PAPER

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Dehydration in water: frustrated Lewis pairs directly catalyzed allylization of electron-rich arenes and allyl alcohols†

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A frustrated Lewis pair (FLP)-catalyzed allylation of allyl alcohols with electron-rich arenes has been developed. Interestingly, in this reaction, the electron-rich arenes and allyl alcohols are dehydrated in water. What's more, water was the sole byproduct of the reaction. In this protocol, various allyl alcohols can be converted into allyl cations and attacked by the electron-rich arenes to form aryl cation intermediates. Finally, the aryl cation intermediates are deprotonated to give the 1,3-diarylpropenes. In this protocol, indole allyl alcohols can undergo a bimolecular ring closure reaction, and structurally diverse tetrahydroindolo[3,2-*b*]carbazoles could be smoothly obtained. The reaction is not sensitive to oxygen and has been performed on a gram-scale.

Introduction

The Tsuji–Trost allylation reaction[1] is an important way to construct C–C and C–X bonds. In recent years, quite a few breakthroughs have been made in transition metal catalyzed allylation. Muzart,[2] Ma,[3] Tunge,[4] Bruneau,[5] and Zhang[6] *et al.* reviewed the latest developments in transition metal catalyzed allylation. At present, the majority of the existing reports are on the reaction of allyl alcohol derivatives as electrophiles.[7] The allylation reaction with allyl alcohols as electrophiles has also been reported.[8] It has attracted the attention of chemists for its good atom economy. At present, the directed distal allylation and alkylation of arenes have been developed.[9] In addition, selective *para*-functionalization of arenes is also an important research direction.[10] The metal-free catalyzed allylation reaction has attracted much attention due to its environmental friendliness, low toxicity and low catalyst loading. Several metal-free catalysts suitable for allylation reactions have been developed, including calix[*n*]arene sulfonic acids,[11] arylboronic acids,[12] water,[13] 1,3-bis(carboxymethyl)imidazolium,[14] graphene oxide CO_2H,[15] and so on.

In recent years, tris(pentafluorophenyl)borane has received widespread attention as an unconventional, non-toxic, air-stable, water-tolerant, and thermal abiding Lewis acid.[16] Piers reported in 1996 that tris(pentafluorophenyl)borane catalyzed

hydrosilation of aromatic aldehydes, ketones and esters.[17] Oestreich demonstrated the mechanism of Piers and confirmed the stereochemical reversal of silicon using chiral silanes.[18] Stephan demonstrated that the new strategy for chemical storage of hydrogen in macroboranes may involve Lewis acid–Lewis base synergistic reactivity. This strategy was used to reduce the imines, nitriles and aziridines.[19] Fontaine introduced the concept of a frustrated Lewis pairs into hydrocarbon activation, and investigated the carbon dioxide hydroboration of FLP catalysts.[20] Repo conducted related research work on the frustrated Lewis pairs in the intramolecular.[21] In addition, the frustrated Lewis pairs are also used to activate small molecules such as CO_2,[22] NO,[23] N_2O,[24] SO_2,[25] alkenes,[26] and alkynes.[27] Although many advances have been made in the catalyzed reaction of frustrated Lewis pairs, there are currently no reports about allylation of electron-rich arenes by using the frustrated Lewis pairs as the catalyst.

At present, there are few reports on the reaction of macroboranes in water (Fig. 1). Tang's group reported α-aryl α-diazoesters O–H bond insertion catalyzed by tris(pentafluorophenyl)borane using water as solvent.[28] Our group has reported the coupling reaction of naphthoquinones with indoles in water catalyzed by $(C_6F_5)_3B$.[29] The use of macroboranes for dehydration in water may be in line with the concept of green chemistry. Herein, we strived to expand the application range of the frustrated Lewis pairs. What's more, we reported the allylation of a catalyzed electron-rich arenes with allyl alcohols in water by the frustrated Lewis pairs.

