

Effects of the reactants concentration in the butadiene telomerization with D-xylose and parallel influence of triethylamine as additive

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Abstract

The efficiency and the selectivity of the palladium-catalyzed telomerization of butadiene with D-xylose in DMF were strongly dependent on the presence of triethylamine as additive for low sugar concentrations. The amine influence, which would mainly be due to its both basic and coordinating properties, disappeared at high sugar concentrations. The selectivity towards the monografting could reach 98% at 50% sugar conversion (with 82% of linear isomers) and could be maintained at 71% at 96% conversion (with a similar ratio of linear isomers).

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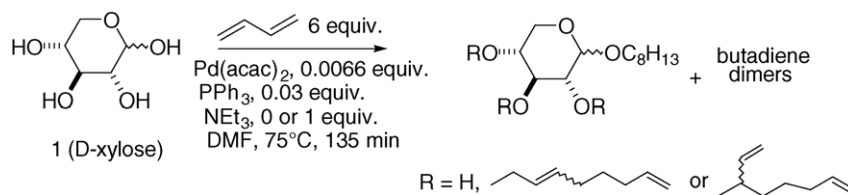
1. Introduction

The telomerization of butadiene with pentoses as telogens leads to surfactant molecules having biodegradable properties [1,2]. The interest in the development of such molecules is growing fast since they correspond to the partial substitution of fossil-based feedstocks with materials from agrosources [3,4]. The minimisation of reactants amounts and waste related to solvents and additives is also of interest in this 100% atom economical reaction. During our studies on the etherification of pentoses using the one pot telomerization strategy, we have demonstrated the beneficial effect of the addition of a tertiary amine on the sugar conversion [1]. Starting however from triacetylated pentoses having free the anomeric hydroxyl, elevated conversion values were observed in the absence of amines [5]. The amine effect may be multiple. In the telomerization of butadiene with methanol, Beller and co-workers have suggested that the possible role of an added tertiary amine is to facilitate the reduction of Pd(II) precatalysts to the active Pd(0) complex [6], following a mechanism proposed by Mc Crindle et al. [7]. The addition of a base in the telomerization reaction may have a ben-

eficial effect [8–10], since it could allow the formation of the telogen derived anion with the counter-cation able to trap the X^- ion corresponding to the PdX_2 precatalyst [8]. Following this ionisation and when the base is a tertiary amine, the protonation step of the intermediate (η^1, η^3 -octadienyl)palladium complex [11,12] could be facilitated in the presence of the resulting ammonium ion, while the nucleophilic character of the telogen would be enhanced. Some improvement in the telomerization reactions have appeared in the literature as, in particular, the use of catalytic amounts of triethylamine with phenols [13] or acetic acid [14] as the telogens. For the hydrodimerization of butadiene with water in a sulfolane/water medium, a remarkable acceleration of the reaction in the presence of increasing concentrations of triethylamine was observed but not explained [15]. In a micellar system, the improvement occurring in the presence of an added amine like dimethyldodecylamine was related to its ability to generate ammonium surfactants which favour mass-transfer between aqueous and organic phases [16]. Lastly, the role of an amine in the metal coordination is known for a long time and this could participate to the catalyst activation [17] or to the catalytic cycle [18] as proposed for the butadiene telomerization with ammonia [19].

In the telomerization reaction of butadiene with alcohols, other parameters influence the reaction course, such as the nature of the ligand L, the ratio L/Pd, the relative amounts of butadiene/

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Scheme 1. Telomerization reaction of butadiene with D-xylose.

substrate, the catalyst precursor and the medium (organic, aqueous or biphasic) [20]. In addition, we have also noticed the influence of the sugar concentration on the regioselectivity of the octadienyl chain grafting (ratio linear/branched telomers) [5].

Pursuing our studies on glycosylation of free pentoses via the palladium-catalyzed telomerization of butadiene with these sugars [1,2], we have been able to remove the amine additive providing that the sugar and butadiene concentrations in the liquid phase were high enough, and the results showing some complementary effects of these parameters are here presented.

