

Copper-Catalyzed Acetoxylation (Hydroacetoxylation) of Butadiene: A Comparison with the Hydrocyanation Reaction

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Copper bromide catalyzes the monoaddition of acetic acid to butadiene (and less effectively to substituted conjugated dienes) yielding mixtures of acetoxybutenes. The presence of LiBr as additive is necessary for efficient catalytic activity. The efficiency of the catalyst can be further improved by adding halogenated additives and strong carboxylic acids. In contrast, complexing ligands (e.g., PPh₃ polyethers) inhibit the catalyst activity. When compared with the copper-catalyzed hydrocyanation of butadiene, the regioselectivity of the acetoxylation is low, easy interconversion of the linear and branched isomeric products being achieved under the reaction conditions, the 1,4-isomer corresponding to the thermodynamically controlled one. © 1986 Academic Press, Inc.

INTRODUCTION

The production of diacetoxybutenes from butadiene and acetic acid under oxidative conditions has received much attention, both copper (1), palladium (2-4), and rhodium (5) derivatives being active catalysts for this reaction. Similarly, the *addition* reaction of carboxylic acids to butadiene in the absence of oxygen is catalyzed by both copper (1) and palladium catalysts (6). On the other hand, HCN addition to conjugated dienes (7) is efficiently catalyzed by copper halides. The subject of the present publication is to report on the Cu-catalyzed addition of acetic acid (Eq. (a)) to butadiene and to compare the activity-selectivity pattern of both systems.

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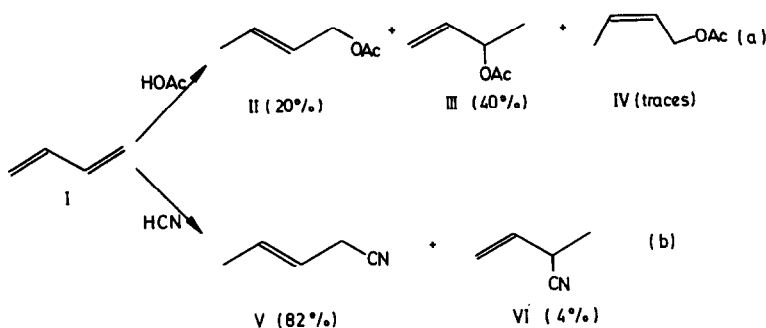
EXPERIMENTAL

Materials. Copper salts (CuBr, CuBr₂, CuCl, CuI, CuCN, Cu(OAc)₂, CuSO₄) and oxides as well as alkali metal salts (LiBr, LiCl, LiI, LiF, LiOAc, KBr, NaBr, CsBr) were commercial products used as such.

Solvents and reagents. Acetic acid (PA quality from Merck) was used as such. Butadiene was dried and handled as reported in Ref. (7).

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

Typical acetoxylation procedure. Most of the experiments were run in sealed glass tubes (15 ml) containing the copper salt (2.5 mmol), the alkali metal halide (10 mmol), the diene (52 mmol), and acetic acid (52 mmol = 3 ml). Each tube was inserted into an aluminum protective sheath and then introduced into a basket rotating in a water bath heated to the required temperature. The tubes were opened after cooling in liquid nitrogen. Butadiene was allowed to es-



cape at room temperature in a hood and the residue was analyzed by GLC (dibutyl phthalate being added as an internal standard for quantitative measurements).

Li-7 NMR studies. Lithium-7 NMR spectra were obtained either with a Bruker WP-80 or a Bruker AM-300 WB spectrometer. The longitudinal relaxation times T_1 were measured with the AM-300 WB apparatus by using the ($T - 180^\circ - t - 90^\circ$) sequence. The 10 t values have been used to calculate the T_1 's by fitting the experimental points to an exponential curve.

