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ASYMMETRIC HYDROFORMYLATION OF THE LINEAR BUTENES BY [(*R*,*R*)-Diop]Pt($SnCl_3$)Cl *

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Summary

The asymmetric hydroformylation of the three isomeric straight chain butenes catalyzed by [(*R*,*R*)-Diop]Pt($SnCl_3$)Cl (Diop is 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane) has been reinvestigated. Depending on the conditions, hydroformylation can be accompanied by extensive isomerization and hydrogenation of the substrate. Enantiomeric excess and regioselectivity depend on the extent of conversion. At least two pathways must be responsible for the formation of the straight chain aldehyde from the 2-butenes. The chirality of the 2-methylbutanal arising from 1-butene (best e.e 46.7%) is opposite to that arising from (*Z*)- and (*E*)-2-butene. Under the conditions used asymmetric induction is determined during or before the formation of the alkyl complexes which are generally postulated as intermediates in the catalytic cycle. The assumption of the existence of different catalytic species responsible for hydroformylation and hydrogenation/isomerization accounts satisfactorily for the results.

Introduction

Conflicting results are reported in the literature [1,2] on the hydroformylation of 1-butene with the catalytic system obtained "in situ" from $SnCl_2 \cdot 2H_2O$ and [(*R*,*R*)-Diop]$PtCl_2$ [3] as the catalyst precursor. In both reports a low enantiomeric excess for 2-methylbutanal was obtained in the reaction but the prevailing chirality was claimed to be (*S*) [1] and (*R*) [2], respectively. Since the relative prevailing chirality obtained for 2-methylbutanal when starting with 1-butene or (*Z*)- and (*E*)-2-butene can have interesting mechanistic implications [4], and since the reproducibility of the above catalytic system prepared "in situ" was found to be poor [5], we have reinvestigated the asymmetric hydroformylation of the isomeric straight

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chain butenes using [(*R*,*R*)-Diop]Pt($SnCl_3$)Cl (**1**) [6] as the catalyst precursor under constant partial pressure of hydrogen and carbon monoxide. As already briefly reported [4,7], under conditions minimizing secondary reactions the prevailing chirality of 2-methylbutanal obtained from 1-butene using the above catalytic system is (*R*). Furthermore the enantiomeric excess (~ 47%) is the highest obtained to date in the hydroformylation of aliphatic olefinic hydrocarbons. We thought it likely that the discrepancy in the literature reports [1,2] could be accounted for by thoroughly investigating the secondary reactions accompanying the hydroformylation.

Results and discussion

1. Racemization of (S)-2-methylbutanal under hydroformylation conditions

In the hydroformylation of butenes achiral n-pentanal and chiral 2-methylbutanal (**2**) are formed. Optically active **2** could racemize under hydroformylation conditions, thus making very difficult the investigation of the asymmetric induction under various reaction conditions. In order to test the extent of racemization during hydroformylation, aldehyde **2** (of 93% optical purity [8]) was first heated at 100°C under 80 atm of an equimolar mixture of hydrogen and carbon monoxide in the presence of the catalyst **1** and small amounts (0.25 mol/l) of 1-butene in ethylbenzene as the solvent. A relatively rapid racemization occurred, with $\tau_{1/2}$ of about 8 h. In order to test the possible influence of the presence of an excess of the olefin on the racemization rate, the hydroformylation of 1-decene was carried out under the above conditions. Optically active **2** was added to the reaction mixture before starting hydroformylation; practically no racemization was observed after 5.5 h, when about 70% of 1-decene had been hydroformylated. Evidently the excess olefin suppresses racemization, and so in the present experiments conversion of olefin into aldehydes was generally kept low (< 80%).

