Telomerization of Butadiene with L-Arabinose and D-Xylose in DMF: Selective Formation of their Monooctadienyl Glycosides

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Conditions to achieve the palladium-catalysed telomerization of butadiene with L-arabinose and D-xylose as telogens have been identified. With DMF as solvent, optimised ratios of substrate, reactants and catalytic system allowed the selective grafting of one octadienyl chain onto the anomeric hydroxy group.

Since its discovery in 1967[1] the palladium-catalysed telomerization of butadiene in the presence of alcohols or phenols as nucleophiles has been extensively studied and applied to a variety of other nucleophiles.[2] The reaction constitutes an elegant method by which to provide a large range of functionalised compounds that can be used as building blocks for fine chemicals and for industrial applications.[2−4] Thanks to the increasing importance of carbohydrates as cheap and renewable starting materials, the use of these compounds as nucleophiles in telomerization is of great interest with regard to the production of biodegradable non-ionic surfactants.[5] A protected galactose was reported as the first carbohydrate derivative used for telomerization with butadiene.[6] Later on, the subject was studied in depth from both academic and industrial perspectives, telomerization being carried out with free sugars, mainly sucrose, but also glucose or its derivatives, and the reaction being developed in organic (mainly 2-propanol mixtures)[7,8] or aqueous media.[9−11] The catalytic system was based on palladium [especially $Pd(acac)_2$ or $Pd(OAc)_2$] associated with a phosphane that could be water-soluble if required.[9−11] Different variations of the reaction conditions were carried out, allowing high efficiency to be attained,[8] but whatever the medium, the transformation gave complex mixtures of polyethers in which the average degree of etherification of hydroxy groups was difficult to control. The best selectivity for the monooctadienyl ether of sucrose was reported with the use of aqueous NaOH and with 2-propanol as a co-solvent, the average degree of etherification being 1.3.[10] However, the process described in aqueous NaOH was not compatible with reducing sugars such as aldoses;[9,10] furthermore, an alcoholic co-solvent competes with the sugar as nucleophilic species.[7,8] The mechanism of telomerization of butadiene with methanol, established in careful studies by several German teams,[12−14] has been substantiated by DFT calculations.[15] The parameters governing the regioselectivity of the linear or branched chain grafting are quite well controlled with nucleophiles such as methanol[13] or ammonia.[16] The proportion of mono- or polysubstitution by the octadienyl chain has also been studied, starting from bifunctional active hydrogen compounds: a high selectivity towards monosubstituted linear telomer has, for example, been achieved from ethylene glycol in biphasic systems[17] or by use of polymer-bound palladium(0) complexes as catalysts.[18]

We were interested in the possibility of making the most of pentoses, mainly L-arabinose and D-xylose, which are now easily extracted from wheat straw and bran.[19] The telomerization of butadiene with these carbohydrates would constitute an attractive route by which to prepare monoethers directly without the use of protection and deprotection steps. Here we report the results of this study, having succeeded in obtaining good control over the monoetherification of the polyols by an octadienyl chain.

Results and Discussion

The telomerization reaction was carried out in an autoclave (50 mL), with 1 g of L-arabinose (**1**) or D-xylose (**2**) and an excess of butadiene. The reaction products (Scheme 1) were analysed by GC/MS after peracetylation of the mixture and subsequent distillation under vacuum to separate the solvent and the butadiene dimers (1,3,7-octatriene and 4-vinylcyclohexene) from the remaining sugar and the sugar-derived products (see Exp. Sect.). These last were first identified as mono- or polyethers by their mass spectra.

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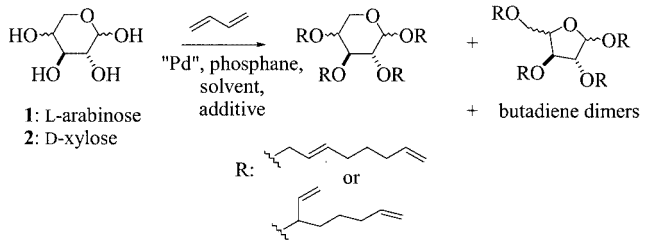


Scheme 1. Telomerization reaction of butadiene with L-arabinose and D-xylose

Our goal in this work was to determine conditions for efficient conversion of the sugar into monooctadienyl ethers, without seeking either a particular regioselectivity or a particular linear/branched C-8 chain ratio in the grafting onto the hydroxy functions. The application of conditions inspired by Hill[7] in an *i*PrOH/H_2O mixture were disappointing, since the degree of conversion attained only 21% and a non-negligible amount of octadienol was observed (Table 1, Entry 1). Since water was a competing reagent, we decided to switch to an exclusive organic medium; DMF, which dissolves the sugar and the reaction products, seemed suitable to us. In this solvent, both pentoses (D-xylose or L-arabinose) exhibited similar behaviour: less than 40% of either sugar was transformed, while the butadiene underwent dimerisation (Entries 2, 3). As the results of telomerization reactions can be improved by addition of base,[20,21] we tested inorganic additives such as Na_2CO_3 and NaOH, but without success. In contrast, addition of triethylamine increased the degree of conversion of the sugar to over 50%, and the selectivity for monoether formation was also improved (Entries 4, 5). Consequently, different tertiary amines were tested (Figure 1).

