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Solid Acid-Catalyzed Dehydration of Pinacol Derivatives in Ionic Liquid: A Simple and Efficient Access to Branched 1,3-Dienes

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ABSTRACT: The selective dehydration of pinacol derivatives to branched 1,3-dienes is extremely challenging due to the predominance of pinacol rearrangement. Herein, we successfully achieve this goal by employing a recyclable solid acid/ionic liquid catalyst system. The dehydration of alkyl and cycloalkyl derived diols in Amberlyst-15/[Emim]Cl system afforded the corresponding 1,3-dienes in good yields, while Nafion/[Emim]Cl was demonstrated to be a better catalyst system for the dehydration of aryl substituted substrates. Our protocol features a straightforward and simple access to branched 1,3-dienes, high chemoselectivity, a recyclable catalyst system, a facile separation of dienes just by decantation, and broad substrate scope.

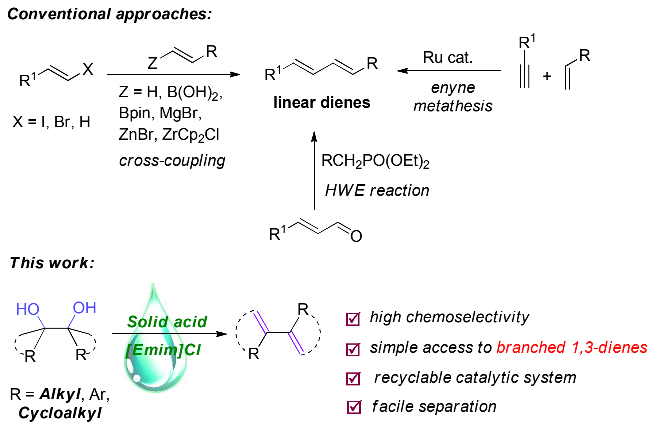
KEYWORDS: branched 1,3-dienes, pinacol dehydration, ionic liquid, solid acid, Amberlyst-15, Nafion, [Emim]Cl

Introduction

1,3-Dienes are key structural motifs in a variety of natural products and bioactive molecules.[1] Moreover, due to their high reactivity in many reactions (such as Diels-Alder cycloaddition, polymerization, *etc*.), 1,3-dienes have found wide applications in organic synthesis[2] and polymer science.[3] Thus, to date, tremendous methods have been developed for their synthesis. The conventional approaches include transition-metal catalyzed cross-couplings,[4] olefination of unsaturated carbonyl compounds (Horner–Wadsworth–Emmons reaction for instance)[5] and enyne metathesis (Scheme 1).[6] However, these methods often suffer from high-cost transition metal catalysts, toxic reagents and solvents, harsh reaction conditions and a multi-step process. Besides, most of them focus on the synthesis of linear dienes, while the selective formation of branched dienes is cumbersome. Consequently, the exploration of new synthetic routes to branched 1,3-dienes, that fulfill the criteria of green chemistry, is highly demanded.

The dehydration of diols is arguably the simplest and most straightforward access to 1,3-dienes. The past decade has witnessed substantial achievements in the gas-phase dehydration of linear diols (such as 1,3-, 2,3- and 1,4-butanediol) towards 1,3-butadiene.[7] In contrast, the dehydration of branched *vic*-diols to highly substituted dienes still lags behind due to the predominance of pinacol rearrangement. Pinacol derivatives, as an intriguing class of *vic*-diols, can be easily synthesized through a low-valent-metal mediated reductive coupling[8] or electrolytic reduction[9] of carbonyl compounds, that is, the so-called pinacol coupling. Very recently, Rueping *et al.* reported a sustainable visible-light-induced pinacol coupling of ketones or aldehydes to diols.[10] With these well-established synthetic methods in hand, we herein develop a recyclable solid acid/ionic liquid system for the selective dehydration of pinacol derivatives to various branched 1,3-dienes (Scheme 1). This approach features a straightforward and simple access to branched 1,3-dienes, high chemoselectivity, a recyclable catalyst system, a facile separation of dienes just by decantation, and broad substrate scope.

Scheme 1. Synthesis Strategy of 1,3-Dienes.



