# Synthetic reactions by complex catalysts. XII. Copper-catalyzed reaction of isocyanide with alcohol

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The reaction of alkyl isocyanide with alcohol to produce alkyl formimidate requires catalysis by metal compounds. The catalysts are classified into two groups. The first group includes metallic copper, and the oxides of copper (Cu (I) and Cu (II)), silver, and mercury, which induce the isocyanide reactions of various alcohols including saturated and unsaturated alcohols and amino-alcohol. The second group catalysts are the chlorides of copper (Cu (I)), silver, zinc, and cadmium, which cause the reactions of isocyanide only with special alcohols having strong coordinating tendencies toward the catalyst, as being exemplified by ally alcohol and  $\beta$ -N,N-dimethylaminoethanol. Among these catalysts, metallic copper and copper oxides are the most effective and give the products almost quantitatively. The difference in catalyst activity between the two groups of catalysts has been explained by assuming a ternary complex consisting of the catalyst, isocyanide, and alcohol as the site of reaction.

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In previous communications (1), we preliminarily reported a new reaction of an isocyanide with an alcohol to produce a formimidate, which was accomplished for the first time by means of catalysts of metallic copper and some copper compounds. This reaction provides a convenient,

[1] ROH + :C
$$\leq$$
N-R' ROCH=N-R'

highly selective method for the preparation of formimidates. The product formimidate may be regarded as being derived by the insertion of the isocyanide carbon bearing lone pair electrons between the oxygen and the hydrogen of the alcohol. In the absence of the copper catalyst, alcohol is quite inert toward isocyanides. Alcohol has been employed as an inert solvent in several reactions of isocyanides (2). The activity of copper catalysts is much affected by the valency of copper and the nature of the ligand. Metallic copper and cuprous and cupric oxides are excellent catalysts, which induce the reactions of isocyanides with various alcohols (1b). On the other hand, cuprous chloride and cyanide catalyze the reactions with specific alcohols such as  $\beta$ -dimethylaminoethanol and  $\beta$ ,  $\gamma$ -unsaturated alcohols (1*a*) including allyl alcohol.

It is well known that isocyanides form complexes with various transition metal salts, especially copper compounds. Therefore, it is suggested that the isocyanide-copper complex plays an essential role in the function of the copper catalyst. In addition, the coordination of alcohol

onto copper catalyst is also assumed to be quite important for the reaction. Thus, it seems likely that the reaction has taken place within the ligand sphere of the so-called mixed ligand complex consisting of copper, isocyanide, and alcohol.

The present paper describes the details of the copper-catalyzed reaction of isocyanides with alcohol, as well as some results of infrared spectral studies upon the interactions between copper catalyst and the reaction components.

### Results

Reactions of Isocyanides with Alcohols Catalyzed by Metallic Copper and Copper Oxides

Metallic copper and copper oxides (Cu (I) and Cu (II)) catalyzed quite effectively the reactions of cyclohexyl isocyanide with various alcohols (Tables I and II).

TABLE I	
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Metallic copper-catalyzed reactions
of cyclohexyl isocyanide
with alcohols*

	Product yield (%)		
ROH	1	2	
EtOH	99†	1	
<i>n</i> -BuOH	99‡		
sec-BuOH	98§	2	
CH <sub>2</sub> =CHCH <sub>2</sub> OH	95	3	

\*Reaction conditions: cyclohexyl isocyanide, 30 mmoles; alcohol, 34 mmoles; Cu, 3 mmoles; 120°; 5 h

20°; 5 h. †Boiling point, 54.5° (8 mm). ‡Boiling point, 81° (21 mm). §Boiling point, 90° (21 mm). ||Boiling point, 90° (26 mm).

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TABLE II

Copper oxide catalyzed reaction of cyclohexyl isocyanide with alcohols\*

		Product yield (%)		
ROH	Catalyst	1	2	3
$\left.\begin{array}{c} \text{EtOH} \\ n\text{-BuOH} \\ sec\text{-BuOH} \\ t\text{-BuOH} \\ \text{CH}_2 = \text{CHCH}_2\text{OH} \end{array}\right\}$	Cu <sub>2</sub> O	95 95 94 94 92	2 1 2 5	1 Trace
EtOH n-BuOH sec-BuOH t-BuOH CH <sub>2</sub> =CHCH <sub>2</sub> OH	CuO	87 81 88 91† 89	$\frac{1}{\frac{1}{3}}$	Trace

\*Reaction conditions: cyclohexyl isocyanide, 30 mmoles; alcohol, 34 mmoles; CuO (or Cu<sub>2</sub>O), 3 mmoles; 120°; 5 h. †Boiling point, 93° (19 mm).

