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Telomerisation of 1,3-Butadiene with 1,4:3,6-Dianhydrohexitols: An Atom-Economic and Selective Synthesis of Amphiphilic Monoethers from Agro-Based Diols

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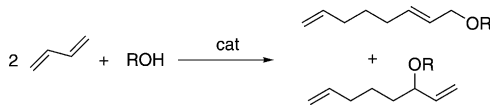
Dedicated to Christian Bruneau on the occassion of his 60th birthday.

The telomerisation of 1,3-butadiene with a Pd/TPPTS catalytic system in water or an organic solvent was used for the synthesis of C8 ethers from isosorbide, an agro-based diol. The use of water/oil biphasic reaction conditions allowed the selective synthesis of monoethers with improved rates upon using inorganic bases as promotors. As isosorbide is a non-symmetric diol, the two hydroxyl groups display different reactivities. 2-*O*-substituted-monoethers were preferentially obtained if water was used as the solvent, whereas in DMSO 5-*O*-substituted monoethers were the major products. Complete conversions of isosorbide with up to 94% monoether selectivities were obtained. The optimized reaction conditions were successfully applied to isomannide and isoidide for the selective synthesis of the derived ethers. An improved reactivity of the *endo*-hydroxy groups of isosorbide and isomannide versus the *exo*-hydroxy groups of isosorbide and isoidide was observed if the reaction was performed in DMSO instead of water.

Introduction

The palladium catalysed telomerisation reaction is a straightforward and atom-economic synthetic tool for the production of alkyl octadienyl ethers from an alcohol and 1,3-dienes (Scheme 1).[1] With methanol and 1,3-butadiene, the transformation was recently industrialised for the production of 1-octene after a further hydrogenation and methanol elimination step. The cost effectiveness of the telomerisation reaction arises from the relatively low cost of 1,3-butadiene compared to previously used ethylene and the efficiency of the catalysts in terms of activities, robustness, and selectivities. In addition to the very efficient and simple palladium/PPh_3 catalytic system, other phosphine- and carbene-modified catalysts have recently allowed further improvements.[2] As an alternative to methanol, hydrophilic polyols readily available from agro-resources have, in the context of sustainable chemistry, attracted particular attention. Polyols with three or more hydroxyl groups,[3] sucrose,[4] as well as starch[5] are suitable substrates under homogeneous or biphasic conditions. However, to date, reactions have not been reported on 1,4:3,6-dianhydrohexitols (isosorbide, isomannide, and isoidide), which are agro-based diols derived from starch. Using a diol as a substrate is attractive, since it lowers the number of possible reaction products, and it also yields interesting mono-substituted compounds. In the case of petroleum-based glycols[6,3e] the telomerisation reaction proved to be an efficient pathway to glycol ethers, which are highly effective organic solvents due to their affinity for hydrophilic and lipophilic organic compounds with numerous applications (e.g., paints, inks, nail polish, de-icers, medicine). However, the established or suspected toxicity of some of them constitutes a serious limitation for their future development. Alternative compounds from agro-based diols are of strong interest and this prompted us to focus our attention on the valorisation of 1,4:3,6-dianhydro-D-glucitol (isosorbide), 1,4:3,6-dianhydro-D-mannitol (isomannide), and 1,4:3,6-dianhydro-D-iditol (isoidide).



Scheme 1. The telomerisation reaction.

Isosorbide is a V-shaped water-soluble asymmetric diol that bears two intracyclic ether functions. Industrially obtained from the double dehydration of sorbitol, isosorbide is an agro-based diol, which can potentially be used in place of glycols. It

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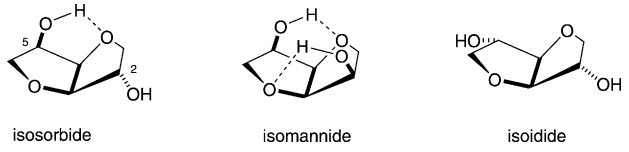
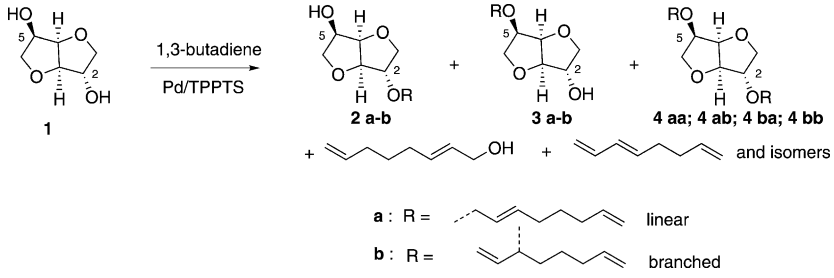
has already found important applications, after chemical modifications, as a vasodilator (isosorbide dinitrate),[7] monomer, and more specifically as polycondensates (polyesters),[8] plasticisers, or solvents (diesters and diethers of isosorbide, and in particular dimethylisosorbide),[9] and shows potential for further new applications. We previously reported the synthesis of isosorbide monoethers by direct alkylation of isosorbide with bromoalkanes and showed the "solvo-surfactant" properties of these compounds.[10] These procedures allowed the synthesis of products with high purity, but suffered from a rather limited efficiency and chemoselectivity; the monoethers were obtained with low yields and as a mixture with the diether. In addition, the synthesis was not environmentally friendly, as large amounts of wastes, mainly salts, were produced. To access isosorbide *O*–C8 monoethers or diethers with high atom economy, selectivities, and chemical yields, we thus turned our attention to the telomerisation reaction of isosorbide with 1,3-butadiene. Difficulties arise with isosorbide in comparison to other diols from the fact that this substrate bears two secondary hydroxyl groups that are supposed to be less reactive than primary alcohols. In addition, the molecule is not symmetric and the two hydroxyl groups are consequently not equivalent, thus increasing the number of products that can be obtained (Scheme 3). The reaction is also performed on isomannide and isoidide, two C2-symmetric isomers of isosorbide (Scheme 2).



Scheme 2. Structures of 1,4:3,6-dianhydro-D-glucitol (isosorbide), 1,4:3,6-dianhydro-D-mannitol (isomannide), and 1,4:3,6-dianhydro-D-iditol (isoidide).



