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Reversibility of palladium-alkyl intermediate formation in deuterioalkoxycarbonylation of 1-hexene

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Abstract

The catalytic pathways of the $Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_2Cl_2$–$SnCl_2$ catalyzed 1-hexene hydroalkoxycarbonylation reaction have been elucidated. Using deuterium labelling, the different reaction products were detected by mass spectral analysis and the deuterium content and its distribution determined by ^{1}H-, ^{2}H- and ^{13}C-NMR methods. The great number of labelled species in residual olefins and carbonylated products does support the assumption that the hydrido (Pd–H) route is operating in the mechanism of this system. Alkyl-metal intermediates undergo reversible β-hydride elimination even at low reaction temperature depending on the catalyst used. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbonylation; 1-Hexene; Deuterium; Palladium; Catalysis; Mechanism

1. Introduction

Hydroalkoxycarbonylation of olefins [1,2] is supposed to take place through two reaction mechanisms [3]: the 'hydrido' [4] and 'carboalkoxy' [5] routes which denote the type of the active palladium species involved. They are claimed to be operative depending on the nature of the substrate and the reaction conditions, though the first one is the most widely accepted [6–8].

Hydride addition to the olefinic double bond to form palladium-alkyls followed by rearrangement through β-hydride elimination are basic processes of many homogeneous catalytic organic reactions. The formation and the fate of the metal–alkyl intermediates is regarded as an important step of the reaction. Recent investigation of the palladium-catalyzed deuterioalkoxycarbonylation of styrene and α-methylstyrene evidenced the different behaviour of the alkyl-palladium intermediates towards β-hydride elimination which accounts for the observed differences in regioselectivity [9]. This approach proved to be suitable to obtain direct information on the origin of the reaction products by using ^{2}H-NMR spectroscopy [10].

Up until now no systematic studies have been reported on the factors governing the similar reaction of alkyl type olefins, assumed to behave differently in comparison to aromatic substrates [11,12]. In order to gain insight into these aspects, deuterioalkoxycarbonylation of 1-hexene has been investigated at various temperatures and conversions in the presence of palladium-monophosphine catalysts. The reaction was also studied using Knifton's $SnCl_2$-modified catalytic system described as changing the ratio of the reaction products, leading to a prevalence of the linear one [12]. Deuterium content of both unconverted terminal and isomeric internal olefins, as well as of the carbonylated products was determined by GC-MS techniques, while the distribution of the isotope was obtained by ^{2}H- and ^{13}C-NMR spectroscopy.

2. Results and discussion

2.1. Deuterioalkoxycarbonylation experiments

Deuterioalkoxycarbonylation of 1-hexene (Scheme 1) has been carried out at various temperatures under 40

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atm CO pressure with $Pd(PPh_3)_2Cl_2$ (**A**) and $Pd(PPh_3)_2Cl_2-SnCl_2$ (**B**) as catalytic precursors in benzene. The reactions have been stopped generally at approximately 30% substrate conversion (Table 1). The exact conversions and the compositon of the reaction mixture were determined by GLC analysis. As expected, in the tin-containing catalytic system (**B**) the normal ester is overwhelming. Conversely, the reaction is not regioselective when system **A** is employed. The ratio of the branched product increases slightly by enhancing the reaction temperature in presence of $SnCl_2$, while in its absence the opposite takes place. The isomerization by-reaction of the substrate intensifies markedly with raising temperatures working with system **B**. Traces of 3-hexene (1% of the species present in the reaction mixture) were found above 100°C.

2.2. Deuterium content and its distribution in residual hexenes

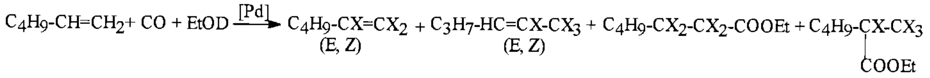
Purified samples of unconverted 1-hexene and samples enriched in 2-hexene were obtained by careful distillation of the reaction mixture at atmospheric pressure. Prior to distillation, unconverted d-ethanol was removed by repeated washing with distilled water, followed by drying with anhydrous $CaCl_2$.

The crude reaction mixtures, as well as the purified samples of hexenes were analyzed by mass spectrometry in order to determine the deuterium content (Table 2) which was calculated from the molecular ion region. Deuterium distribution in 1-hexene and 2-hexene recovered from the reaction mixtures was determined by ^{2}H-NMR analysis of the distilled olefin samples.

