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Lithium Diisopropylamide Catalyzed Allylic C−H Bond Alkylation with Styrenes

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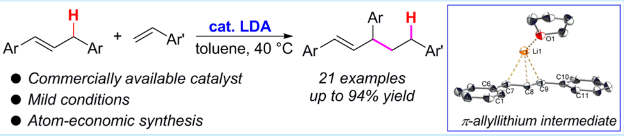
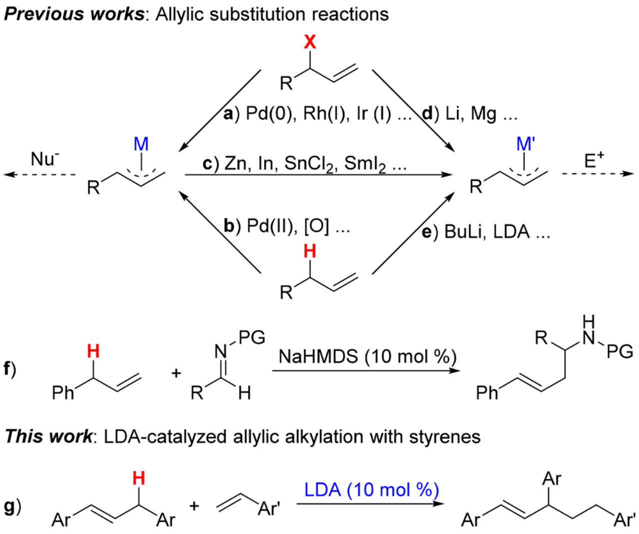
Supporting Information

ABSTRACT: Allylic substitution reactions, a well-established approach for new bond construction, often need transition-metal catalysts and stoichiometric amounts of organometallic reagents, strong bases, or oxidants. Lithium diisopropylamide (LDA), a widely used and commercially available Brønsted base, is herein reported to catalyze the allylic C−H bond addition of 1,3-diarylpropenes to styrenes. Preliminary mechanism studies have provided a solid structure of the π-allyllithium intermediate and revealed the unique catalytic roles of LDA and its conjugate acid diisopropylamine.



Transition-metal-catalyzed allylic substitution reactions are well established as one of the most important and reliable methods for C−C and C−X bond construction reactions.[1] Generally, an olefin bearing an allylic leaving group is necessary for oxidative addition with a low-valent transition-metal complex to produce an electrophilic π-allyl intermediate, which then undergoes nucleophilic substitution with release of the catalyst (Scheme 1a).[2] The electrophilic transition-metal π-allyl intermediates can also be obtained via direct allylic C−H bond activation (Scheme 1b). However, a stoichiometric amount of an oxidant is indispensable to achieve the catalytic transformation.[3,4] The umpolung of electrophilic π-allyl metal species can actually take place via the reactions with stoichiometric amounts of reductants or organometallic reagents such as Zn, In, $SnCl_2$, SmI_2, Et_2Zn, and Et_3B (Scheme 1c).[5] These reagents are incompatible with the oxidation conditions of allylic C−H bond activation, and so the umpolung reactions prefer to take place with substrates bearing a leaving group at the allylic position rather than a simple alkene. Allyl stannanes, allyl silanes, and allyl boron compounds have also been reported to undergo transition-metal-catalyzed electrophilic substitution reactions via nucleophilic π-allyl intermediates.[6,7] The direct synthesis of the nucleophilic π-allyl metal intermediates can also be achieved via either the metalation of allyl halides with main group metals or the deprotonation of an allylic C−H bond with strong base reagents (Scheme 1d,e).[8−10] Even though versatile approaches have been reported for the allylation reactions, these methods have the disadvantages of requiring transition-metal catalysts and stoichiometric amounts of organometallic reagents, strong bases, or oxidants. Therefore, mild, atom-economical methods for allylation would be highly desirable.

