

# 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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**Keywords:** Amine additives; Concentration effects; Palladium; Telomerization; Xylopyranosides

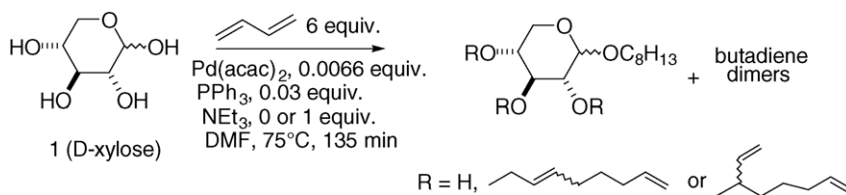
## 1. Introduction

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 ( $\eta^1, \eta^3$ -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<sup>-1</sup>, 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)<sub>2</sub> as the catalyst precursor)

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

<sup>a</sup> Conditions: 1 g of xylose, sugar/Pd/PPh<sub>3</sub>/butadiene = 150/1/3/900 or sugar/Pd/PPh<sub>3</sub>/NEt<sub>3</sub>/butadiene = 150/1/3/150/900, DMF, 75 °C, autoclave of 50 mL.

<sup>b</sup> Determined by GC. Selectivity represents the yield based on the amount of consumed D-xylose.

<sup>c</sup> Linear/branched telomer, determined by GC.

<sup>d</sup> Determined by GC, based on the introduced butadiene.

<sup>e</sup> Polyethers composition: diethers ≥ 93%, triethers ≤ 7%.

<sup>f</sup> Polyethers composition: diethers = 89%, triethers = 11%.

<sup>g</sup> Xylose amount: 3 g in 15 mL instead of 1 g in 5 mL of DMF.

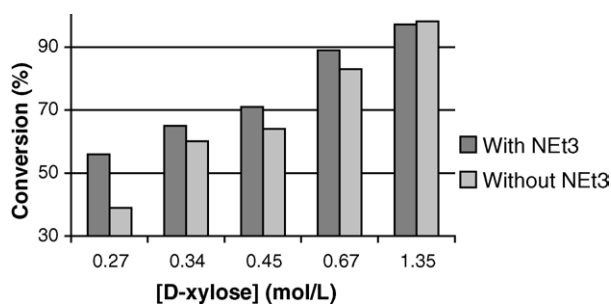


Fig. 1. Influence of triethylamine and xylose concentration on the sugar conversion in butadiene telomerization (reaction time: 135 min).

of triethylamine. Under these conditions, except the use of 3 g of xylose in 15 mL of DMF (runs 13 and 14) instead of 1 g/5 mL, the sugar conversions increased and were close to each other with or without triethylamine, the reaction being very fast in both cases. The differences in runs 13, 14 compared to runs 11, 12 could be related to the amount of gaseous butadiene dissolved in the liquid phase. Indeed in Table 1, the decrease of the DMF volume from 25 mL (runs 1 and 2) to 5 mL (runs 9–12) corresponds to a decrease of the dissolved butadiene; this is borne out by the quantity of butadiene in the gas phase proportional to its pressure at 75 °C at almost constant volume (e.g. runs 1, 2: 1 bar; runs 9, 10: 4–5 bar). In parallel, the amount of butadiene dimers decreased continuously while the sugar concentration

increased in diminishing the DMF volume. The faster reactions observed in runs 13, 14 (initial butadiene pressure of 4.2 and 3.3 bar, respectively) relatively to runs 11, 12 (initial butadiene pressure of 6.0 and 5.1 bar, respectively) could thus be due to the greater amount of dissolved butadiene (which is corroborated by a concomitant increase of the dimers and polyethers formation). Following the results of Table 1, high sugar concentrations entail high sugar conversions and short reaction times if the quantity of dissolved butadiene is sufficient. At low sugar concentration, an excess of butadiene in solution only facilitates the dimers formation; nevertheless, the addition of triethylamine improves the sugar conversion. Concerning the mono/poly-ethers repartition, the presence of triethylamine exhibited a slight effect at low sugar concentration in favour of the monografting, even for a higher sugar conversion (Table 1, runs 1 and 2). The selectivity toward the monoethers formation was about 90% until a sugar concentration of 0.45 mol/L and 70% conversion; after it decreased in both cases, since diethers (runs 7 and 8) and even triethers (runs 9 and 10) were observed, the formed monoethers becoming competitive substrates in the telomerization reaction for prolonged reaction times (runs 9, 10 versus runs 11, 12).

