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B$_{12}$-Catalyzed Generation of Allylic Chromium Reagents from 1,3-Dienes, CrCl$_2$, and Water

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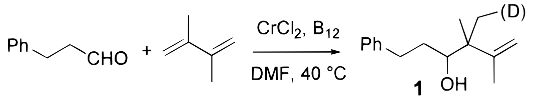
Although allylic chromium reagents are useful tools for stereoselective carbon−carbon bond formation under mild conditions, their source has been almost limited to allylic halides[1] and pseudohalides.[2] Recently, we have reported the generation of allylic chromium compounds by addition of alkyl radicals to 1,3-dienes and successive one-electron reduction with chromium(II).[3] However, the method could not provide a hydrogen radical, and thus, a simple reaction between a diene and an aldehyde was not realized. We report here a novel access to the reagents from 1,3-dienes and a chromium hydride equivalent generated from CrCl$_2$, B$_{12}$ (cyanocobalamin), and water.

Addition of a metal hydride to a 1,3-diene produces an allylic metal compound when the hydride adds to the C-1 of the diene and the metal adds to the C-2 or C-4.[4] Although there is no direct method to provide appropriate chromium hydride species,[5] cobalt hydride species react with a 1,3-diene in the desired fashion to give allylic cobalt compounds.[6,7] An organic moiety on cobalt compounds smoothly transfers to chromium by treatment with chromium(II).[8] In addition, a cobalt hydride species of B$_{12}$ can be prepared by treatment of low-valent B$_{12s}$ with water.[9−11] These observations prompted us to explore the novel preparation of allylic chromium reagents from 1,3-dienes with a cobalt catalyst.

To a mixture of CrCl$_2$ (4.0 equiv) and B$_{12}$ (0.10 equiv) in dry DMF was added a solution of 3-phenylpropanal and 2,3-dimethyl-1,3-butadiene (2.0 equiv) in DMF. The deep green color of the mixture gradually darkened with stirring.[10] Then, the mixture was heated to 40 °C, and a DMF solution of water (0.2 M, 1.0 equiv) was added over a period of 2 h. After usual workup with water, homoallylic alcohol **1** was obtained in 90% yield (eq 1).[12] The coupling reaction only proceeded with the addition of B$_{12}$.[13] For the reaction to go to completion, it is important that the reactions between organochromium reagents and carbonyl compounds are not disturbed by the presence of 1−3 equiv of a proton source.[14] However, the addition of water in one portion caused the reaction to not go to completion, suggesting that the allylic chromium species was protonated to some extent. When D$_2$O in DMF was added in one portion to the reaction mixture, deuterium was introduced at the methyl position with a content of 48%.[15]



(1)

H_2O (slow addition, 2 h)	H_2O quench	90%
H_2O (one portion)	H_2O quench	60%
D_2O (one portion)	H_2O quench	59% (D : 48%)

The results obtained with several kinds of 1,3-dienes are summarized in Table 1. The diastereoselectivity of the reaction between the crotylchromium species and nonanal was 72/28 (Table 1, entry 1), which is almost equal to the ratio observed for the reaction with crotyl bromide and CrCl$_2$ in DMF.[2a] This is explained by a fast equilibrium between (*E*)- and (*Z*)-crotylchromium in the solvent.[2c] Therefore, geometrically fixed allylic chromium compounds derived from 1,3-cyclohexadiene and 3-methylene-1-cyclohexene, respectively, produced each of the diastereomers exclusively (entries 5 and 6). A 1,3-diene having an s-trans configuration also gave the corresponding allylic chromium reagent (entry 6). The result suggests that the hydrocobaltation step proceeds in a 1,2-fashion.[6] In the case of unsymmetrical 1,3-dienes, the cobalt hydride added selectively to form more stable allylic radicals after cleavage of cobalt−carbon bonds (entries 2−8).[6] Selective formation of (*E*)-homoallylic alcohol by the reaction between 2-propenylidenecyclohexane and 3-phenylpropanal possibly stemmed from a six-membered transition state of less steric demand (entry 7). The generated allylic chromium species showed aldehyde-selective addition (entry 4) as did those obtained from allylic halides and CrCl$_2$.[2a] 2-(Benzyloxy)-1,3-butadiene can also be employed for the reaction producing stereoselectively an anti adduct (entry 8).[16]