Results and Discussion

At the outset, we chose the dehydration of pinacol as the model reaction. It is well-known that this process typically involves two competitive pathways: 1) 1,2-elimination of H_2O to form 2,3-dimethylbutadiene (*i.e.* **2a** in Scheme 2). 2) pinacol rearrangement to form pinacolone (*i.e.* **3a** in Scheme 2). In the past decades, a broad range of acid catalysts including Brønsted acids,[11] Lewis acids,[12] solid acids[13] and supercritical water[14] have been used in the dehydration of pinacol. However, almost all of the reactions exclusively proceeded via a rearrangement pathway to produce **3a**. The selective dehydration of pinacol to **2a** was rarely reported.[15] To increase the diene selectivity, we investigated the influence of solvents on the H_2SO_4-catalyzed pinacol dehydration. The results are illustrated in Table 1. Under solvent-free condition, the dehydration gave **3a** as the single product (Table 1, entry 1). Similar results were obtained when we used non-polar solvent (such as toluene) and protic solvent (such as water) (Table 1, entries 2 and 3). In contrast, **2a** was obtained as the main product when the reaction was carried out in some polar aprotic solvents such as dimethyl sulfoxide (DMSO) and *N*-methyl-2-pyrrolidone (NMP) (Table 1, entries 4 and 5). In view of the fact that ionic liquids are a new class of polar aprotic solvents that are endowed with strong electrostatic force,[16] we surmised that ILs could drastically increase the diene selectivity. Just as anticipated, **2a** was afforded in 85% carbon yield with a high chemoselectivity when the dehydration was conducted in [Emim]Cl (Table 1, entry 6). However, the reactions in ammonium and pyridinium salts such as Bu_4NCl and [EtPy]Cl furnished **2a** in low carbon yields, although it still predominated in the products (Table 1, entries 7 and 8). Moreover, the anion and cation of imidazolium-based ILs have evident influences on the results. For example, when the anion of [Emim]Cl (*i.e.* Cl^-) was changed to the large anions BF_4^- and NTf_2^-, the main product switched from **2a** to **3a**, which could be explained by the weak interaction of BF_4^- (or NTf_2^-) with pinacol (Table 1, entries 9 and 10). In contrast, the small anion Cl^- can serve as a good hydrogen bond acceptor, which prefers to interact with the hydroxyl proton of pinacol ($C_{im}^+Cl^- \cdots HO$). Besides its hydrogen-bonding interaction, Cl^- is also prone to stabilize the carbocation intermediate through an ion-pair, thereby enhancing the diene selectivity. The effects of the cation were also studied. Although [Emim]Cl, [Pmim]Cl, and [Bmim]Cl have the same anion, the selectivity and carbon yield of **2a** decreased with the increment of the alkyl chain length (Table 1, entries 6, 11 and 12). The sterically hindered long chain substituent possibly hampers the interaction between IL and pinacol, thus affording low diene selectivity. The utilization of acidic ILs[17] as both catalyst and solvent was attempted as well (Table 1, entries 13–15). The dehydration did not occur in $[Emim]HSO_4$, while stronger acidic IL $[(HSO_3)^4C_4C_1im]HSO_4$ preferred a rearrangement pathway. The reaction in $[(HSO_3)^4C_4C_1im]Cl$ also gave low diene selectivity and yield. In some literature, it is suggested that polyethylene glycol (PEG) has similar physical properties to ILs, thus sometimes serving as an alternative reaction medium.[18] However, PEG was proved to be ineffective in this reaction (Table 1, entry 16).

Scheme 2. Pinacol Dehydration to 2,3-Dimethylbutadiene and Pinacolone.

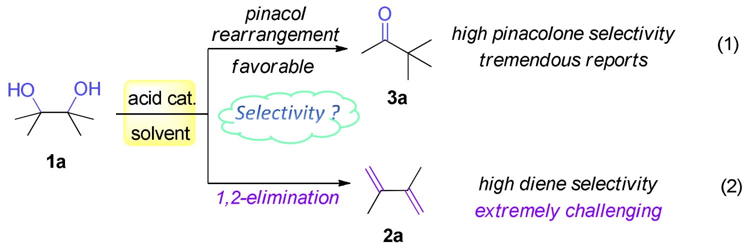
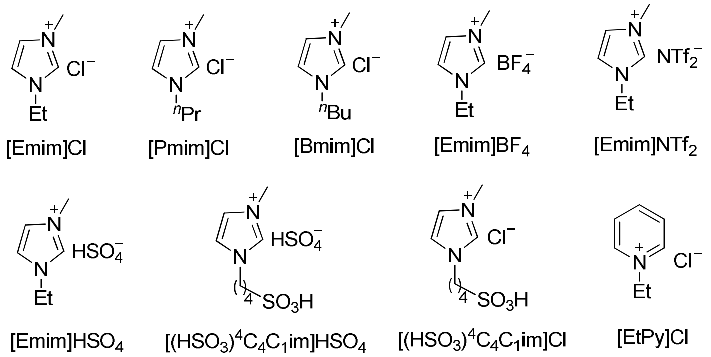


