ELSEVIER

Journal of Molecular Catalysis A: Chemical 116 (1997) 335–342

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Mechanistic aspects of the hydrogenation of some unsaturated mono and diacids and their methyl esters

Agota Bucsai [a,b], Jòzsef Bakos [b], Mohamed Laghmari [a], Denis Sinou [a,*]

[a] *Laboratoire de Synthèse Asymétrique, associé au CNRS, CPE Lyon, Université Claude Bernard Lyon I, 43, boulevard du 11 Novembre 1918, 69622 Villeurbanne Cédex, France*

[b] *Department of Organic Chemistry, University of Veszprèm, P.O. Box 158, H-8201 Veszprèm, Hungary*

Received 6 February 1996; accepted 9 August 1996

Abstract

The study of the reduction of some unsaturated diesters under a deuterium atmosphere shows that β-elimination is a very fast process compared to the reductive elimination. This allows the introduction of deuterium atoms at position α of the double bond and the addition of hydrogen atoms on the double bond.

Keywords: Unsaturated diesters; Rhodium complexes; Reduction; Deuterium; β-elimination

1. Introduction

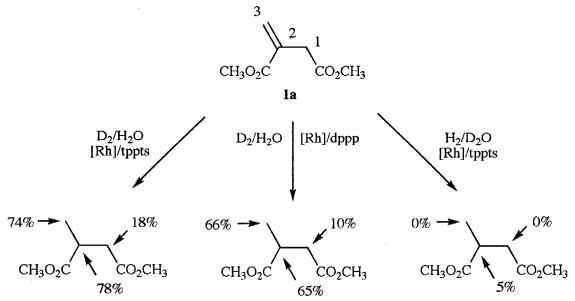
The homogeneous asymmetric catalytic hydrogenation of prochiral olefins is one of the most important applications of enantioselective catalytic reactions [1]. This reaction has been performed with homogeneous catalysts and more recently in biphasic water–liquid systems, allowing an easy recycling of the catalyst [2]. During our work on the reduction of dehydroamino acids in aqueous media using a rhodium complex prepared by mixing $[Rh(COD)Cl]_2$ and a sulfonated phosphine we noticed the participation of water in the reaction [3]. Regiospecific incorporation of a deuterium atom occurred at the position α to the acetamido and the ester group when the reduction was performed in D_2O; conversely carrying out the reaction in H_2O under a deuterium atmosphere showed the incorporation of a hydrogen atom at the same position. Such behavior was also noticed by Joò et al. [4]. In order to have more insight in the present hydrogenation mechanism and eventually to broaden the incorporation of deuterium via such a reaction, we studied the reduction of some unsaturated mono and diacids and their esters in a two-phase and a homogeneous system under a hydrogen or a deuterium atmosphere.

2. Results and discussion

When we studied the reduction of dimethyl itaconate **1a** by gaseous hydrogen in a D_2O/ethyl acetate mixture using $[Rh(COD)Cl]_2$

* Corresponding author. Tel.: +33-72-448160; fax: +33-72-448160.

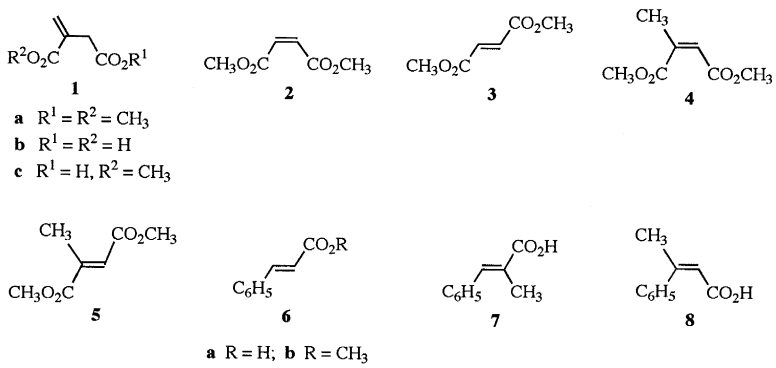
PII S1381-1169(96)00367-6



Scheme 1. Reduction of dimethyl itaconate **1a**.

