Review

Nucleophilic addition of organochromium reagents to carbonyl compounds

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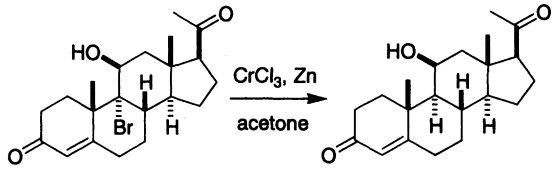
Abstract: One important theme in organic synthesis is to accomplish highly selective transformations under mild conditions, which yield only desirable products. During the past two decades, we have developed several useful tools to achieve this, i.e., organochromium reagents. This review focuses on the following themes: 1) The historical background of organochromium reagents. 2) The development of the allylic chromium reagent (Nozaki-Hiyama reaction). 3) Nickel-catalyzed addition of alkenyl-, aryl-, and alkynyl halides to aldehydes (Nozaki-Hiyama-Kishi (NHK) reaction). 4) Wittig-type olefination with geminal dichromium reagents. 5) Representative applications of organochromium reagents to the total syntheses of biologically active compounds.

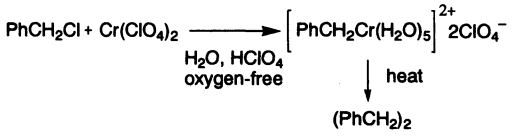
Key words: Synthetic reaction; chromium; nickel; carbonyl addition; organochromium reagent.

Introduction. The chromium(II) ion has been employed as a reducing agent for more than 50 years and can be prepared either by reduction of chromium(III) salts or by dissolving chromium metal in deoxygenated acid. The standard reduction potential (E^0/V) of chromium(III) to chromium(II) measured in water is -0.41, which is weaker than that for zinc(II) to zinc(0) (-0.76). Therefore, zinc has been employed as a reductant for chromium(III) salts under aqueous and non-aqueous conditions eq. [1].[1] The dissolution of chromium metal in an acid provides zinc-free chromium(II) ions, but is limited to aqueous conditions. Chromium(II) salts, such as chromium(II) perchlorate, chromium(II) sulfate, and chromium(II) acetate, are prepared in this way. The chromium(II) ion is then used for a reduction such as deoxygenation or dehalogenation eq. [2].[2] Reductions of reactive halides such as α-halo ketones, allylic halides, benzylic halides and polyhalides with chromium(II) ions proceed smoothly. Since the chromium(II) ion is typically prepared in water, the organochromium compounds produced are usually hydrolyzed to dehalogenated compounds.

The Pauling electronegativity of chromium is 1.6, which is larger than lithium (0.98) and magnesium (1.3). Therefore, the nucleophilicity of organochromium reagents is not as great as for the corresponding organolithium or -magnesium compounds. Organochromium compounds react smoothly with water to give corresponding protonated compounds, although the rate of protonation depends on the amount of water and the presence of a halogen ion in the coordination sphere of chromium.[3] In the absence of a chloride ion in the coordination sphere of the alkylchromium(III) species, the half-life of the carbon-chromium σ bond increases to over 1.5 days under aqueous, oxygen-free conditions.



[1]



[2]

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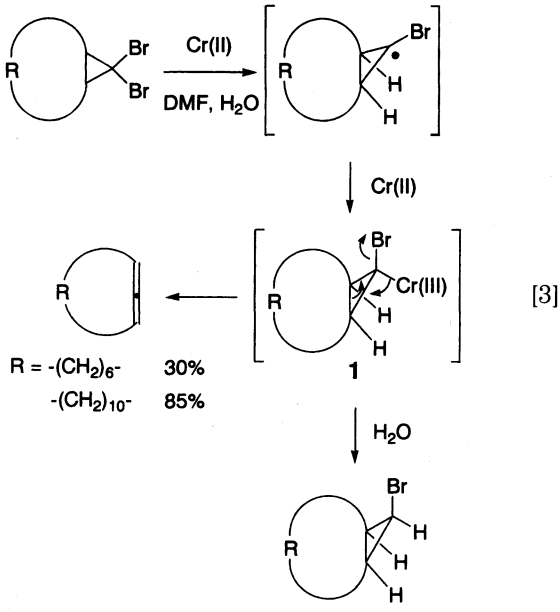
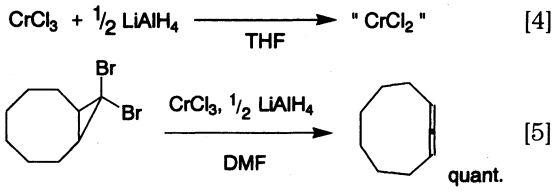
In 1967, Aratani, Noyori, and Nozaki discovered the transformation of a *gem*-dibromocyclopropane to an allene by reduction with an aqueous solution of chromium(II) sulfate eq. [3].[4] The aqueous DMF solution of chromium(II) sulfate derived by reduction of chromium(III) sulfate with zinc showed a sky-blue color, which gradually turned to dark green as the reaction progressed. At that time such transformation was known to proceed with butyllithium under aprotic conditions by Skattebøl.[5] The chromium method proved that the dehalogenation could be accomplished in protic media.



