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A study on the catalytic pathways of the hydroalkoxycarbonylation reaction of styrene

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Abstract

The catalytic pathways of the $Pd(PPh_3)_2Cl_2/SnCl_2$-catalysed styrene 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 ^1H-, ^2H- and ^{13}C-NMR methods. The great number of labelled species supports the assumption that the hydrido (Pd–H) route is the operating mechanism of this system. Alkyl–metal intermediates easily undergo β-hydride elimination. This process is reversible for both isomers even at low reaction temperature © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbonylation; Catalysis; Mechanism; Palladium

1. Introduction

In the hydroalkoxycarbonylation of olefins [1] with different Pd(II) catalysts generally two mechanisms [2] are accepted. The 'hydrido-route', operating in systems producing mainly linear esters [3], involves olefin insertion into Pd–H followed by CO insertion into the Pd–alkyl bond, yielding the final product upon nucleophilic attack of the alkanol. Alternatively, according to the 'carboalkoxy' mechanism, which is often invoked for reactions where the major product is the branched one [4], a Pd–acyl species is formed by the attack of the alcohol on Pd–CO. Insertion of the olefin into the Pd–COOR bond is followed by protonolysis of the metal–alkyl σ bond to give the corresponding ester and regeneration of the active form. These two mechanisms are claimed to be operative depending on the reaction conditions and substrates [5]. In order to differentiate between the two mechanisms in Knifton's [6] $Pd(PPh_3)_2Cl_2/SnCl_2$ catalytic system and to gain an insight into the pathways governing the reaction, the deuterioalkoxycarbonylation of styrene has been carried out.

In this paper we describe a detailed investigation of the reaction performed at various temperatures and different conversions. Using the labelled species determined by MS and NMR (^1H, ^2H, ^{13}C) techniques, we deduce the catalytic pathways leading to these compounds.

2. Results

2.1. Deuterioalkoxycarbonylation of styrene

Deuterioalkoxycarbonylation of styrene (Scheme 1) has been carried out at different temperatures between 60 and 120°C and 40 atm of CO with $Pd(PPh_3)_2Cl_2/$

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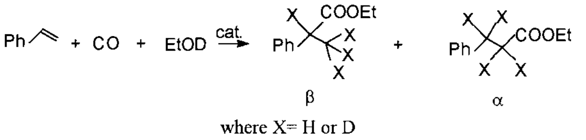


Scheme 1. Deuterioalkoxycarbonylation reaction of styrene.

$SnCl_2/PPh_3$ as the catalyst precursor in toluene (Table 1). At 100°C the reaction has been studied for various degrees of substrate conversion. No high-boiling compounds are formed at these temperatures. The ratio between ethyl-3-phenylpropanoate (β-isomer) and ethyl-2-phenylpropanoate (α-isomer) was determined by GLC analysis. The β-isomer predominates over α, the ratio of the branched product increasing slightly with the reaction temperature (from $\alpha/\beta = 20.3/79.7$ at 60°C to $\alpha/\beta = 26.7/73.3$ at 120°C) and the conversion degree (from $\alpha/\beta = 22.3/77.7$ at 30% conversion to $\alpha/\beta = 25.2/74.8$ at 100% conversion). Pure samples of the linear ester and samples enriched in the branched form were obtained by column chromatography on silica gel.

The crude reaction mixture as well as the purified samples of isomeric esters were analysed by mass spectroscopy and by ^1H-, ^2H-, ^{13}C-NMR spectroscopy in order to determinate the extent and the position of deuterium incorporation in the molecules. Inspection of the ^2H-NMR spectra allowed the rapid and complete identification of all the deuterated species present in solution [7]. Fig. 1 shows the ^2H-NMR spectrum of the reaction mixture in toluene (with residual EtOD removed) formed in the reaction at 100°C with 30% conversion. The main groups of signals are those arising from deuterio-styrenes, deuterio-3-phenylpropanoate and deuterio-2-phenylpropanoate.

Table 1
Degree of regioselectivity in the palladium-catalysed deuterioalkoxycarbonylation of styrene at various reaction temperatures and substrate conversions[a]

Reaction temperature (°C)	Reaction time (h)	Conversion (%)[b]	α/β[c]
60	150	40	20.4/79.6
60	250	99	20.3/79.7
80	20	99	21.8/78.2
100	0.5	30	21.7/78.3
100	1	55	22.3/77.7
100	4.5	99	25.0/75.0
100	35	100	25.2/74.8
120	4	99	26.7/73.3

[a] Toluene solution (10 ml) containing 3.2 mmol of styrene, 28.9 mmol of d-ethanol, 75 mg of $Pd(PPh_3)_2Cl_2$, 55 mg of $SnCl_2$ and 50.1 mg of PPh_3; CO, 40 atm; volume of reaction vessel is 50 ml.

[b] Refers to styrene; determined by GLC with toluene as internal standard

[c] Estimated accuracy ±1%.