+ tppts (or trisodium salt of tri-*m*-sulfonated triphenylphosphine) as the catalyst (Scheme 1), we noticed a very low deuterium incorporation in the molecule at C-2 (less than 5%). Performing the reaction in a H_2O/ethyl acetate mixture under a deuterium atmosphere resulted now in a 78% deuterium incorporation in the molecule at C-2 (instead of 100%), 74% at C-3 (instead of 33%) and 18% at C-1 (respectively 13 and 5% for each diastereotopic hydrogen instead of 0%). This unexpected result prompted us to study the reduction of dimethyl itaconate **1a** under a deuterium atmosphere but in an organic solvent such as THF in the presence of $[Rh(COD)Cl]_2$ and dppp [or 1,3-bis(diphenylphosphino)propane] as the catalyst. We also observed under these conditions a deuterium incorporation of 65% at C-2, 66% at C-3 and 10% at C-1 (respectively 6% and 4%).

The extent of deuterium incorporation was determined by ^1H NMR of the product and calculated from relative areas of the peaks using the signal of the methoxy group as an internal standard. The methine proton appeared at $\delta =$ 2.90 ppm as a very small broadened signal (Fig. 1). The two methylene protons which are diastereotopics gave two large doublets at $\delta =$ 2.41 and 2.75 ppm corresponding to an AB system; however we also noticed two small doublets of doublets at $\delta = 2.75$ and 2.41 ppm corresponding to the coupling with the residual methine proton. The methyl appeared at $\delta = 1.2$ ppm as a broad singlet.



The ^{13}C NMR of the products confirmed the regioselectivity of the incorporation. The most important information was given by the methyl signal (Fig. 2); we observed two triplets at $\delta = 16.77$ ppm ($^1J_{CD} = 20$ Hz) and 16.68 ppm ($^1J_{CD} = 19.5$ Hz) corresponding to a CH_2D– group adjacent to a –CH– and a –CD– group respectively, two quintets at $\delta = 16.75$ ppm ($^1J_{CD} = 19.5$ Hz) and $\delta = 16.65$ ppm ($^1J_{CD} =$ 19.8 Hz) corresponding to a $–CHD_2$ adjacent to a –CH– and a –CD– group, and two singlets at $\delta = 17.04$ ppm and 16.95 ppm corresponding to a CH_3– adjacent to a –CH– and a –CD– group. No signal corresponding to CD_3– was observed. It is clear from these results that water did not play any role as a reactant in the hydrogenation of dimethyl itaconate. In the control experiments carried out with the unsaturated

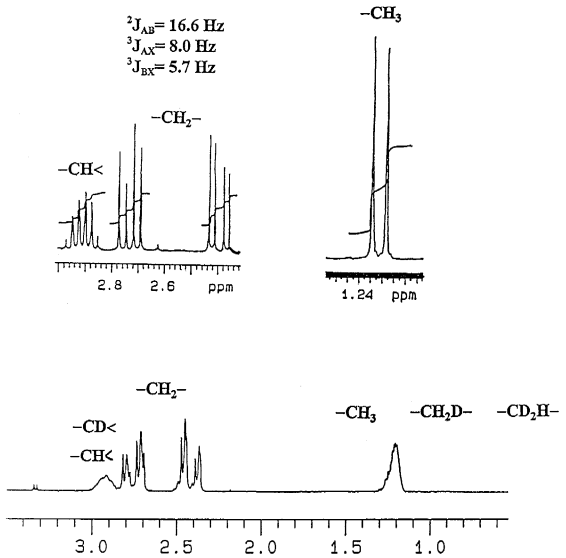


Fig. 1. ^{1}H NMR spectra of products obtained by reduction of **1a** under a hydrogen atmosphere (top) and a deuterium atmosphere (bottom).

substrate in THF under a deuterium atmosphere without catalyst or with the saturated dimethyl ester in the presence of the catalyst no deuterium incorporation was observed. This implies that deuterium scrambling occurred during the catalytic cycle.