Scheme 3. Reaction products obtained from the telomerisation of 1,3-butadiene with isosorbide.

Results and Discussion

The telomerisation reaction was initially performed in melted isosorbide without any additional organic solvent. As the commonly used triphenylphosphine ligand showed very limited solubility in isosorbide, we thus turned to a more hydrophilic phosphine, the TPPTS [tris(3-sulfonatophenyl)phosphine hydrate, sodium salt], initially used in our group for sucrose telomerisation.[4] The solubility of the ligand and palladium precursor in the liquid phase was ensured by the addition of 0.5 mL of a 1 M aqueous solution of sodium hydroxide. The reaction was performed by using 25 mmol isosorbide in the presence of 0.2% [$Pd(OAc)_2$] associated with four equivalents of TPPTS at 80 °C, and the reactor was fed by a continuous flow of 1,3-butadiene at atmospheric pressure. This procedure was advantageous for practical reasons as commonly used glassware equipments were involved, thus avoiding the use of any high-pressure equipment.[11]

The reaction yielded linear diether **4aa** and the two monoethers **2a** and **3a** as the main products (Scheme 3). These compounds were isolated from the crude product by using distillation under reduced pressure and purified by using silica gel chromatography.

The corresponding branched isomers of **2**, **3**, and **4** were formed in low amounts (<3%) and were hard to separate and obtain as pure compounds. Octadienol and products of the butadiene dimerisation were obtained as volatiles in rather limited amounts and were easily separated from the ethers during the distillation procedure. Under these conditions, as the mixture remained homogeneous, the formation of the products could be monitored by using GC analysis of aliquot samples taken at different reaction times (Figure 1). As expected, the initial products were the monoethers **2** and **3**. However, the reactivities of the *exo*-2-hydroxy group of isosorbide and the sterically shielded and hydrogen-bonded *endo*-5-hydroxy group were different. In the case of the telomerisation reaction in the presence of water, the *exo*-2-hydroxy group tends to be the more reactive, and monoethers **2** was obtained as the major isomer. After 4 h, the amount of monoethers reached a maximum as their formation was counterbalanced by their conversion to diethers **4**. The yield of diethers **4** finally reached 60% and did not increase further even at higher reaction times, probably because of catalyst deactivation as indicated by the formation of a black precipitate after 6 h.

Faster reaction rates are expected if a stoichiometric amount of 1,3-butadiene is introduced at the beginning of the reaction. Experiments were thus carried out in a 100 mL stainless steel autoclave under the same reaction conditions of temperature, catalyst loading, and reactants, with the initial loading of 5 equivalents of 1,3-butadiene. At the early stage of the reaction, part of the 1,3-butadiene remains liquid (even at 80 °C according to the volume of the reactor). In addition, isosorbide is a hydrophilic compound with very limited solubility in alkanes, and the miscibility of liquid isosorbide with 1,3-butadiene at 80 °C, although not known, is expected to be rather limited, particularly in the presence of water. The reaction mixture was thus biphasic at the beginning of the reaction. Due to the presence of the two phases, samples taken in the autoclave

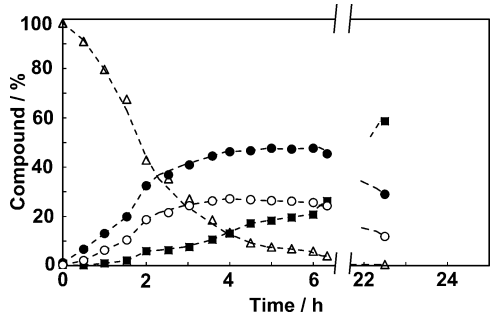


Figure 1. Evolution of isosorbide **1** (△), 2-monoether **2** (●), 5-monoether **3** (○), and diether **4** (■) during the telomerisation reaction under atmospheric 1,3-butadiene pressure (composition of the mixture in %). The dotted lines are drawn to guide the eye. The reaction was performed at 80 °C with 25 mmol isosorbide, 0.2 mol% [$Pd(OAc)_2$] (vs isosorbide), 0.8 mol% TPPTS, and 0.5 mL aqueous 1 M NaOH (0.5 mmol).

Table 1. Effect of the base on the selectivity in the telomerisation reaction of 1,3-butadiene with isosorbide catalysed by [$Pd(OAc)_2$]/4 TPPTS.[a]

Entry	Base [mmol]	Conversion[b] of **1** [%]	Selectivity[b] [%] **2**	**3**	**4**	Mono/di (**2**+**3**)/**4**
1	No base	68	74	23	3	36
2	NaOH (0.025)	72	78	18	4	22
3	NaOH (0.05)	88	67	27	6	16
4	NaOH (0.165)	100	40	9	51	1
5	NaOH (0.3)	100	43	10	47	1.1
6	NaOH (0.5)	100	32	8	60	0.7
7	LiOH (0.5)	99	35	10	55	0.8
8	KOH (0.5)	93	54	27	19	4.3
9	CsOH (0.5)	100	46	23	31	2.2

[a] The reactions were performed at 80 °C with 25 mmol isosorbide, 125 mmol 1,3-butadiene, 0.2 mol% palladium (vs isosorbide), 0.8 mol% TPPTS, and 0.5 mL water with the appropriate base for two hours. [b] Conversions and selectivities were determined by using GC analysis.

are not representative of the whole reaction mixture and changes in the composition during the reaction could not be monitored. Conversion of **1** and yields of the corresponding ethers were thus measured after running the reaction for two hours (Table 1). For all experiments, because of a large consumption of 1,3-butadiene, the pressure dropped from 10 bar (1 bar = 10^5 Pa) to less than 3 bar, and the reaction mixture was homogeneous after being vented.