Several alkyl N-cyclohexylformimidates were produced in almost quantitative yields. In the reactions catalyzed by cuprous and cupric oxides. small amounts of two by-products, N-cyclohexylformamide (2) and alkyl N-cyclohexylcarbamates (3) were formed. Compound 2 may possibly have been produced by the hydrolysis of the isocyanide or formimidate (1) with water which either was present as an impurity in the initial reaction mixture or was produced in situ by the etherification of alcohol. Compound 2 may also be derived from the formimidate according to

#### ROCH=N-R'

 $+ \text{ROH} \rightarrow (\text{RO})_2 \text{CHNHR}' \rightarrow \text{R'NHCHO} + \text{ROR}$ 

The formation of 3 is ascribed to the oxidation of isocyanide to isocyanate by the copper oxide catalysts. The reduction-oxidation between mercuric oxide and isocyanide is known, in which isocyanide is oxidized into isocyanate (3).

As expected, 3 was not formed in the reaction when metallic copper was the catalyst. As to the catalyst activity of metallic copper, it is very important to note that a small amount of metallic copper dissolved in cyclohexyl isocyanide to form a soluble complex. The complex formation from metallic copper and isocyanide will be described later. From these observations, it appears possible that copper oxide catalysts are reduced by isocyanide to form a copper (O)-isocyanide complex which is the actual active species responsible for their catalytic activities. The exact characterization of active species of the metallic copper and copper oxides catalysts is the subject of a future study.

### Cuprous Chloride Catalyst in the Isocyanide-Alcohol Reaction

The catalysis of cuprous chloride in the alcohol-isocyanide reaction was somewhat different from that of metallic copper and of copper oxides. Cuprous chloride did not induce the isocyanide reactions with the usual saturated alcohols such as ethanol and *n*-butanol. It catalyzed only the reactions involving  $\beta$ -dimethylaminoethanol and  $\beta$ , $\gamma$ -unsaturated alcohols such as allyl alcohol. As will be discussed later, these alcohols are characterized by a strong tendency of coordination onto cuprous chloride. The complexes of cuprous chloride and these alcohols are stable and can be isolated. These findings suggest that the coordination of isocyanide as well as alcohol onto cuprous chloride are essential for this reaction.

The reactions of cyclohexyl isocyanide with β.γ-unsaturated alcohols, and β-dimethylaminoethanol by cuprous chloride catalyst are shown in Table III. Benzyl alcohol is among the alcohols which react with isocyanide in the presence of cuprous chloride. Perhaps the phenyl group plays a role similar to that of  $\beta$ ,  $\gamma$ -unsaturated group.

In these reactions, *N*-cyclohexylformamide (2) and N-alkenyl-N-cyclohexylformamide (4) were produced as the by-products. The amount of 2, the product of the hydrolysis of cyclohexyl isocyanide, was much higher than that in the reactions with metallic copper and copper oxides

		TABL	E III		
Cuprous	chloride	catalyze	ed react	tion of	cyclohexyl

isocyanide with alcohol\*

	Product yield (%)		
ROH	1	2	4
CH2=CHCH2OH	67	25	6
CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> OH	50	32	
CH=CHCH2OH	45†	20	
СН20Н	20‡	10	63
(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> OH	67§	16	
$C_nH_{2n+1}OH$	No reaction		

\*Reaction conditions: cyclohexyl isocyanide, 40 mmoles; alcohol, 70 mmoles; CuCl, 8 mmoles; 120°; 5 h. †Boiling point, 130° (3 mm). Boiling point, 155° (3 mm). Bolling point, 85-86° (5 mm). ||Not determined.

catalysts. It may be attributed to a higher concentration of water formed *in situ* by the etherifications of these alcohols. It is known that  $\beta$ , $\gamma$ unsaturated alcohols are easily etherified by cuprous chloride catalyst (4). The by-product **4** was probably produced by the thermal rearrangement (5) of **1** (Chapman rearrangement) which took place, at least partly, during the distillation of the reaction mixture. A higher yield of **4** in the reaction with benzyl alcohol may be due in part to the higher distillation temperature.

