

## Barbier-type Allylation of Aldehydes Mediated by Antimony(III) Chloride–Metallic Iron or Antimony(III) Chloride–Metallic Aluminium

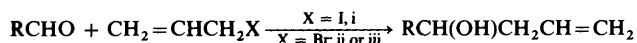
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Active zero-valent antimony generated from antimony(III) chloride–metallic iron or antimony(III) chloride–metallic aluminium, induced allylation of aldehydes with allylic halides at room temperature to give high yields of the corresponding homoallylic alcohols with high regio- and chemo- selectivity.

The allylation of aldehydes to homoallylic alcohols is of synthetic importance and a number of metals have been used to promote Barbier-type allylation of aldehydes with allyl halides.<sup>1</sup> Recently, metallic antimony<sup>2</sup> and trialkylstibine<sup>3</sup> mediated a Barbier-type reaction at 60–80 °C. We now describe the allylation of aldehydes with antimony(III) chloride–metallic iron or –metallic aluminium at room temperature.

A mixture of aldehyde (1 mmol), iron powder (3.6 mmol), antimony(III) chloride (1.5 mmol), and allyl iodide (1.2 mmol) in DMF (4 ml) was stirred at room temperature for several hours to afford the homoallylic alcohol in excellent yield (see Table 1).



*Reagents and conditions:* i, SbCl<sub>3</sub>–Fe, DMF, room temp.; ii, NaI, SbCl<sub>3</sub>–Fe, DMF, room temp.; iii, NaI, SbCl<sub>3</sub>–Al, DMF–H<sub>2</sub>O, room temp.

The less reactive allyl bromide reacted with the same aldehydes (see Table 1) to give the homoallylic alcohols (**1**) (80–98%) at 60 °C (4.5–7 h). However, addition of sodium iodide allowed the reaction temperature to be reduced to ambient. Metallic aluminium when it replaced metallic iron was also effective in a DMF–H<sub>2</sub>O (3:1) medium (see Table 2).

A variety of aldehydes reacted smoothly to give the homoallylic alcohols in good yields.  $\alpha,\beta$ -Unsaturated aldehydes afford only 1,2-addition products (runs 13, 14). Aldehydes containing an hydroxy group gave products containing the OH group unattacked (runs 7–10). Since any acetophenone present in benzaldehyde was recovered, the reaction is chemoselective.

The reaction of crotyl bromide with *p*-chlorobenzaldehyde under similar reaction conditions provided the homoallylic alcohols with the *erythro* isomer predominating.<sup>4</sup>

The reaction mechanism is not yet clear. We assume that some allylantimony reagent is formed through the oxidative addition of an allyl halide to zero-valent antimony generated *in situ* by reduction of antimony(III) chloride with metallic iron or

**Table 1.** SbCl<sub>3</sub>–Fe mediated allylation of aldehydes (RCHO) with allyl iodide (25 °C).

R	Reaction time (hrs)	Isolated yields (%)
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	10	95
C <sub>6</sub> H <sub>5</sub>	20	98
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	34	90
<i>p</i> -HOC <sub>6</sub> H <sub>4</sub>	12	80
<i>o</i> -HOC <sub>6</sub> H <sub>4</sub>	24	99
Me(CH <sub>2</sub> ) <sub>5</sub>	24	79

All the products gave satisfactory <sup>1</sup>H NMR and MS spectra. See text for conditions.

**Table 2.** SbCl<sub>3</sub>–Fe or Al mediated allylation of aldehydes (RCHO) with allyl bromide in the presence of NaI (25 °C).

Run	R	Metal	Reaction time (h)	Isolated yields (%)
1	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Fe <sup>a</sup>	18	89
2		Al <sup>b</sup>	24	99
3	Ph	Fe	18	99
4		Al	12	98
5	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	Fe	34	98
6		Al	24	86
7	<i>p</i> -HOC <sub>6</sub> H <sub>4</sub>	Fe	22	61
8		Al	24	97
9	<i>o</i> -HOC <sub>6</sub> H <sub>4</sub>	Fe	13	98
10		Al	12	67
11	Me(CH <sub>2</sub> ) <sub>5</sub>	Fe	24	89
12		Al	24	63
13	Ph(CH=CH)	Fe	20	95
14		Al	24	98

<sup>a</sup> RCHO:CH<sub>2</sub>=CHCH<sub>2</sub>Br:SbCl<sub>3</sub>:Fe:NaI = 1:1.2:1.5:3:1.2 (mmol) (4 ml DMF). <sup>b</sup> RCHO:CH<sub>2</sub>=CHCH<sub>2</sub>Br:SbCl<sub>3</sub>:Al:NaI = 1:1.2:1.5:2:1.2 (mmol) (3 ml DMF, 1 ml H<sub>2</sub>O).

aluminium. The erythro selectivity seems to proceed *via* a non-cyclic transition state.<sup>5</sup>

### Experimental

A typical procedure is as follows. *p*-Chlorobenzaldehyde (1.0 mmol, 104 mg), sodium iodide (1.2 mmol, 180 mg), antimony(III) chloride (1.5 mmol, 342 mg), metallic aluminium (2.0 mmol, 54 mg), allyl bromide (1.2 mmol, 0.12 ml), DMF (3 ml), and water (1 ml) were mixed under nitrogen and stirred at room temperature. After the reaction was complete (monitored by TLC), ether was added and the reaction mixture was filtered through a little silica gel. The filtrate was washed with water, dried (MgSO<sub>4</sub>), and evaporated under reduced pressure. 1-(*p*-Chlorophenyl)but-3-en-1-ol was isolated by preparative TLC (silica gel) and its identity confirmed by <sup>1</sup>H NMR, IR, and MS spectroscopy.

### Acknowledgements

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