Results and discussion

We commenced our investigations by examining the allylation reaction between *N,N*-dimethylaniline (**1a**) and 1,3-diphenylallyl alcohol (**2a**) under various reaction conditions (Table 1). Initially

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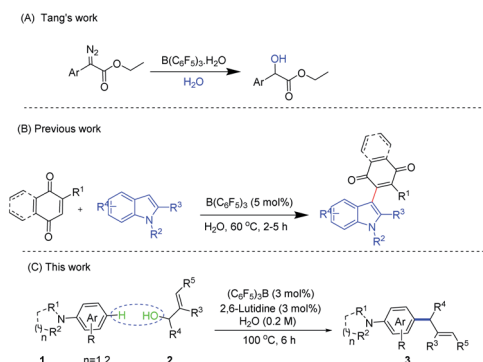
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Fig. 1 The reaction of macroboranes in water.

the reaction was carried out under conditions in which $(C_6F_5)_3B$ was used as a catalyst and triphenylphosphine was used as a base. Gratifyingly, a 1,3-diarylpropene product **3a** was observed and isolated in 71% yield (entry 1). Tris(1,3,5-trifluorophenyl)borane and tris(2,4,6-trifluorophenyl)borane had a small amount of product formation as a catalyst (entries 2–3). Unfortunately, when the reaction was carried out in the absence of a base, the yield of the reaction was lowered (entries 4 and 8). It was demonstrated that the base could promote the reaction. Gratifyingly, when the reaction was carried out in water, the product could be obtained in a comparable yield to that in acetonitrile (entry 5). We attempted to

carry out the reaction without the addition of a catalyst and a base, but the yield of the product was greatly reduced (entry 6). In addition, when the catalyst was omitted, only a small amount of product was formed (entry 7). It was demonstrated that the coordination of the catalyst and the base was more favourable for the occurrence of allylation. Subsequently, we examined the effects of a series of bases on the reaction (entries 9–15). When the reaction was carried out under organic bases, the product was able to be obtained in moderate to excellent yields. But when we used inorganic base, the yield would be greatly reduced. This phenomenon indicated that the inorganic base could not form frustrated Lewis pairs with $(C_6F_5)_3B$ to catalyze the reaction. To our surprise, when the reaction was conducted in 2,6-lutidine as a base, we were pleased to find that the yield of **3a** could be dramatically improved to 90% (entry 10). What's more, when the temperature was adjusted to 60 °C, the expected product could not be observed and a lot of the starting materials remained (entry 16). Interestingly, when the temperature was raised to 100 °C, the yield of the product could be increased to 92% (entry 17). Unfortunately, when we performed the reaction using only 2,6-lutidine as a catalyst, we only got trace product (entry 18). In addition, we also tried to decrease the amount of $(C_6F_5)_3B$ and 2,6-lutidine to 1 mol% but the yield was lower (entry 19). At last, the optimal conditions were confirmed: **1a** (0.3 mmol), **2a** (0.3 mmol), $(C_6F_5)_3B$ (3 mol%), 2,6-lutidine (3 mol%), H_2O (1.5 ml), 6 h.

With the optimized reaction conditions in hand, we next set out to explore the universality of this method (Scheme 1). Therefore, a series of electron-rich arenes with significant structural diversity, including anilines and phenyl ether, were subjected to this process. When the reaction was carried out with N,N,2-trimethylaniline, we obtained 1,3-diarylpropene in moderate yield (**3b**). When we carried out the reaction with a *meta*-substitution or a 2,6-disubstituted N,N-dimethylaniline as a substrate, we were also able

Table 1 Optimization of the reaction conditions[a,b]