Table 1. The influence of solvents on the acid-catalyzed dehydration of pinacol.[a]

Entry	Catalyst	Solvent	Carbon yield of **2a** (%)[b]	**2a**:**3a**[b]
1	H_2SO_4	–	0	–[c]
2	H_2SO_4	Toluene	0	–[c]
3	H_2SO_4	H_2O	Trace	<1:20
4	H_2SO_4	DMSO	58	3:1
5	H_2SO_4	NMP	71	7:1
6	H_2SO_4	[Emim]Cl	85	16:1
7	H_2SO_4	Bu_4NCl	28	23:1
8	H_2SO_4	[EtPy]Cl	28	24:1
9	H_2SO_4	$[Emim]NTf_2$	0	–[c]
10	H_2SO_4	$[Emim]BF_4$	0	–[c]
11	H_2SO_4	[Pmim]Cl	77	11:1
12	H_2SO_4	[Bmim]Cl	63	9:1
13	–	$[Emim]HSO_4$	N.R.	–
14	–	$[(HSO_3)^4C_4C_1im]HSO_4$	0	–[c]
15	–	$[(HSO_3)^4C_4C_1im]Cl$	32	1:1
16	H_2SO_4	PEG-4000	5	1:8

[a] Reaction conditions: **1a** (1.0 g), solvent (4.0 g), catalyst (100 mg), 120 °C for 12 h. [b] Detected by GC using tridecane as the internal standard. [c] Pinacolone **3a** was obtained as the single product. NMP = *N*-methyl-2-pyrrolidone. N.R. = No Reaction. PEG = Polyethylene glycol.



Subsequently, we investigated the catalytic performances of various Brønsted acids. As delineated in Figure 1, the weak acid HOAc and medium acid H_3PO_4 cannot facilitate the dehydration process, while strong acids CF_3SO_3H, H_2SO_4 and CF_3COOH exhibited good activities. The sequence for the carbon yields of **2a** is $CF_3SO_3H \approx H_2SO_4 > CF_3COOH > H_3PO_4$ (HOAc), which is consistent with their acid strength. According to the literature,[19] the *p*Ka values of HOAc, H_3PO_4, CF_3COOH, H_2SO_4, and CF_3SO_3H are 4.76, 2.16, -0.23, -3.0, and -14, respectively. This phenomenon indicates that acid strength is very important for the dehydration. Besides, some Lewis acids were also found to be active for the process. The carbon yields of **2a** over the investigated catalysts decreased in the order of $ZrCl_4 > TiCl_4 > AlCl_3 > FeCl_3$. This is consistent with the acid strength sequence of these catalysts which has been classified by Kobayashi et al.[20] Based on these results, we can see that both strong Brønsted and Lewis acids efficiently catalyzed the dehydration of pinacol to **2a** in [Emim]Cl.

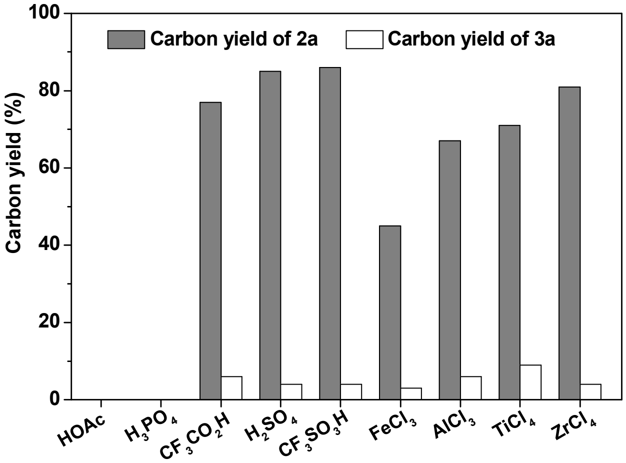


Figure 1. Carbon yields of **2a** and **3a** over different acid catalysts. Reaction conditions: **1a** (1.0 g), [Emim]Cl (4.0 g), catalyst (100 mg), 120 ^{o}C for 12 h.

