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Tetrabutylphosphonium bromide catalyzed dehydration of diols to dienes and its application in the bio-based production of butadiene

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ABSTRACT We report the use of the ionic liquid tetrabutylphosphonium bromide as a solvent and catalyst for dehydration of diols to conjugated dienes. This system combines stability, high reaction rates and easy product separation. A reaction mechanism for the model compound 1,2-hexanediol is proposed and experimentally corroborated. This particular mechanism allows for the selective formation of conjugated dienes, in contrast with purely acidic catalysis. Next, the reaction is also performed on various other diols. As a first application, we assessed the bio-based production of 1,3-butadiene. Starting from 1,4-butanediol, a 94% yield of butadiene was reached at 100% conversion.

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3 KEYWORDS ionic liquids, phosphonium bromide, diol dehydration, conjugated dienes, 1,4-
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5 butanediol, butadiene
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8 9 **Introduction**

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12 Conjugated dienes are a valuable class of chemicals, due to their reactivity in important chemical
13 reactions such as the Diels-Alder reaction and various functionalization and polymerization
14 reactions. As a result, these compounds have tremendous application potential in the production
15 of both fine chemicals¹⁻³ and polymers^{4,5}. The most important diene from an industrial point of
16 view is 1,3-butadiene, which is mostly used for the production of polymers, such as styrene-
17 butadiene rubber and polybutadiene.⁴ An interesting approach towards the synthesis of
18 conjugated dienes in general and 1,3-butadiene in particular is the dehydration of diols, some of
19 which can be obtained from renewable resources.⁶⁻⁸ However, in most cases conjugated dienes
20 are not the predominant products of diol dehydration due to side reactions such as dehydration to
21 aldehydes, cyclodehydration to cyclic ethers or rearrangements like the pinacol rearrangement.⁹
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37 In past research, we have shown the activity of tetraalkylphosphonium chloride ionic liquids (IL)
38 as catalytic solvents in the dehydrochlorination of 1,2-dichloroethane for the production of vinyl
39 chloride.¹⁰ In this reaction, the chloride anion functions as a base to catalyze the elimination
40 reaction. Since this reaction showed the activity of tetraalkylphosphonium halogenides as
41 defunctionalization catalysts, we investigated the use of these ionic liquids as dehydration
42 catalysts. Here we show that tetraalkylphosphonium halogenides, in particular
43 tetrabutylphosphonium bromide, are active catalytic solvents for the dehydration of diols,
44 selectively forming conjugated dienes.
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Experimental section

Catalytic reaction. In a typical reaction 1.7 mmol of an IL was loaded into a glass vial. A reaction mixture containing 0.5 mmol of substrate and 0.5 mmol of internal standards n-hexane or 2,3-dimethylbutane and n-tetradecane in 250 μ L mesitylene was added. For substrates that do not dissolve in mesitylene (for example butanediols), the substrate is weighed and a mixture containing the internal standards in 250 μ L mesitylene is added. Next, 0.022 mmol HBr and, depending on the reaction, other additives were added. After addition of a magnetic stirring bar, the vial was sealed under a N₂ atmosphere using a cap with septum. The mixture was then heated to 200 °C while stirring at 500 rpm. After reaction, the mixture was cooled down until it was safe to handle, but the IL was still liquid. In order to quantitatively extract and analyze the products and the internal standards, 1 mL of mesitylene was added through the septum using a syringe. A picture of the phase separation is shown in figure S1. After a short time of stirring, the mixture was cooled down further on ice. An aliquot of the mesitylene layer was removed with a syringe for gas chromatographic (GC) analysis. This method allowed to quantify a compound as volatile as 1,3-butadiene (with a boiling point of -4 °C); butadiene peaks are observed upon GC analysis of the mesitylene phase if this compound is formed. Next, the cap was removed to add 1.5 equivalent of BSTFA per hydroxyl group in the substrate. The vial was sealed with a new cap and the mixture was heated to 60 °C for 1 hour while stirring at 500 rpm. More BSTFA was added in reactions with large amounts of water or acid. After derivatization, another aliquot was taken for GC analysis.

Product analysis and identification. Substrate conversion and product yields were determined using GC analysis on a Shimadzu GC-2010 with a 60 m CP SIL 5 CB column and an FID detector. Samples taken after reaction were compared to a sample of the mixture before reaction.

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3 The peak areas of substrate and products were normalized by dividing them by the peak area of
4 an internal standard. For volatile compounds (boiling point < 100 °C was chosen as a limit), n-
5 hexane or dimethylbutane were used as internal standard, to account for losses due to
6 evaporation. Less volatile compounds were quantified using n-tetradecane. To compare the peak
7 areas of different compounds, the effective carbon number (ECN) was used. This allowed to
8 calculate product yields. The yield of polar compounds was determined from the silylated
9 samples, since extraction of polar compounds from the IL proved unsuccessful. The calculated
10 conversion of the substrate never differed more than a few percent from the total calculated
11 yield, indicating a good mass balance. Unknown products were identified using gas
12 chromatography coupled to mass spectrometry (GC-MS). The identity of the products was
13 confirmed by comparing the retention time with that obtained for a commercial sample of the
14 compound. This was performed on an Agilent 6890N GC, equipped with a HP-5 MS column,
15 coupled to a 5973N mass spectrometer. Representative gas chromatograms with annotated peaks
16 are shown in figure S2 and S3 for 1,2-hexanediol and S4 and S5 for 1,4-butanediol.
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40 **Results and discussion**