Entry	Catalyst	Base	Solvent	T (°C)	Yield of **3a** (%)
1	$(C_6F_5)_3B$	Ph_3P	CH_3CN	80	71
2	$(1,3,5\text{-}C_6H_2F_3)_3B$	Ph_3P	CH_3CN	80	Trace
3	$(2,4,6\text{-}C_6H_2F_3)_3B$	Ph_3P	CH_3CN	80	Trace
4	$(C_6F_5)_3B$	—	CH_3CN	80	58
5	$(C_6F_5)_3B$	Ph_3P	H_2O	80	74
6	—	—	H_2O	80	3
7	—	Ph_3P	H_2O	80	5
8	$(C_6F_5)_3B$	—	H_2O	80	59
9	$(C_6F_5)_3B$	Morpholine	H_2O	80	71
10	$(C_6F_5)_3B$	2,6-Lutidine	H_2O	80	90
11	$(C_6F_5)_3B$	DABCO	H_2O	80	88
12	$(C_6F_5)_3B$	Me_3P	H_2O	80	78
13	$(C_6F_5)_3B$	$P(OPh)_3$	H_2O	80	86
14	$(C_6F_5)_3B$	$PHPh_2$	H_2O	80	86
15	$(C_6F_5)_3B$	Na_2CO_3	H_2O	100	38
16	$(C_6F_5)_3B$	2,6-Lutidine	H_2O	60	0
17	$(C_6F_5)_3B$	2,6-Lutidine	H_2O	100	92
18	—	2,6-Lutidine	H_2O	100	Trace
19[b]	$(C_6F_5)_3B$	2,6-Lutidine	H_2O	100	79

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.3 mmol), catalyst (3 mol%), base (3 mol%), solvent (1.5 ml), 6 h; yield refers to isolated product. [b] $(C_6F_5)_3B$ (1 mol%) and 2,6-lutidine (1 mol%) was used.
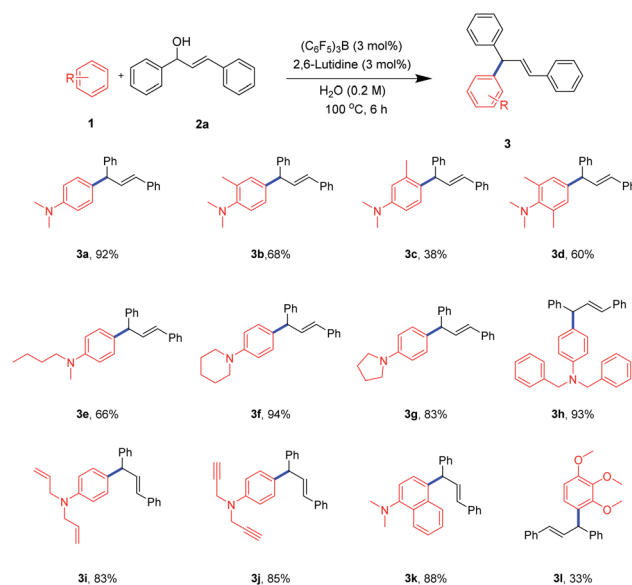
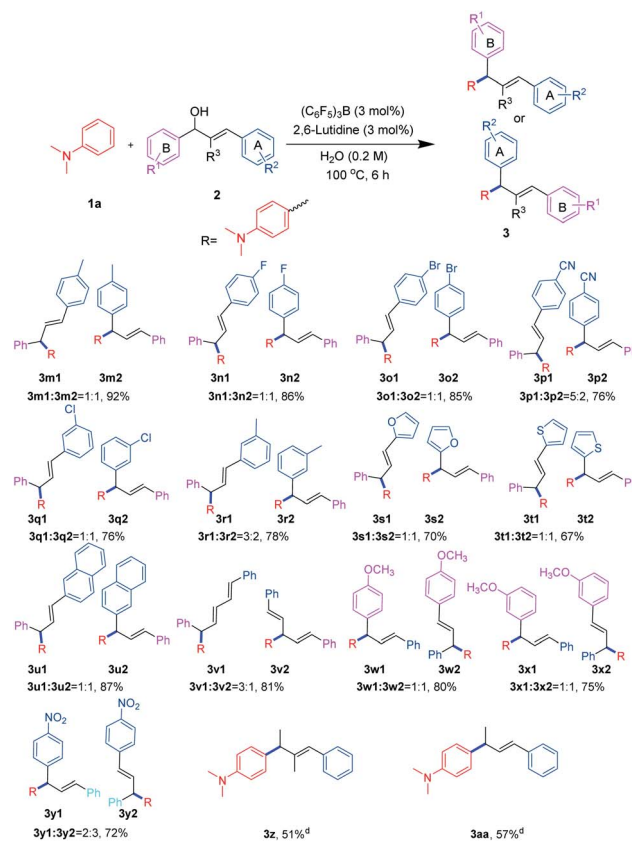**Scheme 1** Substrate scope of electron-rich arenes[a,b]. [a] Reaction conditions: **1** (0.3 mmol), **2a** (0.3 mmol), $(C_6F_5)_3B$ (3 mol%), 2,6-lutidine (3 mol%), H_2O (0.2 M), 100 °C, 6 h. [b] Isolated yields.

