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BARBIER-TYPE ALLYLATION OF ALDEHYDES WITH ACTIVE METALLIC ANTIMONY

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Abstract: Highly reactive antimony, prepared by the $NaBH_4$ reduction of $SbCl_3$, induced allylation of aldehydes with allylic bromide in DMF/H_2O solvent to give good yields of the corresponding homoallylic alcohols with high regio- and chemo- selectivity.

The allylation of aldehydes with allylic halides was a useful method to prepare homoallylic alcohols and a number of metals have been reported.[1] The metallic antimony has also been studied.[2] But in the most cases, the reactions were carried on nonaqueous condition. So, it is necessary to study more common condition. The interest in carrying out the reaction in aqueous media increased,[3] because organometallic compounds usually have to be prepared and treated in anhydrous solvents owing to rapid protonolysis. Recently, we succeeded in allylation of aldehydes with $BiCl_3/NaBH_4$ in THF/H_2O.[4] Now,We describe the reaction with $SbCl_3/NaBH_4$ in DMF/H_2O. (**Scheme 1**)

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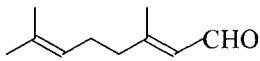
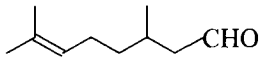
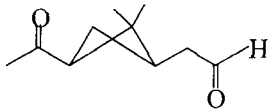
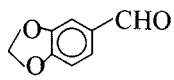
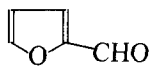
1 **2**

Scheme 1

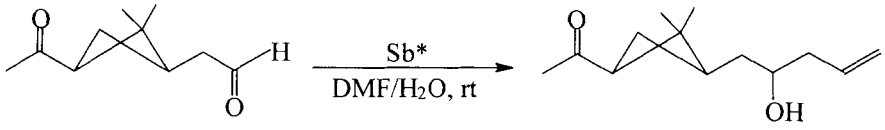
Stirring a mixture of allyl bromide (3 mmol), *p*-chlorobenzaldehyde (2.0 mmol), and active metallic antimony (3 mmol) (*in situ* prepared from $NaBH_4$ and $SbCl_3$ in water) in DMF/H_2O (4:1, 6 ml) for 5h under nitrogen gave 1-(4-chlorophenyl)-3-buten-1-ol in 95.9% yield. The nitrogen was necessary, in the absence of nitrogen, *p*-Chlorophenylaldehyde should be stirred 21h to work up, same phenomenon appeared in benzaldehyde, it didn't react in 24h in absence of nitrogen. **Table 1** summarized the results for aromatic and aliphatic aldehydes. α,β-Unsaturated aldehydes (Entry i, j) afforded 1,2-addition products selectively. The allylation of aromatic aldehydes obtained higher yields than aliphatic aldehydes. For aromatic aldehydes, the allylation afforded the corresponding homoallylic alcohol in good to excellent yields either the presence of electron-withdrawing (Entry a, b, g) or electron-donating (Entry d-f, h, o) substituent. But there are two exceptions. The one was *p*-nitrobenzaldehyde (Entry a), which was all consumed in reaction condition, but the yield (59.6%) of corresponding homoallylic alcohol was low because of the side reaction. The other was *p*-hydroxybenzaldehyde (Entry h), only 66.5% yield was obtained and 24.7% starting material was recovered.

Table 1 The allylation of aldehydes with allylic bromide to homoallylic alcohol

Entry	substrates[a]	reaction time (h)	yield (%)[b]
a	*p*-NO_2PhCHO	4	59.6
b	*p*-ClPhCHO	5	95.9
c	PhCHO	6	91.2
d	*p*-CH_3PhCHO	8.5	97.2
e	*p*-CH_3OPhCHO	5	94.7
f	*o*-HOPhCHO	12	97.6
g	*m*-HOPhCHO	5	79.3
h	*p*-HOPhCHO	16	66.5 [c]
i	PhCH=CHCHO	12	96.3
j	CH_3CH=CHCHO	24	49.1
k	$CH_3(CH_2)_3$CHO	24	75.9
l		10	43.8
m		24	51.0
n		6	66.7
o		9	91.7
p		5	87.0

a. All substrates were carried out on a 2mmol scale, and the molar ratio of aldehyde/antimony chloride/allylic bromide was always 1.0/1.5/1.5.
b. The yield referred to isolated product. All physical data including IR & NMR spectra were consistent with the literature data.
c. 27.4% Starting material was recovered.

