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Palladium catalyzed telomerization of butadiene with water in a two phase system: drastic effect of the amine structure on the rate and selectivity

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Abstract

Telomerization of butadiene with water in the presence of carbon dioxide and a trialkylamine using a palladium–hydrosoluble phosphine system was investigated. 2,7-Octadien-1-ol was obtained as the main product, whilst 1,7-octadien-3-ol, octatrienes, 4-vinylcyclohexene and dioctadienyl ethers were formed as side products. The reaction was carried out exclusively in an aqueous–organic medium in the absence of solvent or co-solvent. The conversion and the selectivity are strongly dependent on the structure of trialkylamine. The role of the amine was discussed.

Keywords: Butadiene; Hydrosoluble phosphine; Micelle; Octadienol; Palladium; Telomerization; Trialkylamine

Palladium catalyzed dimerization of butadiene with incorporation of various nucleophiles such as active methylene compounds, alcohols, phenols and amines have been widely studied during these last years [1,2]. Due to its considerable industrial interest, telomerization of butadiene with water into 2,7-octadien-1-ol has been extensively studied by numerous industrial research groups [3,4]. In contrast with telomerization with alcohols, phenols and amines, efficient telomerization of butadiene with water requires the presence of carbon dioxide and a solvent or co-solvent [3,4]. However, a patent claims the efficient telomerization of butadiene into 2,7-octadien-1-ol in absence of solvent and carbon dioxide [5]. The reaction was carried out in the presence of additives like Na_2CO_3, K_2CO_3 or $KHCO_3$. Although some hypotheses have been suggested, the role of carbon dioxide or additives has not been totally elucidated yet [6].

The increasing number of patents in the literature shows clearly that the telomerization of butadiene with water remains a real challenge and research in this field is still being pursued [3].

We wish to report hereby that telomerization of butadiene into 2,7-octadien-1-ol can be performed in absence of solvent with high conversion and selectivity when a particular trialkylamine such as

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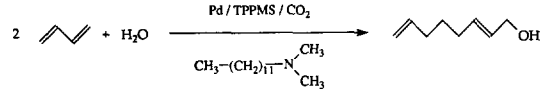

Scheme 1. Telomerization of butadiene with water.

dimethyldodecylamine is used [7]. The catalytic system consists of a palladium salt and a hydrosoluble phosphine such as $Ph_2P(m\text{-}C_6H_4SO_3Na)$ (TPPMS) or $P(m\text{-}C_6H_4SO_3Na)_3$ (TPPTS) (Scheme 1).

In a typical experiment, $Pd(OAc)_2$ (6.5×10^{-4} mol), TPPTS (2×10^{-3} mol), trialkylamine (1×10^{-2} mol), butadiene (0.33 mol) and H_2O (0.66 mol) were introduced, under an argon atmosphere, into a 100 ml stainless steel autoclave equipped with a mechanical stirrer. The autoclave was pressurized to 10 bar of carbon dioxide and heated to 85°C during 1 h 45 min. The autoclave was then cooled and degassed. The crude reaction mixture contained two phases. The organic phase was analyzed by gas liquid chromatography (packed glass column: 5% XE 60 + 10% OV 210; /Chromosorb WHP 80/100; 10 m × 2 mm), using n-octanol as internal standard. Products were identified by comparison of GLC retention times and spectral properties with authentic samples.

Results obtained with various trialkylamines and water-soluble phosphines are shown in Table 1. In contrast with telomerization of butadiene in the presence of solvent, entries 1 and 8 in Table 1 indicate that the use of an amine is essential for the obtention of 2,7-octadien-1-ol in good yields in the absence of solvent.

Table 1 shows also that the structure of the amine has a crucial influence on the rate and selectivity:

(i) Non sterically hindered amines such as triethylamine gave 2,7-octadien-1-ol in poor yields. For example, the yields in the presence of triethylamine were only 5% and 20% with TPPTS and TPPMS, respectively (Entries 3 and 9, Table 1).

