Journal of Organometallic Chemistry, 417 (1991) 77–88
Elsevier Sequoia S.A., Lausanne
JOM 21897

Hydroformylation of olefins in the presence of dicobalt octacarbonyl: some considerations *

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(Received January 7th, 1991)

Abstract

New data for the deuteroformylation of propene and hydroformylation of deuteropropenes are presented, together with revised data for the hydroformylation of but-1-ene-4-d_3. The mechanism of formation of isomeric aldehydes is discussed, and it is concluded that several reaction paths may be followed depending on the reaction conditions and the structure of the substrate.

Introduction

The cobalt-catalyzed hydroformylation of olefins, although long used industrially and the subject of a great number of investigations, is still a reaction whose mechanism is far from being well understood [1–5]. On the basis of the kinetic data and the chemistry of organocobalt carbonyls, a scheme was suggested [6] that rationalizes the formation of the aldehydes in terms of an initial interaction between the substrate and a cobalt carbonyl hydride, followed by the formation of alkyl- and acylcobalt carbonyl intermediates. Although the subsequent stages of the mechanism appear fairly clear, the nature of the initial interaction between the catalyst and substrate is still rather obscure.

The first stage or stages are particularly important since they apparently play a determinant role in the formation of the isomeric aldehydes. Olefin isomerization via reversible decomposition of alkylcobalt carbonyls is still the rationalization most frequently suggested for the formation of the isomeric products [7,8]. The evidence used to support such a suggestion has, however, often been obtained in experiments carried out either under conditions different from those that may be described as oxo conditions [9] or with very sterically hindered substrates [10]. The sensitivity of

* Dedicated to the memory of Professor Piero Pino.

0022-328X/91/$03.50

the catalytic system to the reaction conditions and/or the degree of steric hindrance is such that information useful in formulating an interpretation of the hydroformylation reaction must be obtained under classic oxo conditions, i.e. for a reaction carried out under a pressure of CO and H_2 of 50–100 atm each, at temperatures of 80–120 °C, with simple olefins.

We have therefore studied the hydroformylation of deuterated propenes and the deuteroformylation of propene in order to provide information additional to that previously reported [2,11–13]. We have also investigated the deuteroformylation of 2,3,3-trimethylbut-1-ene in order to bring together the results at 100% conversion [10] with those obtained at intermediate stages of the reaction, by monitoring both the extent of deuterium incorporation and its distribution in the residual olefin and in the reaction product.

Results

The hydrogen content and its distribution in the products from both the hydroformylation of deuterated propenes and the deuteroformylation of propene are shown in Table 1. In these hydroformylation experiments the carbon monoxide pressure was never < 50 atm and the conversion never exceeded 90% (Table 1); reaction times were ca 4 h.

The products and the residual olefin from the hydroformylation of deuterated propenes show complete retention of deuterium. In the deuteroformylation of propene there is no incorporation of deuterium into the residual olefin, and deuterium is present in the aldehydes in exactly the amount expected from the stoichiometry of the reaction.

In the hydroformylation of deuterated propenes and in the deuteroformylation of propene, the deuterium and hydrogen (protium) are found on all the carbon atoms of both linear and branched aldehydes (Table 1). The recovered residual olefin, on the other hand, has retained the original hydrogen or deuterium content at each position.

The mass spectra of the esters related to both straight- and branched-chain aldehydes obtained by hydroformylation of the deuterated propenes show the

Table 1

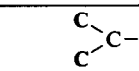
Hydroformylation of deuterated propenes in the presence of $Co_2(CO)_8$ [a]. Hydrogen content and distribution in the reaction products [b] and in the residual olefin [c]

Olefin	$C^4-C^3-C^2-COOCH_3$				$C^3(C^3)C^2-COOCH_3$			$C^3-C^2=C^1$			
	C^4	C^3	C^2	ΣH	C^3	C^2	ΣH	C^3	C^2	C^1	ΣH
$CD_3CH=CH_2$	1.23	1.35	1.42	4.00	3.34	0.66	4.00	0.00	1.00	2.00	3.00
$CH_3CH=CD_2$	2.28	1.33	1.39	5.00	4.34	0.66	5.00	3.00	1.00	0.00	4.00
$CD_3CD=CD_2$	0.31	0.34	0.35	1.00	0.82	0.18	1.00	0.00	0.00	0.00	0.00
$CH_3CH=CH_2$ [d]	2.65	1.65	1.70	6.00	5.30	0.70	6.00	3.00	1.00	2.00	6.00

[a] Olefin 45 mmol, Toluene 25 ml, $Co_2(CO)_8$ 0.30 g, T 100 °C, $p(H_2)$ 90 atm, $p(CO)$ 90 atm, Reaction time 4 h, Conversion < 90%, Butanal/2-Methylpropanal = 4. [b] ^1H NMR on the corresponding methyl esters: carbomethoxy group as internal standard. [c] ^1H NMR on its dibromoderivative: CH_2Br_2 as internal standard. [d] Deuteroformylation, $p(D)_2$ 90 atm.

