

Low-pressure Selective Hydroformylation of 2,3- and 2,5-Dihydrofuran with a Rhodium Catalyst. Unexpected Influence of the Auxiliary Ligand Tris(*o*-*t*-butylphenyl) Phosphite

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Hydroformylation of 2,3- and 2,5-dihydrofuran has been achieved in excellent yields and good selectivities under mild conditions using $[\text{Rh}_2\{\mu\text{-S}(\text{CH}_2)_3\text{NMe}_2\}_2(\text{cod})_2]$ and suitable auxiliary ligands (cod = cyclo-octa-1,5-diene).

Hydroformylation of complex molecules using organometallic catalysts is a field of increasing interest.¹ We have recently reported that $[\text{Rh}_2\{\mu\text{-S}(\text{CH}_2)_3\text{NMe}_2\}_2(\text{cod})_2]$ (**1**) (cod = cyclo-octa-1,5-diene) in conjunction with PR_3 catalyses the hydroformylation of hex-1-ene to give heptanal in good yield and selectivity. Owing to the presence of the amine group the rhodium catalyst can be quantitatively recovered at the end of the reaction as $[\text{Rh}_2\{\mu\text{-S}(\text{CH}_2)_3\text{NHMe}_2\}_2(\text{CO})_2(\text{PR}_3)_2]\text{SO}_4$.²

This work is part of a general study aimed at obtaining formyl-furans and -pyrans to be used in syntheses of natural products. Here we report on the hydroformylation of 2,3-dihydrofuran (**2**) and 2,5-dihydrofuran (**3**) under mild conditions using the rhodium precursor (**1**) and PPh_3 or tris(*o*-*t*-butylphenyl) phosphite, $\text{P}(\text{OPhBu}^t)_3$, as catalyst. The influence of the reaction conditions and the amount of PR_3 on the conversion and selectivity of the reaction has also been studied. Hydroformylation of the unsaturated compounds (**2**) and (**3**) using rhodium catalysts has been reported,⁴ although poor selectivities for formation of tetrahydrofuran-2-carbaldehyde (**4**) were obtained.

Hydroformylation of (**2**) was performed at 80 °C and 5 bar using (**1**) and different excesses of PPh_3 or $\text{P}(\text{OPhBu}^t)_3$ as catalyst precursors. The results and reaction conditions are reported in Table 1. Only tetrahydrofuran-2-carbaldehyde (**4**) and tetrahydrofuran-3-carbaldehyde (**5**)[†] were formed, and no hydrogenation products were detected. The best results were obtained using $\text{P}(\text{OPhBu}^t)_3$, achieving complete conversion into aldehyde and a 77:23 ratio of (**4**) to (**5**). Unexpectedly, the selectivity decreased at lower temperatures, the conversion percentages remaining nearly quantitative. Also, at different temperatures the conversions and regioselectivities appeared to be independent of the phosphite/catalyst molar ratio used (Table 1). Lower selectivities for formation of (**4**) were observed on increasing the pressure (to 30 bar), the H_2/CO ratio (to 2:1), or the catalyst/substrate ratio (to 1:100).

Table 1. 2,3-Dihydrofuran converted (%) [tetrahydrofuran-2-carbaldehyde (**4**) as % of total aldehyde formed].^a

PR ₃ /(1) molar ratio	P(OPhBu ^t) ₃		PPh ₃ 80 °C
	40 °C	60 °C	
2	—	—	80[77]
4	99[60]	99[70]	95[58]
10	99[63]	99[71]	88[56]
20	99[64]	99[71]	58[49]

^a *Conditions:* 2,3-dihydrofuran (20 mmol) and catalyst precursor (**1**) (0.05 mmol) in 1,2-dichloroethane (15 ml); constant pressure, 5 bar; $\text{CO}/\text{H}_2 = 1$; reaction time, 20 h.

[†] Reaction mixtures were analysed by gas chromatography. Tetrahydrofuran-carbaldehydes were identified by comparison with authentic samples prepared from tetrahydrofuran-2-methanol and tetrahydrofuran-3-methanol.