The three resonances at 5.28, 5.75 and 6.70 ppm are due to deuterium nuclei on the vinyl moiety of styrene. The signal at 6.70 comes from the isotopomeric species Ph–CD– having deuterium in position 2 while the two absorptions at 5.28 and 5.75 ppm from the two geometrical isomers (*E*)-1-deuterio-vinylbenzene and (*Z*)-1-deuterio-vinylbenzene arising from the presence of deuterium in the position 1.

In the case of the linear ester, two signals were recognised: that at 2.50 ppm from the methylene group situated α to the CO moiety and that at 2.90 ppm from the methylene group situated β to the CO. Analogously, for the branched ester two resonances were found, one at 1.53 ppm due to the methyl group on the tertiary carbon atom and another at 3.66 ppm due to the deuterium from the methine position.

Other features revealed by the spectrum were: (1) incorporation of deuterium is almost the same in the three possible positions of unconverted styrene; (2) in the linear ester there is a larger incorporation of deuterium on the methylene group adjacent to the phenyl ring than on the methylene near the CO function; (3) in the branched ester deuterium was predominantly incorporated in the methyl group at low conversions and, only to a small extent, in the methine group; (4) neither in unconverted styrene nor in the reaction products isotope labelling of the phenyl ring occurs.

2.2. Deuterium content and distribution in unconverted styrene

Deuterium content of the residual olefin was determined by GC–MS analyses from the crude reaction mixture. As the mass spectrum of styrene at 70 eV complicates the analysis of deuterated styrene [8], the measurements were carried out at 10–12 eV where the peak at m/z 103 $(M-1)$ disappears. Data gathered under these circumstances (Table 2) show that at lower conversions and temperatures the non-deuterated and monodeuterated species predominate over the di- or trideuterated ones which were found in increasing amounts at 100°C with 55% conversion. The average deuterium incorporation shows an increasing tendency with increasing temperature and conversion.

Deuterium distribution in unconverted styrene was easily determined by ^2H-NMR of the reaction mixture after elimination of solvent and residual ethanol-*d* on the base of the incorporation calculated previously for the products by means of ^1H-NMR. The composition of the mixture was determined by GLC. The global incorporation values determined by NMR analyses are in agreement with those found from MS data.

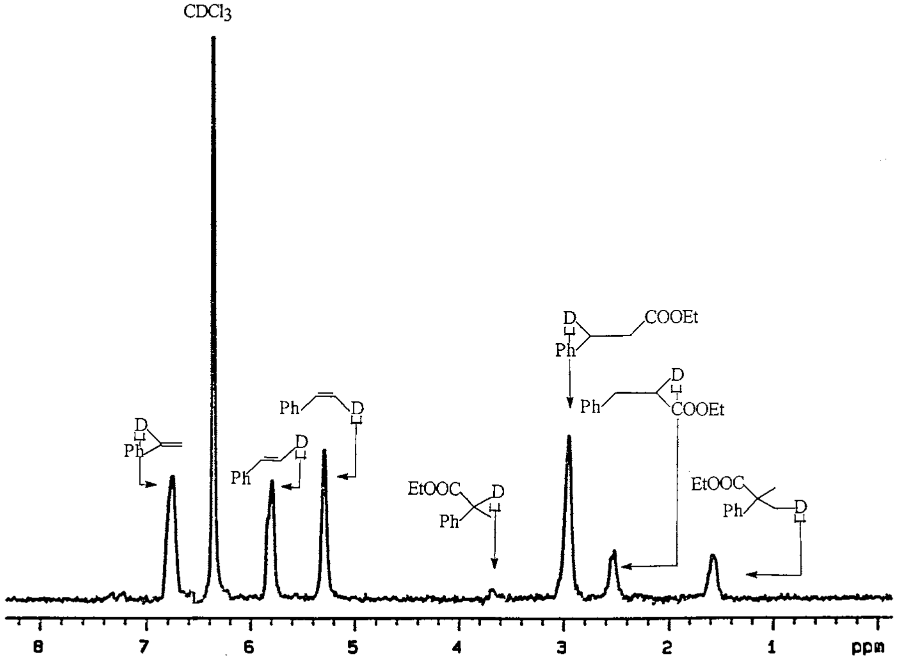


Fig. 1. ^{2}H-NMR spectrum (46 MHz, 20°C) of the reaction mixture in toluene (with EtOD removed) obtained by deuterioalkoxycarbonylation of styrene at 100°C with 30% conversion.

2.3. *Deuterium content of the carbonylated products*

2.3.1. *Mass spectral analysis*

The mass spectra of the products were determined directly from the crude reaction mixture at low ionisation energy. The results obtained (Table 3) served only for the qualitative analysis of low amounts of poly-deuterated species which cannot be observed by NMR. Thus the presence of 0, 1, 2, 3 or 4 deuterium atoms can be noticed. While at lower temperatures and conversions species containing less than two ^{2}H atoms per molecule predominate, in more severe conditions the poly-deuterated ones are favoured.