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43 To compare different tetraalkylphosphonium ILs in the same conditions, and since commercial
44 samples contain different levels of acidity, they were first neutralized using Bu₄POH (see SI).
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46 Then, 0.013 mol HBr (48% in water) per mol of ionic liquid was added. This amounts to 4.4
47 mol% compared to the diol substrate, so the relative molar amounts are diol : ionic liquid : HBr =
48 1 : 3.4 : 0.044. 1,2-Hexanediol (HDO) was chosen as a model substrate to study the reaction
49 system. Selective formation of dienes from vicinal diols is challenging as acid catalyzed
50 dehydration of 1,2-alkanediols typically leads to the formation of aldehydes, through an enol
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intermediate.^{11,12} However, reaction in all tested ILs leads, rather unexpectedly, to predominant formation of different conjugated hexadienes, in selectivities of at least 50% (Table 1). Next to the formation of up to 62% hexadienes after 30 minutes at 200°C, the most important products are 2-hexanone and hexanal, their acetals with 1,2-hexanediol and their aldol products. 2-Hexen-1-ol and 1-halo-2-hexanol (halo corresponding to the anion of the IL) were detected in yields around 1%. For clarity, the reaction products have been divided into 5 groups: hexadienes (HD), 2-hexanone and derived products (HON), hexanal and derived products (HAL), 2-hexen-1-ol (HOL) and 1-halo-2-hexanols (XOH) (see SI). Next to these products, traces of 2,6-dibutyl-1,4-dioxane, the ether of two hexanediol molecules, were detected in all ionic liquids. Throughout the reactions in this paper, this ether product is always detected in yields below 1% for reactions that have not reached full conversion. After full conversion is reached, no ether is detected, indicating the reversibility of etherification in the reaction conditions. Therefore, the role of the ether product will not be further discussed.

Table 1. Product yields in the dehydration of 1,2-hexanediol.

Solvent	Acid	Yield (%)					X (%)
		HD	HON	HAL	HOL	XOH	
Bu ₄ PBr	None	6	2	3	1	0	11
Bu ₄ PCl	HBr	4	1	2	1	<1	8
Bu ₄ PBr	HBr	62	20	16	1	1	99
Bu ₄ PI	HBr	3	1	2	<1	-	6
Bu ₄ NBr	HBr	1	0	1	0	0	2
Mes	PTSA	1	-	9	-	-	11

Conditions: 0.5 mmol 1,2-hexanediol, 1.7 mmol ionic liquid or 2 mL mesitylene, 0.022 mmol acid, 200 °C, N₂ atmosphere, 30 minutes. HD = hexadienes, HON = 2-hexanone, HAL = hexanal, HOL = 2-hexen-1-ol, XOH = 1-halo-2-hexanol, X = conversion, Mes = mesitylene, PTSA = *p*-toluenesulfonic acid.

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3 By using different ILs, the effect of cation and anion on the reaction was tested. Previously, we
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5 thoroughly investigated the influence of the IL cation on basicity for the dehydrochlorination of
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7 1,2-dichloroethane.¹⁰ We concluded that the basicity and thus dehydrochlorination activity of the
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9 IL depend on the strength of the interaction between cation and anion. The higher basicity of
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11 phosphonium ILs compared to inorganic salts can be explained by the decreased electrostatic
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13 interaction between cation and anion, caused by the bulkiness and dispersed charge of the
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15 phosphonium cation.^{13,14} As a result, the anion is more free and its charge is less compensated,
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17 which increases the basicity. Generally, amongst a broad variety of common ILs, the interaction
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19 between cation and anion is weakest for tetraalkylphosphonium cations, resulting in the highest
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21 basicity.^{15,16} In this research, the cation effect was only briefly investigated (table S2), leading to
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23 the result that Bu₄P⁺ is the optimal cation in this reaction, like in the dehydrochlorination of 1,2-
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25 dichloroethane. Anion variation seems to have a larger effect on catalysis than cation variation
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27 (Table 1). All tested ILs show a similar product distribution, but Bu₄PBr strongly outperforms
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29 the other ionic liquids. Therefore, this IL was selected for further experiments. To compare the
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31 system with a purely acidic dehydration, the reaction was also performed in mesitylene as a
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33 solvent with *p*-toluenesulfonic acid as the catalyst. In these conditions, hexanal and its acetal are
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35 almost exclusively formed from 1,2-hexanediol, with a selectivity of 90%. As discussed before,
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37 the selective formation of aldehydes and acetals in the acid catalyzed dehydration of 1,2-
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39 alkanediols is well known.^{11,12} The entirely different product distribution in the presence of
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41 phosphonium ILs clearly indicates a distinct reaction mechanism.
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52 In addition to the activity, also the stability of the catalyst is important. No breakdown of
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54 tetrabutylphosphonium chloride (Bu₄PCl) or bromide (Bu₄PBr) was detected by ¹H NMR of the
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56 ionic liquid, nor were volatile decomposition products detected by GC. This was expected, since
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3 the long-term stability of Bu₄PCl at 240 °C in highly acidic conditions was reported before.¹⁰
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5 However, reaction in tetrabutylphosphonium iodide (Bu₄PI) leads to formation of small amounts
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7 of tributylphosphine, tributylphosphine oxide and butenes and a dark red discoloration of the IL.
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9 This can be caused by the reverse Menshutkin reaction, a typical decomposition pathway for
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11 ammonium ILs.¹⁷ This reaction would lead to 1-iodobutane and tributylphosphine. 1-Iodobutane
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13 can be dehydroiodinated to form butenes, while tributylphosphine is very sensitive to oxidation,
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15 even in the injection port of the GC. This decomposition was not investigated further, since it
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17 does not occur in Bu₄PBr, the most active catalyst by far. For comparison, the reaction was also
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19 performed in Bu₄NBr, resulting in severe decomposition of the ionic liquid to tributylamine, 1-
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21 bromobutane and 1-butene, most likely due to the aforementioned Menshutkin reaction. The
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23 decomposition temperature of ammonium ILs is known to be lower than for their phosphonium
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25 analogs.^{17,18} For example, the thermal stability of a series of phosphonium and ammonium
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27 dicyanamides has been compared and the decomposition temperature of the phosphonium ILs
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29 was about 100 °C higher.¹⁹ Unsurprisingly, the hexadiene yield was very low for this catalyst,
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31 highlighting the strong catalytic performance of the phosphonium ionic liquids, especially
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33 Bu₄PBr.
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42 As a means to elucidate the reaction mechanism, the time profile of the reaction in Bu₄PBr was
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44 investigated, both at 170 °C and 200 °C. At 200 °C, full conversion is already reached after 30
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46 minutes (Figure 1 a). The selectivity towards HD, HON and HAL remains quite constant, around
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48 62, 20 and 18% respectively. Interestingly, the hexadiene products are stable in this system; no
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50 oligomerization products are detected and the hexadiene yield remains constant after reaching
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52 full conversion. In the beginning of the reaction, trace amounts of 1-bromo-2-hexanol (1B2H)
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54 and 2-hexen-1-ol are formed, which might indicate that these are intermediate products. The
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3 reaction profile at 170 °C is more useful to understand the reaction network (Figure 1 b). Full
4 conversion is reached after 120 minutes at this temperature. The HD selectivity rises during
5 reaction, eventually reaching a similar selectivity at full conversion as for the reaction at 200 °C.
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8 The HON and HAL selectivities are quite similar to the values reached at 200°C. The most
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10 interesting observation regards the selectivities towards 2-hexen-1-ol and especially 1-bromo-2-
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12 hexanol. After short reaction times at 170°C, these are higher than at 200 °C, and they gradually
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14 decrease. This is an extra indication that these are intermediate products.
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21 Different reaction parameters were varied to investigate the effects on catalysis. First, increasing
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23 the acid content increases the rate of the reaction (Figure 1 c). The selectivity towards HAL
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25 seems to drop slightly, while the HON selectivity increases with about the same amount. The
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27 selectivity towards HD remains quite stable, especially from 0.01 mmol HBr, or 2 mol%,
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29 onward. Varying the type of acid shows the need for strong acids to obtain a high reaction rate
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31 (Figure 1 d). Furthermore, the reactions with trifluoromethanesulfonic acid (TFSA), p-
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33 toluenesulfonic acid (PTSA) or H₂SO₄ as co-catalyst demonstrate the compatibility of the
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35 reaction system with strong acids other than HBr. For all these acids, similar results were
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37 obtained. Furthermore, the system is also compatible with a strong solid acid catalyst, as
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39 demonstrated by the use of Nafion. The use of HCl and Amberlyst 15 resulted in lower
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41 hexadiene yields. For HCl this is most likely due to the high volatility of hydrochloric acid (28.3
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43 kPa for 38% HCl in standard conditions) compared to the other acids. This results in a much
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45 lower amount of protons in the ionic liquid than expected from the amount of added acid. Also
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47 Amberlyst-15 resulted in lower yields than expected. However, this solid acid is not intended for
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49 use above 120 °C, which can explain the lower yields. Next, increasing the temperature results
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51 in a higher rate, with full conversion already achieved after 5 minutes at 220 °C (Figure 1 e).
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This amounts to an average turn-over frequency (TOF) of 2.1 h^{-1} at full conversion. The selectivities are again quite stable, reaching a slight optimum at $200 \text{ }^\circ\text{C}$. Finally, addition of water to the IL seems to have little effect either on conversion or yield (Figure 1 f). Besides the variation of different reaction parameters, we also confirmed the excellent stability of the catalytic system in recycling experiments (Figure S8).