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[6] (a) $Co(SCN)(PPh_3)_3$, H_2: Nakayama, T.; Kanai, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 16. (b) $HCo(dmgH)_2py$: Howell, A. R.; Pattenden, G. *J. Chem. Soc., Chem. Commun.* **1990**, 103. (c) $HCo(CN)_5^{3-}$: Reger, D. L.; Habib, M. M.; Fauth, D. J. *J. Org. Chem.* **1980**, *45*, 3860. Lee, J.-T.; Alper, H. *J. Org. Chem.* **1990**, *55*, 1854. (d) $Co(acac)_3$, Et_2AlCl, PPh_3: Takacs, J. M.; Mehrman, S. J. *Tetrahedron Lett.* **1996**, *37*, 2749.

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[8] (a) Espenson, J. H.; Shveima, J. S. *J. Am. Chem. Soc.* **1973**, *95*, 4468; Espenson, J. H.; Sellers, T. D., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 94. (b) Takai, K.; Nitta, K.; Fujimura, O.; Utimoto, K. *J. Org. Chem.* **1989**, *54*, 4732.

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[10] Schrauzer, G. N.; Holland, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 4060.

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[12] Under the standard reaction conditions (eq 1), compounds were recovered in the following order: 1-dodecene (90%); 1-dodecyne (92%); 1-chlorododecane (96%); nonanal diethylene acetal (94%); ethyl octanoate (93%); nonanenitrile (90%).

[13] When 2-methyl-1,3-tetradecadiene and 3-phenylpropanal were treated at 25 °C with CrCl$_2$ and water in the absence of B$_{12}$, the 1,3-diene was recovered in 95% yield after 24 h of stirring. The reaction also proceeded by the addition of cobalt phthalocyanine (2.5 mol %), although the yield of **1** was only 58%.

[14] (a) Kauffmann, T.; Abel, K.; Bonrath, W.; Kolb, M.; Möller, T.; Pahde, C.; Raedeker, S.; Robert, M.; Wensing, M.; Wichmann, B. *Tetrahedron Lett.* **1986**, *27*, 5351. Kauffmann, T. *Synthesis* **1995**, 745. (b) Kato, N.; Takeshita, H.; Kataoka, H.; Ohbuchi, S.; Tanaka, S. *J. Chem. Soc., Perkin Trans. 1* **1989**, 165.

[15] Although the reaction slowly proceeded without addition of water, it did not go to completion. Quenching the reaction mixture with D$_2$O did not give the deuterated product, probably because unremoved water in the solvent and hydroxyl group of B$_{12}$ supply protons.

[16] Takai, K.; Nitta, K.; Utimoto, K. *Tetrahedron Lett.* **1988**, *29*, 5263.