Several tertiary amines – *i*Pr_2EtN, Et_3N, *i*Pr_2MeN, *n*Pr_3N, DABCO and *i*Pr_3N – provided a beneficial effect in regard to the conversion of the arabinose, although only *i*Pr_2EtN proved to be slightly superior to Et_3N. In the presence of strong bases such as DBU or TMG (tetramethyl guanidine) no improvement was observed. It clearly appears that there is no correlation between the strength of the base and the conversion values. According to Beller,[22] one possible role of added amines might be to facilitate the reduction of Pd^{II} species to Pd^0 complexes. Such a reduction, a mechanism for which has been proposed by Mc Crindle,[23] is classical in π-allyl palladium chemistry.[24]

With the two best amines, we also studied the influence of the amine/Pd ratios, which could be important if the activation step was to concern the reduction of the metal (Table 2). For the degree of conversion of the sugar, the best

Table 1. Preliminary experiments

Entry[a]	Sugar	Solvent	Additive equiv./Pd	Sugar conv.[b] [%]	Selectivity[c] [%] monoethers	polyethers	By-products [%]
1	**1**	*i*PrOH/H_2O (80:20)	–	21	95	5	11[d]
2	**1**	DMF	–	31	84	16	68[e]
3	**2**	DMF	–	39	89	11	85[e]
4	**1**	DMF	NEt_3 (20)	51	90	10	32[e]
5	**2**	DMF	NEt_3 (20)	56	95	5	77[e]

[a] Conditions: $Pd(acac)_2$ 4.4×10^{-5} mol; molar ratio: sugar/butadiene/Pd/PPh_3 = 150:900:1:3; 1 g of pentose in 25 mL of solvent; 75 °C; 140 min. [b] Determined by GC. [c] Evaluated by GC, the polyethers being mainly diethers. [d] By-products consist of butadiene dimers, octadienol as the major compound and its isopropyl ether. [e] By-products are mainly butadiene dimers.

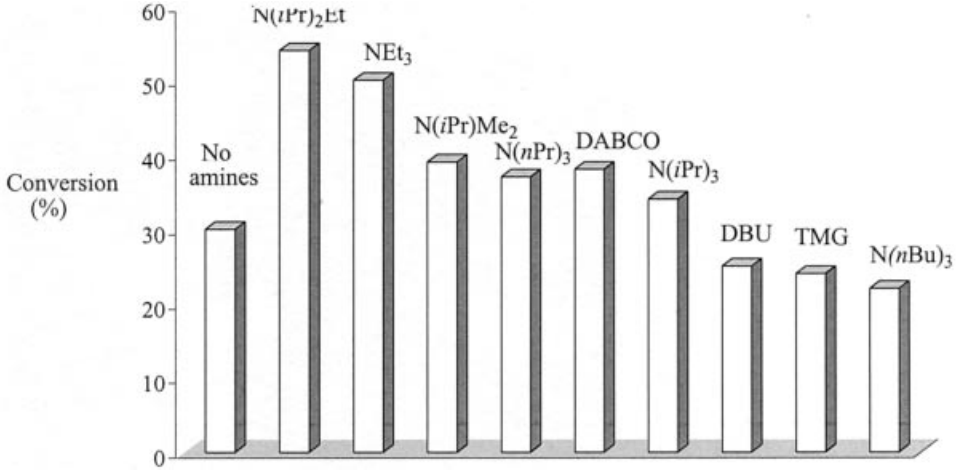


Figure 1. Effect of tertiary amines on the arabinose conversion in butadiene telomerization; conditions: $Pd(acac)_2$ 4.4×10^{-5} mol; molar ratio: L-arabinose/Pd/PPh_3/butadiene/amine = 150:1:3:900:20; temperature 75 °C; time 140 min, 1 g of L-arabinose in 25 mL DMF

Table 2. Influence of the amine/Pd ratios on the arabinose transformation in butadiene telomerization

Entry[a]	Amine molar ratio amine/palladium	Sugar conv.[b] [%]	Selectivity[b] [%] monoethers	polyethers	By-products[c] [%]
1	0	31	84	16	68
2	Et_3N (20)	51	90	10	32
3	Et_3N (84)	53	91	9	10
4	Et_3N (150)	58	91	9	10
5	Et_3N (300)	46	91	9	5
6	$(i\text{Pr})_2\text{EtN}$ (20)	54	94	6	[d]
7	$(i\text{Pr})_2\text{EtN}$ (150)	44	95	5	11
8	$(i\text{Pr})_2\text{EtN}$ (300)	22	100	0	[d]

[a] Conditions: $Pd(acac)_2$ 4.4×10^{-5} mol; molar ratios: sugar/butadiene/Pd/PPh_3 = 150:900:1:3; 75 °C; 140 min, 1 g of L-arabinose in 25 mL DMF. [b] GC determination. [c] By-products are mainly butadiene dimers. [d] Not determined.

ratio was about 150 with triethylamine (Entries 2−5), much lower with diisopropylethylamine (Entries 6−8). In these experiments, the selectivity towards monoetherification was lower in the absence of amine (Entry 1) and remained constant for different amounts of the same amine (Entries 2−4 and 6−8). With triethylamine it seems that an excessive stoichiometry versus the sugar was detrimental to the degree of conversion (Entry 5). No such amine effect has previously been described for a telomerization reaction: even if the amine plays a role during the reduction of palladium salt, it could also stabilise active palladium species by coordination[25,26] or modify the nucleophilic character of the sugar (in establishing hydrogen bonds, for example). When the relative amount of triethylamine was increased, we observed a parallel decrease in the butadiene dimer by-products. Possible explanations could involve both sugar activation or stabilization of a palladium species involved in the telomerization catalytic cycle.