In Fig. 1 the ^{2}H-NMR spectrum of a purified sample of 1-hexene recovered from the deuterioalkoxycarbonylation experiment carried out at 60°C (30% conversion) in presence of catalyst **B** is reported. The resonances present at 6.03 and 6.09 ppm are due to (*E*) and (*Z*) 1-deuterated hexenes, the signal at 6.83 ppm is attributed to 2-deutero-1-hexene. The third group of signals is due to 1-deuterated 2-hexene impurities. The absolute amount of deuterium in each position was calculated by combination of ^{2}H-NMR (relative amount) and MS (total amount) data [13] and the results summarized in Table 3.

In the case of 1-hexene deuterium is incorporated in the vinyl moiety, only negligible amounts being present on the saturated carbon atoms. Furthermore, when Pd-complex **A** was present as catalyst precursor, most of the isotope labelling occurs in the terminal position, while in the presence of $SnCl_2$ 1-hexene-2-*d* predominates.

The ^{2}H-NMR spectrum of a sample enriched in 2-hexene, resulted from the experiment carried out at 100°C and 30% conversion in the presence of catalyst **B** (Fig. 2), shows the following features: two partially superimposed resonances at 2.60 and 2.65 ppm corresponding to *Z* and *E* 1-deuterated 2-hexenes and two signals at 6.58 and 6.62 ppm attributed to *Z* and *E* 2-hexenes labelled in position 2 and 3. Consequently, in the case of 2-hexenes most of the deuterium is incorpo-



$$C_4H_9\text{-}CH{=}CH_2 + CO + EtOD \xrightarrow{[Pd]} \underset{(E, Z)}{C_4H_9\text{-}CX{=}CX_2} + \underset{(E, Z)}{C_3H_7\text{-}HC{=}CX\text{-}CX_3} + C_4H_9\text{-}CX_2\text{-}CX_2\text{-}COOEt + C_4H_9\text{-}\underset{\substack{|\\ COOEt}}{C}X\text{-}CX_3$$

where X= H or D

Scheme 1. Deuterioalkoxycarbonylation of 1-hexene.

Table 1
Selectivity in the palladium-catalyzed deuterioalkoxycarbonylation of 1-hexene at various reaction temperatures and substrate conversions [a]

Reaction temperature (°C)	Catalyst system	Conversion (%) [b]	Composition of the reaction products (%)				N/B
			(*E*)-2-hex	(*Z*)-2-hex	B	N	
60	A	30	10	5	47	38	44/56
80	A	30	10	4	45	41	46/52
100	A	30	8	3	47	42	53/47
100	A	75	7	2	41	50	55/45
125	A	30	13	5	38	44	54/46
60	B	30	9	0	7	74	91/9
80	B	30	9	9	8	75	91/9
100	B	30	13	12	9	66	88/12
100	B	75	15	9	11	65	85/15
125	B	30	22	15	11	52	83/17

[a] 10.4 mmol of 1-hexene, 31.2 mmol of d-ethanol, 0.33 mmol of $Pd(PPh_3)_2Cl_2$(A) or 0.33 mmol of $Pd(PPh_3)_2Cl_2$, 1.65 mmol of $SnCl_2$ (B) in 15 ml benzene; CO, 40 atm; volume of reaction vessel 50 ml.

[b] Refers to 1-hexene; determined by GLC with benzene as internal standard estimated accuracy ± 1%.

Table 2
Deuterium distribution of 1- and 2-hexenes determined via MS analysis [a]

Reaction temperature (°C)	Catalyst system	Conversion (%)	Distribution of isotopic species and D content at 1-hexene (%)			Distribution of isotopic species and D content at 2-hexenes (%)		
			0D	1D	2D	0D	1D	2D
60	A	30	100	0	0	76	21	3
80	A	30	90	10	0	68	29	3
100	A	30	88	11	1	54	45	1
100	A	75	86	12	2	47	45	8
125	A	30	86	11	3	37	50	12 [b]
60	B	30	94	6	0	87	10	6
80	B	30	90	10	1	85	11	4
100	B	30	75	22	3	73	20	7
100	B	75	68	27	5	51	36	12 [b]
125	B	30	72	24	4	42	44	13 [b]

[a] Estimated accuracy ± 3%.

[b] 1% trideuterated species detected.

