Selective synthesis of octadienyl and butenyl ethers via reaction of 1,3-butadiene with alcohols catalyzed by homogeneous palladium complexes

Renata Patrini [a,*], Massimo Lami [a], Mario Marchionna [a], Federica Benvenuti [b], Anna Maria Raspolli Galletti [b], Glauco Sbrana [b]

[a] *SNAMPROGETTI S.p.A., Research Division, Via Maritano 26, I-20097 San Donato Milanese, Italy*
[b] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35, I-56126 Pisa, Italy*

Abstract

The selective synthesis, by telomerization of 1,3-butadiene with alcohols in the presence of palladium catalysts, both of octadienyl ethers (especially from higher linear primary alcohols) and of butenyl ethers is reported. The variation of the alcohol/diene molar ratio plays a decisive role in both the cases, excess of alcohol favouring in the former case the synthesis of octadienyl ethers with respect to octatrienes, being useful in the latter case, together with other factors such as high P/Pd and low Pd/diene molar ratios, to favour the formation of butenyl ethers. It has in fact been discovered that, for palladium catalysts, the formation of butenyl ethers is ruled by a complex mechanism involving both the reversible formation of butenyl ethers and their direct transformation into octadienyl ethers. © 1998 Elsevier Science B.V.

Keywords: Palladium catalysts; Phosphines; 1,3-butadiene; Telomerization; Alcohol addition

1. Introduction

Telomerization reactions of 1,3-butadiene with various hydrogen active compounds (HY) to provide, in good yields, products of dimerization and simultaneous addition of nucleophile are well-known in homogeneous catalysis [1,2].
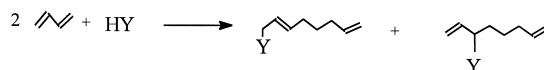

Palladium complexes are generally employed as catalysts to promote 1,3-butadiene telomerization with different nucleophiles (amines, alcohols, water, carboxylic acids salts, enamines, stabilized

---

carbanions, ...). Recently, telomerization of 1,3-butadiene with water gained increasing industrial interest as the resulting product can be hydrogenated to give *n*-octanol, useful raw material for plasticizers [2–4]; this kind of reactivity might also be attractive for industrial production of *n*-octyl-amine from 1,3-butadiene and NH_3 [5,6].

Furthermore, linear ethers have recently focused great deal of attention, as, if their linear chain is sufficiently long (carbon atoms = 9), they display special properties as components of diesel fuels due to their excellent cetane number and cold flow properties [7].

In this respect the telomerization of 1,3-butadiene with methanol (or higher linear alcohols) and the successive hydrogenation of the unsaturated linear ether to the saturated one could represent an attractive synthesis method for these ethers.
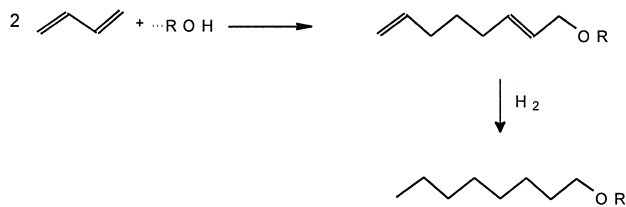
Due to our interest in the development of this synthetic route, the reaction of telomerization of 1,3-butadiene with alcohols has been deeply re-investigated.

In this work, attention is focused on the effect of the variation of the alcohol/diene molar ratio, especially in order to markedly increase the yields in unsaturated linear ethers from higher alcohols. In the course of this experimentation, also a few unexpected results were observed about the selective synthesis of butenyl ethers in the presence of palladium catalysts.

2. Experimental

All manipulations as well as catalytic reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques.

Solvents and alcohols were carefully dried and freshly distilled prior to use; *n*-hexane (Fluka) was dried and distilled from sodium benzophenone ketyl; anhydrous alcohols were obtained by refluxing over Mg/I_2. 1,3-butadiene (99%) was purchased from SIAD and flash distilled prior to use in order to avoid contamination from 4-vinyl-ciclohexene and peroxides. Phosphine ligands purchased from Fluka and $Ni(cod)_2$ purchased from Strem were stored under nitrogen and used as received.

$Pd(dba)_2$ [8] (dba = di-benzylidene-acetone) and $[Pd(allyl)Cl]_2$ [9] were prepared as previously described.

2.1. General procedure and analysis

Catalytic experiments were performed in a 300 ml mechanically stirred stainless steel autoclave, equipped with an inner glass becker, a substrate inlet vessel, a liquid sampling valve and an internal thermocouple for temperature control.