to obtain an allylated product, albeit at a low yields (**3c–3d**). It was possible that the steric hindrance effect of the *ortho* and *meta* positions prevented the attack of allyl cations and led to a decrease in yield. Further, this protocol could be suitably applied after the methyl group on N was replaced by *n*-butyl group, and the allylation product was obtained in a moderate yield (**3e**). Interestingly, the cyclic aniline compounds were capable of obtaining the allylation products in good to excellent yields (**3f–3g**). What's more, when a largely hindered benzyl group was attached to the N of the aniline, the product was obtained in excellent yield (**3h**). The exciting thing was that this protocol showed good compatibility with carbon–carbon double bonds and carbon–carbon triple bonds (**3i–3j**). Moreover, naphthylamine compound could also be used in this process and gave allylation product in good yield (**3k**). Furthermore, the 1,2,3-trimethoxybenzene was used, and the 1,3-diarylpropene product could also be formed, albeit at a low yield (**3l**, 33%). It might be due to the common steric hindrance effect of *ortho* and *meta* positions, which greatly reduced the yield. This is consistent with the previous results (**3c–3d**).

We next explored the scope of allyl alcohols (Scheme 2). Firstly, we focused our attention on the changes in the allyl alcohol **A** ring substituent. Unfortunately, the allyl alcohol double bond was shifted and we got a mixture of double bond migrations. TLC showed as only one point that cannot be separated. The ratio of the double bond migration product to non-migrated product was about 1 : 1 by NMR. The possible reason was that the aromatic rings at the ends of allyl cations had almost the same ability to stabilize the positive charge. When the *para* position of the phenyl group was bonded to an electron-donating substituted group, the product was able to be obtained in excellent yield (**3m**). In addition, the *para* position of the phenyl group was attached to an electron withdrawing group such as fluorine, bromine or cyano, and we could also obtain the products in moderate to good yields (**3n–3p**). In particular, the cyano group of the strong electron withdrawing group caused the uneven distribution of the allyl cation charge, resulting in a product ratio of 5 : 2. In addition, the *meta*-substituted benzene ring could also give the products in a moderate yields (**3q–3r**). Excitingly, this reaction also showed good compatibility with heterocycles (**3s–3t**). When the ring **A** was the naphthalene, we could also carry out the reaction in good yield (**3u**). When the reaction was carried out with (2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-ol, the product was able to be obtained in good yield (**3v**). Next, we would explore the effect of substituent on the **B** ring on the reaction. When the **B** ring was attached to an electron donating substituent, we were able to carry out the reaction in moderate to good yields (**3w–3x**). In addition, when the **B** ring was connected to the electron-withdrawing group, the product was also able to be obtained product in moderate yield (**3y**). Unfortunately, alkyl allyl alcohol and polysubstituted allyl alcohol did not perform the reaction smoothly in water, but the product could be obtained in acetonitrile in moderate yields (**3z–3aa**).

