Copper-Catalyzed Oxycyanation of Conjugated Dienes: A Comparison with the Diacetoxylation Reaction

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Copper bromide-based catalysts promote the formation of 1,4-dicyano-2-butene from butadiene in acetonitrile as solvent. In other solvents such as pyridine or dimethyl sulfoxide, the reaction follows another pathway and 2-cyanopyridine is produced in small yield. These reactions can be applied to other conjugated dienes such as isoprene or 1,3-pentadiene, but the yields are lower than with butadiene. In fact, the described catalyst is poorly active and the yields are moderate to low according to the reactant. The results are discussed in relation to other copper bromide-based catalytic reactions (hydrocyanation, hydroacetoxylation, and diacetoxylation reactions). © 1989 Academic Press, Inc.

INTRODUCTION

The preparation of difunctional compounds from butadiene constitutes a major industrial goal owing to the low cost of butadiene and the application of such derivatives to polymer synthesis.

Some transition metal-based catalysts have important practical applications within this context. For example, the diacetoxylation of butadiene offers an interesting route for the production of butane-1,4-diol when the regioselectivity of the reaction is efficiently controlled. This has not been the case up to now with copper-based catalysts (scheme 1, reaction a) (1): noble metal derivatives such as some rhodium (2) and particularly palladium (3–5) complexes appear to be more selective.

Similarly, the preparation of dinitriles and particularly of adiponitrile from butadiene and HCN (the hydrocyanation process of DuPont) is of major industrial importance in connection with nylon-6,6 synthesis. Hitherto, the catalysts used for this process have been based on nickel[0] complexes (6), copper catalysts being inefficient for the second addition step (scheme 2) but very convenient as far as the monoaddition of HCN is concerned (scheme 1, reaction c) [(8) and therein]. However, a precursor of adiponitrile, 1,4-dicyano-2-butene (dehydroadiponitrile), is formed under oxidative conditions (O₂ pressure) (scheme 1, reaction d) when using a copper halide-based catalyst (7).

As the present catalytic composition is very poorly active when used in batch experiments [the number of catalytic cycles is very limited (<10) and the catalyst appears to be readily deactivated], the interest in the present study lies essentially in providing novel information on essential features related to copper catalysis and to the comparison with related processes based on similar catalysts (1, 8–10).

We report here our observations on this catalyst in relation to our previous reports on copper-catalyzed hydrocyanation [scheme 1, reaction c (8, 9)], hydroacetoxylation (scheme 1, reaction b), and diacetoxylation (scheme 1, reaction a) reactions.
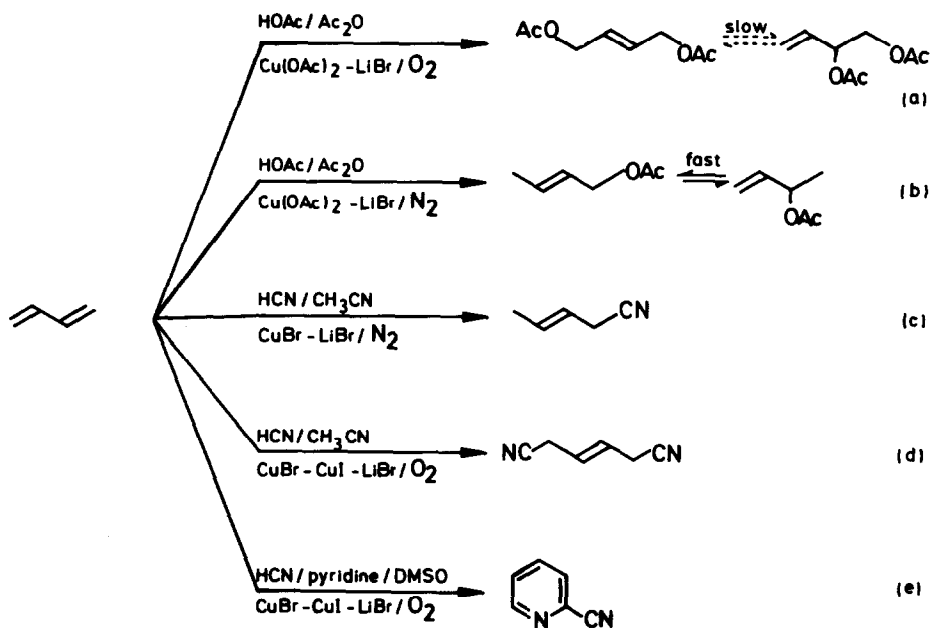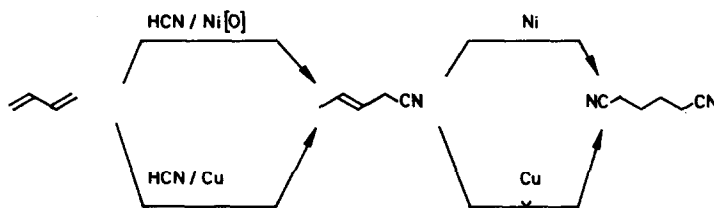
SCHEME 1

