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65. Asymmetric Olefins Hydroformylation. VI. Asymmetric Hydroformylation of Isomeric Butenes Using Platinum Catalysts

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(12. XII. 75)

Summary. The asymmetric hydroformylation of the straight chain butenes with the [(–)-DIOP]$PtCl_2$-$SnCl_2$ catalytic system shows that asymmetric induction, contrary to the rhodium-(–)-DIOP catalytic system, takes place after the intermediate metal-alkyl-complex formation.

Recently the hydroformylation of 1-pentene using hydrido-trichlorostannato-carbonyl-bis(triphenylphosphine)-platinum(II) [$HPt(SnCl_3)(CO)(PPh_3)_2$] has been described [1] and some experiments concerning the asymmetric hydroformylation of 2-methyl-1-butene using platinum(II) catalysts in the presence of $SnCl_2$ and of asymmetric ligands including (–)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane [(–)-DIOP] have been carried out [2].

In the case of the rhodium catalysed asymmetric hydroformylation the investigation of the straight chain butenes as substrates yielded interesting information about the steps in which the asymmetric induction takes place and about the reaction

Table 1. *Hydroformylation of Olefins with [(−)-DIOP]$PtCl_2$ and $SnCl_2$ (molar ratio 1:5) in Aromatic Hydrocarbons* [Olefin 0.14–0.05 mol; Solvent 10 ml; T = 100°; $P_{CO}/P_{H_2} = 1$; Olefin/Pt = $1.3 \cdot 10^2 - 1 \cdot 10^3$]

Olefinic Substrate	$P_{H_2} + P_{CO}$ atm	Reaction Time (h)	Conversion [a]) %	Aldehyde Ratio Straight Chain / Branched	Optically Active Compound Isolated		
					Name	α_D^{25} ($l = 1$)	Opt. Pur. %
1-butene	82	4.5	50	73/27	(*S*)-2-methylbutanal	+0.31	1.2
cis-butene	82	16.8	25	32/68	(*S*)-2-methylbutanal	+0.34	1.2
trans-butene	82	21.5	20	24/76	(*S*)-2-methylbutanal	+0.33	1.2
2,3-dimethyl-1-butene	250	61	95	only s.c.	(*R*)-3,4-dimethylpentanol	+2.68	15.0
styrene	245	1	~100	53/47	(*S*)-2-phenylpropanal	+5.53	2.2
α-methylstyrene	245	3	~100	only s.c.	(*S*)-3-phenylbutanoic acid	+5.60	9.9
α-ethylstyrene	240	5	~100	only s.c.	(*S*)-3-phenylpentanoic acid	+6.52	14.8

[a]) Total conversion of the substrate to hydroformylation and hydrogenation products.

Table 2. *Comparison between the results obtained in the rhodium and platinum catalysed asymmetric hydroformylation using (−)-DIOP as asymmetric ligand*

Substrate	Reaction Product Considered	$HRh(CO)(PPh_3)_3$ + (−)-DIOP		[(−)-DIOP]$PtCl_2$ + $SnCl_2$	
		Prevailing Configuration	Asymmetric Induction, % [a])	Prevailing Configuration	Asymmetric Induction, %
1-butene	2-methylbutanal	(*R*)	18.8	(*S*)	1.2
cis-butene	2-methylbutanal	(*S*)	27.0	(*S*)	1.2
trans-butene	2-methylbutanal	(*S*)	3.2	(*S*)	1.2
2,3-dimethyl-1-butene	3,4-dimethylpentanal	(*S*)	3.5	(*R*)	15.0
styrene	2-phenylpropanal	(*R*)	25.2	(*S*)	2.2
α-methylstyrene	3-phenylbutanal	(*R*)	1.6	(*S*)	9.9
α-ethylstyrene	3-phenylpentanal	(*R*)	1.8	(*S*)	14.8

[a]) Best optical yield reported in [3].

