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Synthesis of new *N*-substituted 2-pyrrolidinones via homogeneous catalytic reactions catalyzed by Pt and Rh complexes

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Abstract

1-Vinyl-2-pyrrolidinone undergoes under oxo-conditions selective dimerization in the presence of Pt complexes and hydroformylation in the presence of Rh complexes, The yield and regioselectivity of the Rh-catalyzed hydroformylation strongly depend on the type of phosphine present on the metal.

Introduction

Homogeneous catalytic hydroformylation of substrates containing functional groups provides a very useful method of preparing various valuable compounds and various bifunctional synthons for synthesis of natural products and biologically active compounds [1]. Unsaturated amides and imides are useful substrates for Rh- and Pt-catalyzed hydroformylation [2–4], since the primary oxo-products can be converted by oxidation and hydrolytic cleavage of the imidoring into the corresponding α-amino acids. The rhodium-catalyzed hydroformylation of unsaturated cyclic amides such as *N*-acyl-2-pyrrolines gives α-formyl derivatives, which are readily oxidized and esterified to *N*-protected proline esters [2].

We have now examined application of this reaction to pharmacologically important lactam 1-vinyl-2-pyrrolidinone (**1**), whose behaviour in the presence of cobalt catalysts has been studied previously [5], and have found that use of Pt-phosphine-$SnCl_2$ and Rh-phosphine homogeneous catalysts give different results.

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Results and discussion

The Pt-containing complex $PtCl(SnCl_3)$DIOP (DIOP = (−)-(4*R*,5*R*)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane) catalyses the selective formation of a dimeric compound (1,4-bis-(pyrrolidin-2-on-1-yl)-1-butene (**3**) under the usual hydroformylation conditions (Scheme 1, eq. 1). Surprisingly, no formyl products were detected even, under more severe conditions (120 °C, 160 bar $CO/H_2 = 1/1$). The only side-product, (**2**), may be derived from the reaction of **1** and 2-pyrrolidinone, the latter being formed by the cleavage of the *N*-substituent (Table 1). Both the dimerization and the reductive cleavage are probably due to the $PtH(SnCl_3)$(DIOP) or $PtH(SnCl_3)(CO)$(DIOP) catalytic species suggested previously to be the active complexes in the homogeneous hydroformylation [6]. Two products, (1-(1,3-butadien-1-yl)-2-pyrrolidinone (**3a**) and 2-pyrrolidinone (**3b**), were isolated from the platinum-catalyzed reaction as a consequence of the quantitative decomposition of **3** at 150 °C.

In contrast, in the rhodium catalyzed hydroformylation of **1** the products mentioned above are detected only in traces or not at all (Table 1). As expected, two formyl-regioisomers (**4** and **5**) are formed (Scheme 1, eq. 2). The branched one (**4**) was isolated from the product mixture by fractional distillation at 106–108 °C/0.5 mmHg in 15–50% yield based on the amount of substrate used. The linear isomer (**5**) was identified by NMR spectroscopy in a mixture (branched/linear = 2/1) of the formyl products.

The rate of the hydroformylation strongly depends on the nature of the phosphine ligand. The rhodium-containing systems prepared "in situ" from $[Rh(nbd)Cl]_2$ and the appropriate phosphine are active in the hydroformylation of **1** even at lower temperature, but reasonable conversion can be achieved only at 100 °C.