In the cuprous chloride catalyzed reaction of cyclohexyl isocyanide with allyl alcohol, the decrease of isocyanide and the increases of the yields of products are plotted against the reaction time (Fig. 1).

There is observed an induction period of 4 h for the formation of 1. The nature of the induction period has not yet been elucidated. As to the induction period, a possibility that the reaction is autocatalytic may be excluded. The addition of formamide or formimidate to the reaction system did not shorten the induction period. Cuprous chloride catalyst itself was not changed throughout the reaction. The hydrolysis of isocyanide to produce a by-product of 2 starts at the beginning of the reaction. Another by-product of 4, however, is produced only after the main product of 1 is accumulated in the reaction system.



FIG. 1. CuCl catalyzed reaction of cyclohexyl isocyanide with allyl alcohol; — , cyclohexyl isocyanide; — O—, N-cyclohexylformamide; — , allyl Ncyclohexylformimidate; — , N-cyclohexyl-N-allylformamide.



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FIG. 2. CuCl<sub>2</sub> – cyclohexyl isocyanide reaction in ethanol; — , CuCl (formed by reduction of CuCl<sub>2</sub>); — , ethyl *N*-cyclohexylcarbamate.

### Catalytic Behavior of Other Copper Compounds

In the cupric chloride catalyzed reaction of isocyanide with saturated alcohols, only small amounts of *N*-substituted carbamate (3) and *N*substituted formamide (2) were produced. The carbamate formation suggests the reduction– oxidation reaction between isocyanide and cupric chloride. A series of reactions of cyclohexyl isocyanide with increasing amounts of cupric chloride in the presence of excess ethanol was carried out (Fig. 2).

It was found that cupric chloride was reduced to cuprous chloride, and the molar ratio of cuprous chloride and carbamate was about two. A separate study by us<sup>1</sup> has shown that the isocyanide – cupric chloride reaction in the absence of alcohol produces cuprous chloride and *N*-substituted imidocarbonyl chloride, the precursor of

$$[2] \quad 2CuCl_2 + RN \cong C: \rightarrow 2CuCl + RN = CCl_2$$

carbamate. The catalytic activity of cuprous cyanide was similar to that of cuprous chloride in the isocyanide–alcohol reaction. Cuprous cyanide induces the isocyanide – allyl alcohol reaction to form allyl formimidate but it does not promote the isocyanide reactions with the usual saturated alcohols.

### Catalytic Activities of Other Metal Compounds

Silver oxide and mercuric oxide also catalyzed the reaction of isocyanide with saturated alcohol. Two runs of the cyclohexyl isocyanide–ethanol

<sup>1</sup>T. Saegusa, Y. Ito, and S. Tomita. To be published.

reaction in the presence of silver oxide and mercuric oxide respectively were carried out under the same conditions as Table I, in which ethyl Ncyclohexylformimidate was formed in yields of 89 and 51%, respectively. However, oxides of zinc, cadmium, and iron were inactive. Oxides of cobalt and nickel caused only the homopolymerization of isocyanide to produce brown colored, insoluble, and infusible polymers.

Chlorides of silver, zinc, and cadmium caused the reaction of isocyanide with allyl alcohol, but they did not induce that with the usual saturated alcohol. Mercuric chloride did not show catalytic activity even for the isocyanide – allyl alcohol reaction. Chlorides of nickel, cobalt, and palladium did not induce the insertion reaction but caused the homopolymerization of isocyanide.

### Mechanisms of Copper Catalysis

According to the catalysis behavior, copper catalysts are divided into two groups. The first group includes metallic copper and cuprous and cupric oxides, which catalyze the reactions of isocyanide with saturated and unsaturated alcohols. The second group of catalysts are cuprous chloride and cyanide which induce the reactions of isocyanide only with  $\beta$ ,  $\gamma$ -unsaturated alcohol and  $\beta$ -aminoalcohol. The infrared (i.r.) spectra of mixtures of cyclohexyl isocyanide and copper catalysts showed a new band at a frequency higher than 2140 cm<sup>-1</sup> of  $v_{N \equiv C}$  of free isocyanide. The new band has been assigned to  $v_{N \equiv C}$  of isocyanide coordinating to metal compound (6). From a Hammett relationship of the argentation constant of styrene derivatives (7), it is assumed that the contribution of the back-donation in the complex of d<sup>10</sup> metal ion is small. The shift of  $v_{N \equiv C}$  to a shorter wavelength is due to the donation of the electrons of isocyanide to d<sup>10</sup> metal ion. Therefore, the magnitude of shift of  $v_{N \equiv C}$ caused by coordination may be utilized as a measure of the strength of the coordination of isocyanide onto copper catalysts. It follows that the coordination of isocyanide with the first group catalysts is weaker than that with the members of the second group.

