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

I.N. NAMALIS *, J. GRANDJEAN ***, A.F. NOELS *, E. PUENTES *
D. WADDAN ****, A.J. HUBERT ** and Ph. TEYSSIE *

* Laboratoire de Chimie Macromoléculaire et de Catalyse Organique
** Laboratoire de Synthèse Organique et de Catalyse
*** Service de Chimie Organique Physique,
Université de Liège, Sart Tilman, 4000 LIEGE, Belgium.
**** Chemistry Department, University of Manchester,
Manchester M13 9PL, England.

SUMMARY

The copper(II) acetate-lithium bromide catalysed diacetoxylation 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 1, 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 7Li NMR and UV spectroscopy, and the kinetics of oxygen absorption by the catalyst were determined; 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 oxidation 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)$_2$: 7.5 mmol; LiBr: 34.5 mmol; butadiene: 80 mmol; H$_2$OAc: 25 mL; Ac$_2$O: 12.5 mL; $P_0$: 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 identified by comparison with authentic samples, using GLC and mass spectrometry. The $^7$Li NMR spectra were determined on a BRUKER WP 80 spectrometer in D$_2$O/acetic anhydride (2:1) 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 anhydride (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)$_2$ concentration. 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 determine 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% (1.1); 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 (PO2 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 H2OAc-Ac2O 2:1, other products than the diacetates being formed in other systems. For example, 4-vinyl-2-butylcyclohexene (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 20% 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: 7Li 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

\[
\begin{align*}
\text{AcO} & \xrightarrow{\text{OAc}} \text{OAc} & \text{AcO} & \xrightarrow{\text{OAc}} & \text{OAc} & \xrightarrow{\text{OAc}} & \text{OAc} & \xrightarrow{\text{(5)}} \\
(2) & & (3) & & (4) & & (5) & \\
\text{Cu(OAc)}_2 & & \text{LiBr} & & \text{O}_2 & & \text{no O}_2 & & \text{(5)} & & \text{AcO} & & \text{OAc} & & \text{OAc} & & \text{OAc} & & \text{OAc} & & \text{OAc} & & \text{OAc} & & \text{OAc} & & \text{OAc} & & \text{OAc} & & \text{OAc} & & \text{OAc} \ \\
\text{HOAc} & & \text{no HOAc} & & \text{Ac}_2\text{O} & & \text{no Ac}_2\text{O} & & \text{(6)} & & \text{(7)} & & \text{(8)} & & \text{(9)} \ \\
191) \text{Mixture of butenehydroxyacetates} & \text{[together with (2), (3), (4)]} & \\
\end{align*}
\]

SCHEME II

MECHANISM OF FORMATION OF (8):

\[
\begin{align*}
\text{[CuO}_2]\text{]^+} & \xrightarrow{\text{CH}_2\text{COOH}} \text{CH}_3\text{COOH} & \xrightarrow{\text{H}^-} \text{Cu}^+ \\
\text{CH}_2\text{COOH} & \xrightarrow{\text{Cu}^{2+}} (8) & + & \text{H}^+ & + & \text{Cu}^+ \\
\end{align*}
\]
FIGURE 1: ABSORPTION OF MOLECULAR OXYGEN BY Cu(OAc)₂·LiBr IN HDAc/Ac₂O

CONDITIONS: Cu(OAc)₂, 2.5mmol; HDAc, 8ml; Ac₂O, 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 HDAc:
EFFECT OF ADDED WATER

CONDITIONS: Cu(OAc)₂, 2.5mmol; HDAc, 12ml; t, 63°C.
CURVES: (1) H₂O = 2.0; HDAc = 12; (2) H₂O = 1.0; HDAc = 12;
(3) H₂O = 0; HDAc = 8; Ac₂O = 4; (4) H₂O = 0; HDAc = 12ml.
the lithium signal in the presence of a copper salt. [δ(0.3M LiCl in D2O : -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 (acetoxylation, diacetoxylation, hydrocyanations (refs 13,14,15) and oxycyanations (ref.13).

