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Copper-Catalyzed Hydrocyanation of Olefins. Kinetic and Mechanistic Aspects

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The CuBr-, $CuBr_2$-catalyzed hydrocyanation of conjugated olefins has been investigated by kinetic methods. The reaction appears to depend on the presence of halogenated species as shown by the effect of additives such as BrCN and crotyl bromide (a possible intermediate in the reaction). Evidence for a mechanism proceeding through protonation of the diolefin by an acidic bromine-containing copper species of the type (HCu(CN)Br) is presented. From a preparative point of view, the reaction gives an excellent yield of pentenenitrile from butadiene, but a poor yield of nitriles from substituted dienes.

INTRODUCTION

The application of HCN to industrial organic synthesis has received much attention in the last few years as it constitutes a material directly available from natural gas (and even coal) and ammonia (*1*).

The addition of HCN to acetylene has been a major (although now obsolete) industrial process for the synthesis of acrylonitrile. However, the application of hydrocyanation to olefins has recently required interest as butadiene hydrocyanation affords a straightforward approach to hexamethylene diamine synthesis (*2*). Major industrial laboratories have devised important processes based either mainly on nickel catalysis (*3–5*) or copper catalysis (*6*). Recently, Benzie and one of us (*6a*) developed a novel process based on copper catalysis. Prior to this, only nickel catalysis had led to efficient *double* addition of HCN onto butadiene with formation of adiponitrile in good yield (*3*) (Scheme 1).

The aim of the present publication is to report and discuss some recent observations related to the copper-catalyzed process (*6a*), the nickel-catalyzed process having already been thoroughly investigated both from the practical and mechanistic point of view (*3, 5*).

EXPERIMENTAL

Methods

Preparation of HCN. HCN was prepared from NaCN and H_2SO_4 and dried over Sikkon (Fluka) and on P_2O_5 in particular cases.

Materials

Copper salts (CuBr, $CuBr_2$, CuCl, CuOAc, CuF_2, CuCN) were commercial products. Copper (I) triflate was prepared as reported by Salomon and Kochi (*7*). Purification of CuBr and CuCl was performed by washing with acetic acid in the presence of SO_2.

Solvents and reagents. Acetonitrile ("purum" quality from Fluka) was used as such or after distillation over P_2O_5 (no significant difference in rates resulted from this treatment). Butadiene was dried by flowing through a column of CaH_2, then through a molecular sieve (5 Å) and finally condensed in a dry-ice bath. It was then transferred by means of a stainless-steel capillary tube into the reactor.

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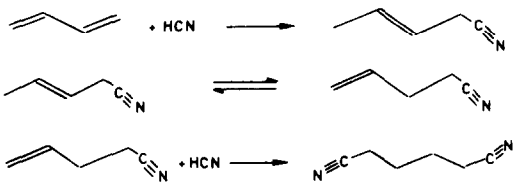


SCHEME 1

Identification of products. The isomeric pentenenitriles were identified by comparison with authentic samples using GLC and mass spectrometry.

Typical hydrocyanation procedure. All experiments were run in an *efficiently* ventilated hood. Most of them and all of the kinetic experiments were run in sealed glass tubes (15 ml) containing the copper salt (2.5 mmol), the diene (51 mmol), hydrocyanic acid (106 mmol), and the solvent (acetonitrile: 80 mmol) according to the reported procedure (*6a*). Each tube was inserted into an aluminum protective sheath and then introduced into a basket rotating in a water bath heated at the required temperature. The tubes were opened after cooling in liquid nitrogen. HCN and butadiene were allowed to escape at room temperature in a *well-ventilated* hood and the residue was analyzed by GLC (benzonitrile being added as an internal standard for quantitative measurements). The relatively large amounts (~0.1 mol) of HCN were destroyed by bubbling the gas through an alkaline solution of sodium hypochlorite.

