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A Novel Synthesis of Isothiocyanates from Amines Using Triphenylphosphine / Carbon Tetrachloride

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Triethylammonium dithiocarbamates ($\text{RNHC(S)S}\cdot\text{HNEt}_3$), prepared from aliphatic and/or aromatic amines, carbon disulfide and triethylamine, were treated with triphenylphosphine/carbon tetrachloride to give the corresponding isothiocyanates in good yields.

Two procedures were examined to convert amines to isothiocyanates, *i.e.*, a direct method which does not include the isolation of dithiocarbamate, and an indirect method.

Aliphatic isothiocyanates were prepared in 70-91% yields using the direct method. The method, however, provided low yield of aryl isothiocyanates. The addition of arylamines to carbon disulfide in the presence of triethylamine is so slow that the formation of aryl dithiocarbamates may compete with the reaction of arylamines with triphenylphosphine/carbon tetrachloride, which may cause the lower aryl isothiocyanates in direct method.

On the other hand, the aryl isothiocyanates were prepared in good yields by using the indirect method, *e. g.*, phenyl isothiocyanate was obtained in 78% yield, while it was obtained only in 51% yield by using the direct method.