53% after recrystallization from diglyme. The product was shown, by melting point and IR-spectrum, to be identical with Ia. The reaction is:

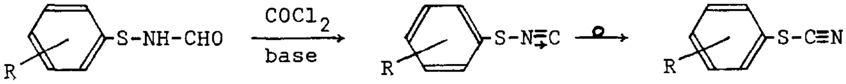


The corresponding p-tolyl compound (Ib) could not be obtained by this reaction because p-toluenesulphenamide is unknown at present.[2)]

The N-formylsulphenamides are soluble in 1 N sodium hydroxide and in concentrated sulphuric acid and hydrochloric acid, but not in dilute acid.

The dehydration of N-substituted formamides, forming the corresponding isocyanides, is well known.[3)] The analogous reaction of N-formylsulphenamides was investigated. A mixture of the formamide and triethylamine or pyridine in methylene chloride was treated with excess phosgene. The IR-spectrum of the product was superimposable with that of an authentic sample of the corresponding thiocyanate.

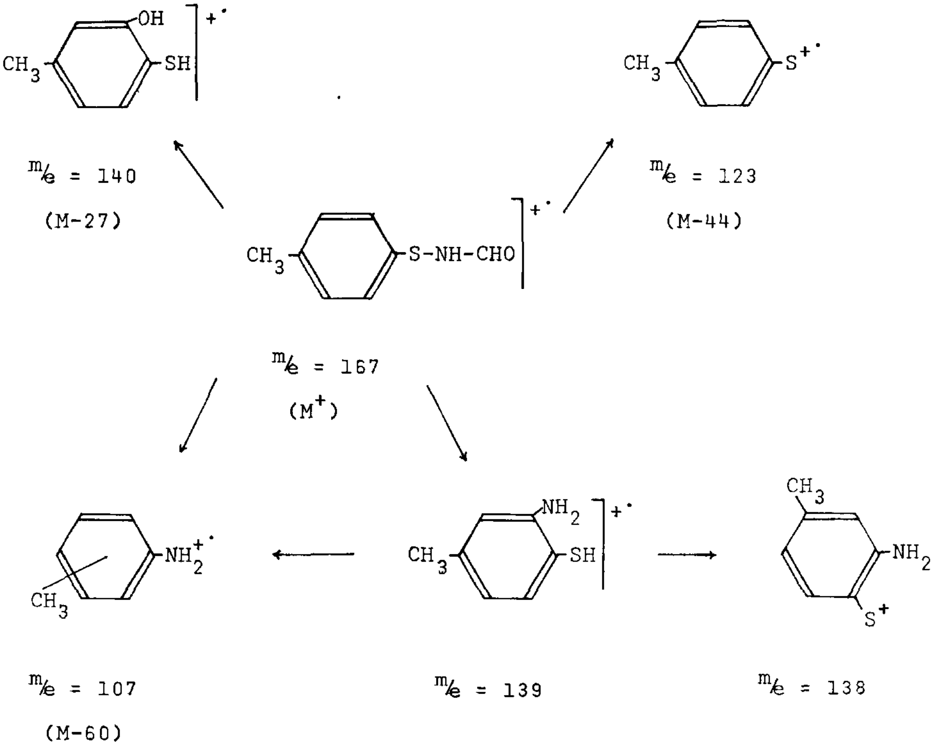
The process is:



The yields of pure o-nitrophenyl thiocyanate and p-tolyl thiocyanate were found to be respectively 20% and 85%. The only by-product from reaction III was the disulphide, $R-C_6H_4-S-S-C_6H_4-R$.

The results indicate that first the sulphenyl isocyanide is formed. The isolated product would then result from a fast isomerization. However, the suggested intermediate has so far not been observed.

A mass-spectrometric investigation of the N-formylsulphenamides was carried out. The characteristic feature of their decompositions was the formation of the fragments (M - 44) and (M - 60). The proposed fragmentation pattern was confirmed using the metastable defocusing technique, and the determination of exact masses by high resolution mass spectrometry. The most important fragmentations of compound Ib are depicted:



The same characteristic fragmentation pattern was found in the mass spectrum of compound Ia. A deviation is that this compound does not show any (M -28)-peak, but instead a (M - 29)-peak.

REFERENCES

1. Senning, A.: Acta Chem. Scand. 21, 1567 (1967).
2. Lecher, H. et. al.: Ber. 58, 409 (1925).
3. Ugi, I. et. al.: Chem. Ber. 77, 2814 (1961).