

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

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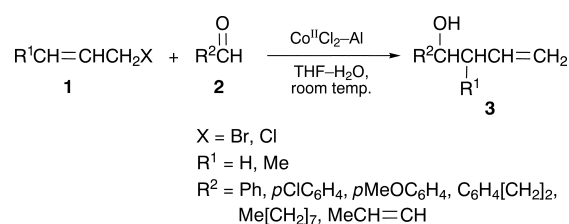
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In the presence of cobalt(II) chloride–metallic aluminium, allylic halides react with aldehydes at room temperature in tetrahydrofuran–water to afford the corresponding alcohols in high yields.

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.<sup>1</sup> 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.<sup>2</sup> Like the aldol reaction, addition can be achieved with high levels of regio- and stereo-selectivity by judicious choice of substrates and reaction conditions.<sup>3</sup> Recently it was reported that cobalt(II) chloride<sup>4,5</sup> 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<sup>6</sup> THF using CoCl<sub>2</sub>–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  $\alpha,\beta$ -unsaturated aldehyde was used, the 1,2-addition product **3f** was obtained selectively. Both



**Scheme 1**

aromatic and aliphatic aldehydes reacted smoothly to afford **3** in good yields.

The use of CoCl<sub>2</sub> is essential in this reaction; *viz.* hardly any expected product was obtained using a Co–Al system in THF–H<sub>2</sub>O. CoCl<sub>2</sub> 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

**Table 1** Synthesis of homoallylic alcohols **3a–h** by allylation of aldehydes in THF–H<sub>2</sub>O and CoCl<sub>2</sub>–Al

Compound <b>3</b>	R <sup>1</sup>	R <sup>2</sup>	Yield (%) <sup>a</sup>	bp/°C (mmHg)	
				Found	Reported
<b>a</b>	H	Ph	95	105–110 (2)	71 (0.75 <sup>7</sup> )
<b>b</b>	H	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	82	140 (2)	102–103 (0.33 <sup>7</sup> )
<b>c</b>	H	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	70	125–130 (2)	85–89 (0.33 <sup>7</sup> )
<b>d</b>	H	C <sub>6</sub> H <sub>4</sub> [CH <sub>2</sub> ] <sub>2</sub>	85	99–101 (2)	Oil <sup>8</sup>
<b>e</b>	H	Me[CH <sub>2</sub> ] <sub>7</sub>	70	115 (2)	Oil <sup>9</sup>
<b>f</b>	H	MeCH=CH	80	110–111 (2)	Oil <sup>10</sup>
<b>g</b>	Me	Ph	84	95–98 (2)	118 (20 <sup>11</sup> )
<b>h</b>	H	Ph	30 <sup>b</sup>	108–110 (2)	71 (0.75 <sup>7</sup> )

<sup>a</sup>Isolated yields of the allylation products and based on the amount of **2**. <sup>b</sup>When CH<sub>2</sub>=CHCH<sub>2</sub>Cl is used.

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

Compound <b>3</b>	$\nu_{\text{max}}/\text{cm}^{-1}$ (CCl <sub>4</sub> ) <sup>a</sup>		$\delta_{\text{H}}$ <sup>a</sup>	<i>m/z</i> (M <sup>+</sup> ) <sup>a</sup>
	OH	C=C		
<b>a</b>	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>b</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
<b>c</b>	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
<b>d</b>	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
<b>e</b>	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
<b>f</b>	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
<b>g</b>	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

<sup>a</sup><sup>1</sup>H NMR and IR spectra of all compounds were in agreement with those previously reported.<sup>9,10,12–14</sup> IR spectra were recorded on a Perkin Elmer 237B spectrometer, <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> using a Varian EM 360L NMR spectrometer with Me<sub>4</sub>Si as internal standard and mass spectra were recorded on a Finnigan 3200 mass spectrometer.

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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<sub>2</sub> with Al in the presence of water.

