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PII: S0040-4039(14)01184-8
DOI: http://dx.doi.org/10.1016/j.tetlet.2014.07.031
Reference: TETL 44874

To appear in: *Tetrahedron Letters*

Received Date: 29 May 2014
Revised Date: 7 July 2014
Accepted Date: 8 July 2014

Please cite this article as: Jadhav, B.D., Pardeshi, S.K., Bismuth chloride mediated allylation of carbonyl compounds in aqueous media: A mechanistic investigation, *Tetrahedron Letters* (2014), doi: http://dx.doi.org/10.1016/j.tetlet.2014.07.031

Bismuth chloride mediated allylation of carbonyl compounds in aqueous media: A mechanistic investigation

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Abstract

The bismuth chloride mediated, aluminum promoted aqueous Barbier type coupling of allyl unit with carbonyl compounds which gives the corresponding homoallyl alcohol is studied. The transient in situ generated allylbismuth (III) bromide intermediate was studied by ^{1}HNMR and GCMS for mechanistic study of allylation. The role of solvent, temperature and additives in their formation is also studied. The results show that the most reactive intermediate species is $CH_2=CHCH_2BiBr_2$ which mediates allylation of aldehydes and ketones with different substituents with good yields.

Keywords: Allylation, Allyl bromide, Bismuth chloride, organobismuth intermediate, homoallyl alcohol

In recent times , organic synthesis in aqueuos media has attracted considerable attention because of their environmental benefits and favorable effects of water on organic transformations.[1] It was noticed in the early 1980s that allylic halides in particular can be used to react with aldehydes in presence of metal powder to afford homoallylic alcohols in aqueous media. This type of allylic carbonyl addition has been called the Barbier-type allylation. Among the reactions in aqueous media, allylation of carbonyl compounds with allylic organometallic reagents or allyl halides are of great interest because they are convenient methods to form C-C bond.[2] They provide an approach to synthesize secondary and tertiary homoallylic alcohols, as valuable synthetic building blocks in natural product synthesis.[3] A number of metals are known to participate in the coupling reaction in aqueous media including zinc, indium, tin, manganese, antimony and magnesium.[4]The most widely used metals in allylation are zinc and indium.

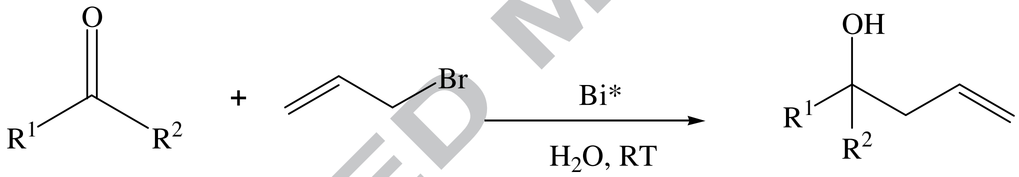
Among VB group elements, bismuth metal and its salts are cheaper and least toxic than arsenic and antimony. Bismuth (III) compounds namely$BiCl_3$, $BiBr_3$, Bi $(NO_3)_3$and Bi $(OTf)_3$ have been used as catalyst in organic synthesis due to its metallic character.[5]Most of these synthetic reactions are performed in organic solvents. The use of water as the reaction medium is usually avoided since a large number of reactants decompose when brought in contact with water. Furthermore, many organic reactants are sparingly soluble in water. Even though these are the disadvantages, water is becoming increasingly popular as a medium for organic reactions. Being the most abundant solvent on earth, it is very cheap, easily available, non-hazardous to the environment and non-toxic. Moreover, aqueous solvents can have beneficial effects on rates and selectivity of important organic transformations.[6] The Barbier reaction is one of synthetic method which became one step alternative to the Grignard reaction due to the simplicity and applicability in organic synthesis.[7] Therefore we focus our attention on potential use of active bismuth metal generated in situ by the action of $BiCl_3$ and metallic aluminum for allylation reaction in aqueous medium.

Wada *et al* reported that bismuth powder (100 mesh) could promote the addition of allyl unit to aldehydes using N, N-dimethylformamide (DMF) as solvent but it requires long period of reaction time.[8] In the absence of Al powder and aqueous tetrahydrofuran (THF) as solvent, trace amount of product was isolated.

