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Synthetic Reactions by Complex Catalysts. XVI. The Dimerization of Acrylonitrile and Acrylate by Means of the Metal-Isocyanide Complex

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Acrylonitrile and acrylate were dimerized to 2-methyleneglutaronitrile and 2-methyleneglutarate respectively by the binary catalyst system of a copper compound and an isocyanide in the presence of a protic solvent such as *t*-butanol. Transition metal acetylacetonates, such as Fe(II and III), Co(II and III), and Ni(II), in combination with isocyanide were also effective for this dimerization. A mechanistic discussion has been presented.

This paper will describe the dimerization of acrylonitrile and acrylate by a new type of catalyst, a metal-isocyanide complex. The catalytic dimerization of acrylonitrile and methyl acrylate has been extensively investigated. Trialkylphosphines and transition metal compounds are known to be excellent catalysts. By the phosphine catalyst, acrylonitrile[1a] and methyl acrylate[1b] can be dimerized to produce α-methylene-glutaronitrile (Ia) and glutarate (Ib) respectively.

$$CH_2{=}CHX \xrightarrow{P(n\text{-}C_4H_9)_3} CH_2{=}\underset{\displaystyle CH_2CH_2X}{\overset{\displaystyle |}{C}}{-}X \qquad (1)$$

a: X=CN [I]
b: X=CO_2CH_3

On the other hand, rhodium- and ruthenium-trichloride catalyzes the dimerization of methyl acrylate[2a] and acrylonitrile[2b] to produce dimethyl 2-hexendioate (IIa) and 1,4-dicyanobutene-1 (IIb) respectively.

$$CH_2{=}CHX \xrightarrow{RhCl_3 \text{ or } RuCl_3} XCH{=}CHCH_2CH_2X \qquad (2)$$

a: X=CO_2CH_3 [II]
b: X=CN

The binary system of cuprous oxide and alkyl isocyanide is a new type of catalyst for the dimerization of polar olefins. Previously, we reported[3a] the dimerization of β-alkyl-α,β-unsaturated carbonyl and such nitrile compounds as methyl crotonate and crotononitrile by means of a cuprous oxide-alkyl isocyanide system:

$$RCH{=}CHX \xrightarrow{Cu_2O\text{-}RNC} RCH{=}\underset{\displaystyle RCHCH_2X}{\overset{\displaystyle |}{C}}{-}X \qquad (3)$$

a: X=CO_2CH_3 [III]
b: X=CN

When acrylonitrile was treated with the system of cuprous oxide and cyclohexyl isocyanide, acrylonitrile was polymerized in an almost quantitative yield, even at room temperature. The IR spectrum of the acrylonitrile polymer thus obtained resembled that of the polymer produced by the anionic catalyst. This finding prompted us to explore the dimerization of acrylonitrile. The treatment of acrylonitrile with the cuprous oxide-cyclohexyl isocyanide system in the presence of a mixture of *t*-butanol and acetonitrile produced Ia, along with a low-molecular-weight polymer.

$$CH_2{=}CH{-}CN \xrightarrow{Cu_2O\text{-}C_6H_{11}NC} \left(CH_2CH(CN)\right)_n \quad [III]$$

$$CH_2{=}CH{-}CN \xrightarrow[\text{in } t\text{-}C_4H_9OH\text{-}CH_3CN]{Cu_2O\text{-}C_6H_{11}NC} CH_2{=}\underset{\displaystyle CH_2CH_2CN}{\overset{\displaystyle |}{C}}{-}CN \quad [Ia]$$

$$+ \quad \left(CH_2CH(CN)\right)_m \quad [IV]$$

$n > m$

The polymeric product was soluble in acetone, and its average molecular weight was about 1500. The yield of the dimer was low (6%). The structure of the dimer was confirmed by a comparison of its IR and NMR spectra with those of the authentic sample prepared by means of a trialkylphosphine catalyst. The combination of copper acetylaceto-

1) a) M. M. Baizer and J. D. Anderson, *J. Org. Chem.*, **30**, 1357 (1965). b) American Cyanamide Co., U.S. 3074999 (1963).

2) a) T. Alderson, E. L. Jenner and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **87**, 5638 (1965). b) A. Misono, Y. Uchida, M. Hidai, H. Shinohara and Y. Watanabe, This Bulletin, **40**, 931 (1967).

