Synthetic Reactions by Complex Catalysts. XV. The Copper(I)–Alkyl Isocyanide Catalyzed Dimerization of α,β-Unsaturated Carbonyl and Nitrile Compounds

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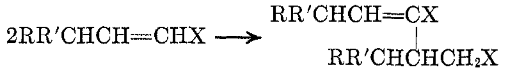
β-Alkyl α,β-unsaturated carbonyl and nitrile compounds have been found to be dimerized by the binary catalyst system of a copper compound and an isocyanide in high yields and high selectivities. Under the same conditions, β-unsubstituted α,β-unsaturated carbonyl and nitrile compounds such as acrylates and acrylonitrile are not dimerized, but they are codimerized with β-alkyl-substituted monomers. A mechanism involving an allyl carbanion complex intermediate is proposed for the dimerization reaction.

There has been much interest in the catalytic oligomerization of olefins by transition metal complexes. This paper describes the dimerization of β-alkyl α,β-unsaturated carbonyl and nitrile compounds (**1**) by the binary catalyst system of a copper compound and an isocyanide (eq 1).



$$2\mathrm{RR'CHCH{=}CHX} \longrightarrow \begin{array}{l}\mathrm{RR'CHCH{=}CX}\\ \qquad\qquad\;\, | \\ \mathrm{RR'CHCHCH_2X}\end{array} \qquad (1)$$

1 **2**

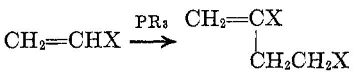
$X = CN, CO_2R', COR'$

As for the dimerization of polar olefins, the hydrodimerization of acrylonitrile has been studied most extensively and is catalyzed by transition metal carbonyls to yield adiponitrile and methylglutaronitrile.[1-4] The dimerization of acrylonitrile by ruthenium chloride[5] and that of acrylates by rhodium chloride[6] are also known and proceed through coupling of the monomer's β-carbon atoms (β–β dimerization).

$$\mathrm{CH_2{=}CHX} \longrightarrow \mathrm{XCH{=}CHCH_2CH_2X} \qquad (2)$$

$X = CN, CO_2CH_3$

Trialkylphosphine causes the dimerizations of acrylonitrile and acrylates through a coupling of the α- and β-carbon atoms of the two respective monomers (α–β dimerization), yielding 2-methyleneglutaronitrile (**3a**) and 2-methyleneglutarate (**3b**), respectively.[7-12]

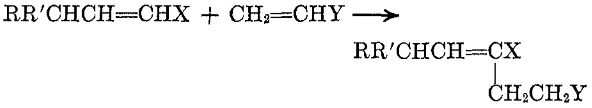


$$\mathrm{CH_2{=}CHX} \xrightarrow{\mathrm{PR_3}} \begin{array}{l}\mathrm{CH_2{=}CX}\\ \qquad\;\, | \\ \qquad\mathrm{CH_2CH_2X}\end{array} \qquad (3)$$

3

3a, $X = CN$
b, $X = CO_2R'$

Both the transition metal catalysts and trialkylphosphine dimerize only β-unsubstituted α,β-unsaturated carbonyl and nitrile compounds, while the copper–isocyanide system of the present study is effective especially toward β-alkyl α,β-unsaturated compounds. The α–β dimerization of ethyl 2-butenoate has been carried out using sodium amide in liquid ammonia.[13] A comparison between the catalytic behavior of the copper–isocyanide system and sodium amide is of interest. β-Unsubstituted α,β-unsaturated carbonyl and nitrile compounds could not be dimerized by the copper–isocyanide catalyst system under the conditions given in Table I. Acrylonitrile afforded polymer, and methyl acrylate was inert using this catalyst system. The copper–isocyanide system also induces codimerization of β-alkyl α,β-unsaturated monomers and β-unsubstituted α,β-unsaturated monomers.



$$\mathrm{RR'CHCH{=}CHX} + \mathrm{CH_2{=}CHY} \longrightarrow \begin{array}{l}\mathrm{RR'CHCH{=}CX}\\ \qquad\qquad\;\, | \\ \qquad\qquad\mathrm{CH_2CH_2Y}\end{array} \qquad (4)$$

$X, Y = CO_2CH_3, CN$

Results and Discussion

The results of the dimerizations of several β-alkyl α,β-unsaturated carbonyl and nitrile compounds by means of the binary catalyst system of copper–isocyanide are shown in Table I. Of the copper compounds, cuprous oxide was the most active. Metallic copper was fairly active, too. Other copper compounds, *e.g.*, copper(II) acetylacetonate, cupric oxide, and cuprous and cupric chlorides, were less active. It is important to notice that a fairly large amount of isocyanide is required for high catalyst activity. A small amount of the isocyanide component affords a poor catalyst (see the second run of Table I). Any single component of the binary system, the copper compound or the isocyanide, was completely inactive for the dimerization. Oxides of silver, zinc, nickel, and iron(II), with or without isocyanide, were inactive. The structures of the product dimers were convincingly determined by nmr and ir spectra, elemental analysis, and molecular weight. Except for the case of methyl 4-methyl-2-pentenoate, all the product dimers were mixtures of *cis* and *trans* isomers. When *cis* and *trans* isomers were easily separated by glpc, each isomer was isolated and was subjected to structure determination. When the separation of *cis–trans* isomers was not easily

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(1) Rhone-Poulenc S. A., French Patent 1,377,425 (1964).

(2) Rhone-Poulenc S. A., French Patent 1,381,511 (1964).

(3) E. I. du Pont de Nemours and Co., U. S. Patent 3,206,498 (1965).

(4) A. Misono, Y. Uchida, K. Tamai, and M. Hidai, *Bull. Chem. Soc. Jap.*, **40**, 931 (1967).

(5) A. Misono, Y. Uchida, M. Hidai, H. Shinohara, and Y. Watanabe, *ibid.*, **41**, 396 (1968).

(6) T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **87**, 5638 (1965).

