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Carbon–carbon bond formation using bismuth in a water medium

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Abstract—In the presence of bismuth and ammonium chloride, allyl halides were found to react with aldehydes in a water medium at room temperature to give the corresponding homoallylic alcohols.

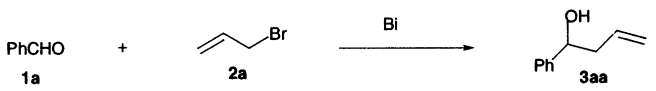
Among group VB elements, bismuth is excepted to be useful for organic synthesis in view of its enhanced metallic character. Wada et al. have reported metallic bismuth-mediated allylation of aldehydes in DMF to give homoallylic alcohols.[1] It has been reported that the synthesis of homoallylic alcohols by the Luche reaction[2] using Zn in DMF[3] or water[4] at room temperature proceeded efficiently. Recently, organic reactions in aqueous media, particularly in water, have received much attention because water is economical and environmentally benign.[5] We report the allylation of aldehydes (**1**) with allyl halides (**2**) using bismuth in a water medium at room temperature to afford the corresponding homoallylic alcohols (**3**) in good yields.

The results of allylation of benzaldehyde (**1a**) with allyl bromide (**2a**) using bismuth for 8 h at room temperature are shown in Table 1. Allylation of **1a** with **2a** using bismuth in the presence of ammonium chloride in a water medium gave 98% yield of **3aa**.[6] Allylation of **1a** with **2a** using Zn in the presence of saturated aqueous ammonium chloride for 0.75 h at room temperature was reported to give 61% yield.[2] Allylation of **1a** with **2a** using bismuth in a water medium gave good yield in comparison to allylation of **1a** with **2a** using Zn in a water medium. Allylation of **1a** with **2a** using bismuth in the absence of a solvent gave low yield. Allylation of **1a** with **2a** using bismuth in THF did not occur and **1a** was recovered.

The results of allylation of aromatic aldehydes (**1a**–**o**) with allyl bromide (**2a**) using bismuth in a water medium at room temperature are shown in Table 2. Allylation of methyl substituted benzaldehydes (**1b**–**d**) afforded good yields. Allylation of chloride substituted benzaldehydes (**1h**–**j**) did not occur and gave only the starting material. Allylation of *p*-methoxy substituted benzaldehyde (**1m**) also did not occur, giving only the starting material.

The results of allylation of aliphatic aldehydes (**1p**–**t**) with allyl bromide (**2a**) using bismuth in a water

Table 1. Allylation of benzaldehyde (**1a**) with allyl bromide (**2a**) using bismuth for 8 h at room temperature



Entry	Additive reagent	Yield (%)		
		In water	In the absence of solvent	In THF
1	NH_4Cl	98	46	0
2	$ZnCl_2$	54	36	0
3	None	65	11	0

Keywords: bismuth; allylation; benzaldehyde; allyl bromide.

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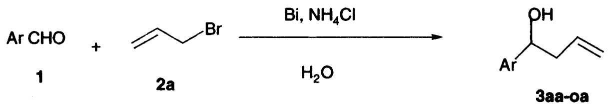
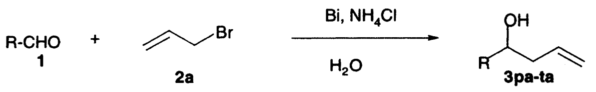
Table 2. Allylation of aromatic aldehydes with allyl bromide in water at room temperature



1	Ar	Time (h)	Yield (%)
a	C_6H_5	8	98
b	*o*-Me-C_6H_4	5	93
c	*m*-Me-C_6H_4	5	88
d	*p*-Me-C_6H_4	5	87
e	*o*-NO_2-C_6H_4	16	53
f	*m*-NO_2-C_6H_4	16	69
g	*p*-NO_2-C_6H_4	16	69
h	*o*-Cl-C_6H_4	5	–[a]
i	*m*-Cl-C_6H_4	5	–[a]
j	*p*-Cl-C_6H_4	5	–[a]
k	*o*-MeO-C_6H_4	16	80
l	*m*-MeO-C_6H_4	16	52
m	*p*-MeO-C_6H_4	40	–[a]
n	1-Naphthyl	16	47
o	2-Naphthyl	16	40

[a] Recovery.

Table 3. Allylation of aliphatic aldehydes with allyl bromide using bismuth for 16 h at room temperature



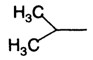
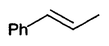
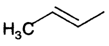
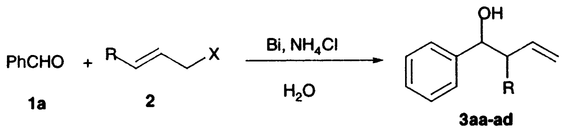
1	R	Yield (%)
p	$CH_3CH_2CH_2$-	82
q	CH_3CH_2-	23
r		74
s		60
t		46

Table 4. Allylation of benzaldehyde with allyl halides using bismuth at room temperature



	2		Time (h)	Yield (%)
	R	X		
a	H	Br	8	98
b	Ph	Br	16	–[a]
c	H	Cl	16	10
d	Ph	Cl	16	–[a]

[a] Recovery.

medium at room temperature are shown in Table 3. Allylation of aliphatic aldehydes (**1p**–**t**) with allyl bromide (**2a**) using bismuth with stirring for 16 h at room temperature gave moderate yield. Allylation of propyl aldehyde (**1p**) with **2a** using bismuth gave 82% yield.

The results of allylation of benzaldehyde (**1a**) with allyl halides (**2a**–**d**) using bismuth in a water medium at room temperature are shown in Table 4. Allylation of benzaldehyde (**1a**) with cinnamyl bromide (**2b**) using bismuth did not occur. Although allylation of **1a** with allyl chloride (**2c**) in DMF did not occur,[1] the allylation of **1a** with allyl chloride (**2c**) in a water medium gave 10% yield. The allylation of **1a** with cinnamyl chloride (**2d**) did not occur.

In conclusion, allylation of aldehydes (**1**) with allyl bromide (**2a**) using bismuth in a water medium at room temperature afforded homoallylic alcohols (**3**) in good yields.

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6. Typical procedure: A mixture of benzaldehyde (**1a**, 0.50 g, 4.71 mmol), allyl bromide (**2a**, 1.71 g, 14.1 mmol), ammonium chloride (0.25 g, 4.71 mmol), bismuth (2.5 g, 11.8 mmol), and water (20 mL) was stirred at room temperature for 8 h. The reaction product was filtered, extracted with ethyl acetate, washed with water, dried with $MgSO_4$, evaporated to give 1-phenyl-3-buten-1-ol (**3aa**, 0.68 g, 4.61 mmol, 98% yield). The purity of **3** was determined by ^1H NMR spectroscopy.