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ASYMMETRIC HYDROFORMYLATION OF UNSATURATED ESTERS WITH $PtCl(SnCl_3)[(R,R)$-DIOP] CATALYST *

LÁSZLÓ KOLLÁR, GIAMBATTISTA CONSIGLIO and PIERO PINO
Technisch-Chemisches Laboratorium, ETH-Zürich, Universitätstr. 6, CH-8092 Zürich (Switzerland)
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Summary

Dimethyl 2-(formylmethyl)butanedioate (**2e**) has been synthesized regioselectively with an enantiomeric excess of more than 82% by the homogeneous catalytic hydroformylation of dimethyl itaconate (**1e**) with $PtCl(SnCl_3)[(R,R)$-DIOP] as the catalyst precursor. Under the conditions used a competitive hydrogenation to dimethyl 2-methylsuccinate (**3e**) takes place. This reaction occurs with an optical yield of up to 51%. For other vinylidene esters **1** the asymmetric induction was lower both in the hydroformylation and in the competitive hydrogenation. The relationship between the absolute configuration of the predominant antipodes and the possible transition states responsible for the enantioface discrimination is discussed in terms of a model developed and successfully used for olefinic hydrocarbons as substrates.

Introduction

Asymmetric hydrocarbonylation of olefinic hydrocarbons has been extensively investigated [1,2]. A simple model of the transition state responsible for the regio- and enantio-selectivity of the reaction has been used successfully, and allows the correct prediction of the predominant structural isomer and enantiomer in over 85% of a large series of experiments (more than 120 reactions with various substrates, chiral ligands, and catalysts) [1,2,10]. When functionalized substrates are used this model should allow identification of possible interactions between functional groups and catalysts by comparison with the results obtained with olefinic hydrocarbons. In this way further information on the structure of the transition states and on the nature of the catalytic centers can be obtained. In this paper we discuss some results

* Dedicated to Professor Luigi Sacconi in recognition of his important contribution to organometallic chemistry.

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TABLE 1

ASYMMETRIC HYDROFORMYLATION OF UNSATURATED ESTERS [a]

Substrate	Reaction time (h)	Conversion [b] (%)	2		3		Selectivity [c] to 2 (%)
			(%)	e.e. (%)	(%)	e.e. (%)	
1a	45	99	83	37.2(*S*)	16	n.c. [f]	83
1a [e]	110	100	42	55.5(*S*)	58	n.c.	42
1b	18	100	56	23.8(*R*)	44	n.c.	56
1b [e]	145	86	21	49.5(*R*)	65	n.c.	25
1c [d]	27	94	40	16.3(*R*)	54	27.7(*S*)	43
1d [d]	24	100	85	10.0(*S*)	15	n.c.	85
1e	21.5	95	51	45.2(*R*)	44	33.7(*R*)	54
1e [e]	45	80	28	81.9(*R*)	52	52.8(*R*)	35
1f [d]	15	100	55	42.5(*S*)	45	35.5(*S*)	55

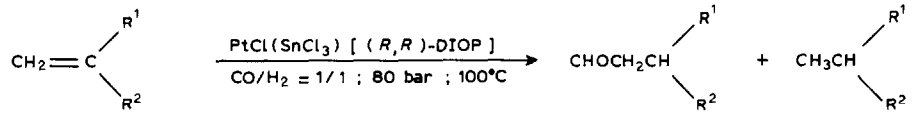
[a] Reaction conditions (unless otherwise stated): 35 ml toluene; 0.1 mol substrate; Pt/substrate 1/2000; $p(CO) = p(H_2) = 40$ bar; 100 °C. [b] (mol reacted substrate/mol initial substrate) $\times 10^2$. [c] (mol aldehyde/mol reacted substrate) $\times 10^2$. [d] 0.05 mol substrate. [e] $p(CO)$ 40 bar, $p(H_2)$ 200 bar, 50 °C. [f] n.c. = nonchiral.

obtained in the hydroformylation of a series of unsaturated esters with $PtCl(SnCl_3)[(R,R)$-DIOP] [3] (DIOP is 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane) as the catalyst precursor.