Assuming a 1/1 stoichiometry for a lithium complex, the observed relaxation rate (T_1)⁻¹ is given by the equation

$$(T_1)^{-1} = p_A(T_{1A})^{-1} + p_B(T_{1B})^{-1}$$

where A and B refer, respectively, to the free (solvated) cation and to the bound cation and p is the mole fraction. An iterative fitting of the data points to this equation, transformed by expressing these mole fractions in terms of binding constant and concentrations, was performed until self-consistency, was obtained.

EPR measurements. EPR spectra were obtained with a Varian E-12 spectrometer working in the X band ($\nu = 9.55$ GHz), the static field being modulated at 100 kHz. The g factors were measured by comparison with the DPPH (diphenylpicrylhydrazyl) signal as a reference.

RESULTS

Under the conditions described under Experimental (standard conditions), the

acetoxylation of butadiene yields 60% (relative to butadiene) of a mixture of 3-acetoxy-1-butene and of 1-acetoxy-2-butene (ratio ~0.5 for conversion ranging from 2 to 60% (12 h), rising to 0.6 for reaction time up to 20 h). Traces of an additional isomer IV (probably *cis*-3-acetoxy-2-butene) are also detected by GLC-MS).

A comparison between acetic and hydrocyanic acid addition to butadiene is particularly informative from the mechanistic point of view. Indeed, the copper-catalyzed addition of acetic acid to butadiene presents some sharp differences when compared to hydrocyanations (7):

(a) The acetoxylation reaction is much less regioselective than the hydrocyanation reaction: the equilibrium between the linear (II) and branched (III) isomers being approached under the reaction conditions (II/III = 0.5; $K_{II/III} \approx 1.0$). In contrast, the hydrocyanation reaction affords a much higher ratio of linear to branched nitriles (95 : 5) (7).

(b) The acetoxylation reaction requires the presence of LiBr as a co-catalyst, in contrast to the hydrocyanation reaction which is efficiently catalyzed by CuBr even in the absence of LiBr both in acetonitrile and *in acetic acid* as solvents. CuBr₂ is also an active catalyst but it is reduced to CuBr under the reaction conditions.

Various other copper derivatives such as CuCl, CuI, Cu(OAc)₂, CuSO₄, and copper oxides have been tested but they afforded much less active catalysts than the copper bromides, the presence of LiBr being more-

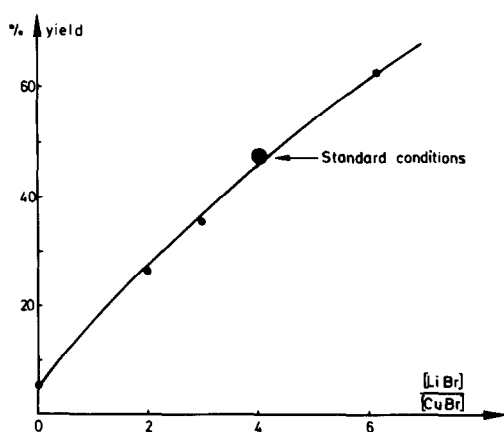
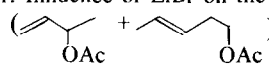


FIG. 1. Influence of LiBr on the yield of acetoxy-butenes () after 20 h. $\text{CuBr} = 0.0025$ mol, butadiene = 0.052 mol, HOAc = 0.052 mol (3 ml). $T = 73^\circ\text{C}$.

over required in every case to obtain notable catalytic activity. The particular case of CuCN will be discussed later. Essentially, *homogeneous solutions* were obtained under the reaction conditions with CuBr, CuBr₂, CuCl, Cu(OAc)₂, the other copper derivatives (particularly CuI) being much less soluble than the former ones.

Influence of additives and co-catalysts. Similarly to the hydrocyanation reaction (7), the copper-catalyzed acetoxylation of butadiene is very sensitive to the presence of different additives: some promote the reaction (particularly LiBr; crotyl bromide, a potential intermediate, presenting also some activating effect), while other types of additive inhibit the reaction (e.g., PPh₃, polyethers, amines). The effect of a radical scavenger has also been considered in order to control the eventual participation of a radical-type mechanism.