To gain a deeper insight into the factors governing this deuterium/hydrogen incorporation we carried out this reduction in various solvents using $[Rh(COD)Cl]_2$ and dppp as the catalyst. The results summarized in Table 1 showed that the amount of deuterium incorporation was not affected by the nature of the solvent, except for acetonitrile (entry 8) where 39% and 36% deuterium incorporation was observed at C-1.

The results concerning the influence of the ligands (basicity, cone angle, chelating ligand) on the deuterium/hydrogen incorporation (Table 2) showed no significant influence of the nature of the phosphine on this phenomena.

This unexpected behavior requires a reversible formation of the complex of dimethyl itaconate with the catalyst and also a reversible formation of an alkylrhodium intermediate. Although this is not usual in hydrogenation using the Wilkinson catalyst, there are some prece-

Table 1
Effect of solvent in the deuterium distribution in the hydrogenation of dimethyl itaconate **1a** using D_2 as deuterium source [a]

Entry	Solvent	Deuterium incorporation (%) [b]		
		C-1	C-2	C-3
1	CH_3OH	5/6	65	66
2	CH_3OD	6/4	85	56
3	CH_2Cl_2	8/6	64	61
4	THF	4/6	65	66
5	$CH_3CO_2C_2H_5$	10/5	73	68
6	toluene	13/8	78	64
7	dioxane	15/9	74	74
8	CH_3CN	39/36	50	56

[a] [**1a**]:[Rh]:[dppp] = 25:1:1; [**1a**] = 0.1 mol l^{-1}; 25°C; $p_{H_2} = 1$ atm; 24 h; quantitative transformation.
[b] Determined by ^{1}H NMR, using the methoxy group as an internal standard.

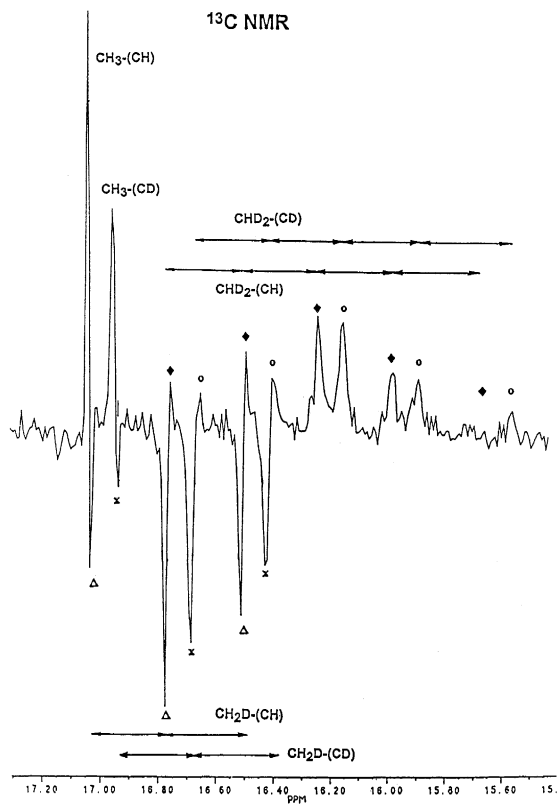


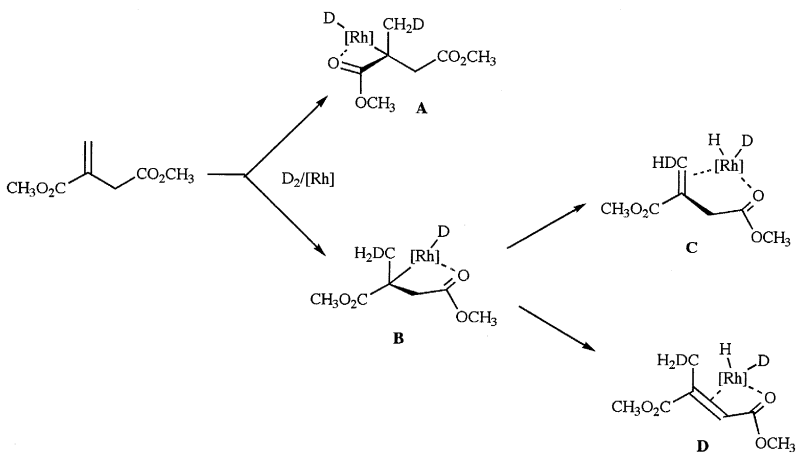
Fig. 2. ^{13}C NMR spectra of products obtained by reduction of **1a** under a deuterium atmosphere between 16–18 ppm (DEPT sequence).

