

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

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Supporting Information



ABSTRACT: The selective dehydration of pinacol derivatives to branched 1,3-dienes is extremely challenging because of 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 an Amberlyst-15/[Emim]Cl system afforded the corresponding 1,3-dienes in good yields, while a Nafion/[Emim]Cl system was demonstrated to be a better catalyst system for the dehydration of aryl-substituted substrates. Our protocol features straightforward and simple access to branched 1,3-dienes, high chemoselectivity, a recyclable catalyst system, a facile separation of dienes just by decantation, and a 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, because of their high reactivity in many reactions (such as Diels-Alder cycloaddition, polymerization, etc.), 1,3-dienes have found wide applications in organic synthesis² 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 multistep 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, which fulfill the criteria of green chemistry, is in great demand.

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) toward 1,3-butadiene.⁷ In contrast, the dehydration of branched *vic*-diols to highly substituted dienes still lags behind because of 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 coupling⁸ or electrolytic reduction⁹ of carbonyl compounds, that is, the so-

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



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 straightforward and simple access to

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branched 1,3-dienes, high chemoselectivity, a recyclable catalyst system, a facile separation of dienes just by decantation, and a broad substrate scope.

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) and (2) pinacol

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



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 diene selectivity, we investigated the influence of solvents on H2SO4-catalyzed pinacol dehydration. The results are illustrated in Table 1. Under solvent-free conditions, the dehydration gave 3a as the single product (Table 1, entry 1). Similar results were obtained when we used a nonpolar solvent (such as toluene) and a protic solvent (such as water) (Table 1, entries 2 and 3, respectively). In contrast, 2a was obtained as the main product when the reaction was performed in some polar aprotic solvents such as dimethyl sulfoxide (DMSO) and N-methyl-2-pyrrolidone (NMP) (Table 1, entries 4 and 5, respectively). 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 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 Bu₄NCl and [EtPy]Cl furnished 2a with low carbon yields, although it still predominated in the products (Table 1, entries 7 and 8, respectively). Moreover, the anion and cation of imidazoliumbased 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, respectively). In contrast, the small anion Cl⁻ can serve as a good hydrogen bond acceptor, which prefers to interact with the hydroxyl proton of pinacol (Cim+Cl-...HO). Besides its hydrogen-bonding interaction, Cl⁻ is also prone to stabilization of the carbocation intermediate through an ion pair, thereby enhancing 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 an increase in alkyl chain length (Table 1, entries 6, 11, and 12, respectively). The sterically hindered long chain

Table 1. 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 ₂ O	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 ₄ NCl	28	23:1
8	H_2SO_4	[EtPy]Cl	28	24:1
9	H_2SO_4	[Emim]NTf ₂	0	
10	H_2SO_4	[Emim]BF ₄	0	
11	H_2SO_4	[Pmim]Cl	77	11:1
12	H_2SO_4	[Bmim]Cl	63	9:1
13	_	[Emim]HSO ₄	no reaction	_
14	-	$[(HSO_3)^4C_4C_1im] \\ HSO_4$	0	_ ^c
15	-	$[(HSO_3)^4C_4C_1im]Cl$	32	1:1
16	H_2SO_4	polyethylene glycol 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.



substituent possibly hampers the interaction between IL and pinacol, thus affording low diene selectivity. The utilization of acidic ILs¹⁷ as both catalyst and solvent was attempted, as well (Table 1, entries 13–15). The dehydration did not occur in [Emim]HSO₄, while stronger acidic IL [(HSO₃)⁴C₄C₁im]-HSO₄ preferred a rearrangement pathway. The reaction in [(HSO₃)⁴C₄C₁im]Cl also gave low diene selectivity and yield. In some of the literature, it is suggested that polyethylene glycol (PEG) has physical properties similar to those of ILs, thus sometimes serving as an alternative reaction medium.¹⁸ However, PEG was proven to be ineffective in this reaction (Table 1, entry 16).

