Journal of Organometallic Chemistry, 385 (1990) 147–152
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20570

Hydroformylation of chiral terpenes with $PtCl(SnCl_3)$-(bis-phosphine) as catalyst

László Kollár, József Bakos, Bálint Heil,

Institute of Organic Chemistry, University of Chemical Engineering, H-8201 Veszprém, P.O. Box 158 (Hungary)

Péter Sándor

Central Chemical Research Institute of the Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17 (Hungary)

and Gábor Szalontai

Research Institute for Heavy Chemical Industries, H-8201 Veszprém, P.O. Box 160 (Hungary)

(Received September 27th, 1989)

Abstract

(+)-*R*-Limonene and (−)-*R*-carvone undergo hydroformylation in the presence of catalytic Pt-bisphosphine-$SnCl_2$ systems to yield exclusively the linear products. The internal double bond and the carbonyl group remain intact in both substrates during the reaction. The variation of the diastereomeric composition of the aldehydes upon variation of the chelating phosphine in the catalyst has been investigated.

Introduction

In the field of catalytic hydroformylation much effort has been directed towards obtaining the homogeneous catalyst which give formyl derivatives containing other functional groups [1]. Some such compounds are potential chiral building blocks or can be converted into commercially important products through simple organic reactions [2]. Among the optically active intermediates derived from the hydroformylation of chiral natural substances there are only a few terpene derivatives [3]. (−)-α-Pinene was hydroformylated under 300–700 bar total pressure to give (−)-2-formylbornane and (−)-3-formylpinane in cobalt- and rhodium-catalyzed reactions, respectively [4]. Similar severe conditions (300 bar, 150 °C) were used for the hydroformylation of (+)-*R*-limonene ((*R*)-4-isopropenyl-1-methyl-1-cyclohexene (**1a**)) in the presence of "Raney-cobalt" as long ago as 1946 [5].

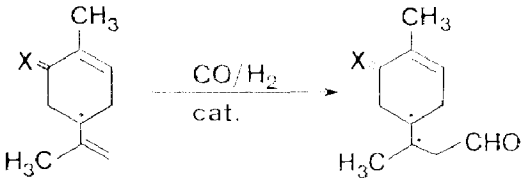
0022-328X/90/$03.50

The especially high regioselectivity of the platinum-catalyzed hydroformylation of vinylidene-type olefins has been observed previously [6,7]. Catalytic systems of this type, namely $PtCl_2$(DPPP) + $SnCl_2$ (where BDPP = (−)-(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane or its (+)-(2*R*,4*R*) enantiomer)) and $PtCl_2$(DPPP) + $SnCl_2$ (where DPPP = 1,3-bis(diphenylphosphino)propane), were used in the synthesis of the formyl terpenoic derivatives starting from (+)-*R*-limonene (**1a**) and (−)-*R*-carvone ((*R*)-5-isopropenyl-2-methyl-2-cyclohexenone (**1b**)).

Results and discussion

Both **1a** and **1b** were hydroformylated regiospecifically to give the linear aldehydes, 3-(4-methylcyclohex-3-enyl)butanal (**2a**) and 3-(4-methylcyclohex-4-en-3-onyl)butanal (**2b**), respectively (Scheme 1). (No trace of the corresponding branched aldehydes could be detected.) The extent of conversion was rather low in both cases, especially in the reaction of **1a** (Table 1). The lower reaction rate may be due to the greater steric hindrance of the 4-methylcyclohex-3-enyl substituent than of the more planar cyclic group containing the CO–C=C conjugated system.