To avoid the corrosion and environmental issues associated with the utilization of homogeneous acids, we also explored the catalytic performances of an array of solid acids. As shown in Figure 2, several commonly used H-type zeolites were active for the process. H-MOR (Si/Al = 24), H-BEA (Si/Al = 25) and H-ZSM-5 (Si/Al = 25) could promote the dehydration but only with low carbon yields. H-USY (Si/Al = 3) showed a slight improvement in the diene yield. In the cases of Amberlyst-15 and Nafion resins, which have strong acidic -SO_3H group, the dehydration proceeded smoothly to afford **2a** in 85% and 86% carbon yield, respectively. These results are comparable with the ones obtained over strong homogeneous catalysts. Considering the lower cost and high activity of Amberlyst-15 resin, we believe it is a promising catalyst for the production of **2a** in a large scale.

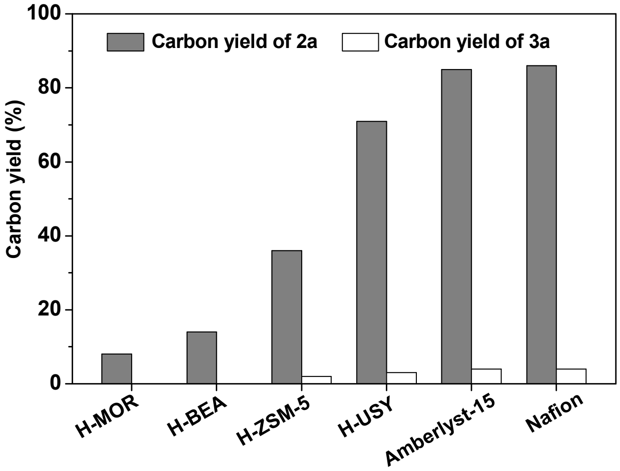


Figure 2. Carbon yields of **2a** and **3a** over various solid acid catalysts. Reaction conditions: **1a** (1.0 g), catalyst (100 mg), [Emim]Cl (4.0 g), 120 °C for 12 h.

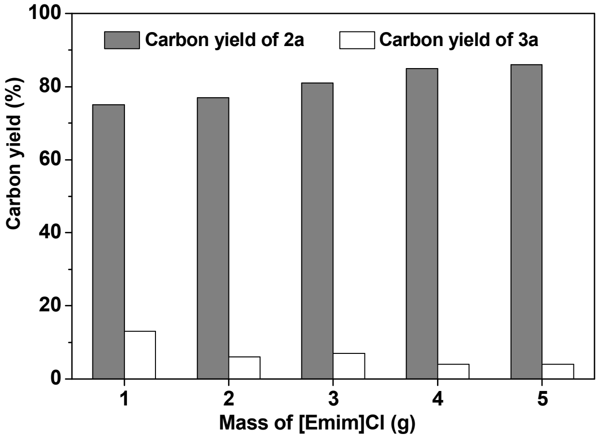


Figure 3. Carbon yields of **2a** and **3a** over Amberlyst-15 resin as a function of [Emim]Cl mass. Reaction conditions: **1a** (1.0 g), Amberlyst-15 (100 mg), 120 °C for 12 h.

Figure 3 depicts the profile for the carbon yields of **2a** and **3a** over Amberlyst-15 resin as a function of the [Emim]Cl mass at 393 K. The carbon yield of **2a** increased with the increment of the [Emim]Cl mass from 1 g to 4 g, then stabilized with a further increase of the [Emim]Cl mass to 5 g. Meanwhile, the opposite trend was observed for the carbon yield of **3a**. Based on this result, we fixed the [Emim]Cl mass as 4 g in the following work.

The influence of the catalyst loading on the pinacol dehydration was also investigated. As shown in Figure 4, the carbon yield of **2a** reached the maximum (85%) when 100 mg of Amberlyst-15 resin was used, then stabilized with further increasing the catalyst loading. Thus, the optimum catalyst loading for the reaction is 10 wt% of pinacol.

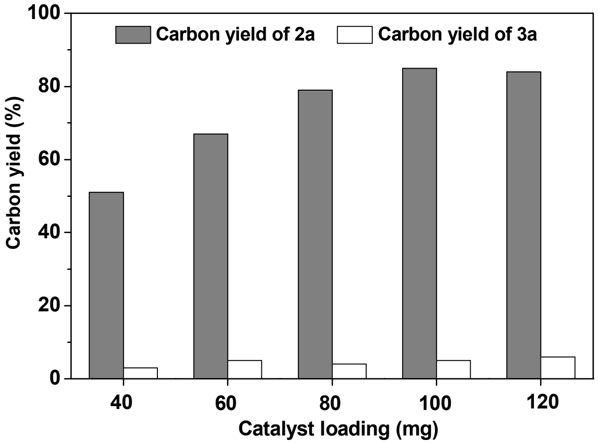


Figure 4. Carbon yields of **2a** and **3a** over Amberlyst-15 resin as a function of catalyst loading. Reaction conditions: **1a** (1.0 g), [Emim]Cl (4.0 g), 120 ^{o}C for 12 h.