[3]

Although the 13-membered ring allene was produced in 85% yield with chromium(II) in a mixed solvent of DMF and water, the yield dropped considerably in the case of the nine-membered ring.[4] This is probably because the ring-opening rate of the cyclopropane fused to cyclooctane is slow due to the strain of the produced allene. Also, the carbon-chromium bond could not survive despite being less labile than a carbon-magnesium or lithium bond, and so most of the **1** decomposed under the protic conditions. In order to overcome this difficulty, preparation of low-valent chromium under water-free conditions was investigated.

Preparation of carbon-chromium bonds under anhydrous conditions and their carbonyl addition. A convenient preparation of chromium(II) species in aprotic solvents was first reported by Hiyama and Nozaki in 1977 by reduction of chromium(III) chloride with 0.5 molar equivalent of lithium aluminum hydride in tetrahydrofuran eq. [4].[6] The anhydrous chromium(II) species enabled organochromium compounds to be prepared in good yields by reduction of organic halides under anhydrous conditions as expected. For example, reduction of a geminal dibromocyclopropane of the eight-membered ring proceeded in a quantitative yield eq. [5].[7]

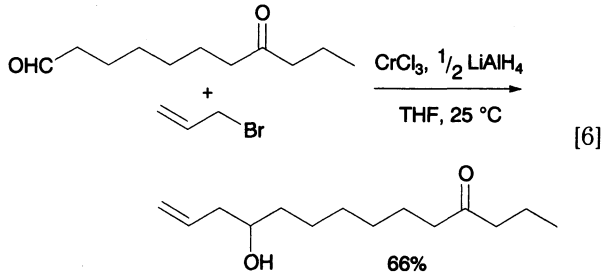


[4]

[5]

The preparation of the anhydrous chromium(II) species greatly expanded the scope of carbon-carbon bond forming reactions via organochromium reagents. Allylic and benzylic halides were reduced with chromium(II) salts in aprotic solvents to furnish allyl- and benzylchromium compounds, respectively, which could then undergo homocoupling.[7] In the presence of electrophiles like carbonyl compounds, the resultant allylic chromium species could be trapped to give homoallylic alcohols.[6]

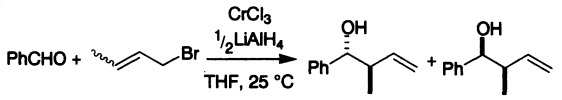
Allylic chromium reagents derived by reduction of allylic halides with the chromium(II) species, add to carbonyl compounds in a chemoselective manner, i.e., the reagents prefer the carbonyl groups of aldehydes to those of ketones or esters eq. [6]. In addition, organochromium compounds that contain keto, ester, or cyano groups can be prepared. Such selectivity of the reagents stems from the mild nucleophilicity and the steric effect of the ligands on chromium. Because of the weak basicity of organochromium compounds, epimerization of a stereocenter α of a carbonyl group is also suppressed.



[6]

Heathcock (1978) and Hiyama (1981) demonstrated that the additions of crotylchromium compounds to aldehydes mainly yield the *anti* addition products regardless of the geometry of the crotyl bro-

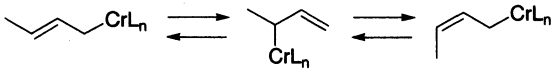
mide eq. [7].[8] These discoveries attracted the attention of more synthetic chemists, and led to the appearance of anhydrous chromium(II) chloride on the market, especially, for 1,2-diastereoselective construction of the carbon skeleton.