Scheme 1. Allylic C−H Bond Functionalization Reactions



Brønsted base-catalyzed C−C bond formation reactions have been extensively used in organic synthesis for their reliability, high efficiency, and ideal atom economy.[11] Kobayashi and co-workers have broadened the scope of the nucleophiles to simple esters, amides, alkylnitriles, alkylazaarenes, and alkanesulfonamides by using a strong Brønsted base such as KH or KHMDS as catalyst.[12] Schneider and co-workers recently reported the first catalytic C−H addition of allylbenzenes to imines with NaHMDS as a catalyst (Scheme 1f).[13] The catalytic alkylation of weakly acidic C−H bonds was also reported by Pines, Knochel, and Kobayashi with styrenes as electrophiles.[14] Very recently, we investigated the base-catalyzed alkylation of alkylpyridines and diarylmethanes.[15]

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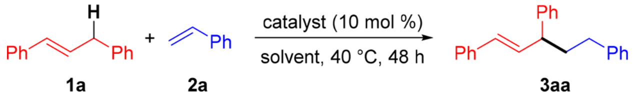
Herein, we further report the catalytic allylic C−H bond alkylation reaction with styrenes (Scheme 1g).

We first investigated the reaction of 1,3-diphenylpropene (**1a**) with styrene (**2a**) in toluene with 10 mol % of KHMDS or potassium zincate, which were efficient catalysts in the alkylation of alkylpyridines or diarylmethanes.[15,16] After being heated at 40 °C for 48 h, the reactions gave the desired alkylation product but in low yields (Table 1, entries 1 and 2).

Table 1. Optimization of Reaction Conditions[a]

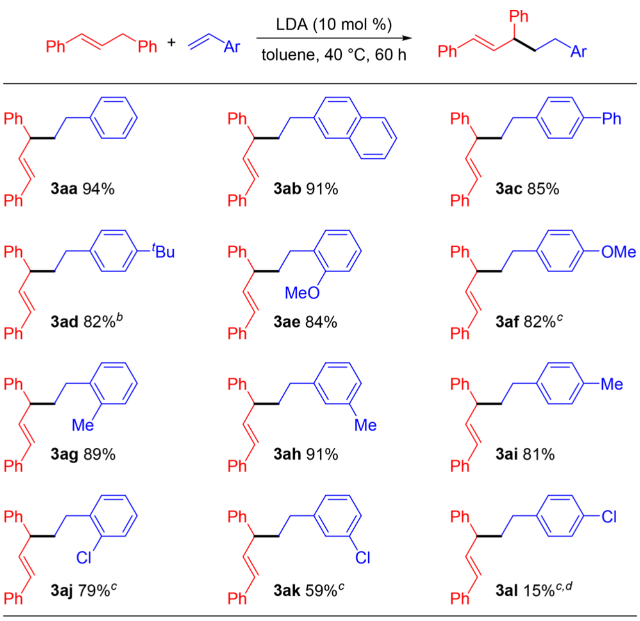


1a **2a** **3aa**

entry	catalysts	solvent	yield[b] (%)
1	KHMDS	toluene	17
2	KZn(HMDS)$_2$Bn	toluene	19
3	KO^{t}Bu	toluene	<5
4	NaHMDS	toluene	<5
5	LiHMDS	toluene	<5
6	KTMP	toluene	<5
7	NaTMP	toluene	<5
8	LiTMP	toluene	23
9	KN^{i}Pr$_2$	toluene	11
10	NaN^{i}Pr$_2$	toluene	9
11	LiN^{i}Pr$_2$ (LDA)	toluene	92
12	LiCH$_2$SiMe$_3$	toluene	<5[c]
13	LiN^{i}Pr$_2$ (LDA)	benzene	91
14	LiN^{i}Pr$_2$ (LDA)	hexane	78
15	LiN^{i}Pr$_2$ (LDA)	THF	8[d]

[a] Conditions: 1,3-diphenylpropene (**1a**) (0.3 mmol), styrene (**2a**) (0.36 mmol), catalyst (10 mol %), solvent (0.5 mL), 40 °C, 48 h. [b] ^{1}H NMR yields based on **1a** with 1,3,5-trimethoxybenzene as an internal standard. [c] Oligomerization of styrene was observed. [d] 64% conversion of **1a**, double and triple styrene insertion products were detected with GC−MS. HMDS = bis(trimethylsilyl)amide, TMP = 2,2,6,6-tetramethylpiperidide.