Since triethylamine and xylose are both reducing species, we attempted to evaluate their possible intervention in the metal reduction step of the reaction, starting with either xylose and a palladium(0) precursor (Table 2), or with methylxylopyranoside and a palladium(II) precursor (Table 3). Whatever the

Table 2  
Effect of xylose concentration in butadiene telomerization (Pd<sub>2</sub>(dba)<sub>3</sub> as the catalyst precursor)

| Run <sup>a</sup> | [Xylose]<br>(mol/L DMF) | Additive         | Time (min) | Sugar<br>conversion <sup>b</sup> (%) | Selectivity             |                         |                                         | Butadiene<br>dimers (%) <sup>d</sup> |
|------------------|-------------------------|------------------|------------|--------------------------------------|-------------------------|-------------------------|-----------------------------------------|--------------------------------------|
|                  |                         |                  |            |                                      | Monoethers <sup>b</sup> |                         | Polyethers <sup>b</sup><br>(%) (di:tri) |                                      |
|                  |                         |                  |            |                                      | Total (%)               | <i>l:b</i> <sup>c</sup> |                                         |                                      |
| 15               | 0.27                    | –                | 135        | 42                                   | 93                      | 90:10                   | 7 (100:0)                               | 92                                   |
| 16               | 0.27                    | NEt <sub>3</sub> | 135        | 50                                   | 98                      | 82:18                   | 2 (100:0)                               | 82                                   |
| 17               | 1.35                    | –                | 135        | 96                                   | 69                      | 83:17                   | 31 (84:16)                              | 17                                   |
| 18               | 1.35                    | NEt <sub>3</sub> | 135        | 97                                   | 63                      | 84:16                   | 37 (80:20)                              | 18                                   |
| 19               | 1.35                    | –                | 15         | 87                                   | 77                      | 91:9                    | 23 (74:26)                              | 17                                   |
| 20               | 1.35                    | NEt <sub>3</sub> | 15         | 96                                   | 73                      | 71:29                   | 27 (88:12)                              | 17                                   |

<sup>a</sup> Conditions: 1 g of xylose, sugar/Pd/PPh<sub>3</sub>/butadiene = 150/1/1/900 or sugar/Pd/PPh<sub>3</sub>/NEt<sub>3</sub>/butadiene = 150/1/1/150/900, DMF, 75 °C, autoclave of 50 mL.

<sup>b</sup> Determined by GC.

<sup>c</sup> Linear/branched telomer, determined by GC.

<sup>d</sup> Determined by GC, based on the introduced butadiene.

Table 3  
Effect of methyl xylopyranoside concentration in butadiene telomerization (Pd(acac)<sub>2</sub> as the catalyst precursor)

| Run <sup>a</sup> | [Sugar]<br>(mol/L DMF) | Additive<br>(amine/Pd = 150) | Time    | Sugar<br>conversion <sup>b</sup> (%) | C-8 grafting: selectivity   |                         |                                         | Butadiene<br>dimers <sup>c</sup> (%) |
|------------------|------------------------|------------------------------|---------|--------------------------------------|-----------------------------|-------------------------|-----------------------------------------|--------------------------------------|
|                  |                        |                              |         |                                      | Monoethers <sup>b</sup> (%) |                         | Polyethers <sup>b</sup><br>(%) (di:tri) |                                      |
|                  |                        |                              |         |                                      | Total (%)                   | <i>l:b</i> <sup>c</sup> |                                         |                                      |
| 21               | 0.24                   | –                            | 135 min | 3                                    | 100                         | 0                       | 0                                       | 83                                   |
| 22               | 0.24                   | NEt <sub>3</sub>             | 135 min | 6                                    | 100                         | 0                       | 0                                       | 85                                   |
| 23               | 0.24                   | –                            | 16 h    | 14                                   | 95                          | 5 (100:0)               | 5 (100:0)                               | 92                                   |
| 24               | 0.24                   | NEt <sub>3</sub>             | 16 h    | 16                                   | 96                          | 4 (100:0)               | 4 (100:0)                               | 91                                   |
| 25               | 1.22                   | –                            | 135 min | 52                                   | 84                          | 16 (81:19)              | 16 (81:19)                              | 17                                   |
| 26               | 1.22                   | NEt <sub>3</sub>             | 135 min | 49                                   | 86                          | 14 (85:15)              | 14 (85:15)                              | 15                                   |

<sup>a</sup> Conditions: 1 g of xyloside, sugar/Pd/PPh<sub>3</sub>/butadiene = 150/1/3/900, DMF, 75 °C, autoclave of 50 mL.