2.3.2. *Nuclear magnetic resonance analysis*

The chromatographically purified reaction products were analysed by ^{1}H-, ^{2}H- and ^{13}C-NMR. It was shown that ^{13}C-NMR spectra of the products permit the identification of some of the species present after the isotope labelling in accordance with the original ^{13}C assignments and the ^{2}H isotope shifts [9]. Thus, in the case of the linear ester (Fig. 2), in the DEPT spectrum [10] the methylene group α to the CO moiety (Fig. 2(a)) shows three anti-phase singlets at $\delta = 35.88$, 35.81 and 35.74 ppm corresponding to $-CH_2-$ adjacent to a $-CH_2-$, $-CHD-$ and a $-CD_2-$ group, respectively, and three in-phase triplets at $\delta = 35.58$ ppm ($^1J_{CD} = 19.9$ Hz), 35.51 ($^1J_{CD} = 19.6$ Hz) and 35.44 ppm ($^1J_{CD} = 19.7$ Hz) corresponding to $-CHD-$ groups adjacent to a $-CH_2-$, a $-CHD-$ and a $-CD_2-$ group. Similarly, the methylene group β to the CO (Fig. 2(b)) shows three singlets at $\delta = 30.94$, 30.87, and 30.80 ppm corresponding to $-CH_2-$ adjacent to a $-CH_2-$, $-CHD-$ and a $-CD_2-$ group, respectively, and three triplets at $\delta = 30.61$ ($^1J_{CD} = 19.9$ Hz), 30.54 ($^1J_{CD} = 20.3$ Hz) and 30.47 ppm ($^1J_{CD} = 19.4$ Hz) corresponding to $-CHD-$ groups adjacent to a $-CH_2-$, a $-CHD-$ and a $-CD_2-$ group. As far as the methyl group of the branched isomer (Fig. 3(a)) is concerned, there is an in-phase singlet at $\delta = 18.58$ ppm corresponding to a CH_3- adjacent to a $-CH-$, two in-phase triplets at $\delta = 18.30$ ($^1J_{CD} = 19.4$ Hz) and 18.19 ppm ($^1J_{CD} = 19.7$ Hz) corresponding to CH_2D groups adjacent to a $-CH-$ and a $-CD-$, respectively and two quintets at $\delta = 18.05$ ($^1J_{CD} = 19.7$ Hz) and 17.91 ppm ($^1J_{CD} = 19.7$ Hz) corresponding to CHD_2- adjacent to a $-CH-$ and a $-CD-$ group. The same spectrum shows four singlets for the methine group (Fig. 3(b)) at $\delta = 45.49$, 45.43, 45.35 and 45.29 ppm, which can be assigned to a $-CH-$ adjacent to a CH_3-, a CH_2D-, a CHD_2- and a CD_3-.

Deuterium content in different positions was calculated from ^{1}H spectra by integration of the signals of the groups where deuterium labelling occurs using the resonance of the methylene group from the ester function as an internal standard. The relative values of incorporations can be followed on the ^{2}H-NMR spectra as well. The results found (Table 4) point out that deuterium is present to a larger extent in the linear isomer than in the branched one but its amount changes more rapidly in the case of the latter when reaction conditions become more severe. As far as the linear ester is concerned, at 99% conversion the amount of deuterium atoms on both carbon atoms increases with increasing reaction temperature. Similarly, at constant temperature (experiments at 100°C) D incorporation becomes greater as the reaction progresses, these effects being more pronounced at C_α atom. In the case of the branched ester, at 99% conversion the deuterium incorporated on the atoms C_α and C_β shows a rapid increase, especially on the methyl group (from 0.60 at 60°C to 1.84 at 120°C), analogously, at 100°C further progress of the reaction produces a significant growth in the amount of D incorporated.

It should be noted that independent control experiments, carried out under reaction conditions, in the presence of the catalyst, proved that H/D exchange between ethanol-*d* and both isomeric products is negligible.

2.4. Deuterium content of residual ethanol-*d*

The deuterium content of the residual ethanol-*d* (Table 5) was determined via ^{2}H-NMR analysis of the crude reaction mixture using $CDCl_3$ as an external standard.

It must be noted that the mass spectrum of toluene recovered from the reaction shows the normal isotopic cluster expected for unlabelled toluene, however at severe reaction conditions slight deuterium incorporation can be observed on the methyl group of the solvent by NMR.

3. Discussion

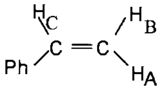
The results of this investigation clearly show that variable deuterium incorporation occurs in the substrate and in the reaction products when deuterioalkoxycarbonylation of styrene is carried out at various temperatures and conversions.