(a) *Influence of alkali bromides.* Lithium bromide is the most efficient promoter of the reaction catalyzed by CuBr, other alkali metal bromides as well as other lithium halides being much less efficient co-catalysts (yields after 12 h at 73°C: LiBr: 35, NaBr: 2, CsBr: 2%. LiCl: 26, LiI: 5, LiF:

0); lithium acetate is also inefficient (yield: 2%). Moreover, the additive (LiBr) must be preferably in excess relatively to copper (Fig. 1). One of the roles of LiBr consists in solubilizing the copper salt (CuBr); however, the importance of the bromide ion is established by the poor yields obtained with other lithium salts, although LiCl is also a rather active promoter.

Moreover, all the above systems lead to practically the same mixture of isomers (1,4/3,4 addition products = 0.5). This distribution is to some extent affected by the equilibrium between the isomers which is efficiently catalyzed by the copper derivatives present in the system. This point was checked after 8 h starting from 3-acetoxy-1-butene and after 12 h from 1-acetoxy-2-butene at 73°C (ratio of branched **III** to linear **II** isomer = 1.0 when starting from both isomers). Moreover, a small amount (~10%) of an additional isomer **IV** (*cis*-1-acetoxy-2-butene) is also present at equilibrium.

The isomer distribution during the reaction (**III/II** = 0.5 after 12 h; 0.6 after 20 h) is, however, notably different from the equilibrium value (**III/II** \approx 1.0, Fig. 3). The formation of the 1,4-addition product appears therefore to be kinetically controlled.

(b) *Influence of carboxylic acids as additives.* As observed in the hydrocyanation reaction, additives affect the reaction rate. Similarly to the HCN case, a very acidic co-catalyst (Br₃CCOOH) increases notably the rate and in fact the promoting activity of the acidic additives correlates to some extent with their pK_a in the bromoacetic acids series (Table 1). However, different promoting activities were observed for CF₃COOH, CCl₃COOH, and Br₃CCOOH (RCOOH) = 0.0025 mol. Respective yields after 12 h: 60, 70, 80%).

The fact that the lowest activity corresponds to the strongest trihalogenoacid (CF₃COOH) indicates that factors other than acidity contribute to these promoting cocatalytic abilities. The acidic additives do not present any catalytic activity of their

TABLE 1

Acetoxylation of Butadiene: Influence of pK_a of the Co-catalyst ($\text{Br}_x\text{CH}_{3-x}\text{COOH}$) on the Yield of Acetoxybutenes after 12 h

RCOOH	pK_a	Yield of diacetoxybutene ^a (%)
(CH_3COOH)	4.75	36
BrCH_2COOH	2.69	42
Br_2CHCOOH	1.40	50
Br_3CCOOH	0.66	60 (80) ^b

Note. Experimental conditions. Butadiene, 0.052 mol; acetic acid, 0.052 mol = 3 ml; CuBr, 0.0025 mol; LiBr, 0.010 mol. $T = 73^\circ\text{C}$. $t = 12$ h. $[\text{RCOOH}] = 0.00125$ mol.

^a Unreacted butadiene accounts essentially for the balance of products.

^b $[\text{Br}_3\text{CCOOH}] = 0.0025$ mol.

own as they are inactive in the absence of CuBr. Besides the promoting effect of alkali metal halides (particularly LiBr), the catalytic activity can also be further improved (as in the hydrocyanation case) by adding crotyl bromide to the medium (Table 2). Other additives such as cyanogen bromide (which increased the rate of the hydrocyanation reaction by a factor of 2), alkyl bromides or HBr/ H_2O present no important effect on the reaction rates. However, the presence of LiBr is required in all the above examples to obtain significant catalytic activity.

Isotropic effects of DOAc which decreases the rate by a factor of 2 is indicative of the participation of a proton transfer in the rate-determining step (a result to be compared with the increase of rate observed in the presence of a strong carboxylic acid).