(7) American Cyanamide Co., U. S. Patent 3,074,999 (1963).

(8) M. M. Baizer and J. D. Anderson, *J. Org. Chem.*, **30**, 1357 (1965).

(9) Rhone-Poulenc S. A., French Patent 1,366,081 (1964); British Patent 1,033,656 (1964).

(10) Badische Anilin- and Soda-Fabrik A.-G., French Patent 1,385,883 (1965).

(11) E. I. du Pont de Nemours and Co., Netherlands Patent Application 670,504 (1967).

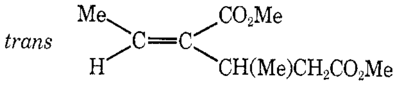
(12) Badische Anilin- and Soda-Fabrik A.-G., British Patent 1,051,821 (1966); Belgian Patent 698,441 (1967).

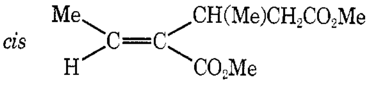
(13) K. Suga, S. Watanabe, and K. Takahashi, *Chem. Abstr.*, **67**, 10965 (1967).

TABLE I
DIMERIZATION OF β-ALKYL α,β-UNSATURATED CARBONYL AND NITRILE COMPOUNDS

Monomer (I), 30 mmol	Catalyst[e] (mmol)		Temp, °C	Time, hr	Dimer II, % yield[a]
trans-$CH_3CH{=}CHCO_2CH_3$	c-$C_6H_{11}NC$ (10)	Cu_2O (0.2)	90	3	70 (*cis/trans*, 4:1)[b]
trans-$CH_3CH{=}CHCO_2CH_3$	c-$C_6H_{11}NC$ (1)	Cu_2O (0.2)	90	7	5
trans-$CH_3CH{=}CHCO_2CH_3$	t-C_4H_9NC (10)	Cu_2O (0.2)	90	12	50
trans-$CH_3CH{=}CHCO_2CH_3$	c-$C_6H_{11}NC$ (10)	Cu (0.2)	90	7	50
trans-$CH_3CH{=}CHCO_2C_2H_5$	c-$C_6H_{11}NC$ (10)	Cu_2O (0.2)	100	14	15
$CH_3CH{=}CHCN$ (*trans/cis*, 1:2)	c-$C_6H_{11}NC$ (10)	Cu_2O (0.2)	90	1	90 (*cis/trans*, 1:7)[c]
trans-n-$C_3H_7CH{=}CHCO_2CH_3$	c-$C_6H_{11}NC$ (10)	Cu_2O (0.2)	110	15	50
trans-i-$C_3H_7CH{=}CHCO_2CH_3$	c-$C_6H_{11}NC$ (10)	Cu_2O (0.2)	110	15	35[d]
trans-$CH_3CH{=}CHCOCH_3$	c-$C_6H_{11}NC$ (10)	Cu_2O (0.2)	60–70	15	50

[a] Combined yield of *cis* and *trans* isomers. [b] For A and B below. [c] For C and D below. [d] Product dimer E. [e] CuCl, $CuCl_2$, and CuO were less effective catalyst components, and afforded only a trace of dimer.


A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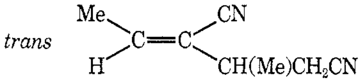
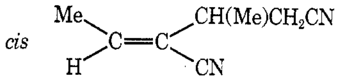

C


D

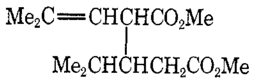
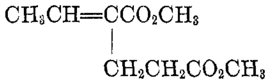
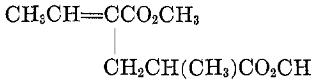
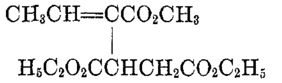
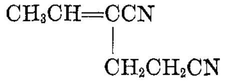

$$\begin{array}{l} Me_2C{=}CHCHCO_2Me \\ \qquad\quad\;\, | \\ \quad Me_2CHCHCH_2CO_2Me \end{array}$$
E

TABLE II
CODIMERIZATION OF α,β-UNSATURATED CARBONYL AND NITRILE COMPOUNDS[a]

Type A monomer (15 mmol)	Type B monomer (15 mmol)	Product, mmol		
		Dimer AA	Codimer AB	
trans-$CH_3CH{=}CHCO_2CH_3$	$CH_2{=}CHCO_2CH_3$	1.73	 $\begin{array}{l} CH_3CH{=}CCO_2CH_3 \\ \qquad\quad\, \vert \\ \qquad CH_2CH_2CO_2CH_3 \end{array}$	4.35
	$CH_2{=}C(CH_3)CO_2CH_3$	1.28	 $\begin{array}{l} CH_3CH{=}CCO_2CH_3 \\ \qquad\quad\, \vert \\ \qquad CH_2CH(CH_3)CO_2CH_3 \end{array}$	4.96
	$H_5C_2O_2CCH{=}CHCO_2C_2H_5$ (*cis*)	0.225	 $\begin{array}{l} CH_3CH{=}CCO_2CH_3 \\ \qquad\quad\, \vert \\ H_5C_2O_2CCHCH_2CO_2C_2H_5 \end{array}$	5.86
$CH_3CH{=}CHCN$ (*cis/trans*, 2:1)	$CH_2{=}CHCN$	0.300	 $\begin{array}{l} CH_3CH{=}CCN \\ \qquad\quad\, \vert \\ \qquad CH_2CH_2CN \end{array}$	1.35

[a] Reaction conditions: 110°, 10 hr; catalyst, c-$C_6H_{11}NC$ (10 mmol)-Cu_2O (0.2 mmol).

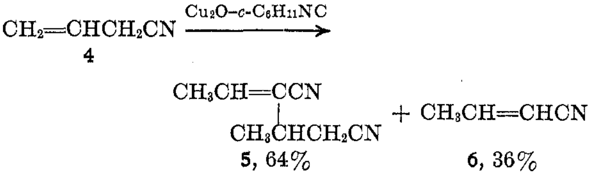
performed by glpc, the mixture was collected by glpc, the structures and the *cis/trans* ratio being determined by nmr.

