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PREPARATIVE AND MECHANISTIC ASPECTS OF COPPER-CATALYZED HYDROCYANATION OF UNSATURATED HYDROCARBONS. PART II*

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Summary

The CuBr-catalyzed hydrocyanation of conjugated dienes and of vinyl ethers has been investigated. The substitution of the diene system affects considerably the yield of the reaction, butadiene affording the best yield of nitrile whereas substituted diene systems react more sluggishly than butadiene and/or lead to extensive polymer formation.

The reaction appears to be very regioselective as one nitrile isomer is very selectively formed in all the investigated cases. The hydrocyanation reaction appears to proceed through the formation of copper–allyl species whereas polymers would be formed by a cationic process.

Introduction

The addition of HCN to unsaturated compounds is an important reaction which has several applications in the field of fine and industrial organic synthesis such as that of cyanhydrins (in relation to the synthesis of acrylates and methacrylates), amino alcohols, hydantoins, prostaglandines, natural products, nitriles, etc. [2 - 6]. However, the main industrial application is the synthesis of nitriles by catalytic hydrocyanation of unsaturated hydrocarbons in relation to the development of important monomers (acrylonitrile, adiponitrile) for the polymer industry.

The most active catalysts for the hydrocyanation of unsaturated hydrocarbons are derivatives of metals from Group VIII, VI and Ib of the Periodic Table, with most investigations having employed catalysts from Group VIII (mainly nickel, such catalysts being involved in the Du Pont process for the

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*For Part I, see ref. 1.

synthesis of adiponitrile [6, 7]). The most important applications of copper catalysts in the field of hydrocyanation reactions involve copper halides (mainly CuBr and CuCl) which have been used to catalyze the hydrocyanation of acetylenes and thus constituting an important industrial process for the production of acrylonitrile [8]. Recent patents have reported on the advantages of copper relatively to nickel as catalysts for the hydrocyanation of butadiene (low price, stability, high selectivity for addition reactions). In comparison with nickel catalysts, copper-based systems have been relatively little studied from a mechanistic point of view, although there have been some interesting recent developments [9 - 11]. However, as the copper-catalyzed hydrocyanation of butadiene has to date been limited to the monoaddition of HCN, this reaction has not as yet been applied on an industrial scale for the preparation of Nylon-6,6, for example.

The present publication completes our recent series of reports in this field and affords additional information relating to the influence of substrate structure on the course of the copper-catalyzed hydrocyanation of unsaturated hydrocarbons.

Experimental

Materials

All the olefins and solvents were commercial products and used after distillation under nitrogen. Copper(I) bromide was purified by washing with acetic acid in the presence of SO_2.

Reaction procedure

The procedure employed for hydrocyanation has been reported previously [1].

Analytical procedure

Gas–liquid chromatography was performed using a Varian 2800 chromatograph equipped with a catharometer detector. The columns consisted of 10% FFAP on Chromosorb W (1/8 in diameter, 6 ft length), the temperature being increased at a rate of 9 °C min⁻¹ from 90 °C to 190 °C. The carrier gas was He at a flow rate of 30 ml min⁻¹. ¹H NMR spectra were recorded on a Varian T60 or a Cameca Model 250 spectrometer, while the IR spectra were recorded on a Perkin–Elmer 21 spectrometer. A Varian Model MAT 112 mass spectrometer coupled to a Varian 1400 chromatograph was used to detect the dimer and trimer byproducts.

Identification of products

All the nitriles displayed the typical absorption for the cyano group which occurs at 2250 cm⁻¹ in the IR spectral range.

Pentene nitriles

The isomers of pentene nitrile were identified by comparison with authentic samples using GLC and mass spectrometric techniques.

2-Ethoxypropionitrile (hydrocyanation product of ethyl vinyl ether)

The NMR spectrum (registered on a Varian T60 spectrometer) showed the presence of an ABX_3 and an AX_3 system. ABX_3: A, δ = 3.52 and 3.74 ppm, qt; $^3J_{AB} \simeq 6.5$ Hz and $^3J_{X_3-A_VB} \simeq 6.5$ Hz. The corresponding methyl absorbed at δ = 1.21 ppm. AX_3: methyne, δ = 4.25 ppm; $^3J_{AX}$ = 6.7 Hz. The corresponding methyl (doublet) absorbed at δ = 1.47 ppm.