The cyclohexyl isocyanide – metallic copper system for i.r. diagnosis was prepared at room temperature by the addition of metallic copper powder to liquid cyclohexyl isocyanide under nitrogen. Metallic copper was prepared by the reduction of cupric sulfate with zinc powder in aqueous solution. The copper–isocyanide mixture was centrifuged. The i.r. spectrum of the liquid phase of copper–isocyanide showed a fairly strong absorption at 2180 cm<sup>-1</sup> as well as the band of  $v_{N \equiv C}$  of free isocyanide at 2140 cm<sup>-1</sup>. This finding indicates the formation of a soluble complex from metallic copper and isocyanide. On treating the centrifuged solution with alcohol, the formimidate was produced. This indicates that the metallic copper-catalyzed reaction proceeds in a homogeneous solution phase, and the solid phase is merely the source of soluble catalyst complexes. The band of coordinating species of cyclohexyl isocyanide appeared at 2181 cm<sup>-1</sup> in the system of cuprous oxide with isocyanide.

On the other hand, the i.r. spectrum of the 1:1 complex of cuprous chloride with cyclohexyl isocyanide showed the band of coordinating isocyanide group at 2192 cm<sup>-1</sup>. Thus, the magnitude of the shift of  $v_{N \equiv C}$  caused by cuprous chloride is larger than that caused by metallic copper and cuprous oxide. These findings are taken to indicate that isocyanide coordinates more tightly with cuprous chloride than with the first group catalysts.

## CH<sub>2</sub>=CHCH<sub>2</sub>OH (liquid film)



FIG. 3. Infrared spectra of allyl alcohol and CuCl allyl alcohol complex.

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The coordination of alcohol with copper catalysts depends upon the nature of the alcohol and of the copper catalysts. Cuprous chloride is almost insoluble in the usual saturated alcohols, whereas it is quite soluble in allyl alcohol and in  $\beta$ -dimethylaminoethanol. This observation suggests a specific interaction between cuprous chloride and these particular alcohols. The complexing of cuprous chloride with these alcohols was indicated by i.r. spectroscopy. In comparison with the i.r. spectrum of allyl alcohol, the spectrum of cuprous chloride dissolved in allyl alcohol had additional bands at 1548 and 1010 cm<sup>-1</sup>, which are assigned to the olefin and alcohol groups, respectively, of the allyl alcohol - cuprous chloride complex (Fig. 3) (8). The strong complexing tendency of β-dimethylaminoethanol with cuprous chloride was also demonstrated by i.r. spectroscopy. From cuprous chloride and βdimethylaminoethanol, a 1:1 complex was successfully isolated, whose i.r. spectrum showed



FIG. 4. Infrared spectra of  $\beta$ -N-dimethylaminoethanol and its complexes.

the shift of  $v_{C-O}$  band from 1039 to 1020 cm<sup>-1</sup> (Fig. 4).

On the basis of these i.r. spectroscopic studies, the difference in catalyst activity between the first group catalysts and those of the second group is explained by a hypothesis of mixed ligand complex. Isocyanide is held rather loosely by the first group catalysts, and hence a part of the isocyanide ligand will be replaced by alcohols including saturated alcohols of weak complexing tendency as well as the particular alcohols mentioned above. The first group catalysts will form a ternary, mixed ligand complex consisting of copper, isocyanide, and various alcohols. On the other hand, isocyanide is held tightly by the second group catalyst, and the isocyanide ligand is partly replaced only by the special alcohols of strong coordinating tendencies. The ternary, mixed ligand complexes of the second group catalysts are feasible only for the special alcohols. It is assumed that the reaction between alcohol and isocyanide will take place in the ligand sphere of the mixed ligand complex. Thus, the formation of the mixed ligand complex is a prerequisite for the occurrence of the reaction.

