COPPER-CATALYSED DIACETOXYLATION OF BUTADIENE.
SPECTROSCOPIC AND PHYSICO-CHEMICAL INVESTIGATIONS
OF THE CATALYST

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SUMMARY

The copper(II) acetate-lithium bromide catalysed diacetoxyla-
tion of butadiene has been investigated in the acetic acid-acetic
anhydride system under oxygen pressure. The distribution of
positional isomers (1,4/3,4) appeared to be little dependent on the
reaction conditions, the 3,4-isomer (Scheme I, compound (4)) being
the kinetically controlled one. A relatively slow interconversion
of the isomers was observed under the reaction conditions. The
catalytic system was investigated by ^{7}Li NMR and UV spectroscopy,
and the kinetics of oxygen absorption by the catalyst were deter-
mined; the roles of acetic anhydride and water at the catalyst
level were thus established. The investigation of the behaviour of
potential intermediates of the diacetoxylation reaction has been
considered as another tentative approach to the understanding of
the reaction mechanism.

INTRODUCTION

The production of butane-1,4-diol is industrially important
mainly in relation to the preparation of valuable polymers. The
selective diacetoxylation of buta-1,3-diene in the presence of
palladium catalysts (ref.1) affords a straightforward route to
butane-1,4-diol through the selective oxidation of buta-1,3-diene.

A variety of other transition metals are active for the oxida-
tion of alkenes to diols, but copper based systems have received
particular attention (ref.2) owing to their activity and the low
cost of the metal. However, these catalysts are not selective as
mixtures of 1,4- and 3,4-addition products onto butadiene

are formed (Scheme I, compounds (2),(3) and (4)), the cis isomer (Scheme I, compound (3) being a minor constituent. We wish now to report on our observations related to the copper-lithium halide system (ref.3).

EXPERIMENTAL

The diacetoxylation reactions were run in a stainless steel autoclave heated in an oil bath at the required temperature.

The STANDARD CONDITIONS were as follows : $Cu(OAc)_2$:7.5mmol; LiBr:34.5 mmol; butadiene:80 mmol; HOAc:25 ml; Ac_2O:12.5 ml. PO_2:10 bar, t:60 min.

Measurements of oxygen uptake by the catalyst were performed by volumetry, using a glass reactor fitted with a gas burette (10 ml) completely immersed in a thermostat.

Analytical techniques : The isomeric diacetoxybutenes were iden- tified by comparison with authentic samples, using GLC and mass spectrometry. The ^7Li NMR spectra were determined on a BRUKER WP 80 spectrometer in DOAc/Ac_2O as solvent (Reference, 3M LiCl).

RESULTS AND DISCUSSION

The diacetoxylation reaction of butadiene was carried in an autoclave under oxygen pressure (generally 10 bar) using $Cu(OAc)_2$ in association with LiBr as catalyst in an acetic acid-acetic an- hydride (2:1) as solvent (for standard conditions, see Experimental Part).

a) Role of LiBr :

The presence of an alkali metal halide is necessary in order to observe a significant catalytic activity, the yield increasing with increasing concentration of LiBr at constant $Cu(OAc)_2$ concen- tration. The total yield of diacetoxybutenes with the LiBr/$Cu(OAc)_2$ ratio in parentheses is : 0%(0); 44%(2.3); 52%(3.1); 62%(4.6); 75%(6.9).

The ratio of 1,4- to 3,4-isomers remains close to 1:1 in all these examples (maximum : 1,4 for (LiBr)=6.9(Cu)).