Table 1
Telomerization of butadiene with water in the presence of various amines and phosphines [a]

Entry	Phosphine	Amine	Butadiene conversion (mol %)	Octadienols yield (mol %)	Octadienols selectivity [c] (mol %)	Selectivity (1-ol/ols) [d] (mol %)	Dimers yield [e] (mol %)	Ethers yield [f] (mol %)	Turnover frequency [h]
1 [b]	TPPTS	–	6	<1	–	–	5	1	9
2 [b,i]	TPPTS	–	26	20	77	70	6	0	38
3 [b]	TPPTS	$(C_2H_5)_3N$	11	5	50	82	5	1	16
4 [b]	TPPTS	$(C_4H_9)_3N$	7	1	14	46	6	0	10
5 [g]	TPPTS	$C_{12}H_{25}N(CH_3)_2$	89	63	71	94	16	8	269
6 [g]	TPPTS	$C_{18}H_{37}N(CH_3)_2$	86	62	72	94	15	8	250
7 [b]	TPPTS	$(C_{12}H_{25})_2NCH_3$	4	1	–	–	3	–	6
8	TPPMS	–	4	0	–	–	4	0	11
9	TPPMS	$(C_2H_5)_3N$	33	20	60	85	10	3	96
10	TPPMS	$(C_4H_9)_3N$	22	12	54	25	10	0	64
11 [g]	TPPMS	$(C_8H_{17})_3N$	17	1	6	–	10	0	50
12	TPPMS	$(C_{12}H_{25})_3N$	1	0	–	–	1	0	3
13	TPPMS	$C_{12}H_{25}N(CH_3)_2$	78	64	82	91	10	4	228
14	TPPMS	$C_{12}H_{25}(C_2H_4OH)_2N$	8	6	75	90	2	0	23

[a] Reaction conditions: $Pd(OAc)_2$ = 0.146 g (6.5×10^{-4} mol); amine = 1×10^{-2} mol; phosphine = 2×10^{-3} mol; C_4H_6 = 18 g (0.33 mol); H_2O = 12 g (0.66 mol); P_{CO_2} = 10 bar; T = 85°C; t = 1 h 45 min.

[b] t = 3 h 30 min.

[c] (moles of octadienols × 2) / (moles of converted butadiene) × 100.

[d] (moles of 1-octadienol/moles of 1- and 3-octadienol) × 100.

[e] The main dimers were 1,3,6-; 1,3,7- and 2,4,6-octatrienes and 4-vinylcyclohexene.

[f] Dioctadienyl ethers.

[g] The deficiency of the mass balance was due to the presence of unidentified high boiling products.

[h] Moles of converted butadiene per hour per mole of palladium.

[i] K_2CO_3 (10 mmol) was used instead of carbon dioxide.

(ii) Amines containing one long alkyl chain afforded 2,7-octadien-1-ol in high yields (Entries 5, 6 and 13, Table 1).

(iii) Trialkylamines having two or three long alkyl chains reduce considerably the conversion and selectivity. For example, when didodecylmethylamine was used instead of dodecyldimethylamine in the presence of TPPTS, the conversion and 2,7-octadien-1-ol yield dropped from 89% to 4% and from 63% to 1%, respectively (Entries 5 and 7, Table 1). A similar type of behaviour was observed with TPPMS (Entries 12 and 13, Table 1).

So, it appears that the amines containing one long alkyl chain (rodlike amines) are the only suitable amines for the telomerization in the absence of solvent in a two phase system.

The influence of the alkyl chain length in such amines has been studied and the results are presented in Table 2. Entries 2 to 9 of this table indicate that the longer the alkyl chain, the higher the rate. This promoted effect is observed when the carbon number of the alkyl chain is higher than six. When the carbon number is more than twelve, the conversion and yield increase no more. Interestingly, a mixture of long chain amines gave also 2,7-octadien-1-ol in good yields (Entry 7, Table 2).

In order to elucidate the role of the amine, we have also tested some tetraalkylammonium salts. Ammonium hydroxides are suitable, but it should be noticed that the hydrodimerization was totally inhibited with ammonium chlorides or bromides. Although no conclusive evidence has been obtained, we believe that chloride or bromide ions block free coordination sites at palladium and inhibit the association–dissociation steps involved in the catalytic process [2]. The results obtained with ammonium hydroxides were similar with those obtained with amines. An ammonium hydroxide containing one long alkyl chain promoted the telomerization, whilst an ammonium

Table 2
Telomerization of butadiene in the presence of amines and ammonium containing one long alkyl chain: effect of the alkyl chain length on the conversion and selectivity [a]