In the absence of a base, the conversion of isosorbide reached 68% after two hours (Table 1, entry 1). Monoethers **2** and **3** were obtained as main products and only 3% diether **4** was formed. The introduction of a strong base had a marked effect on the reaction rates. The introduction of sodium hydroxide in the range from 0.025 to 0.165 mmol dissolved in 0.5 mL of water improved the reaction rate further. In a 0.165 mmol solution of sodium hydroxide, the total conversion of isosorbide was observed, and a 51% yield of diether **4** was obtained. Further increases of the concentration of sodium hydroxide did not allow the formation of a notably larger amount of diether compared to monoether. This demonstrates that with 0.165 mmol sodium hydroxide, the reaction had reached its maximum yield within 2 h. It should be noted that, even with this amount of sodium hydroxide, the base was added in catalytic amounts, which corresponded to only 3.3 equivalents of hydroxide anions per palladium. Other metal hydroxides can be used, but do not increase the yields of diether **4** nor do they improve the selectivities for the monoethers **2** or **3** (Table 1, entries 6–9).

The reaction was performed at three different temperatures, and to avoid the total consumption of the starting material, the runs were quenched and analysed after 30 min reaction time (Table 2). The experiment at 80 °C evidenced that reasonably high reaction rates could be attained in the telomerisation reaction of 1,3-butadiene with isosorbide. Although this derivative is a secondary alcohol, turnover frequencies of 1000 mol of isosorbide converted per mol of palladium per hour were obtained under these conditions. As expected, decreasing the reaction temperature led to drastically reduced conversions of isosorbide.

Table 2. Temperature effect on the telomerisation reaction of 1,3-butadiene with isosorbide catalysed by [$Pd(OAc)_2$]/4 TPPTS.[a]

Entry	*T* [°C]	Conversion[b] of **1** [%]	Selectivity[b] [%] **2**	**3**	**4**	Mono/di (**2**+**3**)/**4**
1	80	99	51	37	12	7.3
2	65	24	66	32	2	49
3	50	5	75	25	<2	n.d.

[a] The reactions were performed with 25 mmol isosorbide, 125 mmol 1,3-butadiene, 0.2 mol% palladium (vs isosorbide), 0.8 mol% TPPTS, and 0.5 mL of aqueous NaOH (1 M) for 30 min. [b] Conversions and selectivities were determined by using GC analysis.

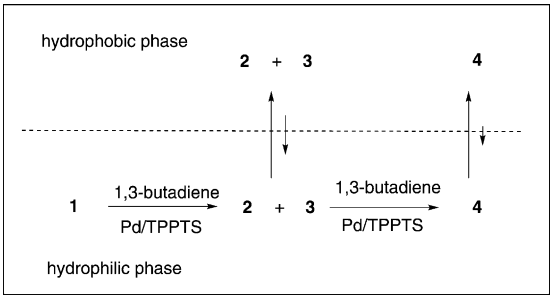
With the aim to reinforce the formation of a biphasic system beneficial to achieve higher monoether/diether (mono/di) ratios, additional experiments were performed by using an organic solvent (ethyl acetate) or increasing the water content (Table 3). Under such conditions, a biphasic water/oil system was maintained during the reaction. As the catalyst is immobi-

Table 3. Selectivity in the telomerisation reaction of 1,3-butadiene with isosorbide using [$Pd(OAc)_2$]/4 TPPTS under reinforced biphasic conditions.[a]

Entry	Solvent (mL/mL)	*t* [h]	Conversion[b] of **1** [%]	Selectivity[b] [%] **2**	**3**	**4**	Mono/di (**2**+**3**)/**4**
1	AcOEt/H_2O (20/0.5)	3	33	57	43	<1	–
2	AcOEt/H_2O (20/0.5)	29	46	56	43	<1	–
3	AcOEt/H_2O (20/0.5)	90	99	58	38	3.2	30
4	H_2O (4)	3	99	65	28	6.6	14

[a] The reactions were performed with 25 mmol isosorbide, 125 mmol 1,3-butadiene, 0.2 mol% palladium (vs isosorbide), 0.8 mol% TPPTS and given amounts of aqueous 1 M NaOH and AcOEt at 80 °C. [b] Conversions and selectivities were determined by using GC analysis.

lized in the aqueous phase by means of the water soluble TPPTS/Pd system, it may be anticipated that, by using this procedure, the monosubstituted products **2** and **3** formed in the course of the reaction could be extracted from the water phase containing the catalyst, thus preventing their subsequent disubstitution (Scheme 4). By using 20 mL ethyl acetate,



Scheme 4. Telomerisation of isosorbide under biphasic conditions.

the reaction turned out to be extremely slow, as 90 h were needed to reach a complete conversion of isosorbide. As expected, the diol was essentially converted into monoethers **2** and **3** and a mono/di ratio of 30 was obtained. High selectivities in monoethers were also obtained if the reaction was performed with 4 mL of water. In that case, the reaction rate turned out to be much higher, and a complete conversion of isosorbide was attained after only 3 h. Surprisingly, although the aqueous catalytic phase was expected to be less prone to solubilise 1,3-butadiene, the reaction rate was not as greatly impeded as in the former case (reaction performed with 20 mL ethyl acetate).

It thus appears that the dilution of 1,3-butadiene in an organic cosolvent results in a reduced concentration of 1,3-butadiene in the water/isosorbide phase, which is responsible for limited reaction rates. This is also in agreement with the lower rates obtained with an atmospheric gas pressure compared to the batch experiments with initial loading of 1,3-butadiene; the concentration of 1,3-butadiene in the catalytic phase is expected to be higher in the latter case.

To confirm the presence of a liquid/liquid biphasic system, the reaction was carried out in an autoclave equipped with quartz windows. The experiment performed with 4 mL of water clearly evidences the existence of two distinguishable phases at 80 °C (Figure 2). The colourless upper phase, expected to be mainly composed of 1,3-butadiene at the beginning of the reaction, remained almost constant in volume as 1,3-butadiene was converted and replaced by monoethers **2** and **3**. On the other hand, the yellowish water/isosorbide phase containing the catalyst was concomitantly reduced in volume as isosorbide was converted and the products were extracted to the organic phase. After 2 h reaction at high conversion of isosorbide, a black precipitate of palladium started to appear, and the reaction medium became sluggish.

