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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-SnCl₂ and Rh-phosphine homogeneous catalysts give different results.

Results and discussion

The Pt-containing complex $\text{PtCl}(\text{SnCl}_3)\text{DIOP}$ ($\text{DIOP} = (-)-(4R,5R)\text{-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane}$) 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 $\text{CO}/\text{H}_2 \approx 1/1$). 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 $\text{PtH}(\text{SnCl}_3)(\text{DIOP})$ or $\text{PtH}(\text{SnCl}_3)(\text{CO})(\text{DIOP})$ 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 $106\text{--}108^\circ\text{C}/0.5\text{ mmHg}$ 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 $[\text{Rh}(\text{nbd})\text{Cl}]_2$ 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 .

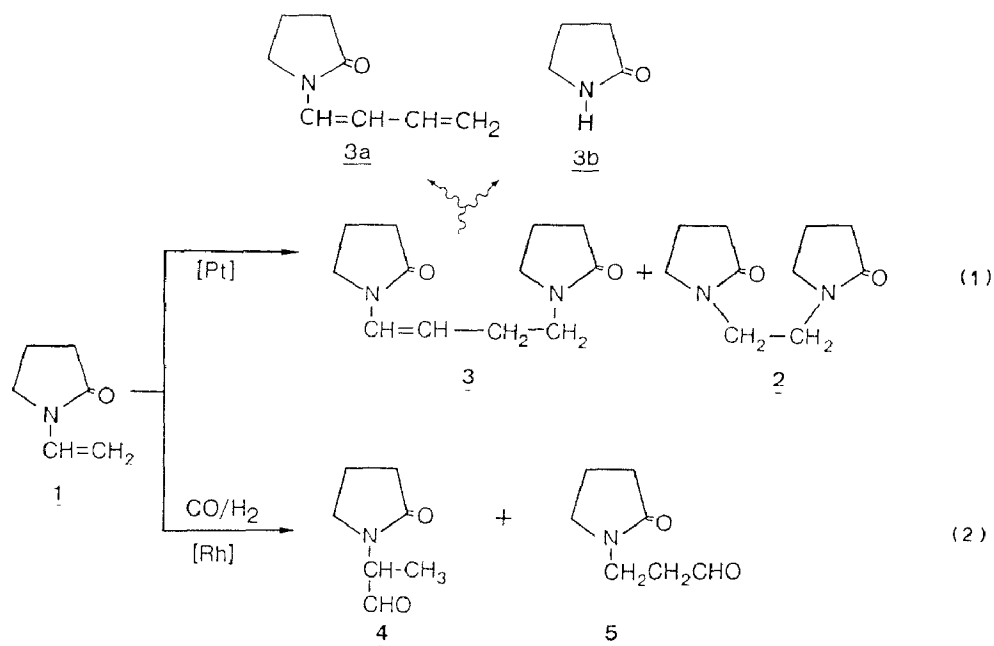


Table 1
Homogeneous hydroformylation of **1**^a

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

^a Reaction conditions (unless otherwise stated): 100 °C; 80 bar CO/H₂ = 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/H₂ = 1/1. ^c 40 °C, 80 bar CO/H₂ = 1/1. ^d (moles of substrate reacted/moles of substrate initially present) × 100.

Catalysts containing the monodentate Ph₃P 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(SnCl₃)(DIOP) and the bidentate 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 CCl₄ or CDCl₃ 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 ¹³C NMR spectra at 100.58 MHz for CDCl₃ 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 ($\text{CO}/\text{H}_2 = 1/1$), placed in a thermostatted electric oven, and agitated with an arm-shaker. (In the platinum-catalyzed reaction $\text{PtCl}(\text{SnCl}_3)(\text{bisphosphine})$ 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-ethane (2). $m/z/\text{rel.int.}$: 196/25 (M^+); 168/3; 130/25; 112/100.

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

1-(1,3-Butadien-1-yl)-2-pyrrolidinone (3a). ^1H NMR (400 MHz, CDCl_3): 7.14(d, J 14.2 Hz, 1H, N-CH); 5.63 (dd, J 14.2, 10.6 Hz, 1H, NCH = CH); 6.35(ddd, J 10.6, 10.0, 16.8 Hz, 1H, CH = CH_2); 5.14(dd, J 16.8, 2.8 Hz, 1H, CH = CH_aH_b); 4.98 (dd, J 10.0, 2.8 Hz, 1H, CH = CH_aH_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, $\text{CH}_2\text{CH}_2\text{CH}_2$); ^{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); $m/z/\text{rel.int.}$: 137/63 (M^+); 122/16; 108/10; 82/100.

2-Pyrrolidinone (3b). ^1H NMR (400 MHz, CDCl_3): 6.86(br. s, 1H, NH); 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); $m/z/\text{rel.int.}$: 85/100 (M^+); 42/54.

2-(Pyrrolidin-2-on-1-yl)-propanal (4). ^1H NMR (80 MHz, CCl_4): 1.1(d, J 8 Hz, 3H, CHCH_3); 2.1(m, 4H, $\text{CO}(\text{CH}_2)_2$); 3.25(t, J 8 Hz, 2H, CH_2N); 4.3(q, J 8 Hz, CHCH_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); $m/z/\text{rel.int.}$: 112/100 ($M^+ - \text{CHO}$); 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); $m/z/\text{rel.int.}$: 141/32 (M^+); 113/80; 98/100.

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