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 strengths. According to ref 19, the pK_a 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 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 following order: $ZrCl_4 > TiCl_4 > AlCl_3 > FeCl_3$. This is



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 °C for 12 h.

consistent with the acid strength sequence of these catalysts that has been classified by Kobayashi et al.²⁰ On the basis of these results, we can see that both strong Brønsted and Lewis acids efficiently catalyzed the dehydration of pinacol to 2a in [Emim]Cl.

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



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.

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 a strong acidic $-SO_3H$ group, the dehydration proceeded smoothly to afford **2a** in 85 and 86% carbon yields, 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** on a large scale.

Figure 3 depicts the profile for the carbon yields of 2a and 3a over Amberlyst-15 resin as a function of [Emim]Cl mass at 393 K. The carbon yield of 2a increased with an increase in the [Emim]Cl mass from 1 to 4 g and then stabilized with a further increase in the [Emim]Cl mass to 5 g. Meanwhile, the opposite trend was observed for the carbon yield of 3a. On the basis of



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.

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



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 °C for 12 h.

carbon yield of **2a** reached its maximum (85%) when 100 mg of Amberlyst-15 resin was used and then stabilized with a further increase in catalyst loading. Thus, the optimal catalyst loading for the reaction is 10 wt % pinacol.

Another advantage of the 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.



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 $^{\circ}$ C, and (c) a biphasic system obtained upon completion of the reaction.

With the increase in reaction time, the mixture switches from monophasic to biphasic, because product diene **2a** is nonpolar and immiscible with [Emim]Cl. Notably, when the final mixture is subjected 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 of >93%) was still liquid, thus allowing a facile separation of **2a** just by decantation.

To fulfill the need of real application, we also checked the reusability of the Amberlyst-15/[Emim]Cl system for the dehydration of pinacol (Figure 6). With the increase in



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.

recycling time, the carbon yield of **2a** slightly decreased while that of unexpected product **3a** increased. 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 the Amberlyst-15/[Emim]Cl system. To do this, we added a different amount of water to the system before reaction. As depicted in Figure 7, an evident decline in the carbon yield of



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.

2a and an increase in the carbon yield of **3a** were observed simultaneously with an increasing 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 a solvent (Table 1, entry 3).

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 the 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 uses.



Figure 8. Carbon yields of **2a** and **3a** over the Amberlyst-15/ [Emim]Cl catalyst system as a function of 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 use.

To gain more insights into the influence of Cl⁻, some control experiments were performed (Scheme 3). The pinacol



dehydration in the Amberlyst-15/DMSO system produced 2a in low yield (16%) and selectivity (2.2:1 2a:3a) (Figure S2). However, after the addition of 20 mmol of LiCl to the mixture, the yield of 2a significantly increased and the molar ratio of 2a and 3a increased to 12.2:1 (Figure S3). On the basis of 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 hydrogen bonding. On the other hand, Cl⁻ could efficiently stabilize the carbocation intermediate, thereby enhancing diene selectivity.

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 listed in Table 2. Compared with the chemical shift of the 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 ¹H and ¹³C shift at position 2 of the imidazole ring (Table 2, entry 5). In contrast, the NMR data of the mixture of [Emim]BF₄ and pinacol showed no difference with neat two components (Table 2, entry 6). These results reveal that [Emim]Cl strongly interacts with pinacol, whereas [Emim]BF₄ does not. In comparison with the weakly coordinating anion BF₄⁻, the small anion Cl⁻ is a good hydrogen bond acceptor, which

		imidazolo	C1 atom of pinacol	
entry		$\delta_{\rm H}$ (H2) (ppm)	$\begin{array}{c} \delta_{\rm C}~({\rm C2})\\ ({\rm ppm}) \end{array}$	$\delta_{\rm C}$ (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, [Em R = ⁿ Bu, X = Cl, [Br R = Et, X = BF ₄ , [Ei	$\begin{array}{ccc} \text{im}]\text{CI} & 5 & \stackrel{1}{\swarrow} \stackrel{1}{\swarrow} 1\\ \text{mim}]\text{CI} & 4 & \stackrel{1}{\swarrow} \stackrel{3}{\searrow} 2 & X^{-1}\\ \text{mim}]\text{BF}_4 & \text{R} \end{array}$	HO OH 2 1 1 2 Pinacol	