In a typical experiment, the desired amounts of *n*-hexane, alcohol, phosphine ligand, palladium complex and toluene (internal standard) were introduced under inert atmosphere in the nitrogen purged autoclave. Then, 1,3-butadiene was charged and the system was pressurized with nitrogen to

1–4 MPa. The autoclave was heated to the desired temperature in a thermostated oil bath. Products samples were periodically removed via the liquid sampling valve, collected in pre-cooled ($-70°C$) capped vials and immediately analysed by gas chromatography.

In the runs carried out in order to produce selectively butenyl ethers the autoclave was at first heated at the reaction temperature and then 1,3-butadiene was rapidly introduced into the autoclave by means of a HPLC pump.

Analyses of the products were performed with a HP 5890 gas chromatograph equipped with FID as the detector and a 50 m capillary column (HP5 5% cross-linked methyl-phenyl-silicone). Products were recognized through both GC/MS and NMR analyses.

2.2. Data presentation

Conversion and selectivity are defined by the following equations:

$$\text{Conv.}\% = \left[(\text{moles } C_4H_6 \text{ in products}) / (\text{moles } C_4H_6 \text{ initial}) \right] \times 100.$$

Selectivities to butenyl ethers (in the tables reported as C_4OMe) are evaluated as:

$$\text{Sel.}\% = \left[(\text{moles of butenyl ethers produced}) / (\text{moles of converted } C_4H_6) \right] \times 100.$$

Selectivities to octadienyl ethers and octatrienes (in the tables reported as telom. and dim., respectively) are evaluated as:

$$\text{Sel.}\% = \left[2(\text{moles of products}) / (\text{moles of converted } C_4H_6) \right] \times 100.$$

Selectivities to telomers containing three butadiene units and butadiene trimers (in the tables comprehensively reported as trim.) are evaluated as:

$$\text{Sel.}\% = \left[3(\text{moles of products}) / (\text{moles of converted } C_4H_6) \right] \times 100.$$

Furthermore, selectivities to linear isomers, both for butenyl and octadienyl ethers, are evaluated as:

$$\text{Sel.}\% = \left[(\text{moles of linear } C_n \text{ ethers}) / (\text{moles of total } C_n \text{ ethers}) \right] \times 100, \quad (n = 4 \text{ or } 8).$$

Metal concentration is relative to the initial total volume of the solution, constituted by the solvent, if present, the diene and the alcohol.

Material balance always resulted higher than 98%.

3. Results and discussion

3.1. Selective synthesis of octadienyl ethers from higher primary alcohols

As regards the telomerization of higher alcohols [1], it was well-known that primary alcohols generally react most easily with 1,3-butadiene to give high yields of telomeric products, whereas secondary and tertiary alcohols give rise only to small amounts of telomers. The length of the alcohol chain seemed to influence the reactivity of the nucleophile: it was reported that the selectivity to octadienyl ethers decreases markedly moving from methanol to higher alcohols [10]. The use of alkyl phosphine ligands instead of aryl phosphines seemed to favour the achievement of higher selectivities to telomers, at least operating with ethanol as the nucleophile. It was also reported that an increase of the alcohol/butadiene molar ratio generally favoured an improvement of the selectivity to unsaturated ethers [10–12] but, despite of that, the yields in octadienyl ethers with higher alcohols were always unsatisfactory.

Table 1
Telomerization of 1,3-butadiene with different alcohols: Effect of the structure of alcohols and phosphines

Run	ROH/C_4H_6	P	P/Pd	Conversion (%)	Selectivity (%)			% tel. lin.
					dim.	telom.	trim.	
MeOH								
1	1.5	PPh_3	2	72	6.9	92.7	0.5	93.0
2	1.5	PBu_3	2	99	2.5	97.3	0.3	93.5
3[a]	1.4	PEt_3	2	100	2.0	97.9	0.1	94.0
EtOH								
4	2	PPh_3	2	50	39.5	60.0	0.5	96.0
5[a]	1.8	PEt_3	2	86	12.2	87.0	0.8	96.6
n-pentanol								
6[b]	1.4	PEt_3	1.5	84	12.7	85.4	1.9	96.7
n-octanol								
7[b]	1.5	PPh_3	2	58	42.3	55.0	2.7	94.8
8[b]	1.5	PBu_3	2	77	16.1	82.1	1.8	96.4
9[b]	1.5	PEt_3	1.5	83	12.2	86.4	1.4	96.4
10[b]	3	PEt_3	1.5	98	7.9	91.0	1.1	97.0
2-methoxy-ethanol								
11[a,b]	3	PEt_3	1.5	99	3.9	95.4	—	96.0

Precursor: $Pd(dba)_2 + P$ ligand; solvent: n-hexane (15–25 ml); $C_4H_6/Pd = 1000$; $Pd = 0.1–0.2$ mmol; $[Pd] = 1–4 \times 10^{-3}$ M; $T = 60°C$; $t = 2$ h.
[a] $C_4H_6/Pd = 2000$.
[b] No n-hexane added.