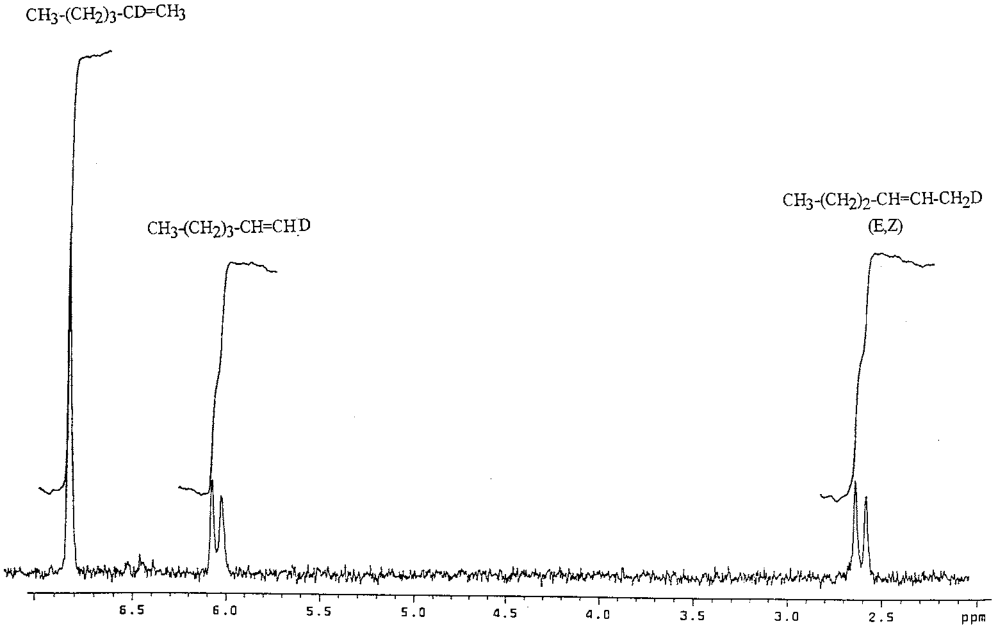


Fig. 1. ^{2}H-NMR spectrum of a purified sample of 1-hexene recovered from deuterioalkoxycarbonylation at 60°C (30% conversion), in the presence of catalyst **B**.

rated on the terminal carbon atom in both catalytic systems.

2.3. Deuterium content and distribution in carbonylated products

In the electron impact ionization mass spectra of the carbonylated deuterium-containing derivatives the abundance of the molecular ion *m*/*z* 158 was ca. 0.1% of the total ion current. This very low value did not enable us to determine the deuterium content with satisfactory accuracy. Chemical ionization with isobutane reagent gas was used to obtain abundant molecular ion cluster. The protonated form of the molecular ions appeared in the spectra, i.e. no significant ion at *m*/*z* 158 was detected. The molecular ion cluster was recorded in the mass range of *m*/*z* 154–168. Data were recorded using 'mass centered average' data acquisition mode.

The mass spectra of the products were determined from the distillation residue resulted after the elimination of olefins and, in some cases, also from the chromatographycally purified samples. The results obtained (Table 4) confirm the presence of 0, 1, 2, 3 or 4 deuterium atoms in the molecules. At temperatures as high as 125°C pentadeuterated species can also be detected in low amounts.

The evaluation of the relative amount of isotope atoms incorporated was again possible by ^{2}H-NMR spectra of the distillation residues. Separation of the ester products by column chromatography was necessary only in a few cases in order to determine the position of deuterium in the isomeric esters. In Fig. 3, showing the ^{2}H-NMR spectrum of the distillation residue of the reaction with catalyst **B** at 100°C and 30% conversion, signals arise from deuterio-ethyl-heptenoate and deuterio-ethyl-2-methyl-hexenoate.

The resonances at 2.07 ppm and 2.65 ppm are due to the deuterium nuclei of the methylene groups situated β and α to the CO moiety, respectively. For the branched ester two signals were detected: one at 1.61 ppm, corresponding to the isotope labelling on the methyl group and an other at 2.88 ppm from the methine position.

At some samples, deuterium incorporation was followed partly also by ^{13}C DEPT-NMR spectroscopy which enabled the identification of some of the labelled species as well, in accordance with the original ^{13}C assignments and the ^{2}H isotope shifts [14]. Thus, as far as the linear ester is concerned, the methylene group

Table 3
Deuterium distribution of 1- and 2-hexenes determined via ^{2}H-NMR analysis [a]

Reaction temp. (°C)	Catalyst system	Conversion (%)	D content at the vinyl and allyl C atoms of 1-hexene				D content at the vinyl and allyl C atoms of 2-hexene			
			$-C_3$	$-C_2$	$=C_1$	NDM [b]	$-C_4$	$-C_3=C_2$	$-C_1$	NDM
60	A	30				0.00			0.27	0.27
80	A	30			0.01	0.01			0.30	0.30
100	A	30			0.13	0.13			0.47	0.47
100	A	75			0.16	0.16			0.64	0.64
125	A	30		0.03	0.14	0.17	0.03	0.04	0.73	0.80
60	B	30		0.04	0.02	0.06			0.09	0.09
80	B	30		0.08	0.04	0.12		0.02	0.17	0.19
100	B	30		0.19	0.09	0.28		0.16	0.18	0.34
100	B	75		0.26	0.11	0.37	0.10	0.28	0.25	0.63
125	B	30		0.22	0.10	0.32	0.09	0.26	0.35	0.70

[a] Estimated accuracy of NMR measurements ±2%.