The deuterated species observed in solution are partially deuterated ethanol-*d*, mono-, di- and trideuteriostyrene labelled at the vinyl group, and mono-, di-, tri- and tetradeuterated isomeric esters (α and β) being labelled at the side-chain (EtOX, $PhCX{=}CX_2$, $PhCX(CX_3)COOEt$ and $PhCX_2CX_2COOEt$, $X = H$, D). The formation of these species can be easily accommodated in terms of the reaction pathways described. Thus, according to Scheme 2, the formation of the two palladium–alkyl intermediates n'_1 and b'_1 is reversible both at lower and higher temperatures; they undergo β-hydride elimination to give the palladium–hydride π-complexes **1** and **2**. In complex **1**, the insertion of the olefin into the Pd–H bond could regenerate the starting linear palladium–alkyl n'_1, leading to the corresponding linear 3-deuterated ester (3-d_1-β), or produce the isomeric branched palladium–alkyl intermediate b'_2, from which the 2-deuterated branched ester (2-d_1-α) can be formed. By the same process, complex **2** gives rise to the linear palladium–alkyl intermediate n'_2 and so to the linear 2-deuterated ester 2-d_1-β or regenerates the branched intermediate b'_1, producing the branched 3-deuterated ester 3-d_1-α. The overall process is, therefore, the isomerisation of the starting branched metal–alkyl intermediate b'_1 to the linear isomeric intermediate n'_2 and, conversely, the isomerisation of n'_1 to b'_2. On the other hand the π-complexes **1** and **2** can undergo an intermolecular exchange process with unlabelled styrene, producing respectively monodeuteriostyrenes 2-d_1-sty and 1-d_1-sty and unlabelled π-complex **3**. The latter can generate the linear (n) or branched (b) unlabelled alkyl and hence the linear and branched esters (β and α).

Once labelled, styrene species may undergo further reaction, resulting in di- and oligodeuterated derivatives

Table 2

Deuterium content via MS and NMR analyses of styrene recovered from the Pd-catalysed deuterioalkoxycarbonylation of styrene, after partial conversions



Reaction temperature (°C)	Conversion (%)	Distribution of deuterium content (%)[a]				Deuterium incorporation at each position[b]				
		0D	1D	2D	3D	NDM[c]	D(H_A)	D(H_B)	D(H_C)	NDM[c]
60	40	43.0	46.3	10.5	0.2	0.68	0.19	0.22	0.32	0.73
100	30	40.8	46.2	12.2	0.8	0.73	0.24	0.24	0.30	0.78
100	55	25.2	38.8	27.5	3.7	1.05	0.25	0.34	0.43	1.02

[a] Via MS analysis.

[b] Via ^{1}H and ^{2}H-NMR.

[c] Average number of deuterium atoms per molecule.

Table 3
Deuterium content of the linear and branched esters determined via MS analysis

Temperature (°C)	Conversion (%)	Deuterium incorporation of the β ester (%)					Deuterium incorporation of the α ester (%)				
		0D	1D	2D	3D	4D	0D	1D	2D	3D	4D
60	99	12.2	40.0	30.7	13.7	3.5	12.9	41.7	30.0	12.4	3.0
80	99	9.7	32.0	30.0	21.0	7.4	9.5	30.7	29.2	22.4	8.2
100	30	9.2	56.7	28.8	4.3	1.0	14.7	52.9	25.5	5.9	0.9
100	55	8.3	35.9	32.2	17.6	5.5	8.1	35	31.6	18.6	6.4
100	99	9.0	28.6	29.8	23.3	9.3	8.5	27.9	29.3	24.4	10.1
100	100	3.8	20.7	29.2	29.7	16.6	3.9	21.9	28.5	28.6	17.0
120	99	3.2	18.0	26.4	33.7	19.7	3.1	17.3	29.5	31.5	19.6

(Scheme 3). Thus, when 1-d_1-sty gives the π-complex **4** with a Pd–D species, dideuterated palladium–alkyls n''_2 and b''_1 can be formed, producing dideuterated isomeric esters (2,3-d_2-β and 3,3-d_2-α). A β-hydride elimination process from b''_1 palladium–alkyl can create the π-complex **5** from which 2,2-dideuterio-3-phenylpropanoate (2,2-d_2-β) is formed. In a similar manner, π-complex **6** leads to the dideuterated branched ester 2,3-d_2-α. After an intermolecular exchange process with styrene, complexes **5** and **6** give rise to labelled dideuteriostyrenes 1,1-d_2-sty and 1,2-d_2-sty, respectively.

With 1,1-d_2-sty as the starting molecule (Scheme 4) metal–alkyls n'''_1 and b'''_1 are generated, from which formation of 2,2,3-d_3-β and 3,3,3-d_3-α is possible. The π-complex **8** can be formed from n'''_1 leading to the isomeric ester 2,3,3-d_3-α and to trideuterated styrene 1,1,2-d_3-sty by elimination and exchange processes which can not occur in the case of palladium–alkyl b'''_1. As far as 1,2-d_2-sty is concerned, the two metal–alkyls n'''_2 and b'''_2 are formed, the first giving rise directly to the trideuterated 2,3,3-d_3-β ester, no β-elimination being possible, while the latter leads to the 2,3,3-d_3-α ester and complex **8** from which the 2,2,3-d_3-β linear ester and 1,1,2-d_3-sty can be derived.