Results

The results obtained in the hydroformylation of the esters **1a–1f** (Scheme 1) are summarized in Table 1. Under the conditions used the hydroformylation is accompanied by hydrogenation of the substrate. The selectivity towards hydroformylation varies between 85% for **1d** and 25% for **1b**. The formylation occurs only at the terminal methylene group, in contrast to the hydroformylation with rhodium catalysts which yields the two expected hydroformylation products [4].

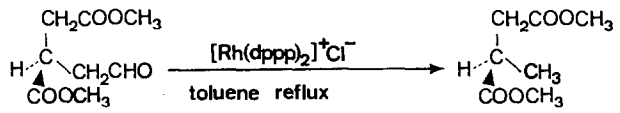
In contrast to the behavior of 2-phenyl-1-butene [5], hydrogenation and hydroformylation of **1e** and **1f** occur predominantly at the same enantioface of the



	R^1	R^2
1a	$COOCH_3$	CH_3
1b	COOPh	CH_3
1c	$COOCH_3$	Ph
1d	CH_3	CH_2COOCH_3
1e	$COOCH_3$	CH_2COOCH_3
1f	COOPh	CH_2COOPh

(**2a–2f**) (**3a–3f**)

SCHEME 1



((−)-**2e**) (*R*-(+)-**3e**)

SCHEME 2

substrate. In contrast, with **1c**, as in the case of the previously reported 2-phenyl-1-butene, the two reactions occur on the opposite enantiofaces.

The absolute configuration of (−)-**2e** was determined by decarbonylation in the presence of [Rh(dppp$_2$)]Cl [4,6] (dppp = 1,3-bis(diphenylphosphino)propane) to the corresponding *R*-(+)-**3e** (Scheme 2). The absolute configuration of (−)-**2f** was determined by decarbonylation (as described previously) to (−)-diphenyl methylsuccinate followed by transesterification to *S*-(−)-**3e**. The absolute configuration of (−)-**2a**, (+)-**2b** and (−)-**2c** was determined by oxidation with Ag_2O to yield, after esterification with methanol, *S*-(−)-**3e** in the first case, *R*-(+)-**3e** in the second, and *R*-(−)-dimethyl 2-phenylbutanedioate in the third. Compound (−)-**2d** was oxidized with Ag_2O to yield *S*-(−)-methyl 3-methylpentanedioate [19]. The enantiomeric excess of the hydroformylation and hydrogenation products was determined by the ^{1}H NMR chiral shift technique with Eu(dcm)$_3$ (tris(dicampholylmethanato)-europium(III)) as chiral shift reagent.

For the esters of both mono- and di-carboxylic acids a change in the type of prevailing chirality occurs on going from the methyl to the phenyl esters. The enantiomeric excess is smaller for **1e**, in which no carboxylic group is present in the α-position with respect to the double bond.

The largest asymmetric induction was observed for the esters of itaconic acid. For dimethyl itaconate the influences of the partial pressures of hydrogen and carbon monoxide and of the temperature on the enantiomeric excess were investigated (Table 2). The enantiometric excess of the hydroformylation product increases with increasing $p(H_2)$ and decreasing $p(CO)$ and decreasing temperature, as previously observed for 2-phenyl-1-butene and 2-phenylpropene [5]. The selectivity to hydroformylation decreases with increasing $p(H_2)$ and with decreasing $p(CO)$. In the competitive hydrogenation of the substrate the enantioselectivity is increased with decreasing temperature. In contrast to results obtained for 2-phenyl-1-butene [5], the enantiomeric excess of the hydrogenation product is also influenced by the partial pressures of hydrogen and carbon monoxide. The maximum enantiomeric excess observed with dimethyl itaconate as substrate is the highest ever reported for asymmetric hydroformylation [7].

Discussion

The negative influence of carbon monoxide partial pressure on the reaction rate and on the enantiomeric excess (Table 1) has been considered in earlier papers [3,5], and has been attributed to the presence in solution of complexes with various

TABLE 2

ASYMMETRIC HYDROFORMYLATION OF DIMETHYL ITACONATE (**1e**) WITH $PtCl(SnCl_3)[(R,R)\text{-DIOP}]$ UNDER DIFFERENT REACTION CONDITIONS [a]