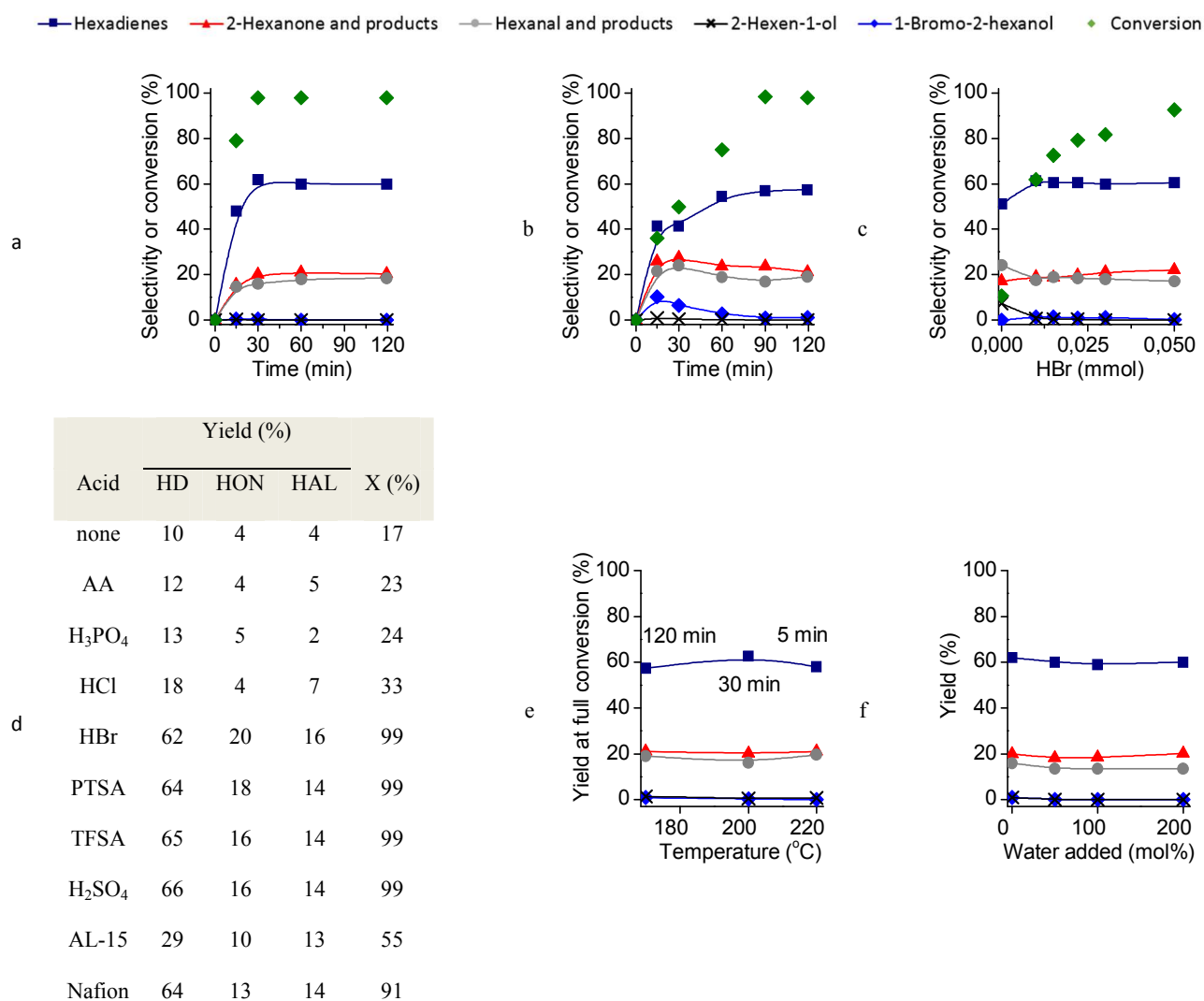
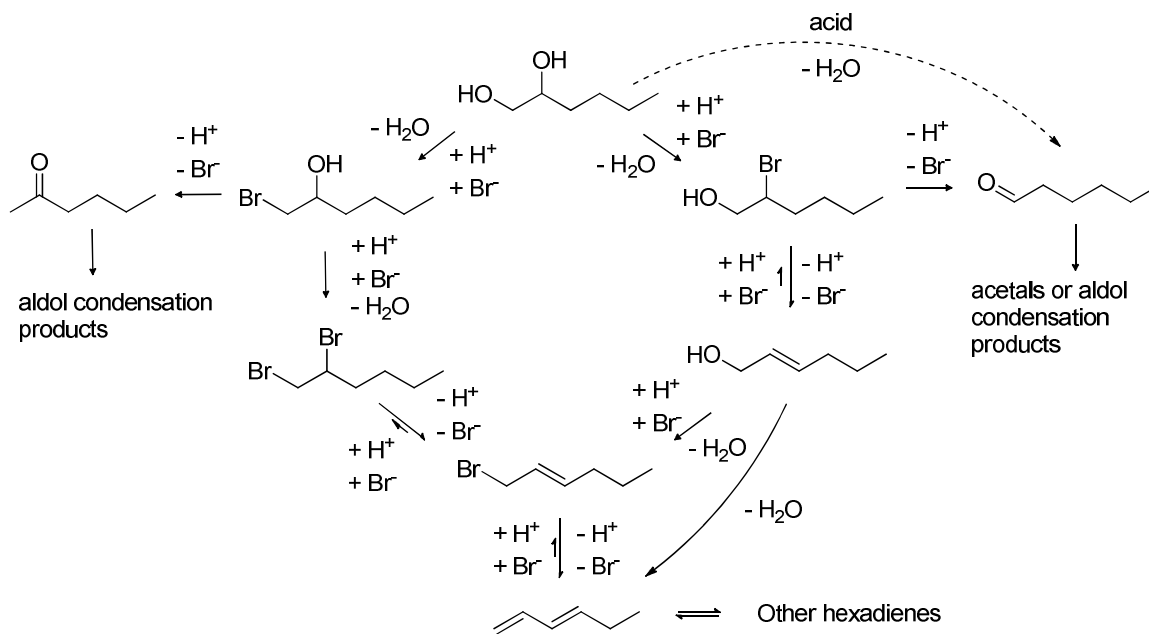