[7]

(*E*)-crotyl bromide 96% *anti* / *syn* = 100 / 0
(*Z*)-crotyl bromide 87% *anti* / *syn* = 100 / 0

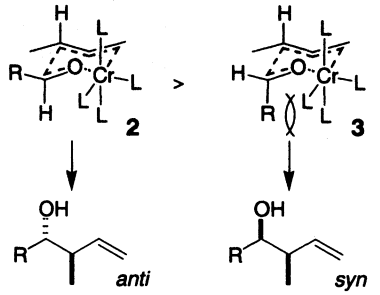
Heathcock and Hiyama's observation, regardless of the geometry of the crotyl bromide, suggests that the crotylchromium reagent prepared *in situ* equilibrates to the more stable and/or more reactive *E* isomer eq. [8].



[8]

The chromium(III) ion has moderate Lewis acidity, and a carbonyl oxygen can coordinate to this ion. This feature affects the geometry of the transition state of reactions of allylic chromium reagents and also facilitates intramolecular cyclization by bringing the organochromium group and the aldehyde carbonyl into proximity. Chromium(III) complexes prefer an octahedral configuration in which the coordination sphere is often supplemented with solvent molecules such as tetrahydrofuran.[9] Ligand displacement at the octahedral (*E*)-crotylchromium with the aldehyde generates a cyclic six-membered transition state. In the absence of any additional stabilization, a chair-like cyclic transition state is more favorable than a boat-like form. Two idealized chair-form six-membered transition states **2** and **3** for the reaction of (*E*)-crotylchromium are shown in Scheme 1.[8] The *anti* selectivity in the addition of crotylchromium reagents to aldehydes is explained by the transition state **2**, in which both the methyl group and R occupy equatorial positions. The diastereoselectivity stems from different steric interactions between R and the aldehydic hydrogen with ligands on chromium(III).

The diastereoselectivity depends on the solvent, and the reaction has lower selectivity in dimethylformamide than in tetrahydrofuran. This is probably because strong coordination of dimethylformamide to chromium(III) can interfere with the formation of a tight six-membered transition state.

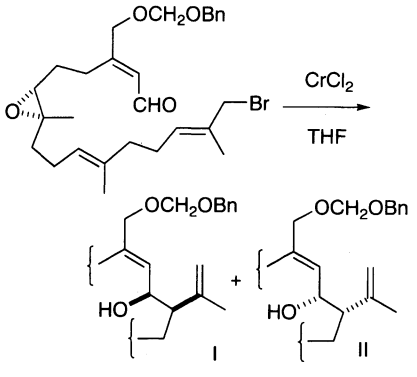


L = halogen or a solvent molecule

Scheme 1

Because chromium(II) is a weaker reducing agent than other low-valent metals such as magnesium(0) and samarium(II), carbonyl compounds including aldehydes can survive in the presence of the chromium(II) ion. Thus, the reduction can be accomplished by either (1) the addition of an electrophile to a solution of chromium(II) before adding the organic halide or (2) a Barbier-type procedure in which the chromium(II) salt is added to a mixture of electrophile and organic halide. The latter procedure is preferred for micro-scale reactions and intramolecular cyclizations.

Because the chromium-mediated coupling reaction of allylic halides and aldehydes proceeds under mild conditions with high 1,2-diastereoselectivity, it has been used to accomplish intramolecular cyclization to give medium-sized and large rings eq. [9].[10] These cyclizations proceed with high 1,2-*anti* selectivity. Macrocyclization proceeds with moderate to high stereocontrol, owing to the influence of the remote asymmetric centers on the transition state.