Table 2

Hydroformylation of deuterated propenes in the presence of $Co_2(CO)_8$ [a]. Contribution (%) of methyl group isotopomers [b] to the chain methyl group of the products

Olefin	C-C-C-COOCH$_3$							
	CH_3	CH_2D	CHD_2	CD_3	CH_3	CH_2D	CHD_2	CD_3
$CD_3CH{=}CH_2$	22.6	14.4	20.8	42.2	23.3	16.0	27.7	33.0
$CH_3CH{=}CD_2$	42.8	34.4	22.8	0.0	26.2	39.1	34.7	0.0
$CD_3CD{=}CD_2$	0.0	0.0	34.4	65.6	0.0	0.0	43.3	56.7
$CH_3CH{=}CH_2$ [c]	64.0	36.0	0.0	0.0	54.3	45.7	0.0	0.0

[a] Olefin 45 mmol, Toluene 25 ml, $Co_2(CO)_8$ 0.30 g, T 100 °C, $p(H_2)$ 90 atm, $p(CO)$ 90 atm, Reaction time 4 h, Conversion < 90%, Butanal/2-Methylpropanal = 4. [b] Determined by mass spectroscopy from the relative intensity of the peaks arising from $[M - \text{chain group methyl}]^+$ ions. [c] Deuteroformylation, $p(D_2)$ 90 atm.

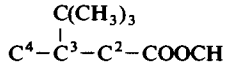
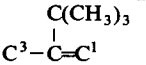
presence of the peaks corresponding to only the expected $[M - OCH_3]^+$ fragment, indicating that no loss or intermolecular transfer of deuterium has taken place.

The contributions of the methyl group isotopomers of the aldehydes were determined and are shown in Table 2. The predominant methyl group in the straight-chain aldehydes derived from either $CD_3CH{=}CH_2$ or $CH_3CH{=}CD_2$ is that having the same isotopic substitution as the starting material; substantial contributions, however, are made by the other isotopomers.

In the deuteroformylation of a highly hindered olefin such as 2,3,3-trimethylbut-1-ene under classic oxo conditions we monitored the evolution of deuterium incorporation as the reaction proceeded by determining the hydrogen content of both the aldehyde and the residual olefin at 40 and 80% conversion (Tables 3 and 4). The olefin gradually loses hydrogen: at 40% conversion the loss of hydrogen per molecule is the same for the residual olefin and the aldehyde produced. At a higher conversion, 80%, the amount of hydrogen lost from the olefin is considerably higher. The fall in the hydrogen content of the aldehyde is less relevant because what is measured in this case is the average content, which includes the aldehyde formed at an earlier stage when the hydrogen loss was lower. Some molecules of both the

Table 3

Deuteroformylation of 2,3,3-trimethylbut-1-ene in the presence of $Co_2(CO)_8$ [a]. Hydrogen content and distribution at various extents of conversion in the main product [b] and in the residual olefin [c]

Olefin conversion (%)	Reaction time (h)							
		C^4	C^3	C^2	ΣH [d]	C^3	C^1	ΣH [e]
40.0	9	2.48	0.63	1.50	4.61	2.66	1.94	4.60
80.0	22	2.21	0.61	1.44	4.26	2.17	1.58	3.75

[a] Olefin 36 mmol, Benzene 20 ml, $Co_2(CO)_8$ 0.40 g, T 100 °C, $p(D_2)$ 100 atm, $p(CO)$ 100 atm. [b] From the ^1H NMR spectra of the corresponding methyl esters: carbomethoxy group as internal standard. [c] ^1H NMR: $-C(CH_3)_3$ group as internal standard. [d] Hydrogen content in the positions C_2–C_4. [e] Hydrogen content in the positions C_1, C_3.