Interestingly, the addition of water also induced a variation of the **3**/**2** ratio. The reaction with 0.5 mL of water as cosolvent yielded predominantly the ethers **2** (ratio **3**/**2** = 0.7) and this

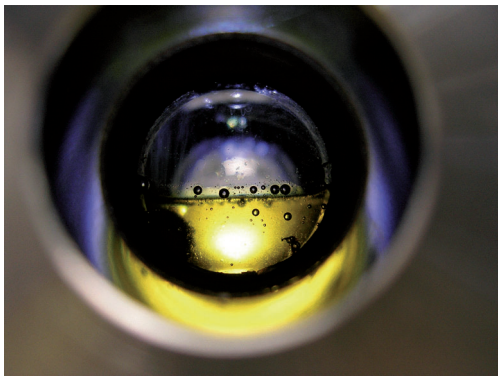


Figure 2. Telomerisation reaction in a high pressure batch reactor. The reaction was performed at 80 °C with 25 mmol isosorbide, 16 mL 1,3-butadiene, 0.2 mol% palladium, 0.8 mol% TPPTS, and 4 mL water (0.5 mmol NaOH). The picture was taken after 30 min reaction.

ratio was significantly improved in favour of **2** by using 4 mL of water (Table 4, entries 1 and 2). This solvent effect on the selectivity was a valuable tool to synthesize **3** more selectively, and a complementary study that involved organic solvents in place of water was therefore conducted. For that purpose, DMSO and *t*BuOH were suitable polar solvents as they also contributed to the solubilisation of the catalyst in the isosorbide phase.

Table 4. Telomerisation reaction of 1,3-butadiene with isosorbide catalysed by [$Pd(OAc)_2$]/4 TPPTS in organic and aqueous solvents.[a]

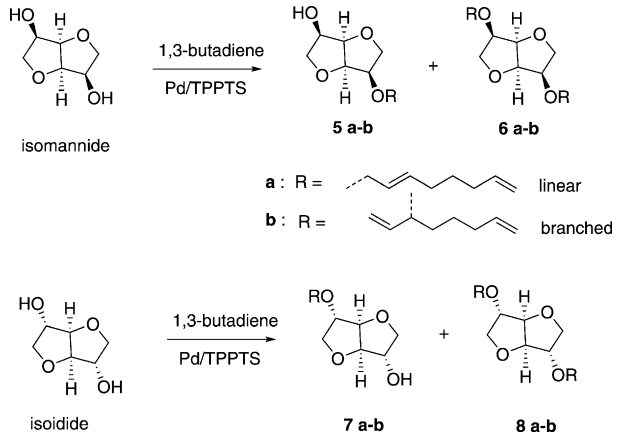
Entry	Solvent [mL]	Conversion[b] of **1** [%]	Selectivity[b] [%]			**3**/**2**
			2	**3**	**4**	
1	H_2O (0.5)	87	54	35	11	0.7
2	H_2O (4)	86	67	27	6	0.4
3	*t*BuOH (0.5)	84	32	42	26	1.3
4	*t*BuOH (4)	34	49	45	7	0.9
5	DMSO (0.5)	74	37	45	18	1.2
6	DMSO (4)	55	46	46	8	1
7[c]	DMSO (0.5)	73	55	17	28	0.3

[a] The reactions were performed with 25 mmol isosorbide, 62.5 mmol 1,3-butadiene, 0.2 mol% palladium (vs isosorbide), 0.8 mol% TPPTS and 0.1 mmol LiOH at 80 °C for 2 h. [b] Conversions and selectivities were determined by using GC analysis. [c] Reaction was performed with PPh_3 in place of TPPTS.

The telomerisation reactions performed by using 0.5 mL of DMSO or *t*BuOH showed the formation of **3** as a major product and the respective **3**/**2** ratios were 1.3 and 1.2. In more diluted media (Table 4, entries 4 and 6), the conversions of isosorbide turned out to be much lower, but the **3**/**2** ratios remained higher than in water thus showing that the selectivity of the reaction of **1** into **2** or **3** could be tuned, to some extent, by changing the nature of the cosolvent. However, owing to the more solubilising properties of organic solvents, it should be noted that the overall yield of the monoethers was limited by the formation of larger amounts of diether **4**. In contrast to water, organic solvents solubilise all the reactants in one

unique phase thus hindering the beneficial biphasic effect for the selective synthesis of monoethers at high isosorbide conversions (cf. entries 5 and 3 with entry 1 in Table 4). However, crude products of reactions performed with DMSO and enriched with **3** were used for purification to access pure **3a**. Moreover, these solvents can be of interest elsewhere as they are compatible with the use of neutral, cheaper, and less sensitive triarylphosphines. By using PPh_3 in place of the TPPTS and with DMSO as solvent, the reaction showed similar conversions of isosorbide, but large amounts of diether **4** were formed (see entry 7). In addition, the selectivity was greatly improved in favour of the monotelomer **2** and a low **3/2** ratio of 0.3 was obtained.

Isoidide and isomannide are C2-symmetric isomers of isosorbide with two *exo* and two sterically shielded and hydrogen-bonded *endo* hydroxy groups (Scheme 3), respectively. These compounds were further efficiently used as telogens in the telomerisation reaction of 1,3-butadiene (Scheme 5).



Scheme 5. Products from the telomerisation reaction of isomannide and isoidide with 1,3-butadiene.

Both diols were selectively converted into octadienyl monoethers **5a**–**b** and **7a**–**b** under biphasic aqueous reaction conditions (Table 5, entries 1 and 2). Similar to isosorbide, linear derivatives **5a** and **7a** were obtained as the main reaction products. The measured conversions after two hours reaction were similar in both cases, and this similarity in reactivity was confirmed by using a competitive reaction performed with equimolar amounts of isomannide and isoidide. Isomannide showed a much larger reactivity compared to isoidide, if the reaction was performed in DMSO instead of water. This is in agreement with the improved reactivity of the *endo*-hydroxy group of isosorbide versus the *exo*-hydroxy group when the reaction was performed in DMSO instead of water. The *endo*-hydroxy groups of isosorbide and isomannide are sterically more crowded than the *exo*-2-hydroxy groups of isosorbide and isoidide. However, *endo*-hydroxy groups are in general more reactive. This higher reactivity is generally attributed to the enhanced acidity of this site, due to the presence of a hydrogen bond with an oxygen atom of the adjacent cycle (Scheme 3),[10a,12] associated with an enhanced deprotonation of the *endo*-hydroxy group, due to the formation of chelates in the presence of alkaline cations.[13] However, exceptions have been reported, in particular in the case of the esterification of isosorbide with acids under phase-transfer catalysed conditions[14] as well as alkylation reactions performed in water.[13] In these cases, water was indeed thought to, at least partially, break the intramolecular hydrogen bonding, thus sterically controlling the reactivity of the hydroxy groups. As a result, the 2-regioisomer becomes the major product under these conditions.