4-Methyl-3-pentene nitrile (hydrocyanation product from isoprene)

The NMR spectrum (registered on a Varian T60 spectrometer) exhibited signals at δ (from HMDS) (CCl_4): 1.63 (s, 3H, CH_3 trans), 1.71 (s, 3H, CH_3 cis), 2.88 (d, $^3J_{AX}$ = 6.8 Hz, 2H, CH_2—CN), 5.06 (t, $^3J_{AX}$ = 6.8 Hz, 1H, olefinic proton) ppm. The singlets observed at 1.63 and 1.71 ppm are broad and arise from long distance couplings.

Trans-2-methyl-3-pentene nitrile (hydrocyanation product from piperylene)

The NMR spectrum (registered on a Cameca Model 250 spectrometer) exhibited signals at δ (from TMS) ($CDCl_3$): 1.35 (d, $3J_{X-K_3}$ = 7.2 Hz, 3H (C^2H_3)); 1.71 (d, d, $^3J_{A-Y}$ = 6.3 Hz, $^4J_{M-Y}$ = 1.3 Hz, 3H (C^1H_3)); 3.28 (q, t, X part of a subsystem AMX, $^3J_{X-K_3}$ = 7.2 Hz, $^3J_{M-X}$ = 6.3 Hz, $^4J_{A-X}$ = 1.5 Hz, 1H, =CH(CN)(CH₃)—); 5.36 (q, $^3J_{A-M}$ = 15.5 Hz, 1H, CH—C(CN)) and 5.81 (st of d, subsystem AMX coupled to Y_3, 1H, CH₃—CH=) ppm. The trans configuration has been attributed to this isomer since $^3J_{A-M}$ = 15.5 Hz. The cis isomer is however present as a minor component (15%) as shown by the superposition of extra peaks, particularly in the δ = 1.35 and 1.71 ppm region, showing the presence of a similar system shifted by 1.5 Hz from the corresponding trans system.

Results

The copper-catalyzed hydrocyanation of butadiene leads essentially to the 1,4-monoaddition product (unsaturated nitrile) with the addition of a second molecule of HCN being undetected under standard hydrocyanation conditions [1]. The influence of substituents on the reactivity of the conjugated diene system as well as on the regioselectivity of the reaction of some typical conjugated dienes is summarized by the data in Table 1.

Nitrile yields decrease sharply as the degree of substitution of the diene is increased. No correlation between the nitrile yields and the coordinative ability of the olefins was observed [12]. However, the substituent position on the diene influences the hydrocyanation reaction since the use of isoprene leads to a nitrile yield three times larger than with piperylene. The decrease in nitrile yield as the degree of substitution of diene increases has also been observed in the nickel-catalyzed hydrocyanation of isoprene and piperylene, these substrates affording nitrile yields of 26 and 74%, respectively [13].

TABLE 1

Hydrocyanation of substituted 1,3-dienes catalyzed by copper bromide[a]

Experiment No.	Diene	Mononitriles	Yield (%)	Other products and remarks
1	butadiene	trans-2-pentene nitrile[c]	68	traces of polymer[e]
		cis-2-pentene nitrile[c]	3	
		2-methyl-3-butene nitrile[c]	4	
2	isoprene[b]	4-methyl-3-pentene nitrile	39	oligomers + telomers[d] (5%) + polymers (22%)
3	piperylene[b]	trans-2-methyl-3-pentene nitrile	12	oligomers + telomers[d] (5%) + polymers (82%)
		cis-2-methyl-3-pentene nitrile	1 - 2	
4	2,3-dimethyl-1,3-butadiene	traces[d]	2	dimers (3%) + polymers (25%)
5	2,4-dimethyl-1,3-pentadiene	—	0	dimers (60%) + polymers (40%)
6	2,5-dimethyl-2,4-hexadiene	—	0	no reaction
7	1,3-cyclohexadiene	—	0	no reaction
8	cyclopentadiene	—	0	polymers (100%)

