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Synthetic Reacions by Complex Catalysts. XXXVIII. A New Preparation of Copper(I) Isocyanate(Alkyl Isocyanide) and Its Reactions

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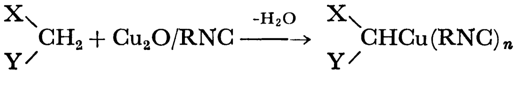
Synopsis. Reaction of ethyl carbamate with Cu_2O in the presence of *t*-butyl isocyanide produces copper(I) isocyanate(*t*-butyl isocyanide) complex, $Cu(NCO)(t\text{-}C_4H_9NC)_{2.5}$ (**1**), in 93% yield. Complex **1** is also produced in high yield by the reaction of ethyl *N*-trimethylsilylcarbamate with Cu_2O in the presence of *t*-butyl isocyanide. Complex **1** reacts with alkyl halides in alcohols and with acyl chlorides to afford *N*-alkylcarbamate (**2**) and acyl isocyanate (**3**), respectively, in moderate yields.

It was already reported that organocopper(I)(alkyl isocyanide) complexes[1] and copper(I) carboxylate (alkyl isocyanide) complexes[2] have been successfully prepared by the reactions of Cu_2O/RNC system with carbon acids such as cyclopentadiene, acetylacetone, and malonate (Eq. (1)), and with carboxylic acid (Eq. (2)).



$$\begin{matrix}X\\ & CH_2\\ Y\end{matrix} + Cu_2O/RNC \xrightarrow{-H_2O} \begin{matrix}X\\ & CHCu(RNC)_n\\ Y\end{matrix} \qquad (1)$$

$$RCO_2H + Cu_2O/RNC \xrightarrow{-H_2O} RCO_2Cu(RNC)_n \qquad (2)$$

We have now found that the treatment of ethyl carbamate with Cu_2O/RNC produces copper(I) isocyanate (alkyl isocyanide) complex in high yields. This reaction presents a convenient one-step preparative method of Cu(I) isocyanate complex(**1**)[3]

$$NH_2CO_2C_2H_5 + Cu_2O/RNC \xrightarrow[-H_2O]{-C_2H_5OH} \underset{\mathbf{1}}{Cu(I)(NCO)(RNC)_n} \qquad (3)$$

The preparation of Cu(I)isocyanate(*t*-butyl isocyanide) complex (**1a**) was carried out as follows. Under nitrogen, a mixture of ethyl carbamate, Cu_2O, and *t*-butyl isocyanide in benzene was refluxed for 6 hr, water and ethyl alcohol produced being removed by azeotropic distillation. The complex of $Cu(I)(NCO)(t\text{-}C_4H_9NC)_{2.5}$ (**1a**) was obtained as a white crystalline solid in 93% yield based upon the starting carbamate. Complex **1a** is not very sensitive to air in solid form, but is readily oxidized in solution. The identity of **1a** has been established by elemental analysis, IR and NMR spectra, and a chemical transformation. Complex **1a** was treated with ethyl alcohol containing dry HCl to produce ethyl carbamate and $Cu(I)Cl(t\text{-}C_4H_9NC)$ complex. It is of interest that complex **1** was also produced in high yields by the reaction of ethyl *N*-trimethylsilylcarbamate[4] with Cu_2O/RNC.

$$(CH_3)_3SiNHCO_2C_2H_5 + Cu_2O/RNC \longrightarrow \underset{\mathbf{1}}{Cu(I)(NCO)(RNC)_n} \qquad (4)$$

A detailed understanding of the reaction mechanism for the formation of copper(I)isocyanate complex **1** must await further studies.

