Telomerization of 1,3-butadiene with various alcohols by Pd/TOMPP catalysts: new opportunities for catalytic biomass valorization

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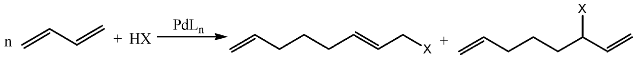
The telomerization of 1,3-butadiene with various alcohols has been investigated using a catalyst based on a Pd(acac)$_2$ precursor and a phosphine ligand, TOMPP (TOMPP = tris-(*o*-methoxyphenyl)phosphine). We were able to demonstrate the capability of the catalyst to telomerize 1,3-butadiene with various multifunctional nucleophiles having primary and secondary alcohol functions. High yields of telomer products (>98%) were obtained in very short reaction times (<2 h). The telomerization activity and selectivity of the Pd/TOMPP complex was strongly influenced by the type of alcohol used as substrate. When diols were used, telomerization of 1,3-butadiene with 1,2-propanediol and 1,2-butanediol afforded the highest yield of mono-telomer (over 70%) and for 1,2-butanediol a turnover frequency (TOF) of 300 000 h^{-1} was reached, combined with a turnover number (TON) of 7800.

1. Introduction

Diminishing oil reserves and the need to develop a sustainable chemical industry have induced growing interest in the biomass-based production of transportation fuels and chemicals.[1] Therefore, efficient technologies for further conversion of biomass derived components are essential, not only to minimize the environmental impact of chemical production, but also to create new economically attractive value chains. Therein, a very promising technology for the conversion of biomass derived components such as glycerol, sugars or starch, is the telomerization of 1,3-butadiene with these nucleophiles.

In general, telomerization describes the addition of a nucleophile toward an alkene bearing a conjugated double bond system and results in the formation of a telomer in a theoretical 100% atom-efficient process (Scheme 1). The first one to describe a telomerization reaction was Smutny in 1967,[2] who studied the oligomerization and dimerization of 1,3-butadiene in the presence of nucleophiles with a Pd based catalyst. Later on, the research focussed on the telomerization of 1,3-butadiene with methanol[3–5] and ammonia[6,7] as nucleophiles, while recently the telomerization of natural products like sugar components[8–12] or starch[13] was reported. The only industrial telomerization process so far is that of 1,3-butadiene with water leading to 2,7-octadien-1-ol.[14–16]



Scheme 1 Telomerization of 1,3-butadiene with nucleophile HX over Pd catalysts.

Pd complexes with phosphine ligands have most frequently been applied[17] as telomerization catalysts but, recently, Pd complexes with carbene ligands have also been shown to be very active telomerization catalysts.[5] Besides methanol, the telomerization of 1,3-butadiene with other alcohols appears to be very interesting, allowing access to molecules with potential surfactant applications or to new chemical building blocks.[18–24]

Substrates produced from renewable feedstocks, either *via* fermentation or even more likely *via* chemo-catalytic conversions,[13–16,25,26] and possessing alcoholic functions like cellulose, starch, vegetable oils or sugars, are particularly interesting due to the possibility of having more than one hydroxyl function.

Such multifunctional nucleophiles offer the opportunity to be used as important chemical building blocks after telomer formation. Particularly, the telomerization of 1,3-butadiene with diols was previously investigated mainly for the case of ethylene glycol.[18–21]

When the telomerization was performed in a single phase system, high amounts of di-telomers were produced with low turnover numbers (TONs) at a high catalyst loading (0.06 mol%).[20] Behr and Urschey succeeded in reducing the formation of the di-telomers by using a biphasic system with a water soluble TPPTS (triphenyl phosphine tris-sulfonate) ligand. The same catalytic system was further applied for telomerization of glycerol.[18]

We have recently shown that a palladium based catalyst system with TOMPP (tris-(*o*-methoxyphenyl)phosphine) exhibits high activity in the telomerization of 1,3-butadiene with glycerol.[27] This catalytic system presented higher activity compared to the previously reported water soluble Pd catalyst with TPPTS as a ligand or other phosphine based ligands.[27] The *in situ* formed