[a]Reaction conditions: catalyst, CuBr (0.0025 mol), Cl$_3$CCOOH (0.0030 mol); solvent, CH$_3$CN (0.0243 mol); reagents, diene (0.052 mol), HCN (0.107 mol); temperature, 79 °C; reaction time, 16 h.
[b]Traces of isonitrile detected in the raw reaction product by IR spectroscopy.
[c]Products identified by GLC comparison with authentic samples.
[d]Products detected by GLC–mass spectrometric techniques.
[e]These polymeric residues are mainly formed by the polymerization of the olefin substrates, although the products and HCN may contribute in some cases to the formation of the polymer fraction. (The yield of polymers reported in the table have been calculated relative to the diene.)

The regioselectivity of HCN addition onto dienes is very high with copper catalysts, as shown by the considerable preference for 1,4-addition in the case of butadiene (ratio of linear to branched nitriles, 18). Furthermore, the present investigation shows that 1,4-addition to isoprene is even more regioselective than for butadiene (100% selectivity). It is worthy of note that in the copper-catalyzed hydrocyanation of isoprene (and piperylene) the regioselectivity seems to be essentially governed by electronic factors (Table 1, expt. 2) and leads to the formation of the very stable allylic cation through protonation of the diene. This result contrasts sharply with that obtained for the nickel-catalyzed reaction where protonation occurs exclusively on the opposite, less-substituted side of the isoprene

molecule [13]. This striking difference between copper and nickel hydrocyanation catalysis is also demonstrated by the much lower regioselectivity of nickel catalysts (ratio of 1,4- to 1,2-addition product with nickel/1,4- to 1,2-addition products with copper is 1/18 for butadiene and 1/∞ for isoprene).

The remarkably high stereoselectivity of copper and nickel catalysts is also demonstrated by the fact that they lead to the preferential formation of the trans isomers with butadiene and pentadiene (Table 1, expts. 1 and 3; see also ref. 13). In contrast, the nickel-catalyzed hydrocyanation of mono-olefins leads almost exclusively to the formation of the cis isomers [14].

Side-reactions such as oligomerization, telomerization and polymerization are also observed with substituted 1,3-dienes. Dimers and trimers are formed from isoprene, piperylene, 2,3-dimethyl-1,3-butadiene and 2,4-dimethyl-1,3-pentadiene. Telomers resulting from the condensation of two molecules of diene and one molecule of HCN (2–1 telomers) are observed with isoprene, piperylene and 2,3-dimethyl-1,3-butadiene. A telomer (3–1) is also formed with the latter substrate together with polymers. Obviously, these reactions are, at least in part, the result of cationic processes since the acidic co-catalyst (Cl$_3$CCOOH) on its own can catalyze the formation of dimers and oligomers (but less efficiently, however, than copper) (see Table 2).

TABLE 2

Formation of dimers from 2,4-dimethyl-1,3-pentadiene under hydrocyanation conditions

Catalyst	Co-catalyst	% Dimer
—	Cl$_3$CCOOH	27
CuBr	—	48
CuBr	Cl$_3$CCOOH	65

The IR spectra demonstrate the formation of small amounts of isonitriles (typical IR absorption at 2150 cm^{-1}) under hydrocyanation conditions, except in the case of butadiene and 1,3-cyclooctadiene. Only a very weak absorption was detected with the high boiling fractions obtained from 2,4-dimethyl-1,3-pentadiene, the dimer of the substrate being the main reaction product in this case.

An isolated olefin double bond is incapable of reacting under the conditions employed as has been demonstrated with 1-hexene, 2-phenyl-2-butene, cyclohexene, allylic cyanide and acrylic acid. However, vinyl ethers such as ethyl vinyl ether react to a reasonable extent (yield, 20%; reaction product, 2-ethoxypropionitrile).

