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Regioselectivity in the cobalt catalyzed hydroformylation of some branched olefins

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Chimica. — *Regioselectivity in the cobalt catalyzed hydroformylation of some branched olefins.* Nota di GIAMBATTISTA CONSIGLIO (*), presentata (**) dal Corrisp. P. PINO.

ABSTRACT. — The hydroformylation of 3-methyl-1-hexene, 4-methyl-1-hexene, trans–4–methyl–2–hexene and 2–ethyl–1–pentene by cobalt carbonyls both under high and low carbon monoxide partial pressure was carried out and the regioselectivity of the aldehyde formation was determined. At high p_{CO} a very small extent of formylation at the saturated methyl groups takes place; this formylation is rather extensive at low p_{CO}, but does not correspond to the equilibrium among the possible carbonylcobaltalkyl intermediates.

KEY WORDS: Hydroformylation; Cobalt carbonyls; Regioselectivity.

RIASSUNTO. — *Regioselettività nella idroformilazione di alcune olefine ramificate catalizzata da cobalto carbonili.* L'idroformilazione del 3–metil–1–esene, 4–metil–1–esene, trans–4–metil–2–esene e 2–etil–1–pentene catalizzata da dicobaltoottacarbonile è stata investigata a bassa ed alta pressione di ossido di carbonio, determinando la regioselettività nella formazione delle possibili aldeidi. Ad alta p_{CO} i gruppi metilici terminali vengono formilati seppure in piccola misura. Tale formilazione è piuttosto notevole a bassa p_{CO} ma non corrisponde ad un completo equilibrio tra tutti i possibili cobalto carbonilalchili intermedi.

It has been pointed out that the preference of transition metals for different carbon atoms during a catalytic process such as olefin isomerization or hydroformylation strongly influences the product composition [1]. The extent of formylation at a carbon atom in an olefinic backbone, however, depends both on the concentration of the corresponding metal alkyl intermediate complex and on the activation energy for carbon monoxide insertion into that particular carbon-metal bond. Particularly, under conditions of low carbon monoxide partial pressure (p_{co} 2–4 atm) (2-4], the latter seems to be the sole determining factor for the aldehydic product composition in the cobalt catalysed hydroformylation of straight chain olefins.

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As a matter of fact, the existence of a very rapid equilibrium [5] among all the possible alkylcobalt complex intermediates is suggested by the fact that under the above conditions the aldehydes obtained from straight chain olefins containing a perdeuterated methyl group show a statistical intermolecular deuterium distribution [2-4]; furthermore, the same product composition is obtained from terminal or internal straight chain olefins [6].

No data existed in the literature on the possibility and on the extent of the migration of the cobalt catalyst along the substrate backbone in the hydroformylation of branched olefins under either high or low carbon monoxide partial pressure. In the hydroformylation of 3-methyl-1-hexene (3-M-1-H) (at 100 atm of carbon monoxide), formylation at the methyl group at position 3 takes place only to a very limited exent ($\simeq 3\%$) [7, 8]; apparently no formylation at position 6 takes place. Investigation in this direction can give deeper insight into the factors controlling the extent of formylation at different carbon atoms. In fact, when this work was at the end a very accurate determination of the regioselectivity in the cobalt catalyzed hydroformylation of linear and branched octenes under high carbon monoxide partial pressure has been published [9].

We report here the results of our investigation of the hydroformylation reactions of 3-methyl-1-hexene (3-M-1-H), 4-methyl-1-hexene (4-M-1-H), trans-4-methyl-2-hexene (4-M-2-H), and 2-ethyl-1-pentene (2-E-1-P) under conditions of low and high carbon monoxide partial pressure.