Generally acidic environment is necessary to promote reactivity of metal and also to increase the solubility of carbonyl compounds in water. However a number of carbonyl compounds bearing different substituent groups are unstable in acidic environment. Moreover the side reactions such as reduction and pinacol type of coupling can take place readily in acidic environment. Yang *et al* reported that phase transfer catalyst promoted allylation of carbonyl compounds in water mediated by tin without NH_4Cl to produce homoallyl alcohols in good yields, [9] however its reaction mechanism is unclear.

Herein we report our studies on the allylation of carbonyl compounds with allyl bromide effected with active bismuth (Bi*) in aqueous medium which is more convenient and environmental friendly. Effect of organic co solvent, amount of catalyst, role of metal salt additives on the yields of homoallyl alcohols along with mechanistic aspect are also discussed.

In aqueous medium, a black suspension of active bismuth (Bi*) was obtained by stirring $BiCl_3$ (5 mmol) with aluminum powder (5 mmol) in ice bath for fifteen minutes. The resulting black suspension was reacted with a solution of allylbromide and carbonyl compounds at room temperature for specified time (Scheme1)



1 **2** **3 a-m**

+

Scheme 1 General allylation reaction

To explore the generality and scope of this reaction further,$BiCl_3$ mediated and Al (0) promoted reaction in aqueous THF at room temperature was examined using other functionality and sterically diverse carbonyls as shown in Table1.

Table 1 $BiCl_3$ mediated aluminum promoted allylation of carbonyl compounds with allylbromide [a,b]

Entry	R^1 Substrates	R^2	Product	Yield (%)/time (h)
1	Ph	H	**3a**	88/16(85/10)[c]
2	4-$CH_3OC_6H_4$	H	**3b**	89/12
3	4-ClC_6H_4	H	**3c**	82/16
4	2-$C_5H_4O_2$	H	**3d**	70/16
5	4-$CH_3C_6H_4$	H	**3e**	85/16[d]
6	2-OHC_6H_4	H	**3f**	96/12(94/10)[c]
7	2-OH-5-$CH_3OC_6H_3$	H	**3g**	94/16
8	3-$NO_2C_6H_4$	H	**3h**	73/16
9	Ph-CH=CH	H	**3i**	85/16[d]
10	n-C_5H_{10}	H	**3j**	78/10(81/6)[c]
11	CH_3-CH=CH	H	**3k**	75/16[d]
12	Ph	Me	**3l**	65/12(83/5)[c]
13	Ph	Ph	**3m**	53/15(50/6)[c]

[a] All reactions were performed with aldehyde (5 mmol), allyl bromide (7.5mmol), $BiCl_3$ (5 mmol)and aluminum powder (5 mmol) in THF: H_2O at room temperature.
[b] Isolated yields. All physical data including IR &NMR spectra were consistent with the literature data
[c] Combined yields.
[d] The yield was estimated by GCMS.

From Table 1 it is clearly seen that all aromatic, heteroaromatic and aliphatic aldehydes reacted smoothly to provide the corresponding homoallyl alcohols in excellent yields of 53-96%.As per Scheme 1, the nature of R^1 and R^2 group and either electron donating or electron withdrawing sustitutents are not significant. 4-methoxybenzaldehyde and4-chlorobenzaldehyde (Entries 2 and 3) showed the tendency of decrease in yield. It is thought that the benzaldehyde with electron-donating groups is more difficult to be attacked by allyl metal reagents. It is interesting to note that unsaturated aldehyde such as cinnamaldehyde affords 1, 2 addition product selectively than 1, 4 addition product (Entry9).