The electronic spectra 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 [CuBr2S2]−, for which a bipyramidal structure has been proposed (refs 7,8)(5 in our case would be acetic acid).

b) Kinetics of oxygen absorption by the catalyst: the diacetoxylation catalyst readily absorbed oxygen at atmospheric pressure even in the absence of substrate. The rate of absorption and the stoichiometry (O2/Cu) was dependent on the presence of LiBr in the HOAc-Ac2O mixture (Fig. 1). In dry acetic acid (in the absence of Ac2O) very little absorption was detected but the addition of water (8-16%) induced rapid absorption of oxygen corresponding to a stoichiometry of O2/Cu close to 0.14. These experiments demonstrate 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 peroxodic 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 dibromobutanes or 3,4-epoxybutene. The copper-catalysed bromination of olefins under oxidative conditions (oxyhalogenation) is a well documented reaction but the participation of direct oxygen transfer from copper peroxydic species has also been established in the oxidation of phenolic substrates (ref. 11). The reactions of dibromo- and dichlorobutanes and of epoxybutene in the presence of the diacetoxylation catalyst \([\text{Cu(OAc)}_2-\text{LiBr}]\) have now been investigated under the reaction conditions (Table 1). It is noteworthy that at 140°C, the \(\text{Cu(OAc)}_2\) 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 temperature (100°C) with epoxybutene as starting material and the Cu(OAc)_2-LiBr system (1,4/3,4 isomer ratio = 0.5) (Table 1, entry 6) is much closer to the distribution obtained during the diacetoxylation reaction of butadiene at this temperature (1,3/3,4 isomer ratio = 0.5) than the one resulting from the dihalogenobutanes (1,4/3,4 isomer ratio = 1.5) (Table 1, entries 7, 8 and 9).

This observation, together with the formation of hydroxycacetates 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 1), the participation of both metal ions in the active species is therefore clearly established.

d) Mechanisms of reactions

The formation of the diacetoxylation products (Scheme I, compounds (2), (3) and (4) can be easily explained both from dibromobutanes 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 H[Cu(OAc)]_3,
<table>
<thead>
<tr>
<th>Reagent</th>
<th>Substrate</th>
<th>Yield(%)</th>
<th>1.4/3.4</th>
<th>Reagent</th>
<th>Substrate</th>
<th>Yield(%)</th>
<th>1.4/3.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Cu(OAc)$_2$</td>
<td>![Substrate Image]</td>
<td>100</td>
<td>0.30</td>
<td>5 Cu(OAc)$_2$</td>
<td>![Substrate Image]</td>
<td>43</td>
<td>0.15</td>
</tr>
<tr>
<td>2 id + LiBr</td>
<td>![Substrate Image]</td>
<td>82</td>
<td>1.60</td>
<td>6 id + LiBr</td>
<td>![Substrate Image]</td>
<td>30</td>
<td>0.5</td>
</tr>
<tr>
<td>3 CuBr$_2$</td>
<td>![Substrate Image]</td>
<td>50</td>
<td>0.40</td>
<td>7 id + LiBr</td>
<td>![Substrate Image]</td>
<td>27</td>
<td>1.5</td>
</tr>
<tr>
<td>4 LiOAc</td>
<td>![Substrate Image]</td>
<td>62</td>
<td>0.10</td>
<td>8 id + LiBr</td>
<td>![Substrate Image]</td>
<td>24</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9 id + LiBr</td>
<td>![Substrate Image]</td>
<td>30</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Conditions: Cu(OAc)$_2$: 1.25 mmoles; LiBr = 5 mmoles; substrate: 1.25 mmole; HOAc = 3 mL; Ac$_2$O = 2 mL; t = 1 h.

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 diacetoxylatation reaction of butadiene remains poorly regioselective under various reaction conditions, the 1,4-to 1,3-isomer ratio 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 occurrence of an epoxide type entity receives some support from the comparison of the behaviour of some potential intermediates in the diacetoxylatation reaction and from the formation of hydroxyacetates in the absence of acetic anhydride.

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

Acknowledgements: We are indebted to SPPS (Belgium) for financial assistance and to FNRS (Belgium) for high pressure and gas liquid chromatograph equipments. We are also indebted to Professor Remson for mass spectrometric measurements performed in his Service.

REFERENCES