Table 4

Deuteroformylation of 2,3,3-trimethylbut-1-ene in the presence of $Co_2(CO)_8$ [a]. Deuterium content (%) of the main product [b] and of the residual olefin [c] at different conversion degrees

Olefin conversion (%)	Ester				Residual olefin			
	3D	2D	1D	0D	3D	2D	1D	0D
40.0	0.0	17.9	64.8	17.3	0.0	7.5	30.0	62.5
80.0	8.6	25.8	52.3	13.3	4.4	21.6	41.4	32.6

[a] Olefin 36 mmol, Benzene 20 ml, $Co_2(CO)_8$ 0.40 g, T 100 °C, $p(D_2)$ 100 atm, $p(CO)$ 100 atm. [b] Determined by mass spectroscopy from the relative intensities of the peaks arising from $[M-OCH_3]^+$ ions. [c] Determined by mass spectroscopy from the relative intensity of molecular ions.

residual olefin and the deuteroformylation product contain up to three deuterium atoms, while some molecules of the aldehyde contain no deuterium in the chain.

It is noteworthy that on the trisubstituted carbon atom, at which a clean addition of a deuteride catalyst should lead to a zero hydrogen content, there is a fairly high hydrogen content that must come either from one of the adjacent carbon atoms or from addition of a cobalt carbonyl hydride instead of a deuteride. Deuterium incorporation in the residual olefin and in the aldehydes produced under the same conditions is thus very different for the two olefins tested, 2,3,3-trimethylbut-1-ene and propene.

Discussion

The results reported help to provide a more complete background to the problem of rationalizing the mechanism of hydroformylation of olefins. With this aim in mind we consider first the reaction performed under classic oxo conditions on simple olefins in the presence of $Co_2(CO)_8$ as catalyst precursor, and with benzene or toluene as solvent.

Evidence arguing against any relevant role of isomerization of the olefin prior to its hydroformylation in determining the formation of the isomeric aldehydes was first obtained from determination of the composition of the unconverted olefin in the hydroformylation of pent-1-ene under a high carbon monoxide pressure [11]. No isomerized olefin was detected up to 70% conversion, and the isomeric distribution of the products remained constant throughout the whole reaction.

Further evidence pointing to the same conclusion was provided by the high optical yield obtained in the formation of (R)-3-ethylhexanal by hydroformylation of (+)-(*S*)-3-methylhex-1-ene [14]. Casey re-examined this aspect by studying the hydroformylation of 3-methylhex-1-ene-3-d_1 and suggested a rationalization based on reversible decomposition of an alkylcobalt carbonyl, with no release of the olefin before hydroformylation [15]. Such a rearrangement without olefin release would also account for the high stereoselectivity found in the hydroformylation of (+)-(*S*)-3-methylhex-1-ene [14].

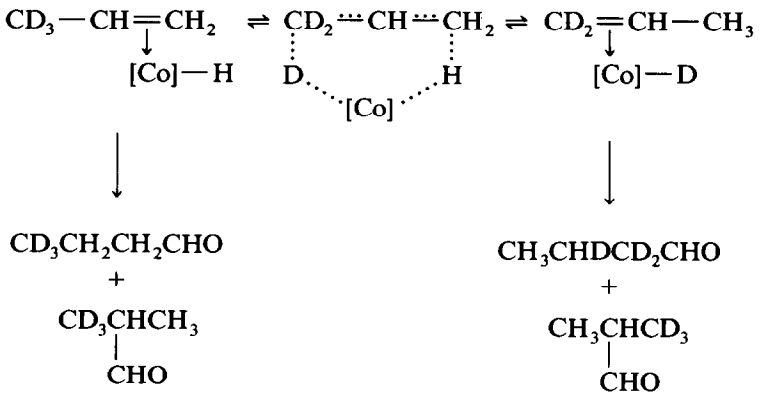
The reversible decomposition of alkylcobalt carbonyls into olefin and cobalt carbonyl hydride had even earlier been considered to be the key reaction for the rationalization of the isomer formation [7,8]. Such reaction, which may take place under appropriate conditions ($p(CO) < 5$ atm, T 20 °C) [9], should not, however,