The dimer of methyl 4-methyl-2-pentenoate had a double bond at the 5,6 position unlike the other dimers which had a double bond at the 4,5 position. Isolation of a dimer having a 5,6 double bond has an interesting bearing upon the reaction mechanism.

Dimerization by the copper–isocyanide system was effective for α,β-unsaturated carbonyl and nitrile compounds having primary and secondary alkyl groups at the β-carbon atom. Those having tertiary alkyl or aryl groups at the β position were not dimerized by this method. Acrylonitrile was polymerized by the cuprous oxide–isocyanide system, whereas acrylate was fairly inert. α–β dimerization of acrylonitrile has been achieved using a metal acetylacetonate–isocyanide system in the presence of *t*-butyl alcohol and/or acetonitrile, and will be reported separately.[14]

Acrylonitrile, methyl acrylate, methyl methacrylate, and diethyl maleate were codimerized with 2-butenoate or with 2-butenenitrile in the presence of a cuprous oxide–isocyanide system. The results of the codimerization are shown in Table II. Treatment of a mixture of two types of monomer (monomers of type A and type B in Table II) with the cuprous oxide–isocyanide system produced two dimeric products, *i.e.*, the dimer of 2-butenoate or 2-butenenitrile (dimer AA in Table II) and a codimer (codimer AB in Table II). Here, type A monomers are 2-butenoate and 2-butenenitrile, whereas type B monomers are acrylonitrile, acrylate, methacrylate, and maleate. In the structure of codimer AB, a hydrogen atom has been transferred from the type A monomer to the type B monomer. It is significant to point out that the alternative codimer of the BA structure in which hydrogen is transferred from a type B monomer to a type A monomer has not been produced.

Using the copper–isocyanide system, 3-butenenitrile (**4**) was isomerized to 2-butenenitrile (**6**) by double-bond migration during dimerization. The structure of the dimer **5** corresponded exactly to that of the dimer


$$\underset{\mathbf{4}}{CH_2{=}CHCH_2CN} \xrightarrow{Cu_2O-c-C_6H_{11}NC} \underset{\mathbf{5},\ 64\%}{\begin{array}{l} CH_3CH{=}CCN \\ \qquad\quad\, | \\ CH_3CHCH_2CN \end{array}} + \underset{\mathbf{6},\ 36\%}{CH_3CH{=}CHCN} \quad (5)$$

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(14) T. Saegusa, Y. Ito, S. Tomita, and H. Kinoshita, *Bull. Chem. Soc. Jap.*, in press.

of 2-butenenitrile. The monomeric species which remained in the reaction system at a 64% conversion into dimer was no longer 3-butenenitrile, but rather a *cis–trans* mixture of 2-butenenitrile (**6**) (*cis/trans*, 2). Any single component of the binary system, copper compound or isocyanide, did not cause both dimerization and isomerization of 3-butenenitrile.

During dimerization catalyzed by the copper–isocyanide system, *cis–trans* isomerization of the monomer also takes place. Table III indicates the *cis–trans* isomerization of *trans*-2-butenenitrile which has occurred during the dimerization. At reaction times of 1, 2.5, and 4 hr, a small portion of the reaction mixture was drawn out and analyzed by glpc. During the dimerization, pure *trans* monomer was isomerized gradually to *cis* monomer. The *cis/trans* ratio was increased progressively, and, at a dimer yield of 58% at 4 hr, it reached 2:1. In the dimerization of methyl *trans*-2-butenoate, a similar phenomenon was observed. After dimerization at 90° for 3 hr, the dimer yield was 70% and the recovered monomer was a mixture of *cis* and *trans* isomers, the *cis/trans* ratio being 1:10. It is important to note that the *cis–trans* isomerization was not caused by any single component of the binary catalyst system.

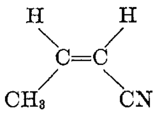
TABLE III

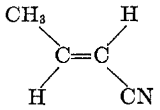
ISOMERIZATION OF *trans*-2-BUTENENITRILE[a]

Reaction time, hr	0	1	2.5	4
cis/trans[b]	0:100	33:66	60:40	66:33

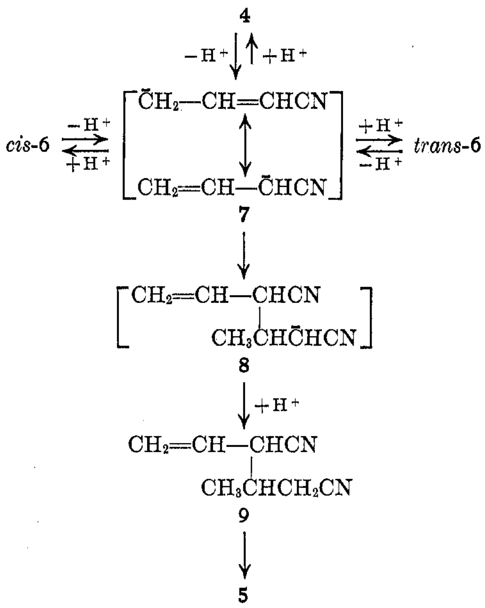
[a] *trans* monomer, 10 mmol; catalyst, Cu_2O (0.15 mmol) and c-$C_6H_{11}NC$ (7 mmol). Reaction at 80°. After 4 hr, the dimer yield was 58%. [b] *cis/trans* ratio of the remaining monomer.

