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Journal of Molecular Catalysis A: Chemical 175 (2001) 17–25

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Preparation of linear long chain dialdehydes by hydroformylation of linear α,ω-dienes or ω-vinylaldehyde acetals

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Received 2 January 2001; received in revised form 19 March 2001; accepted 19 March 2001

Abstract

Linear long chain dialdehydes, a class of valuable intermediates for a wide variety of commercially important products and of interesting cross-linking agents for protein and polysaccharides, can be conveniently prepared by hydroformylation of α,ω-diolefins and protected aldehydes having a terminal olefinic double bond. Thus, 1,5-hexadiene and 1,6-heptadiene were converted in a single *oxo*-process step into the corresponding linear dialdehydes in very high yields (80–98%), using $RhH(CO)(PPh_3)_3$/Xantphos (1:3) as the catalytic system at 40–60°C and 20 atm (CO: H_2 = 1).

If more stable monoprotected dialdehydes are needed, they can be obtained in a >90% yield by hydroformylation of ethylene acetals of ω-vinylaldehydes, like 2-(9-decenyl)- and 2-(10-undecenyl)-1,3-dioxolane, catalysed by the above Xantphos–rhodium complex under analogous reaction conditions. This catalytic system showed to be superior to platinum complexes such as $PtHCl(PPh_3)_3/SnCl_2{\cdot}H_2O$, which require more drastic reaction conditions (100 atm and 100°C) to ensure yields of linear protected aldehydes ranging from 65 to 86%.

Keywords: Hydroformylation; Rhodium; ω-Vinylaldehyde acetals; α, ω-dienes; Dialdehydes

1. Introduction

Bifunctional compounds such as dialdehydes are valuable intermediates for the preparation of a variety of commercially important products; they include bicarboxylic acids and derivatives [1], α,ω-diamines [2], alicyclic and heterocyclic [3] compounds having different structures. Particularly interesting is the use of the dialdehydes as cross-linking agents for polymers like proteins [4–6], polysaccharides [7] and other functionalised macromolecular compounds [8]. For instance, it is known that glutaraldehyde can represent an interesting option for aldehyde tanning [9]. In principle, other higher molecular weight dialdehydes could be utilised in the tanning industry, if available in suitable amount on the market.

The preparation of high molecular weight dialdehydes on semi-industrial scale is strongly dependent upon the availability of economically convenient starting materials. For instance, linear long chain α,ω-diols or dicarboxylic acids, α,ω-diolefins and large ring cyclic olefins, which represent the most valuable precursors of linear dialdehydes are commercially available, but their use is often hampered by limited production. Other problems are connected

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1381-1169/01/$ – see front matter
PII: S1381-1169(01)00174-1

with the production of higher dialdehydes: the numerous traditional experimental methods known to transform various functionalities into the aldehyde group, which are successfully employed for the preparation of monoaldehydes, only in a few instances can be conveniently extended to the preparation of dialdehydes. When it is possible, the chemoselectivities are often unsatisfactory: thus, the oxidative dehydrogenation reaction of α,ω-diols, accessible by catalytic hydrogenation of appropriate diesters, leads to the formation of other products such as cyclic lactons and is often afflicted by side reactions [10].

The peculiar reactivity of dialdehydes makes also their purification particularly troublesome, and compels the adoption of as mild conditions as possible for their manipulation [11,12].

An interesting source of dialdehydes is represented by the double hydroformylation of suitable non-conjugated dienes mostly catalysed by rhodium derivatives [13]; however, only in particular cases this method appears capable to give acceptable results. In 1964 Morikawa reported some interesting results concerning the *oxo*-reaction on 1,4-pentadiene and 1,5-hexadiene: the yield of linear dialdehydes, however, did not exceed 40% [1] and in some cases the formed pimelaldehyde is transformed in the reaction medium in to cyclohexancarboxaldehyde through intramolecular aldol condensation [1].

Better results are generally achieved in the hydroformylation of cyclic non-conjugated dienes: cyclohexan-1,4-dicarbalcoxaldehyde was obtained in 73% yield by *oxo*-reaction of 1,4-cyclohexadiene at 100°C and 100 atm ($CO/H_2 = 1$) catalysed by $Rh(OAc)(CO)(PPh_3)_2$ [14]. Yield up to 94% of the same dialdehyde is reached by subjecting 1,2,3,6-tetrahydrobenzaldehyde to hydroformylation under the same reaction conditions.

