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Iodine/Et_3SiH: a novel reagent system for the synthesis of 3-aryl-1*H*-indenes from 1,3-diaryl propargyl alcohols

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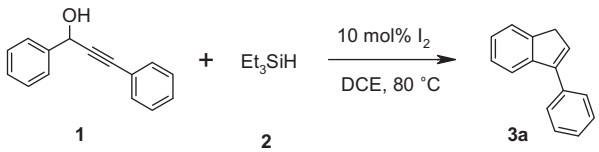
ABSTRACT

1,3-Diaryl propargyl alcohols undergo smooth intramolecular Friedel–Crafts cyclization with triethylsilane in the presence of 10 mol % iodine 3-aryl-1*H*-indene derivatives in good yields in short reaction times. This is the first example on the synthesis of substituted indenes from 1,3-diaryl propargyl alcohols. The use of inexpensive and readily available molecular iodine makes this method quite simple, more convenient, and practical.

The chemistry of alcohols occupies a vital role in organic synthesis. In particular, 'π-activated' alcohols are attracted as proelectrophiles, capable of reacting with various nucleophiles, and their ability to undergo nucleophilic substitution reactions contributes largely to their synthetic value.[1] The use of 'π-activated' alcohols such as benzylic, propargylic, and allylic alcohols makes the C–OH bond activation easier via the formation of stabilized positively charged intermediates.[2] Notably, indene scaffolds are attractive targets for the synthesis of some biologically active molecules.[3] Consequently, transition metal-catalyzed approaches such as Ni- and Co-catalyzed carboannulation of alkynes with *o*-halophenyl aldehydes or *o*-iodophenyl malonates, rhenium-,[4] and palladium-[5] catalyzed annulations and gold(I)-catalyzed intramolecular carboalkoxylations[6] have been introduced for the synthesis of indene derivatives. In addition, substituted indene derivatives were prepared via the Pd-catalyzed annulation of alkynes,[7] and palladium-catalyzed carboannulation of internal alkynes by substituted aryl halides.[8] Subsequently, Lewis acid-catalyzed ring expansion of substituted cyclopropanes and cyclopropenes,[9] and intramolecular hydroarylation of phenyl-substituted alkenes[10] have also been reported for the preparation of indene scaffolds. Recently, $FeCl_3$ has also been utilized to accomplish the synthesis of indenes.[11] Though these methods are quite effective for the synthesis of simple indenes; they have certain drawbacks in the preparation of highly substituted indenes. Many of these methods involve multi-step reaction sequences[12] and often require expensive metal catalysts and strong acidic conditions. Therefore, the development of a simple, convenient, and metal-free catalytic system for the synthesis of indene scaffolds is highly desirable.

Recently, molecular iodine has received considerable interest in organic synthesis because of its low cost and ready availability. The mild Lewis acidity associated with iodine has enhanced its use in organic synthesis to perform several organic transformations using stoichiometric levels to catalytic amounts.[13] A catalytic amount of iodine is able to activate the hydroxyl group and the elimination processes are usually accompanied by rearrangements or intramolecular cyclizations.

Following our interest in the catalytic uses of iodine,[14] we herein, report a direct one-pot method for the synthesis of indenes via an intramolecular Friedel–Crafts cyclization of aryl-substituted propargylic alcohols. Initially, we attempted the deoxygenation of diaryl-substituted propargyl alcohols with triethylsilane using a catalytic amount of molecular iodine. Interestingly, indene derivatives were formed instead of the expected deoxygenation. Thus, treatment of 1,3-diphenyl-2-propyn-1-ol (**1**) with triethylsilane (**2**) in the presence of 10 mol % molecular iodine in 1,2-dichloroethane at 80 °C for 1 h gave the corresponding 3-phenyl-1*H*-indene **3a** in 85% yield (Scheme 1).



Scheme 1. Preparation of 3-phenyl-1*H*-indene.

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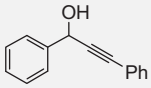
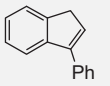
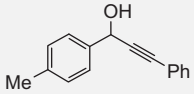
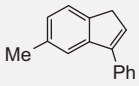
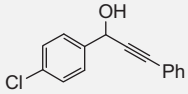
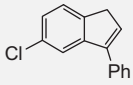
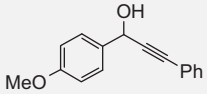
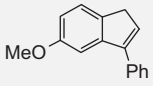
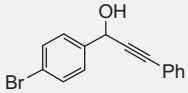
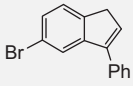
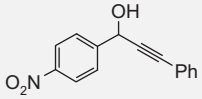
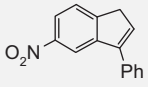
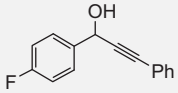
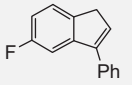
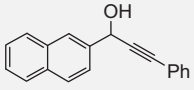
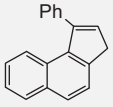
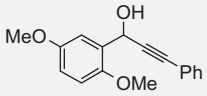
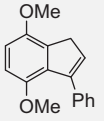
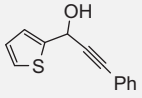
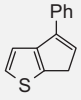
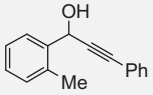
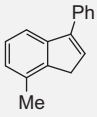
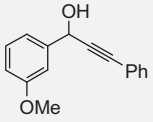
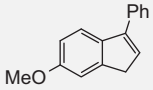
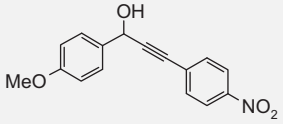
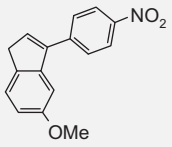
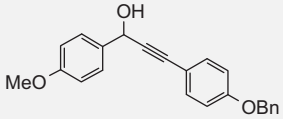
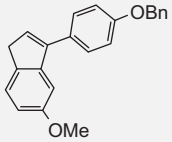
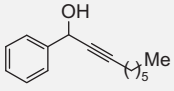
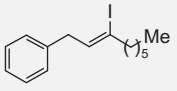
Table 1
Molecular iodine-catalyzed cyclization of propargyl alcohols with triethylsilane

Entry	Propargyl alcohol (**1**)	Triethylsilane (**2**)	Product (**3**)[a]	Time (h)	Yield (%)[b]
a		Et_3SiH		1.0	85
b		Et_3SiH		0.5	86
c		Et_3SiH		1.5	80
d		Et_3SiH		0.5	88
e		Et_3SiH		1.5	82
f		Et_3SiH		2.0	78
g		Et_3SiH		1.5	80
h		Et_3SiH		1.5	84
i		Et_3SiH		1.0	82
j		Et_3SiH		1.5	85
k		Et_3SiH		2.0	75
l		Et_3SiH		1.5	82
m		Et_3SiH		2.0	80
n		Et_3SiH		1.5	85
o		Et_3SiH		2.5	80[c]