Table 2
Effect of the phosphine in the deuterium distribution in the hydrogenation of dimethyl itaconate **1a** using D_2 as deuterium source [a]

Entry	Ligand	Conversion (%) [b]	Deuterium incorporation (%) [c]		
			C-1	C-2	C-3
1	Ph_3P	100	0/0	76	77
2	$(4\text{-}CH_3C_6H_4)_3P$	100	11/0	70	71
3	$(2\text{-}CH_3C_6H_4)_3P$	96	11/0	81	79
4	$(2,6\text{-di}CH_3OC_6H_3)_3P$	100	6/2	77	79
5	$(2,4,6\text{-tri-}OCH_3C_6H_2)_3P$	100	1/3	82	73
6	$(C_5H_4N)(C_6H_5)_2P$	40	17/1	80	52
7	$Ph_2P(CH_2)PPh_2$	100	12/6	75	74
8	$Ph_2P(CH_2)_2PPh_2$	80	15/13	81	67
9	$Ph_2P(CH_2)_3PPh_2$	100	4/6	65	66
10	$Ph_2P(CH_2)_4PPh_2$	100	12/5	77	67
11	$Ph_2P(CH_2)_5PPh_2$	100	14/10	84	70
12	$Ph_2P(CH_2)_6PPh_2$	100	8/4	75	64
13	$(Ph_2PC_5H_4)_2Fe$	86	20/14	86	58

[a] [**1a**]:[Rh]:[P] = 25:1:2; [**1a**] = 0.1 mol l^{-1}; 25°C; p_{H_2} = 1 atm; solvent tetrahydrofuran; 24 h.
[b] Determined by ^{1}H NMR.
[c] Determined by ^{1}H NMR, using the methoxy group as an internal standard.

dents in the literature [5]. The possible steps leading to the different isotopomers of dimethyl esters are illustrated in Scheme 2. The differences with the mechanism of the reduction of α-aminoacid precursors are probably due to the fact that the formed alkylrhodium hydride is less stable and so that the reverse reaction or β-elimination has a faster rate than the transfer of the second hydrogen. If this mechanism occurred, we should observe at low conversion dimethyl itaconate containing deuterium itself. The results compiled in Table 3 showed that exchange had occurred in the recovered dimethyl itaconate **1a** and that the amount of deuterium incorporation in the starting material increased with the conversion; we noticed also that the exchange at the vinylic proton is the same for the two positions. The presence of deuterium in the recovered dimethyl itaconate is in favor of this mechanism and not in favor of the isomer-



Scheme 2. Possible first steps leading to the different isotopomers of 2-methylbutanedioic acid dimethyl ester.

Table 3
Deuterium distribution during the hydrogenation of dimethyl itaconate **1a** using D_2 as deuterium source [a]

Entry	Conversion (%)	Deuterium incorporation (%) [b]				
		starting material		reduced product		
		C-1	C-3	C-1	C-2	C-3
1	20	0	10/8	9/4	70	39
2	25	4	18/16	9/4	72	32
3	44	9	35/34	8/6	73	45
4	77	33	76/75	10/6	71	46
5	100			10/6	72	70

[a] [**1a**]:[Rh]:[P] = 25:1:2; [**1a**] = 0.1 mol·l^{-1}; 25°C; $p_{H_2} = 1$ atm; solvent tetrahydrofuran.
[b] Determined by ^{1}H NMR, using the methoxy group as an internal standard.

ization via a π-allyl hydride rhodium intermediate as recently postulated [5], although both the mechanisms could occur together.