[b] NDM = number of deuterium per molecule determined from MS analyses.

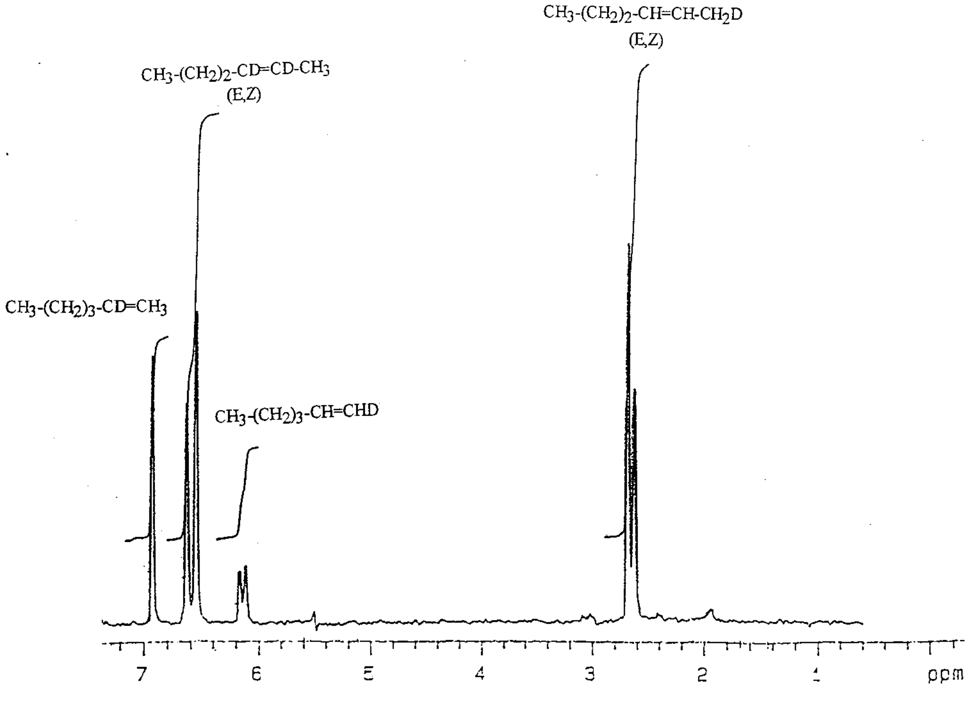


Fig. 2. ^{2}H-NMR spectrum of a sample enriched in 2-hexene resulted from deuterioalkoxycarbonylation of 1-hexene at 100°C (30% conversion), in the presence of catalyst **B**.

Table 4
Deuterium content of the linear and branched esters determined via MS analysis[a]

Reaction temperature (°C)	Catalyst system	Conversion (%)	Deuterium incorporation of the linear (N) ester (%)						Deuterium incorporation of the branched (B) ester (%)					
			0D	1D	2D	3D	4D	5D	0D	1D	2D	3D	4D	5D
60	A	30	60	37	3				65	30	5			
80	A	30	37	55	7	1			42	48	9	1		
100	A	30	35	53	9	2		1	35	51	13	1		
100	A	75	31	53	13	2		1	31	52	14	2	1	
125	A	30	20	56	19	3		2	23	55	16	3	2	1
60	B	30	33	65	2				67	28	5			
80	B	30	31	62	7				44	29	7			
100	B	30	34	55	9	1		1	47	45	8			
100	B	75	29	54	14	2		1	34	52	13	1		
125	B	30	33	46	17	3		1	37	48	13	2		

[a] Estimated accuracy ± 3%.

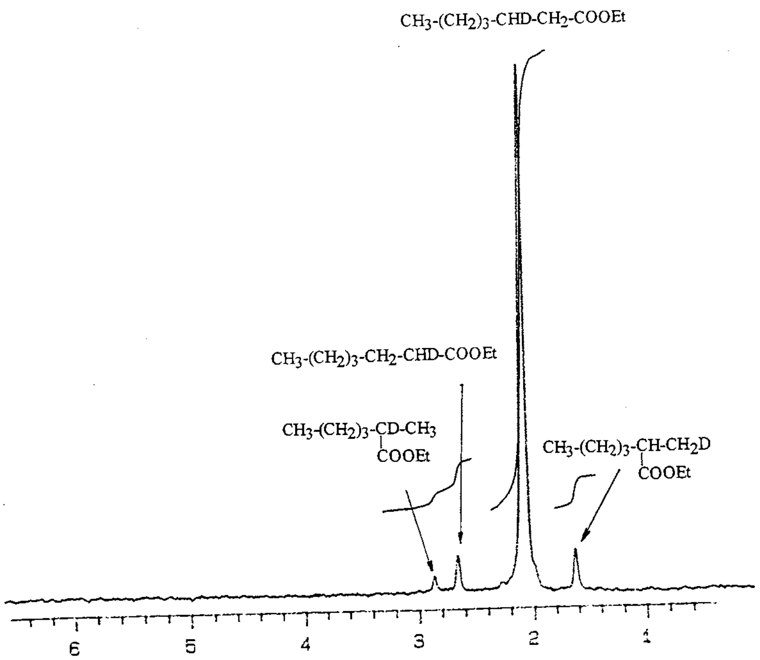
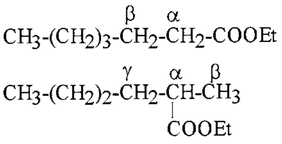