Exclusive formation of the linear (normal) formyl isomer was observed also in the hydroformylation of (+)-dihydrocarvone (5-isopropenyl-2-methyl-cyclohexanone



X=H$_2$ 1a 2a

X=O 1b 2b

Scheme 1

Table 1

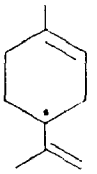
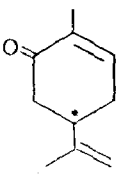
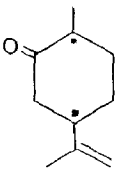
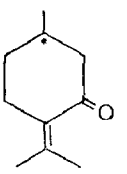
Hydroformylation of **1a** and **1b** with $PtCl_2$(PP) + $SnCl_2$ catalyst [a]

Run	Substrate	Catalyst [b]	Reaction temperature (°C)	Reaction time (h)	Conversion [c] (%)	Diastereomeric ratio [d]	$[\alpha]_D^{20}$ [e]
1	**1a**	$PtCl_2$((+)-BDPP) + $SnCl_2$	100	35	28	38/62	(+83)
2	**1a**	$PtCl_2$(DPPP) + $SnCl_2$	120	35	20	52/48	+100(+87.2)
3	**1a**	$PtCl_2$((−)-BDPP) + $SnCl_2$	120	25	27	60/40	+101.7(+90)
4	**1b**	$PtCl_2$((+)-BDPP) + $SnCl_2$	100	7	60	70/30	−50.2
5	**1b**	$PtCl_2$(DPPP) + $SnCl_2$	100	6	50	57/43	−55.6
6	**1b**	$PtCl_2$((−)-BDPP) + $SnCl_2$	100	7	58	44/56	−59.7
7	**1b**	$PtCl_2$(DPPP) + $SnCl_2$	40	350	21	63/37	−51.8

[a] Reaction conditions: 35 ml toluene; 0.1 mol styrene; Pt/styrene = 1/2000; $P(CO) = P(H_2) = 40$ bar. [b] For abbreviations see: text. [c] (mol of reacted substrate/mol of initial substrate)·100; [d] Ratio of 4*R*,8*R*/4*R*,8*S* (**2a**) or of 5*R*, 8*R*/5*R*,8*S* (**2b**) (it may possibly be reversed). [e] Neat ($l = 0.5$); EtOH ($c = 3.2$, $l = 0.5$) (values in parentheses).

Table 2

Hydroformylation of unsaturated terpenes with Pt-BDPP catalyst. $PtCl(SnCl_3)((-)$-BDPP); toluene; $P(CO) = P(H_2) = 40$ bar; 100 °C; Pt/subst. = 1/2000

Time (h)	Conversion (%)			
	 (1a)	 (1b)	 (1c)	 (1d)
7	5	60	10	0
35	28	96	35	< 1

(**1c**)). In the $PtCl_2BDPP + SnCl_2$ catalyzed reaction the diastereomeric mixture of 3-(4-methylcyclohexan-3-onyl) butanal (**2c**) was isolated in 25% yield after 30 h reaction. The extent of conversions achieved with this substrate (e.g. 10% after 7 h) were between those observed for hydroformylation of **1a** and **1b**. This result may also be associated with the bulk of the cyclic group. As expected, neither hydrogenated nor hydroformylated products were formed from the sterically crowded (+)-*R*-pulegone ((*R*)-2-isopropylidene-5-methylcyclohexanone (**1d**)) (Table 2).

The chemoselectivity of the catalysts specified above is noteworthy. Even at higher temperatures (e.g. run 2) only the terminal double bond was hydroformylated. Even more surprising is the fact, that the selectivity for formation of the aldehyde is very high, less than 0.5% of the hydrogenated product being obtained in each case.

The asymmetric carbon atom of both optically pure substrates of configuration *R* has an influence on the asymmetric induction in the hydroformylation of **1a** and **1b** almost comparable with that of the optically active phosphine (Table 1, run 2,3 and 5,6). In these reactions hydroformylation was carried out with the achiral DPPP as bidentate phosphine. Use of the two enantiomers of the optically active phosphine (BDPP) caused a reversal of the diastereomeric ratio, as expected (run 1,3 and 4,6). The specific rotation values ($[\alpha]_D^{20}$) of the isolated, chemically pure samples are in accordance with the diastereomeric ratios determined by NMR spectroscopy. Apart from that from 7-CH_3, all the carbon signals were separated at 100 MHz (see Fig. 1 and Scheme 2), and so the diastereomeric ratio could be obtained from the integrals of the ^{13}C NMR signals of the products. The ^1H and ^{13}C transitions were assigned by 2D homo- and hetero-nuclear chemical shift correlation experiments.