Finally, at higher temperatures, trideuterated styrene leads to the formation of the tetradeuterated esters 2,2,3,3-d_4-α and 2,3,3,3-d_4-β.

4. Conclusions

Significant deuteration of the unconverted styrene and the ester isomers formed in hydroalkoxycarbonylation of styrene with EtOD using $Pd(PPh_3)_2Cl_2/SnCl_2/PPh_3$ as a catalyst was detected at low reaction temperature (60°C). The composition of the complex reaction mixture was successfully elucidated by mass spectral analysis and NMR methods. The application of ^{2}H-NMR enabled the determination of the deuterium content of styrene directly from the reaction mixture (after the removal of EtOD). Working under severe reaction conditions, oligodeuterated species were formed in a less selective way. Independent control experiments did show that H/D exchange between EtOD and the ester products is negligible. The presence of the deuterium in unconverted olefin confirms the reversibility of the reaction [3] and suggests that dissociation of the alkyl–palladium intermediate takes place.

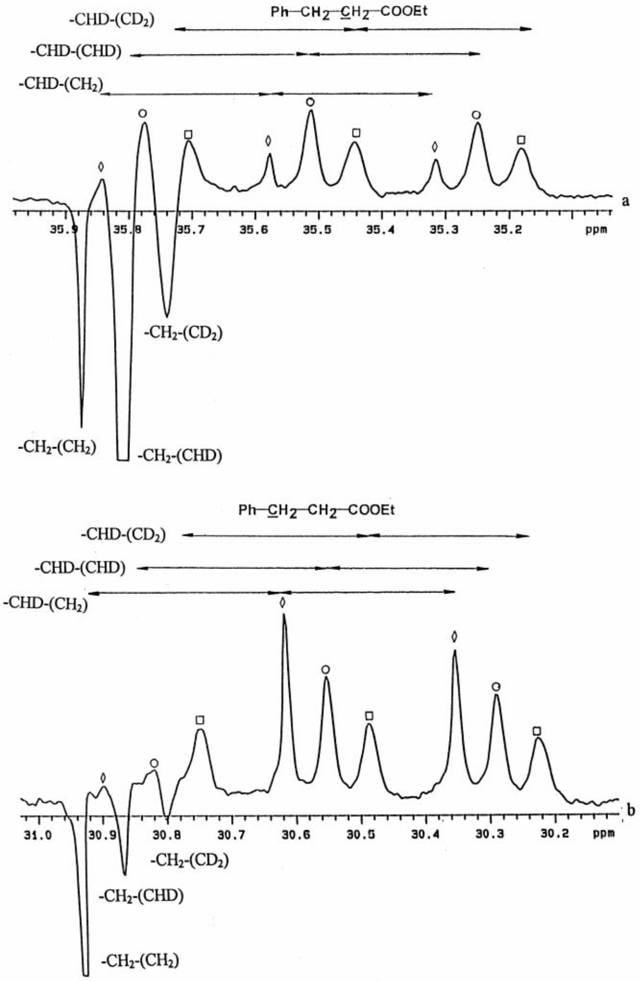


Fig. 2. ^{13}C-NMR DEPT spectrum (75.4 MHz, $CDCl_3$, 20°C) of the methylene groups situated (a) α; (b) β to the CO group of the linear ester obtained from the deuterioalkoxycarbonylation of styrene at 100°C with 99% conversion.