(c) *Influence of ligands and complexants.* A strong inhibition of the reaction is observed with triphenylphosphine (after 12 h at 73°C , Cu/L = 0.5, yield: 2%) and polyethers (respective yields after 8 h at 73°C , Li/ether = 2, with 12-crown-4, 18-crown-6, diethylene glycol dibutyl ether: 4, 4, 8%. Li/ether = 4: 3,—, 13%. No ether present under the same conditions: 25%). Cyclic

polyethers present therefore a stronger inhibiting effect than linear ones but no particular inhibition by 12-crown-4 could be observed: therefore, a specific coordination of lithium does not seem to be responsible for the observed effects which could be rather related to coordination of the ethers to copper, an observation also supported by the fact that, relatively to the ligand L, lithium bromide is in excess in opposition to CuBr (Li/L = 2, Cu/L = 0.5 and Li/L = 4, Cu/L = 1).

(d) *Effect of a radical scavenger.* The limited influence of 2,6-di-*t*-butylcresol, a classical radical scavenger, is an indication for a nonradical mechanism: a moderate (20%) decrease of the rate is observed on adding the inhibitor (1:5 ratio relative to copper). The inhibition seems therefore to be related to an efficient competitive coordination of the phenol to the metal, as in the case of PPh_3 and ethers (see above).

Competition between the acetoxylation and the cyanation reaction. The use of CuCN instead of CuBr in the system acetic acid-acetic anhydride affords some particularly significant information. Copper(I) cyanide alone is inactive both for the hydrocyanation and for HOAc addition. It can however be activated by adding a haloge-

TABLE 2

Acetoxylation of Butadiene: Influence of Crotyl Bromide on the Yield of Acetoxybutenes after 12 h as compared to the Hydrocyanation Reaction (7)

Crotyl bromide CuBr	Yield of acetoxybutenes (%)	Yield of 3-pentenitrile ^a (%)
0	35	9
1	60 ^b	23
3	60 ^b	—
5	—	43

Note. Conditions: see Table 1.

^a Yield obtained after 135 min at 90°C (see Ref. (7)).

^b The accelerator (crotyl bromide) affords also the acetoxybutenes but the maximum amount of acetates resulting from the additive is respectively, 5% (crotyl bromide/CuBr = 1) and 15% (ratio = 3).

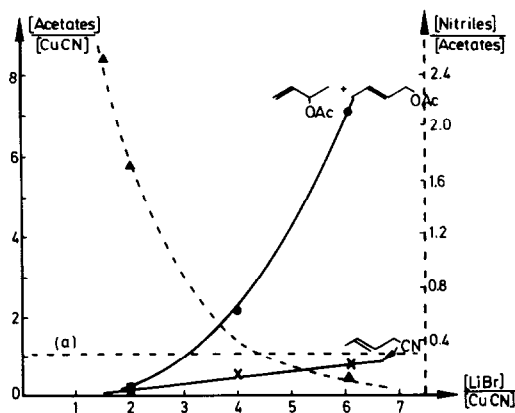


FIG. 2. Influence of LiBr-to-CuCN ratio on the yield of acetoxybutenes (●) and of 3-pentenenitrile (×) per mole of catalyst (CuCN) after 12 h. CuCN = 0.0025 mol, butadiene = 0.052 mol, HOAc = 0.052 mol (3 ml), $T = 73^{\circ}\text{C}$. (a) 100% conversion of CuCN to 3-pentenenitrile.

nated co-catalyst (crotyl bromide or BrCN in the HCN case, LiBr in the HOAc case) (7). It is noteworthy that 3-pentenenitrile is then formed together with the acetoxylation product (Fig. 2). Hydrocyanation therefore competes very efficiently with acetoxylation despite the fact that HOAc is in large excess relative to the cyanide (HOAc/CuCN = 20). The cyanide ion is a much better nucleophile than the acetate anion but the concentration in free cyanide anions must be very low as a consequence of the acidity of the medium. Therefore, this experiment supports the participation of a coordination mechanism for the introduction of the cyanide group into the butadiene moiety as proposed in our previous publication (7): the preferential coordination of the CN group on the copper center would be the determining factor. It is also significant that the hydrocyanation reaction can be very efficiently run both in HOAc and in acetonitrile (7) as solvents.

