Bismuth(III) Chloride–Aluminium-promoted Allylation of Aldehydes to Homoallylic Alcohols in Aqueous Solvent

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In the presence of bismuth(III) chloride–metallic aluminium, allylic halides have been found to react with aldehydes at room temperature in tetrahydrofuran–water to afford the corresponding homoallylic alcohols in high yields.

The addition of allylic organometallics to carbonyl compounds is an important synthetic reaction, and numerous methods utilizing organometallics derived from a number of metallic elements have been developed.[1] Recently, we discovered the first example of chemoselective metallic bismuth and bismuth(III) chloride ($BiCl_3$)–metallic zinc- or –metallic iron-mediated allylation of aldehydes with allylic halides to homoallylic alcohols in *N*,*N*-dimethylformamide and tetrahydrofuran (THF).[2] In the $BiCl_3$-mediated allylation, the desired homoallylic alcohol was not obtained at all in THF when metallic aluminium was used. We found, however, that a Barbier-type allylation of aldehydes with allylic halides could be easily effected in THF–H_2O using $BiCl_3$–metallic aluminium[3,4] although organometallic compounds usually have to be prepared and treated in anhydrous solvents owing to rapid protonolysis. The overall reaction is shown in Scheme 1.

Table 1. Synthesis of homoallylic alcohols (3) with $BiCl_3$–Al.[a]

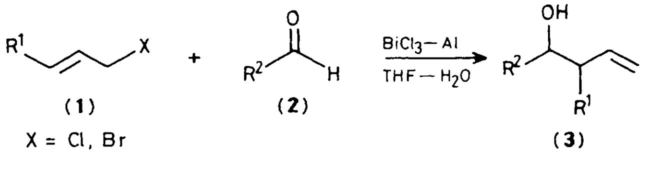
	Allylic halide (1)	Aldehyde (2)	% Yield of (3)
1	CH_2=$CHCH_2Br$	PhCHO	96
2	,,	p-ClC_6H_4CHO	83
3	,,	p-$MeOC_6H_4CHO$	68
4	,,	$Ph[CH_2]_2CHO$	91
5	,,	$Me[CH_2]_7CHO$	70
6	,,	MeCH=CHCHO	82
7	CH_2=$CHCH_2Cl$	PhCHO	30
8	MeCH=$CHCH_2Br$	PhCHO	87 (84 : 16)[b]

[a] All the products gave satisfactory i.r. and ^1H n.m.r. spectra. [b] The ratio of *erythro* : *threo* was determined by ^1H n.m.r. spectroscopy (ref. 2b).

A typical experimental procedure is as follows. Into a mixture of commercial grade Al powder (4.8 mmol) and $BiCl_3$ (2.4 mmol) was added THF (2.5 ml) and H_2O (1 ml) (this reaction is exothermic). Then, a mixture of an aldehyde (**2**) (2.0 mmol) and an allylic halide (**1**) (2.4 mmol) was added, and the reaction mixture was stirred at room temperature for 10—20 h. Workup and purification by flash column chromatography or thin-layer chromatography gave the corresponding homoallylic alcohol. Typical results are summarized in Table 1.

Allyl bromide gave the expected adduct (**3**) in good yield unlike its chloride. When an α,β-unsaturated aldehyde was used, the 1,2-addition product was obtained selectively (run 6). Both aromatic and aliphatic aldehydes reacted smoothly to afford (**3**) in good yields. The reaction of benzaldehyde with but-2-enyl bromide gave predominant *erythro* selectivity (run 8). This shows essential γ-addition of the bismuth reagent.

The use of $BiCl_3$ is essential in this reaction, *viz.*, hardly any expected product was obtained using a Bi–Al system in THF–H_2O.† $BiCl_3$ did not promote the allylation at all in the



Scheme 1. R^1 = H, Me; R^2 = Ph, p-ClC_6H_4, p-$MeOC_6H_4$, $Ph[CH_2]_2$, $Me[CH_2]_7$, MeCH=CH.

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† Addition of a catalytic amount of hydrobromic acid into the medium gave (**3**) (R^1 = H, R^2 = $PhCH_2CH_2$) in 90% yield after stirring for 2 h at room temperature. The reaction was very slow in the absence of Al.

absence of Al, and the action of Al alone gave none of the desired products. Although details of the intermediate species of this reaction are not yet known, we assume that an allylbismuth reagent is formed through the oxidative addition of an allylic halide to Bi generated by the reduction of $BiCl_3$ with Al.

Finally, it is noteworthy that only a catalytic amount of $BiCl_3$ was needed to effect the present reaction.‡

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‡ The benzaldehyde (2.0 mmol)–allyl bromide (2.4 mmol) reaction using $BiCl_3$ (0.24 mmol) and Al (3.0 mmol) gave 82% yield of (**3**) after stirring for 50 h.

References

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