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# HYDROFORMYLATION OF OLEFINS IN THE PRESENCE OF RUTHENIUM CATALYSTS

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## Summary

The hydroformylation of pent-1-ene-5-$d_3$ in the presence of $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_8$ [(–)-DIOP]$_2$ under 7–50 atmosphere pressure of carbon monoxide gives a high percentage of the straight-chain isomer. Deuterium retention is complete only under a high CO pressure. In the presence of $Ru_3(CO)_{12}$ redistribution of deuterium within the molecule takes place whatever the pressure of carbon monoxide. In the presence of $H_4Ru_4(CO)_8$[(–)-DIOP]$_2$ the deuterium is completely retained, and is found in the methyl hexanoate only in $\alpha,\beta$ and $\omega$ positions relative to the carbomethoxy group.

## Introduction

In order to increase knowledge of the course of the hydroformylation of olefins in the presence of ruthenium catalysts, we have studied the reaction in the presence of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_8$[(–)-DIOP]$_2$[1–4]. Useful data may be obtained by determining either (a) the influence of reaction conditions on the isomeric distribution of the products [5,6], or (b) the structures and physico-chemical properties of the products when using optically active olefins [7–10] or olefins labelled with deuterium [11–16] or $^{14}C$ [17,18].

The second of these techniques has been adopted in the present investigation. We have hydroformylated pent-1-ene-5-$d_3$ in the presence of the catalyst precursors mentioned above and then determined the positions and amounts of the deuterium present in the products. Such data may provide information on the extent of the rearrangements involving the catalytically active intermediate; these may involve double bond and/or hydrogen migration in the substrate, giving rise to olefins with a different distribution of deuterium along the chain.

The determination of the amount of deuterium present on the various carbon atoms in the reaction products makes it possible to deduce both the extent and position of the carbonylation process at the carbon atoms of the olefin even in the presence of equivalent carbon atoms in the chain [11–16].

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Possible deuterium-hydrogen exchanges between olefin and synthesis gas may easily be detected by looking at the retention of deuterium.

## Results and discussion

The results for the hydroformylation of pent-1-ene-5-$d_3$ in the presence of various ruthenium based catalyst precursors are shown in Table 1. A temperature of 150°C was chosen in order to achieve moderate conversions within a reasonable reaction time.

When $Ru_3(CO)_{12}$ was used as catalyst precursor a high proportion of the straight-chain isomer was obtained under both low and high CO pressures as previously noticed [2].

At low carbon monoxide pressures, however, alcohols are mainly formed instead of aldehydes.

In the presence of $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ a high percentage of the straight-chain isomer is formed, and the alcohols are in a higher proportion than when using $Ru_3(CO)_{12}$. The hydrogen distribution on the carbon atoms of the chain of methyl n-hexanoate is shown in Table 2.

In the reactions using $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ or $Ru_3(CO)_{12}$ under a high $p(CO)$ as catalyst precursors, deuterium retention was complete. In the presence of $Ru_3(CO)_{12}$ under a low $p(CO)$ however there was considerable loss of deuterium (~ 30%).

In all the experiments except that performed in the presence of $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$, complete redistribution of deuterium in the molecule was observed. Deuterium is also present on the carbon in the $\alpha$-position to the carbomethoxy group, showing that even the $CD_3$ group is involved in the hydroformylation process. With $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ as catalyst precursor, on the other hand, deuterium is detected only in $\alpha,\beta$ and $\omega$ positions relative to the carbomethoxy group. Analogous behaviour has previously been observed with cobalt carbonyl catalysts under a high CO pressure [14].

The course of the hydroformylation in the presence of $Ru_3(CO)_{12}$ as catalyst precursor, has previously been rationalized in terms of the participation of only one catalytically active species [2]. In the earlier study no significant influence of the partial pressure of carbon monoxide on the isomeric distribution of the hydroformylation was observed, probably, because carbon monoxide pressures as low as those we have now adopted were not examined.

The influence of the partial pressure of carbon monoxide on the isomeric distribution of the hydroformylation products of olefins may be rationalized either through the action of two catalytically active species, each giving rise to all the isomers, but in different ratios, as suggested in the case of the hydroformylation in the presence of $Co_2(CO)_8$ [5,6], or, by assuming a change of the isomeric composition of the olefinic substrate prior to its hydroformylation, due to an isomerization process dependent on the carbon monoxide partial pressure. Apparently the isomerizing activity of the hydroformylation catalytic system is particularly high at a low $p(CO)$. The second hypothesis appears to be the more plausible, and in keeping with the results we have obtained.

Pent-1-ene-5-$d_3$ yields 81% of the straight-chain aldehyde under a high carbon monoxide partial pressure and only 72% under 5 atm of carbon monoxide. The latter yield is equal to that obtained in the hydroformylation of *cis*-pent-2-ene under both high and low carbon monoxide partial pressures (Table 3). The unreacted olefin recovered at the end of the hydroformylation of pent-1-ene-5-$d_3$ under a low $p$(CO) is extensively isomerized showing a composition similar to that found after hydroformylation of *cis*-pent-2-ene. Evidently the catalyst active in the hydroformylation is capable of promoting migration of hydrogen within the substrate and does not induce exchange with gaseous hydrogen. Once the olefin has combined with the catalyst to give the intermediate complex, it is not released before hydroformylation.

When the carbon monoxide pressure is low, in addition to the hydroformylation catalyst another species must be present, which is active not only for olefin isomerization but also in the exchange with gaseous hydrogen and in the hydrogenation of both olefin and aldehyde. This species, present in minute quantities even under a relatively high pressure of carbon monoxide, is probably responsible for the formation of the alcohol and of the hydrocarbon always detected in very small amounts among the products.