All these observations prompted us to better investigate the influence of the structure of the alcoholic nucleophile paying particular attention also to the effect of the phosphine ligand, in order to achieve higher selectivities to octadienyl ethers formed by higher alcohols. A few preliminary results are reported in Table 1.

First of all, catalytic runs were carried out with different phosphine ligands using methanol as the nucleophile. The nature of the phosphine does not seem to influence relevantly the telomerization with methanol, also at low $MeOH/C_4H_6$ molar ratios, at least as regards selectivities.

In the case of higher alcohols high selectivities are favoured by the use of alkyl phosphine ligands, especially PEt_3, and higher ROH/C_4H_6 molar ratios. The combination of the two effects allows to achieve very high yields also with higher alcohols such as 2-methoxy-ethanol, n-pentanol and n-octanol: whereas with 2-methoxy-ethanol high yields in telomers were described also by other authors [13], the results for n-pentanol and above all n-octanol, typical examples of higher linear primary alcohol, are absolutely unreported.

In Table 2 the effects of the variation of the ROH/C_4H_6 molar ratio are reported with much more detail referring to the different nature of the alcohol and of the phosphine ligands.

An increase of the $EtOH/C_4H_6$ molar ratio favours an improvement both of conversion and of selectivity to ethers for every kind of phosphine, although selectivities to telomers higher than 90% are obtained only with alkyl-phosphines. An increase of the ROH/C_4H_6 ratio gives also rise to enhanced linearity in the octadienyl ether fractions. However, it is worth noting that, when using secondary alcohol (^sBuOH), the selectivity to ethers are still very poor also with very high ROH/C_4H_6 molar ratios and in the presence of PEt_3 as the phosphine ligand.

Further information on the effect of the nature of the phosphine and of the ROH/C_4H_6 molar ratio for the telomerization of butadiene with methanol are given in Table 3; an increase of the ratio gives rise to enhanced selectivities into ethers using both PPh_3 and alkyl phosphines (PEt_3 and P^nBu_3)

Table 2
Telomerization of 1,3-butadiene with alcohols: Effect of the ROH/C_4H_6 molar ratio

Run	ROH/C_4H_6	P	P/Pd	Conversion (%)	Selectivity (%)			% tel. lin.
					dim.	telom.	trim.	
EtOH								
12	1.5	PPh$_3$	2	48	49.9	49.8	0.3	96.0
4	2	PPh$_3$	2	50	39.5	60.0	0.5	96.0
13	3	PPh$_3$	2	79	28.3	70.3	1.4	96.0
14	1	PBu$_3$	2	57	17.6	82.3	0.1	93.5
15	1.5	PBu$_3$	2	70	15.4	84.3	0.3	94.0
16	2	PBu$_3$	2	75	12.0	87.6	0.4	94.0
17	3	PBu$_3$	2	88	9.5	90.2	0.3	96.0
5[a]	1.8	PEt$_3$	2	86	12.2	87.0	0.8	96.6
18[a]	3.2	PEt$_3$	2	99	5.3	94.0	0.7	97.0
n-Octanol								
19[a,b]	1.4	PEt$_3$	1.5	75	15.0	84.2	0.8	96.3
20[a,b]	4.1	PEt$_3$	1.5	90	9.3	90.3	0.4	96.3
s-Butanol								
21	3	PEt$_3$	1.5	18	80.7	19.3	—	87.8
22[c]	4.6	PEt$_3$	1.5	59	81.1	18.9	—	91.1

Precursor: Pd(dba)$_2$ + P ligand; Solvent: n-hexane (15–25 ml); C_4H_6/Pd = 1000; Pd = 0.05–0.2 mmol; [Pd] = 2–3×10^{-3} M; $T = 60°C$; $t = 2$ h.
[a] C_4H_6/Pd = 2000.
[b] No n-hexane added; [Pd] = 5×10^{-4} M.
[c] $T = 80°C$.

although the effect is stabilized for alcohol/diene ratios ≥ 2. An increase of the P/Pd molar ratio results in a lowering both of conversion and of selectivity. Also with very high $MeOH/C_4H_6$ molar ratios the formation of any amount of butenyl ethers was not observed as achieved for example in the case of the reaction of methanol with isoprene [14,15].

