

Preparation of Aryl Isothiocyanates by Pyrolysis of *N*-Aryldithiocarbamates

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Pyrolysis at 180—200° of *N*-aryldithiocarbamates, prepared from arylamines, affords isothiocyanates in high yield. In contrast to other isothiocyanate syntheses, this method does not require basic conditions or a strongly electron-withdrawing group on the thiol sulphur atom.

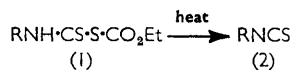
DURING studies of xanthate ester pyrolysis we became interested in the effect of the methyl carbodithioate (S=C-SMe) group on an amine under pyrolytic conditions. In the case of aliphatic compounds it was felt that either or both of two processes could occur, namely rearrangement to the isothiocyanate, similar to the Kaluza re-

action,¹ or elimination to produce an olefin, similar to a xanthate decomposition. The latter was considered possible because pyrolysis of *O*-alkyl dithiocarbamates is reported to give olefins in high yields,² and previous methods for producing isothiocyanates involved basic conditions or strongly electron-withdrawing groups on the thiol sulphur atom. For example, the Kaluza¹ reaction involves the decomposition of ethoxycarbonyl dithiocarbamates. In a modification of this method,

¹ L. Kaluza, *Monatsh.*, 1912, **33**, 363.

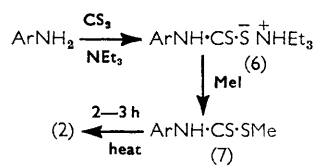
² M. S. Newman and F. W. Hetzel, *J. Org. Chem.*, 1969, **34**, 3604.

base-catalysed decomposition of the ethoxycarbonyl dithiocarbamates (1) gave high yields of alkyl³ and aryl⁴



isothiocyanates (2). Sayigh and his co-workers⁵ and Marquardt⁶ have recently reported an excellent method of preparing the isothiocyanates of aryl compounds containing strongly electron-withdrawing groups by the decomposition of a diethylamino-thiocarbamate intermediate (3). Concurrently, Martin and his co-workers⁷

methyl *N*-aryl dithiocarbamate was then heated for 2–3 h at 180–200° to form the isothiocyanate (2).



Two methods of decomposition were employed. Method A involved heating the neat solid dithiocarb-

Formation of aryl isothiocyanates by thermal decomposition of methyl dithiocarbamates

Amine Ar	Dithiocarbamate ester				Isothiocyanate				
	Yield (%)	M.p. (°C)	Analysis (%)		Reaction time (h)	Yield (%)	B.p. (°C) ^a at 20 mmHg	Analysis (%)	
Ph	82	94–95	Calc. C 52.4 H 4.9 N 7.7	Found 52.3 4.7 7.6	3	72	112–115 ^b	Calc. C 62.1 H 3.7 N 10.3	Found 62.0 3.8 10.3
<i>o</i> -ClC ₆ H ₄	66	119–121	Calc. C 44.1 H 3.8 N 6.4	Found 44.3 3.7 6.5	4	81	143–174 ^c	Calc. C 49.6 H 2.4 N 8.3	Found 39.9 2.5 8.4
<i>m</i> -ClC ₆ H ₄	69	91–93	Calc. C 44.1 H 3.8 N 6.4	Found 44.2 3.9 6.6	3.5	84	136–139 ^c	Calc. C 49.6 H 2.4 N 8.3	Found 49.8 2.6 8.5
<i>p</i> -BrC ₆ H ₄	78	187–189	Calc. C 36.6 H 3.1 N 5.3	Found 36.3 3.2 5.6	3	72	(M.p. 49–50 ^b)	Calc. C 39.3 H 1.9 N 6.5	Found 39.6 2.3 6.7
<i>o</i> -MeC ₆ H ₄	84	140–141	Calc. C 54.8 H 5.6 N 7.1	Found 54.8 5.8 7.3	3	65	140–143 ^b	Calc. C 64.4 H 4.7 N 9.4	Found 64.5 4.9 9.3
<i>m</i> -MeC ₆ H ₄	82	91–92	Calc. C 54.8 H 5.6 N 7.1	Found 55.1 6.0 7.3	2.5	67	143–145 ^b	Calc. C 64.4 H 4.7 N 9.4	Found 64.7 4.8 9.5
<i>p</i> -MeC ₆ H ₄	86	85–86	Calc. C 54.8 H 5.6 N 7.1	Found 54.5 5.7 7.0	2.5	83	124–126 ^b	Calc. C 64.4 H 4.7 N 9.4	Found 64.4 4.8 9.4
<i>m</i> -MeO·C ₆ H ₄	73	120–122	Calc. C 51.1 H 5.2 N 6.6	Found 51.2 5.2 6.7	2	68	148–150 ^c	Calc. C 58.2 H 4.2 N 8.9	Found 58.1 4.0 8.8
<i>p</i> -MeO·C ₆ H ₄	86	90–101	Calc. C 51.1 H 5.2 N 6.6	Found 51.2 5.3 6.4	2	71	171–174 ^b	Calc. C 58.2 H 4.2 N 8.5	Found 57.9 4.0 8.2
1-Naphthyl	74	191–192	Calc. C 61.8 H 4.7 N 6.1	Found 62.1 4.8 6.3	4	38	(M.p. 58–59 ^b)	Calc. C 71.2 H 3.8 N 7.5	Found 71.4 4.1 7.7

^a These b.p.s and m.p.s agree with those reported as indicated. ^b J. E. Hodgkins and W. P. Reeves, *J. Org. Chem.*, 1964, **29**, 3098. ^c G. Dyson, H. George, and R. Hunter, *J. Chem. Soc.*, 1927, 436.

obtained high yields of isothiocyanates from dichloro-phosphinyl dithiocarbamates (4).