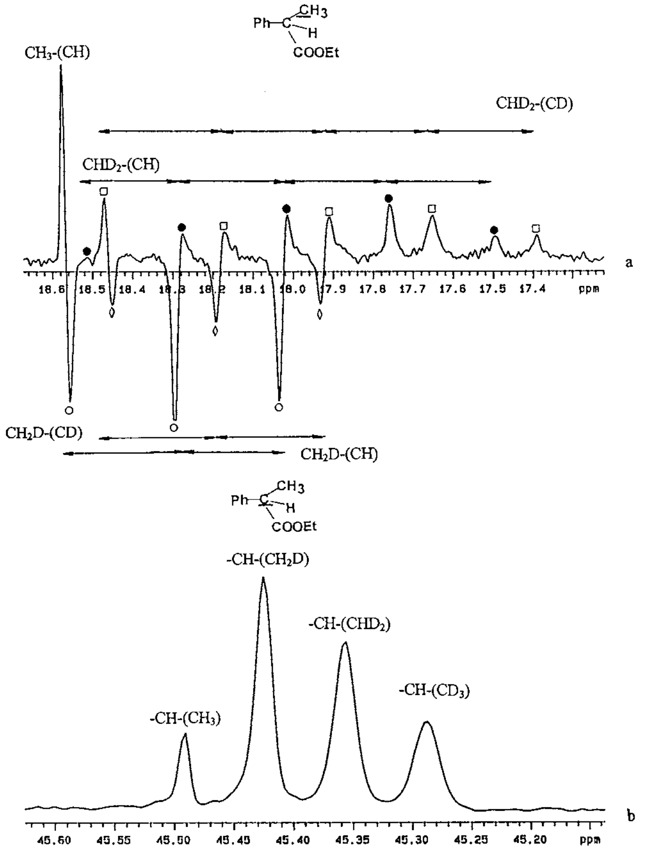


Fig. 3. ^{13}C-NMR DEPT spectrum (75.4 MHz, $CDCl_3$, 20°C) of (a) the methyl group and (b) the methine group of the branched ester obtained from the deuterioalkoxycarbonylation of styrene at 100°C with 99% conversion.

The kinetic deuterium isotope effect which controls β-elimination [11] could account for the observed accumulation of deuterated species. The reaction pathways described in our paper explain the formation of the labelled derivatives and strongly support the 'hydrido' route operating in the catalytic system employed. Reversible olefin insertion/β-hydride elimination prior to carbonylation is responsible for the incorporation of multiple deuterium atoms [5].

Table 5
Deuterium content of the OD group of the residual ethanol-*d*

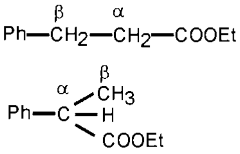
Reaction temperature (°C)	Conversion (%)	Deuterium content of OD group (%)[a]
60	40	90.1
60	99	88.3
80	99	85.9
100	55	87.1
100	99	82.4
120	99	77.9

[a] Data calculated from ^{2}H-NMR spectra using $CDCl_3$ as external standard.

5. Experimental

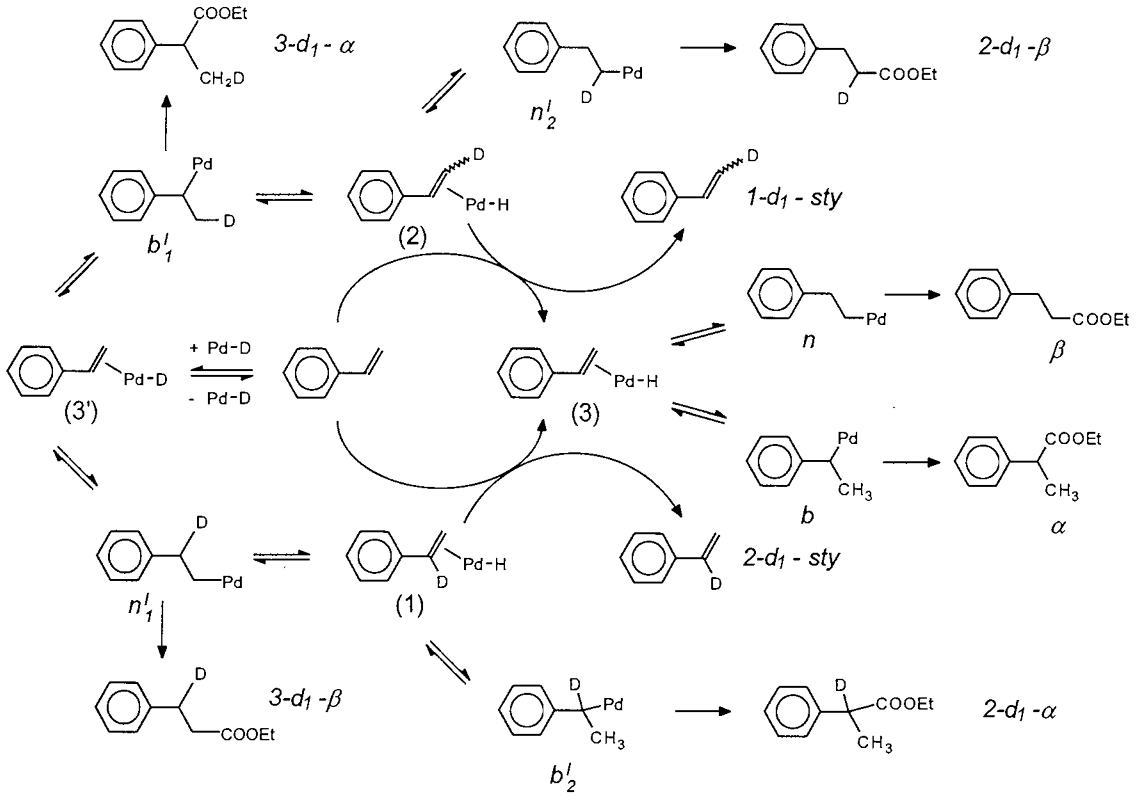
Toluene was distilled from sodium under argon atmosphere. Ethanol-*d* was purchased from Fluka. $Pd(PPh_3)_2Cl_2$ [12] was prepared as reported in the literature. Anhydrous $SnCl_2$ was obtained by reacting $SnCl_2.2H_2O$ with acetic anhydride and washing with ether. GLC analyses were performed on a HP 5830 gas chromatograph equipped with SPB-1 column (30 m × 1 μm film depth) using flame ionisation as the detection method and helium as the carrier gas. Column chromatography was carried out on a silica gel column using hexane, benzene, chloroform, dichloromethane and acetone as eluents.