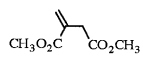
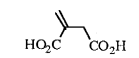
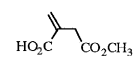
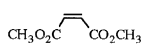
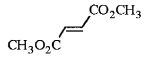
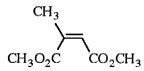
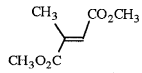
The reduction of itaconic acid **1b** was also carried out under a deuterium atmosphere in THF in the presence of the same catalyst (Table 4); the extent of deuterium incorporation, determined after esterification of the mixture with diazomethane, was 66% at C-2 (instead of 100%), 59% at C-3 (instead of 33%) and 0% at C-1 (entry 2). The reduction of methyl itaconate **1c** (entry 3) gave the saturated product with 68% deuterium incorporation at C-2, 57% incorporation at C-3 and no incorporation at C-1. These values are very similar to those observed for dimethyl itaconate **1a**, and indicated unambiguously that β-elimination with a hydrogen from the methyl group seems to be a fast reaction in the reduction of these substrates compared to reductive elimination.

We also studied the deuterium incorporation in the reduction of other dimethyl esters of dicarboxylic acids in THF as the solvent and $[Rh(COD)Cl]_2$ + dppp as the catalyst. In the case of dimethyl fumarate **2** (entry 4) and dimethyl maleate **3** (entry 5), the extent of deuterium incorporation was approximately 50% as expected for the normal addition of one equivalent of deuterium, with so practically no β-elimination in this case.

The reduction of dimethyl citraconate **4** (entry 6) and dimethyl mesaconate **5** (entry 7) gave more information. We observed practically the same deuterium incorporation for the two compounds at C-1 (95% and 94.5% for **4** and **5**), at C-2 (86% and 84% for **4** and **5**) and C-3 (23% and 26%). This implies that some β-elimination occurred preferentially from the methyl group and not from the methine group. It is to be noticed that deuteriation of these two unsaturated substrates gave diastereoisomers, showing unambiguously that addition of deuterium was a *cis* addition.

Finally we studied the reduction under a deuterium atmosphere of some unsaturated

Table 4
Deuterium distribution in the hydrogenation of various diesters using D_2 as deuterium source [a]

Entry	Substrate	Conversion[b] (%)	Deuterium Incorporation (%)[c] C-1	C-2	C-3
1		100	4/6	65	66
2		100	0/0	66	59
3		100	0/0	68	57
4		100	49		
5		100	51		
6		92	12.5/82.5	86	23
7		97	82/12.5	84	26

[a] [substrate]:[Rh]:[dppp] = 25:1:1.1; [substrate] = 0.1 mol l^{-1}; 25°C; $p_{H_2} = 1$ atm; solvent tetrahydrofuran; 24 h.
[b] Determined by ^{1}H NMR.
[c] Determined by ^{1}H NMR, using the methoxy group as an internal standard eventually after esterification using diazomethane.

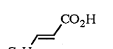
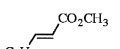
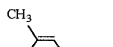
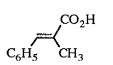
monoacids. The results obtained after esterification using diazomethane and summarized in Table 5 showed for cinnamic acid **6a** deuterium incorporation of 52 and 45% in THF (entry 1) and 60% and 55% in CH_3OD (entry 2), this means that there was virtually no β-elimination in this case. The same behavior was observed for the ester **6b** in THF (entry 3). The reduction under a hydrogen atmosphere in a two-phase system water–ethyl acetate in the presence of $[Rh(COD)Cl]_2$ + tppts (entry 4) gave a product showing by mass spectrometry the incorporation of only one atom of deuterium to an extent of 22%; the ^1H NMR spectrum showed an incorporation of 11% on C-1 and C-2 carbons corresponding to two monodeuterated regioisomers.

If β-methyl cinnamic acid **7** (entries 5 and 6) showed practically 100% deuterium incorporation at C-1 and C-2 (corresponding so to no β-elimination reaction), incorporation of deuterium to an extent of 100% and 50% was noticed in the reduction of α-methyl cinnamic acid **8** (entries 7 and 8), implying in this case a different behavior with an easy β-elimination reaction with the benzylic hydrogen atom. However this result has to be taken with care due to the low conversion of the substrate.