Figure 1. Yields, selectivities and conversions in the dehydration of 1,2-hexanediol: a) time profile at 200°C , conditions: 0.5 mmol 1,2-hexanediol, 1.7 mmol Bu_4PBr , 0.022 mmol HBr, $200 \text{ }^\circ\text{C}$, N_2 atmosphere; b) time profile at 170°C ; c) variation of acid content, 15 minutes; d) variation

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3 of acid type, 0.022 mmol acid, 30 minutes; e) variation of temperature f) variation of added
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5 water content relative to 1,2-hexanediol, 30 minutes; HD = hexadienes, HON = 2-hexanone,
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7 HAL = hexanal, X = conversion, AA = Acetic acid, PTSA = *p*-toluenesulfonic acid, TFSA =
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9 trifluoromethanesulfonic acid, AL-15 = Amberlyst 15.
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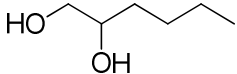
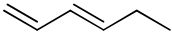
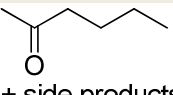
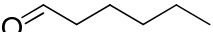
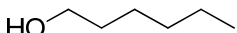
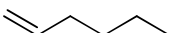
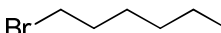
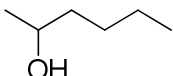
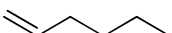
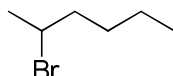
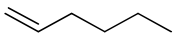

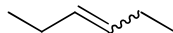
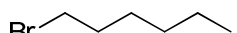
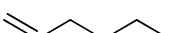
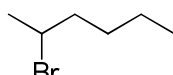
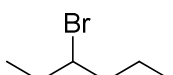
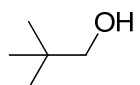
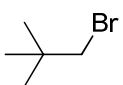