<sup>b</sup> Determined by GC.

<sup>c</sup> Determined by GC, based on the introduced butadiene.

catalyst precursor or the substrate, no telomerization occurred in the absence of a phosphine, meaning its determining role to afford active species. Even if only one equivalent of ligand per palladium is required to promote and sustain the catalytic cycle [11,21], it has to exhibit medium donating properties when pentoses are the telogens [1].

At low sugar concentrations, the conversion induced by  $\text{Pd}_2(\text{dba})_3$  was lower in the absence of amine (runs 15 and 16) but this difference is weaker than in Table 1. At higher xylose concentrations, the difference disappeared in 135 min for high sugar conversions (runs 17 and 18) but remained for a short reaction time (runs 19 and 20). From these observations, it appears that the amine may influence the efficiency of the telomerization even with  $\text{Pd}(0)$  as catalyst precursor.

Methylxyloside was much less reactive than the free sugar and whatever its concentration, the addition of triethylamine had no significant effect on the reaction efficiency (runs 21–26). Thus, and as previously pointed out [22], the addition of a reducing agent is not required in the telomerization reaction. As above, however, the substrate conversion increased strongly with its concentration. These high concentrations conditions (Table 3, run 25) have been applied to the monotelomers ( $l/b = 79/21$ ) leading to 29% conversion and 100% selectivity to the dioctadienyl ethers (Scheme 2), via a telomerization slower than for methylxyloside (Scheme 2 versus run 25), the linear substrate being, however, more reactive than the branched isomer, since the  $l/b$  ratio of the recovered monotelomers was 73/27.

From the experiments reported in Tables 1–3, it appeared that in DMF, a greater reactivity was observed at higher sugar concentrations, whatever the substrate and the catalyst precursor. Under the high concentrations conditions, the telogens reactivity was in the order: free sugar  $\gg$  methylxyloside  $>$  octadienylxyloside.

The data of Table 3 suggest that the role of the tertiary amine towards a free sugar could be the deprotonation of the substrate. The reaction generating charged species  $[(\text{NHEt}_3)^+(\text{xyIO})^-]$ , could only take place from the anomeric hydroxyl, the  $\text{p}K_a$  of which being about 12 [23], and compatible with that of triethylamine ( $\text{p}K_a = 11$ , in water at 25 °C), while the other hydroxyl groups exhibit classical alcohols properties with  $\text{p}K_a$ 's about 16. Since the anomeric hydroxyl is masked in methylxyloside, the acid–base reaction cannot occur. The situation is similar in the case of octadienylxylosides, their lower reactivity could stem from a steric factor.

In the experiments of Table 1, the branched telomers were formed in significant amounts. At the low sugar concentrations, the amine influence concerns not only the conversions and the

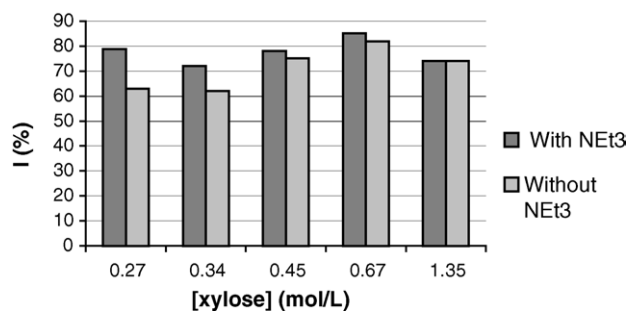
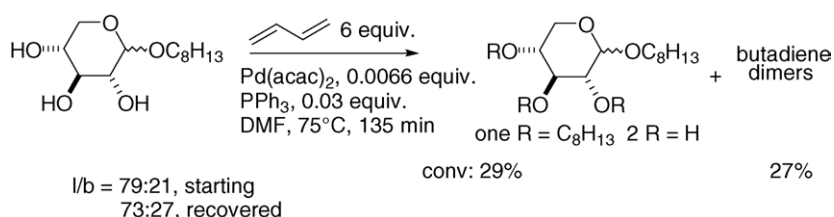


