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Synthesis of Indenes by a BF_3·OEt_2-Mediated, One-Pot Reaction of Aryl Homopropargyl Alcohols, Aldehydes, and Arenes

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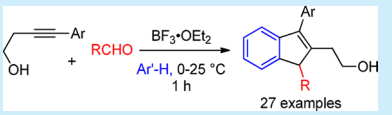
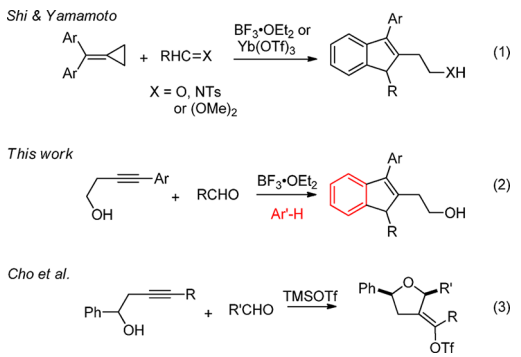
Supporting Information

ABSTRACT: A new and efficient protocol to prepare indenes is reported. Assisted by boron trifluoride diethyl etherate, the one-pot reaction of aryl homopropargyl alcohols and aldehydes in the presence of arenes yielded indene derivatives. The reaction was studied with various substrates, which suggests a cascade reaction including a sequence of Prins, Friedel−Crafts, ring-opening reactions, and Friedel−Crafts to form three C−C bonds leading to indenes.



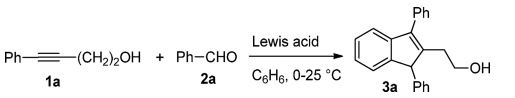
The indene framework is frequently found in natural products,[1] pharmaceutically active compounds,[2] functional molecules,[3] and ligands for metal complexes.[4] It is not surprising that syntheses of indenes and their derivatives continue to receive chemists' attention, and many methods have been developed to prepare this important carbocycle,[5] which include the dehydration of indanols,[6] intramolecular cyclization of conjugated alkenes or alkynes,[7] arene cyclization involving various metal-catalyzed C−H activations,[8] Brønsted or Lewis acid catalyzed intramolecular Friedel−Crafts cyclization of aryl−allylic carbocations,[6a,9] and various cascade reactions using propargyl alcohols.[10] Indenes have also been prepared by Lewis acid catalyzed cycloaddition reactions of arylidenecyclopropanes with aldehydes, acetals, or aldimines (eq 1).[11] Here, we report that indene derivatives could also be



prepared from homopropargyl alcohols, aldehydes and arenes, promoted by boron trifluoride diethyl etherate at room temperature (eq 2). The reactions between homopropargyl alcohols and aldehydes are known to form furans (eq 3)[12] via Lewis acid catalyzed Prins cyclizations.[13,14] In the presence of aromatic solvents and boron trifluoride diethyl etherate, we found that the cascade reaction was further extended to yield indenes.

Our investigation started with the reaction of 4-phenylbut-3-yn-1-ol (**1a**) and benzaldehyde (**2a**) in benzene and the presence of BF_3·OEt_2. The reaction was complete in 1 h according to TLC analysis and the spectroscopic data (IR and ^{1}H, ^{13}C NMR) of the major product were consistent with the reported indene derivative **3a** with a 30% isolated yield.[11b] The structural assignment was also confirmed by X-ray crystallography (see the Supporting Information for the ORTEP of **3a**). In addition to the moieties of **1a** and **2a**, the incorporation of a benzene molecule into product **3a** was interesting and prompted us toward further study. Several reaction factors, such as the stoichiometry of boron trifluoride diethyl etherate, Lewis acids and reaction time were screened. The results are summarized in Table 1. The yields of **3a** increased as the amount of BF_3·OEt_2 increased (entries 1−4); however, more impurities were observed when 5 equiv of BF_3·OEt_2 were applied. Prolonging the reaction time did not improve the yield (entry 5). The reaction also proceeded to yield **3a** with 10 equiv of benzene in CH_2Cl_2 (entry 6) or was promoted by trimethylsilyl triflate and