Complex **1a**, which is soluble in most organic solvents, is conveniently utilized for the preparation of urethane derivatives and acyl isocyanates. Complex **1a** did not react with any alkyl halides but reacted with the halides in the presence of alcohol to afford *N*-alkylcarbamate (**2**) in moderate yields (Eq. (5)). Also, complex **1a** reacted with acyl chlorides to produce acyl isocyanates (**3**) in good yields (Eq. (6)). Results are summarized in Table 1.

$$\mathbf{1a} + RBr + R'OH \longrightarrow \underset{\mathbf{2}}{RNHCO_2R'} \qquad (5)$$

$$\mathbf{1a} + RCOCl \longrightarrow \underset{\mathbf{3}}{RCONCO} \qquad (6)$$

Experimental

*Preparation of Copper(I) Isocyanate(*t*-Butyl Isocyanide) Complex $Cu(I)(NCO)(t\text{-}C_4H_9NC)_{2.5}$ (1a).* Under nitrogen, a mixture of ethyl carbamate (6 mmol), Cu_2O (4 mmol),

Table 1. Reaction of complex **1a** with alkyl halide-alcohol and with acyl chloride

Halide	Alcohol	Reaction[a] °C	hr	Product	(%)
$n\text{-}C_3H_7Br$	C_2H_5OH	80	2	$n\text{-}C_3H_7NHCO_2C_2H_5$	(83)
$n\text{-}C_4H_9Br$	$t\text{-}C_4H_9OH$	75	5	$n\text{-}C_4H_9NHCO_2(t\text{-}C_4H_9)$	(61)
$n\text{-}C_3H_7Br$	$i\text{-}C_3H_7OH$	80	2	$n\text{-}C_3H_7NHCO_2(i\text{-}C_3H_7)$	(73)
$i\text{-}C_3H_7Br$	C_2H_5OH	80	8	$i\text{-}C_3H_7NHCO_2C_2H_5$	(74)
$CH_3CH(Br)CO_2C_2H_5$	C_2H_5OH	80	9	$CH_3CH(CO_2C_2H_5)NHCO_2C_2H_5$	(90)
$BrCH_2CH_2CH_2OH$		100	21	$\lfloor -CH_2CH_2CH_2NHCO_2- \rfloor$	(77)
PhCOCl	——	50	5	PhCONCO	(76)
$n\text{-}C_7H_{15}COCl$	——	25	3	$n\text{-}C_7H_{15}CONCO$	(85)

a) Reaction conditions: **1a** (1 mmol), halide (1.5 mmol), alcohol (1.7 mmol).

t-butyl isocyanide (30 mmol), and benzene (20 ml) was refluxed for 6 hr, water and ethyl alcohol produced being removed by azeotropic distillation. Then, the solvents were removed *in vacuo*, and the residue was recrystallized from benzene to give complex **1a** as a white crystalline solid (mp 103 °C) in 93% yield based upon the carbamate. [**1a**: Found: C, 51.68; H, 7.40; N, 15.78%. Calcd for $Cu(NCO)(C_4H_9NC)_{2.5}$: C, 51.74; H, 7.24; N, 15.64%. IR(KBr) 2220, 2200, 2180, 2140, 1200 cm^{-1}. NMR($CDCl_3$) δ 1.20 (s).]

Complex **1a** was also prepared in 90% yield by the reaction of ethyl *N*-trimethylsilylcarbamate (10 mmol)[4] with Cu_2O (12 mmol) and *t*-butyl isocyanide (50 mmol) at 80 °C for 2 hr. Hexamethyldisiloxane was also isolated.

Reaction of ***1a*** *with Alkyl Halide and Alcohol.* A mixture of **1a** (1 mmol), butyl bromide (1.5 mmol), and *t*-butyl alcohol (1.7 mmol) was heated at 75 °C for 5 hr under nitrogen. The reaction mixture was triturated with ether, and filtered to remove copper(I) bromide (*t*-butyl isocyanide) complex. The filtrate was subjected to distillation *in vacuo*. The product was identified as *t*-butyl *N*-butylcarbamate (61%) by comparison of its IR and NMR spectra with those of an authentic sample.

Reaction of ***1a*** *with Acyl Halide.* To a solution of **1a** (10 mmol) in benzene (10 ml), benzoyl chloride (10 mmol) was added dropwise with stirring, and then heated at 50 °C for 5 hr. The reaction mixture was triturated with hexane and filtered. The filtrate was subjected to distillation. The product was identified as benzoyl isocyanate (bp 95 °C/21 mmHg) by comparison of its IR spectrum with that of an authentic sample[5].

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