Table 4
Deuterium content of the linear and branched esters via NMR analysis

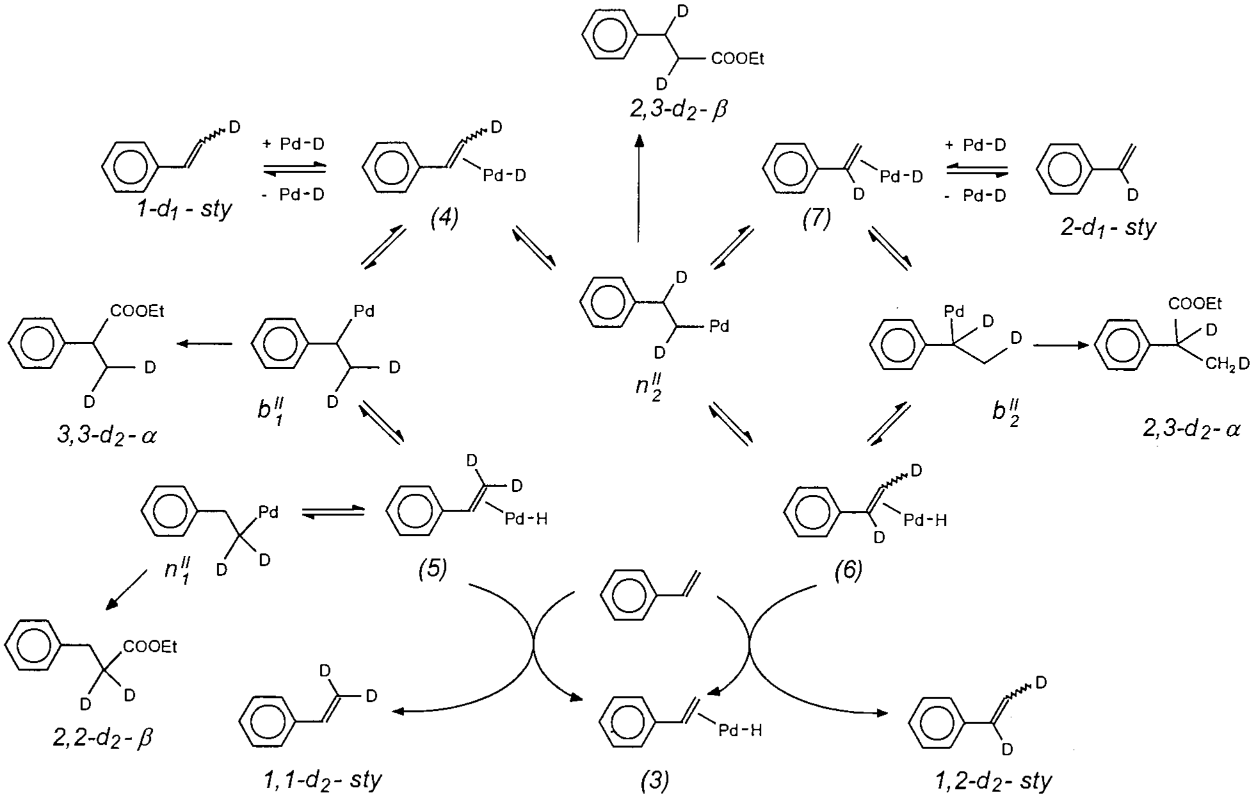


Reaction temperature (°C)	Conversion (%)	D content at the C atoms of the linear ester			D content at the C atoms of the branched ester		
		D(C_α)	D(C_β)	NDM[a]	D(C_α)	D(C_β)	NDM
60	99	0.53	1.09	1.62	0.12	0.60	0.72
80	99	0.63	1.29	1.92	0.33	1.61	1.94
100	30	0.28	0.93	1.21	0.01	0.62	0.63
100	55	0.67	1.21	1.88	0.26	0.95	1.21
100	99	0.90	1.22	2.12	0.43	1.61	2.04
120	99	1.22	1.32	2.54	0.43	1.84	2.27