Another advantage of Amberlyst-15/[Emim]Cl system is the easy separation of the product. As we can see from Figure 5, pinacol merges into [Emim]Cl at the beginning of the reaction. With the increase of reaction time, the mixture switches from monophasic to biphasic, which is because that the product diene **2a** is nonpolar and immiscible with [Emim]Cl. Notably, when submitting the final mixture to a low temperature, the lower layer ([Emim]Cl, Amberlyst-15, and the byproduct water) became solid or highly viscous, while the upper layer (diene **2a**, GC purity > 93%) was still liquid, thus allowing a facile separation of **2a** just by decantation.

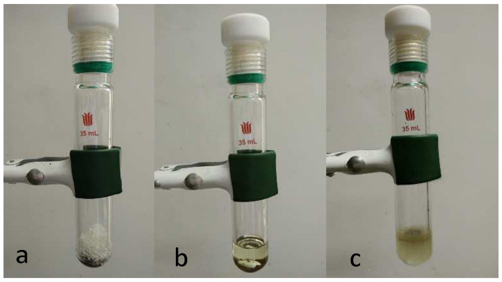


Figure 5. Photographs of the mixture during the reaction. (a) A solid mixture at room temperature; (b) A homogeneous liquid with Amberlyst-15 at 120 ^{o}C; (c) A biphasic system was obtained upon completion of the reaction.

To fulfill the need of real application, we also checked the reusability of Amberlyst-15/[Emim]Cl system for the dehydration of pinacol (Figure 6). With the increment of recycling time, the carbon yield of **2a** slightly decreased, while that of unexpected product **3a** increased at the same time. These results were possibly due to the negative effect of the byproduct water generated during the dehydration. To verify this hypothesis, we studied the effect of water on the catalytic performance of Amberlyst-15/[Emim]Cl system. To do this, we added different amount of water to the system before reaction. As depicted in Figure 7, an evident decline in the carbon yield of **2a** and an increase in the carbon yield of **3a** were observed simultaneously with increasing the amount of external water. These phenomena suggest that pinacol rearrangement is prone to occur in the presence of water, which is in accordance with the result observed using water as solvent (Table 1, entry 3).

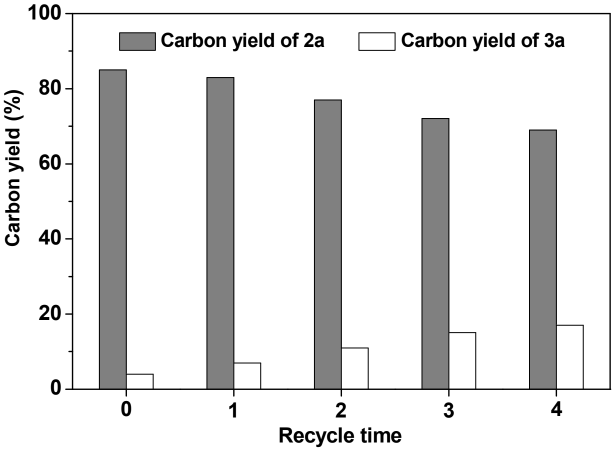


Figure 6. Carbon yields of **2a** and **3a** over the Amberlyst-15/[Emim]Cl catalyst system as a function of recycle time (without removal of the byproduct water). Reaction conditions: **1a** (1.0 g), Amberlyst-15 (100 mg), [Emim]Cl (4.0 g), 120 °C for 12 h.

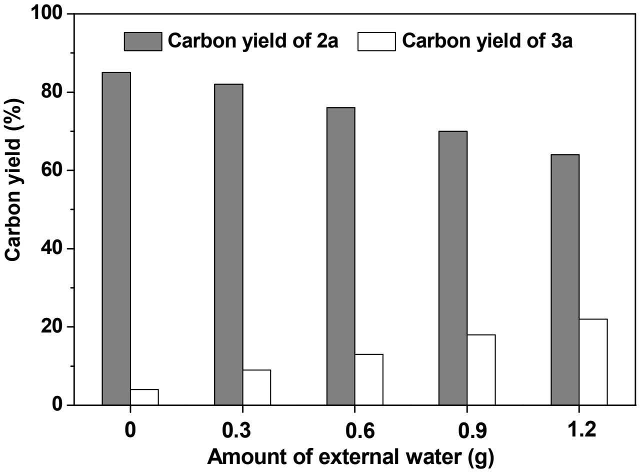


Figure 7. Carbon yields of **2a** and **3a** over the Amberlyst-15/[Emim]Cl catalyst system as a function of the amount of external water added before reaction. Reaction conditions: **1a** (1.0 g), Amberlyst-15 (100 mg), [Emim]Cl (4.0 g), 120 °C for 12 h.