We continued our investigations by studying the influence of the nature and amount of phosphane, usually crucial parameters in telomerization.[2,13,16,22,27,28] The effect of the amount of phosphane is reported in Table 3. With or without amine, one equiv. of phosphane per palladium led to the best degree of conversion of the sugar (Entries 3, 6, 11, 12). The use of one or two equivalents of phosphane also corresponded with a decrease in the loss of butadiene by dimer formation, which could be of interest for practical application (Entries 3, 5, 6, 9−11). The selectivity towards monoethers was influenced by the relative amount of phosphane: the best selectivity was observed for a P/Pd ratio of 3 in the presence of amine (Entries 4, 8) and of 2 in its absence (Entry 2). When the amount of phosphane was below 1 equiv. per palladium, the drop in the level of conversion might be explained by precipitation of palladium black (Entry 7). Such slight precipitation was often observed at the end of the reaction for a P/Pd ratio of 1, while a clear yellow solution resulted for P/Pd = 2 or 3. At this stage of the study, we noticed that a decrease in the amount of solvent may modify the results: both the degree of conversion of the sugar and the selectivity are improved for P/Pd = 2 (Entry 10 versus 9), but they remain similar for P/Pd = 1 (Entry 12 versus 11). We had already noticed some concen-

Table 3. Influence of the amount of triphenylphosphane

Entry[a]	Amine molar ratio amine/palladium	P/Pd	Sugar conv. [%][b]	Selectivity [%] monoethers	polyethers[c]	By-products [%][d]
1	0	3	31	84	16	21
2	0	2	48	88	12	[e]
3	0	1	60	80	20	2
4	$(i\text{Pr})_2\text{EtN}$ (20)	3	54	94	6	15
5	$(i\text{Pr})_2\text{EtN}$ (20)	2	58	90	10	2
6	$(i\text{Pr})_2\text{EtN}$ (20)	1	64	80	20	<1
7	$(i\text{Pr})_2\text{EtN}$ (20)	0.5	38[f]	95	5	[e]
8	Et_3N (150)	3	58	91	9	10
9	Et_3N (150)	2	68	78	22	2
10[g]	Et_3N (150)	2	81	86	12	2
11	Et_3N (150)	1	84	76	24	<1
12[h]	Et_3N (150)	1	85	73	27	[e]

[a] Conditions:. Conditions: $Pd(acac)_2$ 4.4×10^{-5} mol; molar ratios: sugar/butadiene/Pd = 150:900:1; 75 °C; 140 min, 1 g of L-arabinose in 25 mL DMF. [b] GC yields. [c] Diethers are the major products, while yields of triethers remained below 2%. [d] GC yields of butadiene dimers related to the quantity of butadiene introduced (nonane as internal standard). [e] Not determined. [f] Formation of a palladium black precipitate. [g] As Entry 9 in using only 5 mL of DMF. [h] As Entry 11 in using only 5 mL of DMF.

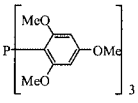
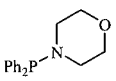
tration effect in the telomerization reaction of butadiene with protected carbohydrates and proposed intervention of these telogens as stabilising ligands.[29]

The above observations prompted us to use more concentrated solutions of sugar (1 g in 5 mL of DMF instead of 25 mL) with a P/Pd ratio of 2, these conditions seeming a good compromise with regard to sugar transformation, monoether formation, the stabilisation of the active palladium species and butadiene dimerisation.

The influence of the nature of the phosphane is reported in Table 4. Since arabinose and xylose gave analogous results under similar conditions (Entries 2 and 3), the runs in this table were carried out indiscriminately with either one of them. In terms of the degree of conversion of the sugar, a methyl or methoxy donating group attached to arylphosphanes seemed more efficient than a chloro group (Entries 3−5 versus 6). We also tested the more strongly donating tris(trimethoxyphenyl)phosphane, the efficiency of which in the telomerization of isoprene with amines was related to its ability to promote the formation of active (L_1Pd^0) complexes,[30] but a drop in the degree of conversion was observed (Entry 7). The use of *o*-tolyl phosphane was beneficial for selectivity towards the monoether, but the degree of conversion of the sugar was slightly reduced (Entry 3). It was interesting to exchange one phenyl group in the PPh_3 for a methyl, since high levels of conversion and selectivity were observed (Entry 8). Other combinations of aryl-alkyl or trialkylphosphanes were less efficient (Entries 9−11). Among the diphosphanes tested, only dppp afforded good results (Entries 12−14), unlike in the telomerization with methanol, where the best activity was observed with dppb, other bidentate ligands being believed to give inactive metallacycles.[28] Some dialkylamino-arylphosphane ligands showed good results (Entries 15, 16), decreasing with monoalkylamino-bis(arylphosphanes) (Entry 17) or triaminophosphane (Entry 18). In this last case, the presence of phosphorus and nitrogen as chelating atoms might entail too strong coordination to the metal, inhibiting the catalytic activity. Finally, triethylphosphite was not suitable for this telomerization reaction (Entry 19).