Linear α,ω-diolefins are industrially accessible by different processes characterised by a production of thousands tons per year scale. Methatesis reaction between cyclic mono or diolefins and ethylene produces various α,ω-diolefins: for instance, Shell produce 1,9-decadiene following this method starting from cyclo-octene and ethylene [15].

1,7-Octadiene is prepared by Chemische Werke Hüls by a bimolecular catalytic reduction process of 1,3-butadiene promoted by $HCOOH/NEt_3$ [15]; the same α,ω-diolefin from 1,3-butadiene is obtained with satisfactory chemoselectivity also using phosphine modified palladium acetate as catalyst [16].

Kuraray in Japan developed a hydrodimerisation process of 1,3-butadiene and water, using aqueous two-phase catalysis to produce 5000 t per year of 2,7-octadien-1-ol [17]: the used catalyst is palladium modified with the lithium salt of monosulphonated triphenylphosphine TPPMS. The intermediate octadienol can be isomerised to 7-octenal, which in turn is converted to nonadialdehyde again by aqueous two-phase hydroformylation catalysed by the system $Rh(CO)_2(acac)$/TPPMS [17].

Linear α,ω-dicarboxylic acids can be converted to the corresponding dialdehydes by Rosemund reduction of acylchloride derivatives in particular conditions [18]. More recently, an interesting catalytic hydrogenation of dicarboxylic acids to dialdehydes promoted by Pd(0) phosphine complexes in the presence of pivalic anhydride appeared in the literature [19]: at 80°C and 30 atm H_2 mono- and dicarboxylic acids are selectively reduced to the corresponding mono- and dialdehydes in the presence of $Pd(PPh_3)_4$ or $Pd(OAc)_2/PPh_3$ (1:4). This reaction method appears to be particularly convenient for the production of straight chain high molecular weight dialdehydes owing to the availability of some dicarboxylic acids like adipic or 1,11-dodecandioic acid [20]. Yields reaching 75% are obtained, if both the catalytic precursor and the ligand are carefully purified by crystallisation before use [21].

In this paper we report some results obtained in the straightforward formation of linear long chain dialdehydes through rhodium catalysed hydroformylation of 1,6-hexadiene and 1,7-heptadiene. Moreover, in order to prevent the chemoselectivity problems connected with the traditional preparation methods to get C_{11} and C_{12} dialdehydes with linearity grade >80%, we have chosen to prepare these compounds by the hydroformylation of linear olefinic substrates containing a protected aldehyde function. Such substrates are easily accessible from starting materials like 9-decen-1-ol (**1**) and 10-undecen-1-al (**2**) [15] available in commercial amount on the petrochemical market. The monoprotected dialdehydes prepared by *oxo*-reaction catalysed by rhodium or platinum complexes are quite stable compounds and can be directly employed in polymer cross-linking processes.

2. Experimental

2.1. Materials

The catalytic precursors (1,5-COD)$PtCl_2$, $(PPh_3)_2PtCl_2$, $HRh(CO)(PPh_3)_3$, $[Rh(CO)_2Cl]_2$, and $[Rh(COD)Cl]_2$ were purchased by Strem and used without further purification. $HPtCl(PPh_3)_2$ [22], (DPPB)$PtCl_2$ [23] were prepared as described in the literature. 10-Undecenal (**2**), 9-decen-1-ol (**1**), 1,5-hexadiene (**9**) and 1,6-heptadiene (**3**) and were Aldrich products. Xantphos was prepared as described by Kranenburg et al. [24] $Rh(CO)_2(acac)$, triphenylphosphine (PPh_3), triphenylphosphite $P(OPh)_3$, 1,3-bis(diphenylphosphinopropane) (DPP), triphenylphospine-3,3′,3″-trisulfonic acid trisodium salt (TPPTS) and tris(2,4-di-*tert*-butylphenyl)phosphite were used as received from Aldrich. Solvents were purified following well-known procedures [25]. Silica gel (70–230 mesh) was purchased by Merck. ^1H NMR spectra (200 and 300 MHz) were measured for solutions in $CDCl_3$.