Fig. 3. ^{2}H-NMR spectrum of the distillation residue of the reaction mixture obtained after deuterioalkoxycarbonylation of 1-hexene at 100°C (30% conversion), in the presence of catalyst **B**.

Table 5
Deuterium content of the linear and branched esters determined via GC-MS and ^{2}H-NMR analysis [a]



$$\mathrm{CH_3\text{-}(CH_2)_3\text{-}\overset{\beta}{C}H_2\text{-}\overset{\alpha}{C}H_2\text{-}COOEt}$$

$$\mathrm{CH_3\text{-}(CH_2)_2\text{-}\overset{\gamma}{C}H_2\text{-}\underset{\displaystyle COOEt}{\overset{\alpha}{C}H}\text{-}\overset{\beta}{C}H_3}$$

Reaction temperature (°C)	Catalyst system	Conversion (%)	D content at the C atoms of the linear (N) ester			D content at the C atoms of the branched (B) ester		
			D(C)	D(C)	NDM [b]	D(C)	D(C)	NDM [b]
60	A	30	0.10	0.33	0.43		0.40	0.40
80	A	30	0.11	0.61	0.72		0.69	0.69
100	A	30	0.12	0.69	0.81		0.80	0.80
100	A	75	0.21	0.68	0.89		0.88	0.88
125	A	30	0.24	0.87	1.11	0.01	1.08	1.09
60	B	30	0.03	0.66	0.69		0.38	0.38
80	B	30	0.05	0.71	0.76	0.03	0.40	0.43
100	B	30	0.06	0.74	0.80	0.19	0.42	0.61
100	B	75	0.17	0.75	0.92	0.21	0.44	0.81
125	B	30	0.14	0.79	0.93	0.26	0.44	0.80 [c]

[a] Estimated accuracy of the NMR measurements ± 2%.

[b] Number of deuterium per molecule determined from MS measurements.

[c] The missing deuterium is incorporated on C_γ.