Both the halide anion and the metal cation contribute to deter- mine the catalytic activity, LiBr being the most efficient :

i) LiX : yield with 1,4/3,4 isomer ratio in parentheses : LiBr 63%(1.1);.LiCl 38%(1); LiI 30%(1.4).

ii) MBr : yield with 1,4/3,4 isomer ratio in parentheses : LiBr 62%(1.1);.KBr 48%(0.5); CsBr 19%(0.7); CuBr 40%(0.4). It is noteworthy that, as a general approximate trend,

the 1,4/3,4-isomer ratios are generally lower with the less active than with the most efficient catalytic compositions. Moreover, it is interesting that the pivalic acid-pivalic anhydride system affords a particularly low 1,4-to 3,4-isomer ratio (0.2), which may be explained by a decrease in the rate of the subsequent isomerisation of the kinetically controlled 3,4-isomer owing to steric hindrance.

b) Role of oxygen pressure :

The yield of diacetoxybutenes depends particularly on the initial oxygen pressure, monoacetoxybutenes (Scheme I, compounds (5),(6) and (7)) being exclusively formed in the absence of oxygen (ref.3).

Even under the best conditions for the diacetoxylation process (PO_2 maintained between 8 and 10 bar during the whole experiment), a small amount (5%) of monoacetoxybutenes is formed together with the diacetoxy derivatives (60%).
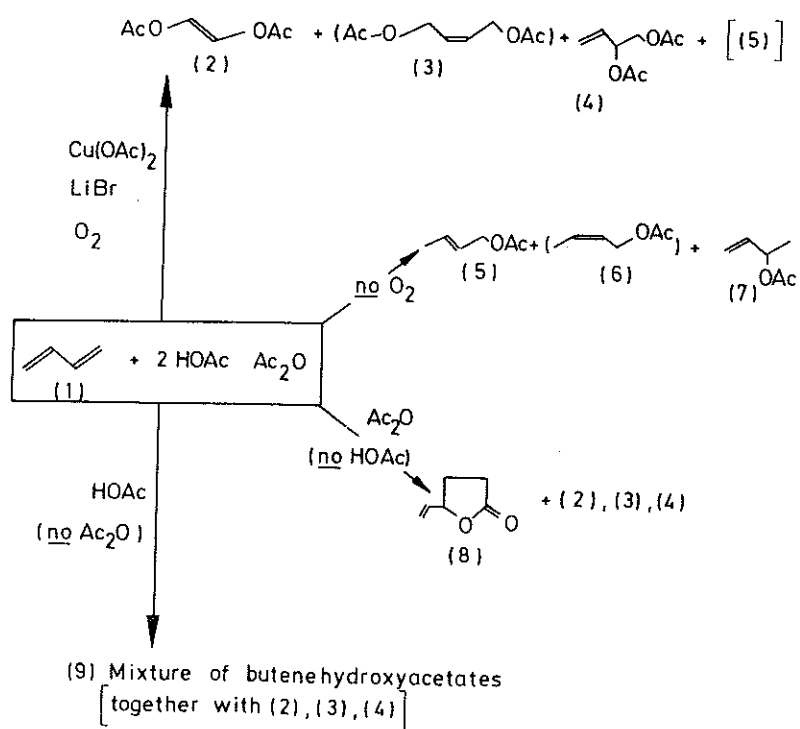
c) The solvent is another important factor, as up to now the best yield of diacetoxybutenes (Scheme I, compounds (2),(3) and (4)) was obtained in the system $HOAc-Ac_2O$ 2:1, other products than the diacetates being formed in other systems. For example, 4-vinyl-4-butyrolactone (Scheme I, compound (8)) (ref.4) (yield 19%) is formed together with the diacetoxybutenes (40%) in pure acetic anhydride whereas a mixture of diacetoxybutenes (44%) and of hydroxyacetates (Scheme I, compound (9))(18%) is obtained in pure acetic acid. The best selectivities for hydroxyacetates production are observed in acetic acid-acetonitrile(1:1) and acetic acid-dioxane (1:1)(yield of diacetoxybutenes : 16% and hydroxyacetates 28% in both systems). However, the selectivity relative to the distribution of the positional isomers remains little affected by the solvent (1,4/3,4-isomer ratio = 0.8-1:1 for both the diacetoxybutenes and the hydroxyacetates.