DISCUSSION

The copper-catalyzed acetic acid addition to butadiene appears to be different from the hydrocyanation reaction, despite

the fact that some similarities are observed between the two reactions. The most significant difference between copper-catalyzed acetic acid and HCN additions is the regioselectivity of the reaction: HCN addition produces very selectively the linear isomer (linear to branched nitrile, V:VI > 95:5). Moreover, the promoting effect of LiBr is essential in the acetoxylation case, whereas this additive is not required in the hydrocyanation case. In fact, the formation of the 1,2-isomer during the acetic acid addition to butadiene is kinetically controlled whereas the equilibrium between the isomers II and III can be achieved in the presence of the acetoxylation catalyst (Fig. 3). It is however noteworthy that this isomerization takes place notably more slowly under the reaction conditions (II/III \approx 0.5 for conversion from 2 to 60%; reaction time up to 20 h: II/III = 0.6) than during the isomerization experiments reported in Fig. 3. The main difference between the two cases is the presence of butadiene during the acetoxylation process: an inhibition effect of the diene on the isomerization reaction could explain the result (the coordination of olefins on copper(I) species is well established).

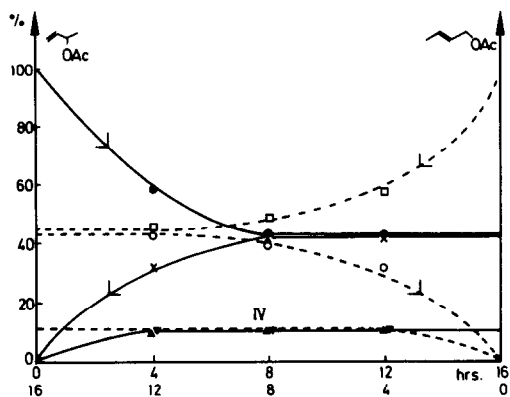


FIG. 3. Isomerization of the acetoxybutenes under the acetoxylation conditions. (—) Starting material = II (1,4-addition product), initially 5 mmol. (---) Starting material = III (1,2-addition product), initially 5 mmol. CuBr = 2.5 mmol, HOAc = 3 ml, LiBr = 10 mmol, $T = 73^{\circ}\text{C}$.

TABLE 3

Investigation of Cu(OAc)₂-LiX Systems by EPR Spectroscopy

Catalyst	Spectral parameters	
	<i>g</i> -value	<i>A</i> (cm ⁻¹)
Cu(OAc) ₂ + LiBr	2.05134	0.00208
	2.38226	0.0161
Cu(OAc) ₂ + LiOAc	2.04358	0.002233
	2.335776	0.0161

Note. Conditions: no Ac₂O, [Cu] = 10⁻⁵ M, [LiOAc] = 4 × 10⁻⁵ M.

The *mechanism* of the reaction cannot yet be explained in much detail owing to the complexity of the catalytic system. However, the role of LiBr is obviously determining for obtaining a significant catalytic activity: one of the effects of LiBr is to ensure the solubilization of CuBr in the acetic acid medium. However, besides the problem of solubility, lithium bromide participates effectively in the formation of the active species because other lithium halides or the bromides of other alkali metals are much less active cocatalysts. Therefore both the lithium and the halide ion participate in the formation of the catalytic species, the role of the halide being particularly determining.

