

A further application of TPPTS in catalysis: Efficient sucrose–butadiene telomerization using palladium catalysts in water

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Abstract

Sucrose–butadiene telomerization is efficiently carried out in water or water–organic medium in the presence of a palladium salt and TPPTS (TPPTS = trisodium tris(*m*-sulfonatophenyl)phosphine as catalyst. Mono- and dioctadienylether compounds are selectively obtained using a NaOH 1 M/isopropanol mixture.

Keywords: Sucrose; Butadiene; TPPTS; Telomerization

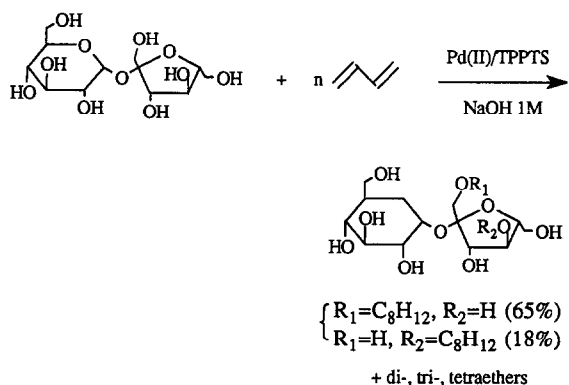
1. Introduction

The telomerization of butadiene with alcohols, for which the most appropriate catalysts are based on palladium compounds, has now been studied for a long time [1,2]. A wide variety of nucleophiles has been used including phenol [3] as well as a protected galactopyranose [4]. The use of carbohydrates as nucleophiles leads to hydrophobic alkyl glucosides. These products show interesting physical–chemical properties of surfactants and have the advantage of being biodegradable. Furthermore, they possess good compatibility properties towards the skin. They are also used in detergent formulations and emulsifiers in cosmetics and food [5]. The selective monoetherification of

unprotected sucrose remains a particularly difficult task because of the small differences in the activation energies among the several classes of the OH groups. Recently, Hill et al. have described a direct route for telomerization of butadiene with sucrose in the presence of a Pd(II)/PPh₃ system in a mixture of propan-2-ol and water [6,7]. Sucrose octadienyl ethers were obtained with an average degree of substitution of 4.7–5.3. However, the presence of 2-propyloctadienylether and butadiene dimers in the crude product was also observed.

We describe here some hydrosoluble palladium catalyst systems that enable the straightforward telomerization of butadiene with sucrose in water or water–organic medium [8]. The mono- and dioctadienylethers were obtained in high yield with a small amount of side products identified as butadiene dimers (< 2%).

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Scheme 1.

Despite the use of water as solvent, no octadienols which could arise from the telomerization of butadiene with water were formed (Scheme 1).

The catalyst system was formed from palladium diacetate and trisodium tris(*m*-sulfonylphenyl)phosphine (TPPTS).

2. Experimental

In a typical experiment, sucrose (8 g, 23.4 mmol), Pd(OAc)₂ (20 mg, 0.09 mmol) and TPPTS (150 mg, 0.27 mmol) were weighed and introduced into a 100 ml stainless steel double walled autoclave equipped with a magnetic stirrer. After a nitrogen purge the degassed solvent were added. The autoclave was frozen at -10°C and liquid butadiene (15 g, 278 mmol) was transferred. The mixture was then heated to 80°C , in which case the pressure increased to 11 bar corresponding to the butadiene vapor pressure at that temperature. After reaction, the autoclave was cooled and degassed. A light yellow monophasic solution was generally obtained unless ketones were used. The solvents were evaporated under vacuo and analyzed by gas chromatography (CP Sil 5CB, length 25 m, internal diameter: 0.22 mm). The crude products were analyzed after peracetylation with a mixture of acetic anhydride and pyridine by GC with a high temperature SGE HT 5 0.1 column (length: 25 m, internal diameter: 0.32 mm). The

telomerization products were also characterized by positive FAB (matrix: thioglycerol/sodium acetate). The different telomers fractions were separated by flash chromatography. From the monoethers fraction, each telomer was isolated by preparative HPLC on a C₁₈ column (Spherisorb ODS 2, 25 cm length, 10.5 mm internal diameter) using MeCN/H₂O (20/80: v/v) as eluent and fully characterised by NMR ¹H and ¹³C DEPT technics [9]. The structure of major monoethers and their relative amounts in this fraction were as depicted in Scheme 1.