Table 5. Telomerisation reaction of 1,3-butadiene with isomannide and isoidide catalysed by $[Pd(OAc)_2]$/4 TPPTS in DMSO and water.[a]

Entry	Solvent [4 mL]	Substrate	Conversion[b] [%]	Selectivity[b] [%] Monoethers	Diethers
1	H_2O	Isomannide	60	>99	<1
2	H_2O	Isoidide	57	>99	<1
3	H_2O	Isomannide	45	98	<2
		Isoidide	58	97	3
4	DMSO	Isomannide	65	83	17
		Isoidide	19	96	4

[a] The reactions were performed with 12.5 mmol isomannide and 12.5 mmol isoidide for the mixture entries 3 and 4, 25 mmol substrate for entries 1 and 2, 62.5 mmol 1,3-butadiene, 0.2% palladium, 0.8% TPPTS, and 0.1 mmol LiOH at 80 °C for 2 h. [b] Conversions and selectivities were determined by using GC analysis.

Conclusions

The telomerisation reaction efficiently allows the synthesis of isosorbide-based mono- or diethers with good yields. The choice of the reaction conditions used for the synthesis is important to improve reaction rates and to tune the product distributions. Simple bases used in catalytic amounts allow higher reaction rates compared to neat water as well as the synthesis of diethers as the main reaction products. Biphasic conditions that involve a sufficient amount of water are preferentially applied for higher selectivity towards monoethers. Under such reaction conditions, the 2-*O*-octadienyl monoethers are the main products. Switching from an aqueous to an organic medium accesses the 5-*O*-octadienyl monoether as the major reaction product, however the overall selectivity for monoethers is less pronounced. The reaction can be applied to the selective synthesis of monoethers derived from isomannide and isoidide with water as the reaction solvent. Competitive reactions between isomannide and isoidide in water or DMSO evidence the improved reactivity of *exo*-hydroxy groups in aqueous media.

Experimental Section

Apparatus: NMR spectra were recorded on a Bruker AC 300 spectrometer (^1H: 300 MHz, ^{13}C: 75.5 MHz) and referenced to TMS. GC analyses were carried out on a Chrompack CP 9002 apparatus equipped with a flame ionisation detector and a CP-Sil 5CB column using 100% dimethylpolysiloxane as internal phase (25 m

length, 0.32 mm id). Undecane was chosen as internal standard for GC analysis. The response factors of the major compounds toward the internal standard were experimentally established. All experiments were performed under a nitrogen atmosphere by using standard Schlenk techniques. Experiments conducted under batch conditions were carried out in a 100 mL stainless steel autoclave with butadiene introduced in liquid form at low temperatures at the beginning of the reaction. Semi-batch reactions were performed in a 50 mL glass reactor connected to a butadiene cylinder through a backpressure regulator to keep the butadiene pressure constant. A rubber septum connected to the reactor allowed to take aliquot samples during the reaction, which were analyzed by GC.

Experimental procedure for telomerisation with atmospheric pressure of 1,3-butadiene: The catalyst [$Pd(OAc)_2$] (11.2 mg, 0.05 mmol), the TPPTS (114 mg, 0.2 mmol), and isosorbide (3.65 g, 25 mmol) were introduced in a glass reactor and flushed under nitrogen. An aqueous soda solution (1 M, 0.5 mL) was degassed and then added to the powders. The reactor was flushed with nitrogen, put under vacuum and filled with 1 bar of butadiene. The reactor was then heated to 80 °C and magnetically stirred while the pressure of the atmosphere of butadiene was kept constant by means of a backpressure regulator (butadiene being introduced in the gas phase) during the overall experiment. During the reaction, the solution remained purely homogeneous, and the kinetics was followed by using GC analysis.

Experimental procedure for the telomerisation of 1,3-butadiene in the autoclave: In a typical telomerisation experiment, the catalyst [$Pd(OAc)_2$] (11.2 mg, 0.05 mmol), the phosphine ligand (114 mg, 0.2 mmol) and isosorbide (3.65 g, 25 mmol) were introduced in a 100 mL stainless steel autoclave, which was bolted and flushed with nitrogen. The base was dissolved in distilled water, degassed under nitrogen flow, and then transferred into the autoclave. The latter was cooled down to −20 °C. A precise volume of butadiene was condensed in a Schlenk tube with an acetone–dry ice mixture and transferred into the autoclave. Finally, the reactor was heated to the chosen temperature and vigorously stirred (at a rate of about 1000 rpm) with a magnetic stirrer for 2 h. After the reaction, the system was cooled and excess gaseous butadiene was vented. The crude product was homogenized by methanol addition, and 0.250 mL of undecane was added. Conversion and selectivities were calculated from the GC analysis of the homogeneous mixture.

Separation of the telomers: 20 mL of water were added to the slurry and the aqueous phase containing isosorbide, and the catalyst was extracted by using acetate (3×20 mL). The organic phase was dried by using Na_2SO_4 and evaporated. Telomers were then partially separated by distillation under low pressure (4.10^{-2} mbar). The distillation separated the two fractions containing mainly monotelomers (108–116 °C: 72% **2**, 13% **3**; 132–145 °C: 17% **2**, 65% **3**) and one fraction essentially consisting of the ditelomer (161–170 °C: 73% **4**).

Pure **2a**, **3a**, and **4aa** were obtained by purification of the enriched distillation fractions by using silica-gel column chromatography with petroleum ether/ethyl acetate (80/20) as the eluent. However, **3a** was best purified from the crude product in a reaction performed in DMSO.