According to Tolman,[31] concerning the structures of phosphanes, some electronic parameters such as the P-donor character [correlated to the ν(CO) frequencies of complexes $LNi(CO)_3$] and steric effects (evaluated as the ligand

Table 4. Effect of the nature of the phosphane on sugar transformation in butadiene telomerization

Entry[a]	Sugar	Phosphane	Conv.[b] [%]	Selectivity[b] [%]		
				Monoethers	Diethers	Triethers
1[c]	**2**	PPh_3	97	69	28	3
2	**1**	P(*p*tolyl)$_3$	97	54	39	7
3	**2**	P(*p*tolyl)$_3$	99	54	41	5
4	**1**	P(*o*tolyl)$_3$	86	69	25	6
5	**1**	P(*p*MeOC$_6$H$_4$)$_3$	98	56	36	8
6	**1**	P(*p*ClC$_6$H$_4$)$_3$	69	82	13	5
7	**1**		6	84	12	4
8	**2**	PPh_2Me	93	78	22	0
9	**2**	P(biph)(*t*Bu)$_2$	11	100	0	0
10	**2**	P(biph)(Cy)$_2$	48	100	0	0
11	**2**	P(*n*Bu)$_3$ or P(*t*Bu)$_3$	< 2	100	0	0
12	**2**	dppe	8	100	0	0
13	**2**	dppp	71	87	13	0
14	**2**	dppb	8	100	0	0
15	**2**	Ph_2PNEt_2	95	55	41	4
16	**2**		97	65	33	2
17[c]	**2**	*n*-$C_{10}H_{21}N[PPh_2]_2$	46	100	0	0
18	**2**	P[NEt$_2$]$_3$	3	100	0	0
19	**2**	P(OEt)$_3$	8	88	12	0

[a] Conditions: $Pd(acac)_2$ 4.4×10^{-5} mol; molar ratios sugar/Pd/P/butadiene/Et_3N = 150:1:2:900:150; 75 °C; 45 min; 1 g of sugar in 5 mL DMF. [b] Determined by GC. Under these conditions, the loss of butadiene by dimerization was generally low (<3%). [c] Reaction time: 30 min. Abbreviations: biph = *o*-biphenylyl, Cy = cyclohexyl, dppe = diphenylphosphanylethane, dppp = diphenylphosphanylpropane, dppb = diphenylphosphanylbutane.

cone angle θ), could influence the reaction efficiency. The steric and electronic maps of the ligands[31,32] we have used are shown in Figure 2. The best ligands associated with the best sugar conversions are situated in a narrow horizontal region corresponding to medium P-donating ligands. The cone angles of these ligands varied from 136° for PPh_2Me to 194° for tri(*o*Tol) phosphane. Such results indicated that electronic parameters were prevailing over steric ones with regard to the degree of conversion of the sugar. Crowding of the phosphane, however, had an influence on the course of the reaction: the reaction rate decreased as shown in Entries 1 and 4, in which the degree of conversion of the sugar reached 97% in 35 min with PPh_3 and 86% in 45 min with $P(o\text{Tol})_3$. In Table 4, a high selectivity for the monotelomer is often concomitant with a low degree of conversion. Accordingly, we might suspect that the low level of conversion observed with the use of tris(trimethoxyphenyl)phosphane (Entry 7) is correlated with its strong basic character,[33] and the good selectivity towards monoethers may be a consequence of the low conversion or due to steric effects.

The observation of a high selectivity towards the monosubstitution product is also an important feature corresponding to our objectives. Obviously, for a high degree of conversion of the sugar, the initially formed monoether became a competitive substrate in telomerization. We have studied the monoethers' ability to undergo such a transformation, carrying out reactions for either 140 or 320 min and with a PPh_3/Pd ratio of 1 (Table 5). Under these conditions, the behaviour of the monoether seemed to depend on the nature of the additive. A prolonged reaction time significantly increased the degree of conversion of the sugar only in the absence of amine (Entries 1, 2 vs. Entries 3, 4 or 5, 6) and curiously the transformation of monoethers into polyethers was not operative with triethylamine as additive. The black palladium precipitate observed at the end of the longer reaction time (Entries 4, 6) may partially explain the catalyst deactivation.