3. Results and discussion

The telomerization reaction was first examined in aqueous medium. The results are reported in Table 1.

Using water alone, the sucrose conversion was only 65% after 5 h (entry 1). The peracetylated reaction mixture was found to be composed mainly of about 36% mono- and 48% di-O-octadienyl compounds. An increase of the reaction time allowed to reach a 90% conversion, but led to an enhancement of the average number of substitutions on the OH groups (entry 2). In this latter case, the di- and trisubstituted ethers were the main products.

The introduction of sodium hydroxide resulted in a large increase of the catalytic activity so that the reaction went to completion within 2.5 h (entry 3). The reaction rate was so effective that after only 26 min, 87% of sucrose was converted into di- and triethers. In this latter case, the degree of substitution remained quite high (entry 4, $N = 2.4$). An optimised time of 23 min has allowed to obtain a good compromise between the sucrose conversion and the substitution degree (entry 5). In order to improve the monotelomers selectively, the butadiene quantity has been decreased but in such cases the activity decreased simultaneously considerably. For example, with a butadiene/sucrose ratio of 3, no reaction occurred.

Table 1
Palladium catalysed telomerization of butadiene with sucrose in aqueous medium

Entry	Solvent	<i>t</i> (min)	Suc. ^b Conv. (%)	But. ^c Conv. (%)	Selectivity ^a				<i>N</i> ^d
					C ₈	2C ₈	3C ₈	4C ₈	
1	H ₂ O	300	65	14	36	48	16	0	1.8
2	H ₂ O	600	90	43	10	37	45	9	2.6
3	NaOH M	150	100	54	1	16	50	33	3.2
4	NaOH M	23	85	19	43	45	9	0	1.6
5	NaOH M	26	87	36	21	34	29	17	2.4
6	NaOH M	30	88	41	14	32	27	27	2.7

Experimental conditions: Pd(OAc)₂ = 20 mg (0.09 mmol), TPPTS = 150 mg (0.27 mmol), sucrose = 8 g (23.4 mmol), butadiene = 15 g (278 mmol), solvent = 2 ml, *T* = 80°C.

^a *m*C₈ = Sucrose substituted by *m* chains containing 8 carbon atoms. Among the octadienylethers, little amounts of C₁₆ telomers could be detected (less than 3%).

^b Sucrose conversion calculated from CG analyzes.

^c Butadiene conversion.

^d *N* = degree of substitution = average number of alkadienyl chains per carbohydrate unit.

The synthesis of the monooctadienylethers was further investigated in the alkali solution but by using an added organic solvent which could allow their extraction into the organic phase. Table 2 summarizes some data for the telomerization in the presence of various organic solvents in combination with water. According to the literature [10], methyl-iso-

butylketone (MIBK) and methyl-ethylketone (MEK) are typical solvents which have been used during the purification by extraction of O-alkylsucrose compounds. The reaction telomerization of sucrose in the mixture alkaline solution/ketone afforded polysubstituted sucroses with a high triethers content (entries 1 and 2, Table 2). In this case, an improvement in cat-

Table 2
Palladium catalysed telomerization of butadiene with sucrose in organic-aqueous medium

Entry	Additive	<i>t</i> (min)	Suc. ^b Conv. (%)	But. ^c Conv. (%)	Selectivity ^a				<i>N</i> ^d
					C ₈	2C ₈	3C ₈	4C ₈	
1	MEK ^e	30	100	57	5	15	58	23	3.0
2	MIBK ^e	30	100	50	9	14	62	15	2.8
3	<i>i</i> PrOH	30	73	13	66	32	2	0	1.4
4 ^f	<i>i</i> PrOH	30	43	10	62	33	5	0	1.4
5 ^g	<i>i</i> PrOH	30	90	32	26	49	23	2	2.0
6 ^h	<i>i</i> PrOH	30	48	11	71	27	2	0	1.3
7 ⁱ	<i>i</i> PrOH	30	50	11	69	27	4	0	1.3
8 ^g	<i>i</i> PrOH	20	43	10	71	27	3	0	1.3
9 ^g	<i>i</i> PrOH	45	98	40	14	41	38	7	2.2

Experimental conditions: Pd(OAc)₂ = 20 mg (0.09 mmol), TPPTS = 150 mg (0.27 mmol), sucrose = 8 g (23.4 mmol), butadiene = 15 g (278 mmol), solvent = NaOH 1 M (2 ml), additive = 5 ml, *T* = 80°C.