Pure monoethers of isomannide and isoidide were obtained by extraction with ethyl acetate of the biphasic aqueous reaction and further purified by using silica-gel column chromatography in the same way as for the telomers of isosorbide.

2a: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.72$ (ddt, 1H, $^3J(H,H) = 17.2$ Hz, $^3J(H,H) = 10.6$ Hz, $^3J(H,H) = 6.5$ Hz, CH_2–*CH*=CH_2), 5.64 (dt, 1H, $^3J(H,H) = 15.5$ Hz, $^3J(H,H) = 7.5$ Hz, CH_2–*CH*=CH–CH_2O), 5.46 (dt, 1H, $^3J(H,H) = 15.5$ Hz, $^3J(H,H) = 6.8$ Hz, CH=*CH*–CH_2O), 4.93 (d, 1H, $^3J(H,H) = 17.2$ Hz, CH=*CH*$_2$), 4.88 (d, 1H, $^3J(H,H) = 10.6$ Hz, CH=*CH*$_2$), 4.53 (dd, 1H, $^3J(H,H) = 4.6$ Hz, $^3J(H,H) = 4.9$ Hz, H_4 isosorbide), 4.39 (d, 1H, $^3J(H,H) = 4.6$ Hz, H_3 isosorbide), 4.19 (dddd, 1H, $^3J(H,H) = 7.1$ Hz, $^3J(H,H) = 5.9$ Hz, $^3J(H,H) = 5.1$ Hz, $^3J(H,H) = 4.9$ Hz, H_5 isosorbide), 3.98 (d, 1H, $^3J(H,H) = 4.2$ Hz, H_2 isosorbide), 3.95 (d, 1H, $^2J(H,H) = 10.3$ Hz, $^3J(H,H) = 4.2$ Hz, H_1 isosorbide), 3.92 (d, 2H, $^3J(H,H) = 6.8$ Hz, CH=CH–*CH*$_2$O), 3.81 (dd, 1H, $^2J(H,H) = 10.3$ Hz, $^3J(H,H) = 3.9$ Hz, H_1 isosorbide), 3.77 (dd, 1H, $^2J(H,H) = 9.2$ Hz, $^3J(H,H) = 5.1$ Hz, H_6 isosorbide), 3.47 (dd, 1H, $^2J(H,H) = 9.2$ Hz, $^3J(H,H) = 5.9$ Hz, H_6 isosorbide), 2.84 (d, 1H, $^3J(H,H) = 7.1$ Hz, OH), 1.99 (m, 4H, CH–*CH*$_2$–CH_2–*CH*$_2$–CH), 1.41 ppm (tt, 2H, $^3J(H,H) = 7.5$ Hz and $^3J(H,H) = 7.5$ Hz, CH_2–*CH*$_2$–CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 138.5$ (1C, *C*H=CH_2), 135.1 (1C, *C*H=CH-CH_2O), 125.9 (1C, CH=*C*H–CH_2O), 114.7 (1C, CH=*C*H$_2$), 86.0 (1C, C_3 isosorbide), 83.1 (1C, C_2 isosorbide), 81.8 (1C, C_4 isosorbide), 73.5 (1C, C_1 isosorbide), 73.3 (1C, C_6 isosorbide), 72.3 (1C, C_5 isosorbide), 70.4 (1C, CH=CH–*CH*$_2$O), 33.2 (1C, *C*H$_2$–CH=CH-*CH*$_2$O), 31.7 (1 C, *C*H$_2$–CH=CH_2), 28.2 ppm (1C, CH_2–*CH*$_2$–CH_2).

3a: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.71$ (ddt, 1H, $^3J(H,H) = 17.3$ Hz, $^3J(H,H) = 10.2$ Hz, $^3J(H,H) = 6.9$ Hz, CH2-*CH*=CH2), 5.64 (dt, 1H, $^3J(H,H) = 15.3$ Hz, $^3J(H,H) = 6.4$ Hz, CH_2–*CH*=CH–CH_2O), 5.49 (dt, 1H, $^3J(H,H) = 15.3$ Hz, $^3J(H,H) = 6.4$ Hz, CH=*CH*–CH_2O), 4.92 (d, 1H, $^3J(H,H) = 17.3$ Hz, CH=*CH*$_2$), 4.87 (d, 1H $^3J(H,H) = 10.2$ Hz, CH=*CH*$_2$), 4.57 (t, 1H, $^3J(H,H) = 4.2$ Hz, H_4 isosorbide), 4.33 (d, 1H, $^3J(H,H) = 4.2$ Hz, H_3 isosorbide), 4.19 (m, 1H, H_2 isosorbide), 3.78–4.12 (m, 5H, H_5 isosorbide, H_6 isosorbide, H_1 isosorbide, CH–*CH*$_2$O), 3.96 (dd, 1H, $^3J(H,H) = 11.6$ Hz, $^3J(H,H) = 6.5$ Hz, CH–*CH*$_2$O), 3.45 (t, 1H, $^3J(H,H) = 8.5$ Hz, H_6 isosorbide), 3.38 (m, 1H, OH), 1.93 (m, 4H, CH–*CH*$_2$–CH_2–*CH*$_2$–CH), 1.35 ppm (m, 2H, $^3J(H,H) = 7.4$ and $^3J(H,H) = 7.4$ Hz, CH_2-*CH*$_2$-CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 138.3$ (1C, CH_2–*C*H=CH_2), 135.1 (1C, CH_2–*C*H=CH_2O), 126.0 (1C, CH=*C*H–CH_2O), 114.6 (1C, CH=*C*H$_2$), 88.1 (1C, C_3 isosorbide), 79.9 (1C, C_4 isosorbide), 78.9 (1C, C_5 isosorbide), 76.2 (1C, C_2 isosorbide), 75.1 (1C, C_1 isosorbide), 71.2 (1C, CH–*C*H$_2$O), 69,7 (1C, C_6 isosorbide), 33.1 (1C, CH_2–*C*H$_2$–CH=CH_2O), 31.5 (1C, CH_2–*C*H$_2$–CH=CH_2), 28.0 ppm (1C, CH_2–*C*H$_2$–CH_2).