The above three observations, *i.e.*, the double-bond shift and *cis–trans* isomerization during the dimerization as well as the necessity of an acidic hydrogen at the γ-carbon atom in the monomer, are explained by Scheme I, which is exemplified by the dimerizations of 2- and 3-butenenitriles. The allyl carbanion complex (**7**) is postulated as a key intermediate, which is formed by γ-hydrogen abstraction of *cis*- and *trans*-2-butenenitriles (**6**) and by α-hydrogen abstraction of 3-butenenitrile (**4**). Both the copper and isocyanide components, which are definitely needed for the catalyst activity, are not incorporated in Scheme I, because direct information about the catalyst behavior has not been obtained. One explanation may be that *cis*-**6**, *trans*-**6**, and **4** are coordinated with a cuprous complex having an isocyanide ligand and that the hydrogen abstraction takes place within the complex to produce an allyl carbanion–cuprous complex which corresponds to **7**. Requirement of a considerable amount of isocyanide may be due to competitive equilibria involving isocyanide, monomer, and the product dimer with copper. Complex **7** may also be regarded as an allyl copper complex having an isocyanide ligand. *cis–trans* isomerization of 2-butenenitrile and the double-bond shift of 3-butenenitrile during the dimerization, as well as the necessity of an acidic hydrogen at the γ-carbon atom of monomer, are well explained by the formation of complex **7** as an essential intermediate. Proton abstraction from 2-butenenitrile producing complex **7** has been supported by the observation of hydrogen–deuterium exchange at the α- and γ-carbon atoms, which occurred during the dimerization of 2-butenenitrile by the cuprous oxide–cyclohexyl isocyanide complex in the presence of D_2O.


cis-**6**


trans-**6**

SCHEME I



$$CH_3CH{=}CHCN \xrightarrow[Cu_2O\text{-}c\text{-}C_6H_{11}NC]{D_2O} CD_3CH{=}CDCN + \text{deuterated dimer} \quad (6)$$

An additional observation of exchange between the α and γ hydrogens of monomer supports proton abstraction. A partially deuterated 2-butenenitrile, in which the γ hydrogens were 42% deuterated and the α hydrogens 88% deuterated, was prepared by treating 2-butenenitrile with deuterium oxide in the presence of alkaline catalyst. The dimerization of the partially deuterated 2-butenenitrile by a copper–isocyanide catalyst at 90° was interrupted at a reaction time of 0.5 hr, at which time the yield of deuterated dimer was 36%. During the dimerization, the distributions of deuterium at the α and γ positions of the partially deuterated monomer equalized; *i.e.*, both were equal to the average degree of deuteration of starting monomer (53%) (Table IV). It was also shown that the β hydrogen was not deuterated. Furthermore, the equalization between the α and γ deuterium was not caused by any single component of the binary catalyst system. The addition of **7** to the second molecule of monomer producing the dimeric anion complex **8** may occur also in a complex; *i.e.*, the second monomer is first coordinated with complex **7**, probably through ligand exchange, and the nucleophilic allyl carbanion ligand adds to the coordinated monomer. The nucleophilic addition of **7** to the monomer corresponds to the base-catalyzed Michael addition. In fact, the copper–

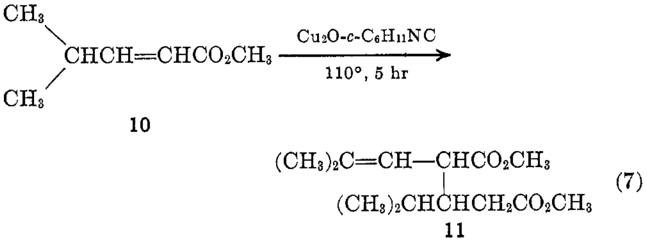
TABLE IV

DIMERIZATION AND DEUTERIUM MIGRATION OF PARTIALLY DEUTERATED 2-BUTENENITRILE

Starting monomer	Catalyst	Reaction time, hr	Recovered monomer	Dimer
$CD_3CH{=}CDCN$[a] (17 mmol) (42%) (88%)[b]	c-$C_6H_{11}NC$ (8.5 mmol) Cu_2O (0.17 mmol)	0.5	$CD_3CH{=}CDCN$[a] (11 mmol) (53%) (53%)[b]	$CD_3CH{=}CCN$[a] (3 mmol) (49%)[b] | CD_3CHCD_2CN (49%) (60%)[b]

[a] Total D content 53%. [b] The deuterium content at the respective hydrogen is given in parentheses.

isocyanide system has been found to induce the Michael reaction, and will be reported separately. The copper–isocyanide system in the Michael-type reaction is characterized by the specific activation of the electrophilic olefin through coordination with the catalyst.[15] The double-bond shift in **9** to produce the final dimer product **5** parallels the isomerization of 3-butenenitrile to 2-butenenitrile, which is probably caused also by coordination with the catalyst system. In most cases, the double-bond shift is rapid, and only the dimer **5** with a 4,5 double bond is isolated. In the dimerization of methyl 4-methyl-2-pentenoate **10**, however, the dimeric product having a 5,6 double bond **11** was isolated. This anomaly may be explained by the



$$(CH_3)_2CHCH{=}CHCO_2CH_3 \xrightarrow[110°,\ 5\ hr]{Cu_2O\text{-}c\text{-}C_6H_{11}NC} (CH_3)_2C{=}CH{-}CHCO_2CH_3 \text{ / } (CH_3)_2CHCHCH_2CO_2CH_3 \quad (7)$$

10

11

assumption that the coordination of **11** with catalyst is hampered by the bulky isopropylidene group, and hence the double-bond shift does not occur.