The 3 position of indoles is electron-rich, and allylization of indoles have been reported more.[30] Herein, we focused our attention to the scope of indoles (Scheme 3). Gratifyingly, various indoles were well applicable in this protocol and were

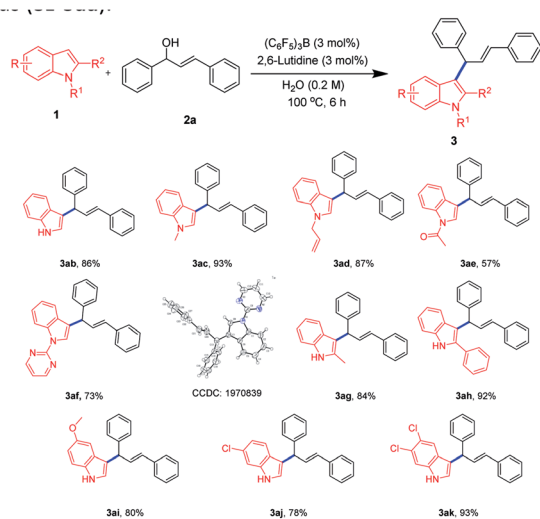**Scheme 2** Substrate scope of allyl alcohols[a,b,c,d]. [a]Reaction conditions: **1** (0.3 mmol), **2a** (0.3 mmol), (C₆F₅)₃B (3 mol%), 2,6-lutidine (3 mol%), H₂O (0.2 M), 100 °C, 6 h. [b]Isolated yields. [c]Mixture ratio determined by NMR. [d]Acetonitrile as solvent (seal).

regioselectively allylated to the 3 position of the indoles. In addition, the single-crystal structure of **3af**, **3al** further confirmed the allylation reaction.[31] As an example, when N1 position of indoles was not attached to a substituent or attached to an electron-donating substituted group such as methyl, allyl, we could proceed smoothly in this process to deliver corresponding allylated products in good to excellent yields (**3ab–3ad**). When N1 position of indoles was substituted by electron-withdrawing groups such as acetyl and pyrimidine we were also able to obtain the products although the yields were slightly reduced (**3ae–3af**). It was possible that the electron-withdrawing group lowered the density of the electrons at the 3-position electrons, thereby reducing the attack activity of the allyl cations. Interestingly, when the C2 position of the indoles was substituted by a methyl group or a phenyl group, we could also obtain the products in a good to excellent yields, demonstrating that the steric hindrance at the C2 position had little effect on the reaction (**3ag–3ah**). In addition, when the C5- or C6-position of the indoles were separately substituted for the substituent, we could obtain the 3-allylated indoles at a good yields (**3ai–3aj**). Excitingly, when the C5 and C6 positions were substituted, we were able to obtain allylated indole in a superior yield (**3ak**).

Surprisingly, (*E*)-3-(1-methyl-1*H*-indol-2-yl)-1-phenylprop-2-en-1-ol (**2q**) and (*E*)-1-(4-bromophenyl)-3-(1-methyl-1*H*-indol-2-

Scheme 3 Substrate scope of indoles[a,b]. [a]Reaction conditions: **1** (0.3 mmol), **2a** (0.3 mmol), $(C_6F_5)_3B$ (3 mol%), 2,6-lutidine (3 mol%), H_2O (0.2 M), 100 °C, 6 h. [b]Isolated yields.

yl)prop-2-en-1-ol (**2r**) were capable of bimolecular ring-closure reaction to obtain tetrahydroindolo[3,2-*b*]carbazoles (**3al**–**3am**). In order to reveal the potential application of this protocol, an amplification scale reaction was implemented. A 1.2 g scale reaction was carried out for *N,N*-dimethylaniline **1a** and (*E*)-3-(1-hydroxy-3-phenylallyl)benzene-1-ylium **2a**, and the product **3a** was isolated in 89% yield (Scheme 4). The result showed that the product yield was not affected after the reaction was scaled up, further indicating that the reaction has great potential for application.