c) Role of temperature : 3,4-Diacetoxybutene (Scheme I, compound (4)) corresponds to the kinetically controlled isomer as it is preferentially formed at the lowest temperature (1,4/3,4-isomer ratio = 0.33 at 98°C). Moreover, the diacetoxybutenes isomerize slowly under the reaction conditions.
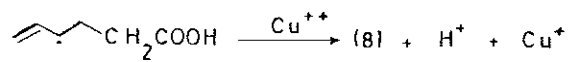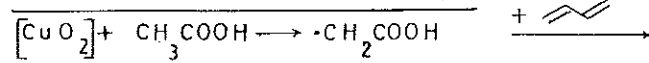
Investigation of the catalyst.

a) Spectroscopy : ^{7}Li NMR showed that the interactions between Cu and Li are significant in the system $Cu(AOc)_2-LiOAc$ (refs 5,6) as shown both by the chemical shifts and the relaxation time of

SCHEME I

AcO⌇⌇OAc + (Ac-O⌇⌇OAc) + ⌇OAc + [(5)]
(2)   (3)   OAc
                                  (4)

Cu(OAc)$_2$
LiBr
O$_2$

⌇OAc + (⌇OAc) + ⌇
(5)   (6)   (7) OAc

no O$_2$

⌇ + 2 HOAc   Ac$_2$O
(1)

Ac$_2$O
(no HOAc)

⌇O⌇O + (2),(3),(4)
(8)

HOAc
(no Ac$_2$O)

(9) Mixture of butene hydroxyacetates
    [together with (2),(3),(4)]

SCHEME II

MECHANISM OF FORMATION OF (8):

[CuO$_2$] + CH$_3$COOH ⟶ ·CH$_2$COOH   + ⌇ ⟶

⌇CH$_2$COOH $\xrightarrow{\text{Cu}^{++}}$ (8) + H$^+$ + Cu$^+$

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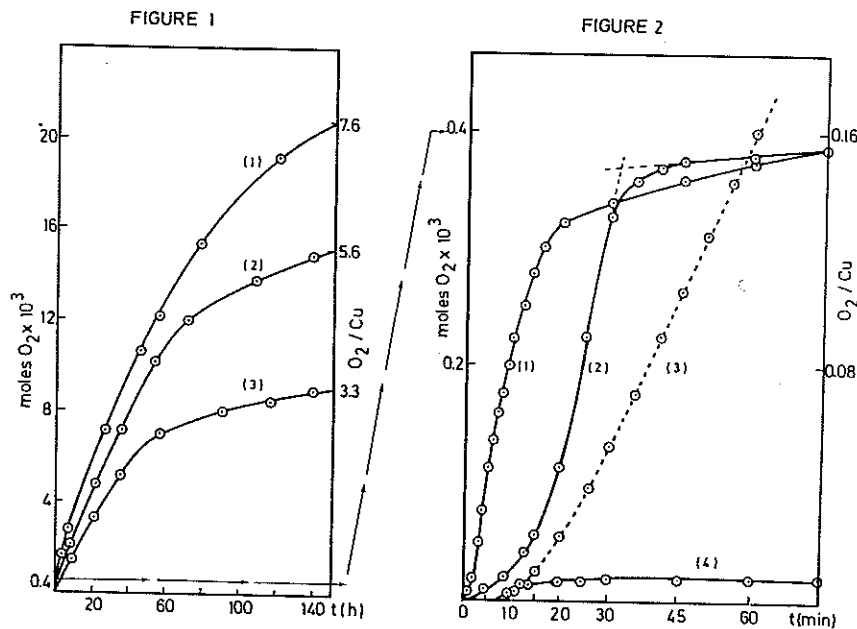
FIGURE 1 : ABSORPTION OF MOLECULAR OXYGEN BY $Cu(OAc)_2$-LiBr IN HOAc/Ac_2O

CONDITIONS : $Cu(OAc)_2$, 2.5mmol; HOAc, 8ml; Ac_2O, 4ml; t, 63°C.
CURVES : Cu/Li = (1) 16; (2) 8; (3) 4.