In order to assess the usefulness of the reaction with other types of aldehydes, reactions were conducted with a heterocyclic aldehyde, 2-furaldehyde (Entry 4, Table 1), which gives the desired homoallyl alcohol with 70% yields. Aliphatic aldehyde for example valeraldehyde (Entry 10) and crotonaldehyde (entry 11) were reacted under these conditions giving moderate yields of corresponding allyl alcohols. When aromatic keto carbonyl compound, such as benzophenone (Entry 13, Table 1) is taken it exhibits reduced electrophilicity, resulted in 53% yields, reflecting improved reactivity of the carbonyl group. This was compared with similar reactions using an allyl gallium reagent in THF hexane.[10] Another noteworthy observation is that no side products resulting from Wurtz or pinacol coupling are observed however, some unreacted starting material is detected. General procedure for allylation of aldehydes with allyl bromide[11] is given in reference section. In order to optimize the reaction conditions such as Lewis acid catalyst, effect of solvent and role of additives, benzaldehyde was chosen as a model substrate.

Considering that Lewis acids were usually employed as auxiliary agents to promote the allylation, we screened different Lewis acids such as $SnCl_2$, $SnCl_4$, and $InCl_3$ to improve the yield of allyl alcohol and compared with $BiCl_3$. The results are summarized in Table 2

Table 2 Lewis acid-aluminum mediated allylation of benzaldehyde with allylbromide[a, b]

Entry	Lewis Acid (mmol)	Time (h)	Yield (%)
1	_	24	30
2	$SnCl_4$(2mmol)	12	39
3	$SnCl_2$(2mmol)	12	56
4	$InCl_3$(2mmol)	12	80 (85) [c]
5	$BiCl_3$(2mmol)	12	80
6	$BiCl_3$(1mmol)	6	92 (88) [c]
7	$BiCl_3$(0.5mmol)	12	55
8	$BiCl_3$ (1 mmol)	12	93

[a] Reaction conditions: PhCHO (1 mmol), allylbromide (1.5 mmol), aluminum powder (1.5mmol)

[b] Lewis acid in NH_4Cl (0.1 mmol) and water (20 ml) at room temperature for a specified time.

[c] Isolated yield

With the help of bismuth trichloride, the reaction rate was accelerated and the product yield improved significantly (Entry 6, Table 2). The amount of bismuth trichloride used had a large influence on the allylation outcome. With 0.5 mmol of bismuth trichloride, the product yield improved from 30% to 55% (Entries 1 and 7, Table 2). When the amount of $BiCl_3$ was increased to 1mmol, the yield improved further with decrease in stirring time. (Entry 6, Table 2). When reaction was continued further for 12 hours with the same mole ratio of $BiCl_3$, yield of the allyl alcohol reaches upto 93% (Entry 8, Table 2).However, when the amount of $BiCl_3$ was 2mmol, the product yield decreased gradually (Entry 5, Table 2).Hence 1mmol bismuth chloride and its different mole ratio were used as Lewis acid catalyst. Under the set of varying catalytic amounts of the different Lewis acids employed in allylation, the yields of the allyl alcohols differ significantly with Lewis acid amount. It is shown graphically in **Figure1.**

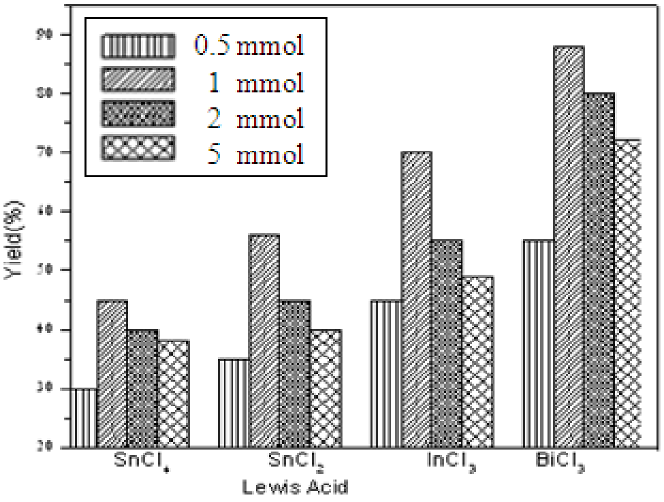


Figure1: Catalyst chemoselectivity study

As seen from the above figure the yields of allylation by $BiCl_3$ in all millimolar ratio are higher than respective $InCl_3$, $SnCl_2$ and $SnCl_4$ respectively.