RESULTS

The catalytic system described in the patent literature (*6a*) consists of a solution of cuprous salt in nitriles or thioethers as solvents, together with an acidic cocatalyst in some cases. Practically all the soluble active systems are based on the bromides and the chlorides (copper iodide is very poorly active), copper bromides being used in the present study as they afford more reproducible results than the chlorides. Copper chromite has, however, been reported by Drinkard (*6c*) as a hydrocyanation catalyst,

TABLE 1

Hydrocyanation of Conjugated Dienes; Influence of the Solvent on the Yield of 3-Pentenenitrile (3-PN) after 12 h

CH_3CN	86%	39%	1.2%
C_6H_6	29.1%	—	—
No solvent	2.6%	28.7%	0

Note. Catalyst: CuCl. Conditions: see Fig. 1.

but the conditions are very different from ours, his system being heterogeneous. Copper (I) cyanide, acetate, fluoride, and even the triflate (a weak ligand) are inactive. The use of *cupric* salt leads readily to reduction to the *cuprous* derivative (copper(II) triflate is reduced to copper (I) under the reaction conditions, as shown by the disappearance of the EPR signal of Cu(II)).

Copper catalysis appears to be a very convenient and efficient method for realizing the monohydrocyanation of butadiene as the yields are good (>90%) and the reaction leads selectively to substituted 2-butenes (≥95% of 1,4-addition); moreover, the catalyst (in contrast to the nickel one) is practically insensitive to traces of water or oxygen.

At the present stage, however, the method suffers from some severe limitations:

- Copper-catalyzed hydrocyanation of olefins is essentially restricted to conjugated olefins (butadiene and substituted butadienes). In fact, the method works satisfactorily only with butadiene itself, substitution of the diene moiety strongly decreasing the yield (Table I).
- Side reactions such as oligomerization and polymerization are the main factors responsible for the yield drop with these reactants and account for the balance of products. The formation of dimers and trimers from isoprene, 1,3-pentadiene, and 2,3-dimethylbutadiene

TABLE 2

Hydrocyanation of Butadiene: Influence of the Concentration of Cl_3CCOOH on the Yield of 3-Pentenenitrile (3-PN) after 12 h

$\frac{[Cl_3CCOOH]}{[CuBr]}$	Yield of 3-PN (%)
0	56 (90)[a]
0.8	61
1.3	63
2.6	70
7.0	83

Note. Conditions: see Fig. 1.
[a] Yield of 3-PN after 50 h.

TABLE 3

Hydrocyanation of Butadiene: Influence of pK_a of the Cocatalyst (RCOOH) on the Yield of 3-Pentenenitrile after 16 h

RCOOH	pK_a	Yield of 3-PN (%)
No cocatalyst	—	40
CH_3COOH	4.8	46
$ClCH_2COOH$	2.85	51
$Cl_2CHCOOH$	1.5	55
Cl_3CCOOH	0.7	65

Note. Conditions: butadiene 0.060 mol, HCN 0.103 mol, propionitrile 3 ml. T = 75°C.

has been observed by GLC coupled with mass spectrometry (the results concerning other dienes than butadiene will be fully reported in a subsequent paper).

The Solvent

The solvent (Table 1) used in the present process is preferably a nitrile such as acetonitrile (*6*). Propionitrile appeared during this study as a particularly convenient solvent for the catalyst and it was therefore used in some cases: see Table 3 and the experiments cited later which were run with an excess of butadiene. The rates are substantially higher in propionitrile than in acetonitrile. However, we observed that the reaction can also be run efficiently in other polar solvents such as acetic acid. Nonpolar solvents (e.g., benzene) afford low yields.

Additives affect the reaction rate. A very acidic cocatalyst such trichloroacetic acid increases the rate (Table 2) and in fact there