FIGURE 2 : ABSORPTION OF MOLECULAR OXYGEN BY $Cu(OAc)_2$-LiBr IN HOAc :
EFFECT OF ADDED WATER

CONDITIONS : $Cu(OAc)_2$, 2.5mmol; HOAc, 12ml; t, 63°C.
CURVES : (1) H_2O = 2.0, HOAc = 12; (2) H_2O = 1.0, HOAc = 12;
         (3) H_2O = 0, HOAc = 8, Ac_2O = 4; (4) H_2O = 0, HOAc = 12ml.

the lithium signal in the presence of a copper salt [δ(from 0.3M LiCl in D_2O : -2.74ppm (0.45M/LiOAc) and -3.24ppm (0.45M/LiOAc + 0.11M $Cu(OAc)_2$]. Interestingly, the Li signals are much less shifted by the addition of the copper salt in the LiBr than in the LiOAc case [δ = -2.59ppm (Li/Cu=4.6), -2.87ppm (Li/Cu=1] indicating lower Cu-Li interactions (probably resulting from more labile clusters) when bromine ions are present. A stability constant of the $Cu(OAc)_2$-LiOAc complex of 90M^{-1} at 34°C was determined from relaxation rates (Li), supporting the existence of a strong Cu-Li interaction in the acetates. Moreover, these measurements confirmed that the presence of bromide ion leads to more labile interactions [the LiBr-$Cu(OAc)_2$ complex is two orders of magnitude less stable than the corresponding LiOAc-$Cu(OAc)_2$ complex (for details related to the above spectral data, see ref. 3).

These observations appear to be particularly significant within the context of rationalizing the activating effect of the bromide ions at the catalytic level in related copper catalysed processes (acetoxylations, diacetoxylations, hydrocyanations (refs 13,14,15) and oxycyanations (ref.13).

The <u>electronic spectra</u> of solutions of $Cu(OAc)_2$-LiBr in pure acetic acid for different Cu/Li ratios (Cu/Li = 2, 5 and 10) show no important variation; additional bands are observed at 436 and 370 nm, whereas $Cu(OAc)_2$ absorbs exclusively at 646 nm (in the 300-650 nm region).

Very similar spectra have been reported for the complex $[CuBr_3S_2]^-$, for which a bipyramidal structure has been proposed (refs 7,8)(S in our case would be acetic acid).

b) <u>Kinetics of oxygen absorption by the catalyst</u> : the diacetoxylation catalyst readily absorbed oxygen at atmospheric pressure even in the absence of substrate. The rate of absorption and the stoichiometry (O_2/Cu) was dependent on the presence of LiBr in the HOAc-Ac_2O mixture (Fig. 1). In dry acetic acid (in the absence of Ac_2O) very little absorption was detected but the addition of water (8-16%) induced rapid absorption of oxygen corresponding to a stoichiometry of O_2/Cu close to 0.14. These experiments demontrate the occurrence of easy electronic transfer reactions involving copper(II) clusters, the bromide ion and the solvent. The role of water may correspond to the hydrolysis of copper peroxidic species (ref. 9, see also significant examples in platinum chemistry in ref. 10).

c) Reactions of potential intermediates under the reaction
   conditions

   Potential intermediates for the present diacetoxylation
reaction could involve dibromobutenes or 3,4-epoxybutene. The
copper-catalysed bromination of olefins under oxidative conditi-
tions (oxyhalogenation) is a well documented reaction but the
participation of direct oxygen transfer from copper peroxidic
species has also been established in the oxidation of phenolic
substrates (ref.11). The reactions of dibromo- and dichlorobutenes
and of epoxybutene in the presence of the diacetoxylation catalyst
$[Cu(OAc)_2-LiBr]$ have now been investigated under the reaction con-
ditions (Table I). It is noteworthy that at 140°C, the $Cu(OAc)_2$
$Cu(OAc)_2-LiBr$ system affords the highest 1,4/3,4 isomer ratio and
presents a different pattern from that displayed by copper or
lithium used separately. Moreover, it is of interest that the
distribution of the positional isomers observed at moderate tempe-
rature (100°C) with epoxybutene as starting material and the
$Cu(OAc)_2-LiBr$ sustem (1,4/3,4 isomer ratio = 0.5) (Table I, entry
6) is much closer to the distribution obtained during the diaceto-
xylation reaction of butadiene at this temperature (1,3/3,4 isomer
ratio = 0.5) than the one resulting from the dihalogenobutenes
(1.4/3.4 isomer ratio = 1.5) (Table I, entries 7, 8 and 9).