As a solution to this problem, we dried the lower layer at 120 °C for 4 h after each usage to remove the byproduct water. As we expected, the reusability of Amberlyst-15/[Emim]Cl catalyst system was significantly improved by such a treatment (Figure 8). No evident change in the activity or selectivity was observed during the four repeated usage.

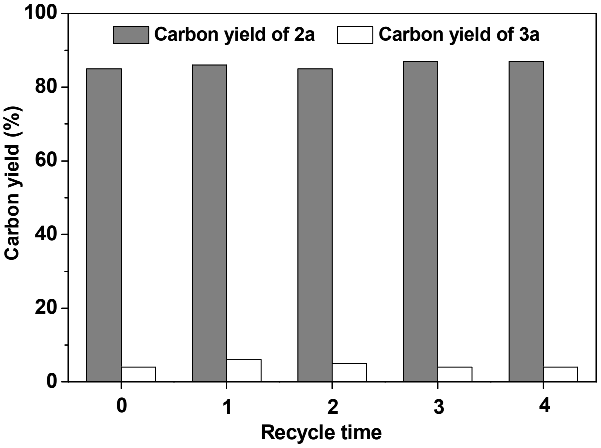
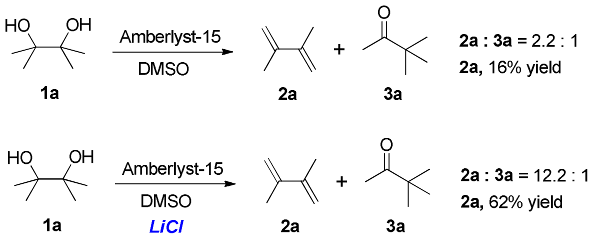


Figure 8. Carbon yields of **2a** and **3a** over the Amberlyst-15/[Emim]Cl catalyst system as a function of the recycle time (removal of the byproduct water). Reaction conditions: **1a** (1.0 g), Amberlyst-15 (100 mg), [Emim]Cl (4.0 g), 120 °C for 12 h. The lower layer was dried at 120 °C for 4 h after each usage.

To gain more insights into the influence of Cl^-, some control experiments were performed (Scheme 3). The pinacol dehydration in Amberlyst-15/DMSO system produced **2a** in low yield (16%) and selectivity (**2a**:**3a** = 2.2:1) (Figure S2). However, after adding 20 mmol of LiCl to the mixture, the yield of **2a** significantly increased and the molar ratio of **2a** and **3a** was up to 12.2:1 (Figure S3). Based on these results, we think that Cl^- possibly plays a predominant role in the selective pinacol dehydration in [Emim]Cl. On one hand, Cl^- interacts with the hydroxyl proton of pinacol through a hydrogen-bonding. On the other hand, Cl^- could efficiently stabilize the carbocation intermediate, thereby enhancing the diene selectivity.

Scheme 3. **Effect of Cl^- on the Pinacol Dehydration.**



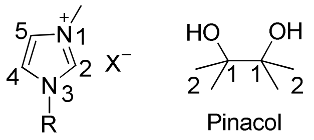
Furthermore, we also conducted the NMR experiments to further investigate the interactions between ILs and pinacol. The NMR data of neat IL, pinacol and the mixture of IL and pinacol are shown in Table

2. Compared with the chemical shift of C1 atom of neat pinacol (75.18 ppm), that in the mixture of [Emim]Cl and pinacol moves upfield (74.82 ppm, $\Delta\delta = 0.36$ ppm). Simultaneously, the mixture led to an increase in the ^{1}H and ^{13}C shift at the 2-position of the imidazole ring (Table 2, entry 5). In contrast, the NMR data of the mixture of [Emim]BF_4 and pinacol showed no difference with neat two components (Table 2, entry 6). These results reveal that [Emim]Cl has a strong interaction with pinacol, whereas [Emim]BF_4 does not. In comparison with the weakly coordinating anion BF_4^-, the small anion Cl^- is a good hydrogen bond acceptor, which possibly interacts with the hydroxyl proton of pinacol ($C_{im}^{+}Cl^{-}\cdots HO$).[21] Besides, when submitting pinacol to [Bmim]Cl, an upfield shift of C1 was also observed (74.96 ppm, $\Delta\delta = 0.22$ ppm). But the upfield shift value of pinacol in [Bmim]Cl (0.22 ppm) was lower than that in [Emim]Cl (0.36 ppm), which indicates that sterically hindered butyl group possibly hampers the interaction between IL and pinacol, thus leading to a decreased diene selectivity in [Bmim]Cl. It has been reported that the acidic H2 proton of the imidazole ring probably also interacts with the oxygen atom of hydroxyl group through a hydrogen bonding ($C_{im}–H\cdots OH$), which cannot be excluded in the process.[22]

Table 2. The NMR data of neat IL, pinacol and the mixture of IL and pinacol.

