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Synthesis of tetralin and chromane derivatives via In-catalyzed intramolecular hydroarylation

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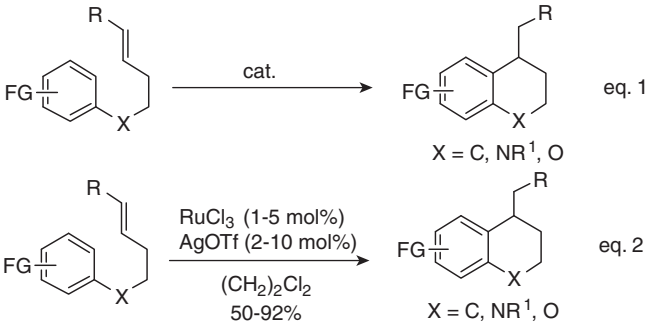
ABSTRACT

$In(OTf)_3$ was found to be an effective catalyst for the cyclization of ω-aryl-1-alkenes to form tetralin and chromane derivatives. Compared with the known Ru-catalyzed version, the In-catalyzed intramolecular cyclization was found to give higher yields and cleaner reactions in some cases. The use of cheaper indium salts instead of the expensive noble metal Ru can be advantageous when the reaction is run on a large scale.

Tetralins and chromanes are important structural motifs and they are present in a wide variety of natural products and pharmaceuticals.[1] To construct the tetralin and chromane structural frameworks, conceptually, one of the simplest ways would involve the intramolecular cyclization of an alkene which is tethered to an arene ring (Scheme 1, Eq. 1). This type of transformation can be formally regarded as a hydroarylation reaction. When the reaction is mediated with sulfuric acid, the reaction is called Dazens tetralin synthesis.[2] Though the Dazens reaction is very simple to run, the need to use a strong acid severely limits its synthetic utility since the acid is not compatible with many different functional groups. As a result, chemists have strived to develop new versions of this useful transformation, aiming to make the reaction milder so that the synthetic scope of the reaction can be greatly expanded.[3] Toward this end, Sames recently developed a $RuCl_3$/AgOTf catalyzed intramolecular hydroarylation of olefins (Scheme 1, Eq. 2),[4] which was based on their earlier works on the Pt-catalyzed intramolecular hydroarylation of alkynes,[5] allowing the facile synthesis of tetralin and chromane derivatives. As simple and straightforward as this reaction is, however, this transformation is not problem-free. In some cases, some isomerization products in addition to the desired intramolecular hydroarylation product were produced. Since the polarities of the isomerization products are similar to the cyclization product, they can complicate the isolation of the final product through column chromatography separation. Indeed, when we treated 5-phenyl-1-pentene with 5 mol % of $RuCl_3$ and 10 mol % of AgOTf in dichloroethane at 80 °C, the desired cyclization product 1-methyl-tetralin (**A**) was produced in 82% yield, which is consistent with the result reported by Sames. However, GC analysis of the crude reaction mixture also indicated the formation of several isomerization products in 8% combined yield (Table 1, entry 1). From these results, it is clear that a similar reaction without producing any of the isomerization products is highly desirable.

We recently became interested in the development of reactions catalyzed by indium and iron salts because of the recent huge influx of reports on In-,[6,7] and Fe-catalysis[8] and their extensive use as Lewis acids. They have attracted much attention lately because of the relatively cheap prices of indium and iron salts, compared to some of the noble metals, and their environmental friendliness due to their low toxicities. Our success of developing an In-catalyzed one-pot synthesis of tetrasubstituted furans from propargyl alcohols and 1,3-diketones[9] prompted us to examine the possibility of using indium or iron salts to catalyze the cyclization of ω-phenyl-1-alkenes to form tetralin and chromane derivatives. Much to our delight, when we treated 5-phenyl-1-pentene with 10 mol % of $In(OTf)_3$ in refluxing anhydrous dichloroethane, the desired product 1-methyl-tetralin **A** was produced cleanly in greater than 97% yield and more importantly, no isomerization product was observed as evidenced by GLC analysis of the crude reaction mixture (Table 1, entry 3). Instead of careful column chromatography, a simple filtration of the reaction mixture through a plug of silica



Scheme 1. Synthesis of tetralins and chromanes via intramolecular hydroarylation.