3.2. Selective synthesis of methoxy-butenes in the presence of palladium catalysts

As it was reported by Commereuc and Chauvin [16] that the formation of butenyl ethers was favoured by the use of Pd(II) complexes (in the absence of alkoxides as activators), the synthesis of butenyl ethers was attempted with [Pd(allyl)Cl]$_2$ as catalyst precursor and under reaction conditions

Table 3
Telomerization of 1,3-butadiene with methanol: Effect of the $MeOH/C_4H_6$ molar ratio

Run	$MeOH/C_4H_6$	P	P/Pd	Conversion (%)	Selectivity (%)			% tel. lin.
					dim.	telom.	trim.	
23[a]	1.5	PPh$_3$	2	100	6.0	92.7	1.3	94.4
24[a]	2.5	PPh$_3$	2	96	3.7	95.6	0.7	95.0
25	1	PEt$_3$	2	100	3.0	96.4	0.6	92.0
26	1.5	PEt$_3$	2	100	2.1	97.4	0.5	92.2
27	1.5	PEt$_3$	4	90	6.4	93.1	0.5	87.6
28	2.5	PEt$_3$	2	100	2.2	97.2	0.6	93.2
29	1.5	PBu$_3$	2	100	2.1	97.3	0.6	92.6
30	3.5	PBu$_3$	2	100	2.1	97.4	0.5	93.3

Precursor: Pd(dba)$_2$ + P ligand; Pd = 0.1 mmol; [Pd] = 1×10^{-3} M; C_4H_6/Pd ca. 5000; no n-hexane added; $T = 65°C$; $t = 5$ h.
[a] [Pd] = 0.2×10^{-3} M; Pd = 0.03 mmol; C_4H_6/Pd = 29000.

Table 4
Synthesis of butenyl ethers with palladium catalysts: Effect of the temperature

Run	t (min)	Conversion (%)	Selectivity %				%	
			C_4OMe	dim.	telom.	trim.	C_4OMe lin.	tel. lin.
$T = 70°C$								
31	10	17	93.1	0.9	5.0	1.0	23.3	81.6
	20	40	89.2	2.1	7.5	1.2	24.3	81.7
	30	66	84.6	2.0	11.4	2.0	24.7	82.0
	60	100	78.1	2.5	17.6	1.8	28.4	80.5
	90	100	74.8	3.1	20.3	1.8	34.5	77.8
$T = 80°C$								
32	10	42	92.3	1.6	5.5	0.6	25.5	82.0
	20	90	86.7	1.6	9.7	2.0	27.9	81.7
	30	94	86.3	2.1	10.6	1.0	32.5	79.5
	60	100	74.9	2.5	17.8	4.8	42.6	75.3
$T = 90°C$								
33	5	51	81.5	2.3	13.9	2.3	25.5	81.5
	10	89	75.6	2.1	20.6	1.7	26.7	81.7
	20	100	75.1	3.7	20.5	0.7	34.1	77.3
	30	100	68.2	4.6	24.8	2.4	41.3	73.7
	60	100	51.4	9.5	34.1	5.0	47.7	68.0

Precursor: $[Pd(allyl)Cl]_2 + PBu_3$; $Pd/P = 1/6$; $[Pd] = 2.4 \times 10^{-3}$ M; Pd = 0.2 mmol; $C_4H_6/Pd = 100$; $MeOH/C_4H_6 = 100$.

(high MeOH/diene and P/Pd ratios) which were shown favourable to maximize the yield into isoprenyl ethers from isoprene and methanol [14,15].

The reaction of 1,3-butadiene with methanol was carried out at different temperatures, evaluating selectivities and diene conversions at different reaction times (Table 4).

In Figs. 1 and 2 are reported the plots of products amounts vs. reaction time for catalytic runs carried out respectively at 70°C and 90°C; at the lower temperature (Fig. 1), butenyl ethers were achieved selectively although at higher conversion they begin to be transformed into octadienyl ethers.
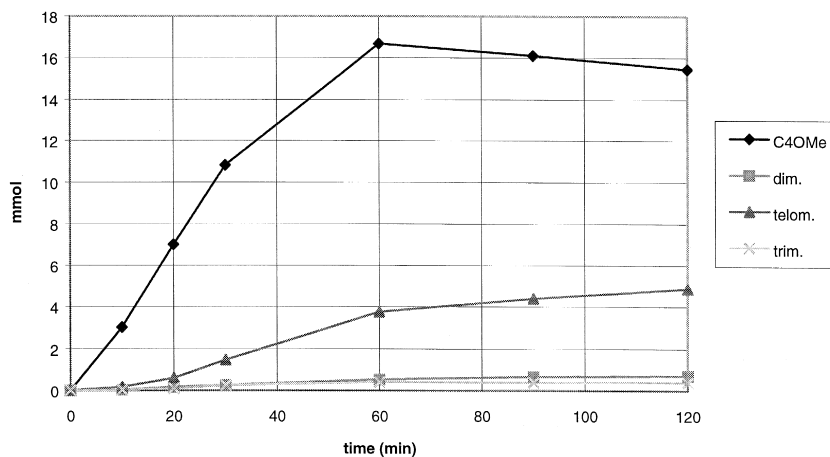