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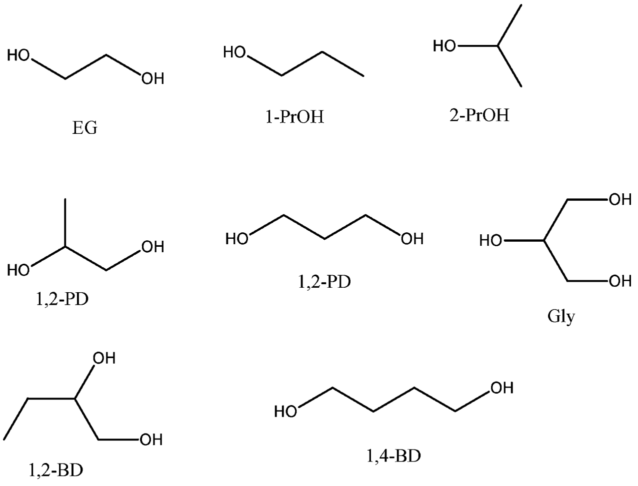
Pd/TOMPP catalytic system did not require the presence of a solvent or a basic initiator as was previously reported for the Pd/TPPTS or Pd/carbene telomerization catalysts.[28,29] Encouraged by these results, we decided to broaden the substrate scope and to further investigate the potential of the Pd/TOMPP catalytic system to telomerize other multifunctional nucleophiles having both primary and secondary alcohols without using any solvent or additive. This investigation aims to give more insight into the telomerization activity of this novel Pd/phosphine system and the relation with the structure of the nucleophile that can later help in developing a large scale telomerization process of 1,3-butadiene with various biomass-based nucleophiles. In other words, the investigated alcohols in this study are biomass-based nucleophiles that include ethylene glycol (EG), 1- and 2-propanol (1- and 2-PrOH), 1,2- and 1,3-propanediols (1,2- and 1,3-PD), glycerol and 1,2- and 1,4-butanediols (1,2- and 1,4-BD) (Scheme 2).

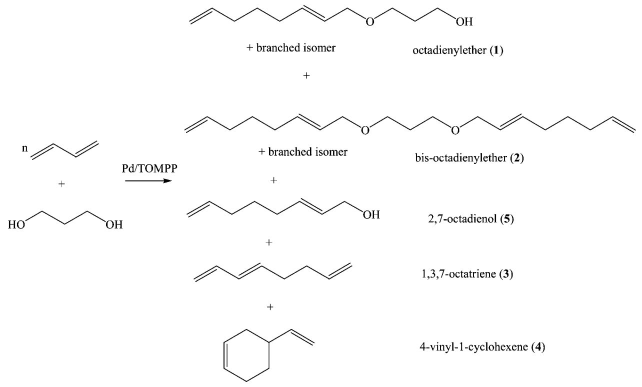


Scheme 2 Overview of the alcohols investigated in this work as nucleophiles in the telomerization of 1,3-butadiene.

2. Results and discussion

2.1. Optimization of telomerization conditions

Telomerization of 1,3-butadiene with 1,3-propanediol (1,3-PD) (Scheme 3) was chosen as a test reaction for the Pd/TOMPP catalytic system. The expected products of this reaction are the mono-telomers (octadienylethers) (**1**), the di-telomers (bisoctadienylethers) (**2**), 2,7-octadienol (**5**) resulting from water impurities, together with the butadiene dimerization products: *e.g.* 1,3,7-octatriene (**3**) and 4-vinyl-1-cyclohexene (**4**).[20] Several reaction parameters (temperature, butadiene : 1,3-propanediol molar ratio) were investigated (Table 1) in order to obtain the highest yield of mono-telomer products. The molar ratio between Pd and TOMPP of 1 : 5 was previously found to give the best catalytic activity/selectivity ratio for telomerization of 1,3-butadiene[27] and was further used in this study. Previous studies on the telomerization of 1,3-butadiene with Pd/PPh3 catalysts indicate that this ratio will minimize branched telomers formation.[17]



Scheme 3 Telomerization of 1,3-butadiene with 1,3-propanediol.

Under all reaction conditions (Table 1), telomerization of 1,3-butadiene with 1,3-PD gave as the major product the mono-telomer (**1**), with yields up to 60% and selectivities over 80%. Di-telomer (**2**) was the main by-product and the non-telomer products were formed in less than 1% yield (Table 1).