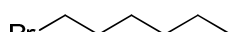
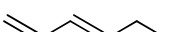
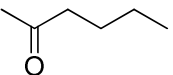
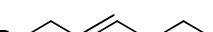
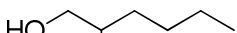
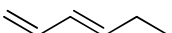
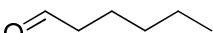
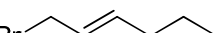
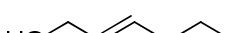
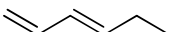
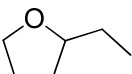
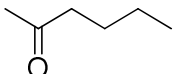
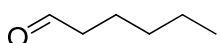
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13
14 Based on these experimental data, the mechanism in Scheme 1 is proposed. This mechanism
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16 consists of acid and IL catalyzed substitutions with bromide followed by IL catalyzed
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18 dehydrobrominations. In the first step, the bromide anion functions as a nucleophile, substituting
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20 either the primary or the secondary hydroxyl group, leading to 1-bromo-2-hexanol (1B2H), a
21
22 detected intermediate, and 2-bromo-1-hexanol (2B1H) respectively. Since similar yields were
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24 reached with strong acids other than HBr, such as H₂SO₄ and PTSA, it is likely that the bromide
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26 of the IL acts as the nucleophile in this substitution reaction. The acid presumably serves only to
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28 protonate the hydroxyl group, making it a better leaving group. In the next step bromide anions
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30 can function as a base to catalyze dehydrobromination reactions. Thus, 2B1H can be
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32 dehydrobrominated to either hexanal or 2-hexen-1-ol, which is a detected intermediate. The latter
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34 can be dehydrated by bromide substitution followed by dehydrobromination (removing the
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36 proton in the C₄ position), but is also expected to be quite reactive in purely acid catalyzed
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38 dehydration, since it is an allylic alcohol. The formed 1,3-hexadiene isomerizes to form 2,4-
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40 hexadienes, through bromohexene intermediates. On the other hand, 1B2H can either be
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42 dehydrobrominated to form 2-hexanone or the remaining secondary hydroxyl group can be
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44 substituted by bromide to form 1,2-dibromohexane, which eventually leads to hexadienes.
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51 Another, purely acid-catalyzed pathway from HDO directly to hexanal is also proposed (dotted
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53 line in Scheme 1).
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Scheme 1. Proposed reaction mechanism for dehydration of 1,2-hexanediol catalyzed by Bu_4PBr and an acid.

To the test the validity of this reaction scheme, different reactants and putative intermediates were tested in the typical reaction conditions in 15 minute reactions at 200°C (Table 2). Entries 2 and 3 show that both primary and secondary alcohols can be dehydrated, with olefins as the main product. Furthermore, the overall dehydration reaction is faster for a secondary alcohol than for a primary alcohol. These results confirm the mechanism via a nucleophilic substitution step, since 1- and 2-bromohexane are formed starting from 1- and 2-hexanol respectively. No other bromohexanes are detected. The elimination of HBr from the primary bromide proves more difficult than from the secondary bromide, as is typical in elimination reactions.²⁰ This can explain why, in the dehydration of HDO, 1B2H is detected intermediately and 2B1H is not.

Table 2. Product yields in the dehydration and/or dehydrobromination of different reactants/putative intermediates.

Entry	Substrate	Products and yield (%)
1	 OH OH	 + isomers 48  + side products 16  + side products 15
2		 + isomers 20 Br-  4 C ₅ H ₁₁ -O-C ₅ H ₁₁ 3
3		 + isomers 86  1
4		 56  18
5	Br- 	 + isomers 62  9  10
6		 3  1  <1
7	Br-  OH	 + isomers 18  + side products 49 Br-  + isomers 3
8	HO-  Br	 + isomers 54  + side products 9 Br-  + isomers 2
9	HO- 	 + isomers 95  <1
10 ^a		Aldol products 47
11 ^a		Aldol products 99

Conditions: 0.5 mmol substrate, 1.7 mmol Bu₄PBr, 0.022 mol HBr, 200 °C, N₂ atmosphere, 15 minutes. ^a 200 mol% water added.

The reaction of 1-hexene (entry 4) shows that double bond isomerization occurs. This isomerization may proceed through a hydrobromination/dehydrobromination sequence, or

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3 simply through a carbenium intermediate. However, entry 5 shows that different 2- and 3-
4 bromohexanes are produced starting from 1-bromohexane. This suggests a (de)hydrobromination
5 equilibrium, which lies mostly towards the olefins, but is pushed towards bromohexanes due to
6 the larger amount of HBr present compared to entries 2 to 4 (as HBr is produced in initial
7 dehydrobromination). The fact that this (de)hydrobromination equilibrium is operative, raises a
8 mechanistic question: the brominated products that are detected could be produced either by
9 nucleophilic substitution of alcohols or by dehydration of alcohols followed by
10 hydrobromination. The first pathway is most likely, as it is corroborated by two experimental
11 findings. First, 2,2-dimethyl-1-propanol (DMP, entry 6) yields 1-bromo-2,2-dimethylpropane
12 (BDMP). As this product cannot be formed from DMP through dehydration followed by
13 hydrobromination, it must be formed through the nucleophilic substitution pathway. The yield of
14 BDMP is rather low, but this is most likely because DMP is a sterically hindered primary
15 alcohol, which is expected to react slowly in substitution reactions. Secondly, 1B2H is detected
16 as a reaction product, especially in short reactions at 170 °C. If this product is formed by
17 hydrobromination, it can only be formed from 1-hexen-2-ol. As this compound is the tautomer of
18 2-hexanone, it should be possible to form 1B2H from 2-hexanone in the reaction conditions. This
19 is however not the case (entry 10), suggesting 1B2H is most likely formed through substitution
20 of bromide into 1,2-hexanediol, as in the proposed mechanism.
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46 To further confirm the reaction mechanism, we examined the fate of different putative
47 intermediates in the typical reaction conditions. As expected, 1B2H (entry 7) leads to the
48 formation of hexadienes and 2-hexanone, while 2B1H (entry 8) leads to hexadienes and hexanal.
49 A more elaborate discussion of these reactions is available in the SI. Next, 2-hexen-1-ol (entry 9)
50 is quickly dehydrated, forming hexadienes with 95% yield after 15 minutes. Finally, 2-hexanone
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3 and hexanal (entries 10 and 11) are shown to be dead-end products, resulting only in their aldol
4 products (or acetals in the presence of HDO).
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9 This mechanism can also explain the most important observations from the variation of
10 parameters. First, only small amounts of bromide substituted products are generally detected.
11
12 This indicates that the nucleophilic substitution is most likely slower than the following
13 dehydrobromination; thus the nucleophilic substitution is the rate determining step. Typically, in
14 such reactions, the hydroxyl group needs to be protonated to make it a better leaving group. This
15 can explain the increase of reaction rate with increased acid content. Furthermore, increasing the
16 amount of acid slightly increases the 2-hexanone selectivity, while decreasing the hexanal
17 selectivity. This might be because the primary substitution is more difficult and therefore is
18 accelerated more by the increased acid content. As the selectivity of 2B1H over 1B2H increases,
19 the HD yield is expected to drop (entries 8 and 9). However, the HD yield can remain stable, as
20 in the next step formation of 1,2-dibromohexane from 2B1H is promoted at higher acid content.
21
22 Finally, the nucleophilic substitution seems to be irreversible in the reaction conditions, as other
23 alcohols than the starting compound are never formed. This explains why the addition of water
24 has almost no effect on yield or selectivity.
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43 Next to these experimental results, the reaction mechanism is also confirmed by literature. We
44 have noticed that this system shows some similarity with the one reported by Zhang et al.²¹ Their
45 system consists of a tetraalkylammonium bromide, combined with a polyoxometalate (POM) as
46 Brønsted acid and a Lewis acidic metal and is used for the dehydration of (primary) mono-
47 alcohols. The Lewis acid is not required for dehydration, but serves to diminish the production of
48 ethers. They propose and experimentally confirm an acid catalyzed nucleophilic substitution of
49 the hydroxyl group of the alcohol by the bromide of the IL, followed by an IL catalyzed
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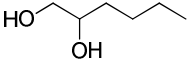
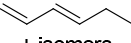
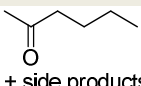
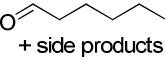
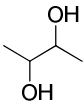


