

Ni/Cr/Al Multi-Metal Redox-Mediated Alkenylation of Aldehydes

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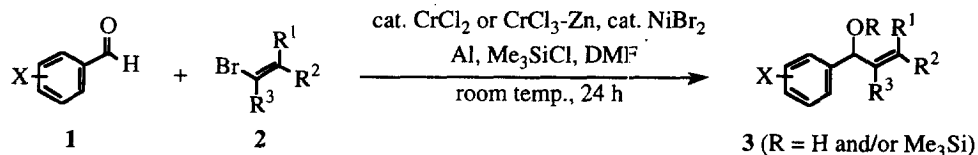
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Abstract: Alkenylation of aldehydes mediated by a catalytic amount of Cr(II)/Ni(0), using aluminium as an electron source, was performed to afford the corresponding allyl alcohol derivatives in good to moderate yields. © 1999 Elsevier Science Ltd. All rights reserved.

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Organometallic reagents are well recognized to show a variety of characteristic reactivity.¹ Furthermore, combinational use of these reagents is expected to promote unique reactions. The chemical behavior of the multi-metal system is highly dependent on the nature of each of the metals, and proper choice of the metals achieves various reductive chemical transformations.² A combination of reducing metal reagents and high-valent transition metal reagents provides a very active, low-valent transition metal species. Among them, combinations of aluminium and a catalytic amount of metal salt have been attracting much attention³ because aluminium is 1) a potent reductant, 2) cheap, and 3) easy to handle, and could be used successfully in construction of cephem derivatives.⁴ Aluminium acts as an electron pool (source) and the metal salts play the role of electron transfer catalyst. Aluminium alone, however, has been scarcely used in organic synthesis owing to its poor electron transfer ability to organic substrates.

The Cr-Ni promoted alkenylation of carbonyl compounds (Nozaki-Hiyama-Kishi reaction) proceeds in a highly chemoselective manner under very mild conditions,⁵ and has been used in the synthesis of complex natural products.⁶ The drawback of this system, however, is that large excess (400 mol%) of CrCl₂ is usually needed, which may cause serious environmental problems. In the reaction, two molar amounts of Cr(II) would be consumed for the reduction of Ni(II) to give Ni(0), liberating Cr(III). To minimize the amount of Cr reagents is a subject of keen study, and re-generation of Cr(II) by the reduction of Cr(III) with Mn^{7a} and electroreduction^{7b} was recently reported. We report herein that the alkenylation of aldehydes with alkenyl halides could be performed by using Al and catalytic amounts of CrCl₂ and NiBr₂, wherein Al acts as an electron source and CrCl₂ and NiBr₂ work as the electron-transfer catalyst (Scheme 1).



A typical procedure is as follows: A mixture of *p*-anisaldehyde **1a** (1.5 mmol), vinyl bromide **2** (3.0 mmol), CrCl₂ (Aldrich, light-green powder, 0.3 mmol, 20 mol%), NiBr₂ (Katayama Chemical Co., 0.03 mmol, 2 mol%), Me₃SiCl (0.57 mL), and freshly cut Al foil (Sun Aluminium Co. Ltd., Wiped with dil. aq. HCl and acetone, 3.4 mmol) in dry DMF (7 mL) was stirred under Ar atmosphere at room temperature for 24 h. After usual work-up, allyl alcohol and its trimethylsilyl ether **3a** (R = H and/or SiMe₃) were obtained in 50% and 33% yield, respectively (Table 1, Entry 1).⁸

Table 1. Vinylation of *p*-Anisaldehyde with Al/Cr/Ni System

$\text{CrCl}_2 \text{ or } \text{CrCl}_3\text{-Zn, NiBr}_2$
 $\text{Al or Zn (3.4 mmol), Me}_3\text{SiCl}$
 DMF (10 mL)
 room temp., 24 h