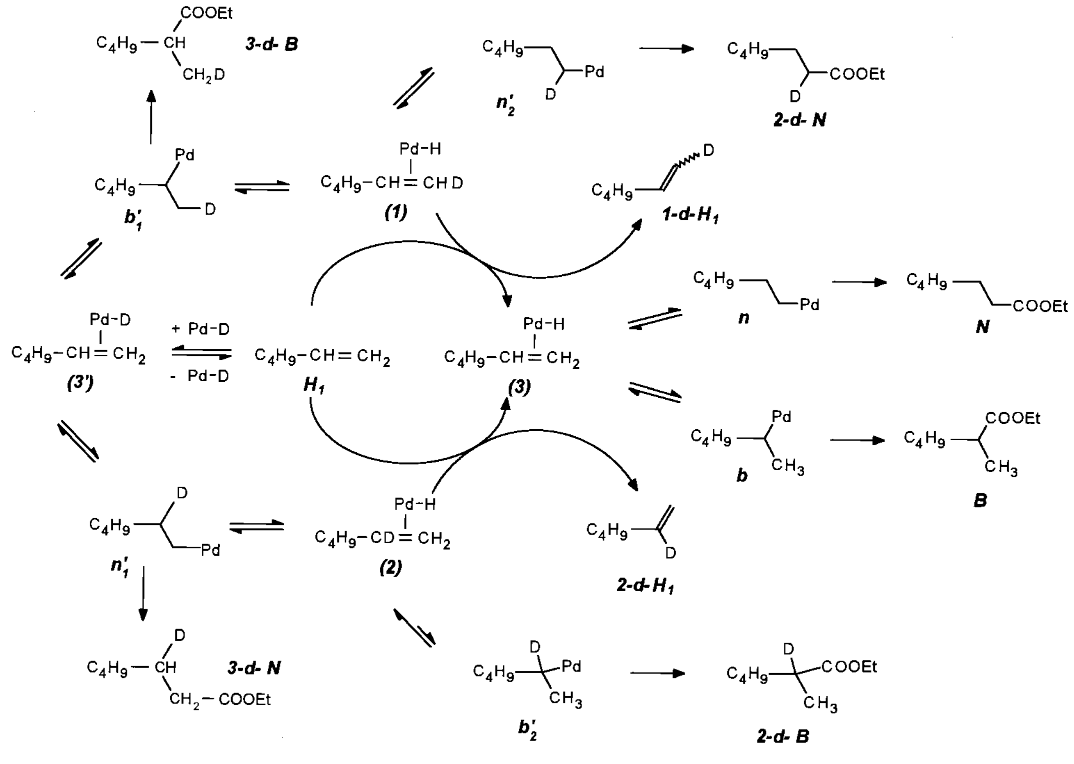
situated α to the CO moiety shows two in-phase singlets at $\delta = 34.25$ and 34.16 ppm corresponding to –CH$_2$– adjacent to –CH$_2$– and –CHD– groups, respectively, and two anti-phase triplets at $\delta = 33.88$ ppm ($J^1_{\mathrm{C,D}} = 19.7$ Hz) and 33.83 ppm ($J^1_{\mathrm{C,D}} = 19.8$ Hz) corresponding to –CHD– adjacent to –CH$_2$– and –CHD–. Similarly, the methylene group β to the CO results two in-phase singlets at $\delta = 24.83$ and 24.77 ppm due to –CH$_2$– group adjacent to –CH$_2$– and –CHD . Two anti-phase triplets at $\delta = 24.47$ ppm ($J^1_{\mathrm{C,D}} = 19.5$ Hz) and 24.41 ppm ($J^1_{\mathrm{C,D}} = 19.5$ Hz) correspond to –CHD– groups adjacent to –CH$_2$– and –CHD–. In the case of the branched ester the deuterium incorporation on the methyl group β to the CO can be followed with help of the resonances of the methine group showing three anti-phase singlets at $\delta = 39.42$, 39.34 and 39.27 ppm corresponding to CH adjacent to $-CH_3$, $-CH_2D$ and $-CHD_2$. The methyl moiety presents an anti-phase singlet at $\delta = 16.95$ ppm due to $CH-CH_3$ and an in-phase triplet centered at 16.67 ppm ($J^1_{C,D} = 19.5$ Hz) due to $CH-CH_2D$ species.

Deuterium amount in different positions of esters was determined similarly to those described for olefins combining the ^2H-NMR and MS data. Results summarized in Table 5 point out that in system **A** no deuterium incorporation occurs on the carbon atom C_α of the branched ester. When the $SnCl_2$-modified catalyst is involved, isotope is observed on both the C_α and C_β atoms of the esters.

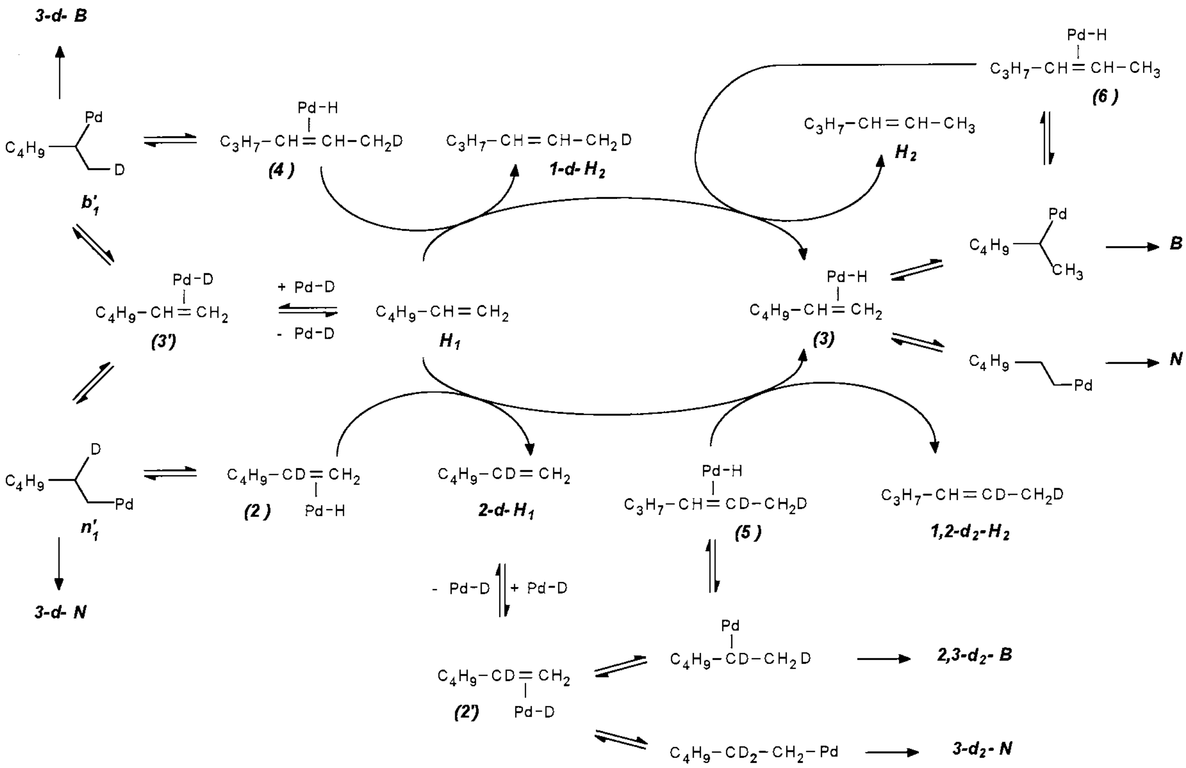
It should be noted that independent control experiments, carried out under typical reaction conditions, in presence of the catalyst, evidenced that direct H–D exchange between d-ethanol and the reaction products is negligible below 125°C.