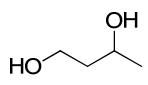

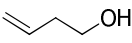
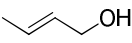
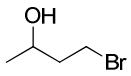
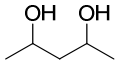
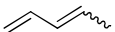
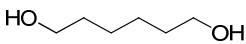
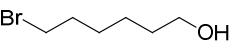
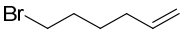
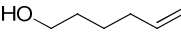
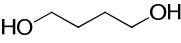


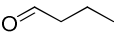


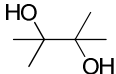


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3 dehydrobromination. In the current work, however, the reaction scope is expanded to include
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5 vicinal diols. Furthermore, the activity of our phosphonium-based system markedly surpasses
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7 that of the ammonium-based system. This is evident from the turn-over frequencies. In the
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9 optimized Zhang system a TOF of 0.005 h^{-1} is reached for 1-octanol to octenes at a total octene
10
11 yield of 24%.²¹ In our system, we reach a TOF of 0.28 h^{-1} for 1-hexanol to hexenes at the same
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13 total hexene yield. For secondary alcohols (2-octanol and 2-hexanol respectively) the difference
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15 is even larger, with 0.0055 h^{-1} compared to 1.0 h^{-1} at 64 and 86% yield respectively.
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19 Furthermore, we have examined the reaction of 1,2-hexanediol in the Zhang system. After 30
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21 minutes, this leads a much lower hexadiene yield of 10%. 3% hexanal, 6% hexanone and 11% 1-
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23 bromo-2-hexanol are formed as side products. In addition, small amounts of 1-bromobutane and
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25 tributylamine were detected, showing some breakdown of the ionic liquid even at a rather low
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27 temperature.
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32 An explanation for the much higher activity in our system lies partly in the higher temperatures
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34 that can be applied ($200 \text{ }^\circ\text{C}$ versus $125 \text{ }^\circ\text{C}$). As we have shown before, increasing the
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36 temperature to $200 \text{ }^\circ\text{C}$ in a system employing Bu_4NBr results in severe decomposition of the
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38 ionic liquid. This might be the reason why increasing the temperature in the Zhang system to 140
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40 $^\circ\text{C}$, decreases the alkene yield.²¹ Thus, simply increasing the temperature would not bridge the
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42 gap in activity. A more fundamental explanation for the increased activity is the higher
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44 dispersion of the positive charge in the phosphonium cation compared to a similar ammonium
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46 cation.^{22,23} For cations with short aliphatic chains, this decreases the electrostatic interaction
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48 between cation and anion, thus increasing the basicity and nucleophilicity of the anion.^{15,24} This
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50 would accelerate both the nucleophilic substitution and the dehydrobromination.
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3 Having developed and studied a stable, highly active dehydrating system for a model substrate,
4 we applied this system to the dehydration of other diols. Different diol patterns are expected to
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6 have reactivities distinct from that of a 1,2-diol such as the model substrate. Therefore, we
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8 investigated the fate of 1,3-, 1,4- and 2,3-butanediol (BDO), 2,4-pentanediol (PDO), 1,6-
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10 hexanediol and pinacol (2,3-dimethyl-2,3-butanediol) in the reaction system (Table 3). Based on
11
12 these results, the diols can be divided into three groups. First, vicinal diols (entries 1 and 2) lead
13
14 to conjugated dienes and carbonyl compounds. Other diols (entries 3 to 6 and 8) do not form
15
16 significant amounts of carbonyl compounds, as expected from the proposed mechanism.
17
18 Secondly, diols with one sp^3 carbon separating the hydroxyl groups (entries 3 and 4) lead only to
19
20 conjugated dienes and, in the case of 1,3-BDO, intermediate products. Finally, as can be seen
21
22 from the reaction of 1,4-BDO and 1,6-HDO (entries 5 and 6), hydroxyls separated by two to four
23
24 sp^3 carbons lead to the formation of cyclic ethers. This cyclodehydration is reversible, as shown
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26 in the reaction of tetrahydrofuran (THF, entry 7).
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Table 3. Product yields in the dehydration of different diols and tetrahydrofuran.

Entry	Substrate	Products and yield (%)					
1		 + isomers	48	 + side products	16	 + side products	15
2			5		85		
3			33		2		2
			3				
4			99				
5		Hexadienes ^a	7	Cyclic ethers ^b	26		2
			1		<1		
6			27		72		1
7			13				
8			73		2		

Conditions: 0.5 mmol substrate, 1.7 mmol Bu₄PBr, 0.022 mmol HBr, 200 °C, N₂ atmosphere, 15 minutes; ^a Hexadienes (yield): 1,3 (< 1%), 2,4 (1%), 1,4 (1%), 1,5 (4%); ^b Cyclic ethers (yield): oxepane (24%), 2-methyltetrahydropyran (2%), 2-ethyltetrahydrofuran (< 1%).