Entry	CrCl ₂ /mmol	CrCl ₃ /mmol	NiBr ₂ /mmol	Zn /mmol	Me ₃ SiCl /mL	Yield ^a /%
1	0.3	0	0.03	0	0.75	83
2	0.3	0	0.03	0	0.28	30
3	0.09	0	0.03	0	0.75	13
4	0.3	0	0.03	0	0	0
5	0.3	0	0	0	0.75	0
6	0	0	0.03	0	0.75	0
7	0	0.3	0.03	0	0.75	0
8	0	0.3	0.03	0.3	0.75	67
9 ^b	0.3	0	0.07	3.4	0.75	0 (87) ^c
10 ^b	0	0.3	0.07	3.5	0.75	0 (55) ^c

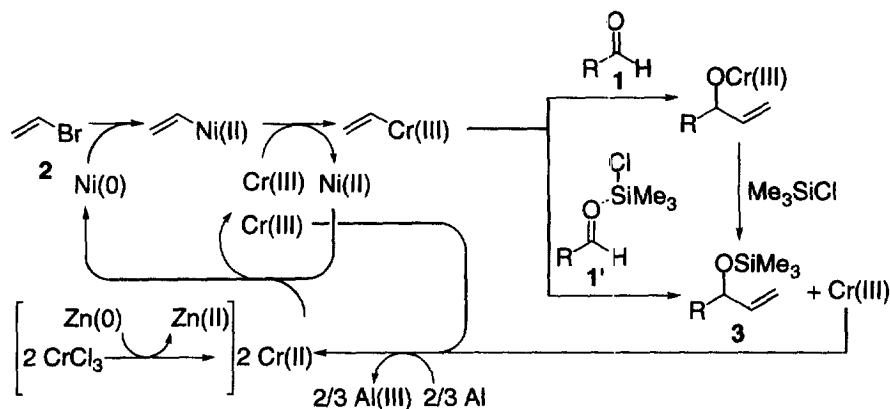
^aIsolated yield. ^bNo Al was used. ^cTotal yield of 1,2-bis(4-methoxyphenyl)ethane-1,2-diol and its trimethylsilyl ether is shown in parentheses.

For this alkenylation, CrCl₂, NiBr₂, Me₃SiCl, and Al were all indispensable: No reaction occurred when any one of them was lacking (Table 1, Entries 4, 5, and 6). When 1.5 eq. of Me₃SiCl was used, the yield of **3** reduced to 30% (Entry 2). Therefore, Me₃SiCl seems to react with Cr(III) alkoxide to release Cr(III) halide as well as with Al to activate by etching of its surface. Reduction of the amount of CrCl₂ to 0.09 mmol (6 mol%) decreased the yield of **3a** (13%, Entry 3).⁹

Since CrCl₂ is highly sensitive to moisture and O₂, the rather stable CrCl₃ may be a more suitable Cr source. This catalytic alkenylation was, however, not promoted with a commercially available anhydrous CrCl₃ (Katayama Chemicals Co. Ltd., 0.3 mmol) instead of CrCl₂ (Entry 7). It is noteworthy that the CrCl₃-promoted alkenylation could be achieved by addition of a catalytic Zn metal (powder, Wako Pure Chemicals, 0.3 mmol) to afford the desired allyl alcohol derivatives **3a** in 67% yield (Entry 8).¹⁰ No allyl alcohol derivatives **3a** but 1,2-bis(4-methoxyphenyl)ethane-1,2-diol and its trimethylsilyl ether were obtained (55 ~ 87%) when Zn was used instead of Al (Entries 9 and 10). Though the mechanism is unclear at present, two important features are noted: 1) Zn can reduce commercially available CrCl₃ to produce the corresponding lower-valent metal species, which starts the catalytic cycle. 2) Electron transfer from Al to these transition metal salts seems not effective, while Al would reduce *in situ* generated Cr(III) (Scheme 1). Silyl ether **3a** may