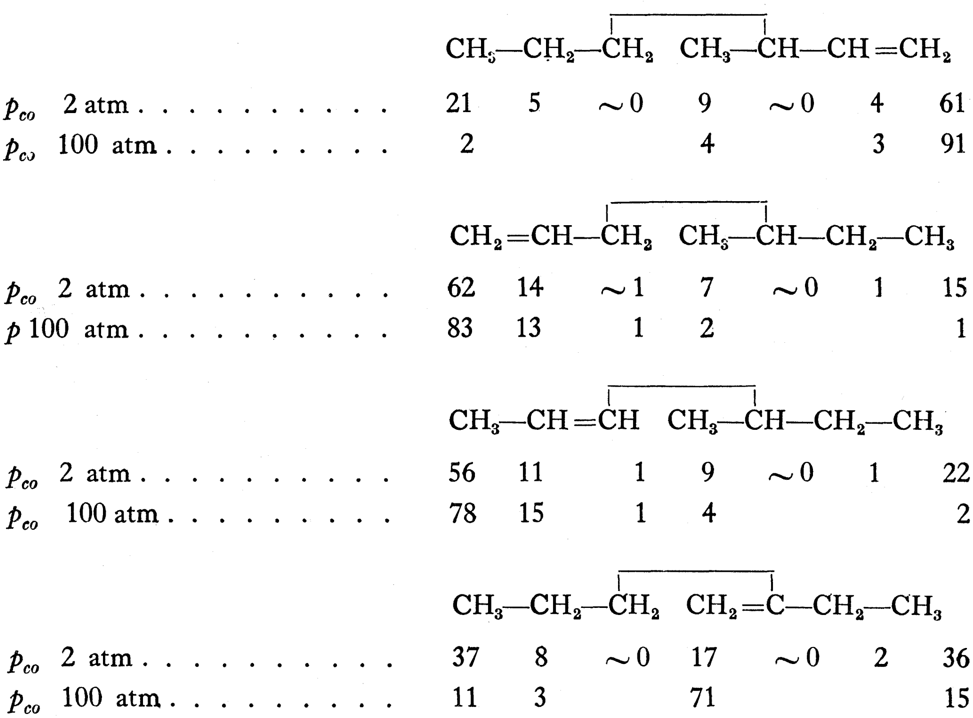
EXPERIMENTAL

3-M-1-H and 4-M-1-H were Fluka products. Trans-4-M-2-H was prepared via an iron catalysed cross-coupling reaction [10] of sec. butyl-magnesium bromide with 1-bromopropene and was separated from the cis-isomer by rectification. 2-E-1-P was prepared by the Wittig reaction from 3-hexanone [11] and was identified by ^{13}C NMR.

The hydroformylation reactions were carried out as previously described, using benzene as the solvent [6, 12]; the conversion was in the range of 80-90%, based on gas absorbtion. The aldehydic products were oxidized immediately after the reaction to the corresponding acids, and these were esterified with diazomethane, as previously described [13].

The mixtures of the esters were analysed by gas chromatography using capillary columns of Squalane (100 m) and Apiezon L (50 m) on a Perkin Elmer F 11 gas chromatograph. Identification of the reaction products was accomplished by comparing their retention times and mass spectra with those of the known products using an Hitachi mass spectrometer RMU-6 L coupled with a Perkin-Elmer F 900 gas-cromatograph.

The retention times of the reaction products on Squalane increase in the following order: methyl 2-methyl-2-ethylpentanoate; methyl 2,4-dimethylhexanoate (first diastereomer); methyl 2–ethyl–3–methylpentanoate (both diastereomers, not separated); methyl 2,4–dimethylhexanoate (second diastereomer); methyl 2,3–dimethylhexanoate (both diastereomers, separated); methyl 3–ethylhexanoate; methyl 4–methylheptanoate; methyl 5–methylheptanoate.



CH_3—CH_2—CH_2 CH_3—CH—CH=CH_2

	CH_3—	CH_2—	CH_2	CH_3—	CH—	CH=	CH_2
p_{co} 2 atm	21	5	~0	9	~0	4	61
p_{co} 100 atm	2			4		3	91

CH_2=CH—CH_2 CH_3—CH—CH_2—CH_3

	CH_2=	CH—	CH_2	CH_3—	CH—	CH_2—	CH_3
p_{co} 2 atm	62	14	~1	7	~0	1	15
p 100 atm	83	13	1	2			1

CH_3—CH=CH CH_3—CH—CH_2—CH_3

	CH_3—	CH=	CH	CH_3—	CH—	CH_2—	CH_3
p_{co} 2 atm	56	11	1	9	~0	1	22
p_{co} 100 atm	78	15	1	4			2

CH_3—CH_2—CH_2 CH_2=C—CH_2—CH_3

	CH_3—	CH_2—	CH_2	CH_2=	C—	CH_2—	CH_3
p_{co} 2 atm	37	8	~0	17	~0	2	36
p_{co} 100 atm	11	3		71			15

SCHEME 1. – Extent of formylation (%) at each carbon atom in the hydroformylation of some branched olefins under low and high carbon monoxide partial pressure. Other reaction conditions: p_{H_2} = 100 atm; t = 100 °C; benzene as the solvent.

RESULTS

a) *Experiments under high carbon monoxide partial pressure.*

The results obtained in the hydroformylation at 100 atm of carbon monoxide of the aforementioned olefins are reported in Scheme 1, where isomeric aldehydes present in concentrations lower than 0.5% have been neglected.

Formylation at position 6 of both 3–M–1–H and 4–M–1–H takes place to a very small extent. Formylation at the lateral methyl group is somewhat higher for both substrates.

The results obtained using 4–M–2–H as the substrate are very similar to those obtained in the case of 4–M–1–H.

The extent of the formylation at the position 2 in 4–M–1–H and 4–M–2–H is higher than that at the same position in 3–M–1–H. Correspondingly, position one is formylated to a greater extent in 3–M–1–H than in 4–M–1–H or in 4–M–2–H.