The allylation of benzaldehyde with allyl bromide was studied as a model reaction in different solvents with catalytically active bismuth metal generated in situ by the action of $BiCl_3$/Al (0). Typical solvent effect on the yield of allyl alcohols and stirring time required for completion of reaction are represented in Table 3.

Table 3 The effect of solvent on the $BiCl_3$mediated, aluminum promoted allylation of benzaldehyde with allylbromide[a, b]

Entry	Solvent	Amount (equiv)	Time (h)	Yield % [c]
1	DMF	6	36	65
2	H_2O	2	24	70
3	H_2O	6	24	65
4	H_2O	6	36	56
5	DCM	6	24	Trace
6	THF/H_2O	6:6	24	95
7	DCM/H_2O	6:6	24	68
8	DMF/H_2O	6:6	36	80
9	CH_3OH	6	48	77
10	CH_3OH / H_2O	3:7	24	80
11	THF	6	24	Trace

[a] All reactions except THF, DCM were performed with aldehyde (5mmol), Allyl bromide (10mmol), aluminum powder (5mmol) and $BiCl_3$ (5 mmol) at room temperature

[b] The reactions were carried out at room temperature for specified time.

[c] Combined yield.

Initially, we treated allyl bromide with benzaldehyde and bismuth chloride in 0.1 N aqueous NH_4Cl for 3 h at room temperature. TLC analysis of the ethyl acetate extract clearly showed a spot that corresponds to the desired allylation product. Subsequently, ^{1}HNMR measurement of the crude reaction mixture showed about 30% of the allylation product. This promising result encouraged us to examine factors that influence the reaction. We then examined in greater detail the effect of the solvent system on the allylation reaction by using various combinations of water and organic co solvents in the reaction.

The results show that the reaction proceeds slow in water and only 56 % yield was obtained even after 36 hours stirring at room temperature (Entry4, Table 3). When reaction was conducted in freshly distilled THF dried over sodium/ benzophenone, or in DCM the reaction between benzaldehyde, allyl bromide, and bismuth chloride generated the expected allylation product only in trace amount (Entry 5 and 11, Table 3). However, when a

THF/H_2O mixture was used as solvent, 95% yields were achieved. Different volume ratios of THF: H_2O were also examined and we found that 10 mL of solvent with 8:2 compositions was sufficient for this reaction. When the composition of the solvent is changed to water (Entry 3, Table 3) alone, a smooth reaction occurred generating the allyl alcohol with a low conversion. This may be attributed to the formation of bismuth oxychloride (BiOCl) as water insensitive material, which may get accumulate on the metal surface and block further reactions.

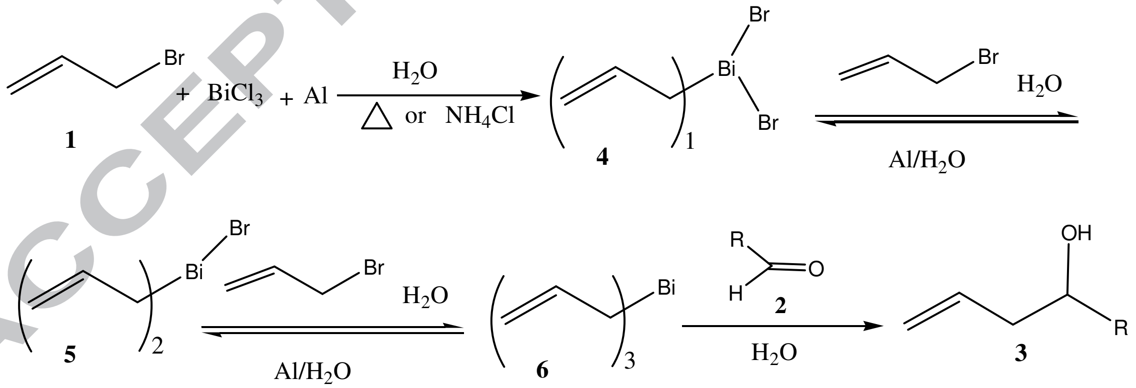
When the reaction was conducted in dimethyl formamide (DMF) it works well but requires a relatively long period of reaction time (Entry 1).The function of water in the reaction has been investigated. We thought that catalytic system generates Bi* metal by redox step and is favorable in aq.THF. We checked this hypothesis by conducting the reaction in absence of Al metal where starting aldehyde gets recovered back. It is possible that the allylbismuth reagent cannot be formed in THF solvent without water probably due to lack of redox step generating Bi (0). On the other hand, it was found that the solution was strongly acidic. Thus, it is thought that the role of water lies in two ways: the first is to accelerate the formation of allylbismuth reagent and the second is to make the aldehyde more liable towards the attack by allylbismuth reagent in acidic media.