EXPERIMENTAL

Materials. Copper salts [CuBr, CuI, Cu(OAc)$_2$, Cu(acac)$_2$, Cu(NO$_3$)$_2$, CuCN, CuSO$_4$] and LiBr, PdCl$_2$, CoCl$_2$, NiCl$_2$, FeCl$_2$, and ZnCl$_2$ were commercial products used as such except for CuBr and CuI, which were purified by being washed with acetic acid in the presence of SO$_2$.

Solvents and reagents. All the solvents used in the present study (acetonitrile, DMSO, DMF, etc.) are commercial products and were used after redistillation.

Typical oxycyanation procedure. The oxycyanation reactions were run in a stainless-steel autoclave (250 ml) containing a

glass jacket and a magnetic stirrer. The conditions are those reported in Ref. (7): CuBr—2.0 g (14 mmol), CuI—1.0 g (5.3 mmol), LiBr—0.5 g (5.7 mmol), diene—120 mmol, HCN—14.3 g (530 mmol) in acetonitrile (10 ml). (*Note:* The mixture was not completely homogeneous even after the reaction.) The oxygen pressure was adjusted to 50 psig at 20°C. The autoclave was heated at 80°C and stirred for 8 h. HCN and the diene were allowed to escape at room temperature into a hood. The residue was taken up in benzene and washed, and the organic layer was dried over drierite (Fluka). The organic solution was concentrated by evaporation and analyzed by a

SCHEME 2

GLC–MS coupled technique. Yields (calculated on butadiene) were determined by GLC methods. In some cases (see below), the product was purified by distillation and the structure established by ^{1}H-NMR spectroscopy.

Identification of products. Identification of 1,4-dicyano-2-butene and of 2-cyanopyridine was readily achieved by comparison with authentic samples using GLC–MS.

For identification of methyl-2-cyanopyridines from 1,3-pentadiene, the product consists of an equimolecular mixture of two isomers: 3-methyl-2-cyanopyridine (C) and 6-methyl-2-cyanopyridine (D) were obtained from isoprene (C/D = 60/40). The structures were proven by ^{1}H-NMR spectroscopy using the shift reagent Eu^{III} tris(dipivalomethanate).

RESULTS

Under the conditions described under Experimental, the oxycyanation of butadiene yields up to 33% 1,4-dicyano-2-butene (scheme 1, reaction d); the yield increases to 60% in the presence of HBr. Small amounts (10%) of the branched isomer were also detected by GLC–MS.

The efficient catalyst systems were based on copper(I) halides (bromide–iodide), other tested copper derivatives [Cu(OAc)$_2$, CuOAc, Cu(acac)$_2$, Cu(NO$_3$)$_2$, CuCN, CuSO$_4$, and Cu$_2$O] being inactive under the standard conditions reported under Experimental.

Influence of Additives

Similarly to hydrocyanation and acetoxylation, the copper-catalyzed oxycyanation of butadiene is very sensitive to the presence of different additives. The latter were selected as examples of (a) representative ligands presenting very different coordinating abilities (pyridine, PPh$_3$), (b) a Lewis acid (ZnCl$_2$), (c) salts of three transition metals classically used in oxidation studies (Co, Fe, and Pd), and (d) LiBr and HBr because their activation effect on bromides

and protonic acids has been established in previous works (*1, 8–10*).