2.1.1. Synthesis of 9-decenal (*10*)

According to a well-known procedure [26] a solution of 5 g (32 mmol) of 9-decen-1-ol and 1.08 g (3.2 mmol) of tetrabutylammonium bisulphate in 80 ml of dichloroethane was shaken in a separating funnel with 3.15 g (10.6 mmol) of $Na_2Cr_2O_7{\cdot}2H_2O$ dissolved in 80 ml of 30% H_2SO_4. After separation of the two phases, the organic layer was dried on Na_2SO_4 and pure aldehyde **10** was obtained in 90% yield by distillation in vacuo (bp 29°C/0.05 mmHg). GC-MS (70 eV) — *m/e*: 154 $[M]^+$; ^1H NMR (200 MHz), δ (ppm): 9.85–9.81 (t, 1H), 5.89–5.72 (m, 1H), 5.05–4.91 (m, 4H), 2.49–2.38 (m, 2H), 2.16–1.97 (q, 2H), 1.68–1.52 (q, 2H), 1.49–1.30 (m, 6H).

2.1.2. Synthesis of acetals *11* and *12*

According to a literature procedure [27], a round bottom flask, equipped with a magnetic stirrer bar and a Dean Stark apparatus, was charged with 13 mmol of aldehyde **10** or **2**, 78 mmol of ethylenglycol, 0.5 mmol of *p*-toluensulfonic acid and 25 ml of benzene and the reaction mixture heated at reflux under stirring overnight. After usual work-up the pure acetal **11** or **12** was obtained by distillation in vacuo.

Compound **11**: yield 78%. bp 58°C/0.05 mmHg. GC-MS (70 eV) — *m/e*: 198 $[M]^+$; ^1H NMR (200 MHz), δ (ppm): 5.93–5.71 (m, 1H), 5.06–5.02 (q, 2H), 4.98–4.82 (m, 2H), 4.03–3.80 (m, 4H), 2.12–1.98 (q, 2H), 1.73–1.59 (m, 2H), 1.47–1.26 (m, 6H).

Compound **12**: yield 88%. bp 65°C/0.05 mmHg. GC-MS (*m/e*): 212 $[M]^+$; ^1H NMR (200 MHz), δ (ppm): 5.98–5.85 (m, 1H), 5.20–4.95 (m, 2H), 4.82–4.70 (m, 2H), 4.12–3.94 (m, 4H), 2.20–1.95 (m, 2H), 1.83–1.65 (m, 2H), 1.51–1.23 (m, 12H).

2.1.3. Hydroformylation of dienes *3* and *9* catalysed by Rh complexes

A 150 ml stainless steel reaction vessel was charged under a nitrogen purge with 4 mmol of **3** or **9**, the rhodium catalyst, the ligand of choice and 5 ml of anhydrous toluene (for the molar ratio used see Tables 1 and 2). The reactor was then pressurised to 20–80 atm with syngas (CO/H_2 = 1) and heated at 40–100°C for the due time (see Tables 1 and 2). The reactor was then cooled to room temperature and the residual gases released. The monoaldehydes (**4** and **5**) and the dialdehydes (**6**–**8**) produced were identified by GC MS analyses.

Compound	$[M]^+$				
4	126	95	86	58	41
5	126	98	83	58	41
6	156	138	126	58	41
7	156	124	112	58	41
8	156	138	110	58	41

^1H NMR analysis carried out on enriched mixtures obtained by flash chromatography (eluent:*n*-hexane/diethyl ether = 6:4) gave the following data:

Compound **4**: 9.56 (d, 1H); 5.82–5.70 (m, 1H); 5.00–4.87 (m, 2H)

Compound **5**: 9.73 (t, 1H); 5.87–5.77 (m, 1H); 5.04–4.91 (m, 2H)

Compound **6**: 9.47 (d, 2H); 1.03–0.99 (m, 6H).

Compound **7**: 9.65 (t, 2H); 2.35–2.29 (m, 4H). Compound **8**: 9.72 (t, 1H); 9.52 (d, 1H)

Hydroformylation of **3** and **9** dienes catalysed by Rh/Xantphos complex. A 150 ml stainless steel reaction vessel was charged under a nitrogen purge with 4.1 mmol of **3** or **9**, 0.039 mmol of $RhH(CO)(PPh_3)_3$, 0.124 mmol of Xantphos in 15 ml of anhydrous

Table 1
Hydroformylation of 1,6-heptadiene (**3**) in the presence of rhodium catalysts