$p(CO)$ (bar)	$p(H_2)$ (bar)	Temperature (°C)	Reaction time (h)	Conversion [b] (%)	**2e**		**3e**		Selectivity [c] to **2e** (%)
					(%)	e.e. (%)	(%)	e.e. (%)	
40	40	100	21.5	95	51	45.2	44	33.7	54
80	40	100	67	97	66	34.5	31	17.7	68
20	40	100	18	99	38	52.5	62	25.8	38
40	80	100	15	100	40	58.7	60	31.0	40
40	200	100	15	100	26	64.0	74	40.1	26
120	120	100	15	99	55	56.6	45	30.3	55
40	40	100	23 [d]	100	83	31.0	17	20.3	83
40	40	50	174	86	66	70.6	20	45.0	77
40	200	50	45	80	28	81.9	52	52.8	35
20	200	50	123	92	19	83.6	73	51.4	21

[a] Reaction conditions (unless otherwise stated): 35 ml toluene; 0.1 mol substrate; Pt/substrate 1/2000. [b] (mol reacted substrate/mol initial substrate) $\times 10^2$. [c] (mol aldehyde/mol reacted substrate) $\times 10^2$. [d] 35 ml 4-methyl-2-pentanone (solvent).

Pt/CO ratios [3] having different catalytic activities and giving rise to different enantioselectivities in hydroformylation (Scheme 3).

$$[P]_2PtH(SnCl_3) \underset{-CO}{\overset{+CO}{\rightleftharpoons}} [P]_2PtH(SnCl_3)CO \underset{+[P],\,-CO}{\overset{+CO,\,-[P]}{\rightleftharpoons}} [P]PtH(CO)_2(SnCl_3)$$
(I) (II) (III)

SCHEME 3. [P] = phosphorus containing ligand.

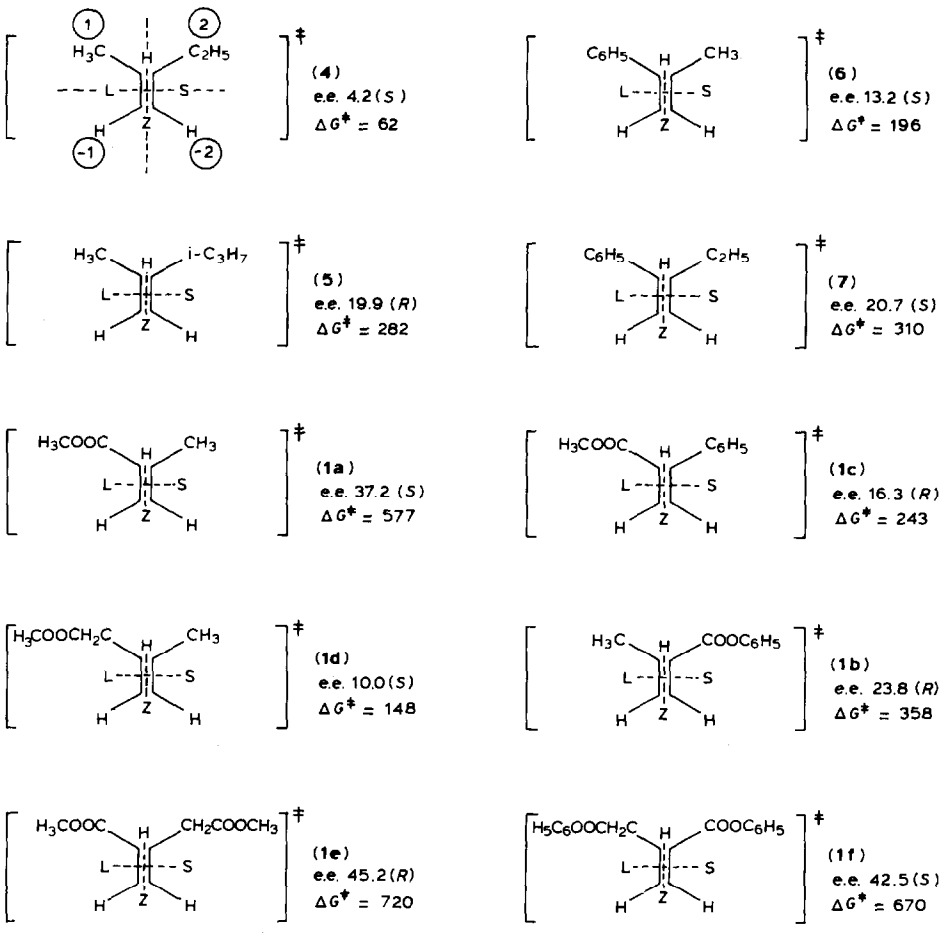
If we further assume that all the species in Scheme 3 are able to catalyze hydrogenation (although at different rates and with different enantioface discriminating abilities), we can also explain the influence of carbon monoxide on enantioselectivity in the competing hydrogenation.