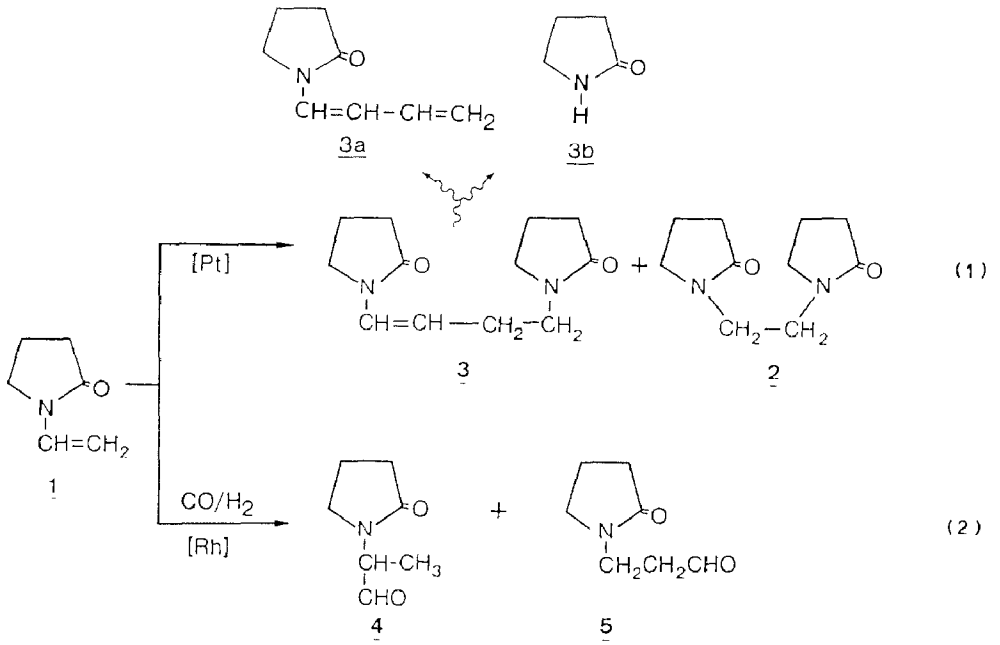

Table 1

Homogeneous hydroformylation of **1** [a]

Catalyst	Reaction time (h)	Conversion [d] (%)	Products (%)			
			2	**3**	**4**	**5**
$PtCl(SnCl_3)$[(*R*,*R*)-DIOP]	10	92	3	89		
$PtCl(SnCl_3)$[(*R*,*R*)-DIOP] [b]	4.5	93	7	86		
$\frac{1}{2}[Rh(nbd)Cl]_2 + 2.2\ Ph_3P$	2	55	–	1	37	18
$\frac{1}{2}[Rh(nbd)Cl]_2 + 2.2\ Ph_3P$	5	90	–	1	60	29
$\frac{1}{2}[Rh(nbd)Cl]_2 + 1.1$(*R*,*R*)-DIOP	8	28	–	–	23	5
$\frac{1}{2}[Rh(nbd)Cl]_2 + 1.1$(*R*,*R*)-DIOP	15	55	–	–	42	13
$\frac{1}{2}[Rh(nbd)Cl]_2 + 1.1$(*S*,*S*)-BDPP [c]	425	22	–	1	20	1

[a] Reaction conditions (unless otherwise stated): 100 °C; 80 bar $CO/H_2 = 1/1$; 30 ml toluene; 0.1 mol substrate; metal/substrate 1/2000; nbd = 2,5-norbornadiene(bicyclo[2,2,1]hepta-2,5-diene). [b] 120 °C; 160 bar $CO/H_2 = 1/1$. [c] 40 °C, 80 bar $CO/H_2 = 1/1$. [d] (moles of substrate reacted/moles of substrate initially present) × 100.

Catalysts containing the monodentate Ph_3P are much more active than those containing bis-phosphines. The regioselectivity of the hydroformylation also changes as the phosphine ligand is varied. Formation of the chiral compound (**4**) is favoured when DIOP is used, and even more when BDPP ((−)-(2*S*, 4*S*)-2,4-bis(diphenylphosphino)-pentane) is used. The ratios of the regioisomers (**4**/**5**) are 82/18 and 95/5, respectively.

Unfortunately, the optical purity of the isolated chiral formyl products is very low in both cases. Determination of the optical purity by chiral "shift-technique" using Eu(facam)$_3$ (tris(trifluoro-acetylcamphorato)europium(III)) as shift-reagent gave values of 5% e.e. for BDPP and < 2% for DIOP.

Experimental

Reagents

The platinum-containing catalytic precursor, $PtCl(SnCl_3)$(DIOP) and the bydentate phosphine, BDPP were prepared as described previously [7,8]. Toluene was distilled under argon from sodium in the presence of benzophenone. *N*-Vinyl-2-pyrrolidinone (Aldrich) was freshly distilled before use.

The ^1H NMR spectra were recorded for CCl_4 or $CDCl_3$ solutions containing TMS as internal standard on a Tesla BS 487C spectrometer at 80 MHz or on a Varian XLDD-400 spectrometer at 400 MHz, and the ^{13}C NMR spectra at 100.58 MHz for $CDCL_3$ with TMS as internal reference. The optical rotation of the product was determined for the neat liquids, after vacuum distillation from the reaction mixture, with a Schmidt Haensch LM visual polarimeter.