Table 1. Optimization of the Reaction Conditions



entry[a]	Lewis acid	equiv	time (h)	yield[b] (%)
1	BF_3·OEt_2	1.0	1	30
2	BF_3·OEt_2	2.0	1	40
3	BF_3·OEt_2	3.0	1	64
4	BF_3·OEt_2	5.0	1	68
5	BF_3·OEt_2	3.0	2	66
6	BF_3·OEt_2	3.0	1	28[c]
7	TMSOTf	3.0	12	26
8	TfOH	3.0	2	19
9	$FeCl_3$	3.0	12	0[d]

[a]Reactions were conducted with **1a** (0.25 mmol), **2a** (0.28 mmol) in benzene (1 mL). [b]Isolated yields. [c]Reactions were conducted with **1a** (0.25 mmol), **2a** (0.28 mmol), benzene (2.5 mmol) in CH_2Cl_2 (1 mL). [d]Unidentified mixture.

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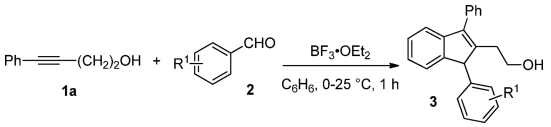
trifluoromethanesulfonic acid; however, the yields were lower (entries 6−8). The reaction using iron(III) chloride was sluggish to yield a complicated mixture (entry 9). Other Lewis acids, such as CF_3CO_2H, $InCl_3$, $Fe(OTf)_2$, and $Zn(OTf)_2$, failed to induce the reactions, and the starting materials were recovered.

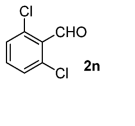
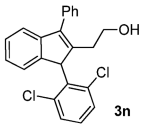
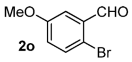
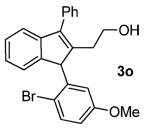
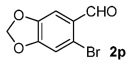
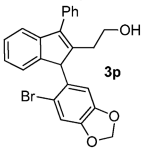
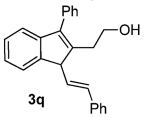
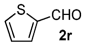
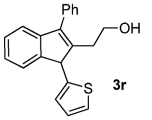
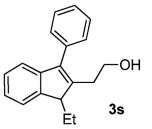
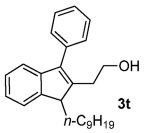
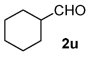
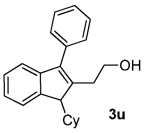
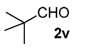
Various aldehydes were applied to examine the reaction scope with this optimized reaction condition (3 equiv of $BF_3{\cdot}OEt_2$ in benzene, 0 °C to rt, Table 2). All of the *para*-substituted benzaldehydes provided the desired indene products (**3b−i**, entries 1−8) with moderate to good reaction yields (55−90%), which indicate that the reaction is not sensitive to the electronic properties of aldehydes imposed by the *para*-substituents. The *ortho*-substituted benzaldehydes also gave satisfactory yields (**3j−l**, entries 9−11), and the reaction was not deterred by the sterically more hindered 2,6-dichlorobenzaldehyde (entry 13). Although 3-methoxybenzaldehyde provided a fair yield (49%, entry 12), slightly better results were observed for other 3-alkoxy-substituted benzaldehydes (entries 14 and 15). Other aromatic aldehydes, such as cinnamaldehyde and thiophene-2-carbaldehyde, were also good substrates and converted to the corresponding indenes (**3q** and **3r**, entries 16 and 17). Aliphatic aldehydes were compatible for this process (entries 18−21); however, their yields decreased as the steric hindrance around the carbaldehyde group increased. Overall, many aryl and alkyl aldehydes could be converted to indenes by this simple, three-component reaction with fair to good yields.