Different explanations can be given for the influence of the partial pressure of hydrogen on enantioselectivity in hydrogenation and hydroformylation. Similar features have been recognized in rhodium-catalyzed asymmetric hydrogenation [8,9].

For **1c** the hydrogenation and hydroformylation products arise from the opposite enantiofaces of the substrate, as previously found for 2-phenyl-1-butene [5]. This fact was accounted for in terms of the assumption that different catalytic species are mainly responsible for the concurrent asymmetric hydrogenation and hydroformylation (e.g., in Scheme 3 species I would be mostly responsible for hydrogenation and species II and III for hydroformylation). In the case of **1e** and **1f**, hydrogenation and hydroformylation occur at the same enantioface; for these substrates, in contrast to the cases of **1c** and 2-phenyl-1-butene, enantioselectivity is higher for hydroformylation than for hydrogenation.

The type and extent of asymmetric induction with different substrates can be classified by use of the simplified stereochemical model for the transition states (Scheme 4) leading to the intermediate alkylplatinum complexes. According to this model, the high regioselectivity observed is connected with the larger steric hindrance in quadrants 2 and -2 (with respect to 1 and -1, compare Scheme 4, [**4**]) arising from the fact that Z is larger than H. The relative positions of the ligand L (large) and S (small) on the metal can be established from the results obtained in the hydroformylation of aliphatic hydrocarbons such as 2-methyl-1-butene and 2,3-dimethyl-1-butene ([**4**] and [**5**] in Scheme 4), for which the only substantial attractive interaction between substrate and catalyst is believed to occur at the double bond. The results obtained with 2-phenylpropene and 2-phenyl-1-butene ([**6**] and [**7**] in Scheme 4), when compared with that from 2,3-dimethyl-1-butene, can be interpreted in terms of attractive interactions between phenyl group and catalyst in quadrant 1. If the bulk of the conjugated phenyl ring is assumed to be similar to that of an isopropyl group, the extent of the attractive interaction in the transition state should be in the range of 400–600 cal/mole. Similarly, there seem to be attractive interactions between the substrate and the catalytic complex when a $COOCH_3$ group conjugated to the double bond of the substrate is situated in quadrant 1 (Scheme 4, [**1a**]).

The results obtained with methyl methacrylate (**1a**), 2,3-dimethyl-1-butene again being used as the reference, indicate that the attractive interaction between $COOCH_3$ and catalytic complex (when $COOCH_3$ is in quadrant 1) is in the region of 800–900 cal/mol. Interactions between carboxylic groups and catalytic complexes have been postulated in, e.g., asymmetric hydrogenation [11].



SCHEME 4. Low energy transition states for the insertion step in the hydroformylation of 1,1-disubstituted ethylenes and free energy differences ($\Delta G^{\ddagger}$ in cal mol^{-1}) between diastereometric transition states responsible for the observed enantiomeric excesses (e.e., %).

Interestingly, for methyl α-phenylacrylate (**1c**) the attractive interaction, associated with the $COOCH_3$ group, prevails over that of the phenyl group, as expected from the above data (Scheme 4, [**1c**]); the resulting interaction, estimated as above, is lower (500 cal/mol) than in the case of methyl methacrylate, and roughly corresponds to the difference between the interaction of the $COOCH_3$ and the phenyl group in quadrant 1 with the catalyst. An unexpected result was obtained in the hydroformylation of phenyl methacrylate (**1b**), for which the enantiomeric excess is only slightly higher than that in the case of 2,3-dimethyl-1-butene, the predominant enantiomer being the (*R*) isomer in both cases (Scheme 4, [**1b**]). A shielding of the ester group arising from the presence of the phenyl group and reducing the attractive interaction between ester group and catalyst is possibly the origin of this effect. A more complex case is represented by methyl 3-methylbut-3-enoate (**1d**), in which the effective size of the CH_2COOCH_3 group and therefore its steric interactions depend on its conformation. The results obtained in the hydrofor-

mylation indicate that the predominant enantiomer is the opposite of that in the hydroformylation of 2-methyl-1-butene (**4**) and 2,3-dimethyl-1-butene (**5**). In terms of the model used (Scheme 4, [**1d**]), the attractive interaction when the CH_2COOCH_3 group is in quadrant 1, can be estimated to be between 200 and 500 cal/mol.