^a *m*C₈ = Sucrose substituted by *m* chains containing 8 carbon atoms. Among the octadienylethers, little amounts of C₁₆ telomers could be detected (less than 3%).

^b Sucrose conversion calculated from CG analyzes.

^c Butadiene conversion.

^d *N* = degree of substitution = average number of alkadienyl chains per carbohydrate unit.

^e MEK = methylethylketone, MIBK = 4-methylpentan-2-one, ketone/NaOH M (v/v) = 5/2.

^f *i*PrOH/NaOH 1 N (v/v) = 10/2.

^g *i*PrOH/NaOH 1 N (v/v) = 2/2.

^h *i*PrOH/NaOH 1 N (v/v) = 1/2.

ⁱ Butadiene/sucrose = 6.

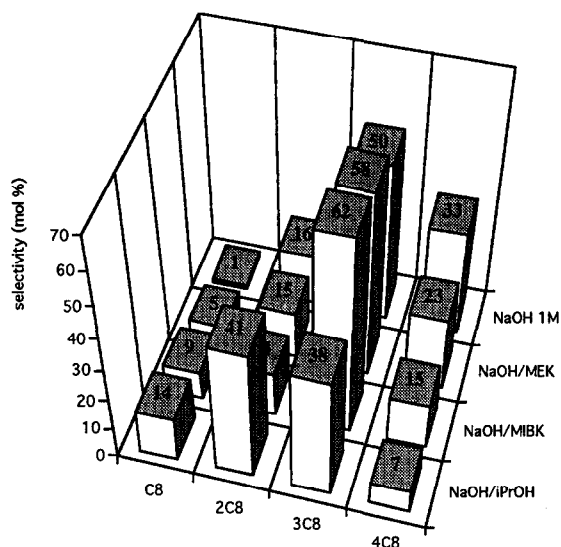


Fig. 1. Sucrose telomers selectivities according to the solvent (Conv. > 98%).

alytic activity was observed, probably due to a better butadiene solubilization into the liquid phase.

Another approach was to use an hydroalcoholic solution of sucrose which has already been reported by H. Cie using triphenylphosphine as ligand [6]. Actually the above results were improved by introducing isopropylalcohol. In our case, a 66% selectivity into mono-octadienylethers was obtained at a 73% conversion which corresponds to a 48% monoethers yield (entry 3, Table 2). Interestingly, no isopropyloctadienylether was observed. Selected results obtained with various solvents are summarised in Fig. 1.

We also studied the effect of a non-hydro-soluble ligand using a mixture of water and isopropanol like those retained for entry 9, Table 2. In this latter case, when PPh_3 was used instead TPPTS, the reaction did not occur at all. This result arose from a too low solubility of PPh_3 in that case.¹

¹ In our hands, Hill telomerization conditions using PPh_3 gave the results obtained by this group, due to a much higher $i\text{PrOH}/\text{H}_2\text{O}$ ratio allowing a good solubilization of the ligand.

A series of experiments to optimize this reaction has been performed. Varying the amount of alcohol had a major effect on the reaction rate and selectivity (entries 3 to 6): a high conversion (90%) was obtained with an alcohol/water ratio of 1 together with a low substitution degree. The use of isopropylalcohol allowed to obtain selectively the sucrose mono- and dioctadienylether compounds, which appear to be less reactive in the mixture alcohol/alkaline solution than in other solvents (entry 9, Table 2 versus entry 3, Table 1 and entries 1–2, Table 2). In this latter case, only small amounts of tetraethers were obtained even at an almost complete sucrose conversion.

The extension of this reaction to others carbohydrates is currently under investigation.

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