Table 2. NMR Data of Neat IL, Pinacol, and the Mixture of IL and Pinacol

possibly interacts with the hydroxyl proton of pinacol $(C_{im}^+Cl^-\cdots HO)$.²¹ In addition, when pinacol is subjected to [Bmim]Cl, an upfield shift of C1 was also observed (74.96 ppm, $\Delta\delta = 0.22$ ppm). However, the upfield shift value of pinacol in [Bmim]Cl (0.22 ppm) was smaller than that in [Emim]Cl (0.36 ppm), which indicates that the 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 the hydroxyl group through hydrogen bonding $(C_{im}-H\cdots OH)$, which cannot be excluded from the process.²²

To illustrate the generality of the Amberlyst-15/[Emim]Cl system, we further explored the dehydration of a series of diols that 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_1 to our surprise, occurred at the adjacent CH₂ position rather than at 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 with high efficiencies. Remarkably, cyclic vic-diols 1e and 1f underwent the process smoothly, providing the corresponding dienes in 86 and 94% yields, respectively. We were disappointed that the dehydration of phenyl-substituted diol 1g in the Amberlyst-15/ [Emim]Cl catalyst system produced 2g in only 18% yield and most of the substrate remained unchanged. Given that the maximal operating temperature of Amberlyst-15 is 120 °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 °C (condition B). Thus, in the cases of aryl-substituted diols, the Nafion/[Emim]Cl system was the optimal 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 strong influence on the results. For example, the dehydration of 1j, possessing an electron-donating OMe group, afforded 2j in 74% yield, whereas electronwithdrawing 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 a substrate. The scope of the reaction can be further extended to

Table 3. Selective	Dehydration of	of Pinacol	Derivatives	to
Various Branched	1,3-Dienes ^f			

	НО	OH R	R = Alk Co	yl, Cy nditic	cloalkyl on A	R	
	R	R-'	R Con	= Ary ditio	l n B	R C	
Entry	Diol	1,3-Diene	Yield (%) ^a	Entry	Diol	L 1,3-Diene	Yield (%) ^a
1	но ОН 1а) 2a	81	8	OH OH 1h		78
2	OH OH 1b	2b	82	9			70
3	OH OH Ic	2c	77	10	MeO HeO HeO 1j	MeO C 2j CMe	74
4	Et OH Et OH 1d	Et Et Et Et 2d	86	11	F ₃ C F ₃ C OH F ₃ C OH	N.R. ^c	-
5	HO HO	[)→ 2e	86	12	Ph OH Ph OH OH	$\begin{array}{c} Ph \\ Ph \\ Ph \\ Ph \\ 2l \\ 2l' $	71 ^{<i>d</i>}
6	HO HO	→2f	94	13	OH OH Im	¢UO y 2m	51
7	Ph OH Ph OH OH 1g	Ph Ph 2g	$75 (18)^b$	14 ^e	HO HO n-hexyl In	N.R. ^c	-

^{*a*}Isolated yield. ^{*b*}An only 18% yield of **2g** was isolated when the dehydration was conducted under condition A. ^{*c*}N.R., no reaction. ^{*d*}A mixture of dienes **2l** and **2l**'. ^{*e*}The dehydration of linear diol **1n** did not occur in either catalyst system. ^{*f*}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.

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 either catalyst system, which was presumably ascribed to the relatively low stability of the secondary carbocation intermediate.

Additionally, this approach also has a potential application in the total synthesis of some intriguing molecules. Vannusals A and B make up a class of marine natural products that were isolated from the interstitial ciliate *Euplotes vannus*. Because of their complex and unusual structures, their synthesis has attracted the interest 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 work, **2e** was prepared by the dehydration of diol **1e** in the presence of POCl₃ 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 POCl₃/pyridine method in the future.