The results obtained in the hydroformylation of the itaconic acid esters are qualitatively in keeping with the above interpretations. For both the dimethyl (**1e**) and diphenyl (**1f**) ester, the predominant enantiomer is that predictable on the basis of the results obtained with the corresponding metacrylic esters, which indicates that there is a large attractive interaction between the catalyst and the $COOCH_3$ group in quadrant 1 which is absent in the phenyl esters (Scheme 4, [**1e**] and [**1f**]). However, from a quantitative point of view a lower enantiomeric excess for **2f** than for **2a** and **2b**, would be expected. This reflects the limitations of the model in quantitative predictions, and the presence of more complicated intramolecular and intermolecular interactions between polar groups in the transition states for [**1e**] and [**1f**].

The simplified model, based on non-bonding interaction only for the transition state leading to the diastereomeric alkylmetal complexes allows us to fit the present results into a scheme which accounts at least qualitatively for the asymmetric induction phenomena in the hydroformylation with platinum/DIOP catalysts. The presence of attractive interactions implied by the model when some substituents are situated in a particular quadrant suggests substrate structures for which high enantiomeric excesses should be expected.

This approach, which consists in tailoring the substrate to the largely unknown catalyst structure, is opposite to the synthetic approach in which the catalyst is adapted to fit the substrate. However, it appears to be useful for elucidating the origin of asymmetric induction in homogeneous catalysis. From the point of view of synthesis the results reveal the possibility of obtaining enantiomeric excesses of practical interest in hydroformylation.

Experimental

Reagents

$PtCl(SnCl_3)[(R,R)$-DIOP] was made from $PtCl_2$ (Johnson–Matthey Chemicals Limited) by a published procedure in which the benzonitrile complex is treated with (R,R)-DIOP to give $PtCl_2[(R,R)$-DIOP], which is then treated with $SnCl_2$ (Fluka) [3]. (R,R)-DIOP was prepared as described previously [12].

Toluene was distilled under nitrogen from sodium-potassium alloy in the presence of benzophenone.

Dimethyl itaconate was used as purchased (Fluka). Methyl methacrylate was freshly distilled under nitrogen.

Methyl phenylacrylate was synthesised by azeotropic esterification of atropic acid, which was prepared by dehydration of tropic acid [13]. Phenyl methacrylate and phenyl itaconate were prepared by treatment of the appropriate acid chlorides with phenol [14]. Methyl 3-methyl-3-butenoate was prepared from methallyl chloride; this was converted to methallyl magnesium chloride which was carboxylated with carbon dioxide, and the resulting unsaturated acid was esterified [15].

Hydroformylation

In a typical experiment the suspension of 0.05 mol (47.7 mg) $PtCl(SnCl_3)[(R,R)$-DIOP] and 35 ml toluene was transferred under nitrogen into a 150 ml stainless steel autoclave which contained 0.1 mol (15.7 g) dimethyl itaconate. The autoclave was pressurized to 80 bar total pressure ($CO/H_2 = 1/1$) and placed in an oil bath which was continuously agitated by an arm shaker. The pressure was monitored throughout the reaction. After cooling and venting, the pale yellow solution was removed and quickly analyzed by GC and fractionally distilled for further characterization.

Characterization of the products

*Methyl 2-methyl-3-formylpropionate (**2a**).* The hydroformylation product from **1a** was separated by fractional distillation at 42°C/1 torr. The enantiomeric excess was determined by ^1H NMR.

^1H NMR (C_6D_{12}): 9.64 (s, 1H, CHO); 3.57 (s, 3H, OCH_3); 2.89 (m, 1H, $CHCOOCH_3$); 2.77 (dd, 1H, CH^aH^bCHO, J 7.2 Hz, 17.6 Hz); 2.3 (dd, 1H, CH^aH^bCHO, J 6 Hz, 17.6 Hz); 1.15 (d, 3H, $CHCH_3$, J 7.1 Hz).