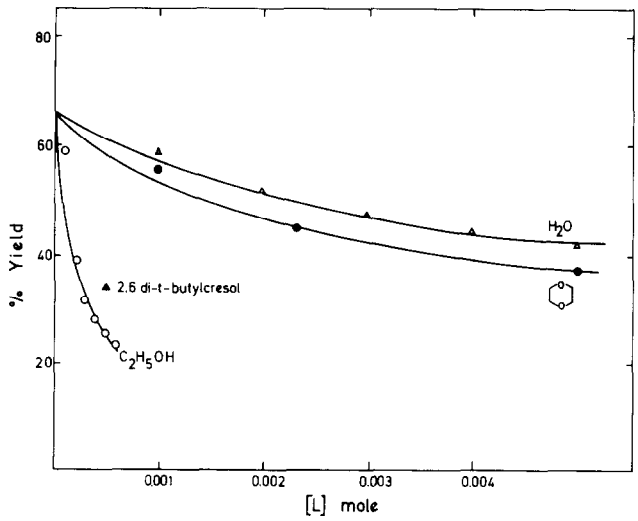


FIG. 1. Influence of additives on the yield of 3-pentenenitrile after 12 h. CuBr: 2.5; Cl_3CCOOH: 3.0; butadiene: 51; HCN: 10.6 mmol; acetonitrile: 1.27 ml. T 79°C.

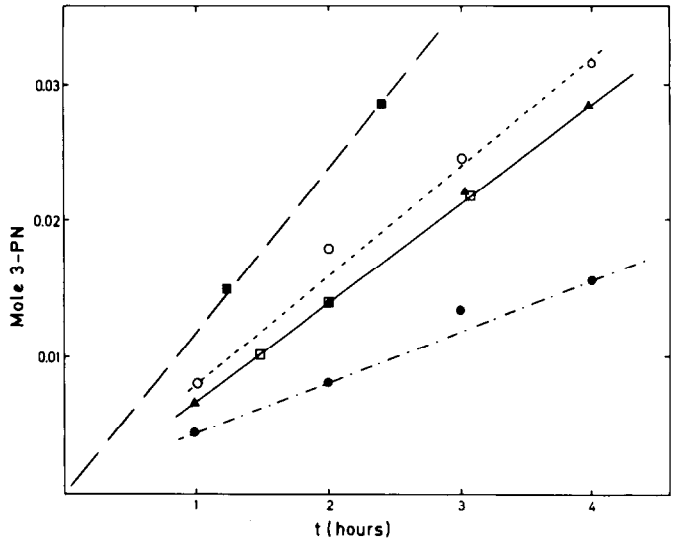


FIG. 2. Activation of copper catalysts by BrCN and $BrCH_2—CH=CH—CH_3$ (●) CuBr, (▲) CuBr + BrCN, (■) CuBr + $BrCH_2—CH = CH—CH_3$, (□) CuCN + $BrCH_2—CH = CH—CH_3$, (○) $CuBr_2$. Conditions: the same as for Fig. 1; equimolecular amounts of BrCN and crotyl bromide relatively to the copper salt.

is a correlation between the promoting activity of the cocatalysts and their p*K*a (Table 3). Lewis bases such as dioxane, water, phenols, and alcohols act as inhibitors (Fig. 1). The limited influence of di-t-butylcresol (a classical radical scavenger) is an indication of a *nonradical* mechanism: the rate decreases only by a factor of 2 on adding an equimolecular amount of the cresol to the catalyst. The very strong inhibiting effect of ethanol may be related to the known HCN-catalyzed reaction of HBr with alcohol to give alkyl bromides (*8*) (see Discussion).

Halides and some halogenated additives promote the catalytic activity. For example, even copper triflate, an inefficient catalyst, displays some activity when lithium chloride is added: the lack of efficiency is therefore not the result of an inhibiting effect of the (weak) triflate ligand. Cyanogen bromide increases the rate of the CuBr-catalyzed reaction (Fig. 2, triangles). Moreover, cyanogen bromide activates efficiently all of the inactive cuprous salts (CuCN, CuOAc) as well as the metal Cu(0). The most efficient additive is, however, crotyl bromide (Fig. 2, solid squares). Stoichiometric amounts of this compound (relative to CuBr) increase the rate by a factor of 3. Moreover, the inactive cuprous cyanide

