GaI_3 catalysed nucleophilic addition of allyltrimethylsilane to aldehydes

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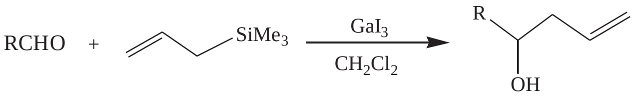
In dichloromethane, the nucleophilic addition of allyltrimethylsilane to aldehydes to give the corresponding homoallyl alcohols in good to excellent yields was catalysed effectively by gallium triiodide which was generated *in situ* by the reaction of gallium metal and iodine.

Keywords: gallium triiodide, aldehyde, allyltrimethylsilane, nucleophilic addition

Homoallyl alcohols are ubiquitous in organic synthesis. They can be used as starting compounds or building blocks for the synthesis of many complicated products.[1-3] One of the important methods for the preparation of homoallyl alcohols is the addition of allyltrimethylsilane to aldehydes. Some powerful Lewis acids such as $TiCl_4$, $BF_3{\cdot}Et_2O$, $SnCl_4$ have been employed to catalyze the reaction because the reactivity of allyltrimethylsilane is not high enough.[4-6] Metal triflates such as $Sc(OTf)_3$ have been found to be effective for this transformation,[7] and $YbCl_3$ has also been used in this reaction.[8] However, there are always some drawbacks with these procedures. For example, some of these Lewis acids are moisture sensitive and require special care in handling and storage, and some of these examples need long reaction times and more catalyst has to be used. Moreover, metal triflates are highly expensive. So the development of new reagents with great efficiency, involving convenient procedures and delivering better yields is of great interest.

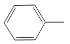
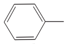
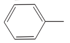
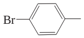
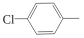
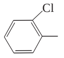
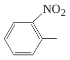
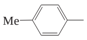
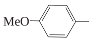
In our research on Lewis acid catalysed organic reactions, gallium triiodide has aroused more and more of our interest. One of the most evident advantages with this reagent is that it can be prepared *in situ* by a simple inorganic reaction of gallium with iodine, which can bring some advantages for its application. We presumed that it may have a great potential to be used in organic synthesis, especially in the formation of C–C bonds. So we decided to use this reagent to catalyse the nucleophilic addition of allyltrimethylsilane to aldehydes. The results showed that in dichloromethane, gallium triiodide catalysed reaction of allyltrimethylsilane with aldehydes gave the corresponding homoallyl alcohols in good to excellent yields.

The Lewis acid catalyst, gallium triiodide was generated easily *in situ* by the reaction of gallium metal and iodine, and a small excess of either Ga or I_2 did not make any difference to the normal course of reaction. The results of the reaction are summarised in Table 1. The reaction proceeded at ambient temperature. GaI_3 exhibited powerful catalytic activity in an amount as low as 5mol%, which was enough to complete the reaction within less than 0.5 hour for all of the substrates we used. A larger amount of catalyst and a high reaction temperature led to some resinification. Several solvents such as acetonitrile, nitromethane and dichloromethane were examined. Among these, dichloromethane was found to be the most effective solvent for this conversion (Table 1, entries 1–3). The catalyst dissolved in it to form a homogeneous solution, and thus the strong electrostatic activation of the carbonyl substrates made the reaction take place smoothly. The reaction was found to be general and applicable to both aromatic and aliphatic aldehydes. With aromatic aldehydes bearing electron-withdrawing substituents, such as a nitro-group or halogen on the benzene ring, the reaction was very fast (completed in a few minutes) and gave excellent yields. However, in the case of aliphatic aldehydes the yields of products were not as high as those from aromatic aldehydes even with longer reaction times due to their intrinsic lower reactivity.