In contrast to the high tolerance of aldehydes, we found that this reaction is sensitive to the substituents on the homopropargyl alcohols (Table 3). The reactions of 4-(4-chlorophenyl)-3-butyn-1-ol (**1b**) with three aldehydes **2d**, **2j**, and **2p**, provided the indenes **3bd**, **3bj**, and **3bp**, respectively (entries 1−3). The location of the chloro substituent was unambiguously determined by X-ray crystallography of **3bj** (Figure 1). However, the reaction of methyl-substituted alcohol **1c** gave a pair of regioisomers **3cg** and **3cg′**, which suggests a competition between the phenyl and tolyl groups during the formation of the indene moiety (vide infra). Interestingly, alcohol **1d** bearing an electron-donating methoxy group afforded the known conjugated enone **4**,[15] derived from a formal alkyne−carbonyl metathesis of **1d** and benzaldehyde.[16] No indene was generated from the reaction of the homopropargyl alcohol bearing an electron-deficient *p*-nitrobenzene (**1e**, entry 6). The inertness of aliphatic 3-pentynol (**1f**) and methyl ether **1g** under this condition (entries 7 and 8) indicates that the aromatic alkynyl moiety and the hydroxyl group are essential for the reaction.

On the basis of the above results and previous studies,[12b,c] a plausible mechanism for the formation of indenes is proposed (Scheme 1). Boron trifluoride initiated the reaction of homopropargyl alcohol and aldehyde to form the oxonium cation **A**. The following Prins-type cyclization yielded the exocyclic vinyl cation **B**, which was the electrophile for the Friedel−Crafts reaction of benzene and the precursor of intermediate **C**. The equilibrated, ring-opening rearrangement gave the allyl carbocation **D**, which was intercepted by the more electron-rich aryl group to produce thermodynamically stable indene **3**. Many aldehydes that can form oxonium cation **A** and allow the following Prins-type cyclization are compatible with this process. On the other hand, the R^2 substituent has a direct influence on the formation of vinyl cation **B**. Thus, the reaction was obstructed by an electron-withdrawing R^2 group, such as the nitro group of **1e** (entry 6, Table 3); however, the electron-donating methoxy group seems to stabilize intermediate **B** well and thwart the following Friedel−Crafts reaction to give **4** (entry 5, Table 3). The reaction using 4-methyl-substituted **1c** proceeded but gave a mixture of regioisomers due to the

Table 2. Synthesis of Indene with Various Aldehydes



entry[a]	R^1/aldehyde	product	yield (%)[b]
1	4-Me, **2b**	**3b**	85
2	4-*i*Bu, **2c**	**3c**	76
3	4-OMe, **2d**	**3d**	84
4	4-SMe, **2e**	**3e**	55
5	4-F, **2f**	**3f**	75
6	4-Cl, **2g**	**3g**	90
7	4-Br, **2h**	**3h**	77
8	4-NO_2, **2i**	**3i**	71
9	2-F, **2j**	**3j**	70
10	2-Cl, **2k**	**3k**	60
11	2-Br, **2l**	**3l**	77
12	3-OMe, **2m**	**3m**	49
13			84
14			61
15			70
16	cinnamaldehyde (**2q**)		78
17			50
18	propionaldehyde (**2s**)		45[c]
19	decanal (**2t**)		57[c]
20			31[c]
21		-	0[c]

[a]Reactions were conducted with **1a** (0.25 mmol), aldehyde (0.28 mmol), and $BF_3{\cdot}OEt_2$ (0.75 mmol) in benzene (1 mL). [b]Isolated yields. [c]Reaction time: 12 h.

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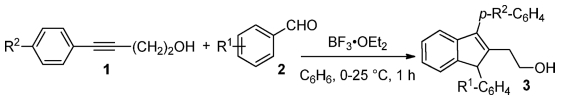
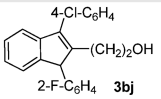
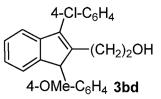
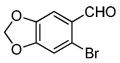
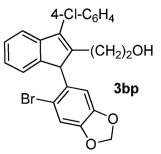
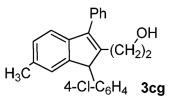
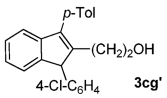
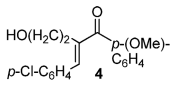
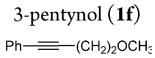
Table 3. Synthesis of Indene with Substituted Alcohols



entry[a]	R^2	R^1	product	yield (%)[b]
1	Cl, **1b**	2-F, **2j**	 **3bj**	60
2	Cl, **1b**	4-OMe, **2d**	 **3bd**	80
3	Cl, **1b**	 **2p**	 **3bp**	64
4	Me, **1c**	Cl, **2g**	 **3cg**	55
			 **3cg'**	
5	OMe, **1d**	Cl, **2g**	 **4**	40
6	NO_2, **1e**	4-OMe, **2d**	-	0[c]
7	3-pentynol (**1f**)	**2a**	-	0[d]
8	 **1g**	**2a**	-	0[d]