Temperature is a key parameter in all chemical transformations. Telomerization of 1,3-butadiene with 1,3-PD occurred with low conversions at temperatures below 353 K. At 333 K, a conversion of 20% was obtained after 90 minutes (entry 1); whereas at 353 K, conversions over 70% were obtained in 25 minutes (entry 2).

A further increase of the reaction temperature to 363 K did not lead to higher conversions or better selectivities. Therefore, 353 K was further used as the reaction temperature for the telomerization of 1,3-butadiene.

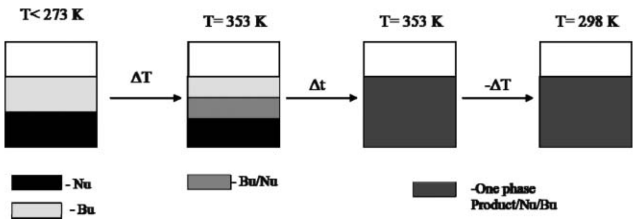
Table 1 Influence of the reaction conditions on the telomerization of 1,3-butadiene with 1,3-PD

Entry	*T*/K	Butadiene : 1,3-PD	Time/min	Conv. (%)	Yield (%)		Sel.[a] (**1**) (%)
					1	**2**	
1	333	2 : 1	94	19.4	18.2	1.2	94.0
2	353	2 : 1	27	76.2	61.4	14.6	80.6
3	363	2 : 1	23	70.0	58.5	10.8	83.6
4	353	4 : 1	29	27.8	26.1	1.6	94.0
5	353	4 : 1	68	96.7	61.1	32.8	63.2
6[b]	353	4 : 1	41	95.9	65.6	30.2	68.4
7[c]	353	2 : 1	36	44.7	39.7	4.9	89.0

Standard reaction conditions: 100 ml autoclave, [Pd] = 0.01 mol%, Pd : TOMPP 1 : 5, 0.125 mol 1,3-PD, conversion and yields calculated with respect to 1,3-PD.[a] Selectivity of mono-telomer **1**. [b] Pd : TOMPP 1 : 10. [c] Reaction carried out with an extra pressure of 0.4 MPa He.

The molar ratio between butadiene and alcohol is another important reaction parameter that influences the product distribution and, therefore, has been investigated. A molar ratio of 1,3-butadiene to 1,3-PD of 2 : 1 should be sufficient to mainly result in the mono-telomer (**1**) formation. According to Scheme 1, two moles of butadiene will react with one mol of nucleophile to give the mono-telomer. The results presented in Table 1 indicate that the reaction behaves differently from the ideal case. Di-telomers were obtained even at a molar ratio of 2 : 1 (entries 1–4) in yields up to 15%. As expected, a higher molar ratio of butadiene to 1,3-PD of 4 : 1 increased the formation of di-telomers (entries 5 and 6).

Besides the presence of larger amounts of butadiene, also the phase behaviour of the reaction mixture affects the product distribution. Formation of the di-telomer in these conditions can be explained by the reaction process depicted in Scheme 4. Initially, a two phase system is obtained: the polar nucleophile (1,3-PD) and the apolar 1,3-butadiene, which at 233 K is liquified. The concentration of TOMPP is higher in the butadiene layer because of the hydrophobic properties of the ligand. During heating to 353 K under continuous stirring, the Pd/TOMPP complex is formed in the butadiene layer and the two phases mix. Formation of the mono-telomer creates a new phase, which is miscible with both the alcohol and butadiene. This results in the formation of a one phase system[28] where both the mono-telomer and the catalyst are present and can easily interact. In this way, the mono-telomer becomes more available to the catalytic species and thereby will be easily re-introduced in the catalytic cycle.[19]



Scheme 4 Schematic representation of phase formation during the telomerization of 1,3-butadiene with 1,3-PD; Nu: 1,3-PD, Bu: 1,3-butadiene.

The solubility of TOMPP in the apolar layer is influenced by the amount of butadiene in the liquid phase. The increase of the molar ratio 1,3-butadiene : 1,3-PD from 2 : 1 to 4 : 1 will increase the solubility of TOMPP.