be held to be responsible for the formation of isomeric aldehydes in a classic hydroformylation. Under classic oxo conditions the carbonylation of the alkylcobalt carbonyls is much more favoured than their decomposition to olefin and cobalt hydride. The evidence for this is provided by the results obtained in the synthesis of alkylcobalt carbonyls from alkyl halides and sodium carbonyl cobaltate under carbon monoxide and hydrogen pressure (200 atm $CO:H_2 = 1:1$) at 80 °C. Only one aldehyde is obtained, that arising from the carbonylation of the alkyl residue as it is in the halide. No isomeric aldehydes are formed from either primary or secondary alkyl halides, and not even head- to tail-isomerization is detected with primary alkyls [16,17]. Recently Cornely et al. [18] confirmed the above results for reactions of 1- or 2-bromododecanes with $NaCo(CO)_4$ under 160 atm CO and H_2 (1 : 1) at 80 °C. The detection of isomeric aldehydes when this reaction was carried out at higher temperatures ($\geqslant 100$ °C) and lower CO pressures (40 atm), already borderline oxo conditions, led these authors to suggest that the decomposition under these new conditions of alkylcobalt tetracarbonyls to the corresponding tricarbonyls is responsible for the isomer formation. Alkylcobalt tricarbonyl isomerization was suggested to account for the formation of isomeric aldehydes in the hydroformylation of olefins. Such a suggestion, based on the isomerization ability of $d^8$4 complexes (alkylcobalt tricarbonyls), is not supported by any evidence for the presence of these intermediates under oxo conditions. The hypothesis would also lead to the conclusion that in the hydroformylation of linear internal olefins, when the CO pressure is lowered and the reaction temperature raised, so leading to an increase in the isomerizing ability of the catalytic system, there should be an increase in the proportion of straight chain aldehyde, but this is exactly the opposite of the observed results [2,19]. The increase in straight chain isomer formation detected by Cornely et al. as the temperature was raised from 80 to 100 °C in the hydroformylation of dodec-6-ene in the presence of stoichiometric amount of $Co_2(CO)_8$ is surprising and unusual.

Evidence in favour of the stability of the alkylcobalt carbonyl intermediates under oxo conditions is provided by the results obtained in carbonylation of orthoesters [20–23]. This reaction, which, as indicated by kinetic evidence and isolation of the acylcobalt carbonyl intermediates in the stoichiometric reaction, involves the same mechanism as the hydroformylation [20,22], except for the initial stage, and therefore goes through alkyl- and acylcobalt carbonyls, yields only one aldehyde isomer. This is that formed by insertion of a formyl group at the carbon atom originally bound to the oxygen in the orthoester and thus attached to the metal in the alkylcobalt carbonyl intermediate [20–23].

If alkylcobalt carbonyl decomposition and isomerization must be excluded, the precursor of the alkyl derivative, formed in the olefin-catalyst interaction, must be responsible for the hydrogen shift along the molecule of the substrate. This precursor must not undergo either olefin release before hydroformylation or hydrogen exchange with the gaseous phase.

Our new data add a further indication that only one molecule of the olefin at a time is involved in the catalytic intermediates. We reinforced the first observation pointing in this direction by examining the hydroformylation of deuterated propenes under classic oxo conditions with the hydroformylation of mixtures of perdeuterated propene and, either ethylene or cyclohexene. In all cases the only deuterium-containing aldehydes were butanal and 2-methylpropanal.



Scheme 1

Deuteroformylation of 2,3,3-trimethylbut-1-ene gave results substantially different from those from the deuteroformylation of propene. In fact the isotopic composition of the products and of the residual substrate changed as the conversion proceeded (Tables 3, 4 and data from ref. 10) in the case of the hindered olefin, while with propene the isotopic composition remains unchanged.

As regards the data obtained in the deuteroformylation of 2,3,3-trimethylbut-1-ene, only alkylcobalt carbonyl decomposition, with olefin release, can account for both deuterium incorporation and distribution.

The significant presence of hydrogen on the trisubstituted carbon atom of the aldehyde, which may be rationalized in terms of a 1,2-hydrogen shift in the substrate, brought about by $HCo(CO)_4$ derived from the decomposition of the alkylcobalt carbonyl formed by an earlier addition of $DCo(CO)_4$ to the starting olefin, shows that the rate of reaction of the hydride with the olefin is faster than that of H/D exchange with the gaseous phase.

The above discussion shows clearly that information derived from experiments on hindered olefins can not be taken as relevant in elucidating the mechanism of hydroformylation of simple olefins such as propene. The decomposition of alkylcobalt carbonyls, which may, as suggested by Consiglio [10], be involved in the hydroformylation of 2,3,3-trimethylbut-1-ene, certainly does not play a significant role when the substrate is propene.

Table 5

Hydroformylation of but-1-ene-4-d_3 in the presence of $Co_2(CO)_8$ [a]. Contribution (%) of methyl group isotopomers [b] to the chain methyl group of the products

Isotopomer	Methyl pentanoate	Methyl 2-methylbutanoate
CH_3	21.5	47.4
CH_2D	3.5	2.6
CHD_2	6.1	7.6
CD_3	68.9	42.4

[a] Olefin 34 mmol, Toluene 25 ml, $Co_2(CO)_8$ 0.25 g, T 100 °C, $p(H_2)$ 80 atm, $p(CO)$ 80 atm, Reaction time 4 h, Conversion < 80%, Pentanal/2-Methylbutanal = 4. [b] Determined by mass spectroscopy from the relative intensities of the peaks arising from $[M -$ main chain methyl group$]^+$ ions.

