Facile Synthesis of Thiocyanate Using Trimethylsilyl Cyanide

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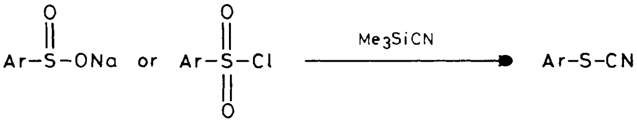
Arenethiocyanate can be prepared by reaction of trimethylsilyl cyanide with sodium arenesulphinate or arenesulphonyl chloride.

Thiocyanates, one of the most fundamental groups of organosulphur compounds, are useful synthetic intermediates for heterocyclic compounds and are of some biological interest.[1] Aromatic thiocyanates have long been prepared from diazonium ions and metal thiocyanates. This traditional method involves intricate experimental procedures as well as a tedious separation of the thiocyanate from the by-product isothiocyanate. An alternative method using arylthallium ions or thiocyanogen is also in limited use.[2] Here we report effective and straightforward syntheses of arenethiocyanates from sodium arenesulphinate or arenesulphonyl chloride using trimethylsilyl cyanide (TMSCN).

Sodium arenesulphinate can be transformed to arenethiocyanate by a reaction with TMSCN in hexamethylphosphoramide (HMPA). The procedure was to add TMSCN (3 mM) in HMPA (1 ml) to an ice-cold suspension of sodium sulphinate (1 mM) in HMPA (2 ml). After stirring (with ice-cooling), the mixture was diluted with water, extracted with ether, and concentrated to give the crude thiocyanate, which was purified by recrystallization or chromatography (see Scheme 1).



Scheme 1. Ar is as defined in Table 1.

Table 1. Results for the reactions in

Ar	Temp/°C	SO_2Na Time/h	% Yields[a]	SO_2Cl % Yields[a,b]
Phenyl	0	6.0	64 (51)	47 (38)
4-Methylphenyl	0	6.0	80 (64)	48 (41)
4-Methoxyphenyl	0	6.0	65 (52)	51 (42)
4-Chlorophenyl	0	6.0	64 (51)	50 (41)
4-Bromophenyl	0	6.0	69 (67)	60 (49)
2,5-Dimethylphenyl	70	2.0	60 (52)	47 (38)
2,4,6-Tri-isopropylphenyl	70	0.5	61 (52)	49 (40)
2-Naphthyl	0	6.0	87 (69)	87 (80)
8-Quinolyl	70	0.5	(20)	(18)

[a] Yields were estimated by G.L.C. by comparison with standard substances; numbers in parentheses are isolated yields. [b] Reactions were carried out in refluxing acetonitrile for 10 min.

Arenethiocyanate can also be synthesised directly from arenesulphonyl chloride using TMSCN in the presence of a reducing agent. Among a variety of methods employed to reduce sulphonyl halides to sulphinic acids,[3] a mixture of sodium sulphite and potasium carbonate gave the best results. The procedure was to add a solution of sulphonyl chloride (2.7 mM) in acetonitrile (2 ml) to a stirred solution of TMSCN (2.0 mM), sodium sulphite (1.8 mM), and potasium carbonate (2.7 mM). After stirring under reflux the reaction mixture was worked up by the same procedure as above. The results of both methods are summarised in Table 1.

Both methods can be applied to obtain mono-, di-, and tri-substituted benzenethiocyanates. Heteroaromatic quinoline derivatives gave a moderate transformation rate. However, considering the simple procedure for the sulphinate to thiocyanate transformation, the methods may be still valuable.

In general, the yields of thiocyanates are better in the reactions with sodium arenesulfinates than with sulphonyl chloride. However, considering the unstable and hygroscopic nature of sulphinic acids, the method using the easily available sulphonyl chloride may still be useful.

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References

1 E. Wenschu and K. Polling, *Z. Chem.*, 1980, **20**, 122; E. E. Reid, 'Organic Chemistry of Bivalent Sulfur', vol. 6, ch. 1, Chemical Pub. Co., 1966.

2 R. G. Guy, 'The Chemistry of Cyanates and Their Thio Derivatives 2', ed. S. Patai, ch. 18, Wiley and Sons 1977; S. Harusawa and T. Shioiri, *J. Synth. Org. Chem. Jpn.*, 1981, **39**, 741 S. Harusawa and T. Shioiri, *Tetrahedron Lett.*, 1982, **23**, 447; D. N. Harp, B. T. F. Lander, and R. A. Smith, *Synthesis*, 1979, 181.

3 F. Muth, 'Methoden der Organischen Chemie' (Houben-Weyl), vol. 9, ed. E. Müller, Georg Thieme Verlag, Stuttgart 1955, p. 285.