Entry	Amine or ammonium	Butadiene conversion (mol %)	Octadienols yield (mol %)	Octadienols selectivity [b] (mol %)	Selectivity (1-ol/ols) [c] (mol %)	Dimers yield [d] (mol %)	Ethers yield [e] (mol %)	Turnover frequency [h]
1	–	4	0	–	–	4	0	11
2	$C_2H_5N(CH_3)_2$	30	21	70	90	8	1	87
3	$C_4H_9N(CH_3)_2$	28	22	78	91	5	1	82
4	$C_6H_{13}N(CH_3)_2$	66	56	85	91	7	3	192
5	$C_8H_{17}N(CH_3)_2$	65	54	83	90	5	6	190
6	$C_{12}H_{25}N(CH_3)_2$	78	64	82	91	10	4	228
7	$(Coco)N(CH_3)_2$ [f]	81	65	80	91	10	6	236
8	$C_{14}H_{29}N(CH_3)_2$	75	52	70	87	10	13	219
9	$C_{18}H_{37}N(CH_3)_2$	80	55	69	87	7	18	233
10	$CH_3N(CH_3)_3^+OH^-$ [g]	16	9	56	89	2	2	46
11	$C_{12}H_{25}N(CH_3)_3^+OH^-$ [g]	84	60	71	90	7	13	245

[a] $Pd(OAc)_2 = 0.073$ g (3.25×10^{-4} mol); amine $= 5 \times 10^{-3}$ mol; TPPMS $= 1 \times 10^{-3}$ mol; $C_4H_6 = 9$ g (0.165 mol), $H_2O = 6$ g (0.33 mol); $P_{CO_2} = 10$ bar; $T = 85°C$; $t = 1$ h 45 min.

[b] (moles of octadienols × 2) / (moles of converted butadiene) × 100.

[c] (moles of 1-octadienol/moles of 1- and 3-octadienol) × 100.

[d] The main dimers were 1,3,6-; 1,3,7- and 2,4,6-octatrienes and 4-vinylcyclohexene.

[e] Dioctadienyl ethers.

[f] $(Coco)N(CH_3)_2$ is a mixture of amines having C_{10} (6%), C_{12} (55%), C_{14} (18%) and C_{16} (10%) alkyl chain. This mixture is obtained industrially from cocoamine which is derived from cocoa plant.

[g] The deficiency of the mass balance was due to the presence of unidentified high boiling products.

[h] Moles of converted butadiene per hour per mole of palladium.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$R(CH_3)_2N + H_2CO_3 \rightleftharpoons R(CH_3)_2\overset{+}{N}H\ HCO_3^-$$

$$R(CH_3)_2\overset{+}{N}H\ HCO_3^- + R(CH_3)_2N \rightleftharpoons (R(CH_3)_2\overset{+}{N}H)_2\ CO_3^{2-}$$

Scheme 2. Various equilibria between carbon dioxide and trialkylamine.

hydroxide containing no long alkyl chains gave 2,7-octadien-1-ol in low yields (Entries 10 and 11, Table 2).

These results can be rationalized if one considers an acid–base reaction between carbon dioxide and trialkylamine to form ammonium salts which have HCO_3^- or CO_3^{2-} like counter anion. Scheme 2 shows the different equilibria involved.

In this hypothesis, amines containing one long alkyl chain – the only suitable amines – are partially transformed into a long alkyl chain ammonium salt. This could explain the similar results obtained with dodecyldimethylamine and dodecyltrimethylammonium hydroxide.

Results obtained with amines having one long alkyl chain could be deduced from their particular structure. Indeed, after reaction with carbon dioxide, amines can behave as cationic surfactants: the straight and long alkyl chain and the quaternary nitrogen constitute the lipophilic and the hydrophilic parts, respectively. So, the effect of amine could be explained by an increase of mass transfer between organic and aqueous phases, due to the formation of micelles. It must be noticed that linear ammonium salts like cetyltrimethylammonium hydroxide, are known to be micellar catalysts [8] and that this property has been used for Wacker oxidation [9] and hydroformylation [10] of higher olefins. Furthermore, it is also known that quaternary ammonium salts having larger and symmetrical cation, e.g. methyltrioctylammonium salt, are excellent phase-transfer catalysts but poor surfactants [8]. This is consistent with the low yields obtained with amines containing two or three long alkyl chains.

Finally, it is worth also mentioning that, if the telomerisation is promoted by the amphiphilic properties of the amine, it is also promoted by the increase in the concentration of carbonate or/and bicarbonate in the medium. Indeed, although the role of carbonate and bicarbonate has not been totally elucidated yet, their beneficial effect is undeniable (compare entries 1, 2 and 3 in Table 1) and has already been reported in a patent [5]. Obviously, the increase in the concentration of carbonate or/and bicarbonate is due hereby to the acid–base reaction of the trialkylamine with the carbon dioxide (Scheme 2).

In conclusion, we have demonstrated that the telomerization of butadiene into 2,7-octadien-1-ol can be achieved in high yields and conversions in the absence of solvent in a two phase system. A more detailed investigation with the aim to confirm the roles of amine is now under way.

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