The large amount of deuterium incorporation at C-3 observed for itaconic acid derivatives, dimethyl mesaconate and dimethyl citraconate could be explained according to Scheme 2. Association of the unsaturated substrate to the rhodium complex followed by the insertion of a deuterium atom gave the σ-alkyl rhodium complex A (4-membered ring) or B (5-membered ring). This complex B could lead by β-elimination from the methyl group to the π-complex C or from the methylene group to the π-complex D. This π-complex is more rigid than the former one and so its formation is less favored. The β-elimination leading to complex C is also favored due to the difficulty for the carbon–rhodium bond and the carbon–hydrogen bond to be in a *syn* position in the ring. It is to be noticed that the σ-alkyl rhodium complex is a common intermediate starting from the different substrates. The complex C could give by insertion of HD and reductive elimination a saturated diester with the incorporation now of two atoms of deuterium in the methyl group. However, due to the large amount of deuterium present, the complex C is probably transformed into a dideuterocomplex which could lead to a three deutered diester by deuteriation or a new π-complex having now two deuterium atoms on C-3. The very short life-time of the σ-alkyl rhodium complex could also explain the observation of practically no deuterium incorporation when the reaction was carried out under a hydrogen atmosphere in a two-phase system D_2O–ethyl acetate in contrast to the reduction of amino acids precursors.

In conclusion, we have shown in the reduction of some unsaturated diesters that β-elimination is a very fast reaction compared to reductive elimination. This allowed the introduction of a certain amount of deuterium into the saturated product at position α of the dou-

Table 5
Deuterium distribution in the hydrogenation of various cinnamic ester derivatives using D_2 as deuterium source [a]

Entry	Substrate	Conditions	Conversion[b] (%)	Deutcrium Incorporation (%)[c] C-1	C-2	CH_3
1		THF/1 atm D_2	27	52	45	
2		CH_3OD/1 atm D_2	90	60	55	
3		THF/1 atm D_2	100	50	50	
4		$H_2O/CH_3CO_2C_2H_5$ /1 atm / D_2	100	7	7	
5		THF/10 atm D_2	48	100	100/3	0
6		CH_3OD/1 atm D_2	37	100	100/20	0
7		THF/1 atm D_2	15	100	100/50	0
8		CH_3OD/1 atm D_2	23	100	100/25	0

[a] [Substrate]:[Rh]:[dppp] = 25:1:1.1; [Substrate] = 0.1 mol l^{-1}; 25°C.
[b] Determined by ^1H NMR.
[c] Determined by ^1H NMR, using the methoxy group as an internal standard eventually after esterification using diazomethane.

ble bond, and of hydrogen on the double bond, when the reduction was carried out under a deuterium atmosphere. Such a behavior was not observed for unsaturated monoesters.

3. Experimental

All manipulation was performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled according to the literature and stored under nitrogen. The following commercial products were used without further purification: D_2 (99.8% D, Alphagaz), $[Rh(COD)Cl]_2$, triphenylphosphine, tri(*p*-tolyl)phosphine, tri(*o*-tolyl)phosphine, tri(2,6-diCH_3O-phenyl)phosphine, tri(2,4,6-triCH_3O-phenyl)phosphine, pyridyldiphenylphosphine, 1,1-bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino) propane or dppp, 1,4-bis(diphenylphosphino)butane, 1,5-bis(diphenylphosphino)pentane, 1,6-bis(diphenylphosphino)hexane, ferrocenylphosphine, itaconic acid dimethyl ester **1a**, itaconic acid **1b**, fumaric acid dimethyl ester **2**, maleic acid dimethyl ester **3**, citraconic acid dimethyl ester **4**, mesaconic acid dimethyl ester **5**, cinnamic acid **6a**, cinnamic acid methyl ester **6b**, α-methyl cinnamic acid methyl ester **7**, β-methyl cinnamic acid methyl ester **8**.

^1H and ^{13}C NMR spectra were recorded on a Bruker AM 200 spectrometer, TMS being used as an internal standard. Mass spectra (EI, 70 eV) were measured with a Nermag R 1010M spectrometer coupled with an OV1 (25-m) silica column.

3.1. General procedure for labelling studies

A solution of 4×10^{-2} mmol of the catalyst prepared in 10 mL of the solvent in a Schlenk tube was injected into a hydrogenation apparatus containing the unsaturated substrate (1 mmol) and placed under deuterium. The catalytic reaction was carried out at room temperature under the indicated pressure. After 24 h, the solvent was evaporated and in the case of the acids, the residue was esterified using diazomethane. The crude product was analyzed by NMR.