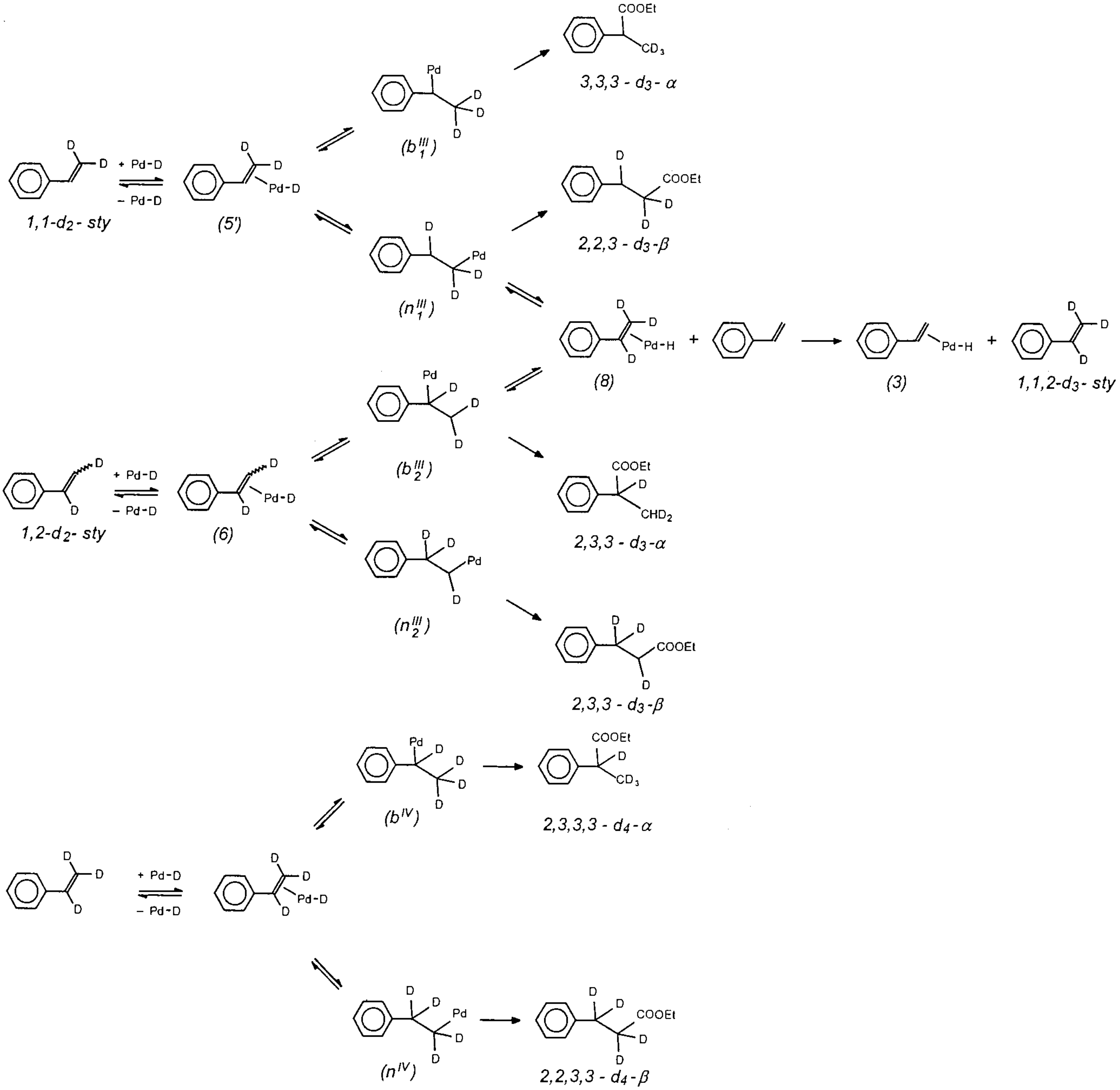
[a] Average number of deuterium atoms per molecule.



Scheme 2. Pathways for monodeuteration of styrene and the derived monodeuterated isomeric esters.



Scheme 3. Pathways for dideuteration of styrene and the derived dideuterated isomeric esters.



Scheme 4. Pathways for oligodeuteration of styrene and the derived oligodeuterated isomeric esters.

The mass spectra were measured using a VG ZAB-SEQ instrument at 10–12 eV ionisation connected to a HP-5890A gas chromatograph with a CP-Sil-8 CB column (25 m × 0.25 μm film depth) using helium as the carrier gas.

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

5.1. Deuterioalkoxycarbonylation of styrene: general procedure

The catalyst (75 mg, 0.11 mmol $Pd(PPh_3)_2Cl_2$; 55 mg, 0.29 mmol anhydrous $SnCl_2$; 50,1 mg, 0.19 mmol PPh_3) was introduced into a 50-ml stainless steel autoclave. After sealing, a solution of styrene (0.37 ml, 3.2 mmol), ethanol-*d* (1,7 ml, 28.9 mmol) in toluene (10 ml) was introduced by suction. Then, carbon monoxide was charged (40 atm pressure at room temperature) and the mixture was magnetically stirred at the reaction temperature until the desired conversion occurred. After cooling, the reaction mixture was siphoned out, and GLC was used to determine the composition using toluene as an internal standard. After ^{2}H-NMR and MS analyses ethanol-*d* and the solvent were removed under vacuum. The residual mixture for partial conversions was analysed by ^{1}H-NMR also. Isomeric esters were separated by column chromatography and studied further.

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