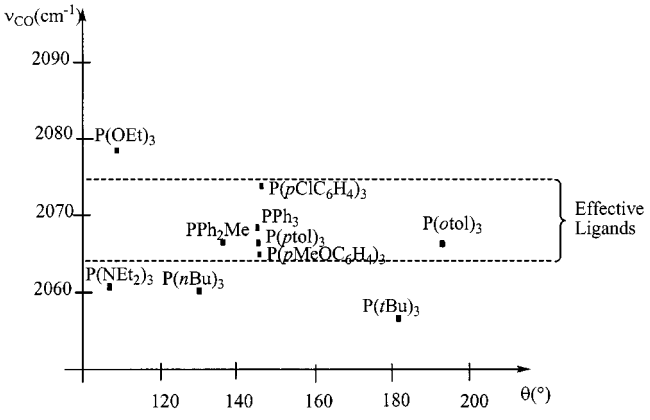


Figure 2. Steric and electronic map of the phosphanes; the ν_{CO} values stem from IR studies of $[Ni(CO)_3PR_3]$ complexes by Tolman[31] and θ correspond to the cone angles of the phosphane[31,32]

Solvents other than DMF were also tested (Table 6). THF, CH_2Cl_2 or toluene, which did not dissolve the sugar

Table 5. Influence of the reaction time on the selectivities of sugar transformation.

Entry[a]	Time (min)	Additive (molar ratio amine/Pd)	Sugar conv. [%][b]	Selectivity [%][b] monoethers	polyethers
1	140	–	60	80	20
2	320	–	72	69	31
3	140	Et_3N (150)	84	76	24
4	320	Et_3N (150)	88	76	24
5	140	$(i\text{Pr})_2\text{EtN}$ (20)	64	80	20
6	320	$(i\text{Pr})_2\text{EtN}$ (20)	67	64	36

[a] Conditions: $Pd(acac)_2$ 4.4×10^{-5} mol; molar ratios sugar/Pd/PPh_3/butadiene = 150:1:1:900/; 75 °C; 1 g of L-arabinose in 25 mL DMF. [b] Determined by GC.

Table 6. Solvent effect in butadiene telomerization with arabinose

Entry[a]	Solvent (g sugar/mL)	Time (min)	Sugar conv. [%][b]	Selectivity [%][b] monoethers	diethers	triethers	Butadiene dimers [%][c]
1	DMF (1/25)	140	68	78	22	0	2
2	THF (0.5/25)	140	0	0	0	0	[d]
3	CH_3CN (0.5/20)	140	96	48	49	3	3
4	CH_2Cl_2 (0.5/20)	180	29	83	17	0	[d]
5	*t*BuOH (1/15)	120	100	21	57	22	[d]
6	DMSO (1/5)	45	85	79	15	5	5
7	Toluene (0.5/20)	180	33	100	0	0	17

[a] Conditions: $Pd(acac)_2$ 4.4×10^{-5} mol; molar ratios L-arabinose/Pd/PPh_3/butadiene/NEt_3 = 150:1:2:900:150 (Entries 1, 5, 6) and 75:1:2:900:150 (Entries 2, 3, 4, 7); 80 °C except Entry 1: 75 °C. [b] Determined by GC. [c] GC yields of butadiene dimers related to the quantity of butadiene introduced (nonane as internal standard). [d] Not determined.

Table 7. Effect of the nature of the palladium precursor in the telomerization of butadiene with L-arabinose

Entry[a]	"Pd"	Sugar conv. [%][b]	Selectivity [%] monoethers (yield[c])	diethers	triethers
1	$Pd(acac)_2$	81	86 (69)	12	2
2	$Pd(OAc)_2$	94	73 (68)	24	3
3	$PdCl_2$	8	100 (8)	0	0
4	$PdCl_2(PhCN)_2$ or $PdCl_2(MeCN)_2$	10	100 (10)	0	0
5[d]	$Pd_2(dba)_3{\cdot}CHCl_3$	79	90 (71)	9	1

[a] Conditions: Pd 4.4×10^{-5} mol; molar ratios L-arabinose/Pd/PPh_3/butadiene/NEt_3 = 150:1:2:900:150; 75 °C; 45 min; 1 g of pentose in 5 mL DMF. [b] GC yields. [c] total yield of monoethers (conv. × selectivity). [d] PPh_3/Pd = 1.

at room temperature, afforded poor levels of conversion (Entries 2, 4 and 7). The enhanced reactivity evident in acetonitrile (Entry 3) and *tert*-butyl alcohol (Entry 5) was detrimental to the monoether selectivity. DMSO (Entry 6) would be the best solvent in terms of the GC results. However, the difficulties in removing this solvent from the products made us prefer DMF.

Other catalytic precursors were examined (Table 7). Except with palladium complexes containing chloride ions (Entries 3, 4), we observed comparable results for the total yields of monoethers (Entries 1, 2, 5). The low reactivity when $PdCl_2$ is employed could not be attributed to its poor solubility in the reaction medium (Entry 3), since the use of the more soluble $PdCl_2(RCN)_2$ [R = Ph or Me] did not provide any improvement (Entry 4). Such an inhibition of palladium reactivity by chloride ions is not a general feature of the telomerization reaction,[30] but has previously been noticed and explained in terms of the strong coordinating properties of halogen in relation to other ligands.[34] With other precursors, the variations concern the conversion and the selectivity values. $Pd(acac)_2$ remained the best catalyst source, if the possible reuse of the unchanged sugar is taken into account (Entry 1). Indeed, $Pd(OAc)_2$ gave the best degree of conversion of the sugar, but with a lower selectivity (Entry 2). With $Pd_2(dba)_3{\cdot}CHCl_3$ as catalyst (Entry 5), the results were similar to those seen with $Pd(acac)_2$. Thus, it appeared to be no advantage in starting from Pd^0 rather than Pd^{II} as the palladium source, as already mentioned for butadiene telomerization with methanol.[35]