Owing to serious overlap of the proton multiplets in the 400 MHz spectra (see Fig. 1) the relative configurations of carbons 4 and 8 in **2a** and that of carbons 5 and 8 in **2b** could not be determined. An attempt to separate the 9-CH_2 methylene signals and so determine the relevant interproton couplings by use of $Eu(fod)_3$ or $Pr(fod)_3$ shift reagents were unsuccesful. The configuration at C(8) of the dominant stereoisomer in product **2a** is probably the opposite of that for the dominant stereoisomer in product **2b** obtained with the same catalyst (see also Table 1). This

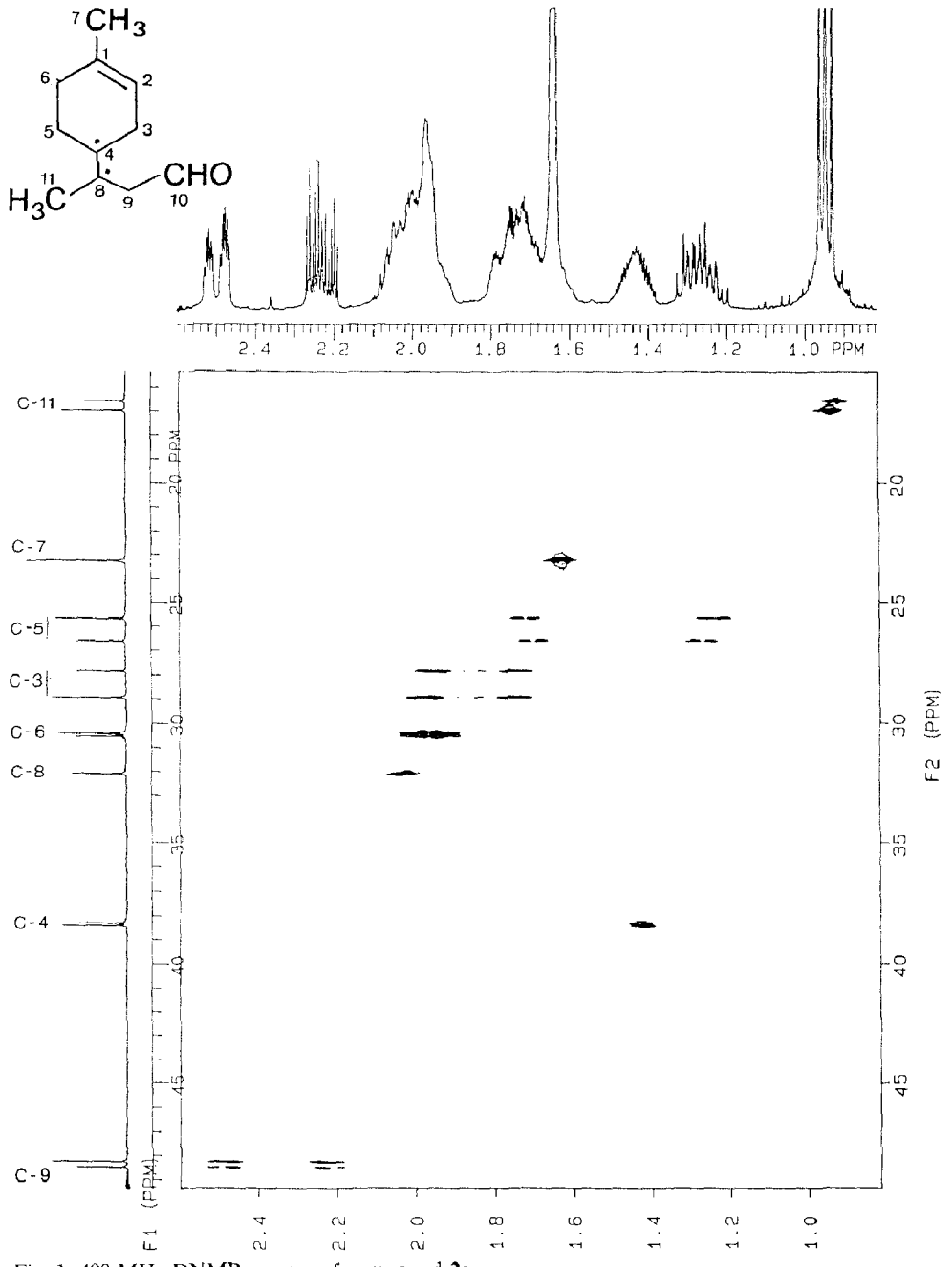


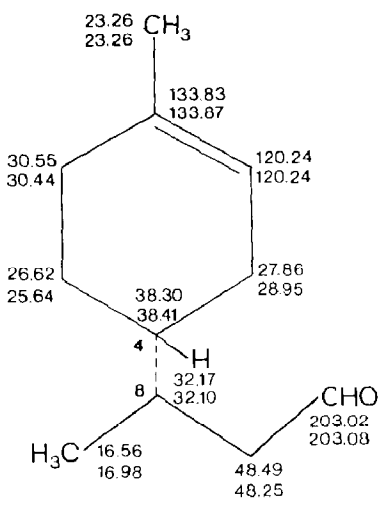
Fig. 1. 400 MHz DNMR spectra of compound **2a**.

conclusion can be drawn from the opposite line intensities of the pertinent carbon signals in the two diastereomers.

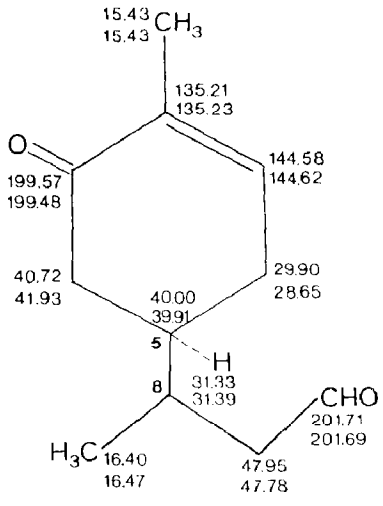
Experimental

Reagents

The $PtCl_2P_2$-type catalytic precursors were prepared from $PtCl_2(PhCN)_2$ by a



4R,8R
4R,8S
2a



5R,8R
5R,8S
2b

Scheme 2

standard method [8]. (−)-(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane (BDPP) and its enantiomer were prepared as described previously [9]. The anhydrous $SnCl_2$ used for the preparation of the "in situ" catalyst was obtained by dehydrating $SnCl_2 \cdot 2H_2O$ with a stoichiometric amount of acetic anhydride and subsequent washing with ether.

Toluene was distilled under argon from sodium in the presence of benzophenone. (+)-*R*-Limonene (Fluka) and (−)-*R*-carvone (Aldrich) were freshly distilled before use.

The ^1H and the ^{13}C NMR spectra were recorded with $CDCl_3$ solutions containing TMS as internal standard on a Varian XL-400 spectrometer operated at 400 MHz and 100.58 MHz, respectively. The optical rotations of the products after isolation from the reaction mixture were determined with neat liquids or ethanol solutions, on a Schmidt Hænsch LM visual polarimeter.

Hydroformylation experiment

In a typical experiment a suspension obtained from 0.05 mmol (35.3 mg) $PtCl_2$ (BDPP) and 0.05 mmol (9.5 mg) $SnCl_2$ in 35 ml of toluene 0.1 mol of substrate was transferred under argon into a 150 ml stainless steel autoclave. The autoclave was pressurized to 80 bar total pressure ($CO/H_2 = 1/1$), placed in a thermostated electric oven, and agitated with an arm shaker. The pressure was monitored throughout the reaction. After cooling and venting, the pale yellow solution was quickly analyzed by GLC and fractionally distilled for further characterization of the products by NMR and mass spectroscopy.