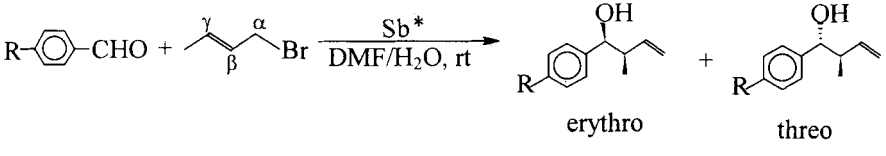
The present allylation induced by antimony is chemoselective, thus aldehydes are much more reactive than ketones so that allyl unit can be selectively introduced at the aldehyde carbon of keto-aldehyde **1n** to give one product **2n**. (**Scheme 2**)



1n **2n**

Scheme 2

The reaction is also highly regio-specific and good stereoselectivity, when *p*-chlorobenzaldehyde and benzaldehyde react with crotyl bromide, both give γ-additional products merely, the product was a mixture of *erythro* and *threo* with predominant *erythro* selectivity. (**Scheme 3**)



erythro threo

3b (R=Cl)	71	:	29
3c (R=H)	71	:	29

Scheme 3

General procedure

In a typical procedure, to a suspension of $SbCl_3$ (3 mmol) in water (10 ml) was

added $NaBH_4$ (9 mmol) in portions in water bath under nitrogen, after the addition completed, the mixture stirred continuously for 5min. Then most of water was decanted out, *p*-chlorobenzaldehyde (2 mmol), allylic bromide (3 mmol) and DMF/H_2O (4:1, 6 ml) was added. The mixture was stirred at room temperature, the progress of the reaction was monitored by TLC. After 5h, the mixture was filtered to remove the antimony and water (20 ml) was added to the filtrate. It was extracted with ether (4 × 20 ml). The extracts were washed with water, dried over anhydrous sodium sulphate. After the solvent was evaporated under reduced pressure, the crude product was purified with flash column chromatography to afforded 1-(4-chlorophenyl)-buten-1-ol in 95.9% yield exclusively.

2n[4] IR ν_{max} (neat): 3400, 1695, 1630, 915 cm^{-1}. ^1H NMR (CCl_4): δ 0.73 (s, 3H, C<u>H</u>$_3$), 1.13-1.67 (m, 6H, C<u>H</u>$_3$, C<u>H</u>$_2$CHO<u>H</u>), 1.70-2.40 (m, 8H, C<u>H</u>$_3$CO, C<u>H</u>$_2$CH=CH$_2$, C<u>H</u>$_2$C<u>H</u>), 2.70 (t, 1H, C<u>H</u>CO), 3.13-3.67 (m, 1H, C<u>H</u>OH), 4.70-5.23 (m, 2H, CH=C<u>H</u>$_2$), 5.33-6.00 (m, 1H, C<u>H</u>=CH$_2$) ppm.

3b[4] Yield 99.2%. IR ν_{max} (neat): 350, 1630, 910 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$): δ 0.87 (*threo*) and 0.98 (*erythro*) (d, 3H, J=6.82 and 6.85, C<u>H</u>$_3$), 1.95 (br, 1H, O<u>H</u>), 2.41-2.52 (*threo*) and 2.53-2.58 (*erythro*) (m, 1H, C<u>H</u>-CH=CH$_2$), 4.34 (*threo*) and 4.60 (*erythro*)(d, 1H, J=7.89 and 5.39, C<u>H</u>OH),

5.02-5.10 (*erythro*) and 5.16-5.23 (*threo*)(m, 2H, CH=C<u>H</u>$_2$), 5.68-5.83 (m, 1H, C<u>H</u>=CH$_2$), 7.21-7.33(m, 4H, Ar-<u>H</u>) ppm.

3c[2a] Yield 97.2%. IR ν_{max} (neat): 3350, 1630, 903 cm^{-1}. ^{1}H NMR (300mhz, $CDCl_3$): δ 0.86 (*threo*) and 1.00 (*erythro*) (d, 3H, J=6.80 and 6.77, C<u>H</u>$_3$), 2.05 (br, 1H, O<u>H</u>), 2.46-2.54 (*threo*) and 2.56-2.61 (*erythro*) (m, 1H, C<u>H</u>-CH=CH$_2$), 4.34 (*threo*) and 4.90 (*erythro*) (d, 1H, J=7.92 and 5.53, C<u>H</u>OH), 5.01-5.08 (*erythro*) and 5.15-5.23 (*threo*) (m, 2H, CH=C<u>H</u>$_2$), 5.69-5.83 (m, 1H, C<u>H</u>=CH$_2$), 7.23-7.36 (m, 5H, Ar-<u>H</u>) ppm.

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