Fig. 1. Dependence of the product distribution (mmol of products) with time (min) (run 31 in Table 4).
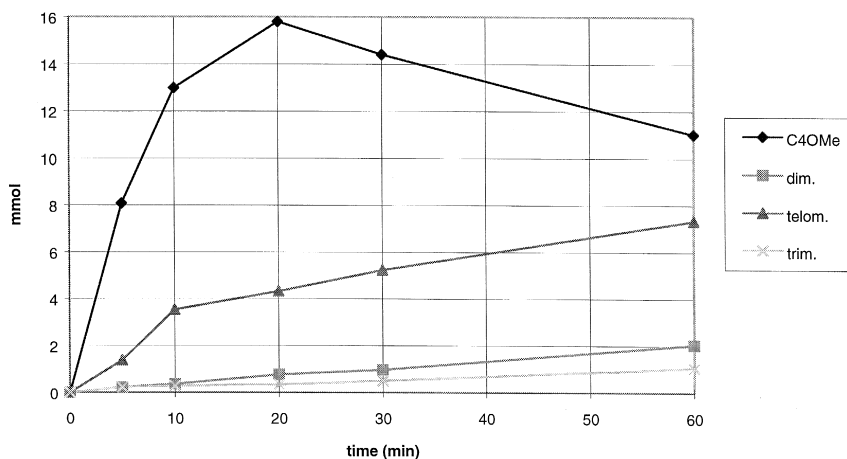
Fig. 2. Dependence of the product distribution (mmol of products) with time (min) (run 33 in Table 4).

At the higher temperature (Fig. 2), total conversion of diene was achieved within a short time; nevertheless, composition evolved during the run: butenyl ethers are converted to octadienyl ethers and, even if to a very reduced extent, the latter ones tend to be transformed into higher telomers containing three or more butadiene units.

As shown in Table 4, the behaviour of the run carried out at 80°C is intermediate, achieving higher conversion (with respect to the run at 70°C) and higher selectivities (with respect to the run at 90°C).

As these runs seemed to suggest the incidence of consecutive reactions in transforming C_4 ethers into C_8 ones, more attention was devoted to the effect of some other variable.

Table 5
Synthesis of butenyl ethers with palladium catalysts: Effect of the C_4H_6/Pd molar ratio

Run	t (min)	Conversion (%)	Selectivity %				%	
			C_4OMe	dim.	telom.	trim.	C_4OMe lin.	tel. lin.
C_4H_6/Pd = 33								
34	10	100	90.4	2.0	3.0	4.6	36.1	77.9
	20	100	82.2	6.7	5.2	5.9	43.0	75.6
	30	100	80.2	3.7	10.1	6.0	46.1	73.6
	60	100	64.3	7.1	20.9	7.7	47.3	71.1
C_4H_6/Pd = 65								
35	10	85	89.5	1.3	5.9	3.3	27.7	83.4
	20	99	86.6	1.8	6.4	5.2	35.9	78.6
	30	100	83.2	2.4	8.8	5.6	41.6	76.2
	60	100	72.0	4.5	17.6	5.9	47.2	71.8
C_4H_6/Pd = 100								
32	10	42	92.3	1.6	5.5	0.6	25.5	82.0
	20	90	86.7	1.6	9.7	2.0	27.9	81.7
	30	94	86.3	2.1	10.6	1.0	32.5	79.5
	60	100	74.9	2.5	17.8	4.8	42.6	75.3
C_4H_6/Pd = 200								
36	10	12	81.4	1.7	13.5	3.4	24.0	80.6
	20	29	73.6	3.4	19.8	3.2	24.4	80.9
	30	45	70.4	3.3	25.8	0.5	24.7	80.7
	60	87	57.3	4.0	37.4	1.3	27.9	79.9

Precursor: [Pd(allyl)Cl]$_2$ + PBu$_3$; Pd/P = 1/6; [Pd] = 7.4×10^{-3}–1.2×10^{-3} M; Pd = 0.2 mmol; T = 80°C; MeOH/C_4H_6 = 100.