Additional side reactions using 0.1 N HCl or NH_4Cl solutions as the reaction solvents gave a quantitative conversion, generating a mixture of the reduced and pinacol coupling products as indicated by TLC and GCMS. Other aromatic aldehydes gave similar results, whereas reactions of aliphatic aldehydes gave more complicated mixtures.

Recent reports indicate that, the performance of bismuth[12] and antimony[13]metals in aqueous Barbier type reactions was enhanced by the presence of fluoride salt which successfully activates C-C bond-forming reactions. Therefore, we investigated the effect of a variety of additives and mole ratios of reactants, beginning with a similar mole ratio as that adopted by Li *et al*[13]in Sb-mediated allylation reactions. We tried various salts like NaF, KBr, KCl, KF, NH4Cl andBu_4NBr in aqueous media as additives. Apart from KF, NH_4Cl and Bu_4NBr most of them are either ineffective or give poor yields. However NH_4Cl, KF or Bu_4NBr were found to be quite effective in activating bismuth, which gave a good yield of the corresponding homoallyl alcohols. Unfortunately, from a green chemistry viewpoint a reaction using KF is not ideal therefore it was not used in further studies. Aliphatic aldehydes (Table 1, Entries10 -11) or aromatic ketone (Table 1, Entry 12), which are usually thought to be unreactive, in presence of Bu_4NBr, get accelerated and transformed to corresponding alcohol in good yield. For rest of the substrates use of NH_4Cl is quite effective. We therefore utilized NH_4Cl or Bu_4NBr in the standard reaction conditions to activate in situ generated bismuth metal in aqueous medium.

The mechanism of the Barbier reaction in aqueous media is not fully understood. For the mechanism of the metal-mediated allylation reaction in aqueous media, Li[4] proposed a radical- carbanion-allyl metal triangle which suggests that the specific mechanism of the reaction is dependent on the metal being used. In case of zinc and tin [14] mediated Barbier allylation it has been found that in aprotic solvents, reaction proceeds through a direct nucleophilic addition, while allylmagnesium bromide reacts through a single electron-transfer process.[15]A recent computational study has shown that allylzinc, allylindium, allyltin, allylantimony, and allylbismuth species are more reactive toward the allylation of carbonyl compounds than towards hydrolysis, while allylmagnesium bromide shows a similar reactivity in the two reactions.[16] NMR studies have shown that indium, tin and antimony react with allylbromide in water to form allylmetal intermediates.[17] However, for different metals, there are still a number of unanswered questions with regard to the nature of the allylmetal species and the involvement of single electron-transfer processes.

Encouraged by a short note from Nesmeyanov[18] indicating that bismuth (III) chloride was reduced by metallic zinc, under similar condition bismuth chloride reacts with metallic aluminum and gave black powder immediately. The assumption of some allylbismuth reagent is formed through the oxidative addition of an allylic halide to the in situ generated bismuth(Scheme 2) was proved by NMR investigations.



Scheme 2: General outline of the allylation of carbonyl compounds by $Al/BiCl_3$

In order to check the nature and detection of the intermediate formed during the reaction course, following set of experiments were performed.

In order to check the transient intermediate formed during the allylation of carbonyl compound by in situ formed active bismuth, aliquots were withdrawn from the reaction mixture at specified time intervals which was followed by its ^{1}HNMR characterization. In order to check the selectivity of the intermediate towards allylation, they are quenched by adding benzaldehyde as model electrophile. Figure 2 represents the ^{1}HNMR assignments in the 2-3 ppm range from the NMR spectra of the allylation intermediates formed during reaction.

