J. Chem. Research (S), 1998, 202–203†

Cobalt(II) Chloride. Aluminium Promoted Allylation of Aldehydes with Allylic Halides†

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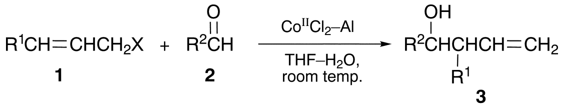
In the presence of cobalt(II) chloride–metallic aluminium, allylic halides react with aldehydes at room temperature in tetrahydrofuran–water to afford the corresponding alcohols in high yields.

The addition of allylic metal compounds to aldehydes and ketones to yield homoallylic alcohols is a useful transformation in organic synthesis and consequently has received considerable attention in recent years.[1] The reaction is synthetically analogous to the aldol condensation but allows for the subsequent introduction of a variety of alternative functional groups by manipulation of the alkene moiety.[2] Like the aldol reaction, addition can be achieved with high levels of regio- and stero-selectivity by judicious choice of substrates and reaction conditions.[3] Recently it was reported that cobalt(II) chloride[4,5] in acetonitrile efficiently catalyses the coupling of acetic anhydride with various aldehydes to the corresponding 1,2-diones and acylation of alcohols and amines with acetic anhydride. Herein we report our findings that Barbier-type allylation of aldehydes with allylic halides can be easily effected in aqueous[6] THF using $CoCl_2$–metallic aluminium.

The overall reaction is shown in Scheme 1. Allylic bromide, unlike allylic chloride, gave the expected adduct **3** in good yield. When an α,β-unsaturated aldehyde was used, the 1,2-addition product **3f** was obtained selectively. Both aromatic and aliphatic aldehydes reacted smoothly to afford **3** in good yields.



$$\underset{\mathbf{1}}{R^1CH{=}CHCH_2X} + \underset{\mathbf{2}}{R^2\overset{\overset{O}{\|}}{C}H} \xrightarrow[\text{THF–}H_2O,\ \text{room temp.}]{Co^{II}Cl_2\text{–Al}} \underset{\mathbf{3}}{R^2\overset{\overset{OH}{|}}{C}H\underset{\underset{R^1}{|}}{C}HCH{=}CH_2}$$

X = Br, Cl
R^1 = H, Me
R^2 = Ph, pClC$_6$H$_4$, pMeOC$_6$H$_4$, $C_6H_4[CH_2]_2$, Me[CH$_2$]$_7$, MeCH=CH

Scheme 1

The use of $CoCl_2$ is essential in this reaction; *viz.* hardly any expected product was obtained using a Co–Al system in THF–H_2O. $CoCl_2$ did not promote the allylation in the 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 allyl cobalt addition product is formed through the oxidative addition of an allyl halide to Co generated by the reduction of $CoCl_2$ with Al in the presence of water.

Table 1 Synthesis of homoallylic alcohols **3a**–**h** by allylation of aldehydes in THF–H_2O and $CoCl_2$–Al

				bp/°C (mmHg)	
Compound **3**	R^1	R^2	Yield (%)[a]	Found	Reported
a	H	Ph	95	105–110 (2)	71 (0.75[7])
b	H	pClC$_6$H$_4$	82	140 (2)	102–103 (0.33[7])
c	H	pMeOC$_6$H$_4$	70	125–130 (2)	85–89 (0.33[7])
d	H	$C_6H_4[CH_2]_2$	85	99–101 (2)	Oil[8]
e	H	Me[CH$_2$]$_7$	70	115 (2)	Oil[9]
f	H	MeCH=CH	80	110–111 (2)	Oil[10]
g	Me	Ph	84	95–98 (2)	118 (20[11])
h	H	Ph	30[b]	108–110 (2)	71 (0.75[7])

[a]Isolated yields of the allylation products and based on the amount of **2**. [b]When $CH_2{=}CHCH_2Cl$ is used.

Table 2 Spectral data for homoallylic alcohols **3a**–**h**

	ν_{max}/cm^{-1} (CCl$_4$)[a]			
Compound **3**	OH	C=C	δ_H[a]	m/z (M$^+$)[a]
a	3500	1640	2.15–2.45 (m,2 H), 4.7 (t, 1 H), 5.15–6.25 (m, 3 H), 7.1 (s, 5 H)	148
b	3500	1645	2.30–2.51 (m, 2 H), 4.8 (t, 1 H), 5.25–6.25 (m, 2 H), 7.15–7.35 (m, 4 H)	182, 184
c	3500	1640	2.15–2.51 (m, 2 H), 3.8 (s, 3 H), 4.75 (t, 1 H) 4.95–6.10 (m, 3 H), 7.05–7.30 (m, 4 H)	178
d	3450	1650	1.5–2.8 (m, 6 H), 3.9 (m, 1 H), 4.95–6.15 (m, 3 H), 7.15 (s, 5 H)	176
e	3400	1640	0.95 (t, 3 H), 2.15–2.75 (m, 18 H), 3.95 (m, 1 H) 5.05–5.95 (m, 3 H)	170
f	3450	1640	1.73 (d, 3 H), 2.32 (m, 2 H), 4.14 (m, 1 H), 5.15–5.93 (m, 5 H)	112
g	3500	1642	0.85 (d, 3 H), 1.75–1.95 (m, 1 H), 4.75 (d, 1 H), 5.05–6.15 (m, 3 H), 7.15 (m, 5 H)	162

[a] ^{1}H NMR and IR spectra of all compounds were in agreement with those previously reported.[9,10,12–14] IR spectra were recorded on a Perkin Elmer 237B spectrometer, ^{1}H NMR spectra were recorded in $CDCl_3$ using a Varian EM 360L NMR spectrometer with Me_4Si as internal standard and mass spectra were recorded on a Finnigan 3200 mass spectrometer.

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Experimental

Typical Experimental Procedure.—To a mixture of commercial grade aluminium powder (4.8 mmol) and $CoCl_2$ (2.4 mmol) was added THF (5 ml) and H_2O (1 ml) A mixture of aldehyde **2** (2.0 mmol) and the allylic halide **1** (2.4 mmol) was then added and the resultant mixture stirred at room temperature for 10–20 h. Progress of the reaction was monitored by TLC. The solution was then poured into water (50 mL) and extracted with dichloromethane (3 × 25 mL). The combined organic extracts were dried (anhy. Na_2SO_4) and the solvent was removed *in vacuo*. The crude product **3** was purified by Kugelrohr distillation or flash chromatography or preparative thin layer chromatography to give the corresponding homoallylic alcohol. The results are summarized in Tables 1 and 2.

Received, 1st July 1997; Accepted, 8th December 1997
Paper E/7/04607C

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