3) a) T. Saegusa, Y. Ito, S. Kobayashi and S. Tomita, *Chem. Commun.*, **1968**, 273. b) T. Saegusa, Y. Ito, S. Tomita and H. Kinoshita, *J. Org. Chem.*, in press.

nate and alkyl isocyanide in the presence of a mixture of *t*-butanol and acetonitrile gave much better results; *i. e.*, this system produced Ia exclusively. The presence of a protic solvent mixture was essential for dimerization. In the absence of a protic solvent mixture, the copper acetylacetonate-isocyanide system induced only the acrylonitrile polymerization. Cuprous and cupric chlorides with isocyanide were quite inactive in the dimerization and polymerization of acrylonitrile.

Besides copper acetylacetonate, the acetylacetonates of iron(II and III), cobalt(II and III), and nickel(II) in combination with isocyanide and a protic solvent were also active in the acrylonitrile dimerization. The results of the dimerization of acrylonitrile are summarized in Table 1.

Table 1. Dimerization of acrylonitrile and methyl acrylate catalyzed by metal compounds—isocyanide*

Olefin	Metal compound	Yield of Dimer (%)	
		t-C_4H_9NC	$C_6H_{11}NC$
CH_2=CHCN	$Cu(acac)_2$	31	34
	$Co(acac)_2$	26	32
	$Co(acac)_3$	40	50
	$Fe(acac)_2$	52	14**
	$Fe(acac)_3$	49	11**
	$Ni(acac)_2$	3	—**
CH_2=$CHCO_2CH_3$	Cu_2O	11	11
	$Cu(acac)_2$	2	1
	$Co(acac)_2$	2	—

* Olefin (20 mM), isocyanide (20 mM), metal compound (0.4 mM), *t*-butanol (2 m*l*), acetonitrile (5 m*l*) at 110°C, 20 hr.

** Cyclohexyl isocyanide was polymerized in these reactions.

When acetylacetonates of iron(II and III), and nickel(II) were used as the catalyst components, cyclohexyl isocyanide was polymerized; hence, the catalyst activity was decreased. Generally, *t*-butyl isocyanide was not polymerized, and so it could be usefully employed.

Acrylate is much less reactive than acrylonitrile in a reaction by a metal-isocyanide system. In the absence of a protic solvent, methyl acrylate is scarcely polymerized at all by the cuprous oxide-cyclohexyl isocyanide system and remains unchanged under room-temperature conditions. The treatment of methyl acrylate in *t*-butanol and acetonitrile by a copper-isocyanide system at a higher temperature produced the dimer Ib in a lower yield. The dimer was identified by a comparison of its IR and NMR spectra with those of dimethyl α-methyleneglutarate.

Mechanism

The catalytic behavior of the cuprous oxide-alkyl isocyanide system has been characterized on the basis of several important observations in the dimerization of β-alkyl-α,β-unsaturated nitrile and carbonyl compounds:[3b] (i) β,γ-unsaturated nitrile compounds are rapidly isomerized to the corresponding α,β-unsaturated species by the catalyst system; (ii) the *cis-trans* isomerization of β-alkyl-α,β-unsaturated nitrile and carbonyl compounds is caused by the catalyst system, and (iii) the exchange between the hydrogen at the α-position and that of the γ-position in β-alkyl-α,β-unsaturated nitrile and carbonyl compounds is caused by the catalyst system. A reaction mechanism involving an allyl carbanion copper isocyanide complex (V) was proposed to explain these findings:

$$\underset{\ominus}{\mathrm{RCHCH{=}CHX}} \longleftrightarrow \mathrm{RCH{=}\underset{\ominus}{C}HCHX}$$

[V] (X=CN, CO_2CH_3)

By analogy with the allyl carbanion copper isocyanide complex obtained from β-alkyl-α,β-unsaturated species, a vinyl carbanion complex (VI) may be assumed to be the key intermediate in the dimerization of acrylonitrile and acrylate. In the complex (VI), the vinyl carbanion probably exists as a ligand of the copper-isocyanide complex. The formation of VI is supported by the deuterium/hydrogen exchange at the α-position of acrylonitrile upon treatment with the copper acetylacetonate-cyclohexyl isocyanide system in the presence of *t*-butanol-d.

$$\mathrm{CH_2{=}CH{-}CN} \xrightleftharpoons{\text{Cu compd.-RNC}} [\mathrm{CH_2{=}\underset{\ominus}{C}CN}]$$

[VI]

The nucleophilic addition of VI to the second molecule of acrylonitrile in a Michael-type addition produces the dimeric anion (VII). The protonation of VII by a protic solvent gives rise to the formation of a dimer. On the other hand, in the absence of a potent proton donor the successive addition of carbanion to the acrylonitrile monomer takes place to produce a polymer.