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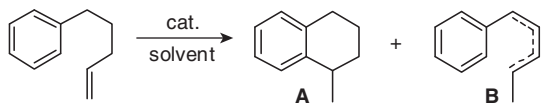
Table 1
Reaction condition optimization for the cyclization of 5-phenyl-1-pentene



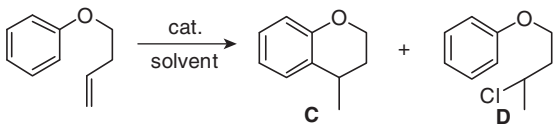
Entry	Catalyst	Solvent	Temperature (°C)	Time (h)	Yield[d] (%)
1	$RuCl_3$/AgOTf	$ClCH_2CH_2Cl$	80	12	**A**(85)**B**(8)
2	$InCl_3$[a]	$ClCH_2CH_2Cl$	90	20	No reaction
3	$In(OTf)_3$[a]	$ClCH_2CH_2Cl$	90	12	**A**(97)**B**(0)
4	$FeCl_3$[a]	$ClCH_2CH_2Cl$	90	12	**A**(8)**B**(0)
5	$FeCl_3$[b]	$ClCH_2CH_2Cl$	90	12	**A**(81)**B**(0)
6	$FeCl_3$[c]	$ClCH_2CH_2Cl$	90	12	**A**(43)**B**(0)

[a] Using 10 mol % of the catalyst.
[b] Using 1.1 equiv of the catalyst.
[c] Using 0.5 equiv of the catalyst.
[d] Yields are determined by GLC using decane as the internal standard.

gel to get rid of the catalyst and evaporation of the solvent afforded the final product **A** that was sufficiently pure enough to give satisfactory ^1H NMR and ^{13}C NMR spectra. The use of $InCl_3$, a weaker Lewis acid, as catalyst was not successful (Table 1, entry 2). The running of the reaction in a less polar solvent such as toluene slowed down the reaction considerably and this might be due to the low solubility of the indium salts in the nonpolar solvent. Surprisingly, the use of $FeCl_3$ (10 mol %), a much weaker Lewis acid, also gave the desired product **A** in 8% yield in refluxing dichloroethane, as determined by GLC analysis and the rest of the starting material was left unchanged (Table 1, entry 4). A further increase of the amount of $FeCl_3$ to 50 mol % resulted in 50% reaction conversion and the desired product **A** was produced in 43% yield (Table 1, entry 6). Finally, by using 110 mol % of $FeCl_3$, a full reaction conversion was realized and the desired product **A** was produced in 81% yield (Table 1, entry 5). The result obtained with $FeCl_3$ was surprising since no reaction was observed with $FeCl_36{\cdot}H_2O$ as reported by Sames.[4]

When we try to cyclize 4-phenoxy-1-butene to produce a chromane derivative **C**, a vastly different result was obtained with $FeCl_3$ from indium salts. As in the case of cyclizing 5-phenyl-1-pentene, $InCl_3$ failed to give any of the desired product **C** in refluxing dry dichloroethane (Table 2, entry 1), whereas the reaction catalyzed by 10 mol % of $In(OTf)_3$ proceeded smoothly to afford the desired cyclization product **C** in 78% yield (Table 2, entry 2). On the other hand, the use of 1.1 equiv of $FeCl_3$ gave a sideproduct, tentatively assigned as the chloro-substituted sideproduct **D**, in 31% yield in addition to the desired chromane product **C** in 52% yield (Table 2, entry 3). However, the sideproduct formation can be completely

Table 2
Reaction condition optimization for the cyclization of 4-phenoxy-1-butene