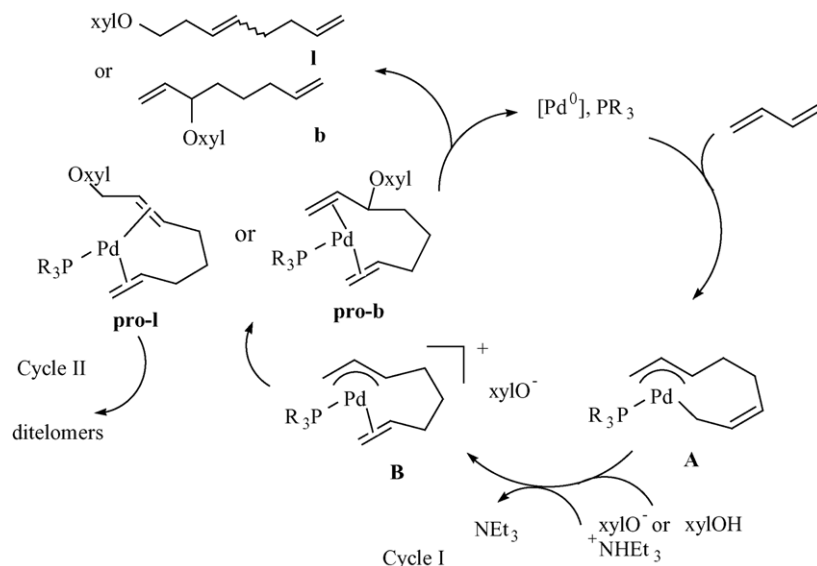
Fig. 2. Influence of triethylamine and xylose concentration on the telomers repartition (% of linear isomers) in butadiene telomerization (runs 1–10).

number of grafted chains, but also the  $l/b$  ratios, the proportion of linear isomers being higher in the presence of  $\text{NEt}_3$  (Fig. 2). In contrast, the  $l/b$  ratios become similar with or without amine for elevated xylose concentrations. The amine effect is less clear with a  $\text{Pd}(0)$  catalyst precursor (Table 2). For these runs, the selectivity towards the  $l$  telomers could be due to the low phosphine/palladium ratio [12,19].

According to the catalytic cycle proposed by Jolly and co-workers [11], the complexes **A** and **B** constitute key intermediates (Scheme 3). The  $(\eta^1, \eta^3\text{-octadienyl})\text{palladium}$  complex **A** is protonated [11,24] by the xylose itself ( $\text{xyIOH}$ ) or its ammonium salt, leading to **B**. Attack of the counter anion ( $\text{xyIO}^-$ ) on the  $\eta^3$ -allyl moiety affords the precursors of the  $l/b$  isomers, the reactivity of **B** governing the results. In the presence of 3  $\text{PPh}_3/\text{Pd}$ , the open complex **C** should be formed (Scheme 4) [12,19,25]. Several other potential ligands exist in the medium, inducing easy exchanges [26]: they include the substrate (xylose), the additive ( $\text{NEt}_3$ ), the reactant (butadiene) and the solvent, leading to various complexes like **D–F**. The telomerization reaction proceeding under kinetic control [5,12], the nucleophilic attack of the xylosyl anion on **B–F** occurs at different rates and with different regioselectivities. Such an attack on  $\pi$ -allylpalladium complexes is strongly dependent on steric and electronic parameters in the classical “Tsuji–Trost” substitution [27] or in the telomerization reactions [12,19]. The differences observed in Fig. 2 may be explained by comparison of the nature of the invoked **B–F** complexes, their relative amounts varying with the reactants concentrations. In complexes of this type, assumed to be square planar [12,19], the electronic influence is very strong for two ligands in the *trans*-position to each other. Thus,  $\pi$ -acceptor ligands, such as phosphine and olefinic linkage will reduce the electron density at the opposite C-1 or C-3 carbon, while an amine or the telogen, which are pure  $\sigma$ -donors, will not modify these electron densities. The presence of the  $\pi$ -acceptor



Scheme 2. Butadiene telomerization with the mono-octadienyl ethers.



Scheme 3. Key steps of the catalytic cycle for the telomerization of butadiene with xylose.

ligand in **B–F** produces a lower electron density at C-1; for **B** and **C**, the presence of the second phosphine ligand increases the electrophilicity of the C-3 position. As a consequence of the electronic effects, the ratio of nucleophilic attack at C-1 should be expected in the order  $E > D > (B, C, F)$ , the difference between **E** and **D** being related to the less donor character of the alcohol function compared to the amino group and to the steric hindrance of the xylose ligand in **D**. The results of Table 1 reflect the above considerations since we observed a more elevated  $l/b$  ratio when  $\text{NEt}_3$  was added at low xylose concentration; in this situation, a complex like **E** could partially govern the reaction. In rising xylose concentration, complex **D** is preferentially formed versus **E** and the proportion of branched isomers increases, due to a ligand steric effect and to a less important deactivation at C-3.