4aa: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.79$ (ddt, 2H, $^3J(H,H) = 17.6$ Hz, $^3J(H,H) = 10.3$ Hz, $^3J(H,H) = 6.4$ Hz, CH_2–*CH*=CH_2), 5.70 (dt, 2H, $^3J(H,H) = 15.3$ Hz, $^3J(H,H) = 6.5$ Hz, CH_2–*CH*=CH–CH_2O-C_2 isosorbide), 5.58 (dt, 1H, $^3J(H,H) = 15.3$ Hz, $^3J(H,H) = 6.2$ Hz, CH_2–*CH*=CH–CH_2O–C_5 isosorbide), 5.52 (dt, 1H, $^3J(H,H) = 15,3$ Hz, $^3J(H,H) = 6,2$ Hz,), 4.99 (d, 2H, $^3J(H,H) = 17.6$ Hz, CH=*CH*$_2$), 4.95 (d, 2H, $^3J(H,H) = 10,3$ Hz, CH=*CH*$_2$), 4.60 (t, 1H, $^3J(H,H) = 4.4$ Hz, H_4 isosorbide), 4.50 (d, 1H, $^3J(H,H) = 4.4$ Hz, H_3 isosorbide), 4.14 (dd, 1H, $^3J(H,H) = 11.7$ Hz, $^3J(H,H) = 6.2$ Hz, CH–*CH*$_2$O–C_2 isosorbide), 4.07–3.84 (m, 8H, H_2 isosorbide, H_1 isosorbide, H_5 isosorbide, 1 H_6 isosorbide, 1H CH–*CH*$_2$O–C_2 isosorbide, CH–*CH*$_2$O–C_5 isosorbide), 3.57 (t, 1H, $^3J(H,H) = 8.2$ Hz, H_6 isosorbide), 2.05 (m, 8H, CH–*CH*$_2$–CH_2–*CH*$_2$–CH), 1.48 ppm (tt, 4H, $^3J(H,H) = 7.4$ Hz and $^3J(H,H) = 7.4$ Hz, CH_2–*CH*$_2$–CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 138.5$ (2C, CH_2–*C*H=CH_2), 135.1 (1C, CH_2–CH=CH–CH_2O–C_5 isosorbide), 134.9 (1C, CH_2–CH=CH–CH_2O–C_2 isosorbide), 126.3 (1C, C8 CH=*C*H-CH_2O–C_2 isosorbide), 126.0 (1C, C16 CH=*C*H–CH_2O–C_5 isosorbide), 114.7 (2C, CH=*C*H$_2$), 86.4 (1C, C_3 isosorbide), 83.5 (1C, C_2 isosorbide), 80.1 (1C, C_4 isosorbide), 79.1 (1C, C_5 isosorbide), 73.4 (1C, C_1 isosorbide), 71.3 (1C, CH–*C*H$_2$O–C_5 isosorbide), 70.3 (1C, CH–*C*H$_2$O–C_2 isosorbide), 69.7 (1C, C_6 isosorbide), 33.2 (2C, CH_2–*C*H$_2$–CH=CH–CH_2O), 31.7 (2C, CH_2–*C*H$_2$–CH=CH_2), 28.2 ppm (2C, CH_2–*C*H$_2$–CH_2)

5a: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.80$ (ddt, 1H, $^3J(H,H) = 17.8$ Hz, $^3J(H,H) = 10.7$ Hz, $^3J(H,H) = 6.5$ Hz, CH_2–*CH*=CH_2), 5.74 (dt, 1H,

^3J(H,H) = 15.2 Hz, ^3J(H,H) = 6.5 Hz, CH_2–*CH*=CH–CH_2O), 5.59 (dt, 1H, ^3J(H,H) = 15.2 Hz, ^3J(H,H) = 6.5 Hz, CH=*CH*–CH_2O), 5.01 (d, 1H, ^3J(H,H) = 17.8 Hz, CH=*CH*$_2$), 4.96 (d, 1H, ^3J(H,H) = 10.7 Hz, CH=*CH*$_2$), 4.52 (m, 2H, H_4, H_3 isomannide), 4.28 (q, 1H, ^3J(H,H) = 5.8 Hz, H_5 isomannide), 4.16 (dd, 1H, ^3J(H,H) = 5.8 Hz, CH–*CH*$_2$O), 4.12–3.95 (m, 4H, H_2, H_6, H_1 isomannide and CH–*CH*$_2$O), 3.71 (m, 2H, H_1, H_6 isomannide), 2.81 (s, 1H, OH), 2.07 (dd, 4H, ^3J(H,H) = 6.5 Hz and ^3J(H,H) = 7.5 Hz, CH–*CH*$_2$–CH_2–*CH*$_2$–CH), 1.49 ppm (tt, 2H, ^3J(H,H) = 7.5 Hz and ^3J(H,H) = 7.5 Hz, CH_2–*CH*$_2$–CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.7 (1C, *CH*=CH_2), 135.5 (1C, *CH*=CH–CH_2O), 126.3 (1C, CH=*CH*–CH_2O), 114.8 (1C, CH=*CH*$_2$), 82.0 (1C, C_4 isomannide), 80.8 (1C, C_3 isomannide), 79.1 (1C, C_2 isomannide), 75.1 (1C, C_6 isomannide), 72.5 (1C, C_5 isomannide), 71.7 (1C, CH=CH–*CH*$_2$O), 71.4 (1C, C_1 isomannide), 33.4 (1C, *CH*$_2$–CH=CH–*CH*$_2O$), 31.8 (1C, *CH*$_2$–CH=CH_2), 28.3 ppm (1C, CH_2–*CH*$_2$–CH_2).