The CuBr–CuI catalyst in the absence of any additives affords the dinitrile in 22% yield; higher yields are obtained when LiBr (yield 33%) or concentrated aqueous HBr (yield 60%) is used as additive ([Cu/[additive] = 2). All the other additives tested have no significant effect (H$_2$O, CoCl$_2$: 24; FeCl$_3$, ZnCl$_2$: 18%) or act as inhibitors [particularly pyridine (3%) and PdCl$_2$ (0%)]. The dramatic inhibiting effect of PdCl$_2$ is not clearly understood at present.

Influence of Oxygen Pressure

The yield of dicyanobutene increases with the oxygen pressure and then remains practically constant for pressures higher than 50 bar (Fig. 1). In the absence of oxygen, the hydrocyanation product of butadiene (3-pentenenitrile) is formed (scheme 1, reaction c) together with traces of the dinitrile. The yield of 3-pentenenitrile is limited
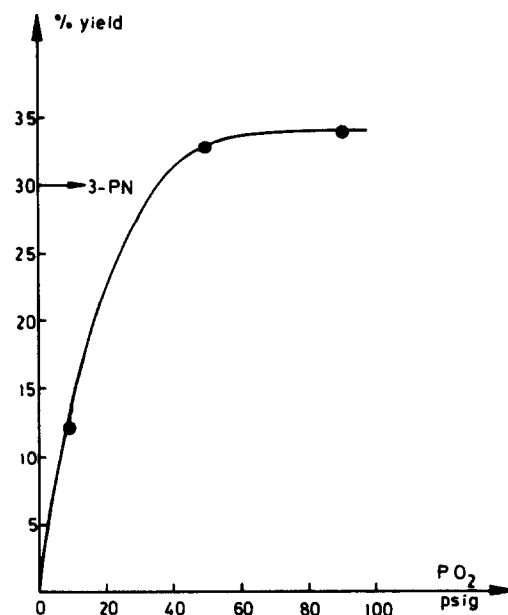

FIG. 1. Influence of oxygen pressure on the yield of dicyanobutene formation. Conditions: see Experimental. *Note.* 3-Pentenenitrile (3-PN) is formed under nitrogen atmosphere (PO_2 = 0); yield = 30%. Traces of dicyanobutene, however, are detected by GLC even under nitrogen.

to 30% under the present conditions in op-position to the 90% yield with the CuBr/LiBr system (*7, 8*).

Influence of the Solvent

Nitriles as solvents can be considered as generally effective for the production of di-cyanobutene. [The yield in acetonitrile is 22% in the *absence* of additives but it increases in the presence of some additives (up to 60% in the HBr case).]

Under the same conditions, most of the other solvents tested, such as acetic acid, methanol, DMF, DMSO, and water, give much smaller yields (<3%). Complete inhi-bition occurs with basic solvents such as pyridine, quinoline, and morpholine.

In pyridine as solvent, small amounts (6%) of 2-cyanopyridines are detected un-der the same conditions when isoprene and 1,3-pentadiene are used instead of butadi-ene; formation of the heterocyclic nitrile cannot therefore be attributed to a substitu-tion reaction on the pyridine solvent. More-over, an even higher yield of-2-cyanopyri-dine (15%) was obtained in DMSO as solvent in the absence of pyridine.

Even in acetonitrile, traces (<0.1%) of 2-cyanopyridines are detected by GLC–MS.

Influence of the Substitution of the Diene

The best yields of dinitrile (33 and 60% in the presence of LiBr and HBr, respec-tively) are obtained in the butadiene case. Much lower yields are observed with iso-prene (3%), 1,3-pentadiene (17%), and 1,3-cyclooctadiene (10%) (LiBr present).

DISCUSSION

Comparison of the oxycyanation and diacetoxylation reactions of butadiene re-veals a trend showing similarities with the cases of hydrocyanation (*8, 9*) (scheme 1, reaction c) and hydroacetoxylation (scheme 1, reaction b) (*10*).