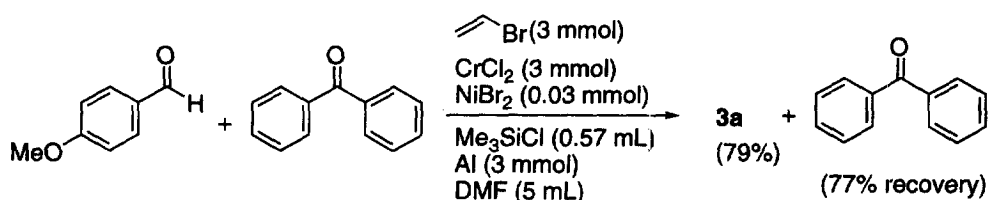
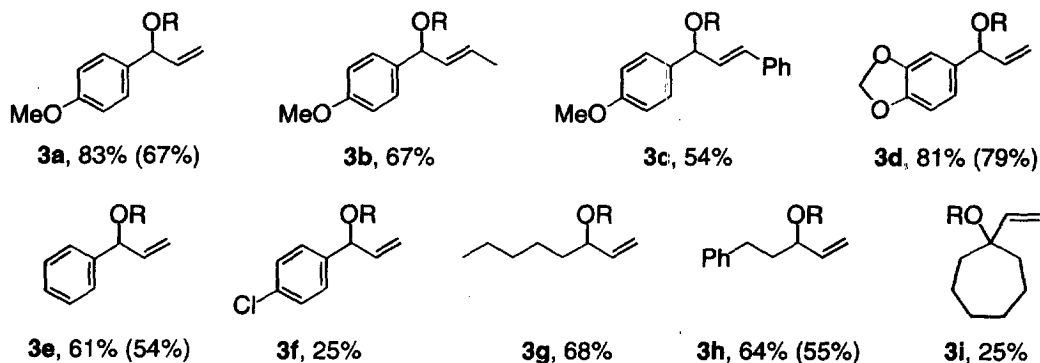
be generated from metal exchange of the chromium alkoxide intermediate with chlorotrimethylsilane to generate chromium(III) halides and/or directly from silyl-coordinated activated aldehyde (**1'** in Scheme 1).

Scheme 1. A Plausible Mechanism of Alkenylation Promoted with Al/Cr/Ni.



Representative results of alkenylation of aldehydes **1** in the Al/CrCl₂/NiBr₂/Me₃SiCl/DMF system are shown below, wherein the yields in the Al/CrCl₃-Zn/NiBr₂/Me₃SiCl/DMF system¹⁰ are given in parentheses. The alkenylation proceeded with both aromatic and aliphatic aldehydes. Aromatic aldehydes bearing electron-donating substituents gave allyl alcohol derivatives (**3a** ~ **3d**) in good yields, whereas electron-poor aromatic aldehydes gave poor results (**3f**), affording the corresponding pinacol derivatives predominantly. A similar alkenylation of ketones also proceeded to give the corresponding allyl alcohol derivatives but in rather low yield (**3i**). Notably, the alkenylation of a 1:1 mixture of *p*-anisaldehyde and benzophenone gave only **3a** in 79% yield, and no alkenylation product of benzophenone was obtained at all.

Products of Alkenylation of Aldehydes in Al/CrCl₂ (or CrCl₃-Zn)/NiBr₂/Me₃SiCl/DMF System



In conclusion, the Al/Cr/Ni system promotes alkenylation of aldehydes effectively. Studies on the mechanism and further synthetic applications are now progressing in our laboratories.

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- A part of the silyl ether was hydrolyzed to afford the corresponding alcohol during purification by silica-gel column chromatography.
- In larger reaction scale (10 mmol of **1**), however, less amount of CrCl₂ and NiBr₂ (0.3 and 0.03 mmol, 3 mol% and 0.3 mol%, respectively) promoted the alkenylation reaction without significant change of the product affording **3a** in 65% yield.
- A typical procedure is as follows: A mixture of *p*-anisaldehyde **1a** (1.5 mmol), vinyl bromide **2** (3.0 mmol), CrCl₃ (Katayama Chemical Co., purple plate, 0.3 mmol), NiBr₂ (Katayama Chemical Co., 0.03 mmol), Zn powder (Wako Pure Chemicals, 0.3 mmol), Me₃SiCl (0.57 mL), and freshly cut Al foil (Sun Aluminium Co. Ltd., Wiped with dil. aq. HCl and acetone, 3.4 mmol) in dry DMF (7 mL) was stirred under Ar atmosphere at room temperature for 24 h. After usual work-up, allyl alcohol and its trimethylsilyl ether **3a** (R = H and/or SiMe₃) were obtained in 47% and 20% yield, respectively.