Table 6

Hydroformylation of but-1-ene-4-d_3 in the presence of $Co_2(CO)_8$ [a]. Contribution (%) of $CXY-COOCH_3$ (X, Y = H or D) isotopomers [b] to methyl pentanoate

$[CH_2=C(OH)OCH_3]^+$	82.6
$[CHD=C(OH)OCH_3]^+$ $[CH_2=C(OD)OCH_3]^+$	9.4
$[CD_2=C(OH)OCH_3]^+$ $[CHD=C(OD)OCH_3]^+$	8.0

[a] Olefin 34 mmol, Toluene 25 ml, $Co_2(CO)_8$ 0.25 g, T 100 °C, $p(H_2)$ 80 atm, $p(CO)$ 80 atm, Reaction time 4 h, Conversion < 80%, Pentanal/2-Methylbutanal = 4. [b] Determined by mass spectroscopy, from the relative intensity, on the peaks derived from Mc Lafferty rearrangements.

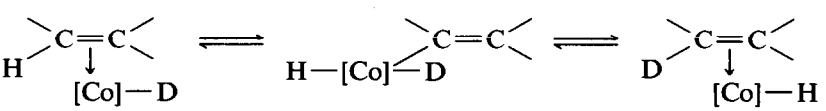
The decomposition of alkylcobalt carbonyls must be excluded as a major process even with the restriction suggested by Casey [15] that there should be no release of the olefin from the complex. Such decomposition in fact would involve isomer formation in the carbonylation of orthoesters and in the synthesis of alkylcobalt carbonyls from alkyl halides and sodium carbonylcobaltate under carbon monoxide and hydrogen [16–20].

Even the hydrogen shift that we suggested previously [24] (Scheme 1) does not provide a satisfactory explanation, since it cannot account for the insertion of deuterium, in position 2 in 2-methylpropanal formed by deuteroformylation of propene (Tables 1 and 2).

A careful re-examination of the earlier data on deuterium distribution in the ω and α positions of the hydroformylation products of but-1-ene-4-d_3 by use of more accurate procedures has shown that deuterium is present (Tables 5 and 6), even if in fairly small amounts, in positions which cannot be accounted for in terms of the isomerization scheme considered above. No suggestion made up to now seems to provide a satisfactory interpretation of all the experimental observations.

The hydroformylation mechanism must account also for the activation, whatever the substrate, of the hydrogen bound to the carbon atoms involved in the double bond; a possible rationalization of this activation is offered by the well documented oxidative addition of a vinylic C–H bond to a transition metal atom in a low oxidation state (Scheme 2) [25–31]. Furthermore, in this stage of the mechanism no release of the olefin must take place. It has, in fact, been shown that a vinyl C–H bond activation may precede π-coordination to the olefin [25,27–30] and may even occur more readily than the reversible addition of the metal hydride to the double bond [25].

Probably several pathways can lead to the hydrogen shifts and isomer distributions in the hydroformylation of olefins. The contribution of each to the overall results is evidently greatly dependent upon the reaction conditions and the structure of the substrate.



Scheme 2

Experimental

GLC analyses were performed with a Perkin–Elmer Sigma 1 chromatograph. Esters were separated by preparative GLC using a Perkin–Elmer F21 instrument. NMR spectra were recorded on a Varian VXR 300 spectrometer operating at 299.945 MHz. Mass spectra were recorded on a Perkin Elmer 270B spectrometer or a Shimadzu GCMS-QP2000 system.

Materials

Propene-3-d_3 [29] and but-1-ene-4-d_3 [24] were synthesized as previously described. 2,3,3-Trimethylbut-1-ene, methyl propanoate, and methyl cyclohexanecarboxylate were Aldrich products.

Synthesis of propene-1-d_2

A solution of propionic acid (22.2 g, 0.30 mol) in diethyl ether (200 ml) was added dropwise, at 0 °C to a suspension of $LiAlD_4$ (10.0 g, 0.24 mol) in diethyl ether (150 ml). The mixture was stirred for 3 h at 20 °C and then heated for 6 h at the reflux temperature. Acetic anhydride (120.0 g, 1 mol) was added to the mixture at 0 °C and the mixture was heated at the reflux temperature for 8 h. An aqueous solution of $NaHCO_3$ was then added (up to pH 6) and the organic layer separated. After the usual work up, propyl-1-d_2 acetate (11.0 g, 0.106 mol, yield 35.3%) having b.p. 101 °C, n_D^{20} 1.3840, was recovered. ^{1}H NMR spectrum (CCl_4 as solvent): δ 1.10 (t, 3H, CH_3CH_2); 1.85 (q, 2H, CH_3CH_2); 2.18 (s, 3H, CH_3COO).