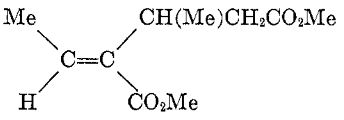
Experimental Section

Reagents. Monomer.—Methyl *trans*-2-butenoate, ethyl *trans*-2-butenoate, 2-butenenitrile, methyl acrylate, methyl methacrylate, diethyl maleate, and acrylonitrile were all commercial reagents, and purified by distillation. Published procedures were utilized for the preparation of methyl *trans*-4-methyl-2-pentenoate,[16] methyl *trans*-2-hexenoate,[17] *trans*-pent-3-en-2-one,[18] 3-butenenitrile,[19] and *trans*-2-butenenitrile.[20]

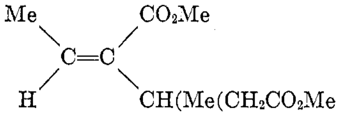
Catalysts. Copper Compounds.—Cuprous oxide and copper acetylacetonate were both commercial reagents. Copper metal was prepared by reducing cupric sulfate with zinc powder in aqueous solution under nitrogen.[21]

Isocyanide.—Cyclohexyl isocyanide and *t*-butyl isocyanide were prepared according to the Ugi's procedure.[22]

Dimerization of Methyl *trans*-2-Butenoate.—A mixture of 1.09 g (10 mmol) of cyclohexyl isocyanide, 30 mg (0.2 mmol) of cuprous oxide, and 3.00 g (30 mmol) of methyl *trans*-2-butenoate was heated at 90° for 3 hr. Then cuprous oxide was removed by filtration and the residue was distilled *in vacuo* to give 2.1 g of a fraction boiling at 70–80° (72 mm), which was shown by the following analyses to be a *cis–trans* mixture of dimethyl 2-methylpent-3-ene-1,3-dicarboxylate, the dimer of methyl 2-butenoate. The combined yield of the *cis* and *trans* isomers was 70%. The nmr spectrum also revealed that a dimer mixture consisted of 80% *cis* and 20% *trans* isomers: nmr of the *cis–trans* mixture (in



cis



trans

CCl_4) τ 8.84 (*cis*) and 8.92 (*trans*) d ($\mathbf{CH_3}CHCH_2$–), 8.16 (*cis*) and 8.14 (*trans*) d ($\mathbf{CH_3}CH{=}$), 7.30–7.70 m (>$CH\mathbf{CH_2}COOCH_3$), 6.50–7.10 m (>$\mathbf{CH}CH_2$–), 6.42 (*cis*) and 6.38 (*trans*) s (-COO$\mathbf{CH_3}$), 3.27 (*cis*) and 4.07 (*trans*) q ($CH_3\mathbf{CH}{=}$). Principal ir bands appeared at 1710 (vs), 1630 (w), 1300–1100 (s) cm^{-1}.

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05; mol wt, 200. Found: C, 59.93; H, 8.15; mol wt (vapor pressure osmometry), 208.

Several runs of the dimerization of methyl 2-butenoate with various catalyst systems were carried out similarly (Table I).

Dimerization of Ethyl *trans*-2-Butenoate.—The reaction was carried out by a similar procedure under the conditions shown in Table I. The dimer, diethyl 2-methylpent-3-ene-1,3-dicarboxylate, was obtained in 15% yield, bp 85–88° (3 mm). This was shown to be a mixture of *cis* and *trans* isomers: nmr (in CCl_4) τ 8.55–8.92, overlap d ($\mathbf{CH_3}CHCH_2$–) and 2t (–CO_2CH_2-$\mathbf{CH_3}$), 8.16 (*cis*) and 8.14 (*trans*) d ($\mathbf{CH_3}CH{=}$), 7.35–7.70 m (>$CH\mathbf{CH_2}COOC_2H_5$), 6.50–7.10 m ($CH_3\mathbf{CH}CH_2$–), 5.67–6.16 2q (–$COO\mathbf{CH_2}CH_3$), 3.30 (*cis*) and 4.08 (*trans*) q ($CH_3\mathbf{CH}{=}$); principal ir bands 1740–1720 (s), 1660 (w), 1300–1100 (s) cm^{-1}.

Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 63.59; H, 9.12.

Dimerization of Methyl *trans*-2-Hexenoate.—The reaction was carried out under the conditions described in Table I. The dimer, dimethyl 2-*n*-propylhept-3-ene-1,3-dicarboxylate, was isolated in 50% yield by fractional distillation: bp 100–102° (3 mm); nmr (in CCl_4) τ 7.60–9.10 m (*n*-$C_3H_7CH{=}C$– and *n*-C_3H_7CH–), 7.42 d (–$CH\mathbf{CH_2}CO_2CH_3$), 7.30–7.55 m (*n*-C_3H_7-$\mathbf{CH}CH_2$–), 6.34 and 6.45 2s (–$CO_2\mathbf{CH_3}$), 3.32 t (*n*-$C_3H_7\mathbf{CH}{=}$); principal ir bands 1700–1750 (s), 1650 (w), 1300–1100 (s) cm^{-1}.

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.29; H, 9.36.

Dimerization of Methyl *trans*-4-Methyl-2-pentenoate.—The reaction was carried out under the conditions described in Table I. The dimer, dimethyl 2-isopropyl-5-methylhex-4-ene-1,3-dicarboxylate, was isolated in 35% yield by fractional distillation: bp 90–93° (2 mm); nmr (in CCl_4) τ 9.07 d [$\mathbf{(CH_3)_2}CHCH$<] 8.20–8.35 s [$\mathbf{(CH_3)_2}C{=}CH$-], 7.50–8.10 m [$(CH_3)_2\mathbf{CH}{-}\mathbf{CH}{-}\mathbf{CH_2}$-], 6.70–7.00 m ($={CH}{-}\mathbf{CH}{-}CO_2CH_3$), 6.40 and 6.37 2s (-$CO_2\mathbf{CH_3}$), 4.93 d ($={\mathbf{CH}}{-}CH$-); principal ir bands 1730 (s) and 1300–1100 (s) cm^{-1}.

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.70; H, 9.62.