3.2. Deuteration of itaconic acid dimethyl ester *1a*

^1H (200 MHz): δ 1.20 (bm, CH_2D and CHD_2), 1.22 (d, CH_3), 2.41 (d, $^2J = 16.6$ Hz, $CH_2CD<$), 2.41 (dd, $^2J = 16.3$ Hz, $^3J = 5.8$ Hz, $CH_2CH<$), 2.75 (d, $^2J = 16.6$ Hz, $CH_2CD<$), 2.75 (dd, $^2J = 16.3$ Hz, $^3J = 8.0$ Hz, $CH_2CH<$), 2.90 (m, $-CH<$), 3.68 (s, OCH_3), 3.70 (s, OCH_3). $^{13}C\{^1H\}$ (50 MHz) δ 16.40 (q, $^1J_{C-D} = 19.8$ Hz, $CHD_2-CD<$), 16.49 (q, $^1J_{C-D} = 19.8$ Hz, $CHD_2-CH<$), 16.68 (t, $^1J_{C-D} = 19.5$ Hz, $CH_2D-CD<$), 16.77 (t, $^1J_{C-D} = 20.0$ Hz, $CH_2D-CH<$), 16.95 (s, $CH_3-CD<$), 17.04 (s, $CH_3-CH<$), 34.9–35.6 ($-CD<$), 35.60 (q, $^2J_{C-D} = 5.4$ Hz, $CHD_2-CH<$), 37.28, 37.32, 37.34, 37.40 and 37.43 (CH_2), 51.70 (s, OCH_3), 51.90 (s, OCH_3), 172.30 (s, CO_2), 175.73 (s, CO_2).

3.3. Deuteration of itaconic acid *1b*

$^{13}C\{^1H\}$ (50 MHz) δ 16.62 (q, $^1J_{C-D} = 18.9$ Hz, $CHD_2-CD<$), 16.71 (q, $^1J_{C-D} = 19.2$ Hz, $CHD_2-CH<$), 16.90 (t, $^1J_{C-D} = 20.0$ Hz, $CH_2D-CD<$), 16.99 (t, $^1J_{C-D} = 19.3$ Hz, $CH_2D-CH<$), 17.18 (s, $CH_3-CD<$), 17.26 (s, $CH_3-CH<$), 35.3–36.0 ($-CD<$), 35.98 (q, $^2J_{C-D} = 5.4$ Hz, $CHD_2-CH<$), 37.47–37.55 (CH_2), 174.00 (s, CO_2), 177.58 (s, CO_2).

3.4. Deuteration of itaconic acid monomethyl ester *1c*

^1H (200 MHz) δ 1.22 (bs, CH_2D and CHD_2), 1.23 (d, CH_3), 2.45 (d, $^2J = 17.0$, $CH_2CD<$), 2.45 (dd, $^1J = 16.1$, $^2J = 4.7$, $CH_2CH<$), 2.79 (d, $^2J = 17.0$, $CH_2CD<$), 2.79 (dd, $^2J = 16.1$, $^3J = 8.0$, $CH_2CH<$), 2.88 (m, $-CH<$), 3.70 (s, OCH_3).

3.5. [2-^{2}H, 3-^{2}H]-hydrocinnamic acid

^{1}H (200 MHz) δ 2.65 (bs, 1H, $CHDCO_2$), 2.90 (bs, 1H, CHD), 7.20–7.50 (m, 5H, C_6H_5); ^{13}C {^{1}H} (50 MHz) δ 30.16 (t, $^1J_{C-D} = 19.8$ Hz, –CHD–), 35.27 (t, $^1J_{C-D} = 19.7$ Hz, –*C*$HDCO_2H$), 126.20, 128.21, 128.66 and 140.16 (C_6H_5), 172.46 (s, CO_2). MS (IE) of the methyl ester *m/z* (%) 166 ($M^{+\cdot}$ + 2D, 49), 165 ($M^{+\cdot}$ + 1D, 43), 164 ($M^{+\cdot}$, 7), 135 (12), 134 (13), 133 (5), 107 (28), 106 (86), 105 (100), 104 (33), 92 (51), 91 (21).