2. Asymmetric hydroformylation of 1-butene

Working under 80 atm of an equimolar mixture of hydrogen and carbon monoxide in the presence of **1** as the catalyst precursor, the rate of hydroformylation rapidly increases with temperature up to 100°C (Table 1). An induction time, which decreases with increasing the temperature and during which no reaction of the substrate occurs, was observed, but its origin was not established. At 140°C a decrease of the rate was noticed, accompanied by partial decomposition of the catalyst. Between 60 and 100°C the straight chain aldehyde greatly predominates, but the isomeric excess (i.e.) [9] decreases from 92 to 86% upon increasing the temperature. The i.e. drastically decreases upon further increase of the hydroformylation temperature, and is 44% at 140°C.

The enantiomeric excess (e.e.) progressively decreases upon increasing the temperature to 100°C, the prevailing enantiomer being the (*R*) one. However at 140°C the (*S*) enantiomer prevails and the enantiomeric excess is very small.

The main secondary reactions are substrate isomerization and hydrogenation; both are insignificant up to 80°C. However, at 100°C, when conversion to aldehydes is 35%, 10% of the substrate is hydrogenated and 25% is isomerized. At 140°C 60% of the substrate undergoes these secondary reactions, whose rates are, at this temperature, similar to that of hydroformylation.

The most striking result is the remarkable change in the isomeric and enanti-

omeric composition at 140°C. Both results can (at least qualitatively) be easily accounted for by taking into account the large extent of isomerization of 1-butene to (*Z*)- and (*E*)-2-butene, which produce **2** having a predominant (*S*) absolute configuration (vide infra). At 140°C, most of 2-methylbutanal arises from (*Z*)- and (*E*)-2-butene, consequently the (*S*) enantiomer predominates. The enantiomeric excess is small, partly because some product arises from 1-butene which is hydroformylated predominantly to the (*R*) enantiomer with a high e.e. The variation in isomeric and enantiomeric excess observed on increasing the temperature from 60 to 100°C has substantially the same origin; in addition one would expect a decrease in regio- and stereo-selectivity due purely to temperature effects [10].

The influence of the partial pressure of carbon monoxide and hydrogen on the hydroformylation of 1-butene has also been investigated (Table 2). At 80°C, an increase of the $p(H_2)$ causes a large increase in the hydroformylation rate, but does not substantially affect the regioisomeric or enantiomeric excess. Isomerization of the substrate ranges between 5 and 12%, but hydrogenation increases significantly upon increasing $p(H_2)$, as expected [11].

An increase of p(CO) brings about a decrease of hydroformylation rate and a very large decrease in the proportion of the secondary reactions; under 10 atm p(CO) these amount to 29%, compared to 45% conversion to aldehydes. The p(CO) has no effect on the isomeric composition; a small but significant decrease of the enantiomeric excess was obtained by working at a p(CO) of 160 atm, as observed in other cases [11].

As far as the isomerization of the substrate is concerned, the catalytic system used has a similar behaviour to $Co_2(CO)_8$, for which the existence of different catalytic species has been postulated [12], with their relative proportion depending on p(CO). A further similarity is provided by the large increase in the extent of hydrogenation at low p(CO) values as previously discussed [11].

The decrease in the rate of the platinum-catalyzed hydroformylation upon increasing the p(CO) at 160 atm is accompanied by a decrease in the enantiomeric excess of **2** (Table 2). This suggests that in addition to the two aforementioned catalytic species I and II, which are responsible for hydrogenation and isomerization of substrate and of hydroformylation respectively [13], species III could be postulated. This third catalytic species must therefore have a lower catalytic activity and

$$\underset{(I)}{P_2PtH(SnCl_3)} \underset{-CO}{\overset{+CO}{\rightleftharpoons}} \underset{(II)}{P_2PtH(SnCl_3)(CO)} \underset{+P,-CO}{\overset{+CO,-P}{\rightleftharpoons}} \underset{(III)}{PPtH(SnCl_3)(CO)_2}$$

a lower enantioface discriminating capacity than either I or II in hydroformylation (P represents a phosphorus atom of the phosphine ligand).