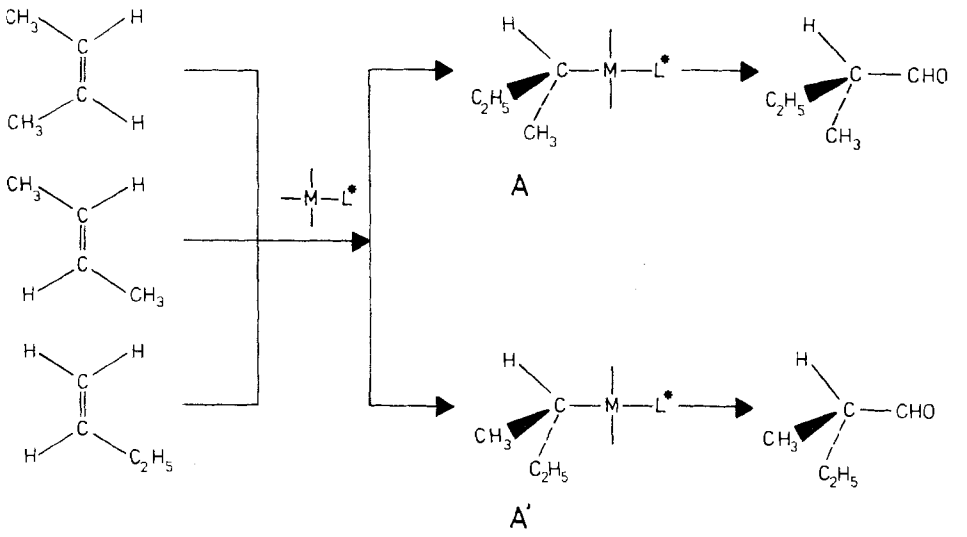
mechanism [3]. It seemed therefore interesting to investigate the above substrates as well as other olefins using chiral platinum complexes as catalysts in order to establish whether the step or steps in which the asymmetric induction takes place are the same, independent of the metal used as catalyst. Furthermore, by comparing experiments involving the same olefinic substrate and the same asymmetric ligand, but different metals in the catalytic complex, information can be obtained about the role that different metal atoms play in asymmetric catalysis.

The results of hydroformylation experiments using [(–)-DIOP]$PtCl_2$-$SnCl_2$ as catalyst precursor are reported in Table 1.

The optical yields reported in Table 1 are compared in Table 2 with the results previously obtained using $HRh(CO)(PPh_3)_3$-(–)-DIOP as catalyst precursor and it appears that:

a) In all cases, excepting the internal olefins, the prevailing chirality of the synthesized products is opposite when platinum- or rhodium-catalysts are used. Therefore, the asymmetric induction is not simply originated by a steric interaction between substrate and asymmetric ligand which is in all cases (–)-DIOP. Other factors, as for instance the prevailing chirality of the metal atom in the catalytic complex [4] and the geometry of the catalyst, must play a role in originating the asymmetric induction.

b) By hydroformylating the straight chain isomeric butenes with platinum catalysts, 2-methylbutanal having the same chirality and practically the same optical purity has been obtained; in the case of *cis*- and *trans*-butene 32% and 24% respectively of the straight chain isomers is formed, showing that either a substrate isomerization or a hydrogen shift in the catalyst-substrate complex takes place [5]. The situation when the platinum catalyst is used is completely different from the case



in which rhodium catalyst is used [3]. In fact, in the latter case the chirality of 2-methyl-butanal is different when obtained from 1-butene than from 2-butene; furthermore, the optical purity is different in the three cases and also only 2-methyl-butanal is obtained starting from *cis*- and *trans*-butene.

Assuming that the mechanism and stereochemistry in the platinum and rhodium catalysed hydroformylation are the same [2], 2-methylbutanal must be originated in all cases from the diastereomeric sec-butylmetal-complexes (*Scheme 1*, A and A'). The conflicting results obtained in the case of platinum and rhodium can be rationalized, assuming that asymmetric induction, which in the case of rhodium has been shown to occur before the CO insertion [3], in the case of platinum takes place after the alkyl-platinum-complex formation. This implies that the diastereomeric alkyl-platinum-complexes undergo an interconversion which is more rapid than the successive step or steps (*i.e.*, either the formation of the acyl-metal-complex or the reduction of the acyl-complex to the aldehyde), in which the asymmetric induction takes place [6]. A rapid interconversion of the platinum-alkyl-complexes intermediates is also in keeping with the formation of two isomeric aldehydes starting from 2-butene.

We do not know if the above conclusion can be extended to other substrates and particularly to the 2-alkylsubstituted terminal olefins. For both platinum catalysed hydroformylation and palladium catalysed hydrocarboxylation the highest asymmetric induction has been obtained with 2-substituted α-olefins, while in the case of rhodium catalyst these substrates are hydroformylated with the lowest optical yield.

This fact might indicate that coordination numbers and/or geometry are different in catalytic complexes containing a metal of the subgroups b or c of the VIII group of the periodic system.

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66. Über die Konstitution von Loroglossin

Vorläufige Mitteilung[1])

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The Constitution of Loroglossine. – *Summary.* Loroglossine, a characteristic constituent of orchids, is shown to be bis-[4-(β-D-glucopyranosyloxy)-benzyl]-(2*R*,3*S*)-2-isobutyl-tartrate (**1**). Hydrolysis and esterification gave 1 mol-equiv. of dimethyl (+)-2-isobutyl-*erythro*-tartrate

[1]) Eine ausführliche Mitt. soll in dieser Zeitschrift erscheinen.