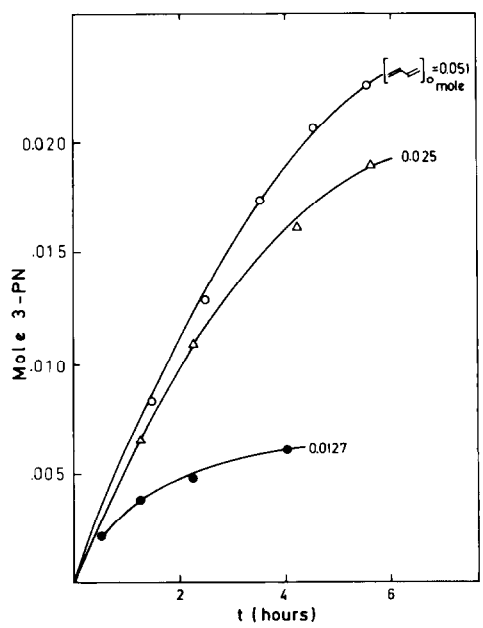


FIG. 3. Kinetics of the CuBr-catalyzed hydrocyanation of butadiene: influence of the initial concentration of butadiene. Conditions: the same as in Fig. 1.

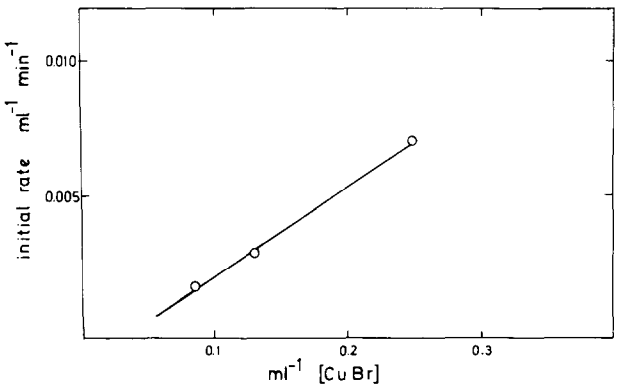


FIG. 4. Correlation between rate constants and catalyst concentration for butadiene hydrocyanation. Conditions: the same as for Fig. 1.

becomes even more efficient than cuprous bromide in the presence of crotyl bromide (Fig. 2, open squares). It appears that allylic halides in general display such activation effects (e.g., 3-chloro-1-butene). Lithium bromide and n-butyl bromide have no kinetic effects on CuBr activity for 3-pentenenitrile formation, but the former does activate inactive Cu (I) salts.

The kinetics of the reaction run in the presence of an excess of HCN have been measured for different initial butadiene concentrations (Fig. 3) when using the reported best conditions from the patent literature (*6a*). The trend of the initial slope is typical for a progressive saturation of the catalytic sites by the reactant (butadiene), the rate becoming progressively independent from the butadiene concentration for the higher concentrations.

Experiments where butadiene is in excess relative to HCN are not relevant owing to the poor solubility of the catalyst under these conditions. However, measurements in the presence of propionitrile (a better solvent of the catalyst than acetonitrile) support an initial order close to unity for HCN; 0.0022 and 0.0043 mol of 3-pentenenitrile are respectively formed from 0.0207 and 0.0415 mol HCN and 0.0623 mol butadiene (CuBr = 0.029 mol, propionitrile = 2 ml, *no* cocatalyst) after 135 min at 75°C.

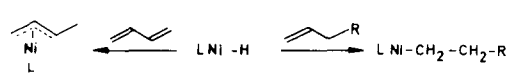
As far as the *catalyst* is concerned, the rate constants linearly correlate with copper concentration (Fig. 4).

DISCUSSION

The copper-catalyzed hydrocyanation of olefins appears to be essentially different from the catalysis by nickel. The latter proceeds through the formation of metal hydride intermediates which add onto the olefin reactants to afford a π-allyl nickel complex (from diolefins) or σ-alkyl nickel derivatives (from an isolated double bond), as in Scheme 2. Copper catalysis, however, under homogeneous conditions, seems to be essentially limited to halide-containing catalytic systems.

It is noteworthy that even the Drinkart process (*6c*) based on solid copper chromite as catalyst, reports on the use of HCl as additive: the initial step of this reaction can therefore be a chlorination step.