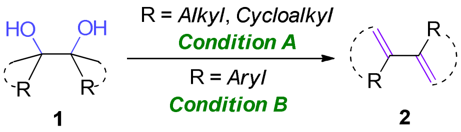
Entry		imidazole ring		C1 atom of pinacol
		δ_H (H2)/ppm	δ_C (C2)/ppm	δ_C (C1)/ppm
1	[Emim]Cl	10.08	136.44	-
2	[Emim]BF_4	8.52	135.82	-
3	[Bmim]Cl	10.23	137.00	-
4	pinacol	-	-	75.18
5	[Emim]Cl/pinacol (4/1)	10.22	136.97	74.82
6	[Emim]BF_4/pinacol (4/1)	8.52	135.82	75.18
7	[Bmim]Cl/pinacol (4/1)	10.39	137.60	74.96

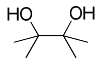
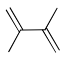
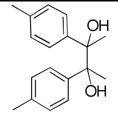
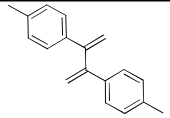
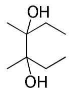
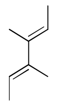
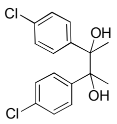
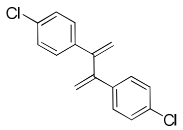
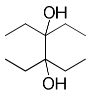
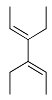
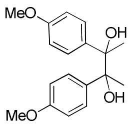
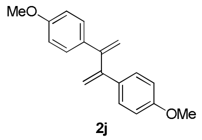
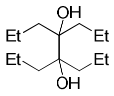
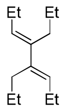
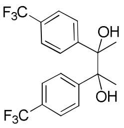
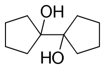
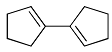
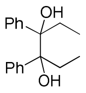
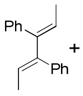
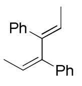
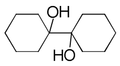
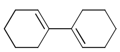
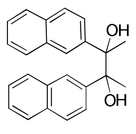
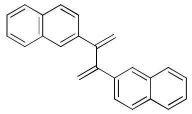
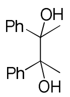
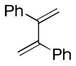
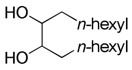
R = Et, X = Cl, [Emim]Cl
R = ^{n}Bu, X = Cl, [Bmim]Cl
R = Et, X = BF_4, [Emim]BF_4



To illustrate the generality of the Amberlyst-15/[Emim]Cl system, we further explored the dehydration of a series of diols which were easily synthesized by the pinacol coupling of the carbonyl compounds. As summarized in Table 3, when unsymmetrical 2-butanone derived diol **1b** was subjected to the standard conditions (Condition A), the elimination of H_2O, to our surprise, occurred at adjacent CH_2 position rather than the CH_3 position, leading to the formation of (*E, E*)-diene **2b** as the main product. Pinacol analogues **1c** and **1d** could also be readily converted into 1,3-dienes in high efficiencies. Remarkably, cyclic *vic*-diols **1e** and **1f** underwent the process smoothly, providing the corresponding dienes in 86% and 94% yield, respectively. Disappointedly, the dehydration of phenyl-substituted diol **1g** in Amberlyst-15/[Emim]Cl catalyst system only produced **2g** in 18% yield and most of the substrate remained unchanged. Given that the maximum operating temperature of Amberlyst-15 is 120 ^{o}C, we then chose Nafion resin with high thermal stability as the catalyst to achieve better results. As expected, the yield of **2g** increased to 75% when the dehydration was conducted at 160 ^{o}C (Condition B). Thus, in the cases of aryl-substituted diols, Nafion/[Emim]Cl was the optimum catalyst system. Diols **1h** and **1i** bearing 4-Me and 4-Cl were tolerated in the reaction. The electronic properties of the substituents on the phenyl ring exerted a great influence on the results. For example, the dehydration of **1j**, possessing electron-donating OMe group, afforded **2j** in 74% yield, whereas electron-withdrawing substrate **1k** cannot undergo the reaction under the investigated conditions. It is noted that a mixture of **2l** and **2l’** was obtained using propiophenone derived pinacol **1l** as substrate. The scope of the reaction can be further extended to 2-naphthyl substituted pinacol **1m** albeit with a slightly decreased yield. However, the dehydration of linear diol **1n**, generated from 1-octanal, did not occur in both catalyst systems, which was presumably ascribed to the relatively low stability of secondary carbocation intermediate.