3. Hydroformylation of (Z)- and (E)-2-butene

Under the conditions in which the highest enantiomeric excess was obtained for 1-butene, the hydroformylation of (*Z*)- and (*E*)-2-butene was investigated (Table 3). At 60°C under 80 atm of an equimolar mixture of hydrogen and carbon monoxide, the overall reaction rate decreased in the order 1-butene > (*Z*)-2-butene > (*E*)-2-butene. Induction times longer than those observed for 1-butene were observed. Even though no double bond shift seems to take place for these substrates under these conditions, 23–24% of n-pentanal is formed. A double bond shift leading to 1-butene followed by its very rapid hydroformylation would imply that about 8% of

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TABLE 1

INFLUENCE OF THE TEMPERATURE ON THE HYDROFORMYLATION OF 1-BUTENE WITH [(−)-Diop]Pt($SnCl_3$)Cl (**1**) AS THE CATALYST PRECURSOR UNDER 80 atm H_2/CO (1/1) [a]

Reaction temperature (°C)	Reaction time (min)	Residual olefin				Hydrogenation (%)	Aldehydes		2-Methylbutanal	
		%	Isomeric composition (%)				Yield (%)	Normal/branched	Optical purity (%)	Absolute configuration
			1-B	(*Z*)-2-B	(*E*)-2-B					
60	390 [b]	60	95	2	3	1	32 [c]	96/4	46.7	(*R*)
80	75 [d]	47	89	4	6	4	49	95/5	36.2	(*R*)
100 [e]	13	55	55	18	27	10	35	93/7	21.9	(*R*)
140 [f]	162	33	13	31	56	30	38	72/28	2.6	(*S*)

[a] 80 mg **1**; 30 ml (at −60°C) of 1-butene; 50 ml ethylbenzene. [b] Induction time 480 min. [c] A small amount of high boiling product was also found. [d] Induction time 60 min. [e] 160 mg of **1** and 60 ml of 1-butene were used; induction time 8 min. [f] 50 mg **1**, 20 ml 1-butene, 25 ml ethylbenzene; some reduction of the catalyst was observed.

TABLE 2

INFLUENCE OF THE HYDROGEN AND CARBON MONOXIDE PARTIAL PRESSURE ON THE ASYMMETRIC HYDROFORMYLATION OF 1-BUTENE WITH [(−)-Diop]Pt($SnCl_3$)Cl AS THE CATALYST PRECURSOR AT 80°C [a]

p(CO) (atm)	*p*(H_2) (atm)	Reaction time (min)	Residual olefin				Hydrogenation (%)	Aldehydes		2-Methylbutanal	
			%	Isomeric composition, %				Yield (%)	Normal/branched	Optical purity (%)	Absolute configuration
				1-B	(*Z*)-2-B	(*E*)-2-B					
40	10	420	55	78	7	15	2	37	93/7	33.3	(*R*)
40	40	75	47	89	4	6	4	49	95/5	36.2	(*R*)
40	160	20	37	84	5	11	15	48	96/4	29.9	(*R*)
10	40	90	42	62	12	26	13	45	95/5	33.6	(*R*)
160	40	120	52	96	2	2	1	47	96/4	27.6	(*R*)

[a] 80 mg **1**, 30 ml 1-butene, 50 ml ethylbenzene. Induction times between 5 and 60 min were observed.