Run	Catalytic precursor	Conversion (%)[a]	Olefin isomer (%)	Aldehyde yields (%)				
				4	**5**	**6**	**7**	**8**
1	$Rh(CO)_2(acac)$	98.0	2.2	2.1	3.7	12.4	33.2	41.0
2	$Rh(CO)_2(acac)/PPh_3$	96.2	1.2	3.4	2.1	11.4	34.2	41.2
3	$Rh(CO)_2(acac)/P(OPh)_3$	98.4	1.3	1.8	4.1	9.2	36.3	41.1

[a] Small amounts (up to 4.6%) of mixtures of other unidentified isomeric mono- and dialdehydes were detected. Reaction conditions: substrate = 4.0 mmol; solvent = toluene, 5 ml; $p(CO) = p(H_2) = 40$ atm; temperature 100°C; substrate-to-catalyst molar ratio = 250:1; Rh-to-ligand molar ratio = 1:3; reaction time 24 h.

toluene (see Table 2). The reactor was then pressurised to 20 atm with syngas ($CO/H_2 = 1$) and heated at 40–60°C for the due time (see Table 2). The reactor was then cooled to room temperature and the residual gases released. The reaction mixture was first analysed by GC to determine the conversion and the normal to branched aldehyde ratio and then the linear dialdehyde **7** and octandiale (**13**) were purified by careful distillation.

Compound **7**: bp 89°C at 1 mmHg, ^{1}H NMR (300 MHz), δ (ppm): 9.65 (t, 2H); 2.35–2.29 (m, 4H); 1.53–1.50 (m, 4H); 1.24–1.19 (m, 4H); 1.10–0.92 (m, 2H). GC-MS (70 eV) — *m/e*: 156 $[M]^+$, 139, 124, 112, 97, 58, 41.

Compound **13**: bp 73°C at 1 mmHg, ^{1}H NMR (300 MHz), δ (ppm): 9.67 (t, 2H); 2.39–2.33 (m, 4H); 1.58–1.53 (m, 4H); 1.30–1.26 (m, 4H). GC-MS (70 eV) — *m/e*: 142 $[M]^+$, 98, 86.

*2.1.4. Hydroformylation of **11** or **12** catalysed by Pt complexes*

A 150 ml stainless steel reaction vessel was charged under a nitrogen purge with 2.3 mmol of **11** or **12**, 0.023 mmol of Pt complex, 0.12 mmol of $SnCl_2 \cdot 2H_2O$ and 5 ml of anhydrous toluene (see Table 4). The reactor was then pressurised to 100 atm with syngas ($CO/H_2 = 1$) and heated at 80–100°C for the due time (see Table 4). The reactor was then cooled to room temperature and the residual gases released. The reaction mixture was first analysed by GC to determine the conversion and the normal to branched aldehyde ratio and then the acetal aldehydes **14–17** were transformed into the corresponding diacetals by reaction with diethylenglycol in benzene at reflux and in the presence of *p*-toluensulfonic acid, overnight. After usual work-up the diacetals were isolated from the reaction mixture by flash silica gel chromatography (hexane/diethylether 6:4).

Compound **18**: ^{1}H NMR (200 MHz), δ (ppm): 4.90–4.82 (t, 2H, 2CH), 4.04–3.82 (m, 8H, $4CH_2$), 1.73–1.58 (m, 4H, $2CH_2$), 1.35–1.24 (m, 16 H, $8CH_2$).

*2.1.5. Hydroformylation of **11** or **12** catalysed by Rh complexes*

A 150 ml stainless steel reaction vessel was charged under a nitrogen purge with 2.35 mmol of **11** or **12**,

Table 2
Hydroformylation of dienes **3** and **9** catalysed by $RhH(CO)(PPh_3)_3$/Xantphos

Run	Substrate	Catalytic precursor	Reaction time (h)	Temperature (°C)	Conversion (%)	Linear dialdehyde (%)
1[a]	1,5-Hexadiene (**3**)	$RhH(CO)(PPh_3)_3$/Xantphos	24	100	>99	80[b]
2	1,5-Hexadiene (**3**)	$RhH(CO)(PPh_3)_3$/Xantphos	24	60	90	>99
3	1,6-Heptadiene (**9**)	$RhH(CO)(PPh_3)_3$/Xantphos	24	40	77	>99
4	1,6-Heptadiene (**3**)	$RhH(CO)(PPh_3)_3$/Xantphos	120	40	>99	>99

[a] Reaction conditions: substrate 4.0 mmol; $p(CO) = p(H_2) = 40$ bar; temperature 100°C; substrate-to-catalyst molar ratio = 250:1; Rh-to-ligand molar ratio = 1:3.