$$\mathrm{CH_2{=}CHX} \xrightleftharpoons{\text{catalyst}} [\mathrm{CH_2{=}\underset{\ominus}{C}X}] \xrightarrow{\mathrm{CH_2{=}CHX}}$$

[VI]

$$\left[\mathrm{CH_2{=}CX \atop \quad CH_2\underset{\ominus}{C}HX}\right] \xrightarrow{H^+} \mathrm{CH_2{=}CX \atop \quad CH_2CH_2X}$$

[VII] $\xrightarrow{\mathrm{CH_2{=}CHX}}$ polymer $\left(\mathrm{-CH_2\underset{X}{CH}-}\right)_n$

The copper acetylacetonate-isocyanide system also catalyzes the Michael-type addition.[4] The addition of VI to the second monomer corresponds to the

4) T. Saegusa, Y. Ito, S. Tomita and H. Kinoshita, unpublished results.

addition of the anion to an α,β-unsaturated nitrile in the usual Michael addition. Furthermore, the Michael addition catalyzed by the copper-isocyanide system is characterized by the coordination of α,β-unsaturated compounds to the catalyst.[4] In the dimerization, the coordination of acrylonitrile may facilitate the addition of VI.

Experimental

Reagents. The acrylonitrile and the methyl acrylate were commercial reagents and were purified by distillation. The cuprous oxide and the acetylacetonates of copper, iron(II and III), cobalt(II and III), and nickel(II) were commercial reagents; all were used without purification. The cyclohexyl and the *t*-butyl isocyanide were prepared according to Ugi's procedure.[5]

Oligomerization and Dimerization of Acrylonitrile. A mixture of 2.18 g (20 mmol) of cyclohexyl isocyanide, 40 mg (0.28 mmol) of cuprous oxide, and 1.06 g (20 mmol) of acrylonitrile in 2 m*l* of *t*-butanol and 5 m*l* of acetonitrile was heated at 65°C for 20 hr. The reaction mixture was then poured into about 100 m*l* of methanol, after which the insoluble oligomer of acrylonitrile was removed by filtration. The oligomer was dissolved in acetone, and the acetone solution was filtrated and poured into methanol. The purified oligomer (0.334 g (32%)) was soluble in acetone and *N,N*-dimethylformamide. The methanol solutions were concentrated and subjected to gas-liquid-phase chromatography (glpc) analysis. The yield of the dimer was 6%. The dimer was isolated by preparative glpc and was identified by a comparison of its glpc retention time and NMR and IR spectra with those of an authentic sample which had been prepared by means of a tri-*n*-butyl phosphine catalyst.

NMR of the dimer (in CCl_4): τ 4.00 ppm and 4.11 $\left(2s, \underline{H}\!>\!C\!=\!C\!<\underline{H}\right)$, 7.39 (s, $-C\underline{H}_2C\underline{H}_2-$).

Principal IR bands (neat): 2325 (w) and 1624 (w) cm^{-1}.

Dimerization of Acrylonitrile. A mixture of 2.18 g (20 mmol) of cyclohexyl isocyanide, metal acetylacetonate (0.4 mmol), and 1.06 g (20 mmol) of acrylonitrile in 2 m*l* of *t*-butanol and 5 m*l* of acetonitrile was heated at 110°C for 20 hr. The reaction mixture was then distilled at 62—64°C/0.1 mmHg. The distillate was subjected to glpc analysis.

Dimerization of Methyl Acrylate. A mixture of 2.18 g (20 mmol) of cyclohexyl isocyanide (or 1.66 g (20 mmol) of *t*-butyl isocyanide), cuprous oxide (57 mg (0.4 mmol)), and 1.72 g (20 mmol) of methyl acrylate in 2 m*l* of *t*-butanol and 5 m*l* of acetonitrile was heated at 110°C for 20 hr. The reaction mixture was then distilled at 82—84°C/3 mmHg. The distillate was subjected to glpc analysis. The product was identified by a comparison of its glpc retention time and NMR and IR spectra with those of an authentic sample which had been prepared by the tri-*n*-butyl phosphine-catalyzed reaction of methyl acrylate. The yield of the dimer was 11%.

NMR of dimer (in CCl_4): τ 3.89 ppm and 4.42 $\left(2d, J_{H-H}=2.0\ Hz, \underline{H}\!>\!C\!=\!C\!<\right)$, 6.26 and 6.37 (2s, $-COO-C\underline{H}_3$), 7.50 (s, $-C\underline{H}_2C\underline{H}_2-$).

Principal IR bands (neat): 1725 (s) and 1629 (w) cm^{-1}.

5) I. Ugi and R. Meyr, *Chem. Ber.*, **93**, 239 (1960).