When allyl bromide, bismuth chloride and aluminum powder were stirred in D_2O at room temperature for 30 min to 10 h without addition of NH_4Cl,no allyl bismuth type intermediate **4,5,6** (Scheme 2) was detected as indicated by ^{1}HNMR of the reaction mixture (Figure 2A,B).When mixture was warmed without additive to 60 °C, the appearance of small doublet at 2.33ppm in the ^{1}HNMR suggesting probable insertion of active bismuth in C-Br bond and formation of some triallyl bismuth (III) intermediate **6** (Scheme 2) . Such upfield shift of methylene proton of allyl bromide from 3.97 ppm suggests the diamagnetic shielding effect caused by bismuth on adjacent methylene protons (Figure 2C). In another set with 3mmol allyl bromide in the temperature range between 60-80°C methylene proton signal was readily seen at 2.53ppm in the form of doublet in ^{1}H NMR (Figure 2D), which was attributed to the intermediate **4 or 5**. Such down field shift by 0.3 ppm units might be due to electron withdrawing nature of bromine attached to bismuth in the intermediate. The signal appearing at 2.33 ppm in the first set at 60 °C is assigned to triallylbismuth (III)intermediate **6**(Scheme 2) by comparison with an authentic sample prepared independently[19] (Figure 2E).

The effect of catalytic amount of NH_4Cl on the formation of intermediates formed by the action of bismuth chloride, aluminum powder and allyl bromide in D_2O at room temperature was evaluated by adding NH_4Cl under optimized time. It is interesting to note that the rate of formation of the intermediates **4 and 5** (Scheme 2) has been accelerated as observed by ^{1}HNMR (Figure 2F). At the end of 10 h, we have quenched the intermediates formed in the reaction mixture by adding benzaldehyde as model electrophile. Further stirring of reaction mixture for 2-3 h completely consume benzaldehyde to 1-phenylbut-3-en-1-ol suggesting selectivity of intermediates for chain extending reactions.

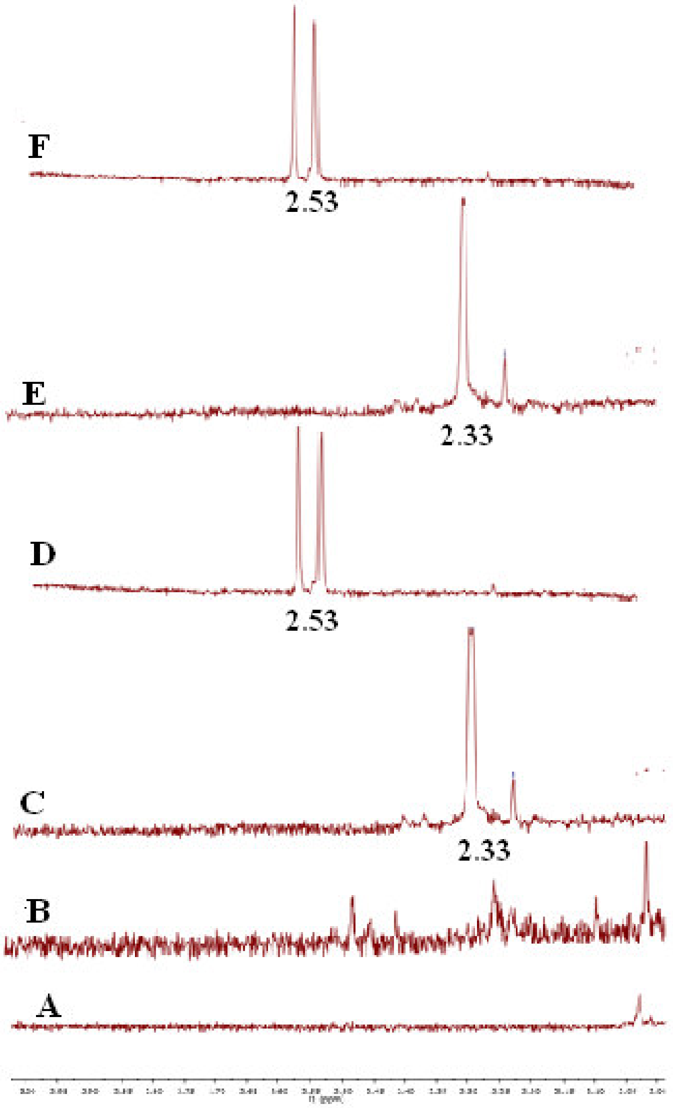


Figure 2 Partial ^{1}HNMR spectra of allyl bromide and bismuth stirred in D_2O solution