## Experimental

*Typical Experimental Procedure.*—To a mixture of commercial grade aluminium powder (4.8 mmol) and  $\text{CoCl}_2$  (2.4 mmol) was added THF (5 ml) and  $\text{H}_2\text{O}$  (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 ( $3 \times 25$  mL). The combined organic extracts were dried (anhydrous  $\text{Na}_2\text{SO}_4$ ) 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.

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## References

- 1 Y. Yamamoto and N. Asao, *Chem. Rev.*, 1993, **93**, 2207; T. M. Cokley, R. L. Marshall, A. McCluskey and D. J. Young, *Tetrahedron Lett.*, 1996, **37**, 1905; A. Yanagisawa, H. Nakashima, A. Ishiba and H. Yamamoto, *J. Am. Chem. Soc.*, 1996, **118**, 4722; K. Sugimoto, S. Aoyagi and C. Kibayashi, *J. Org. Chem.*, 1997, **62**, 2322.
- 2 J. A. Marshall and K. W. Hinkle, *J. Org. Chem.*, 1996, **61**, 4247.
- 3 J. S. Carey, T. S. Coutler, D. J. Hallet, R. J. Maguire, A. H. McNeil, S. J. Stanway, A. Teerawutgulrag and E. J. Thomas, *Pure Appl. Chem.*, 1996, **68**, 707.
- 4 S. Ahmad and J. Iqbal, *J. Chem. Soc., Chem. Commun.*, 1987, 692.
- 5 For other catalytic reactions of cobalt(II) chloride see: J. Marquet and M. Moreno-Manas, *Chem. Lett.*, 1981, 173; H. Matsuda and H. Kanai, *Chem. Lett.*, 1981, 395; J. Iqbal, B. Bhatia and N. K. Nayyar, *Chem. Rev.*, 1994 **94**, 519; M. Mukhopadhyay and J. Iqbal, *J. Org. Chem.*, 1997, **62**, 1843.
- 6 Other similar allylation of carbonyl compounds in aqueous media has been reported to be a Borbier-type reaction: J. Nokami, I. Otera, T. Sudo and R. Okawara, *Organometallics*, 1983, **2**, 191; C. Petrier, J. Eihorn and J. L. Luche, *Tetrahedron Lett.*, 1985, **26**, 1449; C. Petrer and J. L. Luche, *J. Org. Chem.*, 1985, **50**, 910; K. Uneyama, N. Karmaki, A. Moriya and S. Torri, *J. Org. Chem.*, 1985, **50**, 5396; K. Uneyama, H. Nambu and S. Torri, *Tetrahedron Lett.*, 1986, **27**, 2395; A. Yanagisawa, H. Inoue, M. Morodome and H. Yamamoto, *J. Am. Chem. Soc.*, 1993, **115**, 10 356; A. Lubineau, J. Auge and Y. Queneau, *Synthesis*, 1994, 741; M. B. Isaac and T. H. Chan, *Tetrahedron Lett.*, 1995, **36**, 8957.
- 7 G. L. Smith and K. J. Voorhees, *J. Org. Chem.*, 1970, **35**, 2182.
- 8 M. F. Lipton and R. H. Shapiro, *J. Org. Chem.*, 1978, **43**, 1409.
- 9 Y. Kanagawa, Y. Nishiyama and Y. Ishii, *J. Org. Chem.*, 1992, **57**, 6988.
- 10 S. R. Wilson and M. E. Guazzar, *J. Org. Chem.*, 1989, **54**, 3087.
- 11 D. Abenhaim, E. Henry Basch and P. Freon, *Bull. Soc. Chim. Fr.*, 1969, **11**, 4038.
- 12 T. Mandai, J. Nokami, Y. Yano, Y. Yoshinaga and J. Otera, *J. Org. Chem.*, 1984, **49**, 172.
- 13 K. Sugimoto, S. Ayoyagi and C. Kibayashi, *J. Org. Chem.*, 1997, **62**, 2322.
- 14 M. Wada, H. Ohki and K. Y. Akiba, *Tetrahedron Lett.*, 1986, **27**, 4771.