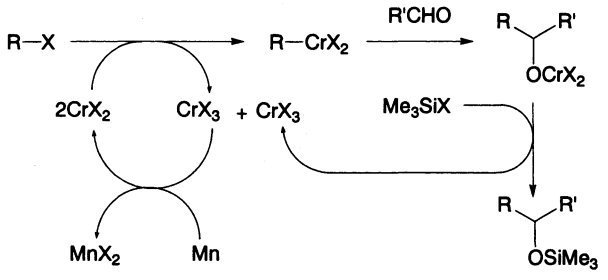


[9]

64% (I : II = 80 : 20)

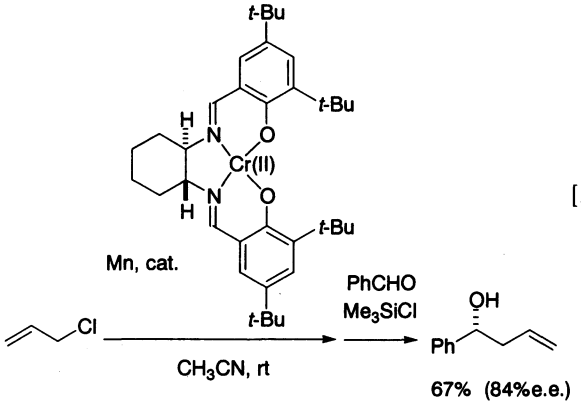
Formation of a catalytic cycle of chromium(II). Chromium(II) salt is a one-electron reductant; therefore 2 equivalents of the salt are required for the formation of organochromium reagents. From a stand-

point of ecology, it is desirable to reduce the amount of chromium salts. Moreover, chromium(II) chloride of high purity especially without contamination by nickel salt is rather expensive. Therefore, several approaches for recycling a catalytic amount of chromium(II) salts have been explored. Fürstner found that among the metals, a combination of manganese and chlorotrimethylsilane is suitable for the following reasons (Scheme 2).[11] (1) Manganese metal does not directly reduce organic halides (R-X) under the reaction conditions. (2) The chromium(III) bonded to the oxygen of the product is smoothly replaced with chlorotrimethylsilane to liberate chromium(III) salt. This combination can be applied to chromium(II)- and chromium(II)-nickel(II)-mediated reactions.



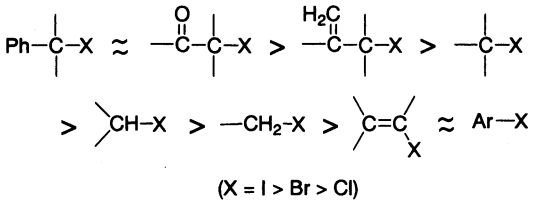
Scheme 2

Although there have been several reports of asymmetric versions of chromium(II)-mediated reactions,[12] stoichiometric use of chiral auxiliaries has prevented the development of asymmetric carbon-carbon bond formations. Achievement of a catalytic cycle of chromium enables a practical asymmetric reaction using a catalytic amount of a chiral ligand eq. [10].[13]



[10]

Preparation of alkenylchromium reagents under nickel catalysis. The rate of reduction of organic halides with chromium(II) salts depends on the nature of the organic group, the halide, and the reaction conditions (solvents, ligands, temperature). The reactivity of the various halides toward chromium(II) salts decreases in the order shown in Scheme 3.[14] Active halides, such as allyl and benzyl halides are smoothly reduced with chromium(II) salts in aprotic solvents to furnish allyl- and benzylchromium compounds, respectively, which then undergo homocoupling. The rate of reduction of alkyl iodides depends on their substitution pattern. For example, although treatment of a primary alkyl iodide with chromium(II) chloride produces the corresponding alkyl chloride as a major product, reduction of secondary or tertiary alkyl iodides leading to radical or anionic species proceeds easily under the same conditions.[15] In contrast, no reduction of alkenyl and aryl iodides takes place with chromium(II) salts in aprotic solvents. In fact, the reduction of halogens connected to sp^2 carbons proceeds under a nickel catalysis, although it was proved accidentally as explained below.

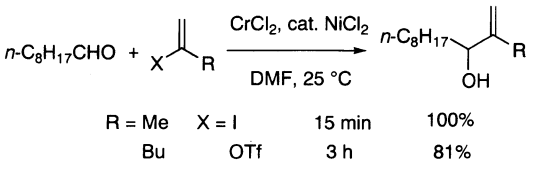


Scheme 3

Anhydrous chromium(II) chloride produced by the reduction of chromium(III) chloride with hydrogen has been commercially available since the early 1980's, but from a limited number of suppliers such as ROC/RIC. Recently, major suppliers such as Aldrich and Strem have begun commercial production of chromium(II) chloride. The chromium(II) chloride is gray, very hygroscopic, and oxidizes rapidly in air, especially under moist conditions, to give green-colored chromium(III). The chromium(II) salt is usually used without further purification. Chromium(II) chloride is only slightly soluble in anhydrous tetrahydrofuran or dioxane, and reactions performed in these solutions are usually heterogeneous. The salt, however, is soluble in dimethylformamide and dimethyl sulfoxide.