#### Experimental

### (a) Metallic Copper-catalyzed Reaction of Cyclohexyl Isocyanide with Ethanol

Metallic copper was prepared by treating an excess of aqueous solution of cupric sulfate maintained below  $70^{\circ}$  with zinc powder under a nitrogen atmosphere. The metallic copper precipitate was collected and washed successively with water and dry acetone, and then dried.

A mixture of cyclohexyl isocyanide 3.27 g (0.030 mole), ethanol 1.56 g (0.034 mole), and metallic copper 0.43 g (0.003 g-atom) was heated at  $120^{\circ}$  for 5 h. After the insoluble catalyst was removed by filtration, the filtrate was subjected to gas-liquid chromatography (g.l.c.) analysis (PEG 20000 on Celite). Two products, 1a and 2a, were detected. The product 1a was also isolated by distillation *in vacuo*, b.p. 54.5° (8mm).

On the basis of the following analyses, 1a was identified as ethyl *N*-cyclohexylformimidate.

Nuclear magnetic resonance (CCl<sub>4</sub>) of 1*a*:  $\delta$  1.21 (3H, triplet), 1.00–2.00 (10H, complex multiplet), 2.70–3.10 (1H, broad singlet), 3.98 (2H, quartet), 7.43 (1H, singlet). Infrared (i.r.) (neat): 1650 (s), 1200 cm<sup>-1</sup> (s). The structure of 1*a* was further confirmed by comparisons of the g.l.c. retention time and i.r. spectrum with the authentic sample. The authentic sample of 1*a* was prepared as follows (9). *N*-Cyclohexylformamide (0.5 mole) was added dropwise to triethyloxonium fluoroborate (0.5 mole) (10) in ether at room temperature. Ethyl *N*-cyclohexylformimidate hydrogen fluoroborate, which separated as a viscous liquid in the lower layer, was treated with triethylamine to give ethyl *N*-cyclohexylformimidate.

Compound 2a, b.p. 103° (3mm) was identified as Ncyclohexylformamide by comparison with the authentic sample prepared from cyclohexylamine and ethyl formate.

### (b) Cuprous Oxide Catalyzed Reaction of Cyclohexyl Isocyanide with sec-Butanol

A mixture of cyclohexyl isocyanide 3.27 g (0.030 mole), sec-butanol 2.52 g (0.034 mole), and cuprous oxide 0.43 g (0.003 mole) was heated at 120° for 5 h. After working up the mixture as described above, sec-butyl N-cyclohexylformimidate, b.p. 90° (21mm) (1b), N-cyclohexylformamide, and sec-butyl N-cyclohexylcarbamate (3b), were detected by g.l.c. and identified.

Nuclear magnetic resonance (CCl<sub>4</sub>) of  $1b: \delta 0.87$  (3H, triplet), 1.15 (3H, doublet), 1.00-2.00 (12H, complex multiplet), 2.70-3.10 (1H, broad singlet), 4.73 (1H, multiplet), 7.33 (1H, singlet). Infrared (neat) : 1650 (s), 1205  $cm^{-1}$  (s). The authentic sample of 3b was prepared by the reaction of cyclohexyl isocyanate with sec-butyl alcohol.

#### (c) Cupric Oxide Catalyzed Reaction of Cyclohexyl Isocvanide with t-Butanol

A mixture of cyclohexyl isocyanide 3.27 g (0.030 mole), t-butanol 2.52 g (0.034 mole), and cupric oxide 0.24 g (0.003 mole) was heated at 120° for 5 h. According to the same procedure, t-butyl N-cyclohexylformimidate, b.p. 93° (10mm) (1c), N-cyclohexylformamide, and t-butyl N-cyclohexylcarbamate (3c) were identified.

Nuclear magnetic resonance (CCl<sub>4</sub>) of  $1c: \delta 1.40$  (9H, singlet), 1.00-2.00 (10H, complex multiplet), 2.70-3.10 (1H, broad singlet), 7.36 (1H, singlet). Infrared (neat): 1650 (s), 1220 (s), 1170 (s) cm<sup>-1</sup>.

#### (d) Cuprous Chloride Catalyzed Reaction of Allyl Alcohol with Cyclohexyl Isocyanide

A solution of cyclohexyl isocyanide 4.36 g (0.040 mole), allyl alcohol 4.06 g (0.070 mole), and cuprous chloride 0.80 g (0.008 mole) was heated at 120° for 5 h. Then the reaction mixture was subjected to g.l.c. analysis and the products were identified. Allyl N-cyclohexylformimidate (1d), b.p. 90° (26mm), cyclohexylformamide, and N-allyl-N-cyclohexylformamide (4d) were the products.