The formation of the species detected can be accomodated in terms of the reaction pathways described. Thus, according to Scheme 2, the π-complex **3′**, formed by coordination of 1-hexene to a palladium-deuteride species, gives rise to the palladium-alkyl intermediates n'_1 and b'_1. Deuterated esters can be formed via carbonylation or π-complexes **2** and **1** through β-hydride elimination of a hydrogen atom (kinetic deuterium isotope effect [15]). This last step is reversible only for the branched isomer in both catalytic systems. Working with system **A**, the linear alkylpalladium is not involved in rearrangement processes, being transformed directly into the corresponding ester N. It forms however complex **2** when $SnCl_2$ is present. Intermolecular exchange processes of π-complexes with unlabelled 1-hexene lead to the nondeuterated π-complex **3** releasing in the same time 2- or 1-deuterated 1-hexenes (1-*d*-H_1 and 2-*d*-H_1). Consecutive additions lead to isomeric, unlabelled σ-complexes n and b and so to nondeuterated esters N and B. On the other hand, isomerization of the starting metal-alkyls n'_1 and b'_1 is possible via **2** and **1**, and thus b'_2 and n'_2 can be formed, leading to 2-deuterated esters (2-*d*-B and 2-*d*-N).

An analogous sequence accounts for the formation of 2-hexene species (Scheme 3). When the β-hydride elimination process from b'_1 takes place in the direction of the alkyl chain, complex **4** is formed which gives rise to 1-deuterated 2-hexene (1-*d*-H_2) via intermolecular exchange with 1-hexene. Similarly, nondeuterated 2-hexene (H_2) can be deducted from the unlabelled branched Pd-alkyl b through π-complex **6**. 1,2-Dideuterated 2-hexene (1,2-d_2-H_2) derives from 2-*d*-H_1 to which a Pd-D coordinates. Rearrangement through addition and elimination, followed by exchange with 1-hexene



Scheme 2. Pathways of deuterioalkoxycarbonylation of 1-hexene and the derived deuterated products.



Scheme 3. Pathways for the formation of deuterated hexene species during deuterioalkoxycarbonylation of 1-hexene.

afford the labelled olefin. At the same time, dideuterated isomeric esters (2,3-d_2-B and 3-d_2-N) are formed.

3. Conclusions

The results of this investigation show variable deuterium incorporation occuring in the unconverted substrate, isomeric olefins and carbonylated products when deuterioalkoxycarbonylation of 1-hexene is carried out at various temperatures and conversions employing $Pd(PPh_3)_2Cl_2$ (**A**) or $Pd(PPh_3)_2Cl_2$–$SnCl_2$ (**B**) catalysts. The compositon of the rather complex reaction mixture was elucidated succesfully by the combination of mass spectroscopy and NMR techniques. The species detected by MS and ^{2}H-NMR were evidenced also by ^{13}C-DEPT-NMR as an independent method. The formation of the deuterated species detected can be explained in the framework of the 'hydrido' route, in terms of the supposed reaction pathways.

As far as the catalyst precursor is concerned, $Pd(PPh_3)_2Cl_2$ (**A**) is known to lead to a slight prevalence of the branched isomer when medium-chain aliphatic olefins are hydroalkoxycarbonylated [11]. As some authors suppose, upon addition of $SnCl_2$ formation of the $SnCl_3^-$ ligand occurs, and this coordinates to the central palladium atom, providing thus a sterically particularly hindered catalyst [12,17], a phenomenon proved in details at related platinum complexes [18,19]. This shifts the equilibrium concentrations of the Pd-alkyl isomers towards the sterically less hindered terminal ones, i.e. anti-Markownikoff addition will be favoured [12].