Characterization of the products

3-(4-Methylcyclohex-3-enyl)butanal (2a). MS (*m/z*/ rel.int.): 166/50(M^+); 148/370; 133/270; 121/220; 106/340; 93/1000. ^1H NMR (400 MHz, $CDCl_3$): δ

0.95(d, 7Hz, 3H, CH_3CH); 1.2–1.35(m, 1H, $CH_2CH^aH^bCH$); 1.45(m, 1H, CH_2CHCH_2); 1.64(s, 3H, CH_3C=); 1.60–1.82(m, 2H, $CH^aH^bCHCH_2$ + $CH_2CHCH^aH^b$); 1.9–2.1(m, 4H, $CH_2CHCH^aH^b$ + $CH_2C(CH_3)$ + CH_3CH); 2.2–2.28(m, 1H, CH^aH^bCHO); 2.48–2.52(m, 1H, CH^aH^bCHO); 5.36(br s, 1H, CH=); 9.76(br s, 1H, CHO). IR(neat): 1720 cm^{-1} (ν(CO), CHO, br, vs).

*3-(4-Methylcyclohex-4-en-3-onyl)butanal (**2b**).* MS (*m/z*/rel.int.): 180/30(M^+); 162/30; 136/520; 109/1000; 82/430. ^1H NMR (400 MHz, $CDCl_3$): δ 0.98(d, 6.8 Hz, 3H, CH_3CH); 1.77(m, 3H, CH_3C=); 1.98–2.2(m, 4H, $CH^aH^bCHCH_2$ + $CH_2CHCH^aH^b$ + CH_2CHCH_2 + CH_3CH); 2.25–2.38(m, 2H, $CH_2CHCH^aH^b$ + CH^aH^bCHO); 2.46–2.55(m, 2H, $CH^aH^bCHCH_2$ + CH^aH^bCHO); 6.75(br s, 1H, CH=); 9.78(br s, 1H, CHO). IR(neat): 1675 cm^{-1} (ν(CO), CO–C=C, br, vs); 1720 cm^{-1} (ν(CO), CHO, br, vs).

*3-(4-Methylcyclohexan-3-onyl)butanal (**2c**).* MS (*m/z*/rel.int.): 182/10(M^+); 164/60: 138/1000; 111/880. ^1H NMR (80 MHz, CCl_4): δ 0.95(d, 7 Hz, 6H, CH_3CHCH + CH_3CHCO); 1.2–2.6(m, 11H); 9.7(br s, 1H, CHO). IR(neat): 1703 cm^{-1} (ν(CO), $COCH_2$, br, vs); 1720 cm^{-1} (ν(CO), CHO, br, vs).

References

1 C. Botteghi, R. Ganzerla, M. Lenarda and G. Moretti, J. Mol. Catal., 40 (1987) 129.
2 G. Parrinello and J.K. Stille, J. Am. Chem. Soc., 109 (1987) 7122.
3 H. Siegel and W. Himmele, Angew. Chem., 92 (1980) 182.
4 W. Himmele and H. Siegel, Tetrahedron Lett., 12 (1976) 907.
5 Food Machin. and Chem. Corp. U.S.P. 2 584539, 1946.
6 G. Consiglio and P. Pino, Top. Curr. Chem., 77 (1982).
7 L. Kollár, G. Consiglio and P. Pino, J. Organomet. Chem., 330 (1987) 305.
8 L. Kollár, J. Bakos, I. Tóth and B. Heil, J. Organomet. Chem., 350 (1988) 277.
9 J. Bakos, I. Tóth, B. Heil and L. Markó, J. Organomet. Chem., 279 (1985) 23.