We report the preparation of aryl isothiocyanates from the corresponding amines by the thermal decomposition of a methyl dithiocarbamate intermediate. The arylamines (5) were treated with carbon disulphide and base to form the dithiocarbamate salt (6). This intermediate was then treated with methyl iodide to form the methyl dithiocarbamate (7), which was a solid in all cases. The

amate in a simple distillation apparatus under reduced pressure for 2–3 h. The isothiocyanate was collected as the distillate as the reaction proceeded. Method B involved heating the dithiocarbamate ester in a reflux apparatus for a similar period of time. The product was then recovered by distillation under reduced pressure. The latter method produced a slightly higher yield and was the method used to obtain the results summarized in the Table.

A mechanism considered for this decomposition reaction involves resonance structure (8). Holloway

⁵ A. A. Sayigh, H. Illrich, and J. S. Potts, *J. Org. Chem.*, 1965, **30**, 2465.

⁶ F. H. Marquardt, *Helv. Chim. Acta*, 1966, **49**, 1717.

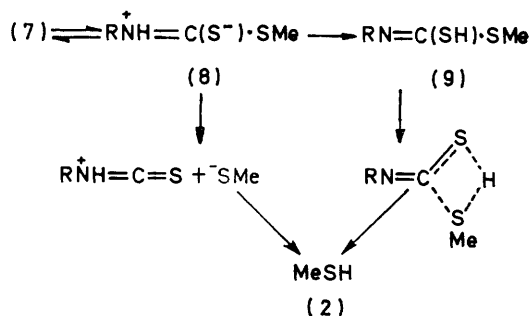
⁷ D. Martin, E. Beyer, and H. Gross, *Chem. Ber.*, 1965, **98**, 2425.

³ J. E. Hodgkins and M. G. Ettlinger, *J. Org. Chem.*, 1956, **21**, 404.

⁴ J. E. Hodgkins and W. P. Reeves, jun., *J. Org. Chem.*, 1964, **29**, 3098.

and Gitlitz⁸ have reported that an appreciable amount of C=N bonding exists in alkyl dithiocarbamates. This suggestion was based on an estimated rotational barrier about the C-N bond of *ca.* 10–12 kcal mol⁻¹ and the presence of a thioureide band in the i.r. spectrum.

One mode of decomposition proposed involves the elimination of the methanethiolate ion from resonance form (8) and the subsequent removal of the proton from the quaternized nitrogen atom by this anion to produce isothiocyanate and methanethiol. Another possible mode of decomposition involves an equilibrium between (8) and the tautomeric dithiohemiacetal (9).



The latter could undergo concerted elimination of methanethiol to produce the isothiocyanate (2).

We were not able to prepare the dithiocarbamate salts of arylamines carrying strongly electron-withdrawing groups, such as *p*-nitro and *p*-cyano-anilines. Hodgkins and Reeves⁴ reported similar difficulty with the modified Kuluza method. Our method is thus useful for preparing aryl isothiocyanates from the

⁸ C. E. Holloway and M. H. Gitlitz, *Canad. J. Chem.*, 1967, **45**, 2659.

corresponding amines if they do not have strongly electron-withdrawing groups. The applicability of the method to alkyl systems is being investigated.

EXPERIMENTAL

The following are the general procedures used for the preparation of the aryl isothiocyanates reported. The Table shows yields and properties of the dithiocarbamate esters and of the corresponding isothiocyanates.

Methyl Dithiocarbamates.—A mixture of arylamine (0.25 mol) (distilled samples of commercial products were used) and triethylamine (0.25 mol) was added dropwise with stirring to carbon disulphide (150 ml) cooled in ice. The triethylammonium dithiocarbamate was usually completely precipitated in 2–3 h. The salt could be isolated at this stage (higher yields were obtained when it was not). To the stirred suspension was added methyl iodide (0.25 mol) in carbon tetrachloride (50 ml). After 2 h diethyl ether (100 ml) was added to precipitate triethylammonium iodide salt, which was filtered off. Evaporation removed the ether and the excess of carbon disulphide, and the residual oil was taken up in chloroform (50 ml) and treated with charcoal. Crystallization was induced with pentane.

Isothiocyanates.—*Method A.* The ester (20 g) was placed in a simple micro-vacuum distillation apparatus. The system was kept under reduced pressure (20 mmHg) to remove methanethiol during pyrolysis, which was carried out at 180–200 °C for 2–3 h. The distillate was diluted with chloroform (30 ml) and treated with charcoal. The solvent was removed and the remaining liquid was distilled under reduced pressure.

Method B. The dithiocarbamate (20 g) was heated in a reflux apparatus for 2–3 h at 190–200°. The product was recovered by distillation under reduced pressure.

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