The fact that a small amount of cyclohexyl bromide is detected when cyclohexene is added to the copper-catalyzed hydrocyanation process is not particularly significant as far as the mechanism of the reaction is concerned; alkyl bromides do not participate in the catalytic cycle whereas allylic

bromides do. In fact, alkyl bromides do not appear to have any activating effect on copper(I) catalysts in contrast to allylic bromides such as crotyl bromide [1].

Discussion

Kinetic studies of the copper-catalyzed hydrocyanation of butadiene have enabled the key activating role of halides to be demonstrated in the catalytic cycle, and have led to the proposal of a mechanistic scheme based on initial protonation of the diene, the participation of copper–π-allyl type species being probably involved in the subsequent steps [1].

With conjugated dienes, the decrease in the nitrile yield as a result of the hindered formation of π-allyl substitution may be, in part, the result of the hindered formation of π-allyl type intermediates (A–B) (Scheme 1) as reported with nickel(0) catalysts [15], but the competition of cationic side-reactions (oligomerization) is obviously enhanced by the presence of electron-donating methyl substituents on the diene group. The position of the methyl groups on the diene has a noticeable effect on the relative rates of hydrocyanation and the side-reactions, as shown by the inversion of the nitrile to polymer ratio in the cases of isoprene and piperylene (Table 1, expts. 2 and 3; compare also expts. 4 and 5).

Copper–allyl complexes present in solution probably appear in the form of an equilibrium between the π and σ forms. The preferential

dimers, polymers, isonitriles, telomers (favoured with some substituted dienes)
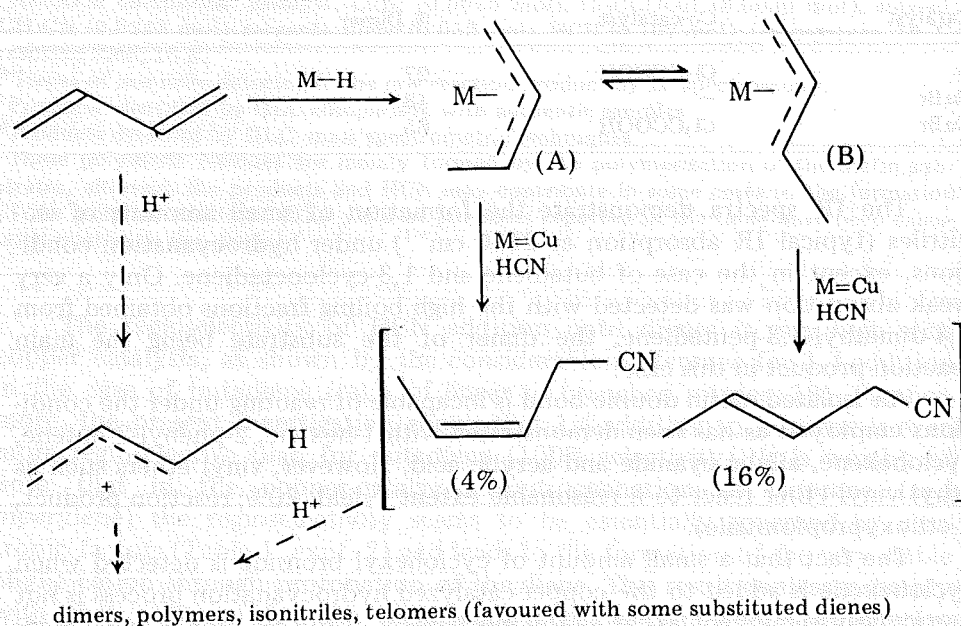
Scheme 1.

nucleophilic attack of the σ_{-1} forms will explain the observed selectivity for the linear nitrile isomer (ratio of linear to branched nitriles is 18 with butadiene), the selectivity in favour of the *trans* isomer resulting from the higher stability of B (*syn*) relatively to A (*anti*) conformations.

Thus the regioselectivity of the reaction should result both from electronic and steric effects. The exclusive attack of the cyano group onto the less hindered site of isoprene indicates that the latter effect predominates.