[a]Reactions were conducted with **1a** (0.25 mmol), aldehyde (0.28 mmol) in benzene (1 mL). [b]Isolated yields. [c]Unidentified mixture. [d]Starting materials recovered.

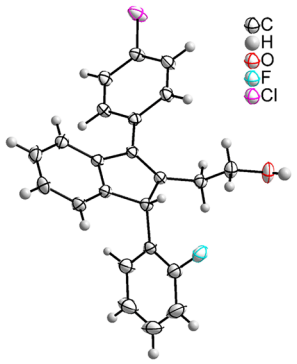
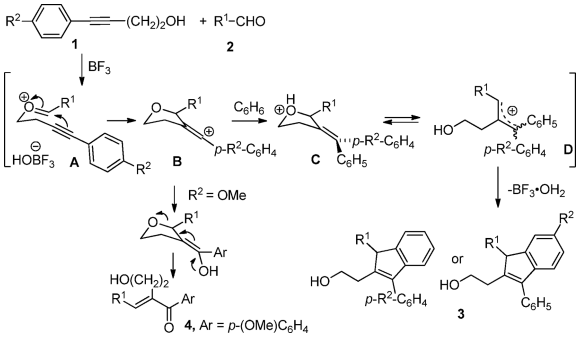


Figure 1. ORTEP of **3bj**.

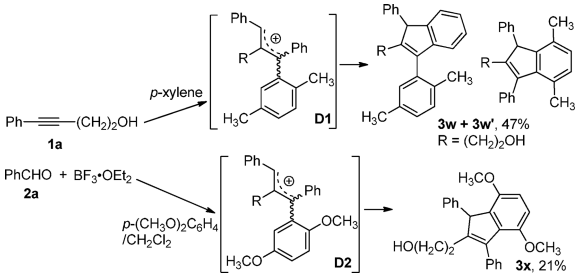
competition between the two aryl groups in the intramolecular Friedel–Crafts-type cyclization of **D** to form indenes **3cg** and **3cg′** (entry 4, Table 3). The issue of competition was relieved in **1a** (R^2 = H) and the chloro-substituted **1b** (R^2 = Cl), which gives a symmetrical **D** or has a deactivated chlorophenyl group for the Friedel–Crafts-type reaction, respectively.

The above mechanism was also supported by the results obtained from the reactions performed in *p*-xylene or 1,4-dimethoxybenzene/CH_2Cl_2 (Scheme 2). The ^1H and ^{13}C NMR spectra indicated that the reaction in *p*-xylene provided a pair of regioisomers (**3w** and **3w′**), and the reaction in 1,4-

Scheme 1. Proposed Mechanism for the Formation of indene 3



Scheme 2. Reactions Conducted in Different Solvents



dimethoxybenzene gave single product **3x**. The results are consistent with the relative reactivity of the corresponding aryl groups toward to the allyl cation in the intermediates **D1** and **D2**. No indene product could be found when the reaction was carried out in bromobenzene.

In summary, a new approach to access indenes is developed through a sequence of Prins, Friedel–Crafts, ring-opening and Friedel–Crafts reactions including three C–C bond formations. This method has the advantages of broad substrate scope in aldehydes, readily available substrates and a metal-free, simple one-pot procedure. The intermolecular Friedel–Crafts reaction between the vinyl cations and arenes is especially attractive because the effort needed to prepare the highly strained arylidenecyclopropanes is circumvented. Further studies on the tandem Prins/Friedel–Crafts reactions and their application in synthesis are in progress.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01929.

Experimental procedures and spectral data of compounds described herein (PDF)

Accession Codes

CCDC 1846842 and 1847193 contain 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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