Table 3. The selective dehydration of pinacol derivatives to various branched 1,3-dienes



Entry	Diol	1,3-Diene	Yield (%)[a]	Entry	Diol	1,3-Diene	Yield (%)[a]
1	 **1a**	 **2a**	81	8	 **1h**	 **2h**	78
2	 **1b**	 **2b**	82	9	 **1i**	 **2i**	70
3	 **1c**	 **2c**	77	10	 **1j**	 **2j**	74
4	 **1d**	 **2d**	86	11	 **1k**	N.R.[c]	–
5	 **1e**	 **2e**	86	12	 **1l**	 **2l** +  **2l'** **2l** : **2l'** = 2 : 1	71[d]
6	 **1f**	 **2f**	94	13	 **1m**	 **2m**	51
7	 **1g**	 **2g**	75 (18)[b]	14[e]	 **1n**	N.R.[c]	–

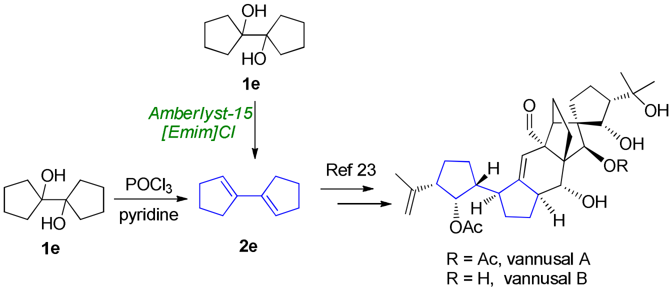
Condition A: Diol (1.0 g), Amberlyst-15 (100 mg), [Emim]Cl (4.0 g), 120 °C for 12 h.

Condition B: Diol (1.0 g), Nafion (100 mg), [Emim]Cl (4.0 g), 160 °C for 12 h.

[a] Isolated yield. [b] Only 18% yield of **2g** was isolated when the dehydration was conducted under condition A. [c] N.R. = No Reaction. [d] A mixture of diene **2l** and **2l'**. [e] The dehydration of linear diol **1n** did not occur in both catalyst systems.

Additionally, this approach also has potential application in the total synthesis of some intriguing molecules. Vannusals A and B are a class of marine natural products that were isolated from the interstitial ciliate *Euplotes vannus*. Owing to their complex and unusual structures, their synthesis has attracted the interests of synthetic chemists. As described by Nicolaou and co-workers, diene **2e** is the important building block for the total synthesis of vannusals A and B (Scheme 4).[23] In their works, **2e** was prepared by the dehydration of diol **1e** in the presence of $POCl_3$ and pyridine. From an economical and environmental point of view, our protocol provides a recyclable alternative for the production of **2e**, which can further undergo the same processes to elaborate vannusals A and B. We believe that our approach will replace the conventional $POCl_3$/pyridine method in the future.

Scheme 4. Potential Application in the Total Synthesis of Vannusals A and B.



Conclusion

In summary, a recyclable solid acid/ionic liquid system has been developed for the catalytic dehydration of pinacol derivatives to branched 1,3-dienes. The reaction of alkyl and cycloalkyl derived diols in Amberlyst-15/[Emim]Cl system afforded the corresponding 1,3-dienes in good yields, while Nafion/[Emim]Cl was demonstrated to be the optimum catalyst system for the dehydration of aryl substituted substrates. The presence of [Emim]Cl significantly improved the diene selectivity. Furthermore, the high polarity of ionic liquid also allows a facile separation of dienes just by decantation. Our protocol features a straightforward and simple access to branched 1,3-dienes, high chemoselectivity, a recyclable catalyst system, a facile work-up process, and broad substrate scope. Due to the ubiquitous role of 1,3-dienes in cycloadditions and polymerizations, this work will have potential applications in organic synthesis and polymer science.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Experimental details. Characterization data of the reactants and products. Copies of GC chromatograms and NMR spectra. (PDF)

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Notes

The authors declare no competing financial interests.

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