Tetrahedron Letters No. 18, pp 1771 - 1774, 1972. Pergamon Press. Printed in Great Britain.

REACTION OF ISONITRILES WITH THALLIUM(III) NITRATE: AN EFFECTIVE SYNTHESIS OF CARBAMATES.

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(Received in UK 20 March 1972; accepted for publication 22 March 1972)

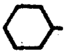
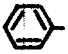
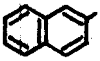
Isonitriles have become easily available through dehydration of formamides[1] and have gained increased importance in synthetic organic chemistry.[2]

We wish to report that thallium(III) nitrate trihydrate (TTN)[3] reacts fast and cleanly with isonitriles to give carbamates in high yield. Thus a solution of the isonitrile in methanol is added to a stirred solution of an equimolar amount of TTN in methanol at room temperature. Thallium(I) nitrate precipitates immediately and the reaction is complete within a few minutes. The inorganic salt is removed by filtration and the filtrate is evaporated. The residue is taken up in ether and the ether solution is washed once with a small portion of water. The organic layer is dried over anhydrous sodium sulfate, filtered and evaporated to give the crude carbamate. Purification is achieved by distillation or recrystallization. Representative conversions are listed in Table 1.

Isonitriles react with mercury(II) nitrate, too, but less efficiently. However, in contrast to TTN which seems to be stable only in methanolic solution, mercury(II) nitrate may be used in other alcohols as well.* Some examples are listed in Table 2.

Table 1

$$\text{R-NC} + \text{Tl(NO}_3)_3 \xrightarrow[\text{H}_2\text{O}]{\text{CH}_3\text{OH}} \text{R-NH-COOCH}_3 + \text{TlNO}_3 + 2\ \text{HNO}_3$$

R	Yield[a] %
$C_2H_5OCOCH_2$-	84
	90
$CH_3)_3C$-	35
	93
	85
	97

[a] Identity of products was established by comparison with authentic material and/or by spectral data. The yield is based on pure product.

Table 2

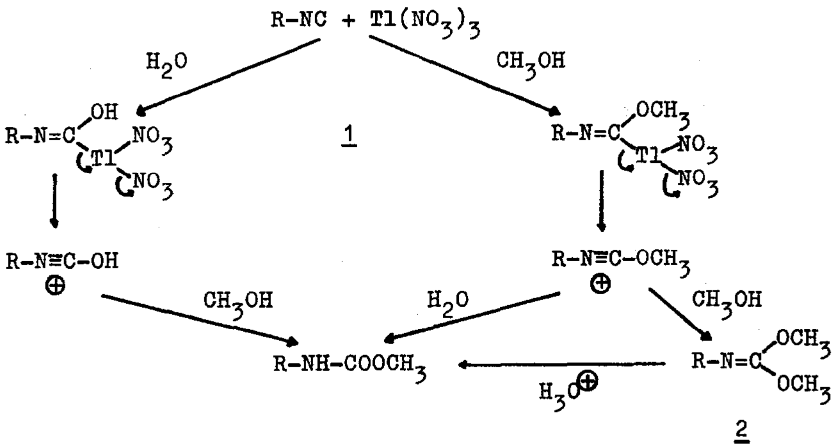
$$\text{R-NC} + \text{Hg(NO}_3)_2 \xrightarrow[\text{H}_2\text{O}]{\text{R'OH}} \text{R-NH-COOR'} + \text{HgNO}_3 + \text{HNO}_3$$

R	R'	Yield[a] %
$C_2H_5OCOCH_2$-	CH_3-	36
$C_2H_5OCOCH_2$-	$CH_3)_2CH$-	40
	$CH_3)_2CH$-	23

[a] See Footnote 'a' in Table 1.

The capability of isonitriles to undergo α-addition is well documented and carbamate formation may be explained in terms of the reactions outlined in Scheme 1. The heterolysis of the carbon-thallium bond in the intermediate 1 would proceed readily[3,4] and, depending on the nature of the nucleophile, would lead either directly to the carbamate or to the easily hydrolyzable[5,6] imino carbonate 2.

Scheme 1



The oxidation of isonitriles to isocyanates (and hence in the presence of alcohols to carbamates) has been achieved by means of ozone[7], t-butyl hypochlorite[8], dimethyl sulfoxide[9], and nitrile oxide[10] with variable success. The oxidation with TTN is characterized by its extreme simplicity and high yield and should, in the absence of complicating factors[3,11] become the method of choice.

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