The phosphine-containing ruthenium carbonyl hydride yields not only more of the straight-chain aldehyde but also small quantities of 2-ethylbutanal and of alcohols. Even more interesting is that deuterium while completely retained is found in neither of position 4 or 5. Apparently the catalytic intermediate originating from this precursor promotes migration of hydrogen through a mechanism which leads to its activation in certain positions accompanied by retention, as already noted for the cobalt-catalyzed reaction [14].

Ruthenium carbonyl cluster catalyst precursors show a catalytic activity different from that of the analogous mononuclear complexes [3]: they give rise to products which may be regarded as formed through isomerization either of the substrate or of the alkyl intermediate. They also catalyze the hydrogenation of both substrate and product.

## Experimental

GLC analyses were performed on a Perkin–Elmer F30 instrument. The isomeric mixture of esters were separated by preparative GLC using a Perkin–Elmer F21 instrument equipped with 3 m column packed with Ucon oil LB-550-X (15%) (polypropyleneglycol) on Chromosorb A (85%) at 100°C.

NMR spectra were recorded on a Perkin–Elmer R32 spectrometer. Mass spectra were recorded on a Perkin–Elmer 270B instrument.

Hydrogen distributions (Table 2) were determined by integration of the NMR spectra of solutions of esters in $C_6D_6$ using $Eu(DPM)_3$ as shift reagent.

The methyl group of the $COOCH_3$ moiety was used as internal standard.

### *Materials*

$Ru_3(CO)_{12}$ [19], $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ [20] and pent-1-ene-5-$d_3$ [14] were prepared by known procedures. *cis*-Pent-2-ene (99% purity) was a Fluka product.

### *Hydroformylation of olefins and identification of products*

The hydroformylations were carried out as described elsewhere [8].

The composition of the product mixture was determined by GLC using 2 m columns packed with bis-2-methoxy ethyl adipate (13.5%) and di-2-ethylhexyl seba-

TABLE 1

HYDROFORMYLATION OF PENT-1-ENE-5-$d_3$ IN THE PRESENCE OF RUTHENIUM CATALYSTS

(Olefin 25 mmol; benzene 25 ml; $p$(CO) 50 atm; $p(H_2)$ 45 atm; $T$ 150°C; catalyst precursor 0.3 g)

| Catalyst precursor | Conversion (%) | Product composition (mol%) | | | Isomeric distribution of aldehydes (mol%) | | |
|---|---|---|---|---|---|---|---|
| | | Aldehydes | Alcohols | Paraffin | Hexanal | 2-Methylpentanal | 2-Ethylbutanal |
| $Ru_3(CO)_{12}$ | 95.0 | 83.0 | 4.2 [a] | 12.8 | 81.0 | 17.0 | 2.0 |
| $Ru_3(CO)_{12}$ [b] | 97.0 | 5.1 | 35.9 [c] | 59.0 | 71.9 | 24.3 | 3.8 |
| $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ [d] | 23.0 | 64.0 | 10.5 [a] | 25.5 | 85.3 | 14.2 | 0.5 |

[a] mol hexanol/mol total alcohols 80.5%. [b] $p$(CO) 7 atm, $p(H_2)$ 85 atm. [c] mol hexanol/mol total alcohols 72.0%. [d] Olefin 18 mmol, catalyst precursor 0.1 g. [e] mol hexanol/mol total alcohols 85.7%.

TABLE 2

HYDROGEN DISTRIBUTION ON THE CARBON ATOMS OF METHYL HEXANOATE DERIVED FROM THE HYDROFORMYLATION OF PENT-1-ENE-5-$d_3$

| Catalyst precursor | Number of hydrogens on carbon atoms | | | | | $\Sigma$(H) [a] |
|---|---|---|---|---|---|---|
| | C(6) | C(5) | C(4) | C(3) | C(2) | |
| $Ru_3(CO)_{12}$ [b] | 1.22 | 1.83 | 1.80 | 1.62 | 1.59 | 8.06 |
| $Ru_3(CO)_{12}$ [c] | 2.30 | 1.92 | 1.88 | 1.45 | 1.42 | 8.97 |
| $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ | 0.37 | 1.99 | 1.99 | 1.83 | 1.81 | 7.99 |

[a] Number of hydrogen atoms per molecule of ester, with the exception of methoxylic group. [b] $p$(CO) 50 atm. [c] $p$(CO) 7 atm.

TABLE 3

HYDROFORMYLATION OF *cis*-PENT-2-ENE IN THE PRESENCE OF $Ru_3(CO)_{12}$ (Olefin 25 mmol; benzene 25 ml; $p(H_2)$ 45 atm; catalyst precursor 0.3 g; $T$ 150°C)

| Conversion (%) | $p$(CO) (atm) | Product composition (mol%) | | | Isomeric distribution of aldehydes (mol%) | | |
|---|---|---|---|---|---|---|---|
| | | Aldehydes | Alcohols | Pentane | Hexanal | 2-Methylpentanal | 2-Ethylbutanal |
| 45.1 | 5 | 36.5 | 7.4 | 56.1 | 73.0 | 23.2 | 3.8 |
| 41.0 | 50 | 72.5 | Trace | 27.5 | 72.6 | 24.0 | 3.4 |

cate (6.5%) mixture on Chromosorb P (80%) at 40°C for the hydrocarbon components, and 2 m columns packed with Ucon oil LB-550-X (15%) (polypropyleneglycol) on Chromosorb A (85%) at 80°C for the oxygenated products.

Aldehydes were converted into the methyl esters of the corresponding acids [8]; the esters were then analysed and separated by GLC. The results obtained are reported in Tables 1 and 3.

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