Table 6
Synthesis of butenyl ethers with palladium catalysts: Effect of the P/Pd molar ratio

Run	t (min)	Conversion (%)	Selectivity %				%	
			C_4OMe	dim.	telom.	trim.	C_4OMe lin.	tel. lin.
P/Pd = 4								
37	5	9	59.2	7.3	32.1	1.4	24.8	79.0
	10	19	50.4	4.8	43.4	1.4	24.7	79.1
	20	42	37.8	6.7	55.0	0.5	25.0	80.1
	30	76	27.0	5.6	66.7	0.7	25.2	81.5
	60	100	26.0	7.4	65.2	1.4	31.9	77.4
P/Pd = 6								
38	5	15	77.6	3.0	17.8	1.6	25.1	80.2
	10	33	69.6	2.6	25.8	2.0	25.2	80.7
	20	71	55.5	4.3	39.2	1.0	26.3	81.5
	30	98	49.7	4.8	44.6	0.9	28.6	80.9
	60	100	44.0	7.4	46.5	2.1	40.2	74.0
P/Pd = 8								
39	5	17	81.8	2.9	13.6	1.7	25.2	81.4
	10	38	77.0	2.8	18.5	1.7	25.6	81.9
	20	83	66.8	3.6	29.2	0.4	27.2	82.7
	30	100	63.5	4.0	31.6	0.9	30.9	80.8
	60	100	55.2	6.6	36.4	1.8	42.1	74.3
P/Pd = 10								
40	5	23	86.8	1.6	9.0	2.6	25.2	82.6
	10	52	84.5	1.8	12.7	1.0	26.0	83.3
	20	96	80.5	2.5	16.1	0.9	29.3	82.7
	30	100	78.1	3.0	18.0	0.9	35.1	80.1
	60	100	69.4	4.9	24.4	1.3	44.1	74.0

Precursor: $[Pd(allyl)Cl]_2 + PBu_3$; Pd/P = 1/6; $[Pd] = 1.2 \times 10^{-3}$ M; Pd = 0.1 mmol; $T = 90°C$; initial ratio C_4H_6/Pd = 200; initial ratio $MeOH/C_4H_6 = 100$.

In Table 5 the effect is reported of the C_4H_6/Pd molar ratio at a fixed temperature of 80°C and at a molar ratio $MeOH/C_4H_6$ of 100.

The initial enhancement of the C_4H_6/Pd molar ratio from 33 to 100 gives similar results with selectivity to butenyl ethers of 80–90%, higher at low 1,3-butadiene conversion. At total conversion, as usual, butenyl ethers begin to be converted into octadienyl ethers. A further increase of the C_4H_6/Pd molar ratio to 200 results in an enhanced selectivity to octadienyl ethers.

With this higher C_4H_6/Pd molar ratio the selectivity to butenyl ethers can be increased by enhancing the PBu_3/Pd molar ratio. In Table 6 is, in fact, reported the effect of the variation of the PBu_3/Pd molar ratio at a fixed temperature of 90°C, which should furtherly disfavour the achievement of high selectivities in butenyl ethers.

It was observed that an increase of the P/Pd ratio from 4 to 10 favoured the formation of more butenyl ethers. Higher ratios also favour the achievement of higher conversions. This unexpected behaviour is related to the instability of the palladium catalysts with low P/Pd ratios in the activation phase at high temperature (see also experimental).

Finally, in Table 7 some selected runs carried out in order to maximize the production of butenyl ethers are reported: nearly total selectivities (92–96%) were achieved increasing temperature but further reducing the reaction time to 3 min and, above all, the C_4H_6/Pd molar ratio.

When the reaction product was rapidly quenched in iced water, the composition of the sample was observed unchanged for days (after storage at room temperature with the catalyst still present in the solution).

Table 7
Selective synthesis of butenyl ethers with palladium and nickel catalysts

Run	C_4H_6/M	MeOH/C_4H_6	t (min)	T (°C)	Conversion (%)	Selectivity %				%	
						C_4OMe	dim.	telom.	trim.	C_4OMe lin.	tel. lin.
41[a]	33	100	3	100	42	95.6	1.2	1.3	1.9	30.0	76.9
42	33	100	3	120	58	92.5	1.4	2.9	3.2	42.2	76.0
43[b]	110	30	10	80	85	0.7	2.4	95.1	1.8	17.0	92.6
32	100	100	10	80	42	92.3	1.6	5.5	0.6	25.5	82.0
44[c]	540	5	210	120	18	96.9	0.7	0.7	1.7	28.0	73.6

Precursor: [Pd(allyl)Cl]$_2$ + PBu$_3$; Pd/P = 1/6; [Pd] = 6.5×10^{-3} M; Pd = 0.6 mmol; M: metal (Pd or Ni).
[a] PEt$_3$ used instead of PBu$_3$.
[b] Precursor: Pd(dba)$_2$ + PEt$_3$.
[c] Precursor: Ni(cod)$_2$/DPPE (P/Ni = 4); Ni = 1 mmol; [Ni] = 6.5×10^{-3} M.

