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A CONVENIENT METHOD FOR THE PREPARATION OF ISOTHIOCYANATES USING 2-CHLOROPYRIDINIUM SALT

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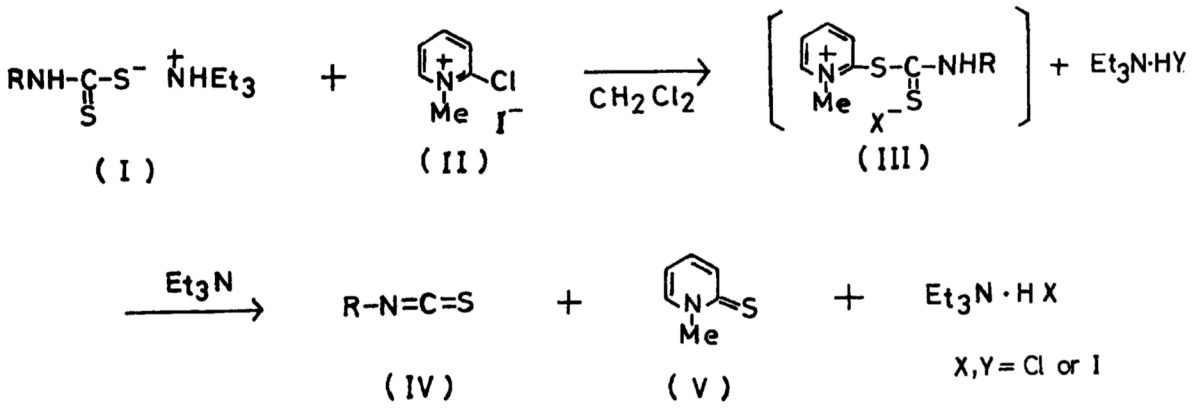
Various isothiocyanates are prepared in high yields by treating triethylammonium dithiocarbamates with 2-chloro-1-methylpyridinium salt in the presence of triethylamine.

In the course of our synthetic investigation utilizing 2-halopyridinium salts,[1] it was found that triethylammonium dithiocarbamates, easily prepared from amines, carbon disulfide and triethylamine, reacted readily with 2-chloropyridinium salt in the presence of triethylamine to give the corresponding isothiocyanates in high yields.

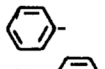
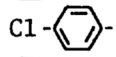
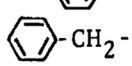
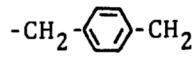
A typical procedure is described for the preparation of p-chlorophenyl isothiocyanate: A solution of triethylamine (111 mg, 1.1 mmol) in dichloromethane (4 ml) was slowly added at room temperature under an argon atmosphere to a mixture of triethylammonium p-chlorophenyldithiocarbamate (304 mg, 1 mmol) and 2-chloro-1-methylpyridinium iodide (281 mg, 1.1 mmol), and then the reaction mixture was stirred at room temperature for an additional 2 hr. After removal of the solvent, the residue was separated by silica gel thin layer chromatography to afford p-chlorophenyl isothiocyanate in a quantitative yield.

In a similar manner, various isothiocyanates were prepared in high yields as summarized in the Table.



As described in the equation, triethylammonium dithiocarbamate (I) initially reacts with 2-chloropyridinium salt (II) to give a key intermediate (III), which is in turn converted to the corresponding isothiocyanate (IV) and 1-methyl-2-pyridinethione (V).

Table. The Preparation of Isothiocyanates[6)]

R-N=C=S R	Isolated Yield (%)	R-N=C=S R	Isolated Yield (%)
	95		91
	quant.	$CH_3(CH_2)_7$-	94
	91		84[a)]

a) Triethylammonium dithiocarbamate was treated with each 2.2 molar amounts of 2-chloro-1-methylpyridinium iodide and triethylamine.

Concerning the preparation of isothiocyanates, there have been reported a variety of methods such as the Kalza reaction,[2)] phosgene method, [3)] thiophosgene method,[4)] and decomposition of thiourea derivatives.[5)] In comparison with the above mentioned methods, the present method is unique in preparing various isothiocyanates from triethylammonium dithiocarbamates in high yields under mild conditions using readily available 2-chloropyridinium salt.

References and Note

1) K. Hojo and T. Mukaiyama, Chem. Lett., 619 (1976), and the other references cited therein.
2) J. E. Hodgkins and W. P. Reeves, J. Org. Chem., 29, 3098 (1964).
3) K. H. Slotta and H. Presseler, Chem. Ber., 63, 888 (1930).
4) E. Dyer and T. B. Johnson, J. Am. Chem. Soc., 54, 781 (1932).
5) J. Cymerman-Craig, M. Moyle, and R. A. White, Org. Synth., Coll. Vol. 4, 700 (1963).
6) IR and NMR spectra of all the compounds were well agreed with the assigned structures.

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