The rearrangement of the isomeric metal-alkyl intermediates through succesive β-hydride eliminations and additions depends on the reaction parameters, the catalyst applied and the structure of the alkyl group bonded to the metal. In presence of $Pd(PPh_3)_2Cl_2$ neither the branched ester nor the hexenes were deuterated in position 2. So, the linear palladium-alkyl intermediate n'$_1$ must be transformed entirely into the corresponding linear ester (3-d-N). On the other hand detection of terminally labelled hexenes (1-d-H_1 and 1-d-H_2) and 2-deuterated linear carbonylated product (2-d-N) denotes the β-hydride elimination process occuring at the preferentially formed branched palladium-alkyl (b'$_1$). As a consequence, all the deuterated hexenes and part of the linear ester [corresponding to the $D(C_\alpha)/D(C_\beta)$ ratio, see Table 5] originates from the rearrangement processes of the branched Pd-σ-complex which accounts for the observed decay in the regioselectivity towards ethyl-2-methyl-hexanoate.

If $SnCl_2$ is present, a significant isomerization of the normal Pd-alkyl occurs even at lower temperatures since 2-deuterated hexenes (2-d-H_1 and 1,2-d-H_2) and branched ester (2-d-B) are present in addition to the species specified above. In this system β-eliminations and additions are reversible for both the isomeric alkylpalladium species in the temperature range investigated. The intensification of these processes causes a decrease in the regioselectivity towards the linear ester as the conditions become harsher.

Comparing this results with those previously reported for deuterioalkoxycarbonylation of styrene and α-methyl-styrene [9] the following should be noted. In presence of $Pd(PPh_3)_2Cl_2$ the reactions leading to the styrene-derived linear alkylpalladium are inhibited due to the stabilization of the branched species by the π-benzylic interaction of Pd. This results in a marked regioselectivity towards the branched ester. In the case of α-methyl-styrene the branched Pd-alkyl is also preferentially formed, however a fast β-hydride elimination from this tertiary Pd-σ-complex causes the dominant fomation of the linear product. Where β-elimination is possible, the formation of the primary alkylpalladiums is reversible, contrarily to those observed for 1-hexene. If $Pd(PPh_3)_2Cl_2$–$SnCl_2$ is employed, both aryl and alkyl olefins lead mainly to terminal esters and the formation of isomeric Pd-alkyls is reversible in each case.

4. Experimental

Benzene was distilled from sodium under argon atmosphere. d-Ethanol and 1-hexene were purchased from Fluka. $Pd(PPh_3)_2Cl_2$ [16] was prepared as reported in the literature. Anhydrous $SnCl_2$ was obtained by reacting $SnCl_2{\cdot}2H_2O$ with acetic anhydride and washing with diethylether.

GLC analyses were performed on a HP 5830 gas chromatograph equipped with SPB-1 columns (30 m × 1 μm film depth) and a flame ionization detector, helium was used as carrier gas.

Mass spectra were recorded on a VG ZAB2-SEQ instrument. Samples were introduced via a HP-5890A gas chromatograph with an HP-5MS (50 m × 0.25 μm film depth, 0.25 mm. i.d.) column, using helium as carrier gas.

The ^1H-, ^2H-, ^{13}C-NMR spectra were recorded on a Varian Unity 300 spectrometer, operating at 300, 46 and 75.4 mHz, respectively. Chemical shifts of the ^2H-NMR measurements were determined by reference to $CDCl_3$ as external standard.

4.1. Deuterioalkoxycarbonylation of 1-hexene: general procedure

The catalyst [225 mg, 0.33 mmol $Pd(PPh_3)_2Cl_2$ (**A**) or 225 mg, 0.33 mmol $Pd(PPh_3)_2Cl_2$ and 196.4 mg, 1.65 mmol anhydrous $SnCl_2$ (**B**)] was introduced into a 50 ml stainless steel autoclave. After sealing, a solution of olefin (1.3 ml, 10.4 mmol), d-ethanol (1.8 ml, 31.2 mmol) in benzene (15 ml) was introduced by suction. Then, carbon monoxide was charged (40 bar pressure at room temperature) and the mixture was magnetically stirred at the reaction temperature until the conversion desired. After cooling, the reaction mixture was syphoned out, and GLC was used to determine the composition with toluene as internal standard.

d-Ethanol and the solvent were removed under vacuum before ^2H, ^1H-NMR and MS analyses. Isomeric esters were separated by column chromatography and studied further. Column chromatography was carried out on a silicagel column using hexane, benzene, chloroform, dichloromethane and acetone as eluents.

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