TABLE 3

HYDROFORMYLATION OF 1-, (Z)-2- AND (E)-2-BUTENE WITH [(−)-Diop]Pt($SnCl_3$)Cl AS THE CATALYST PRECURSOR AT 60°C AND UNDER 80 atm $H_2/CO(1/1)$ [a]

Substrate	Reaction time) (h)	Residual olefin				Hydrogenation (%)	Aldehydes		2-Methylbutanal	
		%	Isomeric composition (%)				Yield (%)	Normal/branched	Optical purity (%)	Absolute configuration
			1-B	(Z)-2-B	(E)-2-B					
1-Butene [b]	6.5	60	95	2	3	1	32 [c]	96/4	46.7	(R)
(Z)-2-Butene [d]	5.5	68	~0	75	25	1	31	24/76	14.5	(S)
(E)-2-Butene [d]	8	64	~0	12	88	1	35	23/77	24.2	(S)

[a] 80 mg **1**, 50 ml ethylbenzene. [b] 30 ml substrate; induction time 8 h. [c] Small amounts of high boiling material were produced. [d] 20 ml substrate; induction time ~10 h.

TABLE 4

INFLUENCE OF THE CONVERSION ON THE PRODUCTS COMPOSITION IN THE HYDROFORMYLATION OF 1-, (*Z*)-, AND (E)-2-BUTENE WITH [(−)-Diop]Pt($SnCl_3$)Cl AS THE CATALYST PRECURSOR[a]

Substrate	Reaction time[b] (min)	Residual olefin				Hydrogenation (%)	Aldehydes		2-Methylbutanal	
		(%)	Isomeric composition (%)				Yield (%)	Normal/branched	Optical purity (%)	Absolute Configuration
			1-B	(*Z*)-2-B	(*E*)-2-B					
1-Butene	85	10	10	30	60	22	68	85/15	2.8	(*S*)
	43	26	8	31	61	11	63	91/9	11.7	(*R*)
	25	40	23	41	36	9	51	92/8	22.8	(*R*)
	13[c]	55	55	18	27	10	35	93/7	21.9	(*R*)
	7[c]	75	79	9	12	6	19	94/6	24.8	(*R*)
(*Z*)-2-Butene	195	6	1	37	62	9	85	64/36	8.3	(*S*)
	90	25	2	36	62	7	68	62/38	8.3	(*S*)
	25	74	1	64	35	2	24	57/43	8.0	(*S*)
	10	94	2	89	9	~ 0	6	45/55	7.7	(*S*)
(*E*)-2-Butene	285	10	1	32	67	8	82	60/40	9.7	(*S*)
	105	24	2	30	68	8	68	63/37	11.1	(*S*)
	35	76	1	21	78	2	22	56/44	12.8	(*S*)
	15	93	2	8	90	~ 0	7	49/51	13.4	(*S*)

[a] Reaction conditions: *T* 100°C; *p* 80 atm (100°C), constant pressure; 80 mg **1**, 30 ml olefin, 25 ml ethylbenzene. [b] Induction period 2–15 min. [c] The amount of the catalyst, olefin and solvent was doubled.

the substrate has isomerized; under the same conditions only 3% of 1-butene is isomerized to 2-butenes. Since the ratio between the sum of the rate constants for the reactions 1-butene → (*Z*)-2-butene and 1-butene → (*E*)-2-butene and the sum of the rate constants for the reverse reactions (as evaluated from the equilibrium constants) is about 20 at room temperature, it must be concluded that under the condition used formylation at position 1 for the 2-butenes does not occur via isomerization to 1-butene followed by hydroformylation, in keeping with the absence of 1-butene in the reaction mixture. A similar conclusion was reached for the hydroformylation of 2-butene using $CO_2(CO)_8$ as the catalyst precursor [12]; in this case formylation of the 2-butenes at position 1 was explained in terms of a rearrangement of the substrate-catalyst complex preceding CO insertion [14]. However, as in the case of the platinum catalysis, the structure of the postulated catalyst-substrate complex was not clarified.

In contrast to 1-butene, (*Z*)- and (*E*)-2-butene give 2-methylbutanal with a predominant (*S*) absolute configuration, the enantiomeric excess being larger for the (*E*) than for the (*Z*) isomer. Taking into account the (*E*) ⇄ (*Z*) isomerization of the substrates, the actual asymmetric induction must be slightly lower for the (*Z*) and slightly higher for the (*E*) isomer. In both cases competitive hydrogenation of the substrate takes place to a very limited extent.