The ester was pyrolyzed by the usual procedure at 480 °C to give propene-1-d_2 (1.9 g, 0.045 mol, yield 42.8%). The ^{1}H NMR spectrum of its dibromo-derivative obtained in the presence of CH_2Br_2 as internal standard showed peaks at (CCl_4 as solvent): δ 1.84 (d, 3H, CH_3CHBr); 4.23 (q, 1H, CH_3CHBr).

Synthesis of hexadeuteropropene

A solution of hexadeuteroacetone (61.1 g, 0.95 mol) in diethyl ether (100 ml) was added at 0 °C to a suspension of $LiAlD_4$ (10.0 g, 0.24 mol) in 100 ml of diethyl ether. The mixture was heated at the reflux temperature for 6 h, then cooled at 0 °C, and acetic anhydride (240 g, 2 mol) was added. The mixture was heated at the reflux temperature for 6 h and then cooled to room temperature. An aqueous solution of $NaHCO_3$ was finally added (up to pH 6) and the organic layer separated. After the usual work up, propyl-d_7 acetate was recovered (65.0 g, 0.59 mol, yield 62.1%) having b.p. 102 °C, n_D^{25} 1.3725. ^{1}H NMR spectrum (C_6D_6 as solvent): δ 1.72 (s, CH_3COO). This ester (18.0 g, 0.16 mol) was pyrolyzed at 480 °C to give hexadeuteropropene (3.2 g, 0.067 mol, yield 41.2%). The ^{1}H NMR spectrum of its dibromo-derivative (30% w/w, CCl_4 as solvent) showed no signals.

Hydroformylation of olefins and identification of products

Olefins were hydroformylated as previously described [33]. The conditions used are indicated in the Tables. Aldehydes were converted into the corresponding methyl esters in the usual manner [33]. Esters and residual olefins were analyzed and separated by GLC, and spectroscopic data are reported below. The hydrogen distribution was determined by integration of the NMR spectra in the appropriate solvent; when necessary $Eu(DPM)_3$ was used as shift reagent. In the case of the

esters, the methyl group of the $COOCH_3$ moiety was used as the internal standard. Residual propenes were converted into the corresponding 1,2-dibromo-derivative; dibromomethane was used as internal standard. The $C(CH_3)_3$ group present in 2,3,3-trimethylbut-1-ene was used as the internal standard for this olefin. Some significant peaks of the mass spectra (normalized) are shown; their intensities were corrected for relative isotopic abundance.

Hydroformylation of propene-3-d_3

Residual olefin. ^{1}H NMR spectrum of the dibromo-derivative (CCl_4 as solvent): δ 3.65 (m, 2H, CH_2Br); 4.23 (m, 1H, CHBr).

Methyl butanoate. ^{1}H NMR spectrum (C_6D_6 as solvent): δ 0.71 (m, 1.23H, CH_3CH_2); 1.42 (m, 1.35H, CH_3CH_2); 2.00 (m, 1.42H, CH_2COOCH_3); 3.35 (s, 3H, $COOCH_3$). The mass spectrum showed peaks at m/e 74 $[M - OCH_3]^+$ (100%), 87 $[M - CD_3]^+$ (15.1%), 88 $[M - CHD_2]^+$ (7.4%), 89 $[M - CH_2D]^+$ (5.2%), 90 $[M - CH_3]^+$ (8.1%).

Methyl 2-methylpropanoate. ^{1}H NMR spectrum (C_6D_6 as solvent): δ 0.98 (m, 3.34H, $(CH_3)_2CH$); 2.28 (m, 0.66H, $(CH_3)_2CH$); 3.35 (s, 3H, $COOCH_3$). The mass spectrum showed peaks at m/e 74 $[M - OCH_3]^+$ (100%), 87 $[M - CD_3]^+$ (23.9%), 88 $[M - CHD_2]^+$ (20.1%), 89 $[M - CH_2D]^+$ (11.6%), 90 $[M - CH_3]^+$ (16.9%).

Hydroformylation of propene-1-d_2

Residual olefin. ^{1}H NMR spectrum of its dibromo-derivative (CCl_4 as solvent): δ 1.84 (d, 3H, CH_3); 4.23 (q, 1H, CHBr).