Dimerization of a *cis–trans* Mixture of 2-Butenenitrile.—The monomer was a *cis–trans* mixture of 2-butenenitrile, the *cis/trans* ratio being 2. The fraction boiling at 82–83° (3 mm) was obtained from the reaction mixture, and was shown to be a *cis*–

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trans mixture of the dimer, 1,3-dicyano-2-methylpent-3-ene. The yield was 90%. Each isomer was isolated by preparative glpc, 1:7 *cis*/*trans* ratio. Nmr data (CCl_4) follow: *trans* isomer, τ 8.70 d ($\mathbf{CH_3}\overset{|}{C}HCH_2-$), 7.94 d ($\mathbf{CH_3}CH=$), 7.00–7.65 m ($CH_3\overset{|}{\mathbf{C}}\mathbf{HCH_2}CN$), 3.60 q ($CH_3\mathbf{CH}=$); *cis* isomer, τ 8.63 d ($\mathbf{CH_3}\overset{|}{C}HCH_2-$), 8.07 d ($\mathbf{CH_3}CH=$), 7.53 d ($CH_3\overset{|}{C}H\mathbf{CH_2}CN$), 6.65–7.18 m ($CH_3\overset{|}{\mathbf{C}}\mathbf{H}CH_2CN$), 3.49 q ($CH_3\mathbf{CH}=$). Principal ir bands were at 2340–2380 (m) and 1630 (s) cm^{-1}.

Anal. Calcd for $C_8H_{10}N_2$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.87; H, 7.65; N, 20.64.

Dimerization of *trans*-Pent-3-en-2-one.—The *cis* dimer, 4-methyl-5-acetyl-hept-5-en-2-one, was isolated by preparative glpc from the reaction mixture in a yield of 50%. The dimer could not be isolated by means of vacuum distillation, because it was easily dehydrated during distillation: nmr (in CCl_4) τ 8.93 d ($\mathbf{CH_3}\overset{|}{C}HCH_2-$), 8.05 d ($\mathbf{CH_3}CH=$), 8.00 s ($-CH_2CO\mathbf{CH_3}$), 7.83 s ($=\underset{|}{C}CO\mathbf{CH_3}$), 7.10–7.40 m ($>CH\mathbf{CH_2}COCH_3$), 6.60–7.10 m ($CH_3\overset{|}{\mathbf{C}}\mathbf{H}CH_2-$), 3.42 q ($CH_3\mathbf{CH}=$); principal ir bands 1700 (s), 1660 (s), 1630 (s) cm^{-1}.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.38; H, 9.59. Found: C, 71.78; H, 9.84.

Codimerization of Methyl *trans*-2-Butenoate with Methyl Acrylate.—A mixture of 1.50 g (15 mmol) of methyl *trans*-2-butenoate, 1.29 g (15 mmol) of methyl acrylate, 1.09 g (10 mmol) of cyclohexyl isocyanide, and 30 mg (0.2 mmol) of cuprous oxide was heated at 110° for 10 hr. The cuprous oxide was removed by filtration, and the filtrate was subjected to vacuum distillation. The fraction boiling at 60–70° (3 mm), 1.5 g, was collected and shown by glpc to contain two compounds. By comparison of the glpc retention time with an authentic sample, one component was identified to be the dimer of methyl 2-butenoate (*cis–trans* mixture). The other was isolated by preparative glpc and shown by nmr and elemental analysis to be dimethyl pent-3-ene-1,3-dicarboxylate, *i.e.*, codimer of methyl 2-butenoate with methyl acrylate. The yields of the dimer of methyl 2-butenoate and the codimer were 1.73 and 4.35 mmol, respectively: nmr of the codimer (in CCl_4) τ 8.14 d ($\mathbf{CH_3}CH=$), 7.40–7.66 overlap 2t ($-\mathbf{CH_2CH_2}-$), 6.38 s ($-CH_2CO_2\mathbf{CH_3}$), 6.30 s ($=\underset{|}{C}CO_2\mathbf{CH_3}$), 3.16 q ($CH_3\mathbf{CH}=$).

Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.47; H, 7.39.

Codimerization of Methyl *trans*-2-Butenoate with Methyl Methacrylate.—The reaction conditions and procedures were the same. The fraction boiling at 60–80° (2 mm), 1.5 g, was collected, from which the 2-butenoate dimer (1.28 mmol) and codimer, dimethyl 1-methylpent-3-ene-1,3-dicarboxylate (4.96 mmol), were isolated separately by preparative glpc: nmr of the codimer (in CCl_4) τ 8.90 d [$-CH_2CH(\mathbf{CH_3})COOCH_3$], 8.20 d ($\mathbf{CH_3}CH=\underset{|}{C}-$), 7.20–7.83 m [$-\mathbf{CH_2CH}(CH_3)COOCH_3$], 6.44 and 6.34 2s ($-CO_2\mathbf{CH_3}$), 3.19 q ($CH_3\mathbf{CH}=\overset{|}{C}-$); principal ir bands 1730–1710 (s), 1645 (m), 1300–1100 (s) cm^{-1}.

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.71; H, 8.08.

Codimerization of Methyl *trans*-2-Butenoate with Diethyl Maleate.—The reaction was carried out under the conditions given in Table II. The fraction boiling at 100–130° (3 mm), 1.0 g, was collected from the reaction mixture. From this fraction the dimer of methyl 2-butenoate (0.225 mmol) and the codimer, 1,2-dicarbethoxy-3-carbomethoxypent-3-ene (5.86 mmol), were isolated by preparative glpc: nmr of the codimer (in CCl_4) τ 8.75 and 8.80 2t ($-COOCH_2\mathbf{CH_3}$), 8.10 d ($\mathbf{CH_3}CH=C<$), 6.33 s ($-COO\mathbf{CH_3}$) 5.94 2q ($-COO\mathbf{CH_2}CH_3$), 3.11 q ($CH_3\mathbf{CH}=C<$).

Anal. Calcd for $C_{13}H_{20}O_6$: C, 57.35; H, 7.35. Found: C, 57.12; H, 7.75.

Codimerization of 2-Butenenitrile with Acrylonitrile.—The reaction was carried out similarly (see Table II). From the reaction mixture, cyclohexyl isocyanide and unreated monomers were removed by vacuum distillation. Owing to the polymerization of a part of the acrylonitrile, the distillation residue was viscous and was thoroughly extracted with diethyl ether. The ether extract was concentrated and subjected to glpc analysis. The dimer of 2-butenenitrile (0.300 mmol) and the codimer of 2-butenenitrile with acrylonitrile, 1,3-dicyanopent-3-ene (1.35 mmol), were isolated: nmr of the codimer τ 7.92 d ($\mathbf{CH_3}CH=$), 7.44 s ($-\mathbf{CH_2CH_2}CN$), 3.58 q ($CH_3\mathbf{CH}=$); principal ir bands 2280–2240 (s), 1640 (s) cm^{-1}.