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



cycloalkyl-derived diols in the Amberlyst-15/[Emim]Cl system afforded the corresponding 1,3-dienes in good yields, while the Nafion/[Emim]Cl was system demonstrated to be the optimal catalyst system for the dehydration of aryl-substituted substrates. The presence of [Emim]Cl significantly improved diene selectivity. Furthermore, the high polarity of ionic liquid also allows a facile separation of dienes just by decantation. Our protocol features straightforward and simple access to branched 1,3-dienes, high chemoselectivity, a recyclable catalyst system, a facile workup process, and a broad substrate scope. Because of 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 Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b00066.

Experimental details, characterization data of the reactants and products, and copies of GC chromatograms and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Nicolaou, K. C.; Snyder, S. A.; Montagnon, T.; Vassilikogiannakis, G. Angew. Chem., Int. Ed. 2002, 41, 1668-1698. (b) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. Angew. Chem., Int. Ed. 2005, 44, 4442-4489.

(2) (a) Taarning, E.; Madsen, R. Chem. - Eur. J. 2008, 14, 5638– 5644. (b) Kersten, L.; Roesner, S.; Hilt, G. Org. Lett. 2010, 12, 4920– 4923. (c) Ohashi, M.; Takeda, I.; Ikawa, M.; Ogoshi, S. J. Am. Chem. Soc. 2011, 133, 18018–18021.

(3) (a) Kamachi, M.; Kajiwara, A. *Macromolecules* **1996**, *29*, 2378–2382. (b) Gholami, M.; Tykwinski, R. R. *Chem. Rev.* **2006**, *106*, 4997–5027. (c) Uemura, T.; Nakanishi, R.; Mochizuki, S.; Murata, Y.; Kitagawa, S. *Chem. Commun.* **2015**, *51*, 9892–9895.

(4) (a) Zheng, C. W.; Wang, D.; Stahl, S. S. J. Am. Chem. Soc. 2012, 134, 16496–16499.
(b) Delcamp, J. H.; Gormisky, P. E.; White, M. C. J. Am. Chem. Soc. 2013, 135, 8460–8463.
(c) Jiang, H. F.; He, L.; Li, X. W.; Chen, H. J.; Wu, W. Q.; Fu, W. Chem. Commun. 2013, 49, 9218–9220.
(d) Xia, Y. M.; Xia, Y.; Liu, Z.; Zhang, Y.; Wang, J. B. J. Org. Chem. 2014, 79, 7711–7717.
(e) Prasan Ojha, D.; Ramaiah Prabhu, K. J. Org. Chem. 2013, 78, 12136–12143.
(f) Amaya, T.; Suzuki, R.; Hirao, T. Chem. Commun. 2016, 52, 7790–7793.

(5) Negishi, E. I.; Huang, Z. H.; Wang, G. W.; Mohan, S.; Wang, C.; Hattori, H. Acc. Chem. Res. 2008, 41, 1474–1485.

(6) (a) Diver, S. T.; Giessert, A. J. Chem. Rev. 2004, 104, 1317–1382.
(b) Clark, J. R.; Griffiths, J. R.; Diver, S. T. J. Am. Chem. Soc. 2013, 135, 3327–3330.

(7) Makshina, E. V.; Dusselier, M.; Janssens, W.; Degreve, J.; Jacobs, P. A.; Sels, B. F. *Chem. Soc. Rev.* **2014**, *43*, 7917–7953.

(8) (a) Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S. J. Org. Chem. 1976, 41, 260-265. (b) Nomura, R.; Matsuno, T.; Endo, T. J. Am. Chem. Soc. 1996, 118, 11666-11667. (c) Hirao, T.; Hatano, B.; Imamoto, Y.; Ogawa, A. J. Org. Chem. 1999, 64, 7665-7667.
(d) Kronenwetter, H.; Husek, J.; Etz, B.; Jones, A.; Manchanayakage, R. Green Chem. 2014, 16, 1489-1495. (e) Billamboz, M.; Len, C. ChemSusChem 2015, 8, 1664-1675. (f) Sotto, N.; Billamboz, M.; Chevrin-Villette, C.; Len, C. J. Org. Chem. 2015, 80, 6375-6380.