Methyl butanoate. ^{1}H NMR spectrum (C_6D_6 as solvent): δ 0.71 (m, 2.28H, CH_3CH_2); 1.42 (m, 1.33H, CH_3CH_2); 2.00 (m, 1.39H, CH_2COOCH_3); 3.35 (s, 3H, $COOCH_3$). The mass spectrum showed peaks at m/e 73 $[M - OCH_3]^+$ (100%), 87 $[M - CHD_2]^+$ (9.2%); 88 $[M - CH_2D]^+$ (13.9%), 89 $[M - CH_3]^+$ (17.3%).

Methyl 2-methylpropanoate. ^{1}H NMR spectrum (C_6D_6 as solvent): δ 0.98 (m, 4.34H, $(CH_3)_2CH$); 2.28 (m, 0.66H, $(CH_3)_2CH$); 3.35 (s, 3H, $COOCH_3$). The mass spectrum showed peaks at m/e 73 $[M - OCH_3]^+$ (100%), 87 $[M - CHD_2]^+$ (27.8%), 88 $[M - CH_2D]^+$ (31.3%), 89 $[M - CH_3]^+$ (21.0%).

Hydroformylation of hexadeuteropropene

Residual olefin. ^{1}H NMR spectrum of its dibromo-derivative: (10% w/w, CCl_4 as solvent): no signals.

Methyl butanoate. ^{1}H NMR spectrum (C_6D_6 as solvent): δ 0.71 (s broad, 0.31H, CH_3CH_2); 1.42 (s broad, 0.34H, CH_3CH_2); 2.00 (s broad, 0.35H, CH_2COOCH_3); 3.35 (s, 3H, $COOCH_3$). The mass spectrum showed peaks at m/e 77 $[M - OCH_3]^+$ (100%), 90 $[M - CD_3]^+$ (16.4%), 91 $[M - CHD_2]^+$ (8.6%).

Methyl 2-methylpropanoate. ^{1}H NMR spectrum (C_6D_6 as solvent): δ 0.98 (s broad, 0.82H, $(CH_3)_2CH$); 2.28 (s broad, 0.18H, $(CH_3)_2CH$); 3.35 (s, 3H, $COOCH_3$). The mass spectrum showed peaks at m/e 77 $[M - OCH_3]^+$ (100%), 90 $[M - CD_3]^+$ (29.3%), 91 $[M - CHD_2]^+$ (22.4%).

Deuteroformylation of propene

Residual olefin. ^{1}H NMR spectrum of its dibromo-derivative (CCl_4 as solvent): δ 1.84 (d, 3H, CH_3); 3.53 (dd, 1H, CH_2Br); 3.87 (dd, 1H, CH_2Br); 4.23 (m, 1H, CHBr).

Methyl butanoate. ^{1}H NMR spectrum (C_6D_6 as solvent): δ 0.71 (m, 2.65H, CH_3CH_2); 1.42 (m, 1.65H, CH_3CH_2); 2.00 (m, 1.70H, CH_2COOCH_3); 3.35 (s, 3H, $COOCH_3$). The mass spectrum showed peaks at m/e 72 $[M - OCH_3]^+$ (100%), 87 $[M - CH_2D]^+$ (16.6%), 88 $[M - CH_3]^+$ (29.5%).

Methyl 2-methylpropanoate. ^{1}H NMR spectrum (C_6D_6 as solvent): δ 0.98 (m, 5.30H, $(CH_3)_2CH$); 2.28 (m, 0.70H, $(CH_3)_2CH$); 3.35 (s, 3H, $COOCH_3$). The mass spectrum showed peaks at m/e 72 $[M - OCH_3]^+$ (100%), 87 $[M - CH_2D]^+$ (24.1%), 88 $[M - CH_3]^+$ (28.6%).

Hydroformylation of but-1-ene-4-d_3

Methyl pentanoate. The ^{1}H NMR spectrum was identical to that previously reported [21]. The mass spectrum showed peaks at m/e 74 $[CH_2{=}C(OH)OCH_3]^+$ (100%), 75 $[CHD{=}C(OH)OCH_3]^+$ or $[CH_2{=}C(OD)OCH_3]^+$ (11.4%), 76 $[CD_2{=}C(OH)OCH_3]^+$ or $[CHD{=}C(OD)OCH_3]^+$ (9.7%), 101 $[M - CD_3]^+$ (1.80%), 102 $[M - CHD_2]^+$ (0.16%), 103 $[M - CH_2D]^+$ (0.09%), 104 $[M - CH_3]^+$ (0.57%).