Besides allowing to group different diols based on their structure, several of these results indicate that formation of more substituted, thus more stable, alkenes is preferred. First, this can be concluded from the higher dehydration rate for 2,4-PDO compared to 1,3-BDO. Next, this also explains the slow dehydration of primary diols such as 1,4-BDO and 1,6-HDO. Furthermore, the immediate product of 1,6-HDO dehydration is 1,5-hexadiene. However, 1,4-hexadiene and

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3 conjugated dienes are also formed, which shows that isomerization to more stable dienes occurs.
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5 Next, the high selectivity for 2-butanone in the dehydration of 2,3-butanediol (entry 2) is most
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7 likely caused by preferential formation of the internal alkene 2-buten-2-ol over the terminal
8
9 alkene 3-buten-2-ol. 2-Buten-2-ol then tautomerizes to butanone. In the reaction of pinacol (entry
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11 8) formation of the internal double bond is avoided, because there is no proton available in the C₂
12
13 or C₃ position. However, the dehydration rate is still high, since the terminal alkenes that can be
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15 formed are also disubstituted. This leads to a high selectivity for the conjugated diene. Only a
16
17 small amount of pinacolone is formed, most likely through acid catalyzed pinacol rearrangement.
18
19 This striking result highlights once more the distinct selectivity in this IL system, since in a
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21 purely acid catalyzed reaction, pinacolone is typically the major product.⁹ Very recently, the
22
23 dehydration of pinacol derivatives to dienes using a solid acid catalyst in an imidazolium IL has
24
25 been reported.²⁵ However, the activity of our system is again significantly higher (TOF 0.86 h⁻¹
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27 compared to 0.022 h⁻¹ at similar conversions) for the same reasons as discussed before for the
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29 Zhang system.
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37 As discussed before, the reaction of 1,4-BDO results in the formation of 1,3-butadiene (BD),
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39 with THF as the only side product. We decided to investigate this reaction more thoroughly,
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41 since it presents an interesting step towards the bio-based production of BD. Production of BD
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43 from renewables, including butanediols, has been highlighted in a few recent reviews.⁶⁻⁸ 1,4-
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45 BDO can be produced by bacterial fermentation of sugar streams, including crude biomass
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47 hydrolysates.²⁶ Recently, the fermentative production of 1,4-BDO has been patented by
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49 Genomatica and licensed for commercial plants by BASF and Novamont, indicating greatly
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51 increasing bio-based availability of this compound in the near future.^{27,28} This could enable an
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53 economically viable bio-based production of BD from 1,4-BDO. However, the dehydration of
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3 1,4-BDO to BD through acidic catalysis is hampered by selective formation of THF.⁹ For
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5 example, an old route for production of BD was the dehydration of 1,4-BDO over a supported
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7 H_3PO_4 and Na_3PO_4 catalyst bed.²⁹ This leads to almost pure THF, so BD can only be formed
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9 through lengthy recycling of THF. Some basic catalysts, such as CeO_2 , can avoid the formation
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11 of THF and lead to a 90% BD selectivity at 275 °C, but only at low conversion (6%).³⁰ Another
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13 acid catalyzed side reaction is the cleavage of 3-buten-1-ol, the first dehydration product of BD,
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15 to propylene.^{31–33} Again, Ce based catalysts can suppress this reaction.³¹ To our knowledge, the
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17 only reported example of a process directly leading to BD yields over 90% is the gas phase
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19 dehydration of 1,4-BDO over NiO and CoO on ZrO_2 .³⁴ Very high yields can be achieved starting
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21 from a 10 wt.% aqueous solution, but high temperatures (400 °C) are required and coke is
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23 formed, leading to deactivation and necessitating frequent regeneration.
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30 In view of these problems, we examined the dehydration of 1,4-BDO using the phosphonium IL
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32 system. First, we tested the purely acid-catalyzed reaction in mesitylene and N-
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34 methylpyrrolidone. As expected, this leads to the formation of THF as the only product (Table
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36 4), showing that the IL is necessary for the formation of significant amounts of BD. Next, to
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38 increase the yield of BD, we examined the effect of higher temperature and acid concentrations.
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40 The main products in all these reactions are BD and THF. A small amount of butanal is
41
42 produced, presumably through isomerization of 3-buten-1-ol to 1-buten-1-ol and rapid
43
44 tautomerization. 4-bromo-1-butene, 1-bromo-2-butene, 1,4-dibromobutane, 4-bromo-1-butanol
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46 and 3-buten-1-ol are detected as side products with yields lower than 1%. Moreover, they react
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48 away over time. Interestingly, although 3-buten-1-ol is a reaction intermediate, no propylene is
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50 detected. A possible explanation for this is the lower temperature applied in this system,
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52 compared to the gas phase dehydrations of butadiene or 3-buten-1-ol, which are typically
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performed at temperatures above 250 °C and often above 300 °C.^{31–33} Furthermore, this reaction is acid catalyzed and only small amounts of acid are present in our system.

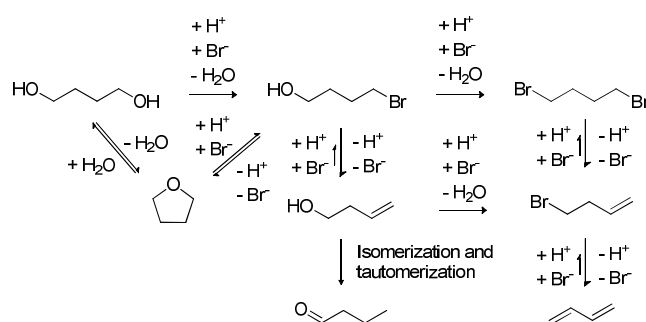
Table 4. Product yields in the dehydration of 1,4-butanediol.