(9) (a) Slotterbeck, O. C. Trans. Electrochem. Soc. 1947, 92, 377–390.
(b) Popp, F. D.; Schultz, H. P. Chem. Rev. 1962, 62, 19–40.

(10) Nakajima, M.; Fava, E.; Loescher, S.; Jiang, Z.; Rueping, M. Angew. Chem., Int. Ed. 2015, 54, 8828–8832.

(11) (a) De Lezaeta, M.; Sattar, W.; Svoronos, P.; Karimi, S.; Subramaniam, G. *Tetrahedron Lett.* **2002**, *43*, 9307–9309. (b) Liang, T.; Zhang, Z. J.; Antilla, J. C. *Angew. Chem., Int. Ed.* **2010**, *49*, 9734– 9736.

(12) (a) Bhushan, V.; Chandrasekaran, S. *Chem. Lett.* **1982**, *11*, 1537–1538. (b) Rashidi-Ranjbar, P.; Kianmehr, E. *Molecules* **2001**, *6*, 442–447.

(13) (a) Bezouhanova, C. P.; Jabur, F. A. J. Mol. Catal. **1994**, 87, 39– 46. (b) Bucsi, I.; Molnar, A.; Bartok, M.; Olah, G. A. Tetrahedron **1994**, 50, 8195–8202.

(14) Ikushima, Y.; Hatakeda, K.; Sato, O.; Yokoyama, T.; Arai, M. J. Am. Chem. Soc. 2000, 122, 1908–1918.

(15) There is only one report of the pinacol dehydration to diene **2a**, in which a corrosive liquid acid, careful control of the temperature, and an additional distillation process were required: Kyriakides, L. P. *J. Am. Chem. Soc.* **1914**, *36*, 987–1005.

(16) (a) Wilkes, J. S. Green Chem. 2002, 4, 73–80. (b) Dong, K.;
Zhang, S. J.; Wang, J. J. Chem. Commun. 2016, 52, 6744–6764.
(c) Mao, C.; Wang, Z.; Wang, Z.; Ji, P.; Cheng, J.-P. J. Am. Chem. Soc. 2016, 138, 5523–5526.

(17) Amarasekara, A. S. Chem. Rev. 2016, 116, 6133-6183.

(18) Chen, J.; Spear, S. K.; Huddleston, J. G.; Rogers, R. D. Green Chem. 2005, 7, 64–82.

(19) Rinaldi, R.; Meine, N.; vom Stein, J.; Palkovits, R.; Schüth, F. ChemSusChem 2010, 3, 266–276.

(20) Kobayashi, S.; Busujima, T.; Nagayama, S. *Chem. - Eur. J.* **2000**, 6, 3491–3494.

(21) (a) Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. J. Am. Chem. Soc. **2002**, 124, 4974–4975. (b) Shi, C. Y.; Zhao, Y. L.; Xin, J. Y.; Wang, J. Q.; Lu, X. M.; Zhang, X. P.; Zhang, S. J. Chem. Commun. **2012**, 48, 4103–4105.

(22) Lu, B. L.; Xu, A. R.; Wang, J. J. Green Chem. 2014, 16, 1326–1335.

(23) (a) Nicolaou, K. C.; Ortiz, A.; Zhang, H. J.; Dagneau, P.; Lanver, A.; Jennings, M. P.; Arseniyadis, S.; Faraoni, R.; Lizos, D. E. J. Am. Chem. Soc. **2010**, 132, 7138–7152. (b) Nicolaou, K. C.; Ortiz, A.; Zhang, H. J.; Guella, G. J. Am. Chem. Soc. **2010**, 132, 7153–7176.

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