The structures of the major resulting materials (Figure 3) were established by their transformation into peracetylated derivatives, followed by purification. The obtained products were compared with the peracetylated starting sugars[36] and the compounds resulting from the telomerization of butadiene with 2,3,4-tri-*O*-acetylated pentopyranoses.[29]

The major ethers consist of approximately 50% of **3α** and 26% of **3β** from D-xylose and 39% of **4α**, 22% of **4β**, 4% of **5α** and 4% of **5β** from L-arabinose. The other products included isomers of the above compounds with branched chains instead of linear ones and isomeric forms of di- and tri-octadienylethers, no C-4 or C-16 adducts being detected by GC/MS. During this work we did not determine the linear/branched ratio exactly, in view of the complicated mixtures obtained, the branched compounds being found, however, in non-negligible amounts (l/b around 80:20 from D-xylose). During the first chain grafting, etherification occurred mainly at the anomeric hydroxy group, which is probably due to its higher acidity. Indeed, the anomeric hydroxy group ($pK_a \approx 12$) is more acidic than simple alcohols ($pK_a \approx 16$), due to inductive electron withdrawal by the endocyclic oxygen.[37] As a consequence, the anomeric hydroxy proton is more active during the key step of protonation of the (η^1,η^3-octadienyl)palladium intermediate,[12,13] inducing the observed selectivities. The xylose derivatives adopted the pyranose forms while the furanose forms were also present in the arabinose derivatives. As we have previously discussed,[29] the ratios of the glycoside tautomers are different from those in the starting materials.

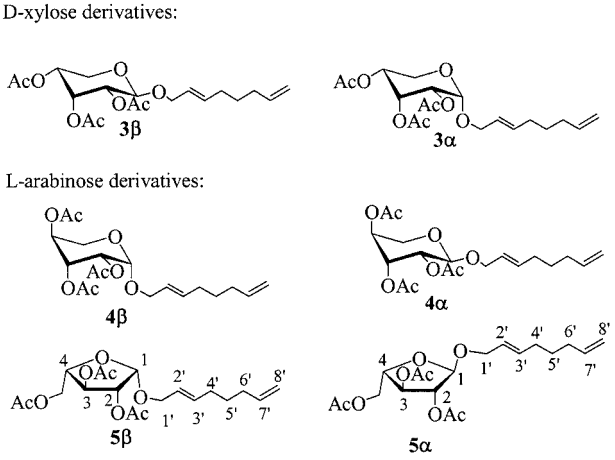


Figure 3. Structures of the major compounds resulting from the telomerization after their acetylation

Conclusion

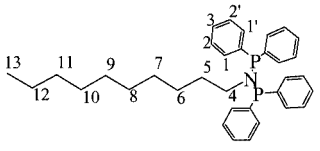
By careful modification of the experimental conditions, we have succeeded in the selective glycosidation of free pentoses by a Pd-catalysed telomerization of butadiene in DMF. The catalytic system has been optimised by adjustment of quantities of amines and phosphanes, the latter having medium donating properties. The process, which re-

quires neither activation nor protection of the sugar and the glycosyl acceptor, provides surfactant molecules with non-ionic and biodegradable heads.[38]

Experimental Section

General: ^{1}H and ^{13}C NMR were recorded on a Bruker AC 500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125.7 MHz) and referenced to TMS. Elemental analyses were carried out on a Perkin−Elmer CHN 2400 instrument. GC analyses were recorded on a Hewlett−Packard HP-6890 gas chromatograph, fitted with a DB-1 capillary column (25 m, 0.32 mm), a flame ionisation detector and a HP-3395 integrator. GC/MS spectra (EI or CI-NH_3) were performed on a Finnigan Trace GC 2000 Series Thermoquest spectrometer, fitted with a DB-1 capillary column (25 m, 0.32 mm) and under the following conditions (for the sugar derivatives): helium as vector gas (0.5 bar), injector: 250 °C, column: 150−300 °C (5 °C/min). Chromatography was carried out on SDS Silica 60 (40−63 μm), Art 2050044 (flash chromatography, petroleum ether/ethyl acetate, 1:1 for L-arabinose derivatives and 7:3 for D-xylose derivatives), silica 60 F_{254} (TLC plates) or semi-preparative HPLC, LC-10AS Shimadzu, UV detection (210 nm), column Si-60 LiChrospher, 10 μm (elution with hexane/2-propanol, 97:3, 3.5 mL/min for L-arabinose derivatives and 99:1, 5 mL/min for D-xylose derivatives).