Hydroformylation experiments

In a typical experiment 0.025 mmol (11.6 mg) of $[Rh(nbd)Cl]_2$ and 0.055 mmol (27.4 mg) of DIOP were dissolved in 30 ml of toluene under argon in a Schlenk tube. After addition of 0.1 mol (10.5 ml) of 1-vinyl-2-pyrrolidinone the mixture was transferred to a 100 ml stainless steel autoclave, which was pressurized to 80 bar

total pressure ($CO/H_2 = 1/1$), placed in a thermostatted electric oven, and agitated with an arm-shaker. (In the platinum-catalyzed reaction $PtCl(SnCl_3)$(bisphosphine) was used as the precursor.) The pressure was monitored throughout the reaction. After cooling and venting, the solution was removed and analyzed by GC(OV-1, 12 m capillary column), and fractionally distilled to permit further characterization of the products.

Characterization of the products

1,2-Bis(pyrrolidin-2-on-1-yl)-1-etane (**2**). *m/z*/rel.int.: 196/25 (M^+); 168/3; 130/25; 112/100.

1,4-Bis(pyrrolidin-2-on-1-yl)-1-butene (**3**). *m/z*/rel.int.: 22/58 (M^+); 204/100; 124/66; 81/96.

1-(1,3-Butadien-1-yl)-2-pyrrolidinone (**3a**). ^{1}H NMR (400 MHz, $CDCl_3$): 7.14(d, *J* 14.2 Hz, 1H, N–C*H*); 5.63 (dd, *J* 14.2, 10.6 Hz, 1H, NCH = C*H*); 6.35(ddd, *J* 10.6, 10.0, 16.8 Hz, 1H, C*H* = CH_2); 5.14(dd, *J* 16.8, 2.8 Hz, 1H, CH = C$H_a$$H_b$); 4.98 (dd, *J* 10.0, 2.8 Hz, 1H, CH = $CH_a$$H_b$); 3.58 (t, *J* 8.08 Hz, 2H, CH_2N); 2.41 (t, *J* 8.15 Hz, 2H, CH_2CO); 2.13 (q, *J* 8.08, 8.15 Hz, 2H, $CH_2CH_2CH_2$); ^{13}C NMR (100.58 MHz, $CDCl_3$); 17.4(CH_2CH_2); 31.0($COCH_2$); 45.2 (NCH_2); 112.7(CH = CH_2); 114.2(CH = CH_2); 126.7(NCH = CH); 135.1(NCH); 173.3(CO); *m/z*/rel.int.: 137/63 (M^+); 122/16; 108/10; 82/100.

2-Pyrrolidinone (**3b**). ^{1}H NMR (400 MHz, $CDCl_3$): 6.86(br, s, 1H, N*H*); 3.42(t, *J* = 8 Hz, 2H, CH_2N); 2.32(t, *J* 8.1 Hz, 2H, CH_2CO); 2.13(q, *J* 8.0, 8.1 Hz, 2H, CH_2); ^{13}C NMR(100.58 MHz, $CDCl_3$): 20.8(CH_2CH_2); 30.2($COCH_2$); 42.3 (NCH_2); 179.1(CO); *m/z*/rel.int.: 85/100 (M^+); 42/54.

2-(Pyrrolidin-2-on-1-yl)-propanal (**4**). ^{1}H NMR (80 MHz, CCl_4): 1.1(d, *J* 8 Hz, 3H, $CHCH_3$); 2.1(m, 4H, $CO(CH_2)_2$; 3.25(t, *J* 8 Hz, 2H, CH_2N); 4.3(q, *J* 8 Hz, C*H*CH_3); 9.4(s(br),1H, CHO); ^{13}C NMR (20.1 MHz, $CDCl_3$): 11.1(CH_3); 18.3(CH_2CH_2); 30.6 ($COCH_2$); 44.6(NCH_2); 56.4($CHCH_3$); 175.3(CO); 199.5(CHO); *m/z*/rel.int.: 112/100 (M^+ – CHO); 84/22; 69/55.

3-(Pyrrolidin-2-on-1-yl)-propanal (**5**). ^{13}C NMR (20.1 MHz, $CDCl_3$): 18.0 (CH_2CH_2); 30.7(CH_2CO); 36.2(CH_2CHO); 41.8(NCH_2); 47.3(CH_2N); 175.0 (CO); 200.8(CHO); *m/z*/rel.int.: 141/32 (M^+); 113/80; 98/100.

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