3.6. 3-Methyl-[2-^{2}H, 3-^{2}H]-hydrocinnamic acid

^{1}H (200 MHz) of the methyl ester δ 1.30 (s, 3H, CH_3), 2.60 (bs, 1H, CHD), 3.64 (s, 3H, OCH_3), 7.20–7.60 (m, 5H, C_6H_5); ^{13}C {^{1}H} (50 MHz) δ 21.72 (s, CH_3), 35.63 (t, $^1J_{C-D} =$ 19.7 Hz, –*C*$HDCO_2H$), 42.26 (t, $^1J_{C-D} = 19.7$ Hz, –CD$<$), 126.38, 126.47, 128.22 and 141.97 (C_6H_5), 172.46 (s, CO_2). MS (IE) of the methyl ester *m/z* (%) 180 ($M^{+\cdot}$ + 2D, 17), 121 (10), 120 (45), 119 (25), 107 (13), 106 (100), 105 (17), 92 (51).

3.6.1. 2-Methyl-[2-^{2}H, 3-^{2}H]-hydrocinnamic acid

^{1}H (200 MHz) of the methyl ester δ 1.18 (bs, 3H, CH_3), 2.60 (bs, 1H, CHD), 3.65 (s, 3H, OCH_3), 7.17–7.45 (m, 5H, C_6H_5); ^{13}C {^{1}H} (50 MHz) δ 16.28 (s, CH_3), 38.86 (t, $^1J_{C-D} =$ 19.8 Hz, $>$*C*DCO_2H), 40.63 (t, $^1J_{C-D} = 19.7$ Hz, –CHD–), 127.77, 128.33, 129.62 and 140.77 (C_6H_5), 172.30 (s, CO_2). MS (IE) of the methyl ester *m/z* (%) 180 ($M^{+\cdot}$ + 2D, 11), 121 (19), 120 (32), 119 (18), 93 (25), 92 (100), 91 (21).

Acknowledgements

Financial support from the C.N.R.S., the Hungarian National Science Foundation (OTKA-T016269) and the Ministry of Culture and Education is gratefully acknowledged. One of us (A.B.) thanks the M.E.S.R. for a grant.

References

[1] J.D. Morrison (Ed.), Asymmetric Synthesis, Vol. 5 (Academic Press, New York, 1985); R. Noyori and M. Kitamura, in: R. Scheffold (Ed.), Modern Synthetic Methods (Springer Verlag, Berlin, 1989) p. 115; H. Brünner and W. Zettlmeier, Handbook of Enantioselective Catalysis (VCH, Weinheim, 1993); I. Ojima (Ed.), Catalytic Asymmetric Synthesis (VCH, Weinheim, 1993); R. Noyori (Ed.), Asymmetric Catalysis in Organic Synthesis (Wiley Interscience, New York, 1994).

[2] Y. Amrani, L. Lecomte, D. Sinou, J. Bakos, I. Toth and B. Heil, Organometallics 8 (1989) 542; I. Toth, B.E. Hanson and M.E. Davis, Tetrahedron: Asymmetry 1 (1990) 913; K. Wan and M.E. Davis, J. Chem. Soc. Chem. Commun. (1993) 1262; K. Wan and M.E. Davis, Tetrahedron: Asymmetry 4 (1993) 2461; J. Bakos, B. Heil, A. Orosz, M. Laghmari, P. Lhoste and D. Sinou, J. Chem. Soc. Chem. Commun. (1991) 1684; C. Lensink and J.G. de Vries, Tetrahedron: Asymmetry 3 (1992) 235.

[3] J. Bakos, R. Karaivanov, M. Laghmari and D. Sinou, Organometallics 13 (1994) 2951.

[4] J. Joò, P. Csiba and A. Bényei, J. Chem. Soc. Chem. Commun. (1993) 1602.

[5] A.S. Hussey and Y. Takeuchi, J. Am. Chem. Soc. 91 (1969) 672; J.F. Biellmann and M.J. Jung, J. Am. Chem. Soc. 90 (1968) 1673.