Reduction of alkenyl and aryl iodides (or bromides) to alkenyl- and arylchromium reagents with chromium(II) chloride and subsequent Grignard-type carbonyl addition was first performed without any catalyst in 1983.[16] However, the results were not consistent with the observation that alkenyl and aryl halides are dif-

ficult to reduce with chromium(II) in aprotic solvents.[14] Later, it was found that the success of the reaction depended on the source and batch of chromium(II) chloride. The reaction proceeded smoothly with a certain specimen of chromium(II) chloride purchased from ROC/RIC, but others failed to give reproducible results. Analysis of a fluorescent X-ray of the effective lots revealed that nickel was the major contaminant. Addition of a catalytic amount of nickel(II) chloride to pure chromium(II) chloride was necessary to promote the Grignard-type carbonyl addition of halo alkenes to aldehydes with good reproducibility eq. [11].[17] Kishi at Harvard University also noticed the nickel catalysis,[18] and applied the chromium(II)-nickel(II) system to a total synthesis of palytoxin.[19]

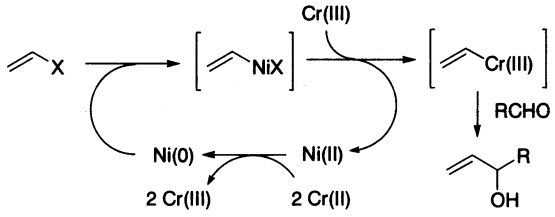


[11]

In order to perform the reaction, normally 0.1-1% w/w of nickel(II) chloride is added to chromium(II) chloride, although nickel acetylacetonate is reportedly effective in some reactions. It is important to keep the content of nickel(II) chloride low (about 0.01-1%w/w) to avoid the formation of dienes by homocoupling of the halo alkenes. Other potential catalysts, such as manganese(II) chloride, iron(III) chloride, cobalt(II) chloride, copper(I) chloride, and palladium(II) chloride are not as effective. A soluble form of chromium(II) chloride is essential to promote a smooth reaction. Little or no reaction occurs in ether or tetrahydrofuran. Iodoalkenes are more reactive than bromoalkenes, and product yields are generally better with the former. The Grignard-type reaction between alkenyl triflates (or mesylates) and aldehydes also proceeds under the same conditions.[17]

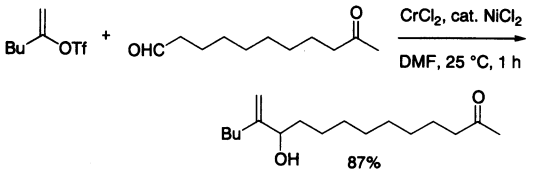
In contrast to traditional reactions with alkenyllithium, -magnesium, and -cuprate reagents, the alkenylchromium reaction is experimentally simple. The reaction can be accomplished by adding a mixture of an aldehyde and a halo alkene to a stirred mixture of chromium(II) chloride and a catalytic amount of nickel(II) chloride in dimethylformamide or dimethyl sulfoxide (or *vice versa*). Conventional organolithium or -magnesium reagents are sometimes difficult to generate from highly-oxygenated, multifunctional substrates, and the chromium protocol offers a solution to anionic coupling at the alkenyl positions of such substrates.[19]

The nickel-catalyzed Grignard-type addition of alkenylchromium reagents to aldehydes proceeds according to the mechanism shown in Scheme 4. Nickel(II) chloride is first reduced to nickel(0) with 2 equivalents of chromium(II) chloride. Oxidative addition of an alkenyl halide to the nickel(0) occurs, then the transmetalation reaction between the resulting alkenylnickel species and the chromium(III) salt affords an alkenylchromium reagent, which reacts with an aldehyde to produce the allylic alcohol.