The access of the polar nucleophile to the catalytic centre will become more difficult and longer reaction times will be necessary to reach higher conversions (entries 4 and 5, Table 1). An identical effect was obtained when an external gas pressure was introduced. Using a molar ratio butadiene : 1,3-PD of 2 : 1 and a 0.4 MPa external helium pressure, a longer reaction time was needed to achieve a 50% yield of telomers (entry 7). In order to regain the initial activity, the Pd to TOMPP molar ratio was changed from 1 : 5 to 1 : 10 (entry 6). The reaction time required to convert all the diol to telomers products decreased from 68 minutes (entry 5) to 41 minutes (entry 6) and the selectivity to the mono-telomer increased from 63% to 68%. A molar ratio of butadiene : nucleophile of 2 : 1 and a ratio of Pd : TOMPP of 1 : 5 were further used in the telomerization reaction with the other substrates.

2.2. Substrate scope

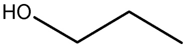
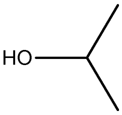
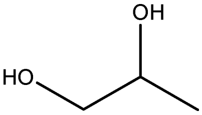
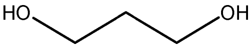
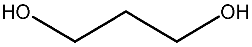
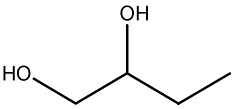
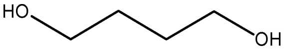
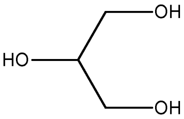
Beside 1,3-PD, other polyols were tested as nucleophiles in the telomerization of 1,3-butadiene in order to show the versatility of the Pd/TOMMP catalytic system (Table 2).

For all substrates, the mono-telomer was obtained as the major product. Besides the telomerization products, 2,7-octadienol was the major side product in yields <1%. The product distribution and the time necessary to reach almost total conversion of the substrate varied with the alcohol. For 1-propanol, 2-propanol and glycerol, a higher amount of catalyst (0.06 mol%) was used to achieve reasonable conversions after 70, 70 and 30 minutes of reaction, respectively (entries 1, 2 and 9). 1-Propanol (entry 1) gave a higher yield of telomer than 2-propanol (entry 2) with product selectivities in both cases over 99%. For glycerol, tri-telomers were obtained together with the mono- and di-telomers (entry 9).[27] Better results were obtained in the case of diols (entries 3–8). Mono-telomers remained the major products in the series. The highest yield of mono-telomer, over 70% (entries 4 and 6), was obtained with 1,2-PD and 1,2-BD, whereas the highest yield of di-telomer, 38% (entry 3), was obtained for EG. The selectivity of the telomerization was influenced by the position of the second –OH group. With the 1,3-PD and 1,4-BD substrates, the selectivity to the mono-telomers was lower compared to the corresponding 1,2-diols (entries 4, 5, 7 and 8). TONs were also influenced by the type of the alcohol. The lowest TONs were obtained for 1-propanol, 2-propanol and glycerol (entries 1, 2 and 9, Table 2). High TONs were obtained for all investigated diols. While the TON indicates the activity of the catalyst, a very high value is not necessarily good for the selective mono-telomerization of 1,3-butadiene with diols. The formation of one mol of mono-telomer accounts for one reaction cycle and corresponds to a TON of 1, whereas the di-telomer formation corresponds to a TON of 2. Therefore, for EG (entry 3), a higher TON (9831) than for the other diols is reached, since high amounts of di-telomer are formed. A higher TON can be obtained by increasing the amount of 1,3-butadiene (entry 6), which also increases the production of di-telomers. For 1,3-PD, the TON increased from 7584 to 10 562 when the molar ratio between 1,3-butadiene and 1,3-PD was increased from 2 : 1 to 4 : 1.

2.3. Influence of the structure of the diol on the telomerization activity of Pd/TOMPP

In order to understand the variation in the catalytic activity of the Pd/TOMPP system in the case of the diols, the initial activities were measured. By stopping the reaction at conversions below 20%, the formation of the di-telomer is strongly reduced and the activity is determined only by the formation of the mono-telomer. In all cases, selectivities above 90% were obtained. This is important, since the competition between the un-transformed alcohol and the mono-telomer for telomerization is avoided. A surprising trend in turnover frequency (TOF) values was obtained (Table 3). The highest TOF was obtained for 1,2-BD (321 085 h^{-1}) and the lowest for EG (7206 h^{-1}), which is contradictory to the results of Behr and Urschey.[18] Using the