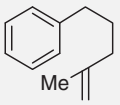
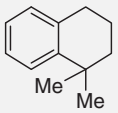
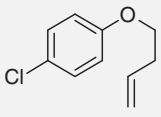
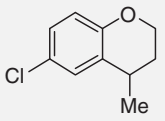
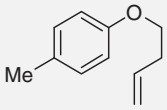
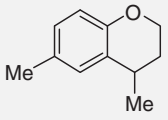
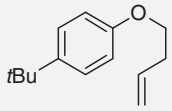
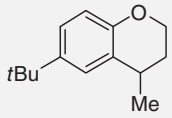
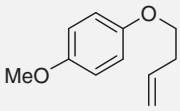
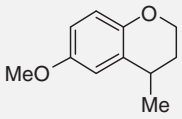
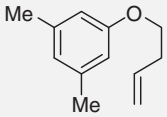
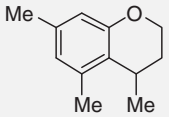
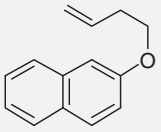
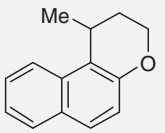
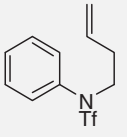
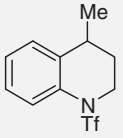
Entry	Catalyst	Solvent	Temperature (°C)	Time (h)	Yield[c] (%)
1	$InCl_3$[a]	$ClCH_2CH_2Cl$	90	20	No reaction
2	$In(OTf)_3$[a]	$ClCH_2CH_2Cl$	90	12	**C**(78)**D**(0)
3	$FeCl_3$[b]	$ClCH_2CH_2Cl$	90	12	**C**(52)**D**(31)
4	$FeCl_3$[b]	CH_3NO_2	105	12	**C**(73)**D**(0)

[a] Using 10 mol % of the catalyst.
[b] Using 1.1 equiv of the catalyst.
[c] Isolated yields.

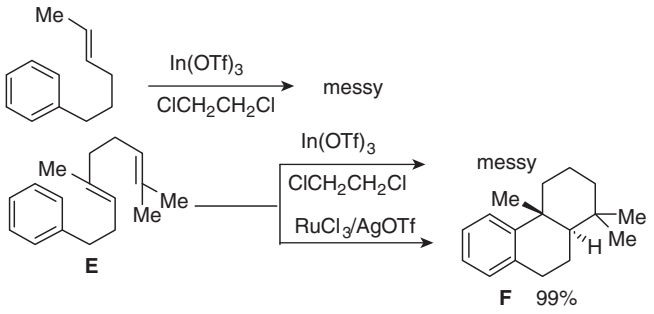
suppressed by switching the solvent to nitromethane (Table 2, entry 4). The test also showed that 1.1 equiv of $FeCl_3$ was necessary for the reaction to reach completion even in nitromethane. Though the price of $FeCl_3$ is very cheap, the need to use it in more than stoichiometric amounts made the approach much less attractive. As a result we chose running the reaction in the presence of 10 mol % of $In(OTf)_3$ in refluxing dichloroethane as our standard reaction condition.[10]

With a satisfactory protocol in hand, we next set out to examine the scope of the reaction. As summarized in Table 3, a variety of tetralins and chromanes could be synthesized smoothly from 5-ary-1-pentenes and arylhomoallyl ethers. A methyl substituent at the 2-position of the alkenes did not impede the reaction. For example, when 5-phenyl-2-methyl-1-pentene was treated with 10 mol % of $In(OTf)_3$ in refluxing dichloroethane, the desired product was produced in 89% yield (Table 3, entry 1). As for the synthesis of chromane derivatives, the yields are generally lower, ranging from 52% to 80% (Table 3, entries 2–6). The lower yields might be due to the deprotection of the ether substrate to a minor extent. The reaction is also compatible with various functional groups such as alkyl, methoxy, and chloride on the aryl ring. Replacing the phenyl ring with a naphthyl ring also gave the tricyclic chromane derivative in 61% yield (Table 3, entry 7). It is also important