[b] The remaining 20% of the mixture is constituted by isomeric aldehydes: 13% of 2,5-dimethylhexandial, 5% of 2-methylheptandial and 2% of other not identified aldehydic isomers. Reaction conditions: substrate = 0.05 mol; solvent = toluene, 5 ml; $p(CO) = p(H_2) = 10$ bar; substrate/catalyst molar ratio = 100:1; Rh-to-ligand molar ratio = 1:3.

Table 3
Hydroformylation of **11** and **12** catalysed by rhodium complexes[a]

Run	Substrate	Catalyst	Temperature (°C)	Reaction time (h)	Conversion (%)	Aldehyde yield (%)	Linear aldehyde (%)	Branched aldehyde (%)
1	**11**	$HRh(CO)(PPh_3)_3$	80	4	99	99	59	41
2	**11**	$HRh(CO)(PPh_3)_3/PPh_3$ (1/10)	80	4	95	95	68	32
3	**11**	$[Rh(COD)Cl]_2$/DPP (1/1)	100	48	71	71	53	47
4	**12**	$HRh(CO)(PPh_3)_3$	80	4	99	99	57	43
5	**12**	$HRh(CO)(PPh_3)_3/PPh_3$ (1/10)	80	4	98	98	63	37
6	**12**	$[Rh(COD)Cl]_2$/DPP (1/2)	80	3	99	99	56	44
7	**12**	$[Rh(COD)Cl]_2$/DPP (1/10)	100	72	82	82	42	58
8	**12**	$[Rh(CO)_2Cl]_2$/L (1/6)	80	4	99	99	51	49

[a] Reaction conditions: substrate = 2.35 mmol; solvent = toluene, 5 ml; substrate-to-catalyst molar ratio = 1000:1; P = 100 atm ($CO/H_2 = 1$). DPP = 1,3-bis(diphenylphosphino)propane; L = tris(2,4-di-*tert*-butylphenyl)phosphite. COD = *cis*,*cis*-1,5-cyclooctadiene.

the rhodium catalyst, the ligand of choice and 5 ml of anhydrous toluene (for the molar ratio used see Tables 3 and 5). The reactor was then pressurised to 20 or 100 atm with syngas ($CO/H_2 = 1$) and heated at 40–100°C for the due time (see Tables 3 and 5). It was then cooled to room temperature and the residual gases released. The obtained acetal aldehydes **14**–**17** were identified by GC-MS analyses.

Compound **14**: GC-MS (70 eV) — *m*/*e*: 228 $[M]^+$; 199, 185, 73. ^{1}H NMR (300 MHz), δ (ppm): 9.70 (t, 1H); 4.78 (t, 1H); 3.86 (m, 4H).

Compound **15**: GC-MS (70 eV) — *m*/*e*: 242 $[M]^+$; 241, 214, 199. ^{1}H NMR (300 MHz), δ (ppm): 9.78 (t, 1H); 4.81 (t, 1H); 3.87 (m, 4H).

Compound **16**: GC-MS (70 eV) — *m*/*e*: 228 $[M]^+$; 199, 171, 73. ^{1}H NMR (300 MHz), δ (ppm): 9.60 (d, 1H); 4.80 (t, 1H); 3.91 (m, 4H), 1.11 (d, 3H).

Compound **17**: GC-MS (70 eV) — *m*/*e*: 242 $[M]^+$; 241, 185, 73. ^{1}H NMR (300 MHz), δ (ppm): 9.65 (d, 1H); 4.78 (t, 1H); 3.82 (m, 4H), 1.09 (d, 3H).

*2.1.6. Hydroformylation of **12** catalysed by Rh complexes in heptan-1-ol*

A 150 ml stainless steel reaction vessel was charged under a nitrogen purge with 2.35 mmol of **12**, the rhodium catalyst (0.0235 mmol) and the ligand when necessary (Xantphos 0.070 mmol) (see Table 6) and 15 ml of heptan-1-ol. The reactor was then pressurised to the desired pressure with syngas ($CO/H_2 = 1$) and heated at 60°C for the due time (see Table 6). The reactor was then cooled to room temperature and the residual gases released. The obtained acetal aldehydes **15** and **17** were identified by GC-MS analyses.

