Photochemical Thiocyanation of Aromatic Compounds[1]

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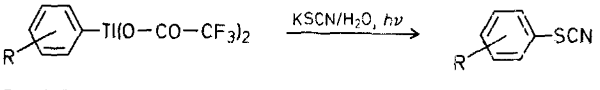
Direct introduction of a thiocyano group into aromatic compounds is possible only with very reactive substrates such as amines and phenols, utilizing thiocyanogen as the effective reagent[2]. Less reactive substrates such as aryl ethers and anilides, which are unreactive towards thiocyanogen, may be thiocyanated by the use of thiocyanogen chloride[3]. No general procedure exists, however, for the introduction of the thiocyano grouping into relatively unreactive or deactivated aromatic compounds. We describe herein a simple procedure for the introduction of a thiocyano grouping into a variety of activated as well as non-activated aromatic substrates in moderate yield, which involves photolysis of the readily accessible arylthallium bis-trifluoroacetates[4] in aqueous potassium thiocyanate solution.



R = 4-CH$_3$	yield: 36%[a]
R = 4-C$_2$H$_5$	38%[b]
R = 4-OCH$_3$	46%[c]
R = 4-Cl	41%[d]
R = 2,4-di-CH$_3$	53%[e]
R = 2,5-di-CH$_3$	58%[f]
R = 3,4-di-CH$_3$	41%[g]

[a] 90% 4-methyl-thiocyanobenzene + 10% of a mixture of the 2- and 3-methyl isomers.

[b] 96% 4-ethyl-thiocyanobenzene + 4% of an unidentified (probably the 2-ethyl) isomer.

[c] 94% 4-methoxy-thiocyanobenzene + 6% of an unidentified (probably the 2-methoxy) isomer.

[d] 85% 4-chloro-thiocyanobenzene + 15% 2-chloro-thiocyanobenzene.

[e] >99% 2,4-dimethyl-thiocyanobenzene.

[f] >99% 2,5-dimethyl-thiocyanobenzene.

[g] 95% 3,4-dimethyl-thiocyanobenzene + 5% of an unidentified isomer.

Since the thiocyano grouping enters the aromatic ring at the position to which thallium was originally attached[5], and aromatic thallation has been demonstrated to be subject to orientation control[6], this new procedure should provide access to a wide variety of aryl thiocyanates.

Thiocyanation of Substituted Benzenes; General Procedure:
A solution of an arylthallium bis-trifluoroacetate (3 g) in aqueous potassium thiocyanate (20 g in 100 ml of water) was irradiated in a quartz tube with 3000 Å light (Rayonet Reactor) for 5 hr. Addition of water (50 ml), extraction with ether (3 × 50 ml), and evaporation of the ether extracts gave a residue which was taken up in 60 ml of ether/hexane (1:1). Decolorization with charcoal, filtration, and evaporation of the filtrate then gave the aryl thiocyanate.

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[1] Thallium in Organic Synthesis. Part XXIX. For the preceding paper in this series, see A. McKillop, O. H. Oldenziel, B. P. Swann, E. C. Taylor, R. L. Robey, J. Amer. Chem. Soc., in press.

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[3] R. G. R. Bacon, R. G. Guy, J. Chem. Soc. **1960**, 318.

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[5] Similar regiospecificity has been observed in the photolysis of arylthallium bis-trifluoroacetates in aqueous potassium cyanide to give aromatic nitriles [E. C. Taylor, H. W. Altland, R. H. Danforth, G. McGillivray, A. McKillop, J. Amer. Chem. Soc. **92**, 3520 (1970)] and in benzene suspension to give unsymmetrical biphenyls [E. C. Taylor, F. Kienzle, A. McKillop, J. Amer. Chem. Soc. **92**, 6088 (1970)]

[6] E. C. Taylor, F. Kienzle, R. L. Robey, A. McKillop, J. Amer. Chem. Soc. **92**, 2175 (1970).