The solvents, the substrates L-arabinose and D-xylose and the Pd^{II} catalysts were commercially available (Aldrich, Acros or Strem Chemicals) and were used as received. $Pd_2(dba)_3{\cdot}CHCl_3$ was prepared by a literature method.[39] Butadiene N25 from Air Liquide was used without further purification. The amines employed were distilled from KOH before use. Commercial phosphanes from Strem Chemicals were used as supplied and aminodiphenylphosphanes prepared according to the literature,[40,41] morpholinodiphenylphosphane[40] and *N,N*-diethylaminophosphane[41] having been described.



N,N-bis(diphenylphosphanyl)decylamine

A solution of Ph_2PCl (10 mmol, 1.8 mL) in diethyl ether (10 mL) was added over 2 h, at −20 °C under argon, to a solution of decylamine (5 mmol, 1 mL) in Et_3N (5 mL). After further stirring at room temperature for 4 h, the suspension was filtered through Celite to remove the triethylammonium salt. Diethyl ether was evaporated under reduced pressure to afford the labile *N,N*-bis(diphenylaminophosphanyl)decylamine as a yellow oil: 1.05 g, 40%. IR: $\tilde{\nu}$ = 2923, 2853, 1961, 1893, 1819, 1774, 1590−1436, 1206, 1122, 743 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.75−1.25 (m, 19 H, 5−13 H), 3.15 (m, 2 H, 4-H), 7.15 −7.35 (m, 20 H, 1-H, 1′-H, 2-H, 2′-H, 3-H) ppm. ^{13}C NMR (250 MHz, $CDCl_3$): δ = 14.0 (C-13), 22.6−29.3 (m, C6−10, C-12), 31.2 (C-11), 31.8 (C-5), 53.0 (t, J_{C-N} = 11 Hz, C-4), 127.9−139.6 (m, C_{arom}) ppm. ^{31}P NMR (250 MHz, $CDCl_3$): δ = 62.6 ppm. $C_{34}H_{41}NP_2{\cdot}HCl$ (561.5): calcd. C 72.65, H 7.53, N 2.49; found C 71.41, H 7.70, N 2.42 (the compound is easily oxidized, explaining the deviation of the elemental analysis). GC/MS (EI): *m/z* = 526 [M +1] (100).

General Procedure for the Telomerization of Butadiene with Pentoses: $Pd(acac)_2$ and the ligand were charged into a sealed 50-mL stainless-steel autoclave (Parr Instrument Company). The autoclave was evacuated and filled with argon three times. A degassed DMF solution of the pentose was transferred under argon from a Schlenk tube into the autoclave. Gaseous 1,3-butadiene was condensed at −20 °C in a Schlenk tube and then transferred into the cooled autoclave. After closure, the autoclave was placed in an oil bath at 75 °C. Stirring was started for the time indicated in Tables 1−7. After cooling, remaining butadiene, volatile dimers and solvent were condensed in a Schlenk tube. Nonane was then added as internal standard in order to quantify the butadiene dimers by GC (isotherm 50 °C; 15 min, and then: 50−150 °C, 10 °C/min).

The residual mixture containing unreacted pentoses and octadienyl ethers of pentoses was acetylated with an excess of acetic anhydride/pyridine over 12 h. After extraction with ether the mixture was analysed by GC/MS, with 9-decen-1-ol as standard. The groups of compounds were separated by successive chromatography.

Three fractions were then collected:

The least polar fraction (R_f > 0.8, petroleum ether/ethyl acetate, 7:3) was a mixture of peracetylated polyoctadienyl ethers of pentoses and butadiene oligomers. GC/MS-CI (NH_3) confirmed the presence of peracetylated di- and trioctadienyl ethers of pentoses.

Peracetylated trioctadienyl ethers of L-arabinose: T_r = 30.49, 30.73, 31.04, 31.36, 31.41, 31.70, 31.02. MS/CI (NH_3): *m/z* (%) = 534 (100) [M + 18], 391 (25) [M − OC_8H_{13}].

Peracetylated dioctadienyl ethers of L-arabinose: T_r = 25.97, 25.07, 25.37, 25.34, 25.69, 25.77 min. MS/CI (NH_3): *m/z* (%) = 468 (57) [M + 18], 325 (100) [M − OC_8H_{13}].

The fraction corresponding to a R_f of 0.6 (petroleum ether/ethyl acetate, 7:3) was a mixture of peracetylated monooctadienyl ethers as analysed by GC/MS-CI (NH_3).

T_r = 15.48, 15.95, 17.74, 17.98 min. MS/CI (NH_3): *m/z* (%) = 402.2 (100) [M + 18].

The most polar fraction contained the peracetylated residual pentose in four forms (pyranosic, furanosic and anomeric isomers).

T_r = 9.44, 9.64, 9.90, 10.04 min. MS/CI (NH_3): *m/z* (%) = 336 (100) [M + 18], 259 [M − OAc].