The use of more basic phosphines, such as PEt$_3$, seems to afford even higher selectivity into butenyl ethers (run 41).

It is worth noting that this behaviour is typically achieved with Pd(II) precursors (see Run 32) whereas, under similar conditions, in the presence of a Pd(0) complex such as Pd(dba)$_2$ (run 43) only octadienyl ethers are obtained, although with higher conversion.

Such a high selectivity into butenyl ethers in the presence of palladium catalyst was so far absolutely unreported (best precedent selectivity < 50% [16]); in Table 7 is also reported a comparative example (Run 44) with a nickel complex [17], a typical catalyst for this reaction [17,18]. The run with the nickel complex was carried out with a higher 1,3-butadiene/metal molar ratio because higher ratios are generally requested to assure a sufficient activity of the catalysts [17].

Otherwise, it is to point out that the activity of the palladium catalyst is markedly higher than the nickel one (at 100–120°C and for selectivities into butenyl ethers > 90%, Turnover Frequency in C_4 ethers of 250–400 h^{-1} were achieved with Pd catalysts with respect to the 25–40 h^{-1} for nickel catalysts under similar conditions).

As regards the selectivity into the butenyl ethers fraction, the formation of the branched ether 3-methoxy-1-butene is generally favoured with respect to that of the linear 1-methoxy-2-butenes, although higher temperatures and longer reaction times give rise to similar selectivities between linear and branched ethers. For selectivities into butenyl ethers of ca. 90% the linear butenyl ethers percentage increases from 23 to 42% moving to higher temperatures (runs 31–33, 41 and 42): the linear isomers, product of 1,4 addition, are in fact thermodinamically favoured by higher temperatures. However, it has been observed in addition that when substantial amounts of butenyl ethers are formed, the selectivity into linear octadienyl ethers (with respect to branched ones) is sensibly lower (70–80%) than usual. This is partly due to the high P/Pd ratio employed (see also Run 27 in Table 3) but it has been also noticed that, on increasing the reaction time, not only the percentage of linear butenyl ethers increases but also that of branched octadienyl ethers with respect to the overall octadienyl ethers fraction (see Fig. 3). This could be related to a preferential conversion of 3-methoxy-1-butene into 3-methoxy-octadienes.

In conclusion, butenyl ethers can be selectively formed under particular reaction conditions, although at longer reaction times they tend to be transformed into octadienyl ethers. The butenyl ethers formation is favoured by the use of Pd(II) complexes (not promoted by alkoxide ligands), by high phosphine/Pd molar ratios (the more basic the phosphine the more seems to be preferred) and by low diene/Pd and high MeOH/diene molar ratios.
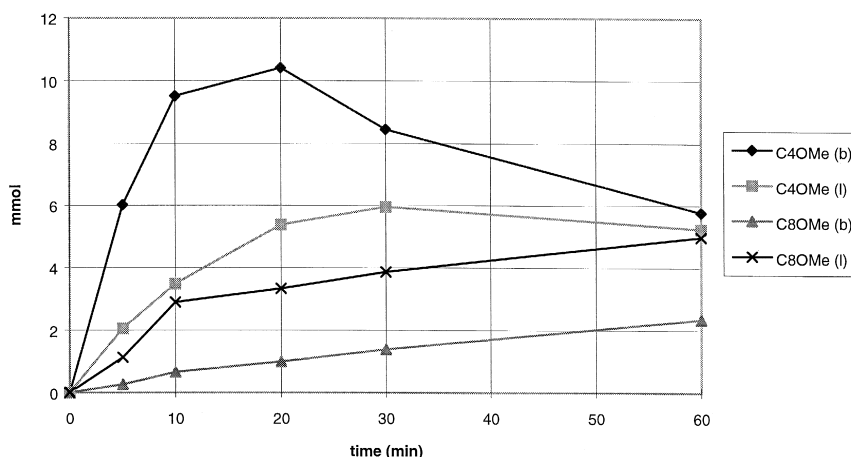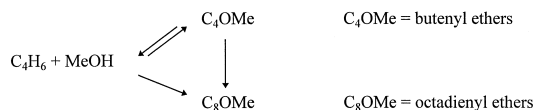
Fig. 3. Linear (l) and branched (b) products distribution (mmol of products) with time (min) (run 33 in Table 4).

All these factors concur to increase the steric crowding around the palladium center and favour the coordination of only a butadiene molecule, which can be rapidly attacked by methanol, present in strong excess.