Scheme 2. Substrate Scope of Styrenes[a]



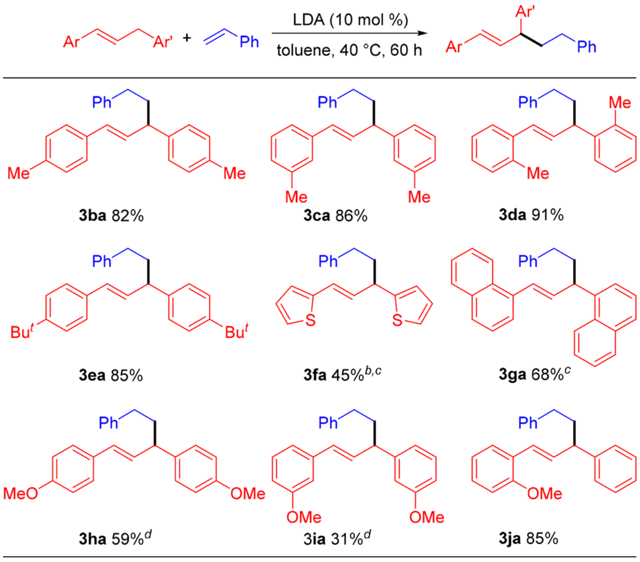
[a] Conditions: 1,3-diphenylpropene (**1a**) (0.3 mmol), styrenes (**2**) (0.36 mmol), LDA (10 mol %), toluene (0.5 mL), 40 °C, 60 h; isolated yields are based on the amount of **1a**. [b] 72 h. [c] 96 h. [d] LDA (20 mol %).

Some other widely used Brønsted bases were also tested as catalysts in the reaction. KO^{t}Bu, NaHMDS, LiHMDS, KTMP, and NaTMP failed to provide any alkylation product (entries 3−7). Compared with KTMP and NaTMP, LiTMP could catalyze the alkylation reaction and gave the product in 23% yield (entries 6−8). Using KDA and NaDA as catalyst, the alkylation products were obtained only in yields of about 10% (entries 9 and 10). We were pleased to find that LDA (lithium diisopropylamide) efficiently catalyzed the reaction and gave the alkylation product in a high yield of 92% (entry 11). Since it is a commonly encountered reagent, LDA was extensively studied but mostly used as a reagent rather a catalyst.[17] Even stronger Brønsted base alkyllithium reagents were studied as reaction catalysts. However, the styrene underwent oligomerization easily but left the 1,3-diphenylpropene intact (entry 12). The LDA-catalyzed alkylation reaction also took place in benzene to give a yield comparable to that of toluene (entry 13). Hexane could achieve the catalytic alkylation but not as efficiently as toluene or benzene (entry 14). In THF, 64% of 1,3-diphenylpropene was consumed, but the desired product was produced in only 8% yield. The double styrene insertion product could also be detected with GC−MS, which suggested the easy multiple insertion of styrene (entry 15). Prolonging the reaction time to 60 h actually led to the alkylation product in an even higher isolated yield of 94% (Scheme 2, **3aa**). We also attempted to raise the reaction temperature to accelerate the reaction, but multiple styrene insertion products were detected. The synthesis of the allylic alkylation product **3aa** was reported by coupling reactions but needed allylic carbonate substrates, transition-metal catalysts, and phosphine ligands.[18]

Having the optimized conditions in hand, we examined the styrene scope of the LDA-catalyzed alkylation of 1,3-diphenylpropene (Scheme 2). 2-Vinylnaphthalene, 4-phenylstyrene, 4-*tert*-butylstyrene, 2-methoxylstyrene, 4-methoxylstyrene, 2-methylstyrene, 3-methylstyrene, and 4-methylstyrene all smoothly underwent the reaction and afforded the corresponding alkylation products (**3ab−ai**) in good to high yields. 2-Methylstyrene and 2-methoxystyrene displayed similar good reactivity with their *para*-substituted analogues, which means that the steric hindrance in the styrenes has little effect on the reaction. Chlorostyrenes were also subjected to the alkylation reaction but showed poor reactivity. By prolonging the reaction time, 3-chlorostyrene and 2-chlorostyrene provided the alkylation products in moderate and good yields (**3aj−ak**). 4-Chlorostyrene, however, failed to achieve the alkylation catalytically (**3al**). The possible reason might be the inhibitory effect resulting from the coordination interaction between the chlorine atom and the lithium metal center.[15b]