The following glycosides exhibit spectroscopic data analogous to those previously described:[29] 2′-(*E*)-7′-octadienyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (**3β**), 2′-(*E*)-7′-octadienyl 2,3,4-tri-*O*-acetyl-α-D-xylopyranoside (**3α**), 2′-(*E*)-7′-octadienyl 2,3,4-tri-*O*-acetyl-α-L-arabinopyranoside (**4α**), 2′-(*E*)-7′-octadienyl 2,3,4-tri-*O*-acetyl-β-L-arabinopyranoside (**4β**). Two monooctadienyl ethers, 2′-(*E*)-7′-octadienyl 2,3,4-tri-*O*-acetyl-β-L-arabinofuranoside (**5β**) and 2′-(*E*)-7′-octadienyl 2,3,4-tri-*O*-acetyl-α-L-arabinofuranoside (**5α**), were also isolated and characterized.

2′-(*E*)-7′-Octadienyl 2,3,5-Tri-*O*-acetyl-β-L-arabinofuranoside (5β): IR: $\tilde{\nu}$ = 2926, 2843, 1742, 1441, 1375, 1223, 700 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.45 (quint, 2 H, $J_{5',4'} = J_{5',6'}$ = 7.3 Hz, 5′-H), 2.00−2.10 (m, 13 H, −COC*H*$_3$, 4′-H, 6′-H), 3.95 (dd, 1 H, $J_{1'b,1'a}$ = 12.2, $J_{1'b,2'}$ = 6.8 Hz, 1′b-H), 4.07 (ddd, 1 H, $J_{4,3}$ = 6.7, $J_{4,5a}$ = 4.1, $J_{4,5b}$ = 5 Hz, 4-H), 4.12−4.22 (m, 2 H, 5b-H, 1′a-H), 4.45 (dd, 1 H, $J_{5a,4}$ = 4.1, $J_{5a,5b}$ = 11.5 Hz, 5a-H), 4.95−5.05 (m, 3 H, 2-H, 8′a-H, 8′b-H), 5.12 (d, 1 H, $J_{1,2}$ = 4.6 Hz, 1-H), 5.38 (dd, 1 H, $J_{3,2}$ = 6.7, $J_{3,4}$ = 6.7 Hz, 3-H), 5.44 (ddd, 1 H, $J_{2',1'a}$ = 7.1, $J_{2',1'b}$ = 6.8, $J_{2',3'}$ = 15.5 Hz, 2-H), 5.70 (dt, 1 H, $J_{3',2'}$ = 15.5, $J_{3',4'}$ = 6.7 Hz, 3′-H), 5.80 (ddt, 1 H, $J_{7',6'a}$ = 6.8, $J_{7',8'a}$ = 10, $J_{7',8'b}$ = 18 Hz, 7′-H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 20.5, 20.6, 20.7 (3 *C*H$_3$), 28.1 (C-5′), 31.5, 33.1 (C-4′, C-6′), 65.3 (C-5), 68.3 (C-1′), 75.8 (C-3), 76.7 (C-2), 78.6 (C-4), 99.0 (C-1), 114.6 (C-8′), 125.2 (C-2′), 135.2 (C-3′), 138.5 (C-7′) 170.2, 170.3,

170.6 (3 *C*O) ppm. $C_{19}H_{28}O_8$ (384.4): calcd. C 59.36, H 7.34; found C 59.52, H 7.63. GC/MS (NH_4^+): *m*/*z* = 402 [M + 18] (100), 259 [M − 125], 78%.

2′-(*E*)-7′-Octadienyl 2,3,5-Tri-*O*-acetyl-α-L-arabinofuranoside (5α): IR: $\tilde{\nu}$ = 2926, 2843, 1742, 1441, 1375, 1223, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.45 (quint, 2 H, $J_{5',4'} = J_{5',6'} = 7.5$ Hz, 5′-H), 2.00−2.15 (m, 13 H, −COC*H*$_3$, 4′-H, 6′-H), 4.10−4.20 (m, 3 H, 3-H, 5b-H, 1′b-H), 4.30 (m, 3 H, 4-H, 5a-H, 1′a-H), 4.95−5.05 (m, 3 H, 2-H, 8′a-H, 8′b-H), 5.15 (d, 1 H, $J_{1,2} = 2.5$ Hz, 1-H), 5.50 (ddd, 1 H, $J_{2',1'a} = 6.8$, $J_{2',1'b} = 5.6$, $J_{2',3'} = 12.3$ Hz, 2′-H), 5.70 (dt, 1 H, $J_{3',2'} = 12.3$, $J_{3',4'} = 6.7$ Hz, 3′-H), 5.80 (ddt, 1 H, $J_{7',6'} = 6.6$, $J_{7',8'a} = 6.7$, $J_{7',8'b} = 17.1$ Hz, 7′-H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 20.5, 20.6, 20.7 (3 *C*H$_3$), 28.1 (C-5′), 31.6, 33.1 (C-4′, C-6′), 63.6 (C-5), 68.7 (C-1′), 76.8 (C-3), 79.5 (C-2), 83.0 (C-4), 107.4 (C-1), 114.6 (C-8′), 125.3 (C-2′), 134.6 (C-3′), 138.4 (C-7′) 170.2, 170.3, 170.6 (3 *C*O) ppm. $C_{19}H_{28}O_8$ (384.4): calcd C 59.36, H 7.34; found C 59.52, H 7.63. GC/MS (NH_4^+): *m*/*z* = 402 [M + 18] (100), 259 [M − 125], 78%.

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