4. Asymmetric hydroformylation of the isomeric butenes at various extents of conversion

In order to gain a better understanding of the effect of the olefin concentration upon the main and upon the secondary reactions during the hydroformylation catalyzed by **1**, the regio- and enantio-selectivity was determined at various extents of conversion. The three straight chain butenes were hydroformylated under constant pressure (80 atm) and 100°C, with the extent of reaction varying between 15 and 99% (Table 4). Because of the coexistence of numerous parallel reactions, determination of the rate constants would be subject to many assumptions and was not attempted.

Under the conditions used the overall hydroformylation rate decreases in the order 1-butene ≫ (*Z*)-2-butene > (*E*)-butene, and the rate of hydrogenation decreases in the order 1-butene > (*Z*)-2-butene ≃ (*E*)-2-butene. In all cases regioisomeric and enantiomeric excesses vary with the extent conversion, but to a different degree. The most interesting results concern 1-butene; in this case the regioisomeric excess varies from 88% at 40% substrate conversion to 70% at 99% conversion. The corresponding variation in the enantiomeric excess is from 24.8% (*R*) to 2.8% (*S*). Over the same range of conversion hydrogenation increases from 6 to 22%. As previously discussed, the variation of the isomeric excess can be explained by the fact that products arise in part from 1-butene hydroformylation (i.e. 88%) and in part from the 2-butene hydroformylation (i.e. 2–20%). Analogously the enantiomeric excess reflects the sum of the 2-methylbutanal arising from 1-butene (24.8% e.e., the (*R*) enantiomer predominating) and from (*Z*)- and (*E*)-2-butene (7.7% and 13.4% e.e., respectively, with a predominance of the (*S*) enantiomer).

In the case of the 2-butenes also, regioisomeric and enantiomeric excess vary with the conversion; in both cases the branched isomer predominates at very low conversions, whereas a preference for the normal isomer is observed at higher conversions. As far as the enantiomeric excess is concerned, it decreases for (*E*)-2-butene and increases for (*Z*)-2-butene with increasing conversion, the (*S*) enantiomer always predominating. These different trends can be explained in terms

of the fact that for (*E*)-2-butene the 2-methylbutanal arising from isomerization products has in all cases a lower proportion of the (*S*) enantiomer. For (*Z*)-2-butene the increase in e.e. is due to the fact that the contribution by the product arising from (*E*)-2-butene (which have a larger e.e. (*S*)) is larger than the contribution by the product arising from 1-butene, which has a large e.e. (*R*).

As already mentioned, there are two mechanisms leading to the straight chain aldehyde from the internal olefins. Most of this aldehyde arises from the rearrangement of the catalyst-olefin complex, as previously discussed for the low temperature hydroformylation, additional small amounts of the linear isomer are formed from the hydroformylation of 1-butene slowly produced by double bond shift of 2-butenes. The dependence on the 2-butene concentration of the rate of formation of the linear isomer through the two pathways can be different, and therefore the isomeric excess can change with the time.

Conclusions

The results permit understanding of the origin of the discrepancies existing in the literature [1,2] on the hydroformylation of linear butenes. Thus 1-butene can yield a predominantly (*S*)- or (*R*)-2-methylbutanal depending on the extent of isomerization to 2-butenes, since 1-butene yields predominantly the (*R*) antipode whereas 2-butenes, arising from isomerization, yield predominantly the (*S*) antipode. Under conditions under which isomerization, of 1-butene is faster than the hydroformylation of the 2-butenes the substrate composition is continuously shifted in favour of the 2-butenes, and thus the relative amount of the (*S*) antipode increases with the extent of conversion. The reported low values of e.e. of 2-methylbutanal obtained from 1-butene arise from the fact that at high conversion and/or at a long reaction time the amount of aldehyde arising from 2-butene is overwhelming (Table 4). The relatively low isomeric excess for the straight chain isomer reported in the literature (72% [2] and 46% [1], respectively) is in keeping with the above explanation.