3. Results and discussion

3.1. Linear dialdehydes from α,ω-dienes

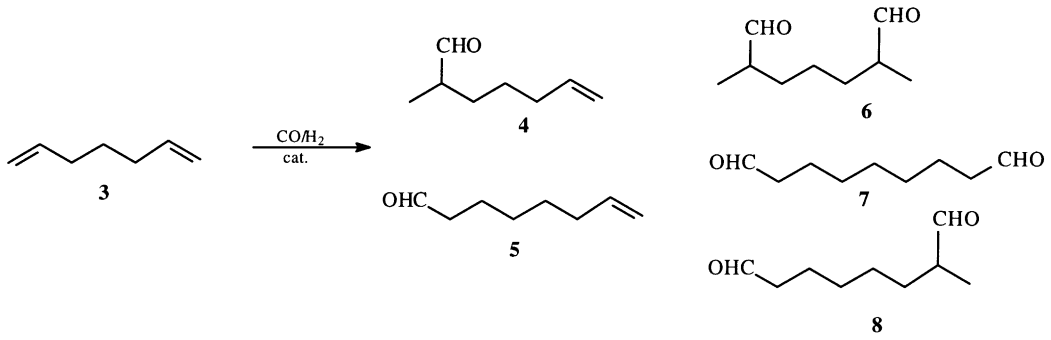
In the first phase of this experimental work 1,6-heptadiene (**3**) was subjected to rhodium-catalysed hydroformylation in the presence of some rhodium carbonyl complexes at 100°C and 80 atm ($CO/H_2 = 1$) using a substrate-to-catalyst molar ratio = 250. Whereas the chemoselectivity was very high (96–98%), the regioselectivity towards the linear dialdehyde nonandial (**7**), resulted to be very poor ($\leq$36%) (Scheme 1).

In all three cases investigated rather complex mixtures of dialdehydic compounds are obtained (Table 1), which are very difficult to be separated and identified. The structures of all *oxo*-products were determined by GC-mass spectroscopy and ^{1}H-NMR analysis on partially by flash-chromatography separated mixtures (see Section 2).

Hence, the hydroformylation of α,ω-dienes catalysed by simple rhodium carbonyls modified with monodentate ligands like PPh_3 or $P(OPh)_3$ does not represent a viable method to linear dialdehydes.

In 1995 Kranenburg et al. [24] developed diphosphines based on xanthene-type backbones such as Xantphos, which showed to promote an exceptionally high regioselectivity towards the formation of linear aldehydes in the rhodium catalysed hydroformylation of olefins. This peculiar behaviour of Xantphos was ascribed to the large "natural" bite angle formed by coordination with the metal [28] (Fig. 1).

Diolefins 1,5-hexadiene (**9**) and 1,6-heptadiene (**3**) are then hydroformylated under different reaction



Scheme 1.

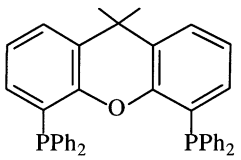


Fig. 1. Xantphos: Bite angle 109.8°.

conditions using the complex formed in situ from $RhH(CO)(PPh_3)_3$/Xantphos as catalytic precursor. The results obtained in some *oxo*-experiments are reported in Table 2.

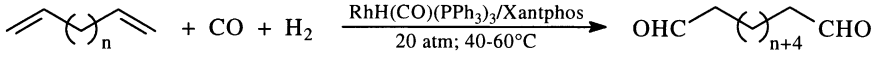
Thus, the *oxo*-reaction carried out at 100°C produces high yield of dialdehydes, but only 80% of the linear isomer. The effect of the temperature on the regioselectivity of this catalytic process is remarkable: the linear dialdehyde is practically formed only in the temperature range 40–60°C.

This result is rather surprising taking into account that in the hydroformylation of 1-alkenes such as 1-octene using similar catalytic system upon raising the temperature from 40 to 80°C the regioselectivity is practically not affected [24]. It is difficult to give a reasonable explanation of this strong influence of the reaction temperature on the isomer distribution in the case of dienes hydroformylation, because many equilibria among different rhodium complexes could be involved; however, it is possible that the hydride rhodium complex with Xantphos (postulated as the catalytically active intermediate [29]) is not sufficiently tight, in the reaction medium, so that it equilibrates the corresponding not chelate complex [29]: increasing temperature of course could enhance the concentration of the more active but less regioselective monodentate species (Scheme 2).