(a) The oxycyanation reaction (scheme 1, reaction d) appears to be more regioselec-tive than the diacetoxylation process

(scheme 1, reaction a). This can be attrib-uted to promotion, by the catalysts used, of the isomerization of the diacetoxybutenes (1,4 to 3,4 addition = 1.8 at equilibrium). Such side reactions were not observed with the nitriles.

The distribution of isomers remains very different in the case of diacetoxybutenes [linear to branched products = 1.0 (*1, 10*)] relative to the dicyanobutenes (linear to branched product > 9). Note that this isom-erization proceeds also with monoacetoxy-butenes 1,4 to 3,4 addition = 0.6 at equilib-rium), but at a much higher rate than in the diacetoxylation reaction, equilibrium not being reached under the reaction conditions in the latter case (*10*).

(b) The oxycyanation reaction requires that the catalyst contain a halogen ion; the most effective system contains bromide an-ion. Such a requirement was also encoun-tered in other reactions shown in Scheme 1.

The presence of substantial amounts of CuI in the particular case of the oxycyana-tion system is necessary to avoid the forma-tion of cyanogen by oxidation of HCN. However, despite some similarities, the copper-catalyzed oxycyanation (scheme 1, reaction d) of conjugated dienes has some aspects essentially different from the oxida-tive diacetoxylation reaction of butadiene (scheme 1, reaction a) (*1*), as indicated be-low.

(1) The most significant difference be-tween diacetoxylation and dicyanation is regioselectivity; the cyanation reaction pro-duces the linear isomer [linear (I) to branched (II) dinitrile > 90:10] with good selectivity.

I   II

(a) X = CA
(b) X = OAc
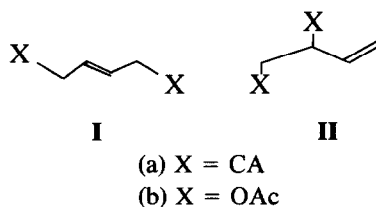
In contrast, the diacetoxylation reaction leads to a mixture of isomers generally

$$2 \text{ HCN} + 2 \text{ Cu}^{++} \longrightarrow 2 \text{ Cu}^{+} + 2 \text{ H}^{+} + 2(\text{CN})\cdot$$
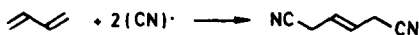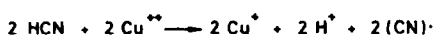
SCHEME 3

close to equimolecularity with copper catalysts.

(2) A marked effect of the solvent on the course of the reaction was observed in the dicyanation process: the formation of dinitriles in appreciable yields remains limited to the use of acetonitrile, whereas other solvents (pyridine, DMSO) favor the formation of cyanopyridines. This last aspect is discussed further in the subsequent sections.

The mechanism of the reaction cannot yet be explained in great detail owing to the complexity of the catalytic system. However, as in the hydrocyanation and acetoxylation reactions, the halogen ion (Br⁻, I⁻) plays a definite role as shown by the effect of added LiBr and HBr.

The participation of a halogenation step is very probable in the present case as shown by the GLC–MS detection of traces of 1,4-dibromo-2-butene and of a monobromoderivative (probably a bromocyanobutene) with butadiene, as well as the formation of traces of isomeric dibromo derivatives with isoprene. The role of oxyen would consist of a generation of halogenating entities (Br_2, $CuBr_2$, etc.), and a mechanism proceeding through bromide addition to the diene followed by nucleophilic substitution appears plausible (copper-catalyzed oxyhalogenation is the basis of important industrial processes).