(A) 30 min at room temperature without NH_4Cl
(B) 10 h at room temperature without NH_4Cl. no signal from 1.0 to 3.0 ppm
(C) 30 min at room temperature with NH_4Cl and at 60°C without additive
(D) At 60-80°C with NH_4Cl
(E) Allylbismuth (III) bromide prepared from allyl magnesium bromide and bismuth (III) chloride in ether, and extracted into D_2O for NMR
(F) At 70°C for 10 h with NH_4Cl

The above experiments strongly support that the aqueous Barbier reaction with in situ generated bismuth proceeds through allylbismuth (III)dibromide(**4**),diallylbismuth(III)bromide(**5**)and triallylbismuth (III) **(6)** as the organometallic intermediates according to Scheme 2. The formation of **6** is the slow step and requires heating or the use of catalyst (Al).The conversion of **4 and 5 to 6** depends largely on the relative amount of allyl bromide and in situ generated Bi* in the reaction system. Intermediate compound react with benzaldehyde in water to give the corresponding homoallylic alcohol.

From GCMS studies the presence of allylbismuth and allylbismuth bromide species were detected in the organic extracts of the reactions. Theoretically, one equivalent of allyl bromide would be required to produce $(CH_2{=}CH\text{-}CH_2)_1BiBr$ **(4)** while two equivalents for $(CH_2{=}CH\text{-}CH_2)_2\ BiBr_2$ **(5)** which efficiently leads to the homoallylic alcohols. However, it is observed that in reactions when only 2 equivalents were added it significantly reduces the reaction yields but 4 equiv. of allyl bromide were necessary to give high yields. The reason is physical rather than chemical and stems from the volatility of allyl bromide under prolonged stirring. In GC-MS spectra of the reaction mixture extracted in ethyl acetate it has been seen that the peak at RT 15 min corresponding to m/e = 410 suggest the presence of intermediate **4** $(CH_2{=}CH\text{-}CH_2)\ BiBr_2$ (Scheme 2) during the reaction course.

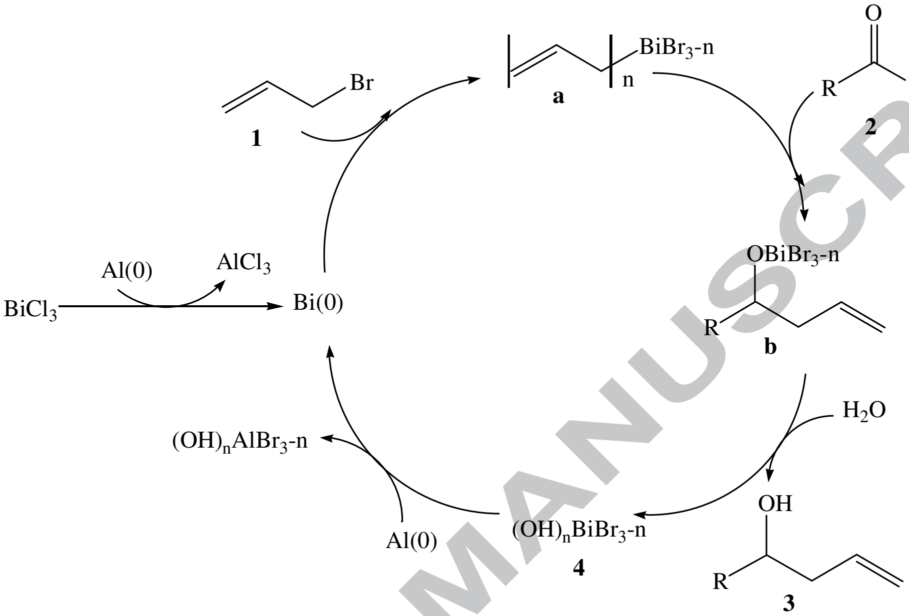
Unlike Grignard reagents, many organometallic complexes cannot be prepared in preformed fashion due to their low thermal stability. Hence easy way to overcome the stability problem of such organometallic complexes is its genesis in presence of electrophiles. This is very common for the organometallic complexes to be generated in situ and then react with electrophile in real time before it undergoes decomposition.