3.2. Linear dialdehydes from 2-(9-decenyl) (**11**)and2-(10-undecenyl)-1, 3-dioxolane(**12**)

The unsaturated cyclic acetal 2-(9-decenyl)-1,3-dioxolane (**11**) was prepared in 76% overall yield by sodium dichromate oxidation of the commercially available 9-decen-1-ol (**1**) to the corresponding aldehyde **10** [26], followed by the conventional carbonyl group protection by acetalysation with ethylene glycol in benzene catalysed by *p*-toluensulphonic acid (see Section 2) [27]. 2-(10-Undecenyl)-1,3-dioxolane (**12**) was obtained directly by acetalisation of 10-undecenal (**2**) under the same reaction conditions (see Section 2).

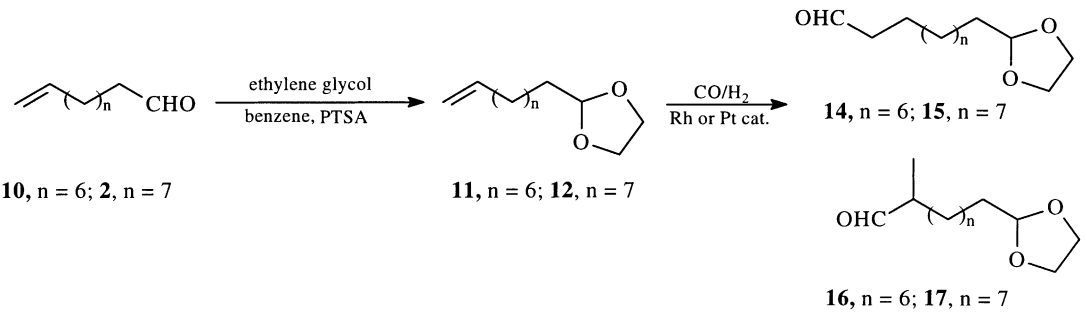
In a first phase of our research work we subjected substrates **11** and **12** to hydroformylation catalysed by



n = 2, **9**
n = 3, **3**

n = 2, **15**
n = 3, **17**

Scheme 2.



Scheme 3.

some rhodium–phosphine complexes under standard conditions [30] (Scheme 3).

For both substrates **11** and **12** rhodium carbonyl complexes modified with triphenylphosphine or 1,3-bis(diphenylphosphino)propane or tris(2,4-di-*tert*-butylphenyl)phosphite affords high conversion and practically quantitative chemoselectivity, but the regioselectivity towards the linear aldehyde-monoacetal is low, not exceeding in the best case 68% (run 2).

An *oxo*-experiment on substrate **12** was carried out in the biphasic water–toluene medium in the presence of the catalytic system $[Rh(COD)Cl]_2$/TPPTS [31]: after 24 h 81% substrate was converted, but the chemoselectivity to aldehydes was only 30% because of the extensive simultaneous substrate hydrogenation (42%) and the formation of unidentified high boiling by-products (9%); moreover, the regioselectivity towards the linear isomer was only 30%.

Generally, platinum mono- and chelating diphosphine complexes promote the formation of the linear *oxo*-product for both substrates **11** and **12** in the hydroformylation reaction (Table 4); however, the chemoselectivity is lowered by the formation of transacetalisation products. It is to point out that the regioselectivity does not appreciably change using platinum complexes with chelating diphosphines with respect to those with monophosphines; our results seem to be in contrast with those obtained by Hayashi et al. using 1-alkenes as substrates [32].

To determine the regioselectivity of this reaction, the mixture of free dialdehydes and the corresponding mono- and diacetals must be further reacted with excess ethylene glycol in the presence of PTSA to be transformed quantitatively into a mixture of isomeric diacetals (see Section 2).

In order to improve the regioselectivity vs. linear isomer, both substrates **11** and **12** were subjected to hydroformylation catalysed by the system $HRh(CO)(PPh_3)_3$/Xantphos; the results obtained are collected in Table 5.

