

CATALYSIS BY METAL COMPLEXES. XIII.*

A NEW COPPER CATALYST FOR CYANOETHYLATION OF TRICHLOROSILANE AND METHYLDICHLOROSILANE

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Binary systems of a copper compound (Cu_2O , CuCl or $\text{Cu}(\text{acac})_2$) and an isocyanide (tert-butyl or cyclohexyl isocyanide) were found to be effective catalysts for hydrosilylation of acrylonitrile by trichlorosilane and methyldichlorosilane. The reaction proceeds at elevated temperatures to give exclusively corresponding 2-cyanoethyl derivatives.

Among the catalysts used to effect the addition of chloro-substituted silicon hydrides to acrylonitrile (*cf.*^{1,2} and references therein), the binary or ternary systems of cuprous chloride (oxide) and tertiary amine(s) occupy specific position in that in their presence the reaction proceeds selectively to give corresponding 2-cyanoethyl derivative in good yields also with otherwise little reactive methyldichlorosilane^{1,3}. Although the action of these catalyst systems is not quite clear from mechanistic point of view¹, by comparison with group VIII metal catalysts, which induce the formation of 1-cyanoethyl derivatives², the different mode of the addition may be associated with the different polarisation of the Si—H bond of the silicon hydride ($\text{Si}^- \text{H}^+$) or of the metal—hydrogen bond in a complex transiently formed from it³. It may further be reasonably assumed that also the activation of the olefinic substrate, acrylonitrile, *via* coordination to the metal complex is one of crucial reaction steps.

Starting from these considerations we expected that copper-isocyanide complexes, known to activate cyano olefins^{4,5}, might be potential catalysts for the above hydrosilylation reaction. To verify this assumption, we used binary mixtures of a copper compound and an isocyanide as catalyst systems and tested their activity in the addition of trichlorosilane and methyldichlorosilane to acrylonitrile. The systems employed are listed in Table I. We have found that the copper-isocyanide complexes under study do act as selective catalysts for preparing 2-cyanoethyl derivatives. However, they display catalytic activity only at elevated temperatures. With most of them the best results were achieved when the reaction was carried out at temperatures of from 90 to 120°C (Table I, for further results see ref.⁶). The yields of 2-cyanoethyltrichlorosilane recorded for several catalyst systems in Table I were obtained under the conditions which on the basis of preliminary experiments seemed to be

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TABLE I

The Yields of (2-Cyanoethyl)trichlorosilane Obtained by Hydrosilylation of Acrylonitrile by Trichlorosilane Catalysed by Binary Systems of a Copper Compound and an Isocyanide
7.5 mmol of acrylonitrile, 7.9 mmol of trichlorosilane, 120°C, 2 h.

Copper compound mmol	Isocyanide mmol	Yield, %
Cu ₂ O (0.084)	C ₆ H ₁₁ CN (0.29)	70 ^a
	t-C ₄ H ₉ CN (1.00)	42
CuCl (0.01)	C ₆ H ₁₁ CN (0.037)	78
	t-C ₄ H ₉ CN (0.02)	56
Cu(acac) ₂ (0.009)	C ₆ H ₁₁ CN (0.073)	75 ^b

^a 100°C. ^b 45% yield at 80°C, 10% yield at 60°C.

optimum ones. Although no definitive conclusions concerning the difference in the catalytic activity of individual systems can hence be made, the data indicate that as the isonitrile component cyclohexyl isocyanide is superior to tert-butyl isocyanide. As to the copper component, all the copper salts used turned out to be precursors of catalytically active complexes. We have further found that within the range of the copper compound to isonitrile molar ratios used (1:3–1:10) the reaction yields are little affected by relative amounts of both components. Similar results were obtained also with methyldichlorosilane.

When compared to copper-amine catalysts¹, similar yields of the silane were obtained here at much shorter reaction time and with the concentration of the copper component by about one order of magnitude lower. Comparable yields of the trichlorosilyl and methyldichlorosilyl derivatives obtained under identical conditions with the copper-isocyanide complexes are of interest, as they indicate that, by contrast to copper-amine catalysts⁷, the ease of the addition is not strongly dependent on the structure of the reactant silicon hydride. The copper-isocyanide complexes might hence turn out to be effective in the addition of dialkylchlorosilanes, such as dimethylchlorosilane, the reaction which has not been accomplished with copper-amine catalysts⁷.

EXPERIMENTAL

Compounds used. CuCl, Cu₂O, and Cu(acac)₂, commercial products, were used without further purification. Cyclohexyl isocyanide and tert-butyl isocyanide were prepared according to the procedure reported by Walborsky and Niznik⁸. Acrylonitrile, trichlorosilane, and methyldichlorosilane were commercial products and were used without further purification. Their purity

was checked by g.l.c. The standards for chromatographic analysis of reaction products were prepared independently: (1-cyanoethyl)trichlorosilane and methyl(1-cyanoethyl)dichlorosilane by hydrosilylation of acrylonitrile catalysed⁹ by Ni(CO)₄, (2-cyanoethyl)trichlorosilane by the (C₆H₅)₃P-catalysed hydrosilylation¹⁰, and (2-cyanoethyl)methyl-dichlorosilane by the copper-amine catalysed addition³.

Hydrosilylation. All experiments were carried out in sealed glass ampoules under nitrogen. The composition of reaction mixtures was analysed by gas chromatography (the chromatograph equipped with thermal conductivity detector, the column (3 m long and 0.6 cm across) filled with 16% Trifluoro Propyl Methyl Silicone (Pye, London) on Chromosorb W. 150°C oven temperature and 30 ml/min nitrogen flow rate). The so obtained yields of the reaction products are presented in Table I, along with reaction conditions. The structure of the 2-cyanoethyl derivatives formed was confirmed by NMR spectroscopy.

Reaction with methyl-dichlorosilane. A mixture of 7.5 mmol of acrylonitrile, 7.5 mmol of trichlorosilane, $8.5 \cdot 10^{-3}$ mmol of copper acetylacetonate, and $3.7 \cdot 10^{-2}$ mmol of cyclohexyl isocyanide was heated under nitrogen in sealed glass ampoule to 120°C for 2 h, giving the corresponding 2-cyanoethyl derivative as a sole reaction product (80% yield, by g.l.c.). Again, tert-butyl isocyanide turned out to be less effective (60% yield).

REFERENCES

1. Bluestein B. A.: J. Am. Chem. Soc. 83, 1000 (1961).
2. Chalk A. J.: J. Organometal. Chem. 21, 207 (1970).
3. Bluestein B. A.: US-Pat. 2 971 970; Chem. Abstr. 55, 12 356 (1961).
4. Saegusa T., Ito J., Kinoshita H., Tomita S.: Bull. Chem. Soc. Japan 43, 877 (1970).
5. Saegusa T., Ito J., Tomita S., Kinoshita H.: Bull. Chem. Soc. Japan 45, 496 (1972).
6. Svoboda P., Hetflejš J., Bažant V.: Czech. pat. appl. 437-73.
7. Bluestein B. A., Ashby B. A.: IInd Symposium on Organosilicon Chem., Bordeaux, 1968.
8. Walborsky H. M., Niznik G. E.: J. Org. Chem. 37, 187 (1972).
9. Čukovskaja E. C., Frejdlina R. C.: Izv. Akad. Nauk, Otd. Chim. Nauk 1963, 761.
10. Jex V. B., McMahon J. E.: US-Pat. 2 907 784; Chem. Abstr. 54, 4388 (1960).

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