The extent of formylation on the methylene carbon atom in 2–E–1–P is rather large ($\simeq 71\%$). Formylation on either of the two alkyl groups bound to the carbon atom in position 2 takes place to almost the same extent; however, formylation at the terminal methyl groups takes place to different extents.

b) *Experiments under low carbon monoxide partial pressure.*

The results obtained in the experiments are also reported in Scheme I. Under the conditions used, formylation of the methyl group at position 6 is remarkable both with 3–M–1–H (21%) and with 4–M–1–H (15%). The lateral methyl group is formylated to a smaller extent (7-9%) in spite of its closeness to the double bond. Analogous to the results obtained under high carbon monoxide partial pressure, equivalent carbon atoms in 4–M–1–H and in 4–M–2–H are formylated to similar extents; furthermore, the extent of formylation at position 2 is larger with 4–M–1–H and 4–M–2–H than with 3–M–1–H.

Contrary to the results obtained under high carbon monoxide partial pressure, the extent of formylation at position 1 in 2–E–1–P is smaller than that for the two terminal methyl groups, which are formylated to about the same extent. Furthermore, the propyl chain on carbon 2 is formylated a little more than the ethyl chain (45% respectively 38%).

DISCUSSION

In the hydroformylation of 1–hexene (1–H) under high carbon monoxide partial pressure, [14] formylation a position 1 amounts to about 74% of the formylation at all carbon atoms: formylation at position 1 in 3–M–1–H and 4–M–1–H is higher than in 1–H (91% and 83% respectively); this is probably due to the decreasing steric intrance on position 1 in the series 3–M–1–H, 4–M–1–H, 1–H. Correspondingly, formylation at position 6 is smaller in 3–M–1–H and in 4–M–1–H (2% and 1% respectively) than in 1–H (6%); if we consider, however, formylation at the lateral methyl groups in 3–M–1–H and in 4–M–1–H, we can conclude that formylation at the methyl groups in a branched olefin is comparable with that observed in the straight chain olefin.

The statistical intramolecular deuterium distribution observed in the n–heptanal obtained from hydroformylation of 6,6,6–tri–deutero–1–hexene carried out under low (2 atm) carbon monoxide partial pressure [4], can be taken as an indication that position 1 and 6 are formylated to equal extents, as already discussed. Under similar reaction conditions, formylation at position 6 in 3–M–1–H and in 4–M–1–H is rather extensive (21% respectively 15%) but does not correspond to a rapid equilibrium between the two possible alkyl cobalt complex intermediates [8] because the ratio between the amount of 4–

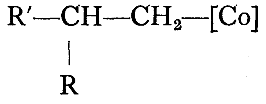
methylhexanal and 5–methylhexanal obtained from the above substrates is very different in each case (2.86 and 0.24 respectively).

Formylation of the lateral methyl group takes place to a smaller extent than formylation at position 6 in 3–M–1–H, 4–M–1–H and in 4–M–2–H in the hydroformylation under high carbon monoxide partial pressure, thus reflecting a greater proximity to the double bond. Similar results have been obtained for the branched octanes [9].

This does not hold for conditions of low carbon monoxide partial pressure, where also, the terminal methyl groups in 2–E–1–P are formylated to a larger extent than position 1.

Under these low p_{co} conditions there is a larger possibility for the cobalt catalytic complexed to migrate along the olefinic backbone, probably due to the presence of unsaturated catalytic species and to the fact that carbon monoxide insertion can become the rate determining step.

Species of type (1) give rise to aldehyde formation less than species of the type (2) do probably for steric reasons



$$R'{-}\underset{\substack{| \\ R}}{CH}{-}CH_2{-}[Co]$$

(1)

$$R''{-}CH_2{-}CH_2{-}[Co]$$

(2)

Iron complexes of the type (1) have been found to be thermodynamically less stable than the corresponding alkyl complexes of the type (2) [1]. Unfortunately there are no data about the activation energy required for carbon monoxide insertion in complexes of the type (1) and (2). As we do not have conditions suitable for rapid equilibration of the possible alkyl cobalt complex intermediates, the above data should, however, reflect, at least in part, the relative thermodynamic stabilities of the intermediate complexes (1) and (2) [5].

The reverse trend of formylation observed under high carbon monoxide partial pressure is probably connected with the activation energies responsible for the formation of the alkyl complexes, which then rapidly insert carbon monoxide.

The presence of a lateral chain in the γ or δ position with respect to the cobalt atom seems not to influence the rate of formylation of the primary carbon atoms, as shown by the equal extents of formylation of the two terminal methyl groups in 2–E–1–P at low carbon monoxide partial pressure.

The very similar results obtained in the hydroformylations of 4–M–1–H and 4–M–2–H under both high and low carbon monoxide partial pressures, may probably be explained by the similarities in the regioselectivities of the first attack of the intermediate cobalt carbonyl hydride catalyst. This attack should, for both sybstrates, take place prevalently at position 2, due to electronic reasons in 4–M–1–H 14 and to steric reasons in 4–M–2–H. Experiments are in progress to test the above hypothesis.

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