Time (min)	T (°C)	mmol HBr	Yield (%)			
			BD	THF	BA	X (%)
15	200	0	<1	98	<1	99
15	200	0.022	0 ^a	22	0	78
15	200	0.022	0 ^b	53	0	47
15	200	0.022	27	72	1	100
15	220	0.022	31	66	<1	100
120	220	0.022	58	40	1	100
120	220	0.03	65	31	1	100
120	220	0.04	74	25	1	100
120	220	0.05	94	5	1	100
120	220	0.05	93 ^c	/	<1	94

Conditions: 0.5 mmol 1,4-butanediol, 1.7 mmol Bu₄PBr, N₂ atmosphere. BD = 1,3-Butadiene, THF = Tetrahydrofuran, BA = Butanal, X = conversion. ^a 2 mL mesitylene as solvent. ^b 2 mL N-methylpyrrolidone as solvent. ^c THF as substrate.

Since cyclodehydration to THF is reversible, while dehydration to BD is not, higher rates for both dehydration reactions lead to higher BD yield. As a result, a butadiene yield of 94% was reached after 2 hours using 0.05 mmol HBr at 220°C. Keeping in mind the very strong tendency for THF formation, this is, most likely, only possible with a highly active and selective catalyst. To illustrate this, we have conducted the same experiment in the Zhang system. After 30 minutes, only tetrahydrofuran (95%) and 1-bromo-4-butanol (1%) are formed; no butadiene was detected. A mechanism can be proposed inspired by the one for HDO dehydration (Scheme 2).

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3 Interestingly, all the intermediates in this reaction scheme are detected, providing further proof
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5 of the validity of the mechanism. As THF is the only intermediate in this scheme that is not
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7 analogous to the intermediates in the reaction of 1,2-hexanediol, we performed the reaction in
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9 optimized conditions using THF as the substrate. This leads to a comparably high BD yield of
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11 93%, which is consistent with the proposed mechanism and demonstrates the use of THF as an
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13 alternative substrate for the production of BD.
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Scheme 2. Proposed mechanism for the dehydration of 1,4-butanediol

Conclusions

In conclusion, a new catalytic system for dehydration of alcohols and polyols has been developed, consisting of the ionic liquid tetrabutylphosphonium bromide and an acid. Its advantages include thermal stability, easy product separation and greatly increased activity compared to similar systems. Its effect on a vicinal diol has been investigated, demonstrating selective formation of conjugated dienes, which is generally not achieved by acid catalyzed dehydration. A mechanism relying on both the basic and nucleophilic properties of the bromide anion has been proposed and confirmed experimentally. Furthermore, the reactivity of other diols in this reaction system was also investigated. Also for some of these compounds, typical side reactions can largely be avoided. Next, in light of renewed interest in bio-based production of butadiene, we focused on the dehydration of 1,4-butanediol. Using the reported system, 1,4-

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3 butanediol, which is available from waste fermentation, is converted to butadiene with 94% yield
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5 in relatively mild conditions.
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8 ASSOCIATED CONTENT

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12 **Supporting Information.** Experimental detail, information on product grouping, ionic liquid
13 acidity and the effect of different cations on activity, discussion on the dehydration and
14
15 dehydrobromination of bromohydrins (PDF).
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29 **Author Contributions**

30
31
32 The manuscript was written through contributions of all authors. All authors have given approval
33 to the final version of the manuscript.
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35
36

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51 **Notes**

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55 The authors declare no competing financial interest.
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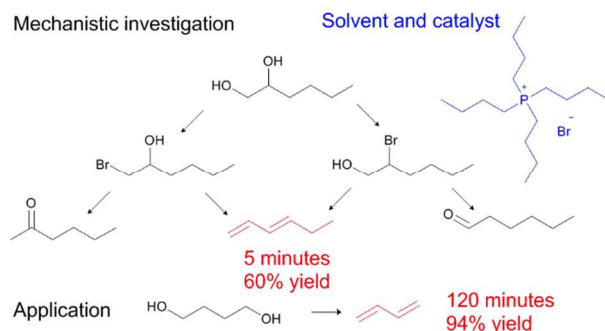
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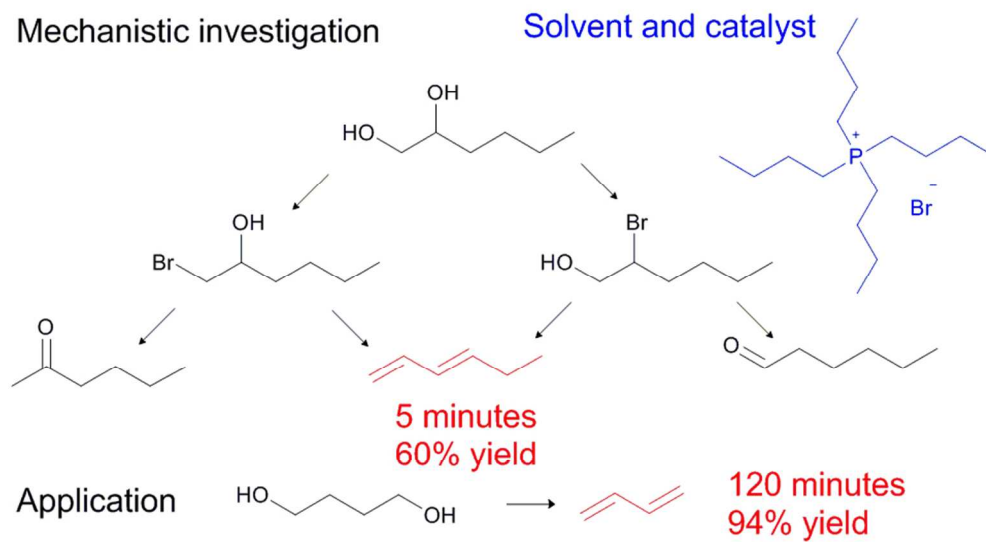
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