However, the butenyl ethers, once formed, can be coordinated again to the palladium center, differently from the nickel case, and the formation of octadienyl ethers could be therefore favoured at high 1,3-butadiene conversion and higher reaction times, according to the following mechanism:

$$
\begin{array}{lll}
 & C_4OMe & C_4OMe = \text{butenyl ethers} \\
C_4H_6 + MeOH & \downarrow & \\
 & C_8OMe & C_8OMe = \text{octadienyl ethers}
\end{array}
$$

This kind of mechanism, that involves both the reversibility of the formation of butenyl ethers and their direct evolution to octadienyl ethers, was not pointed out by previous studies [16], but plays a fundamental role in determining the overall behaviour of the system. It is not yet clear why Pd(0) complexes are not able to give butenyl ethers. Likely, the direct formation of octadienyl ethers is preferred in this case as also indicated by the high selectivity into octadienyl ethers and their higher linearity.

4. Final remarks

The most important and original result of this work is represented by the selective synthesis, in the presence of palladium catalysts, both of octadienyl ethers from 1,3-butadiene and higher linear primary alcohols and of butenyl ethers from methanol and the diene.

The ROH/C_4H_6 molar ratio plays a decisive role in the case of higher alcohols: an excess of alcohol favours the synthesis of octadienyl ethers with respect to octatrienes, as it increases the reaction rate and the probability that an intermediate octadienyl complex can be attacked by an alcohol molecule to afford the ether.

In the case of the selective synthesis of butenyl ethers excess of alcohol is useful but is not the only factor that plays a relevant role. Also other precautions are in fact to be adopted: the use of unpromoted Pd(II) complexes, of high P/Pd and low C_4H_6/Pd molar ratios, of relatively short reaction times.

It is crucial the formation of a sterically hindered species able to coordinate only a molecule of 1,3-butadiene to produce a butenyl palladium intermediate which can rapidly react with methanol, present in large excess.

It has been discovered that for palladium catalysts, the formation of butenyl and octadienyl ethers is ruled by a complex mechanism involving both the reversible formation of butenyl ethers and their direct transformation into octadienyl ethers. In the case of nickel complexes, either butenyl ethers are not easily transformed into octadienyl ones or their formation is not reversible. Otherwise, this study has pointed out that palladium catalysts are much more active than nickel ones.

Acknowledgements

References

[1] A. Behr, in: R. Ugo (Ed.), Aspects of Homogeneous Catalysis, vol. 5, Reidel, Dordrecht, 1984, p. 3.
[2] N. Yoshimura, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, VCH, Weinheim, 1996, p. 351.
[3] E. Monflier, P. Bourdauducq, J.-L. Couturie, J. Kervennal, I. Suisse, A. Mortreux, Catal. Lett. 34 (1995) 201, and references therein.
[4] E. Monflier, P. Bourdauducq, J.-L. Couturie, J. Kervennal, I. Suisse, A. Mortreux, Appl. Catal. A: Gen. 131 (1995) 167, and references therein.
[5] T. Prinz, W. Keim, B. Driessen-Hölscher, Angew. Chem. Int. Ed. 35 (1996) 1708.
[6] W. Keim, personal communication.
[7] M. Marchionna, R. Patrini, F. Giavazzi, G.C. Pecci, Preprints 212th National Meeting of the American Chemical Society, 1996, Div. Petr. Chem., vol. 41, p. 585.
[8] M.F. Rettig, P.M. Maitlis, Inorg. Synth. 28 (1990) 110.
[9] W.T. Dent, R. Long, A.J. Wilkinson, J. Chem. Soc. (1964) 1585.
[10] J. Beger, H. Reichel, J. Prakt. Chem. 315 (1973) 1067.
[11] S. Takahashi, T. Shibano, N. Hagihara, Bull. Chem. Soc. Jpn. 41 (1968) 454.
[12] Y. Tamaru, M. Kagotani, R. Suzuki, Z. Yoshida, Chem. Lett. (1978) 1329.
[13] U.M. Dzhmilev, R.V. Kunakova, N.Z. Baibulatova, G.A. Tolstikov, A.A. Panasenko, USSR Zh. Org. Khim. 16 (1980) 1157.
[14] R. Patrini, M. Marchionna, M. Lami, F. Ancillotti, Snamprogetti, European Patent 450 707 (1991).
[15] W. Gaube, H. Stegemann, J. Prakt. Chem. 326 (1984) 947.
[16] D. Commereuc, Y. Chauvin, Bull. Soc. Chem. Fr. (1974) 656.
[17] M.J. Mullins, Dow Chemical, US Patent 4 843 180 (1989).
[18] T.C. Shields, W.E. Walker, J. Chem. Soc. Chem. Commun. (1971) 193.