BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (11), 3415—3416 (1975)

# Oxidation of Isocyanides by Hg(II), Tl(III), and Pb(IV) Acetates

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(Received May 2, 1975)

**Synopsis.** Isocyanides were oxidized to isocyanates in acetic acid in the presence of Hg(II), Tl(III), or Pb(IV) acetate through acetoxymetallation. The reaction of an isocyanide with Tl(III) acetate in various alcohols gave the corresponding carbamates in good yields.

Oxymetallations of isocyanides ($\alpha$-addition) have recently been proposed in the carbamate formation from isocyanides by use of Tl(III) nitrate[1] and Hg(II) salts.[2] We now report the oxidation of isocyanides to the corresponding isocyanates by Hg(II), Tl(III), or Pb(IV) acetate in acetic acid which seems to proceed through acetoxymetallation. Various other reagents for such oxidation are cited in a review by Saegusa and Ito.[3]

## Results and Discussion

When cyclohexyl isocyanide was treated with Hg(II), Tl(III), or Pb(IV) acetate in a mixture of benzene and acetic acid (9:1 by volume) at 5—10 °C, cyclohexyl isocyanate was obtained as the product. The reaction also proceeded in acetic acid at 20 °C, but the yield of isocyanate was slightly lower. The metal acetates were reduced to Hg metal and Tl(I) and Pb(II) acetates, respectively. Some typical results are listed in Table 1. In the absence of metal acetates, no isocyanate was formed under any conditions shown in Table 1. An

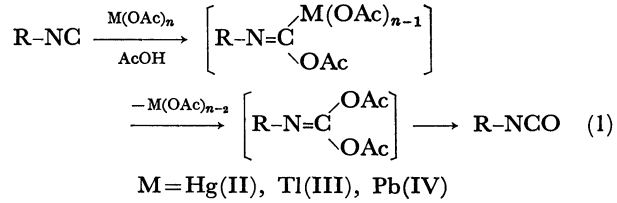
Table 1. Isocyanates from isocyanides[a]

| R–NC (10 mmol) R | Metal acetate (10 mmol) | React. temp. (°C) | React. time (h) | Yield of R–NCO (%)[b] |
|---|---|---|---|---|
| *c*-$C_6H_{11}$ | $Hg(OAc)_2$ | 5—10 | 2.5 | 69 |
| *c*-$C_6H_{11}$ | $Hg(OAc)_2$ | 20 | 3 | 64[c] |
| *c*-$C_6H_{11}$ | $Tl(OAc)_3$ | 5 | 3 | 54 |
| *c*-$C_6H_{11}$ | $Pb(OAc)_4$ | 5 | 3 | 54 |
| *c*-$C_6H_{11}$ | $Pb(OAc)_4$ | 80 | 0.2 | 19 |
| $C_6H_5$ | $Pb(OAc)_4$ | 5 | 3 | 41 |

a) Solvent: Benzene+AcOH (9:1 by volume) 20 ml. b) Determined by glc. c) Solvent: AcOH 20 ml.

elongation of the reaction time or an elevation of the temperature resulted in a decrease of the yield of isocyanate because of the formation of formamide from isocyanide and acetic acid and also of the secondary reaction of isocyanate with acetic acid. The reaction with Mn(III) and Co(III) acetates[4] instead of the above metal acetates gave only a trace amount of the isocyanate and almost all of the starting isocyanide was recovered. Moreover, although the oxidations of alkylbenzenes and olefins with Pb(IV), Mn(III), and Co(III) acetates are known to involve radical pathways,[5] no products which seemed to result from a radical reaction could be detected even at higher reaction temperatures.

Considering the well-known nature of Hg(II), Tl(III), and Pb(IV) acetates to afford oxymetallates of olefins and acetylenes and a proposal of oxymetallation of isocyanides,[1,2] it seems to be reasonable to assume that the reaction proceeded through acetoxymetallation as shown in Scheme 1. All attempts to isolate the intermediate acetoxymetallate of cyclohexyl and phenyl isocyanides were unsuccessful.



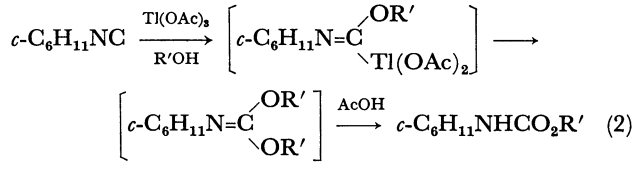
M=Hg(II), Tl(III), Pb(IV)

Table 2. Carbamates from cyclohexyl isocyanide[a]

| Alcohol (20 ml) R′ in R′OH | React. temp. (°C) | React. time (h) | Yield of *c*-$C_6H_{11}NHCO_2R'$[b] (%) |
|---|---|---|---|
| Me | 65 | 1 | 62 |
| Et | 65—70 | 1 | 68 |
| *n*-Pr | 65—70 | 1 | 72 |
| *i*-Pr | 65—70 | 1 | 75 |
| *t*-Bu | 65—70 | 2 | 49 |
| $CH_2CH_2OH$ | 65—70 | 1 | 36[c] |

a) *c*-$C_6H_{11}NC$ 10 mmol, $Tl(OAc)_3$ 10 mmol. b) Determined by glc. A small amount (<10%) of *c*-$C_6H_{11}NHCOCH_3$ was always formed. c) *c*-$C_6H_{11}NHCO_2CH_2CH_2OAc$.