Product distribution with the nickel process is determined by the orientation of the H–Ni addition (*4*) onto the double bond and also by thermodynamic factors (isomerization of the addition products): this H–Ni addition to olefins is in many respects quite reminiscent of hydroboration (steric con-



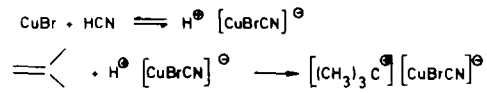
SCHEME 2

trol and apparent "contrathermodynamic" isomerization) as pointed out by Keim (*13*). It is possible that the reaction may be the result of a pathway different from simple H–Ni addition and proceed through initial coordination of the olefin followed by the double-bond insertion as a result of *cis* rearrangement: however, the analogy with hydroboration remains of interest as the process is also governed by steric factors. Moreover, the Lewis acid character of the boron hydride is certainly a key factor in the hydroboration of olefins.

At the practical level, however, the more significant difference between nickel and copper catalysis is the poor reactivity of nonactivated double bonds with the copper system. For example, hydrocyanation of butadiene is strictly limited to the monoaddition product (pentenenitrile), at least under standard reaction conditions, with a good selectivity for the 1,4-addition product relative to the 1,2-addition product (95 : 5).

The mechanism of the catalysis by nickel has been extensively studied (*3, 4*). However, the copper-catalyzed hydrocyanation has not yet been reported outside the patent literature. The main facts which must be accounted for in any tentative mechanism for the copper case are the key role and activating effect of halides, together with the observed selectivities.

Cuprous cyanide is known (*9*) to form highly acidic complexes with HCN, such as $HCu(CN)_2$ and $H_2Cu(CN)_3$. However, these entities are inactive both in the hydrocyanation of butadiene and in isonitrile formation from isobutene (*10*). The fact that CuBr can catalyse either the formation of a *nitrile* (from a conjugated olefin) or of an *isonitrile* (from isobutene) can be explained as the result of Pearson HSAB interactions between a cationic intermediate (soft allylic cation or a "harder" t-butyl cation) and the soft ($C^{\ominus}$) or hard ($N^{\ominus}$) ends of the cyanide anion. A related explanation implies the occurence of a S_N1 mechanism for isonitrile formation, and a S_N2-type process for nitrile formation: this may indeed be the case if crotyl bromide is an intermediate.

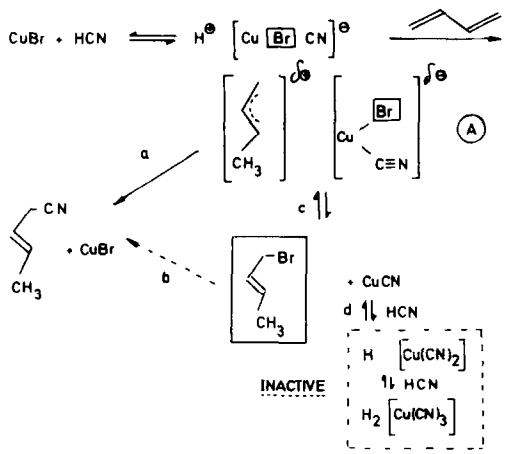


SCHEME 3

Thus the key intermediates in copper-catalyzed hydrocyanation and isonitrile formation (*10*) might be very similar (see Schemes 3 and 4). It is noteworthy that small amounts of isonitriles (as shown by ir spectroscopy, R–N≡C = 2120–2180 cm^{-1}, R–C≡N = 2200–2250 cm^{-1}) are formed during the hydrocyanation of conjugated dienes in the absence of acetonitrile as solvent.

The high regioselectivity in favor of the 1,4-addition product would be the result of steric interactions with the bulky $[CuBrCN]^{\ominus}$ group during the transfer of the $CN^{\ominus}$ moiety in a complex such as A in Scheme 4. It is to be stressed that the amazing regioselectivity in isoprene hydrocyanation, where $(CH_3)_2C{=}CH{-}CH_2{-}CN$ is the exclusive isomer, parallels the regioselectivity of the HCl addition to isoprene.