Based on others previously reported in literature,[19,28,32,33] a plausible mechanism was proposed in Scheme 5. Initially, tris(pentafluorophenyl)borane and 2,6-lutidine formed a frustrated Lewis pairs **A**. **A** interacted with allyl alcohol to form
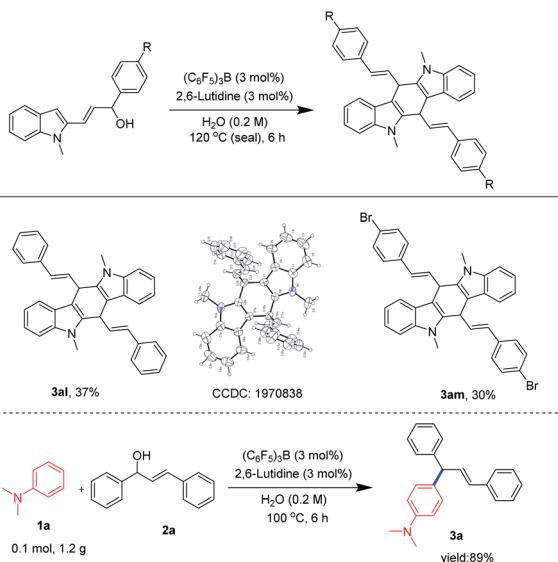
Scheme 4 Bimolecular ring closure and scale-up reaction.
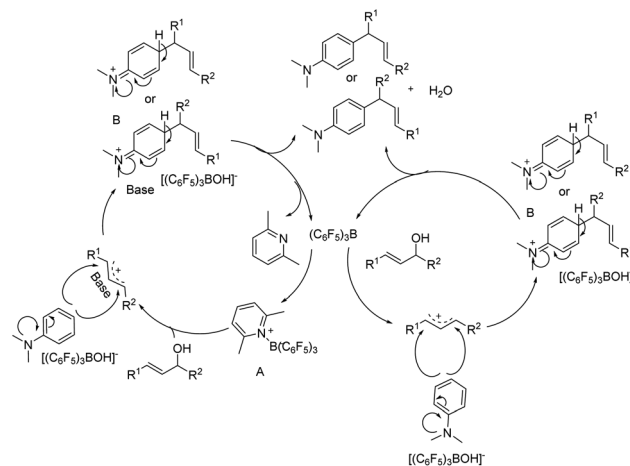
Scheme 5 Proposed mechanism.

$[(C_6F_5)_3B(OH)]^-$ and an allyl cation stabilized by base. The electron-rich aromatic ring attacked the allyl cation to form aromatic cation intermediate **B**. **B** deprotonated and reacted with $[(C_6F_5)_3B(OH)]^-$ to produce water and target products, while the catalyst and base were circulated. In addition, when there was no base, $(C_6F_5)_3B$ could also convert allyl alcohol to allyl cation, thereby completing the reaction process. However, in the absence of a base, the yield of the reaction product was only moderate (Table 1 entries 5 and 8). It might be that the base helped stabilize the allyl cation and improved the yield.

Conclusions

In summary, a FLP-catalyzed allylization of allyl alcohols with electron-rich arenes in water has been reported for the preparation of 1,3-diarylpropenes. In this protocol, the electron-rich aromatics and allyl alcohols are dehydrated in water. What's more, the reaction has very good atom economy and water is the sole byproduct. This protocol is not only featured with mild conditions and broad scope, but also reveals FLP-catalyzed allylization of electron-rich aromatic rings in water, which would offer a new insight for synthesis of 1,3-diarylpropenes and dihydrocarbazoloindoles.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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