Scheme 1

Table 1 Addition reaction of allyltrimethylsilane to aldehydes

Entry	R	Solvent	*t*/min	Yield[a]/%	lit.[b]
1		CH_3CN	60	75	ref. 9
2		CH_3NO_2	60	65	
3		CH_2Cl_2	30	88	
4		CH_2Cl_2	15	92	ref. 9
5		CH_2Cl_2	15	88	ref. 9
6		CH_2Cl_2	15	90	ref. 9
7		CH_2Cl_2	5	90	ref. 10
8		CH_2Cl_2	30	78	ref. 9
9		CH_2Cl_2	30	80	ref. 9
10	$CH_3CH_2CH_2$—	CH_2Cl_2	30	72	ref. 11
11	$(CH_3)_2CHCH_2$—	CH_2Cl_2	30	75	ref. 12

[a] Isolated yields based on aldehydes. All of the products are known compounds, and the structures of the products were confirmed by ^{1}HNMR and IR spectra.

[b] Literature references of the products.

In summary we have developed a new and efficient procedure for the nucleophilic addition of allyltrimethylsilane to aldehydes catalysed by GaI_3. The method offers several advantages like mild reaction conditions, short reaction time, high yields of products, and simple experimental operation, which leads to a useful and attractive process for the preparation of homoallyl alcohols. It is also revealed that GaI_3 is an effective Lewis acid catalyst for the formation of C–C bonds. Its further application in organic synthesis is currently being explored in our laboratory.

Experimental

Typical experimental procedure. Gallium (single piece of metal, 0.05mmol) was added to a stirring solution of iodine (0.075mmol) in dry dichloromethane (2ml). The mixture was stirred under a nitrogen atmosphere until the reaction was complete (the reactants disappeared, it needed about 0.5h). To this solution was added the aldehyde (1mmol) followed by allyltrimethylsilane (1.3 mmol). The resulting mixture was stirred at room temperature for an appropriate time (see Table 1) and quenched with aqueous $NaHCO_3$. The mixture was then extracted with CH_2Cl_2 three times. After being combined and washed with saturated brine the organic layers were dried over anhydrous Na_2SO_4. The solvent was removed and the residue was subsequently purified by column chromatography on silica gel with hexane/ethyl acetate (20:1–10:1) as eluent to yield the product.

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Selected ^1H NMR data, δ($CDCl_3$, 300MHz)
1-Phenyl-3-buten-1-ol: 2.24(br, 1H), 2.50(m, 2H), 4.70(dd, *J*=7.2, 5.7Hz, 1H), 5.16(m, 2H), 5.82(m, 1H), 7.22–7.40(m, 5H).

1-(4-Bromophenyl)-3-buten-1-ol: 2.28(s, 1H), 2.50(m, 2H), 4.70(dd, *J*=7.2, 6.0Hz, 1H), 5.19(m, 2H), 5.78(m, 1H), 7.24(d, *J*=8.1Hz, 2H), 7.48(d, *J*=8.1Hz, 2H).

1-(2-chlorophenyl)-3-buten-1-ol: 2.28(br, 1H), 2.53(m, 2H), 4.74(dd, *J*=7.2, 6.0Hz, 1H), 5.16(m, 2H), 5.80(m, 1H), 7.25(m, 2H), 7.63(d, *J*=7.5Hz, 1H), 7.72(d, *J*=7.2Hz, 1H).

1-(2-nitrophenyl)-3-buten-1-ol: 2.10(br, 1H), 2.52(m, 2H), 4.85(dd, *J*=7.5, 5.7Hz, 1H), 5.22(m, 2H), 5.93(m, 1H), 7.40(m, 1H), 7.65(m, 1H), 7.80(d, *J*=7.8Hz, 1H), 7.92(d, *J*=4.2Hz, 1H).

1-(4-Methylphenyl)-3-buten-1-ol: 2.00(br, 1H), 2.35(s, 3H), 2.50(m, 2H), 4.70(dd, *J*=7.2, 6.0Hz, 1H), 5.15(m, 2H), 5.75(m, 1H), 7.16(d, *J*=8.1Hz, 2H), 7.28(d, *J*=8.1Hz, 2H).

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