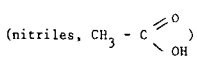
The role of bromide ion could be explained by the increased acidity that it imparts to the HCuCNX complex, but the particularly high activating effect of crotyl



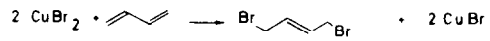
SCHEME 4

bromide (Fig. 2, solid squares) indicates a more intimate participation of the halide ion in the mechanism. Actually, crotyl bromide may even be a key intermediate in the process (Scheme 4), reactions (a) and (b) corresponding in fact to mechanisms of exchange of crotyl bromide and CuCN through the formation of the complex A as intermediate, this last postulate explaining the high regioselectivity of the reaction. The complex A may also directly form 3-pentenenitrile ((a) in Scheme 4). However, a free allylic cationic species, e.g., according to a S_N1 mechanism for (b) (in Scheme 4) is very unlikely owing to the high selectivity in favor of 3-pentenenitrile and to the absence of any acetoxylation product when the reaction is run in acetic acid as solvent. The activation effect of crotyl bromide may be explained by a shift of the equilibria (c) and (d) from the inactive forms (shown in the dashed frame in Scheme 4) toward the active species. One has to recall here that the addition of an equimolecular amount of crotyl bromide to the *inactive* CuCN gives a catalytic system that is even *more efficient* than neat CuBr (Fig. 2, open squares). This may be the result of a favorable formation of the active complex A through equilibrium shift, as shown in Scheme 4.

An ionic type mechanism would also be suggested by the beneficial effect of high *solvent* polarity



as well as the increased yield of polymeric products with substituted dienes. On the other hand, the fact that the hydrocyanation process competes very efficiently with an acetoxylation pathway in the presence of acetic acid as solvent is strong evidence for a reaction proceeding through activation of HCN by preferential coordination of HCN to copper, leading to the very acidic H[CuBrCN] species (Scheme 4), which leads in turn to the formation of the allyl moiety which remains to some extent con-



SCHEME 5

trolled by the copper center (otherwise the formation of some crotyl acetate would be expected in acetic acid as solvent). However, the synthesis of trans-3-pentenenitrile from butadiene and of 4-methyl-3-pentenenitrile from isoprene strongly supports the hypothesis of a nucleophilic attack of a *noncoordinated* CN^- on a (cationic?) π-allyl Cu species (trans addition, see Ref. (14)).

The observed regioselectivity is probably the result of steric control within complex A, particularly if A is an oversimplification for more elaborate structures (polymetallic?). The problem of the mononuclear or polynuclear state of the active species remains, however, open, as well as the reality of copper (III) π-allyl type intermediates as proposed in the literature (*12*) for some copper-catalyzed reactions.

The higher initial reactivity of $CuBr_2$ relative to CuBr can be explained by the well-known halogenating properties of this salt (Scheme 5). The resulting dibromobutene can play the same activating role as crotyl bromide in Scheme 4. Similarly, the activating role of BrCN is probably the result of its halogenating properties (Scheme 6). In fact the characteristic deep-green color of $CuBr_2$ appears readily when BrCN is added to a solution of CuBr in acetonitrile in the absence of butadiene.

Catalyst deactivation is the result of the formation of inactive CuCN: after one run under "standard conditions" (see Experimental), the Cu-to-Br ratio is indeed equal to 2.5 in the recovered catalyst instead of 1 initially. Some halide is therefore incorporated in the organic part of the medium and progressively lost during the recovery of the product by distillation. Significantly,

SCHEME 6

the recommended procedure to restore the catalytic activity consists in treating the used catalyst with HBr or HCl (*11*). In fact, we observed that BrCN or (better) crotyl bromide are particularly convenient additives for the activation of the copper catalysts (Fig. 2).

CONCLUSIONS

The results of the present investigation have shown that copper-catalyzed monoaddition of HCN onto conjugated dienes proceeds very conveniently with butadiene. The regioselectivity is high in favor of 3-pentenenitrile and seems to be mainly controlled by steric effects.

The bromide ion present in the catalyst plays an essential role in the process and participates directly in the reaction mechanism as shown by the rate-accelerating effect of bromine-containing additives and the inhibition by halide removal (quenching by ethanol). We have, therefore, proposed a mechanism involving the participation of the bromide ion in the coordination sphere of the copper ion and even in further reaction intermediates. The results can very probably be extrapolated to the chlorides which are also active catalysts.

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