A further discrepancy exists in the literature concerning the enantiomeric excess of the 2-methylbutanal obtained starting with (*Z*)- or (*E*)-2-butene. The lower values (1.2%) were obtained using long reaction times; under these conditions the [(*R*,*R*)-Diop] $PtCl_2/SnCl_2 \cdot 2H_2O$ system could act as a racemization catalyst. In the light of the results of the racemization experiments on 2-methylbutanal it is understandable that in experiments carried out with long reaction times (16–22 h) and relatively high conversions, lower enantiomeric excesses should be obtained [1] than in the experiments in which the reaction time was 3–4 h [2].

The results reported in this paper show that, in contrast with previous proposals [1], in the platinum catalysed hydroformylation using [(*R*,*R*)-Diop]$Pt(SnCl_3)Cl$ as the catalyst precursor, the regioselectivity and asymmetric induction are determined during or before the formation of the key alkylplatinum intermediates. The fact that in the case of 1-butene a relatively large enantiomeric excess (45%) is obtained shows that the alkylplatinum-complexes-involved in hydroformylation have sufficient configurational stability under the reaction conditions used.

At 100°C in the case of 1-butene the initial rate of double bond shift and of hydroformylation are closely similar. If the double bond shift occurred through the same the alkylplatinum intermediates this would require a facile β-hydrogen elimination, which would be in conflict with the configurational stability of the alkylplatinums required for a satisfactory asymmetric induction. These facts could be

reconciled by assuming that different catalytic complexes are responsible for the double bond shift and the hydroformylation, as is the case for hydrogenation and hydroformylation [13]. The fact that for 1-butene an increase of carbon monoxide pressure significantly lowers both the extent of hydrogenation and the double bond shift can be taken as an indication that both secondary reactions are catalyzed by the same coordinatively unsaturated catalytic complex or complexes, which are deactivated by carbon monoxide.

A change of the isomeric composition with the extent of conversion, as observed in our experiments at 100°C, is not a common phenomenon in hydroformylation. This phenomenon has a different origin in the hydroformylation of 1-butene and 2-butenes. It is related in the first case to the fact that substrate hydroformylation and isomerization have similar rates, and in the second case to the fact that there are two mechanisms of formation of the straight chain isomer from the 2-olefins, respectively involving a rearrangement of the catalyst substrate complex and a substrate isomerization.

Experimental

General

GC analyses were carried out with Perkin–Elmer Sigma 4 with flame ionization detector using a 2 m column packed with Carbowax 20 M 20% on chromosorb A and a 4 m column packed with dimethylsulfolane 25% on Kieselgur. Mass spectra were recorded with a Hitachi–Perkin–Elmer RMU-6L spectrometer. NMR spectra were recorded on a WH 90 Bruker spectrometer using TMS as the internal standard or H_3PO_4 as the external standard. Optical rotations were measured on a Perkin–Elmer 141 polarimeter. The optical purity of 2-methylbutanal was calculated by assuming the value $[\alpha]_D^{25}$ 35.14 as the maximum rotatory power [8].

Carbon monoxide was prepared by decomposition of formic acid; purity $\geqslant 99.5\%$ by GC. Hydrogen was a product of Sauerstoff- und Wasserstoffwerken AG, Luzern, Switzerland, with a purity $> 99.5\%$. Ethylbenzene (Fluka product) was purified through distillation over Na-K-alloy under nitrogen. 1-Butene, (*Z*)- and (*E*)-2-butene were Fluka products purum (99%) and were used without further purification.

