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A NEW METHOD FOR THE PREPARATION OF ISOCYANATES FROM METHYL THIOCARBAMATES BY THE USE OF 2-CHLOROBENZOXAZOLIUM SALT

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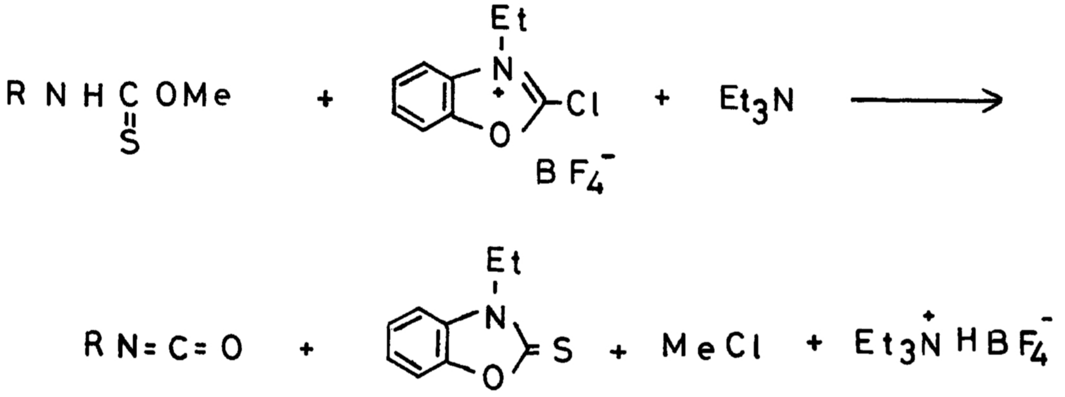
Treatment of methyl thiocarbamates with 2-chloro-3-ethylbenzoxazolium tetrafluoroborate and triethylamine at room temperature affords isocyanates in good yields under neutral condition.

The onium salts of azaaromatics have been shown to be useful reagents for the elimination of certain sulfur functions. For example, thioureas[1] and triethylammonium dithiocarbamates[2] are converted to carbodiimides and to isothiocyanates, respectively, on treatment with 2-chloropyridinium salts.

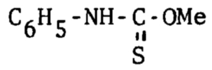
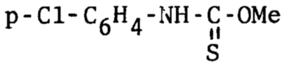
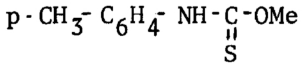
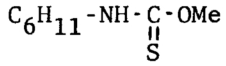
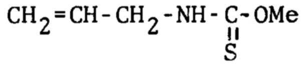
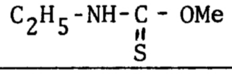
We have now found that methyl thiocarbamates are easily converted to the corresponding isocyanates in good yields on treatment with 2-chloro-3-ethylbenzoxazolium tetrafluoroborate[3] [4] [5] in the presence of equimolar amount of triethylamine as shown in the following equation.



A typical procedure is described for the preparation of p-tolyl isocyanate: A solution of triethylamine (182 mg, 1.8 mmol) in dichloromethane (5 ml) was slowly added at 0°C under an argon atmosphere to a mixture of methyl N-p-tolylthiocarbamate (271 mg, 1.5 mmol) and 2-chloro-3-ethylbenzoxazolium tetrafluoroborate (484 mg, 1.8 mmol), and then the reaction mixture was stirred at room temperature for 2 hr. After evaporation of the solvent p-tolyl isocyanate (82%, 184 mg) was isolated by short path distillation (130°C/52-53 mmHg). On the other hand, when the above reaction mixture was quenched with excess amount of benzylamine, N-P-tolyl-N'-benzyl urea was isolated (87%, 379mg).

In a similar manner, various isocyanates were prepared in good yields as shown in the Table.

Table The Yield of Various Isocyanates from Methyl Thiocarbamates

Methyl Thiocarbamate	Isocyanate	Yield (%)
 $C_6H_5\text{-NH-}\underset{\underset{S}{\|}}{C}\text{-OMe}$	$C_6H_5\text{-N=C=O}$	78
 $p\text{-Cl-}C_6H_4\text{-NH-}\underset{\underset{S}{\|}}{C}\text{-OMe}$	$p\text{-Cl-}C_6H_4\text{-N=C=O}$	83
 $p\text{-}CH_3\text{-}C_6H_4\text{-NH-}\underset{\underset{S}{\|}}{C}\text{-OMe}$	$p\text{-}CH_3\text{-}C_6H_4\text{-N=C=O}$	82
 $C_6H_{11}\text{-NH-}\underset{\underset{S}{\|}}{C}\text{-OMe}$	$C_6H_{11}\text{-N=C=O}$	79
 $CH_2\text{=CH-}CH_2\text{-NH-}\underset{\underset{S}{\|}}{C}\text{-OMe}$	$CH_2\text{=CH-}CH_2\text{-N=C=O}$	66[a]
 $C_2H_5\text{-NH-}\underset{\underset{S}{\|}}{C}\text{-OMe}$	$C_2H_5\text{-N=C=O}$	64[b]

a) The products obtained by short path distillation (40°C/55 mmHg) consisted of allyl isocyanate and dichloromethane, and the yield of allyl isocyanate was determined by the integral peak ratio of nmr spectrum.
b) The yield was calculated based on the yield of N-ethyl-N'-benzyl urea obtained by quenching the reaction mixture with benzylamine.

The present method can be applied to both aliphatic and aromatic isocyanate synthesis at room temperature under neutral condition , and is of general utility. It is also applicable to the preparation of allyl isocyanate which is known to be prepared in low yield by the conventional methods.6) 7)

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