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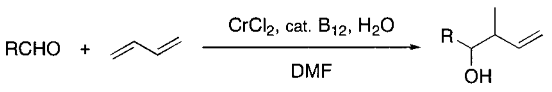
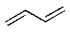
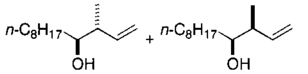
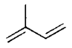
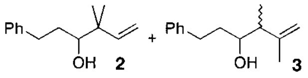
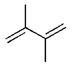
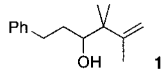
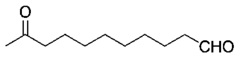
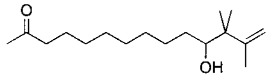
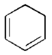
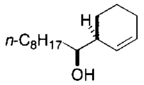
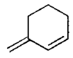
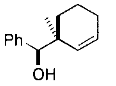
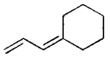
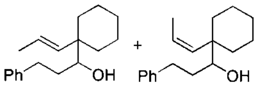
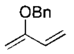
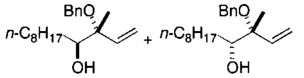
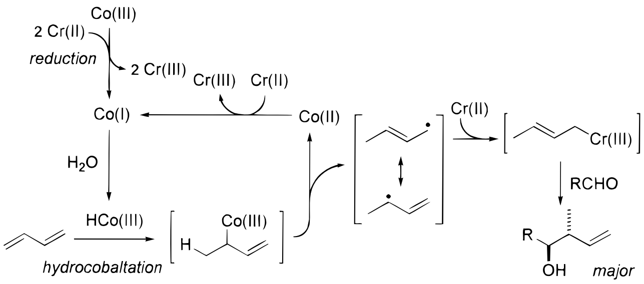
Table 1. Reactions between 1,3-Dienes and Aldehydes Mediated by $CrCl_2$, B_{12}, and Water[a]



entry	aldehyde	1,3-diene	temp, °C	time, h	product(s)	yield, %	isomeric ratio[b]
1	n-$C_8H_{17}CHO$		25	3.5		88[c]	*anti* / *syn* = 72 / 28
2	$Ph(CH_2)_2CHO$		40	1	 2, 3	94	**2** / **3** = 86 / 14 *anti*-**3** / *syn*-**3** = 64 / 36
3	$Ph(CH_2)_2CHO$		40	2	 1	90	
4			40	2		81	
5	n-$C_8H_{17}CHO$		40	2		93	*anti* / *syn* = <1 / >99
6	PhCHO		40	0.5		84	*anti* / *syn* = <1 / >99
7	$Ph(CH_2)_2CHO$		40	3		85[d]	*E* / *Z* = 95 / 5
8	n-$C_8H_{17}CHO$		40	0.5		94	*anti* / *syn* = 86 / 14

[a] The reactions were conducted on a 1.0-mmol scale. 1,3-Diene (2.0 mol), $CrCl_2$ (4.0 mol), water (1.0 mol), and B_{12} (0.10 mol) were used per mol of a carbonyl compound. [b] Diastereomeric ratios were determined by isolation and/or ^1H NMR spectroscopy. [c] An excess amount of butadiene was used. [d] 1,3-Diene (3.0 equiv), $CrCl_2$ (6.0 equiv), water (1.5 equiv), and B_{12} (0.15 equiv) were employed.

Scheme 1



We are tempted to assume the following mechanism for the reaction (Scheme 1).[17] Cobalt(I) species, B_{12s}, derived by the reduction of B_{12} with 2 equiv of chromium(II) chloride,[9] affords hydridocobalamin by reaction with water.[10] Hydrocobaltation of the cobalt hydride species to a 1,3-diene produces an allylcobalt(III) species.[7] Homolytic cleavage of allylcobalt(III) to an allyl radical followed by trapping with chromium(II) gives allylchromium(III),[6b,19] which adds to the carbonyl compounds in a selective manner.[2] Reduction of cobalt(II) with chromium(II) regenerates the cobalt(I) species.

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Supporting Information Available: General procedure and spectroscopic and analytical data of compounds in Table 1 (4 pages).

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[17] Another possible mechanism is as follows: (1) insertion of a low-valent cobalt to a carbon−hydrogen bond of an aldehyde; (2) hydroacylation;[18] (3) successive reduction of a ketone. However, when we prepared 1-deuterio-3-phenylpropanal and used it in the reaction with 2,3-dimethyl-1,3-butadiene, deuterium was found only at the carbon attached to a hydroxyl group of the adduct **1**. In addition, a ketone functionality remained untouched during the reaction (Table 1, entry 4). These results argue against the hydroacylation−reduction mechanism.

[18] Lenges, C. P.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 3165.

[19] Direct transmetalation of an allylic group from cobalt(III) with chromium(III) could not be eliminated.[8]