Methyl 2-methylbutanoate. The ^{1}H NMR spectrum was identical to that previously reported [21]. The mass spectrum showed peaks at m/e 101 $[M - CD_3]^+$ (89.5%), 102 $[M - CHD_2]^+$ (16.0%), 103 $[M - CH_2D]^+$ (5.5%), 104 $[M - CH_3]^+$ (100%).

Deuteroformylation of 2,3,3-trimethylbut-1-ene

Conversion 40%

Residual olefin. ^{1}H NMR spectrum (C_6D_6 as solvent): δ 1.02 (s, 9H, $C(CH_3)_3$); 1.68 (s, 2.66H, $CH_3C{=}CH_2$); 4.79 (d, 1.94H, CH_2). The mass spectrum showed peaks at m/e 98 $[C_7H_{14}]^+$ (100%), 99 $[C_7H_{13}D]^+$ (48.0%), 100 $[C_7H_{12}D_2]^+$ (12.0%).

Methyl 3,4,4-trimethylpentanoate. ^{1}H NMR spectrum (C_6D_6 as solvent): δ 0.71 (s, 9H, $C(CH_3)_3$); 0.85 (d, 2.48H, CH_3CH); 1.87 (m, 1.50H, CH_2COO); 2.35 (m, 0.63 H, CH_3CH); 3.38 (s, 3H, $COOCH_3$). The mass spectrum showed peaks at m/e 127 $[C_9H_{18}O_2 - OCH_3]^+$ (26.7%), 128 $[C_9H_{17}DO_2 - OCH_3]^+$ (100%), 129 $[C_9H_{16}D_2O_2 - OCH_3]^+$ (27.6%).

Conversion 80%

Residual olefin. ^{1}H NMR spectrum (C_6D_6 as solvent): δ 1.02 (s, 9H, $C(CH_3)_3$); 1.68 (s, 2.17H, $CH_3C{=}CH_2$); 4.79 (d, 1.58H, CH_2). The mass spectrum showed peaks at m/e 98 $[C_7H_{14}]^+$ (78.7%), 99 $[C_7H_{13}D]^+$ (100%), 100 $[C_7H_{12}D_2]^+$ (52.2%), 101 $[C_7H_{11}D_3]^+$ (10.6%).

Methyl 3,4,4-trimethylpentanoate. ^{1}H NMR spectrum (C_6D_6 as solvent): δ 0.71 (s, 9H, $C(CH_3)_3$); 0.85 (d, 2.21H, CH_3CH); 1.87 (m, 1.44H, CH_2COO); 2.35 (m, 0.61H, CH_3CH); 3.38 (s, 3H, $COOCH_3$). The mass spectrum showed peaks at m/e 127 $[C_9H_{18}O_2 - OCH_3]^+$ (25.4%), 128 $[C_9H_{17}DO_2 - OCH_3]^+$ (100%), 129 $[C_9H_{16}D_2O_2 - OCH_3]^+$ (49.3%), 130 $[C_9H_{15}D_3O_2 - OCH_3]^+$ (16.4%).

Hydroformylation of a mixture of hexadeuteropropene and ethylene

A mixture of hexadeuteropropene (3.2 g, 66 mmol), ethylene (1.5 g, 53 mmol), and $Co_2(CO)_8$ (0.300 g) in toluene (25 ml) under hydrogen (100 atm) and carbon monoxide (100 atm) was heated at 100 °C for 4 h. The resulting mixture was treated

as described above. The methyl butanoate and methyl 2-methylpropanoate thus obtained had the same deuterium content and spectroscopic properties as the products obtained by hydroformylation of hexadeuteropropene, as reported above. Methyl propanoate had the same ^1H NMR and mass spectra as an undeuterated reference sample.

Hydroformylation of a mixture of hexadeuteropropene and cyclohexene

A mixture of hexadeuteropropene (1.7 g, 35 mmol), cyclohexene (3.3 g, 40 mmol), and $Co_2(CO)_8$ (0.300 g) in toluene (25 ml) under hydrogen (100 atm) and carbon monoxide (100 atm) was heated at 100 °C for 5 h. The resulting mixture was treated as described above. The methyl butanoate and methyl 2-methylpropanoate thus obtained had the same deuterium content and spectroscopic properties as the products obtained by hydroformylation of hexadeuteropropene, as reported above. Methyl cyclohexanecarboxylate had the same ^1H NMR and mass spectra as an undeuterated reference sample.

Acknowledgements

We thank M.P.I. and C.N.R. "Progetto Finalizzato Chimice Fine e Seconderia" for financial support.

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