Various substituted 1,3-diarylpropenes were evaluated in the LDA-catalyzed allylic C−H alkylation reaction with styrene (Scheme 3). 1,3-Di-*p*-tolylpropene, 1,3-di-*m*-tolylpropene, 1,3-di-*o*-tolylpropene, and 1,3-bis(4-*tert*-butylphenyl)propene smoothly reacted with styrene and afforded the alkylation products in good to high yields (**3ba−ea**). Rather than leading to a sluggish reaction due to increased steric hindrance, the *o*-methyl group of 1,3-diarylpropene actually gave the alkylation product in an even better yield (**3da**). 1,3-Di(thiophene-2-yl)propene and 1,3-di(naphthalen-1-yl)propene could also undergo the catalytic reaction under enhanced conditions

Scheme 3. Substrate Scope of 1,3-Diarylpropenes[a]

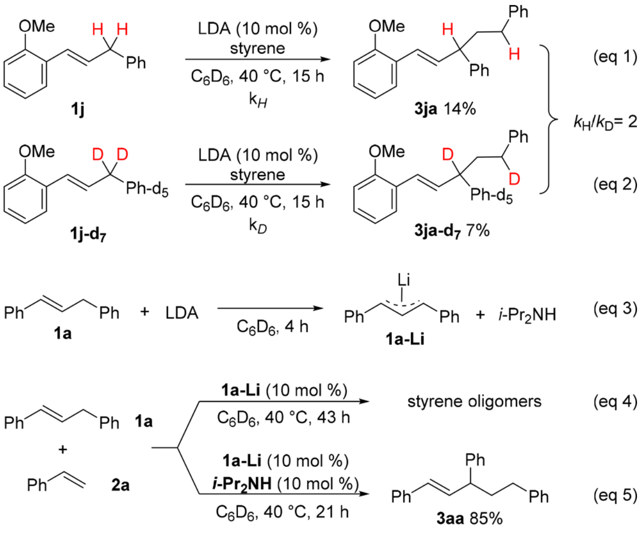


[a]Conditions: **1** (0.3 mmol), styrene (**2a**) (0.36 mmol), LDA (10 mol %), toluene (0.5 mL), 40 °C, 60 h; isolated yields are based on the amount of **1**. [b]LDA (20 mol %). [c]96 h. [d]100 °C.

and gave the alkylation products in moderate yields (**3fa**−**ga**). 1,3-Bis(4-methoxyphenyl)propene and 1,3-bis(3-methoxyphenyl)propene were subjected to the reaction, and the alkylation products were obtained in moderate and low yields even under elevated temperature (**3ha**−**ia**). 1,3-Bis(2-methoxyphenyl)propene was also tested but failed to provide any alkylation product. 1-(2-Methoxyphenyl)-3-phenylpropene and 3-(2-methoxyphenyl)-1-phenylpropene smoothly reacted with styrene, and both isomers gave the same alkylation product **3ja** with good efficiency and regioselectivity. This result suggested that the deprotonation of the allylic C−H bond took place easily to provide a delocalized allylic lithium species, which could be a key intermediate in the catalytic alkylation reaction. Allylbenzene was also subjected into the reaction with styrene but failed to provide alkylation product selectively.[19] To evaluate the practicability of this reaction, the catalytic allylic C−H alkylation of 1,3-diphenylpropene (**1a**) was carried out on gram scale with styrene (**2a**), and the alkylation product was obtained in 80% yield (Supporting Information).

We measured the initial rates of the catalytic alkylation reaction of 1-(2-methoxyphenyl)-3-phenylpropene (**1j**) and its deuterated analogue (**1j-d$_7$**) under exactly the same conditions (Scheme 4). The kinetic isotope effect value (k_H/k_D = 2.0) suggested that the cleavage of the allylic C−H bond is the rate-determining step. To gain insight of this catalytic transformation, we further carried out the control experiments and monitored them with ^{1}H NMR and ^{7}Li NMR. The deprotonation reaction of 1,3-diphenylpropene with LDA in C_6D_6 took place slowly at room temperature. After about 4 h, the deprotonation was complete and produced a mixture of diisopropylamine and an allyllithium intermediate. Further addition of styrene into this mixture gave alkylation product **3aa** in 78% yield after 19 h and regenerated LDA (see the Supporting Information). The allyllithium intermediate was prepared, isolated, and characterized by NMR. A red crystal suitable for X-ray crystallographic study was obtained from crystallization in toluene/THF (10/1), and its structure is shown in Figure 1. In the solid state, the complex is composed of a 1,3-diphenylallyl anion and a cationic [Li(THF)]$^+$ moiety.