Preparation of [(−)-Diop]Pt($SnCl_3$)Cl

4.8 g of [(−)-Diop]$PtCl_2$ and 1.23 g of anhydrous $SnCl_2$ were stirred in 350 ml of degassed CH_2Cl_2 for 60 min. The resulting bright yellow solution was filtered under nitrogen and concentrated to 200 ml. Hexane was added to the boiling solution until it became turbid. After filtration followed by cooling, the resulting clear solution was kept at −25°C for 24 h, to give colourless crystals. These were filtered off, washed with 50 ml of pentane, and dried under vacuum. Yield: 3.8 g (63%), m.p. 270°C. Analysis: Found: C, 38.12, H, 3.35, Cl, 14.92. $C_{31}H_{32}Cl_4O_2P_2PtSn$ calcd.: C, 38.01; H, 3.38; Cl, 14.86%. ^{31}P NMR($CDCl_3$, −50°C): 8.9 and −0.8 ppm; ^1J(Pt, P) 2850 and 3510 Hz; ^2J(P, P) 18 Hz; ^2J(Sn, P) 4180 and 214 (average for ^{117}Sn and ^{119}Sn).

Hydroformylation experiments

The second run of Table 4 is described as an example. A 250 ml stainless steel autoclave filled with 80 mg of [(−)-Diop]Pt($SnCl_3$)Cl was evacuated and cooled to −11°C. 30 ml of 1-butene (measured in a Schlenk tube at −60°C) and 25 ml of ethylbenzene were introduced by suction. The autoclave was charged with 20 atm of

CO and heated at 100°C in an oil bath. After 1 h the reaction was started by introducing an equivalent amount of H_2 and by connecting the autoclave to a reservoir to maintain the pressure in the reaction vessel constant at 80 atm. After a gas uptake of 12.5 litres (corresponding to an olefin conversion of 70%) the reaction was stopped by cooling, first with water and then with ice to 0°C. The solution was analyzed by GC using a Carbowax column at 100°C for aldehyde analysis and a dimethyl-sulfolan column at room temperature for olefin analysis. The aldehyde yield was determined by using the solvent as internal standard.

A sample of 1 ml of aldehyde was fractionationally distilled from the product mixture, and its linear to branched ratio was determined by GC. The optical rotation (neat at 589 nm and 25°C) was $-1.15°$ ($l = 1$). By extrapolation to a 100% branched sample, pure 2-methylbutanal was judged to have $[\alpha]_D^{25}$ $-4.1°$ (o.p. 11.7%). The assumption of linearity for the extrapolation was justified by measuring the rotations of various mixtures of almost optically pure (*S*)-2-methylbutanal [8] and pentanal.

Racemization of 2-methylbutanal under hydroformylation conditions

(a) In the presence of small amounts of 1-butene. 2.5 ml of (*S*)-2-methylbutanal having $[\alpha]_D^{25}$ + 32.7 (o.p. 93% [8]), 30 mg of **1** and ~ 2 mmol of 1-butenes were dissolved in 6 ml of ethylbenzene. The mixture was kept in an autoclave at 100°C under 80 atm of an equimolar mixture of hydrogen and carbon monoxide. After various times, the aldehyde was recovered by rectification. The residual optical rotations were: $[\alpha]_D^{25}$ + 29.3 after 1.5 h; $[\alpha]_D^{25}$ + 21.4 after 5 h; $[\alpha]_D^{25}$ + 0.3 after 22 h.

(b) During 1-decene hydroformylation. 15 ml of (*S*)-2-methylbutanal having $[\alpha]_D^{25}$ + 22.3 (o.p. 63.5%). 80 mg of **1**, 50 ml of 1-decene and 50 ml of ethylbenzene were introduced into a 250 ml autoclave as described for the hydroformylation experiments. The mixture was kept at 100°C and 80 atm of H_2/CO. Samples of the solution were taken after 0.7, 1, 8, 3.2 and 5,5 h, and the 2-methylbutanal was recovered by distillation after gas chromatographic determination of the extent of hydroformylation of 1-decene. After 5.5 h (70% conversion of 1-decene) the optical rotation of 2-methylbutanal was unchanged.

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