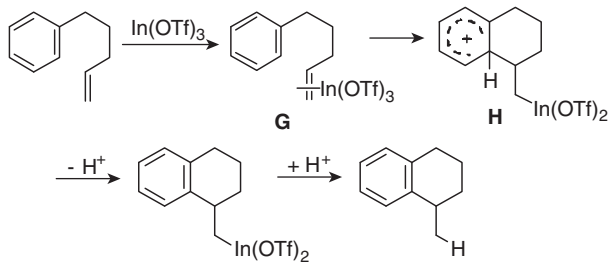
Table 3
Indium-catalyzed intramolecular hydroarylation

Entry	Substrate	Product	Yield[a] (%)
1			89
2			62
3			58
4			70
5			80
6			52
7			61
8			76

[a] All reactions were carried out using $In(OTf)_3$ (0.1 mmol), ω-aryl-1-alkene (1.0 mol) in anhydrous dichloroethane (3 mL) at 90 °C for 12 h. Isolated yields.



Scheme 2. Attempt to cyclize internal alkenes.



Scheme 3. Possible mechanism for the In-catalyzed intromolecular hydroarylation.

to point out that an attempt to cyclize 4-phenyl-1-butene under otherwise the same reaction conditions did not succeed. Though most of the starting materials were gone, only several isomerization products were produced in 20–30% combined yield (not shown in Table 3). We suspect that the majority of the starting materials underwent polymerization instead of the desired cyclization. In the case of cyclizing a substrate with a nitrogen tether (Table 3, entry 8), we also found that the use of Tf group as the protection group of the amine was essential for the reaction to succeed, as reported by Sames.[4] The reaction of the free amine was very sluggish. Compared with the excellent yields obtained with terminal alkenes, rather disappointing results were obtained with internal alkenes. For example, the reaction of cyclizing 2*E*-6-phenyl-2-hexene, a simple internal alkene substrate, was quite messy (Scheme 2). Attempts to cyclize substrate **E** to produce the tricyclic product **F** also failed completely. In sharp contrast, cyclization using $RuCl_3$/AgOTf as the catalyst gave the desired product **F** in 99% yield. These results show that the scope of the In-catalyzed reaction is narrower than the Ru-catalyzed version.

Even though the exact mechanism of this reaction is unknown at the present stage, we believe that the reaction is not based on the C–H activation.[11] A tentative mechanism is proposed and depicted in Scheme 3. First, the indium catalyst interacts with the double bond to form an olefin–metal complex **G**. Then the complex can undergo Friedel–Crafts reaction with the aromatic ring to form intermediate **H**. After the loss of a proton, the aromatic ring is regenerated and subsequent protonolysis of the carbon–indium bond furnishes the final product. Though HOTf generated in situ[12] could also be responsible for the catalysis, this possibility has been ruled out by Sames.[4]

In summary, we have developed a method for the synthesis of tetralin and chromane derivatives via an intramolecular hydroarylation of ω-aryl-1-alkenes via In-catalysis. The use of $In(OTf)_3$ was found to be critical for the reaction to be successful while the use of less Lewis acidic $InCl_3$ was ineffective. While $FeCl_3$ could also be used to catalyze the cyclization, a stoichiometric amount of the catalyst is necessary for the reaction to reach completion. Compared to the Ru-catalyzed version, the use of $In(OTf)_3$ gave cleaner reactions in some cases. The use of cheaper indium salts instead of the expensive noble metal Ru could be advantageous when the reaction is run on a large scale. Though narrower in substrate scope, the indium catalyzed reaction could potentially be useful in selected cases and complementary to the Ru-catalyzed version.

Acknowledgments

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Supplementary data

Supplementary data (detailed experimental procedures and characterization data; ^1H and ^{13}C NMR spectra for all new compounds) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.06.091.

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