Anal. Calcd for $C_7H_8N_2$: C, 69.97; H, 6.71. Found: C, 69.52; H, 6.47.

Codimerization of Methyl *trans*-2-Butenoate with Methyl *trans*-4-Methyl-2-pentenoate.—According to procedures similar to the above, the fraction boiling at 80–100° (3 mm), 1.3 g, was collected, which was subjected to glpc analysis. By preparative glpc, the dimer of methyl 2-butenoate (0.825 mmol) and the codimer, dimethyl 2,5-dimethylhex-4-ene-1,3-dicarboxylate (4.50 mmol), were isolated separately: nmr of the codimer τ 9.10 d ($\mathbf{CH_3}CH-$), 8.35 and 8.25 2s [$(\mathbf{CH_3})_2C=$], 6.70–8.00 m ($=CH\overset{|}{\mathbf{C}}\mathbf{H}COOCH_3$ and $CH_3\overset{|}{\mathbf{C}}\mathbf{HCH_2}COOCH_3$), 6.41 s ($-COO\mathbf{CH_3}$), 4.95 d ($=\mathbf{CH}-CH<$).

Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.33. Found: C, 62.98; H, 8.57.

Isomerization and Dimerization of 3-Butenenitrile.—A mixture of 1.34 g (20 mmol) of 3-butenenitrile, 1.09 g (10 mmol) of cyclohexyl isocyanide, and 70 mg (0.5 mmol) of cuprous oxide was heated at 90° for 5 min. Then the reaction was quenched by cooling to 0°. By glpc analysis, the reaction mixture was shown to contain 2-butenenitrile and the dimeric product. The dimeric product was identical to the dimer from 2-butenenitrile, *i.e.*, a mixture of *cis* and *trans* isomers of 1,3-dicyano-2-methylpent-3-ene. The yield of dimer was 64%. 3-Butenenitrile was not detected in the reaction mixture, and the monomeric species was recovered exclusively as 2-butenenitrile.

Dimerization of 2-Butenenitrile in the Presence of Deuterium Oxide.—A mixture of 2.8 g (40 mmol) of 2-butenenitrile, 2.18 g (20 mmol) of cyclohexyl isocyanide, 56 mg (0.4 mmol) of cuprous oxide, 0.8 g (40 mmol) of deuterium oxide, and 3 ml of dimethylformamide (solvent) was heated at 100° for 4 hr. The glpc analysis of the reaction mixture revealed that the dimer was produced in a yield of 1–2%. From the reaction mixture, cuprous oxide was removed by filtration, and the filtrate was fractionally distilled at 200–300 mm at room temperature. The distillate was subjected to preparative glpc to isolate the monomeric species. By nmr, the monomer was shown to be deuterated 58% at the α position and 24% at the γ position. The average degree of hydrogen–deuterium exchange was calculated to be 33%.

Dimerization and Deuterium–Hydrogen Exchange of Partially Deuterated 2-Butenenitrile.—2-Butenenitrile partially deuterated at the α and γ positions was prepared by the following procedure. 2-Butenonitrile (6.70 g, 0.1 mol) was heated with stirring at 100° for 4 hr with the sodium deuterioxide from 50 mg of sodium and 20 g of deuterium oxide. The organic layer was separated from the deuterium oxide–water mixture, and treated again with the sodium deuterioxide from 50 mg of sodium and 15 g of deuterium oxide at 100° for 4 hr. The organic layer from the second treatment was dried with calcium chloride and distilled to yield 1.9 g of partially deuterated 2-butenonitrile. The degree of deuteration determined by nmr was 88% at the α position and 42% at the γ position. The average deuteration degree was calculated to be 53%.

Partially deuterated monomer was then subjected to dimerization. A mixture of 1.14 g (17 mmol) of partially deuterated monomer, 0.93 g (8.5 mmol) of cyclohexyl isocyanide, and 20 mg (0.15 mmol) of cuprous oxide was heated for 30 min at 90°. Cuprous oxide was removed by filtration, and the filtrate was distilled *in vacuo* at room temperature. Using preparative glpc, the monomer was recovered from the distillate and the dimer was isolated from the distillation residue. The nmr of the recovered monomer showed that the deuteration degrees of α and γ hydrogens were both 53%, the average value of the starting monomer. The deuterium content of the product dimer was determined also by nmr. As has been shown in Table IV, the average degree of deuteration was the same as that of the starting monomer (53%). By nmr analysis using nitromethane as the standard, it was shown that no hydrogen–deuterium exchange occurred at the β hydrogen. Moreover, the dimerization and the hydrogen–deuterium equalization were not observed using any single component of the cyclohexyl isocyanide and cuprous oxide system under the same experimental conditions.

Registry No.—Dimethyl *cis*-2-methylpent-3-ene-1,3-dicarboxylate, 16657-04-8; dimethyl *trans*-2-methylpent-3-ene-1,3-dicarboxylate, 16657-03-7; diethyl *cis*-2-methylpent-3-ene-1,3-dicarboxylate, 22485-82-1; diethyl *trans*-2-methylpent-3-ene-1,3-dicarboxylate, 22528-27-4; dimethyl *cis*-2-*n*-propylhept-3-ene-1,3-dicarboxylate, 22485-83-2; dimethyl *trans*-2-*n*-propylhept-3-ene-1,3-dicarboxylate, 22528-28-5; dimethyl 2-isopropyl-5-methylhex-4-ene-1,3-dicarboxylate, 22482-50-4; *trans*-**5**, 22485-84-3; *cis*-**5**, 22485-85-4; *cis*-4-methyl-5-acetylhept-5-en-2-one, 22485-86-5; dimethyl pent-3-ene-1,3-dicarboxylate, 22482-51-5; dimethyl 1-methylpent-3-ene-1,3-dicarboxylate, 22483-45-0; 1,2-dicarbethoxy-3-carbomethoxypent-3-ene, 22485-87-6; 1,3-dicyanopent-3-ene, 22485-88-7; dimethyl 2,5-dimethylhex-4-ene-1,3-dicarboxylate, 22485-89-8.