Scheme 4. Control Experiments



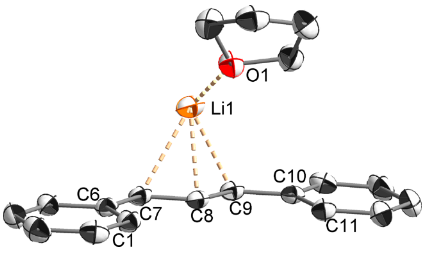
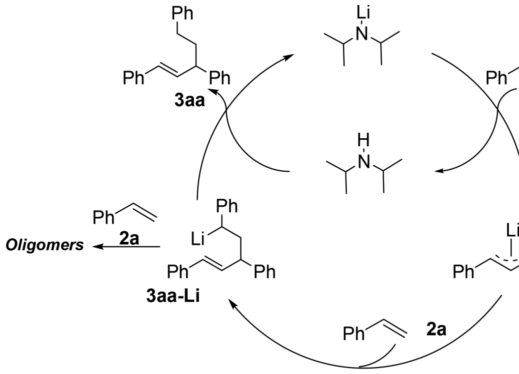


Figure 1. Molecular unit of **1a**−Li·THF with H atoms omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths (Å) and angles (deg): Li(1)−O(1) 1.894(3), Li(1)−C(8) 2.302(3), Li(1)−C(9) 2.327(3), Li(1)−C(7) 2.534(3), C(7)−C(8) 1.387(2), C(8)−C(9) 1.397(2); C(1)−C(6)−C(7)−C(8) 3.1(2), C(8)−C(9)−C(10)−C(11) 2.8(2).

The intermolecular interaction between the lithium atom with diphenylallyl anion of another unit extends the structure supramolecularly (see the Supporting Information). All of the carbon atoms of the two phenyl group are located in the allylic plane. The lithium atom lies above the plane and coordinates with the allylic anion in an η^3 fashion. It is interesting that this allyllithium intermediate smoothly underwent the deprotonation reaction with HMDS to produce LiHMDS and 1,3-diphenylpropene (see the Supporting Information). These results hint that the basicity of the allyllithium intermediate is located between that of LDA and LiHMDS. The basicity difference well explains the quite different behaviors in the catalytic alkylation reactions (Table 1, entry 5 vs 11). As a widely used intermediate, allyllithium species have been extensively studied with NMR analysis. The exact structures, to our best knowledge, have not been determined.[20] Herein, we reported the first solid structure of a π-allyllithium complex. The isolated allyllithium intermediate itself could not catalyze the alkylation reaction but led to the formation of styrene oligomers. However, in the presence of the diisopropylamine, the allyllithium species smoothly achieved the catalytic reaction. These results suggest that the diisopropylamine generated via deprotonation also plays an important role in the catalytic transformation.

According to the results described above, we propose the possible mechanism shown in Scheme 5. The catalyst LDA first undergoes the deprotonation reaction with 1,3-diphenylpropene **1a** to produce diisopropylamine and the allyllithium intermediate **1a-Li**. The insertion reaction between allyllithium species and styrene then generates the intermediate **3aa-Li**, which undergoes the protonation reaction with diisopropylamine to give the alkylation product and regenerate the catalyst. Using the allyllithium species itself as catalyst, the absence of amine turns off the protonation pathway. Then intermediate **3aa-Li** undergoes further styrene insertion reactions to produce oligomers rather than alkylation products.

Scheme 5. Proposed Mechanism



In summary, we have reported the first catalytic allylic C−H bond addition of 1,3-diarylpropenes to styrenes. LDA, a commercially available and widely used Brønsted base, displayed good catalytic activity. For the easily available catalyst and substrates, this method provides a practical and atom-economic approach for allylic alkylation reactions. The nucleophilic *π*-allyllithium intermediate was isolated, and its solid structure was characterized for the first time by X-ray analysis. Preliminary mechanism studies indicate the important and special roles of the LDA catalyst and its conjugate acid, diisopropylamine. Further applications and mechanism studies are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03108.

Experimental details and complete analytical data (PDF)

Accession Codes

CCDC 1849989 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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