For determination of the absolute configuration the product was oxidized with Ag_2O [16] and the formed carboxylic acid esterified. The reactions starting from (−)-**2a**$[\alpha]_D^{20} - 2.02°$(neat) resulted in (−)-**3e**$[\alpha]_D^{20} 2.16°$(neat) having an absolute configuration *S*.

*Phenyl 2-methyl-3-formylpropionate (**2b**).* The hydroformylation product from **1b** was separated by fractional distillation at 97–100°C/1 torr. The enantiomeric excess was determined by ^1H NMR spectroscopy using $Eu(tfc)_3$ (tris(trifluoracetylcamphorato)europium(III)) as chiral shift reagent.

^1H NMR (C_6D_{12}): 9.69 (t, 1H, CHO, J 0.7 Hz); 6.98–7.24 (m, 5H, Ph); 3.8 (m, 1H, $CHCOOPh$); 2.87 (ddd, 1H, $CHCH^aH^b$, J 18 Hz, 7.7 Hz, 0.7 Hz); 2.44 (ddd, 1H, $CHCH^aH^b$, J 18 Hz, 5.7 Hz, 0.7 Hz); 1.29 (d, 3H, CH_3, J 7.2 Hz).

For determination of the absolute configuration, **2b** was hydrolyzed and the resulting 2-methyl-3-formylpropionic acid oxidized to methyl butanedioic acid as described for **2a** then esterified with methanol. The reaction of (+)-**2b**$[\alpha]_D^{20}$ + 2.36°(neat) gave (+)-**3e**$[\alpha]_D^{20}$ + 1.60°(neat) having an absolute configuration *R*.

*Methyl 2-phenyl-3-formylpropionate (**2c**).* The hydroformylation product from **1c** was separated from the reaction mixture by fractional distillation at 97–100°C/1 torr. The enantiomeric excess was determined by the ^1H NMR shift technique using $Eu(dcm)_3$ as chiral shift reagent.

^1H NMR (C_6D_{12}): 9.6 (s, 1H, CHO); 7.17 (m, 5H, Ph); 4.03 (dd, 1H, $CHCOOCH_3$, J 4.5 Hz, 9.9 Hz); 3.53 (s, 3H, OCH_3); 3.25 (dd, 1H, $CHCH^aH^b$, J 9.9 Hz, 18.1 Hz); 2.53 (dd, 1H $CHCH^aH^b$, J 4.5 Hz, 18.1 Hz).

For determination of the absolute configuration, **2c** was oxidized with Ag_2O [16] and the formed carboxylic acid derivate esterified. This procedure with (−)-**2c**$[\alpha]_D^{20}$ − 22.4°(neat) gave (−)-dimethyl 2-phenylbutanedioate $[\alpha]_D^{20}$ − 19.63°(neat) with an absolute configuration *R* [17].

*Methyl 2-phenylpropionate (**3c**).* The hydrogenation product from **1c** was separated by fractional distillation at 58–60°C/0.8 torr. The optical purity was determined from the specific rotation $[\alpha]_D^{20}$ − 19.28° (*R*) (neat) [18].

^1H NMR (C_6D_{12}): 7.2 (m, 5H, Ph); 3.57 (q, 1H, $CHCH_3$, J 7.2 Hz); 3.52 (s, 3H, OCH_3); 1.41 (d, 3H, $CHCH_3$, J 7.2 Hz).

Methyl 3-methyl-4-formylbutanoate (2d). The formyl derivate of **1d** was separated by fractional distillation from the reaction mixture at 44–46 °C/1 torr. An attempt to determine the enantiomeric excess directly by ^{1}H NMR spectroscopy was unsuccessful. Thus **2d** was oxidized to methyl 2-methylpentanedioate and the optical purity of the latter was determined from its optical rotation, using $[\alpha]_D^{20}$ 0.58° (*R*) (neat) [19].

^{1}H NMR (C_6D_{12}): 9.64 (t, 1H, CHO, *J* 1.5 Hz); 3.55 (s, 3H, OCH_3); 2.45 (m, 2H, $CHCH_2 + CH^aH^bCOOCH_3$); 2.20 (m, 3H, $CH^aH^bCOOCH_3 + CH_2CHO$); 0.98 (d, 3H, $CHCH_3$, *J* 6.8 Hz).

