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Photochemical Thiocyanation of Halobenzenes with Thiocyanate Anion

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Synopsis. Halobenzenes having such an electron-donating group as amino, hydroxyl or methoxyl group at their para position were thiocyanated with sodium thiocyanate under irradiation. Also, the ring isomer of *o*-thiocyanatoaniline, 2-aminobenzothiazole, was obtained by the photoreaction of *o*-chloroaniline with sodium thiocyanate.

In spite that photochemically induced nucleophilic aromatic substitution including the photocyanation has been extensively studied[1] very few examples of photothiocyanation of aromatic compounds are known other than the reaction of phenylthallium(III) compounds with potassium thiocyanate[2] and the formation of *p*-thiocyanatoaniline from *p*-chloroaniline.[3] We now report the photothiocyanation of monosubstituted halobenzene with thiocyanate anion.

By the irradiation of *p*-substituted halobenzenes and sodium thiocyanate in water or *t*-butyl alcohol-water through quartz by a high pressure mercury lamp the corresponding *p*-substituted thiocyanatobenzenes were obtained. The results are summarized in Table 1. Under the similar conditions, *m*-chloroaniline, *m*-chlorophenol, *m*-chloronitrobenzene, or *m*-nitroanisole did not give a detectable amount of *m*-thiocyanatobenzene derivatives.

TABLE 1. PHOTOTHIOCYANATION OF *p*-SUBSTITUTED HALOBENZENES

$$\mathrm{R{-}C_6H_4{-}X} + \mathrm{NaSCN} \xrightarrow{h\nu} \mathrm{R{-}C_6H_4{-}SCN} + \mathrm{NaX}$$

R	X	Solvent	Time (h)	Yield (%)
NH_2	Cl	20% *t*-butyl alcohol	6	10.5
NH_2	Br	20% *t*-butyl alcohol	6	5.0
OH	Cl	water	18	25.0
OH	Br	water	6	13.6
OCH_3	Cl	20% *t*-butyl alcohol	11	15.3
OCH_3	Br	60% *t*-butyl alcohol	3	7.0

Irradiation of a solution of *o*-chloroaniline and sodium thiocyanate in 20% aqueous *t*-butyl alcohol afforded 2-aminobenzothiazole. There was no remarkable acceleration in the photoreaction of *p*- or *m*-chloroaniline in the presence of 18-crown-6 ether potassium thiocyanate complex in anhydrous acetonitrile. As shown in Table 1, halobenzenes having an electron-donating group at their para position can be substituted by photothiocyanation.

Experimental

UV spectra were recorded on a Hitachi EPS-3T recording spectrophotometer and IR spectra on a Hitachi EPI-G3 spectrophotometer. A Taika 100W high pressure mercury lamp was used as the irradiation source.

General Procedure for Analysis of Photothiocyanation Products from Halobenzenes. A solution of a halobenzene (0.2 mmol) and sodium thiocyanate (2 mmol) in a solvent (20 ml) was irradiated. The reaction was cheked with TLC and UV spectrum. An aliquot of the reaction mixture was analyzed by liquid partition chromatography and UV spectrum to determine the yields of products. The reaction mixture was always proved to contain unreacted halobenzene.

Photothiocyanation of p-*Chloroaniline.* A typical example for isolation and identification of photothiocyanation products from monosubstituted halobenzenes is as follows. A solution of *p*-chloroaniline (5 mmol) and sodium thiocyanate (50 mmol) in 20% aqueous *t*-butyl alcohol (500 ml) was irradiated through quartz with stirring for 4.5 h. A small amount of dark brown precipitates which appeared during the irradiation was filtered off. The filtrate was concentrated to dryness. The residue was mixed with water and extracted with ether. The ethereal layer was dried over anhydrous sodium sulfate and ether was removed under reduced pressure. The residue was crystallized from ethanol water to give colorless crystals, mp 55.5 °C,[4] which was identified with an authentic sample by mixed-melting point, UV and IR spectrum: $\lambda_{\max}^{\mathrm{EtOH}}$ 262 nm, ν(KBr) 2141 cm^{-1} (SCN).

Photothiocyanation of o-*Chloroaniline. Formation of 2-Aminobenzothiazole.* The preceding procedure was used except that the *t*-butyl alcohol solution was irradiated for 50.5 h to give colorless crystals, mp 128—129.5 °C,[5] which was identified with an authentic sample by mixed-melting point and UV spectrum: $\lambda_{\max}^{\mathrm{EtOH}}$ 264 nm.

Photothiocyanation of p- *or* m-*Chloroanilne in the Presence of 18-Crown-6 Ether Potassium Thiocyanate Complex.* Potassium thiocyanate (1 mmol) and 18-crown-6 ether (1 mmol) were dissolved in methanol (10 ml) and then methanol was removed under reduced pressure to give a colorless complex. A solution of the complex and *p*- or *m*-chloroaniline (0.1 mmol) in acetonitrile (10 ml) was irradiated for 5 h. The yield of the product did not increase compared with that of the reaction product in the absence of the complex.

References

1) a) J. Cornelisse and E. Havinga, *Chem. Rev.*, **75**, 353 (1975); b) J. Cornelisse, *Pure Appl. Chem.*, **41**, 433 (1975).

2) E. C. Taylor, F. Kienzle, and A. McKillop, *Synthesis*, **1972**, 38.

3) A. V. Eltsov, O. V. Kulbitskaya, and A. N. Frolov, *Zh. Org. Khim.*, **8**, 76 (1972).

4) The reported value is 56—57 °C; A. Kaji, *Nippon Kagaku Zasshi*, **81**, 1776 (1960).

5) The reported value is 132 °C; Z. H. Skraup, *Ann.*, **419**, 65 (1919).