Studies of Nitriles. III.[1a] Synthesis of Chlorocyanoacetylene and Cyanoacetylene, and a Novel Malononitrile Synthesis from Chlorocyanoacetylene[1b]

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Pyrolysis of trichloropropionitrile and dichloropropionitrile at 900–1000° under reduced pressure provided a novel synthesis of chlorocyanoacetylene (*ca.* 80%) and cyanoacetylene (40–60%). Chlorocyanoacetylene reacted with ammonia to give malononitrile in high yields.

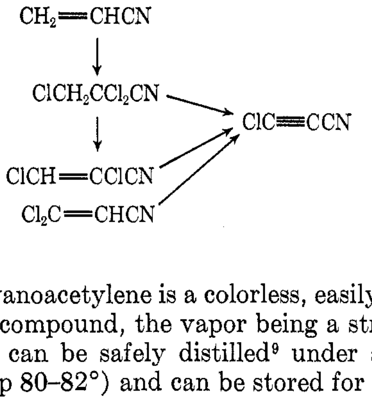
Cyanoacetylene is a compound of considerable interest, because it has two conjugated triple bonds in the molecule and, perhaps, will find wide application in the synthesis of a variety of heterocyclic compounds. It may also be useful as a monomer in the chemistry of polymers. Although cyanoacetylene has been known for many years, its chemical properties remain uninvestigated, largely owing to lack of a convenient synthesis. The most orthodox method for its synthesis has been recorded by Moureu,[2] and involves the dehydration of propiolamide with phosphorus pentoxide. Since propiolamide has to be prepared from acetylene by a series of reactions including carbonylation, esterification, and amidation, this approach is far from being practical. Several workers[3] thereafter somewhat improved Moureu's method but could not alter its lengthy nature.

Recently, several patents claim that cyanoacetylene can be prepared by the dehydration of propargylaldehyde oxime[4] or by some gas-phase reactions of acetylene[5] or acetonitrile[6] with hydrogen cyanide at high temperatures.

Chlorocyanoacetylene was first prepared by Kloster-Jensen[7] by the reaction of chlorine with lithium cyanoacetylide and its melting point (42–42.5°) and ir and uv spectral data were recorded by the same author. Recently, Bjorvatten[8] reported the X-ray crystallographic study of chlorocyanoacetylene with the sample supplied by Kloster-Jensen. However, for lack of a convenient synthesis the investigation of its chemical properties has been hampered for years.

In the preceding paper[1a] we reported that chlorocyanoacetylene was produced by the copyrolysis of carbon tetrachloride and acetonitrile. Further, it was suggested that its formation would be explained by the pyrolytic dehydrochlorination of β,β-dichloroacrylonitrile, which was the main product of the copyrolysis.

The present paper deals with a convenient one-step synthesis of chlorocyanoacetylene from trichloropropio- or dichloroacrylonitriles, and a synthesis of cyanoacetylene from dichloropropio- or chloroacrylonitriles, together with a novel synthesis of malononitrile from chlorocyanoacetylene.



(1)

Chlorocyanoacetylene is a colorless, easily sublimable crystalline compound, the vapor being a strong lachrymator. It can be safely distilled[9] under atmospheric pressure (bp 80–82°) and can be stored for months in a refrigerator or even at room temperature with only slight decomposition. It should be mentioned, however, that chlorocyanoacetylene appears to have rather

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(1) (a) Paper II: N. Hashimoto, Y. Kawano, and K. Morita, *J. Org. Chem.*, **35**, 828 (1970); (b) Part of this work was presented at the symposium on The Chemistry of Heterocyclic Compounds, Osaka, Japan, Oct 1968, and at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, Japan, April 1969.

(2) C. H. Moureu, and J. Ch. Bongrand, *Ann. Chem.*, **14**, 53 (1920).

(3) S. Murahashi, T. Takizawa, S. Kurioka, and S. Maekawa, *Nippon Kagaku Zasshi*, **77**, 1689 (1956); *Chem. Abstr.*, **53**, 5163 (1959); Union Carbide Corp., Netherlands Application Patent 296,042 (1965); *Chem. Abstr.*, **63**, 17907 (1965).

(4) J. Happel, C. J. Marsel, and A. A. Reidlinger, U. S. Patent 3,006,948 (1958); *Chem. Abstr.*, **56**, 8574 (1962).

(5) L. J. Krebaum, U. S. Patent 3,079,424 (1963); *Chem. Abstr.*, **59**, 3777 (1963); *J. Org. Chem.*, **31**, 4103 (1966).

(6) L. J. Krebaum, U. S. Patent 3,055,738 (1962); *Chem. Abstr.*, **58**, 2375 (1963).

(7) E. Kloster-Jensen, *Acta Chem. Scand.*, **18**, 1629 (1964).

(8) T. Bjorvatten, *ibid.*, **22**, 410 (1968).

(9) Chlorocyanoacetylene burns in air only moderately with a sooty flame but it may cause a hazardous explosion if it burns in a nearly closed vessel. In a large-scale synthesis, it was found that the pyrolytic dehydrochlorination of trichloropropionitrile was accompanied by a minute but nonnegligible amount of hazadous low boiling materials. These low boiling substances were isolated and identified as $ClC{\equiv}CH$ (trace), $ClC{\equiv}CCl$, and ClCN, by mass spectra. The former two compounds are extremely flammable, and it was proved that they were the cause of small explosions met sometimes at the early stage of the investigations, but it was soon discovered, thanks to the excellent work of Ott, *et al.*, that the addition of very small (*ca.* 1%) amount of ethyl ether to the material greatly hampered both ignition and explosion.