Dimethyl 2-(formylmethyl)-butanedioate (2e). The hydroformylation product from **1e** was separated by fractional distillation at 54–56 °C/0.1 torr. The enantiomeric excess was determined by the ^{1}H NMR chiral shift technique using Eu(dcm)$_3$ as chiral shift reagent, the signal from the CHO group being used.

^{1}H NMR (C_6D_{12}): 9.62 (t, 1H, CHO, *J* 0.8 Hz); 3.57 (s, 3H, OCH_3); 3.55 (s, 3H, OCH_3); 3.28 (m, 1H, $CHCH_2$); 2.82 (ddd, 1H, CH^aH^bCHO, J_1 6.4 Hz, J_2 18.1 Hz, J_3 0.8 Hz); 2.66 (dd, 1H, $CH^cH^dCOOCH_3$, J_1 5.6 Hz, J_2 16.8 Hz); 2.62 (ddd, 1H, CH^aH^bCHO, J_1 6.4 Hz, J_2 18.1 Hz, J_3 0.8 Hz); 2.50 (dd, 1H, $CH^cH^dCOOCH_3$, J_1 7.2 Hz, J_2 16.8 Hz).

The absolute configuration of **2e** was determined by homogeneous catalytic decarbonylation using [Rh(dppp)$_2$]Cl (where dppp = 1,3-bis(diphenylphosphino)propane) as a catalyst [6]. A solution of the rhodium complex and the hydroformylation product in toluene was refluxed for 2 days. Decarbonylation of the (−)-**2e**$[\alpha]_D^{20}$ − 1.37° (neat) then gave (+)-**3e** with $[\alpha]_D^{20}$ + 2.6° (neat) having absolute configuration *R*.

Dimethyl methylbutanedioate (3e). The pure hydrogenated derivative of **1e** was separated by fractional distillation at 28 °C/0.1 torr. For the determination of the optical purity the optical rotation, $[\alpha]_D^{20}$ + 6.44° (*R*) [20], and the density, d_4^{20} 1.076, were used.

^{1}H NMR ($CDCl_3$): 3.56 (s, 3H, OCH_3); 3.55 (s, 3H, OCH_3); 2.81 (m, 1H, $CHCH_3$); 2.65 (dd, 1H, $CH^aH^bCOOCH_3$, *J* 16.4 Hz, 7.1 Hz); 2.23 (dd, 1H, $CH^aH^bCOOCH_3$, *J* 16.4 Hz, 6.7 Hz); 1.14 (d, 3H, CH_3, *J* 7.1 Hz).

Diphenyl methylsuccinate (3f). The hydrogenated product from **1f** was separated by fractional crystallization from toluene under nitrogen. An attempt to determine the enantiomeric excess directly by ^{1}H NMR spectroscopy was unsuccessful. After transesterification of **3f** with methanol the optical purity of the resulting **3e** was determined as before (see above); (−)-**3f**$[\alpha]_D^{20}$ − 19.4° (acetone, *c* 2.7) gave (+)-**3e**$[\alpha]_D^{20}$ − 2.8° (neat) with absolute configuration *R*.

^{1}H NMR ($CDCl_3$): 7.42 (m, 4H, Ph); 7.26 (m, 2H, Ph); 7.13 (m, 4H, Ph); 3.25 (m, 1H, $CHCH_3$); 3.1 (m, 2H, CH_2COOPh); 1.45 (d, 3H, CH_3, *J* 7.2 Hz).

Diphenyl 2-(formylmethyl)-butanedioate (2f). The hydroformylated product from **1f** was separated as white crystals by fractional crystallization of the reaction mixture under nitrogen. **2f** was decarbonylated by the method used in the case of **2e**. The product was transesterified with methanol and the optical purity of **3e** determined. Starting from (−)-**2f**, the procedure gave (−)-**3e** with absolute configuration *S*.

^{1}H NMR ($CDCl_3$): 9.87 (s, 1H, CHO); 7.37 (m, 4H, Ph); 7.23 (m, 2H, Ph); 7.08 (m, 4H, Ph); 3.68 (m, 1H, $CHCH_2CHO$, *J* 6.3 Hz); 3.25 (m, 4H, $CH_2COOPh + CH_2CHO$).

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