It has been reported that Tl(III) nitrate is a good reagent for synthesis of carbamates from isocyanides, but unfortunately only in methanol.[1] As we found that Tl(III) acetate could be used successfully in various alcohols for this purpose, we would like to add here the results obtained by using cyclohexyl isocyanide (Table 2). Carbamates may be formed mainly *via* alkoxythallation of the isocyanide, followed by redox decomposition to iminocarbonates which react with acetic acid (Scheme 2).



The protolysis of iminocarbonates to give carbamates has already been reported.[6] When ethylene glycol was used as an alcohol component, the expected carbamate, *c*-$C_6H_{11}NHCO_2CH_2CH_2OAc$, which may be derived from ethylene *N*-cyclohexyl iminocarbonate, was obtained as the only product.

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## Experimental

The IR spectra were taken with a Hitachi EPI-S2 spectrometer. Glc analyses were carried out with a Shimadzu 5APTF apparatus, using Apiezon L(30%)-Celite (1m) and EGSS-X(30%)-Chromosorb W (1m) columns ($N_2$ as the carrier gas).

*Materials.* Isocyanides (R–NC) were prepared by the method of Ugi *et al*:[7] R=*c*-$C_6H_{11}$, bp 65—69 °C/20 mmHg (lit,[7] bp 56—58 °C/11 mmHg); R=$C_6H_5$, bp 57.5 °C/19.5 mmHg (lit,[7] bp 50—51 °C/11 mmHg). Other organic materials including the solvents were purified before use by distillation. Commercial inorganic materials were used without further purification. $Tl(OAc)_3$ was prepared from $Tl_2O_3$ and acetic acid. Mn(III) and Co(III) acetates were prepared by the reported method.[4]

*Reaction of Isocyanides with Metal Acetates in Acetic Acid.* A typical experimental procedure is given below. To a stirred suspension of $Tl(OAc)_3$ (3.82 g, 10 mmol) in a mixture of benzene (18 ml)–AcOH (2 ml) was added slowly cyclohexyl isocyanide (1.09 g, 10 mmol) under cooling with an ice-bath and the resulting mixture was stirred for 3 h at 5 °C. After the precipitated TlOAc was filtered off from the reaction mixture, the filtrate was combined with benzene (50 ml) and washed with 50 ml of cold water and with aq. $NaHCO_3$ (50 ml). After being dried over $Na_2SO_4$, the benzene was evaporated to leave *ca.* 5 ml of a residue. Glc analysis of the residue by using iodobenzene as an internal standard revealed the presence of 5.4 mmol (54% yield based on $Tl(OAc)_3$ charged) of cyclohexyl isocyanate. Distillation gave 0.25 g of a pure compound: bp 52 °C/24 mmHg; IR, 2250 ($\nu_{N=C=O}$) $cm^{-1}$.

*Reaction of Cyclohexyl Isocyanide with $Tl(OAc)_3$ in Alcohols.* As an example, the reaction in ethanol is given below. To an orange suspension of $Tl(OAc)_3$ (3.82 g, 10 mmol) in ethanol (20 ml) was added cyclohexyl isocyanide (1.09 g, 10 mmol) at room temperature and the resulting mixture was heated for 1 h at 65—70 °C. After being cooled down to room temperature, the precipitated TlOAc (1.4 g, 5.3 mmol) was filtered off. The filtrate was treated as described above. Glc analysis of the residue by using ethyl benzoate as an internal standard showed the presence of 6.8 mmol (68% yield) of ethyl *N*-cyclohexyl carbamate. Distillation gave 0.5 g of crude product, which was recrystallized from *n*-hexane: mp 53.5—55 °C (lit,[8] mp 55—56 °C).

In a similar way, the following carbamates (*c*-$C_6H_{11}NHCO_2R'$) were obtained: R'=Me, mp 72—73.5 °C (lit,[8] mp 75 °C); R'=*n*-Pr, mp 40—41 °C from *n*-hexane; R'=*i*-Pr, mp 65—66.5 °C (lit,[9] mp 66.5—67 °C); R'=*t*-Bu, mp 65—68 °C (lit,[10] mp 68—69 °C); R'=$CH_2CH_2OAc$, mp 77—79 °C (lit,[11] mp 83.5 °C). The last compound was identified by comparison of IR and NMR spectra with an authentic sample prepared from the reaction of ethylene *N*-cyclohexyl iminocarbonate with acetic acid in ethylene glycol or benzene.[6]

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