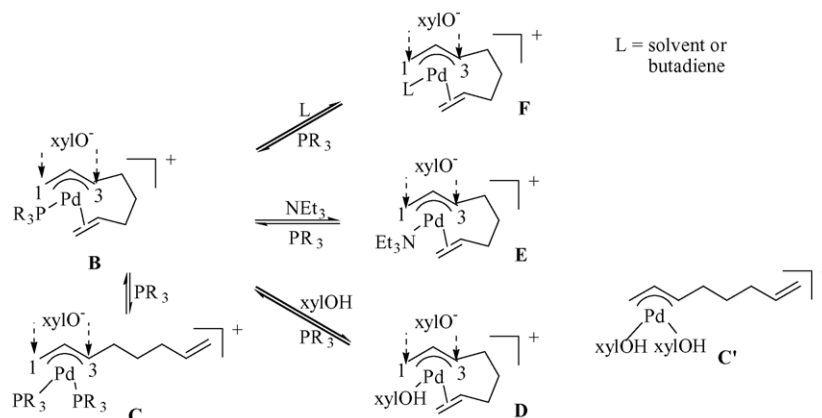
The above examination of the electrophilic character of C-1 and C-3 allows to explain the variation of the  $l/b$  ratios, but seems not compatible with the observed reactivities, since (i) **C** or **B** should react faster due to the presence of electrophilic C-1 and C-3 and (ii) a fast reaction is observed only at high xylose

concentration, i.e. when **D** would be involved. The examination of the different equilibria suggests some explanations.

At low xylose concentrations, in the presence of large amounts of DMF and dissolved butadiene, the equilibrium would lie on the side of **F**, which should favour the formation of butadiene dimers via a  $\beta$ -H elimination process, rather than an attack by the telogen. Under these conditions, the addition of triethylamine would allow the telogen activation, accelerating the transformation of **A** to **B** and/or the participation of **E** in the catalytic cycle. These possibilities could also explain the highest reactivity observed at short reaction times (runs 11 and 12).

The strong acceleration of the telomerization occurring under high sugar concentration conditions could be due to the coordination of the sugar to the palladium. The intervention of the closed complex **D** is proposed since an open species like **C'** obtained from the displacement of the double bond by a  $\sigma$ -donor ligand, would react much slower [19].

The last remark concerns the slow formation of the dioctadecyloxides which seems slightly more efficient starting from the free sugar (about 4% in 15 min and 38% in 135 min, entries



Scheme 4. Equilibria between different palladium complexes.



11 and 9, respectively) than from the corresponding monoethers (29% in 135 min, Scheme 2). The multiple C-8 chain grafting could obviously occur in successive reactions but also in parallel reactions as proposed for the octadienyl ethylene glycol [22], the mono- and ditelomers being produced simultaneously (cycle II, Scheme 3). Actually, a complex like **pro-I** which allows the formation of the main monoethers compounds, could be a highly active catalyst in the telomerization reaction [25] and may start a new catalytic cycle for a second chain grafting. This proposal is in agreement with the higher reactivity of the linear compared to the branched monotelomers (Scheme 2).

### 3. Conclusion

The parameters which influence the palladium-catalyzed telomerization of butadiene with pentoses have been identified [28]. The presence of one phosphine is required to start and/or sustain the catalytic cycle, although the triethylamine and the sugar substrate are also involved as coordinating species. At low sugar concentration, the efficiency of the sugar transformation remains quite low, but the addition of  $\text{NEt}_3$  improves the sugar conversion and the selectivities to both monooctadienylethers and linear telomers. The tertiary amine, as a base, could activate the telogen and, as a ligand, take part in the catalytic cycle. At high sugar concentrations, the reaction is very fast and the substrate could become itself an effective ligand. Nevertheless, the amine activating effect remains, except if the amount of dissolved butadiene is sufficient. As for the formation of butadiene dimers, it would mainly result from a  $\eta^3$ -allylpalladium intermediate bearing the diene or the solvent as a ligand.

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