Table 2 Telomerization of 1,3-butadiene with various alcohols

Entry	Substrate	Time/min	Yield			
			Mono- (%)	Di- (%)	Sel.$_{\text{mono-telomer}}$ (%)[c]	TON[a]
1[b]		70	80.0	—	100.0	1340
2[b]		70	41.5	—	100.0	692
3		66	42.4	37.8	52.8	9831
4		34	73.2	6.6	89.4	7188
5		27	61.4	14.6	80.6	7584
6[d]		68	61.1	32.8	63.2	10 562
7		22	70.1	11.4	84.1	7779
8		19	64.2	16.2	79.8	8048
9[b]		30	37.0	18.0	60.0	1529

Standard reaction conditions: 100 ml autoclave, [Pd] = 0.01 mol%, Pd : TOMPP 1 : 5, 353 K, 1,3-butadiene : nucleophile 2 : 1. [a] TON calculated based on nucleophile conversion, where formation of 1 mol of mono-telomer is one reaction cycle TON = 1, where for 1 mol of di-telomer TON = 2. [b] [Pd] = 0.06 mol%. [c] Sel.$_{\text{mono-telomer}}$ = (Yield mono/Conv.) × 100. [d] 1,3-butadiene : 1,3-PG 4 : 1; mono-: mono-telomer, di-: di-telomer.

Table 3 Physical properties *versus* TOF for diols

Substrates	pK_a (1°)[a]	pK_a (2°)[a]	E_T^N[b]	TOF/h^{-1}
ED	15.1	—	0.790	7206
1,2-PD	15.1	15.13	0.722	30 991
1,3-PD	15.42	—	0.747	21 183
1,2-BD	15.1	15.13	0.676	321 085
1,4-BD	15.63	—	0.704	227 498

[a] pK_a was calculated using the online program SPARC,[31] pK_a (1°) – pK_a of the primary –OH and pK_a (2°) – pK_a of the secondary –OH. [b] Taken from ref. 30.

water soluble Pd/TPPTS, they concluded that the catalyst was most active when ethylene glycol was used as a substrate.

Several factors may be responsible for this activity trend in the case of the Pd/TOMPP telomerization of 1,3-butadiene with diols. Hydrophobicity, pK_a and the coordination properties of the diols are the major factors that seem to influence the activity of the telomerization catalyst.

The hydrophobic nature of the ligand has already been pointed out as responsible for the formation of the di-telomer products (*vide supra*). The hydrophobic nature of the diol is influencing both the solubility of the TOMPP ligand and the interaction with the butadiene. Based on the E_T^N values of the investigated diols (Table 3), butanediols are expected to present the highest hydrophobic properties, where ethylene glycol is the most hydrophilic.[30]

The solubility of the TOMPP ligand in the above diols was measured using UV-Vis spectroscopy. TOMPP presents a strong absorption band around 292 nm corresponding to the intraligand π–π* and n–π* transitions, and the intensity of this band was used to measure the solubility of the ligand in the tested diols. At room temperature, TOMPP was mostly insoluble in all tested diols. After heating to 353 K, the solubility varied in the order of 1,2-BD > 1,2-PD > EG > 1,4-BD > 1,3-PD. Concentrations of TOMPP equivalent to the ones used during telomerization experiments were used. The presence of the second –OH group in the alpha position to the primary –OH seems to increase the solubility of the TOMPP ligand.

TOMPP is more soluble in 1,2-BD compared to 1,4-BD and 1,2-PD compared to 1,3-PD. A longer alkyl chain increased, as expected, the solubility of TOMPP in the series EG, 1,2-PD and 1,2-BD, since it increases the hydrophobic properties of the diol. Whereas TOMPP is less soluble in 1,4-BD compared to 1,2-PD and EG, the TOF obtained for 1,4-BD is much higher than the TOF of 1,2-PD and EG (Table 3). Based on the E_T^N, 1,4-BD is more hydrophobic than 1,2-PD and EG (Table 3).

Furthermore, 1,3-butadiene solubility in the diols was tested taking toluene as a reference molecule for the diene as previously suggested by Behr and Roll.[28] The results showed that butanediols dissolved the highest amount of toluene at room temperature, where the poorest solubility was in ethylene glycol. These results explain the high TOF obtained for 1,2-BD, since it can easily dissolve both more ligand and more butadiene. The same conclusion can be drawn for propanediols for which 1,2-PD has a higher TOF than 1,3-PD (Table 3).