As expected, Xantphos strongly affects the regioselectivity towards the formation of linear isomer at 60°C; however the behaviour of the acetal **11** is rather different from that of the higher homologue: 97% of

Table 4
Hydroformylation of **11** and **12** catalysed by platinum complexes

Run	Substrate	Catalyst	Temperature (°C)	Reaction time (h)	Conversion (%)	Aldehyde yield (%)	Linear aldehyde (%)[a]	Branched aldehyde (%)[a]
1	**11**	$PtHCl(PPh_3)_2/SnCl_2{\cdot}2H_2O$	100	17	98	98	85	15
2	**11**	$(DPPB)PtCl_2/SnCl_2{\cdot}2H_2O$	100	24	77	77	88	12
3	**12**	$PtHCl(PPh_3)_2/SnCl_2{\cdot}2H_2O$	100	17	99	99	87	13
4[b]	**12**	$(DPPB)PtCl_2/SnCl_2{\cdot}2H_2O$	80	22	98	85	85	15
5[b]	**12**	$(DPPB)PtCl_2/SnCl_2{\cdot}2H_2O$	100	21	99	77	82	18

[a] Determined on the mixture of the corresponding diacetals.

[b] High Boiling products were detected. Reaction conditions: substrate = 2.35 mmol; solvent = toluene, 5 ml; substrate-to-catalyst molar ratio = 100:1; Pt-to-$SnCl_2{\cdot}2H_2O$ molar ratio = 1:5; P = 100 atm (CO/H_2 = 1). DPPB = 1,4-bis(diphenylphosphino)butane.

Table 5
Hydroformylation of **11** and **12** catalysed by the catalytic system $HRh(CO)(PPh_3)_3$/Xantphos[a]

Run	Substrate	Temperature (°C)	Reaction time (h)	Conversion (%)	Aldehyde yield (%)	Linear aldehyde (%)	Branched aldehyde (%)
1	**11**	60	72	94	94	73	27
2	**11**	40	90	30	30	97	3
3	**12**	60	24	93	93	93	7
4	**12**	60	72	99	99	91	9

[a] Reaction conditions: substrate = 2.35 mmol; solvent = toluene, 5 ml; substrate-to-catalyst molar ratio = 600:1; P = 20 atm (CO/H_2 = 1). Rh-to-Xantphos molar ratio = 1:3.

Table 6
Hydroformylation of **12** catalysed by rhodium complexes in heptan-1-ol as the solvent

Run[a]	Catalytic precursor	Reaction time (h)	P (atm)	Linear aldehyde (%)	Branched aldehyde (%)
1	$RhH(CO)(PPh_3)_3$	23	20	73	27
2[b]	$RhH(CO)(PPh_3)_3$	19	100	70	30
3[b]	$RhH(CO)(PPh_3)_3$/Xantphos	20	20	59	41

[a] In all cases quantitative conversions were achieved.
[b] Substrate/catalyst molar ratio = 1000:1. Substrate = 2.35 mmol; solvent = heptan-1-ol, 5 ml; substrate-to-catalyst molar ratio = 600:1; ligand-to-catalyst molar ratio = 3:1; reaction temperature 60°C.

aldehyde **14** is achieved only when the hydroformylation is carried out at 40°C, at this temperature the reaction being rather sluggish (run 2, Table 5).

Some years ago Divekar et al. reported the hydroformylation of 1-decene in the presence of rhodium carbonyl complexes (substrate/catalyst molar ratio = 530:1) using different alcohols as solvents: high regioselectivity towards linear aldehyde (up to 82%) was claimed when the catalytic process was carried out in long chain linear alcohol such as 1-heptanol at 50°C and 27 atm [33].

We hydroformylated the substrate **12** under the above conditions obtaining the results collected in Table 6.

Whereas the chemoselectivity of this reaction is in any case excellent the regioselectivity has never achieved the value found by Divekar et al. for 1-decene [33]. However, the amount of linear aldehyde **14** obtained by us from the substrate **12** using unmodified $RhH(CO)(PPh_3)_3$ is the highest found in our *oxo*-experiments (see Table 6); the use of Xantphos as catalyst external ligand gave no benefit in the regioselectivity, which underwent a sharp decrease.

In conclusion, the present paper points out that the hydroformylation process represents a very convenient route to linear dialdehydes or their monoacetals: in particular, it was demonstrated that α,ω-dienes can be converted in a straightforward way into the corresponding linear dialdehydes in about 90% yield, when subjected to *oxo*-reaction catalysed by rhodium carbonyl complexes modified with Xantphos under mild conditions (20 atm and 60°C).

Whereas free dialdehydes have to be used preferably in a short time after their preparation, the monoprotected ones are quite stable for a long time: the best route to these last compounds showed to be the hydroformylation of ω-vinyl aldehydes ethylene acetals catalysed again by rhodium complexes with Xantphos at 20 atm and 60°C, ensuring linear isomer yields up to 90%.

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