2. Results and discussion

The telomerization reactions have been carried out at 75 °C, using an autoclave of 50 mL, containing D-xylose, a butadiene excess, DMF as solvent and the palladium catalyst. After elimination of volatile and peracetylation of the resulting mixture, the reaction products analysed by GC/MS consist mainly of mono-octadienyl xylopyranosides (Scheme 1) [1].

To study the sugar concentration effect, we used standard conditions, i.e. 1 g of sugar, with or without triethylamine (1 equiv./sugar), and only modified the DMF amounts (5–25 mL) (Table 1). At low xylose concentration (0.27 mol/L), the addition

of triethylamine clearly increased the sugar conversion (runs 1 and 2); this improvement was much more limited in diminishing the DMF amount (runs 3–10). When the sugar concentration reached 1.35 mol/L, the amine addition has no more effect on the reaction efficiency since the results with or without amine were similar (entries 9 and 10). The experiments of runs 1, 2 and 9, 10, which correspond to the lowest and highest sugar concentrations, respectively, have been repeated several times and the results varied from less than 1% to 2%. The same behaviour was observed starting from L-arabinose as sugar [1] (sugar conversion = 31% and 51% under the conditions of runs 1 and 2, respectively, the conversion reaching more than 90% under the conditions of entries 9 and 10). With or without amine, the xylose conversion increased remarkably with the telogen concentration and was almost complete at 1.35 mol/L (Table 1; Fig. 1). We have evaluated the performance of each system at high sugar concentration for a short reaction time (15 min, runs 11 and 12): surprisingly an improvement was observed in the presence of triethylamine (TOF relative to the sugar transformation of 400 and 450 h⁻¹, without and with amine, respectively); such a result was in agreement with the previous Beller's observation [6], that the time to reach the maximum catalyst activity in the butadiene/methanol telomerization is shortened in the presence

Table 1
Effect of xylose concentration in the butadiene telomerization (Pd(acac)₂ as the catalyst precursor)

Run ^a	[Xylose] (mol/L DMF)	Additive	Time (min)	Sugar conversion ^b (%)	Selectivity			Butadiene dimers (%) ^d
					Monoethers ^b		Polyethers (%)	
					Total (%)	<i>l:b</i> ^c		
1	0.27	–	135	39	89	63:37	11 ^e	85
2	0.27	NEt ₃	135	56	95	79:21	5 ^e	77
3	0.34	–	135	60	90	62:38	10 ^e	73
4	0.34	NEt ₃	135	65	93	72:28	7 ^e	66
5	0.45	–	135	64	88	75:25	12 ^e	65
6	0.45	NEt ₃	135	71	91	78:22	9 ^e	55
7	0.67	–	135	83	80	82:18	20 ^e	35
8	0.67	NEt ₃	135	89	78	85:15	22 ^e	35
9	1.35	–	135	98	62	74:26	38 ^f	17
10	1.35	NEt ₃	135	97	62	74:26	38 ^f	22
11	1.35	–	15	63	94	75:25	6	16
12	1.35	NEt ₃	15	74	92.5	75:25	7.5	15
13 ^g	1.35	–	15	88	86	75:25	14	39
14 ^g	1.35	NEt ₃	15	85	86	76:24	14	40

^a Conditions: 1 g of xylose, sugar/Pd/PPh₃/butadiene = 150/1/3/900 or sugar/Pd/PPh₃/NEt₃/butadiene = 150/1/3/150/900, DMF, 75 °C, autoclave of 50 mL.

^b Determined by GC. Selectivity represents the yield based on the amount of consumed D-xylose.

^c Linear/branched telomer, determined by GC.

^d Determined by GC, based on the introduced butadiene.

^e Polyethers composition: diethers ≥ 93%, triethers ≤ 7%.

^f Polyethers composition: diethers = 89%, triethers = 11%.

^g Xylose amount: 3 g in 15 mL instead of 1 g in 5 mL of DMF.

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