   This observation, together with the formation of hydroxyacetates
in the absence of acetic anhydride (see above) might support the
hypothesis of the participation of oxygen transfer to the substrate
(particularly with the formation of an epoxide as intermediate).
Moreover, the $Cu(OAc)_2-LiBr$ system promotes the formation of the
1,4-diacetate in contrast to the single-component systems (compare
entry 2 with 1, 3 and 4 and entry 6 with 5 in Table I), the parti-
cipation of both metal ions in the active species is therefore
clearly established.

d) Mechanisms of reactions

   The formation of the diacetoxylation products (Scheme I, com-
pounds (2),(3) and (4)can be easily explained both from dibromobute-
nes or 3,4-epoxybutene by classical nucleophilic substitution
(from the dibromo intermediate) or ring opening reaction (from the
epoxide).

   The monoacetates (Scheme I, compounds (5), (6) and (7) are
obviously the result of an electrophilic addition of acetic acid
onto butadiene, the copper ion increasing the protonating ability
of acetic acid through complex formation such as $HCu(OAc)_3$,

TABLE

Reactions of 3,4-epoxy-1-butene and dihalobutenes with the diacetoxylation catalyst

T = 140°C

	Reagent	Substrate	Yield(%)	1.4/3.4
1	Cu(OAc)$_2$	(epoxide)	100	0.30
2	id + LiBr		82	1.60
3	CuBr$_2$	(epoxide)	50	0.40
4	LiOAc		62	0.10

T = 100°C

	Reagent	Substrate	Yield(%)	1.4/3.4
5	Cu(OAc)$_2$	(epoxide)	43	0.15
6	id + LiBr		30	0.5
7	id + LiBr	Cl,Cl	21	1.5
8	id + LiBr	Cl,Cl	24	1.5
9	id + LiBr	Br,Br	30	1.6

Conditions : Cu(OAc)$_2$: 1.25 mmoles; LiBr = 5 mmoles; substrate : 1.25 mmole; HOAc = 3 mL;
Ac$_2$O : 2 mL; t = 1h.
N.B. : entry 5 : heterogeneous solution at the end of the reaction. Other examples : homogeneous.

$H_2Cu(OAc)_4$, complexation of butadiene being possibly an additional activation mode of this substrate. The most intriguing reaction corresponds to the formation of the lactone (Scheme I, compound(8)), which is however reminiscent of the $Mn(OAc)_3$ promoted lactone formation from olefins (ref.16)(a radical process). Copper peroxidic species would act as the radical generating species in our case (Scheme II)(NB: Cu(II) is readily reduced to Cu(I) species in the presence of butadiene; the formation of copper-oxygen complexes is therefore possible).

CONCLUSIONS

This work has shown that the copper(II) acetate-LiBr- catalysed diacetoxylation reaction of butadiene remains poorly regioselective under various reaction conditions, the 1,4-to 1,3-isomer ratios lying close to unity in most instances. The 3,4-isomer appears to be the kinetically controlled one.

^{7}Li NMR and UV spectroscopy and the kinetics of oxygen uptake by the catalyst show that the formation of the active catalytic species is probably linked to the formation of oxygen activating species, the cleavage of Cu acetate clusters by the bromide ions being an essential requirement. The nature of the key organic intermediates of the reaction are not clearly established but the occurence of an epoxide type entity receives some support from the comparison of the behaviour of some potential intermediates in the diacetoxylation reaction and from the formation of hydroxyacetates in the absence of acetic anhydride.

The above results are also particularly significant in relation to the hydrocyanation and oxycyanation processes, these last reactions appearing, however to be more regioselective (1,4-isomer) than the acetoxylation-type processes (refs 13-15).

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