Nuclear magnetic resonance (CCl<sub>4</sub>) of 1d: δ1.00-2.00 (10H, complex multiplet), 2.70-3.20 (1H, broad singlet), 4.49 (2H, doublet), 4.90-6.20 (3H, multiplet), 7.53 (1H, singlet). Infrared (neat) : 1650 (s), 1190 (s), 990 (m), 910  $cm^{-1}$  (s). The authentic sample of 1d was synthesized by the reaction of triallyloxonium fluoroborate with N-cyclohexylformamide.

Nuclear magnetic resonance (CDCl<sub>3</sub>) of 4d: 1.00-2.00 (10H, complex multiplet), 2.90-3.50 (1H, broad singlet), 3.84 (2H, doublet), 4.80-6.10 (3H, multiplet), 8.04 and 8.20 (1H, two singlets).

### (e) Cuprous Chloride Catalyzed Reaction of Cyclohexyl Isocyanide with Benzyl Alcohol

A solution of cyclohexyl isocvanide 4.36 g (0.040 mole), benzyl alcohol 7.56 g (0.070 mole), and cuprous chloride 0.80 g (0.008 mole) was heated at 120° for 5 h. The whole product could not be analyzed by g.l.c. Distillation of the reaction mixture gave benzyl N-cyclohexylformimidate (1e), b.p. 155° (3mm), N-cyclohexylformamide, and Nbenzyl-N-cyclohexylformamide (4e), b.p. 133° (3mm).

Nuclear magnetic resonance (CDCl<sub>3</sub>) of 1e: δ 1.00-

2.00 (10H, complex multiplet), 2.80-3.20 (1H, broad singlet), 4.49 (2H, singlet), 7.24 (5H, singlet), 7.60 (1H, singlet).

Nuclear magnetic resonance (CCl<sub>4</sub>) of  $4e: \delta 1.00-2.00$ (10H, complex multiplet), 2.90-3.30 (1H, broad singlet), 4.28 and 4.40 (2H, two singlets), 7.15 (5H, singlet), 8.02 and 8.15 (1H, two singlets).

#### Cupric Chloride Catalyzed Reaction of Cyclohexyl (f)Isocvanide with Ethanol

A solution of cyclohexyl isocyanide 4.36 g (0.040 mole), ethanol 5.52 g (0.120 mole), and cupric chloride 2.69 g (0.020 mole) was heated at  $120^{\circ}$  for 5 h. The insoluble matter was separated by filtration, and the filtrate was analyzed by g.l.c. Ethyl N-cyclohexylcarbamate (0.0084 mole) was obtained in a yield of 42% (based on CuCl<sub>2</sub>). CuCl in the insoluble portion was analyzed according to the thiocyanate method. It was found that 76% of CuCl<sub>2</sub> was reduced to CuCl (0.0152 mole).

#### (g) Complex of Cyclohexyl Isocyanide – Cuprous Chloride (1:1)

Cuprous chloride was added slowly to excess cyclohexyl isocyanide at room temperature, and the precipitation was collected by filtration. The white crystalline product was recrystallized from chloroform-ether, m.p. 95-96°. Elemental analysis revealed that the crystalline product consisted of 1 mole cyclohexyl isocyanide and 1 mole cuprous chloride.

Anal. Calcd. for C<sub>7</sub>H<sub>11</sub>NClCu : C, 40.40; H, 5.22; N, 6.60; Cl, 17.01. Found : C, 40.40; H, 5.29; N, 6.73; Cl, 17.07.

#### (h) Complex of $\beta$ -Dimethylaminoethanol – Cuprous Chloride (1:1)

A dark blue solution of cuprous chloride (0.01 mole) in  $\beta$ -dimethylaminoethanol (0.04 mole) was treated with excess petroleum ether, and the precipitating green crystalline mass was collected and dried, m.p. 144-145°

Anal. Calcd. for (C<sub>4</sub>H<sub>11</sub>NOClCu)<sub>2</sub> : C, 25.53; H, 5.86; N, 7.45; Cl, 18.88. Found : C, 25.93; H, 5.42; N, 7.27; Cl, 18.78.

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