The stability of the allylating agent prepared *in situ* in aqueous environment was checked by leaving the reaction of allyl bromide with Al-$BiCl_3$ in THF-H_2O (4 : 1) at 0-5°C for a number of hours (the molar ratio of allyl bromide : Al : $BiC1_3$: benzaldehyde = 1.5 : 2.25 : 1.5 : 1.0). Benzaldehyde was added to the reaction mixture as per the delay time span indicated in Table 4.Yields of allyl alcohol are reported after standard workup.

Table 4 Investigation of the stability of the allylating agent in aqueous environment

Entry	Delay Period (h)	Yield (%)
1	1	82
2	3	77
3	5	65
4	7	53

It is interesting to note that the reactivity of the allylating agent prepared *in situ* did not disappear for several hours in aqueous media at low temperature which is mere indication of its stability. Up to 1-3 h (Entry 1 and 2) the yield of final allyl alcohol is moderate. Hence we quenched the reaction mixture starting from 10 minutes to 3 h, extracted with D_2O and analyzed it by ^{1}HNMR.



Scheme 3: Possible mechanism of allylation using active bismuth in aqueous medium

Bismuth (III) chloride in presence of Al(0) metal gets reduced to Bi (0) (Scheme 3) which undergoes insertion most probably at weak C-Br bond in allylbromide (**1**)and forms terminal organobismuth (III) derivative (**a**). This derivative combines in the next step with aldehyde (**2**)and forms tetrahedral intermediate(**b**)which in the aqueous media hydrolyses to homoallyl alcohol(**3**)and bismuth (III) compound (**4**).

In freshly dried THF, redox reaction between bismuth chloride and aluminum powder leading to Bi (0) is sluggish and generation of organobismuth via C-Br bond insertion is very slow process. However, in presence of NH_4Cl as additive and THF: H_2O as solvent system there is rapid exothermic reaction generating Bi (0) very effectively and hence fast generation of organobismuth reagent. The organobismuth halide generated during the reaction might act as a Lewis acid which in a tandem manner, catalyze the organometallic addition to carbonyl centre and produce linear homoallyl alcohols as per Scheme1.

This is supported by the recent computational study by Dam*etal.*[20]

We have developed a simple and convenient method for allylation of carbonyl compounds with less expensive allyl bromide by using Al / $BiC1_3$bimetal system in aqueous media. Homoallyl alcohols were not obtained when Al alone was used in THF-H_2O which signifies that some water-tolerant allylating agent prepared *in situ* is stable in aqueous media. It is shown that the allylbismuth compounds persist during the reaction and that the most reactive species is CH_2=$CHCH_2BiBr_2$.

Acknowledgments

B.D.J is grateful to the University Grant Commission, New Delhi for awarding Teacher Fellowship under F.I.P.

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11) General procedure for the allylation of aldehydes with ally1 bromide:
In a 50 mL round bottom flask a mixture of carbonyl compound (5mmol), allylbromide (10.8mmol) and bismuth trichloride (5 mmol) in 20mLdistilled water was prepared. Then solid NH_4Cl (4 mmol) was added followed by aluminum powder (5mmol) in one portion with stirring. The resultant mixture was vigorously stirred at room temperature for a specified time as given in Table1.The mixture was then extracted with ethyl acetate (20mLx2) and the combined organic layer was dried over anhydrous $MgSO_4$. After filtration and evaporation of the solvent, the residue was purified by column chromatography over silica gel to give the pure product. The corresponding product was identified by^{1}HNMR,^{13}CNMR, FTIR and GCMS.

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