The halogenation of conjugated dienes by $CuCl_2$ in acetonitrile has been reported as notably regioselective in favor of the 1,4-addition product (1,4/3,4 = 85/15) (13). However, nucleophilic substitution of the 1,4- and 3,4-dihalogenobutenes resulted in very different distributions of products relative to the diacetoxylation of butadiene (1). Thus, the mechanism in the diacetox-

ylation reaction appears to be more intricate than a simple halogenation–nucleophilic substitution sequence. Nevertheless, HCN is more oxidizable than Br⁻ or I⁻ (11) in aqueous solution, the oxidation of HCN being the basis of the industrial production of cyanogen ($E^0CN_2/2HCN = 0.3$, $E^0I_2/2I^-$ = 0.53, $E^0Br_2/2Br^- = 1.06$, $E^0Cu^{2+}/Cu(CN)_2^- = 1.12$ V).

Hence, the participation of a radical mechanism based on the generation of cyanide radicals (Scheme 3) would appear to be a plausible alternative. However, the reported oxidoreduction scale has been determined in water and cannot necessarily be extrapolated to acetonitrile. Moreover, a radical inhibitor such as diter-butylcresol presents no significant effect.

The copper ions are certainly more intimately involved in the process than suggested by Scheme 3, copper ions participating probably in electron transfer to intermediate radical species as proposed tentatively in Scheme 4 (path a).

The Cyanopyridines

The formation of cyanide radicals can
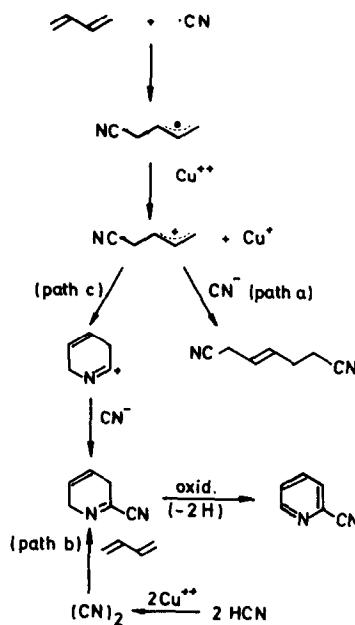
SCHEME 4

best explain the formation of cyanopyri-dines which may result from formal Diels–Alder addition of cyanogen onto the diene: formation of small amounts of cyanogen has in fact been observed during our experiments (scheme 4, path b). Other pathways, however (e.g., scheme 4, path c), cannot be completely excluded at the present time. Although nitriles are known as poor dienophiles, it has been reported that they are sufficiently activated for cycloadditions if they bear an electron-attracting group (12) (as is the case for cyanogen).

It is noteworthy that traces of an additional isomer, 4-cyanopyridine, are detected when the reaction is run in pyridine as solvent. This shows that substitution of this solvent occurs but constitutes a minor pathway in this reaction (such a substitution reaction, however, is not responsible for the formation of 2-cyanopyridine as methylated-2-cyanopyridines are produced from isoprene and 1,4-pentadiene in pyridine as solvent and as the reaction proceeds in DMSO in the absence of pyridine).

The different behavior of the solvents promoting dinitriles relative to the formation of 2-cyanopyridines could be associated with modification of the relative rate of the bromine addition mechanism (a typically ionic process that would favor the dinitrile formation) and of the radical process (which would be responsible for cyanopyridine formation). It is noteworthy that the dinitrile is effectively produced even in the presence of large amounts of phenolic radical scavengers. Moreover, conditions (such as the use of CuI in the catalytic composition) that impede the formation of cyanogen (a product of the radical oxidation of HCN) actually promote the formation of the dinitrile. These two observations therefore support the hypothesis that two fundamentally different mechanisms are responsible for the duality of reaction pathways.

It is concluded that, because of the relatively low yields and the poor activity, of the catalyst, copper-catalyzed oxydicyanation of butadiene is of less interest than the

corresponding hydrocyanation from the preparative point of view. In contrast to the diacetoxylation reaction, however, the reaction is very regioselective.

The present study stresses that the application of copper catalysis is potentially very rich in various possibilities as shown by the formation of such different products as nitriles, cyanopyridines, and esters from conjugated dienes.

The key role of bromide ions in all these copper-catalyzed processes is further confirmed. A mechanistic hypothesis for dinitrile formation is based on bromination of the diene, but participation of a radical mechanism involving cyanide radical (and eventually of cyanogen) to explain cyanopyridine formation must also be considered.

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