The high stereoselectivity of the copper-catalyzed hydrocyanation of 1,3-dienes must therefore result from the configuration adopted by the allyl–copper complex. The preferential formation of the *trans* isomer could be explained by the substantially higher stability of the *syn* relative to the *anti* configuration. The participation of such *syn,anti* configurations provide the basis for the explanation for *trans,cis* selectivities in typical nickel-catalyzed oligomerization reactions, typically in the formation of 1,3-hexadienes from butadiene and ethylene [16].

Side-reactions, particularly oligomerizations, are therefore obviously the result of cationic processes, the cationic species being formed by attack of either an acid copper complex of type H[Cu(CN)$_2$] or Cl$_3$CCOOH on the diene as shown by dimer formation from 2,4-dimethyl-1,3-pentadiene in the presence of the latter acid (no CuBr being present). Isonitrile formation probably results from the competitive reaction to cationic oligomerization of the dienes. The formation of isonitriles, which is equivalent to a reverse addition of HCN to the diene, should result from an attack of the hard cation on the harder site (N) of the cyanide moiety, as observed in the case of the copper-catalyzed hydrocyanation of terminal disubstituted mono-olefins which leads exclusively to isonitrile formation [17].

The activity of copper compounds as catalysts for HCN addition seems to be linked to the facile formation of stabilized intermediates brought about by initial protonation of the olefin. Hence the formation of stabilized cations (*e.g.* the t-butyl cation) or of a species stabilized by coordination to copper (*e.g.* the allylic cation, (CH$_3$–$^+$CH–OR), ...) seems an essential feature necessary to enable the catalytic cycle to proceed.

In the copper-catalyzed hydrocyanation of 1,3-dienes and other activated olefins it has not proved possible to detect any copper–allyl intermediates to date, but the formation of such species as transient intermediates provides the best explanation for the results. It is likely that such copper–allyl species are highly unstable and hence have only been proposed as tentative explanations for some copper-catalyzed reactions [18, 19]. In fact, the occurrence of highly unstable entities is very frequently encountered in copper-catalyzed processes such as in typical carbene oxidation reactions and reactions of organic halides with copper carboxylates [20].

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A COMPARISON OF POLYMER-SUPPORTED CHLOROTRIS-(TRIPHENYLPHOSPHINE)RHODIUM(I) TO ITS HOMOGENEOUS ANALOG IN THE SELECTIVE REDUCTION OF POLYNUCLEAR HETEROAROMATIC COMPOUNDS

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Summary

A comparison between polymer-supported chlorotris(triphenylphosphine)rhodium(I) catalyst, P —Ph$_2$PRh(Ph$_3$P)$_2$Cl, and its homogeneous analog in the selective hydrogenation of polynuclear heteroaromatic compounds provides evidence for differences in initial rates and in ability to exchange aromatic hydrogens for deuterium. Crosslinking of the polymer-supported catalyst also affected the hydrogenation rates, but diffusion into the polymer bead and surface mass transfer effects were not rate-limiting. High regioselectivity for the reduction of the nitrogen heterocyclic ring was found in the hydrogenation of a model coal liquid with the polymer-supported catalyst.

Introduction

Recently, we found that a wide variety of transition-metal compounds catalyze the regiospecific reduction of polynuclear heteroaromatic nitrogen and sulfur compounds [1 - 3]. These findings may, in fact, have important effects on various synthetic fuel processes. Hydrogen gas consumption is known to be an economically limiting factor in the up-grading of synthetic fuels and in the removal of nitrogen and sulfur from these complex matrices. Hydrogen gas consumption by selective hydrogenation will be lower; furthermore, the reactions described in our previous homogeneous studies were carried out at lower temperatures and pressures than are used in conventional industrial processing.

Homogeneous catalysts have their own limitations in that recovery is often difficult or impossible. In addition, thermal stability and solubility may also present problems in practical applications. The use of polymer supports, such as crosslinked polystyrene–divinylbenzene (PS–DVB), as well as silica and alumina, to anchor homogeneous transition-metal catalysts

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