The fact that 1,4-BD is more active than 1,2-PD and 1,3-PD than EG can be explained by the increased butadiene solubility but also by the coordination properties of the diol. Diols can coordinate in a chelate fashion to Pd. This chelate-type coordination may decrease the telomerization activity, since less coordination sites remain available for butadiene coordination. 1,2-Diols may coordinate stronger to the Pd, since the distance between the –OH is smaller. Increasing the distance between the –OH groups from 1,2-diols to 1,4-diol will decrease the strength of the chelate.[32,33] For 1,4-BD, a poor bidentate coordination is expected, which explains the high telomerization activity obtained for this support even if the butadiene solubility is not favourable.

The pK_a values of the –OH groups also influence the product distribution and catalyst activity. For 1,2-diols like 1,2-PD and 1,2-BD there is a difference in the pK_a of the –OH groups. The secondary –OH presents a higher pK_a value than the primary alcohol (Table 3). For these diols, the primary alcohol reacts predominantly and this explains the higher selectivity for the mono-telomer (more than 85%) (Table 2). 1,2-BD is less selective but more active than 1,2-PD even if their pK_a values are similar, which can be explained by the higher hydrophobicity of the 1,2-BD. For linear diols like EG, 1,3-PD and 1,4-BD, both –OH groups present the same pK_a value, so the formation of the mono-telomers and further on the di-telomers can occur at each of the two hydroxyl group with higher probability. Having a lower pK_a value for the two –OH groups makes EG more nucleophilic and the addition to the double bond of the diene is faster compared to 1,3-PD and 1,4-BD and, therefore, a lower selectivity for the mono-telomer is obtained (Table 2, entry 3).

3. Conclusions

The telomerization of 1,3-butadiene with various alcohols and diols was achieved using the Pd/TOMPP catalytic system in the absence of a solvent. Very high TON and TOF values for a telomerization catalyst were obtained in a single reaction run. The mono-telomers were obtained in all cases as the main reaction products, with the highest yields obtained for 1,2-PD and 1,2-BD. By using a low molar ratio 1,3-butadiene to diol of 2 : 1, the formation of di-telomers is reduced. The product distribution and the activity were strongly influenced by the acidity, coordination property and the hydrophobicity of the alcohol. A hydrophobic alcohol with a low pK_a value of the –OH groups affords the highest telomerization activity.

4. Experimental

4.1. Catalytic experiment

In a typical telomerization experiment, 1.5×10^{-5} mol (4.57 mg) of $Pd(acac)_2$ and 7.5×10^{-5} mol of the TOMPP ligand were added to 0.125 mol of alcohol. For 1-propanol and 2-propanol, 7.5×10^{-5} mol of $Pd(acac)_2$ and 3.75×10^{-4} mol of ligand were used to achieve reasonable conversions in comparable reaction times. The alcohol, the Pd source and the phosphine were directly mixed inside a 100 ml stainless steel Parr autoclave and flushed three times with argon. The autoclave was cooled down to 233 K using an acetone–dry ice mixture. 1,3-Butadiene was directly condensed in the reactor and the autoclave was heated to the reaction temperature of 353 K and kept until the pressure had dropped to less than 3 bar. The starting point of the reactions was defined as the time the reaction temperature was reached. After the reaction, the reactor system was cooled to room temperature and flushed several times with argon.

4.2. Analytical methods

The reaction mixture was analyzed using a GC 2010 system from Shimadzu with a CP-WAX 57CB (internal calibration). As the reaction products are rarely commercially available, authentic samples of each were prepared and were purified using column chromatography. Their purities were checked by ^{13}C NMR, ^1H NMR and GC-MS. The GC calibration was performed afterwards using these purified products. Conversions and yields were calculated based on the alcohol. Branched products have been observed in amounts below 9% using ^1H NMR. 1,3-Butadiene and argon were purchased from Linde Gas Benelux, all other chemicals were obtained from Aldrich and were used without any purification. UV-Vis measurements were made on a Varian Cary 50 Conc. spectrometer in absorbance mode.

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