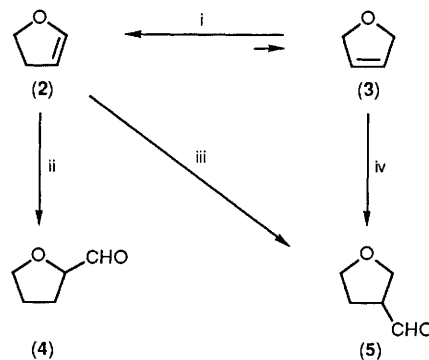
When PPh_3 was used as auxiliary ligand conversions were high as well, but similar amounts of (**4**) and (**5**) were formed (Table 1). Furthermore, in this case the conversion decreased markedly when the PPh_3 /(**1**) molar ratio was increased; however, the regioselectivity was only slightly affected.

Surprisingly, hydroformylation of (**3**) at 80 °C and 5 bar (1 bar = 10⁵ Pa) using (**1**) and $\text{P}(\text{OPhBu}^t)_3$ produced similar results to those obtained in hydroformylation of (**2**), therefore the selectivity for formation of the expected product (**5**) was low (Table 2). To gain more insight into this process, the reaction mixture was analysed at different times. Extensive isomerisation of (**3**) to (**2**) occurred at the beginning of the reaction while hydroformylation was still incipient (Scheme 1); this isomerisation took place only under hydroformylation conditions [*i.e.*, the presence of the catalyst, hydrogen, and also carbon monoxide is required, (**3**) being stable otherwise]. The slight differences in the final reaction mixtures when compared with the hydroformylation of pure (**2**) were due to the small variations in the isomerisation rate (path i) vs. the

Table 2. 2,5-Dihydrofuran converted (%) [tetrahydrofuran-3-carbaldehyde (**5**) as % of total aldehyde formed].^a

PR ₃ /(1) molar ratio	P(OPhBu ^t) ₃	PPh ₃
2	98[31]	66[48]
4	98[28]	—
10	97[25]	51[79]
10 ^b	—	67[89]
10 ^c	—	94[90]
10 ^d	—	99[99]

^a *Conditions:* 2,5-dihydrofuran (20 mmol) and catalyst precursor (**1**) (0.05 mmol) in 1,2-dichloroethane (15 ml); constant pressure, 5 bar; $\text{CO}/\text{H}_2 = 1$; temperature, 80 °C; reaction time, 20 h. ^b 2,5-Dihydrofuran (5 mmol). ^c Total pressure, 30 bar; reaction time, 8 h. ^d 2,5-Dihydrofuran (5 mmol); total pressure, 30 bar; reaction time, 8 h.



Scheme 1. Processes observed in the hydroformylation of 2,3-dihydrofuran and 2,5-dihydrofuran.

hydroformylation (paths ii—iv), caused by the different excesses of phosphite (Scheme 1).

When (1) and PPh_3 were used in the hydroformylation of (3) under the same conditions used for $\text{P(OPhBu}^t)_3$, higher selectivities for formation of (5) were obtained, but the conversions were lower (Table 2).

To increase the rate of hydroformylation vs. isomerisation, more drastic conditions were used for the catalytic system (1) + PPh_3 ; the pressure was increased to 30 bar and the catalyst/substrate ratio increased to 1:100. Under these conditions (5) was quantitatively formed, which implies that hydroformylation of (3) (path iv) is much faster than its isomerisation (path i).

In conclusion, 2,3-dihydrofuran (2) was hydroformylated quantitatively to give tetrahydrofuran-2-carbaldehyde (4) as principal regioisomer. Modification of the reaction conditions allowed the hydroformylation of 2,5-dihydrofuran (3) to give either tetrahydrofuran-2-carbaldehyde (4) or tetrahydrofuran-3-carbaldehyde (5) in good yields. Finally, for a given temperature, the selectivity of the catalytic system (1) + $\text{P(OPhBu}^t)_3$ is independent of the phosphite/(1) molar ratio; this unexpected result has been recently observed in the system $[\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_2]$ and 1,2,5-triphenylphosphole,⁵ suggesting the presence of a unique active catalytic species.

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