Complexes such as LiCuX₂ and Li₂CuX₄ (X = Cl, OAc) are well known (8a). Some information relative to the structural surroundings of copper(II) ion in acetic solutions has also been obtained from EPR studies (8b, 8c): Cu(OAc)₂ is a diamagnetic dimer in dry acetic acid solution but signals are observed in the presence of added water as the monomeric Cu(OAc)₂ · 2H₂O complex is formed. In fact, we observed that the addition of LiOAc or of LiBr to the solution of Cu(OAc)₂ in acetic acid affords similar spectra, which allows us to infer that the environmental situation around the copper ion corresponds an octahedral geometry elongated along the *z*-axis (Table 3). However, copper-lithium interactions

TABLE 4

⁷Li NMR Spectra of the Butadiene (BD) Acetoxylation Catalyst

	Li/Cu	Conditions	(LiCl) ppm
LiBr	∞	BD	-2.65 (1)
		No BD	-2.59 (2)
LiOAc	∞	BD	-2.74 (3)
		No BD	-2.67 (4)
LiBr/Cu(OAc) ₂	1	No BD	-2.59 (5)
	2	No BD	-2.70 (6)
	4	No BD	-2.87 (7)
	4	BD	-2.66 (8)
LiOAc/Cu(OAc) ₂	4 ^a	No BD	-3.24 (9)
	4	BD	-4.25 (10)
	4	Isoprene	-3.90 (11)
	4	Toluene	-3.31 (12)

Note. Solvent: HOAc/Ac₂O = 2 [LiX] = 0.45 M. [hydrocarbon]/[LiX] [hydrocarbon]/[LiX] = 20. T = 25°C. Reference: LiCl (3M).

^a The solubility of Cu(OAc)₂ decreases for lower lithium acetate concentration.

seem to depend strongly on the nature of the anion. We have observed that, with lithium *acetate*, the signal of lithium (⁷Li NMR measurements) is notably shifted when Cu(OAc)₂ is added to the medium (Table 4, compare lines, 3, 4 to 9, 10). Conversely, the lithium signal of lithium *bromide* is little affected by the presence of copper acetate (Table 4, lines 5-8). These observations show that Li-Cu interactions are much more important in the absence of bromide ions, probably as the result of the bridging properties of the acetate ion.

Determination of the lithium-7 longitudinal relaxation rate versus copper concentration affords a means to estimate the strength of this interaction.⁵ Assuming 1/1 stoichiometry for the lithium complex, a reasonably good fit of the experimental points to the theoretical curve is obtained (see experimental part for details) (Fig. 4). A stability constant of ca. 90 M⁻¹ has been

⁵ We are indebted to a referee for having suggested investigation of ⁷Li relaxation.

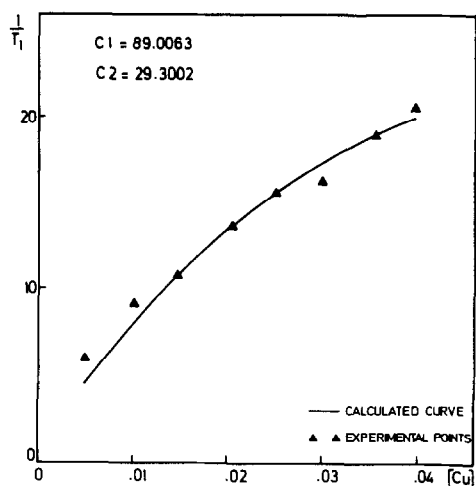


FIG. 4. Plot of the ${}^7\text{Li}$ relaxation rate versus copper ion concentration. $\text{LiOAc} = 0.0245 \text{ M}$, $T = 34^\circ\text{C}$.

calculated for the formation of such a complex: a significant interaction does occur between lithium and copper ions.

Conversely, with lithium bromide, the lithium-7 relaxation rate is less affected by the presence of copper ions. For instance, at a Cu/Li ratio of 0.2 the increase of the lithium relaxation rate is 4.2 times less with the bromide. If a similar complex is formed, its formation constant is about two orders of magnitude weaker.

