

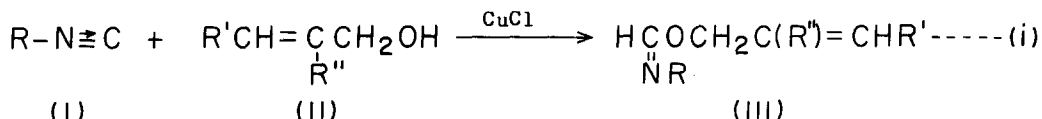
SYNTHETIC REACTION BY COMPLEX CATALYST V.
A NEW SYNTHETIC METHOD OF FORMIMIDATE

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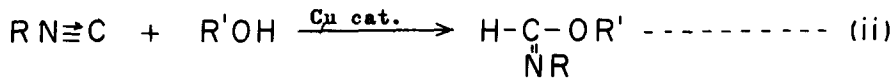
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Recently we have reported that in the presence of cuprous chloride as catalyst isocyanide (I) reacts with β,γ -unsaturated alcohol (II) to produce the corresponding formimide (III)¹).

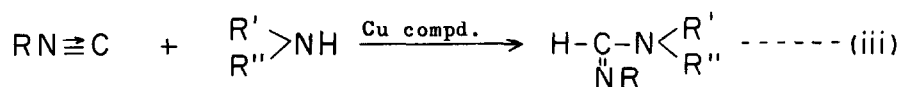


The above reaction by cuprous chloride catalyst is not applied to aliphatic saturated alcohols such as ethyl, *sec*-butyl and *t*-butyl alcohol. Chlorides of nickel, cobalt and palladium do not catalyze the above reaction but induce the polymerization of isocyanide.

In the course of the extension studies, we have now found that metallic copper as well as copper oxides (Cu(I) and Cu(II)) catalyze the reaction of isocyanide with various alcohols including saturated alcohols to produce the corresponding formimides in almost quantitative yields.

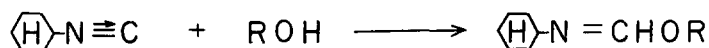


This reaction presents a convenient synthetic method of N-substituted formimide. The above reaction can be regarded as the insertion of the isocyanide carbon atom bearing lone-pair electrons between oxygen and hydrogen of alcohol, which is a counterpart of the insertion reaction of isocyanide between nitrogen and hydrogen of amine by copper compound catalysts²).



A mixture of 28 mmol of cyclohexyl isocyanide, 50 mmol of alcohol and copper catalyst was heated at 120°C for 5 hrs. The reaction mixture was then distilled to isolate N-cyclohexylformimidate, which was identified by infra-red and n.m.r. spectra and elemental analysis. A part of the reaction mixture was subjected to v.p.c. analysis in order to examine the by-product and determine the yield of N-cyclohexylformimidate by means of an internal standard. The results are illustrated in Table 1.

TABLE I. Reaction of Cyclohexyl Isocyanide with Alcohol



	ROH	Products (Yield %)	
		$\text{C}_6\text{H}_{11}\text{N}=\text{CHOR}^{\text{b}}$	$\text{C}_6\text{H}_{11}\text{NHCHO}$
Cu Catalyst ^{a)} (5 mg-atom)	C ₂ H ₅ OH	94	1
	n-C ₄ H ₉ OH	99	—
	sec-C ₄ H ₉ OH	98	2
	CH ₂ =CHCH ₂ OH	95	3
Cu ₂ O Catalyst (5 mmol)	C ₂ H ₅ OH	95	2
	n-C ₄ H ₉ OH	95	1
	sec-C ₄ H ₉ OH	94	2
	t-C ₄ H ₉ OH	94	—
CuO Catalyst (5 mmol)	C ₂ H ₅ OH	87	11
	n-C ₄ H ₉ OH	81	—
	sec-C ₄ H ₉ OH	88	—
	t-C ₄ H ₉ OH	91	—

a) Copper powder was prepared by the reduction of CuSO₄ with zinc powder according to the procedure given in Organic Syntheses, Coll. Vol. II, p.432, John Wiley and Sons. Inc., New York, (1941).

b) Boiling points of N-cyclohexylformimidates, $\text{C}_6\text{H}_{11}\text{N}=\text{CHOR}$: R=C₂H₅, 85°C/27 mm Hg; R=n-C₄H₉, 81°C/21 mm Hg; R=sec-C₄H₉, 90°C/21 mm Hg; R=t-C₄H₉, 93°C/19 mm Hg; R=CH₂=CHCH₂, 105°C/32 mm Hg.

The N-cyclohexylformimidates were produced almost quantitatively. As a by-product, N-cyclohexylformamide was sometimes produced in a quite small yield. In the cases of copper oxides catalysts, N-cyclohexylcarbamates were produced also in small yields, usually about 1 %.

In the absence of copper catalyst, neither β,γ -unsaturated alcohol nor saturated alcohol reacted with cyclohexyl isocyanide. Both alcohol and cyclohexyl isocyanide remained unchanged and were recovered quantitatively from the heat-treated reaction mixture.

The catalysis features of copper compounds as well as silver, zinc and cadmium compounds in the isocyanide-alcohol reaction are now being studied in connection with those of the above metal compounds in the isocyanide-amine reaction.

REFERENCES

- 1) T. Saegusa, Y. Ito, S. Kobayashi and K. Hirota, Tetrahedron Letters, No.6 (1967).
- 2) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota and H. Yoshioka, Tetrahedron Letters, No.49, 6121 (1966).