6a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.79 (ddt, 2H, ^3J(H,H) = 17.5 Hz, ^3J(H,H) = 10.4 Hz, ^3J(H,H) = 6.8 Hz, CH_2–*CH*=CH_2), 5.72 (dt, 2H, ^3J(H,H) = 15.8 Hz, ^3J(H,H) = 6.8 Hz, CH_2–*CH*=CH–CH_2O), 5.58 (dt, 2H, ^3J(H,H) = 15.8 Hz, ^3J(H,H) = 6.8 Hz, CH=*CH*–CH_2O), 5.00 (d, 2H, ^3J(H,H) = 17.5 Hz, CH=*CH*$_2$), 4.95 (d, 2H, ^3J(H,H) = 10.4 Hz, CH=*CH*$_2$), 4.52 (m, 2H, H_3 isomannide), 4.16–3.94 (m, 8H, CH–*CH*$_2$O, H_2 isomannide, H_1 isomannide), 3.61 (t, 2H, ^3J(H,H) = 11.3 Hz, H_1 isomannide), 2.05 (dd, 8H, ^3J(H,H) = 6.8 Hz and ^3J(H,H) = 7.5 Hz, CH–*CH*$_2$–CH_2–*CH*$_2$–CH), 1.47 ppm (tt, 4H, ^3J(H,H) = 7.5 Hz and ^3J(H,H) = 7.5 Hz, CH_2–*CH*$_2$–CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.6 (2C, *CH*=CH_2), 135.1 (2C, *CH*=CH–CH_2O), 126.3 (2C, CH=*CH*–CH_2O), 114.7 (2C, CH=*CH*$_2$), 80.3 (2C, C_3 isomannide), 79.4 (2C, C_2 isomannide), 71.5 (2C, CH=CH–*CH*$_2$O), 71.0 (2C, C_1 isomannide), 33.2 (2C, *CH*$_2$–CH=CH–*CH*$_2O$), 31.6 (2C, *CH*$_2$–CH=CH_2), 28.1 ppm (2C, CH_2–*CH*$_2$–CH_2).

7a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.81 (ddt, 1H, ^3J(H,H) = 17.1 Hz, ^3J(H,H) = 10.3 Hz, ^3J(H,H) = 6.5 Hz, CH_2–*CH*=CH_2), 5.72 (dt, 1H, ^3J(H,H) = 15.3 Hz, ^3J(H,H) = 6.5 Hz, CH_2–*CH*=CH–CH_2O), 5.54 (dt, 1H, ^3J(H,H) = 15.3 Hz, ^3J(H,H) = 6.5 Hz, CH=*CH*–CH_2O), 5.01 (d, 1H, ^3J(H,H) = 17.1 Hz, CH=*CH*$_2$), 4.96 (d, 1H, ^3J(H,H) = 10.3 Hz, CH=*CH*$_2$), 4.68 (d, 1H, ^3J(H,H) = 4.0 Hz, H_3 isoidide), 4.53 (d, 1H, ^3J(H,H) = 4.0 Hz, H_4 isoidide), 4.32 (m, 1H, H_5 isoidide), 4.00 (m, 3H, H_2 isoidide, and CH–*CH*$_2$O), 3.84 (m, 4H, H_1, H_6 isoidide), 2.34 (s, 1H, OH), 2.07 (dd, 4H, ^3J(H,H) = 7.5 Hz and ^3J(H,H) = 6.5 Hz, CH–*CH*$_2$–CH_2–*CH*$_2$–CH), 1.49 ppm (tt, 2H, ^3J(H,H) = 7.5 Hz and ^3J(H,H) = 7.5 Hz, CH_2–*CH*$_2$–CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.7 (1C, *CH*=CH_2), 135.3 (1C, *CH*=CH–CH_2O), 126.0 (1C, CH=*CH*–CH_2O), 114.8 (1C, CH=*CH*$_2$), 87.3 (1C, C_4 isoidide), 85.4 (1C, C_3 isoidide), 82.7 (1C, C_2 isoidide), 76.2 (1C, C_5 isoidide), 74.5 (1C, C_6 isoidide), 72.6 (1C, C_1 isoidide), 70.6 (1C, CH=CH–*CH*$_2$O), 33.4 (1C, *CH*$_2$–CH=CH–*CH*$_2O$), 31.8 (1C, *CH*$_2$–CH=CH_2), 28.3 ppm (1C, CH_2–*CH*$_2$–CH_2).

8a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.80 (ddt, 2H, ^3J(H,H) = 17.4 Hz, ^3J(H,H) = 10.6 Hz, ^3J(H,H) = 6.8 Hz, CH_2–*CH*=CH_2), 5.71 (dt, 2H, ^3J(H,H) = 15.4 Hz, ^3J(H,H) = 6.8 Hz, CH_2–*CH*=CH–CH_2O), 5.54 (dt, 2H, ^3J(H,H) = 15.4 Hz, ^3J(H,H) = 6.8 Hz, CH=*CH*–CH_2O), 5.01 (d, 2H, ^3J(H,H) = 17.4 Hz, CH=*CH*$_2$), 4.96 (d, 2H, ^3J(H,H) = 10.6 Hz, CH=*CH*$_2$), 4.62 (s, 2H, H_3 isoidide), 4.00 (m, 4H, H_2 isoidide and CH–*CH*$_2$O), 3.84 (m, 4H, H_1 isoidide), 2.06 (dd, 8H, ^3J(H,H) = 7.5 Hz and ^3J(H,H) = 6.8 Hz, CH–*CH*$_2$–CH_2–*CH*$_2$–CH), 1.49 ppm (tt, 4H, ^3J(H,H) = 7.5 Hz and ^3J(H,H) = 7.5 Hz, CH_2–*CH*$_2$–CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.6 (2C, *CH*=CH_2), 135.0 (2C, *CH*=CH–CH_2O), 125.9 (2C, CH=*CH*–CH_2O), 114.7 (2C, CH=*CH*$_2$), 85.4 (2C, C_3 isoidide), 82.5 (2C, C_2 isoidide), 72.3 (2C, C_1 isoidide), 70.4 (2C, CH=CH–*CH*$_2$O), 33.2 (2C, *CH*$_2$–CH=CH–*CH*$_2O$), 31.7 (2C, *CH*$_2$–CH=CH_2), 28.1 ppm (2C, CH_2–*CH*$_2$–CH_2).

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Keywords: biomass · homogeneous catalysis · palladium · selectivity · telomerisation

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