The additional shift induced by butadiene corresponds obviously to a solvation effect of the diene onto the Li-Cu cluster (Table 4, lines 9–10). Isoprene induces also a notable shift whereas toluene presents a negligible effect (Table 4, lines 11 and 12). The easy reduction of CuBr_2 to CuBr by butadiene must also be considered as the second coordinates efficiently the diene: the striking differences between the butadiene effect in the LiBr-Cu(OAc)_2 case (Table 4, lines 7–8) and the LiOAc-Cu(OAc)_2 system (Table 4, lines 9–10) may be the result of such oxido-reduction problems in the LiBr case. The bromide ions may also lead to the cleavage of clusters affording free coordination sites on the metal.

Moreover, as discussed in the previous article (7), CuCN forms acidic addition

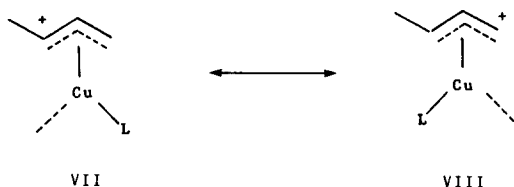
products with HCN (such as HCu(CN)_2 and $\text{H}_2\text{Cu(CN)}_3$) (9). Similar activation of acetic acid may occur through formation of complexes of the type $\text{H[LiCuBr}_x\text{OAc}_y]$ ($x + y = 4$). Protonation of the substrate would be therefore a key step in the reaction as indicated also by the increase of the rate observed in the presence of strong carboxylic acids. Transient π -allyl copper type species could thus be formed as proposed for the hydrocyanation reaction, but the difference of regioselectivities results from a delicate balance of steric and electronic effects: in fact, the extreme sensitivity of reactions where π -allyl complexes are implicated is well documented (10).

It is noteworthy that π -allyl copper type intermediates have been frequently postulated in mechanistic discussions (11) but such complexes have never been detected and appear as very elusive entities (a situation which is reminiscent of the copper carbenoid case). Indirect evidence concerning the mechanisms of this kind are often obtained from observations on the effect of the ligand on the selectivity, competition reactions between different substrates, and other influences, but in our case the isomer ratio remained practically unchanged ($\text{II/III} \sim 0.5$). Therefore the full understanding of the mechanism involved in this reaction remains an open question owing to the complexity of the catalytic system and of the elusive character of the key intermediates.

The mechanistic question that remains open is whether cationic intermediates are involved. It is noteworthy that extensive (cationic?) polymerization of isoprene and piperylene occurs under the conditions used for the acetoxylation and hydrocyanation reactions.

By analogy with the acid-catalyzed Markownikov addition of nucleophiles to olefins, a positive charge should be preferentially stabilized of the more substituted position (VII vs VIII). The formal charge of the π -allyl complex may thus have an influence on the reactivity but it is probable that the added ligands also play a very impor-

tant role. Ligand promoting carbenium ion character would thus direct the reaction to the more substituted position.



The mechanistic problem is further complicated by the fact that two distinct mechanistic pathways are possible for nucleophilic attack of the π -allyl ligand, namely, external attack at the activated ligand or initial attack at the metal atom, followed by reductive elimination.

The observation that nitriles are formed even in acetic acid as solvent is indicative of a metal-directed cyanation while the regiocontrol of acetoxylation might result from a more marked ionic character of the intermediates (OAc^- is a harder ligand than CN^-).

In conclusion, because of its low regioselectivity, copper-catalyzed acetoxylation of butadiene shows less interest than the corresponding hydrocyanation from the preparative point of view. LiBr is necessary as a co-catalyst for promoting catalytic addition of butadiene, and ^7Li NMR spectroscopy indicates determining interactions in mixed Cu–Li salts. The presence of bromide ions is of importance as they help to cleave carboxylate bridges and also participate actively in the catalytic cycle (bromide-containing additives increase the reaction rate). A proton transfer is implied as a key step in the reaction. The resulting copper allyl species undergo nucleophilic substitution, the stereochemical outcome

of which is the result of a delicate balance between steric and ionic parameters.

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