Scheme 4

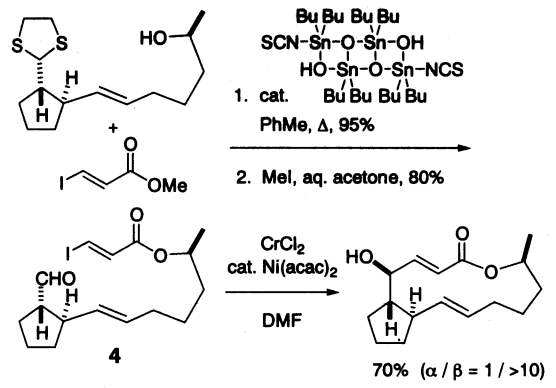
Alkenylchromium reagents add to ketones in ca. 40% yield owing to the low nucleophilicity of the reagents. Aldehyde-selective additions can be accomplished in good-to-excellent yields without affecting the coexisting ketone, ester, amide, acetal, cyano and sulfinyl groups similar to allyl- and alkynylchromium reagents eq. [12].



[12]

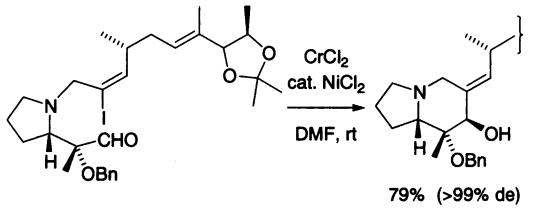
The regiochemistry of double bonds is maintained during the coupling reaction, and the stereochemistry of *trans*- and *cis*-disubstituted halo alkenes and trisubstituted *trans*-halo alkenes is also retained.[17),18]

In 1988, Schreiber employed the nickel-catalyzed chromium-mediated coupling of alkenyl iodides and aldehydes to the total synthesis of a brefeldin series eq. [13].[20] In the synthesis a new carbon-carbon bond was formed between a β-iodo-acrylate and an aldehyde group. The alkenylchromium reagent was not very basic; epimerization at the α-position of aldehydes did not normally occur. The starting ester **4** was prepared by transesterification using Otera's distanoxane catalyst which can now be purchased from Aldrich.



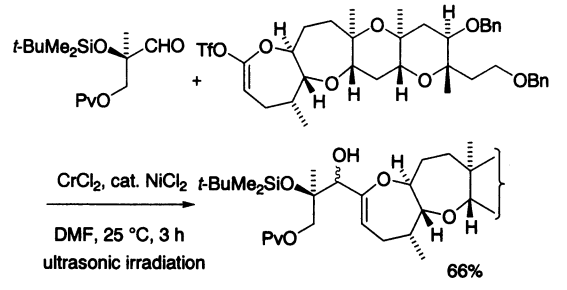
[13]

In the total synthesis of (+)-allopumiliotoxin 339A, Kibayashi obtained the cyclohexanol by an intramolecular coupling reaction eq. [14].[21] One diastereomer was obtained due to the stereochemistry at the α carbon of the aldehyde.



[14]

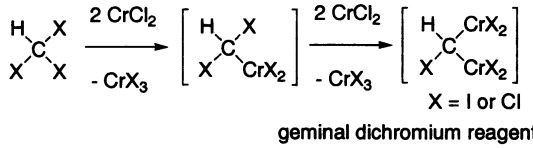
Coupling reactions between alkenyl triflates and aldehydes were employed in the total synthesis of brevetoxin B by Nicolaou eq. [15].[22] As shown, the chromium reagent could be prepared with many oxygen functional groups, although this could not be achieved with organomagnesium and -lithium reagents.



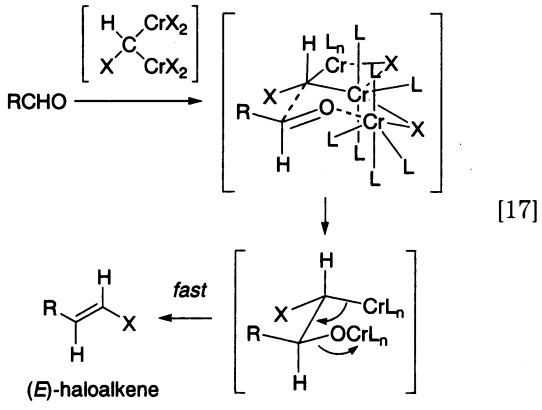
[15]

Preparation of (*E*)-iodoalkenes with organochromium reagents and its applications. There are several important coupling reactions using alkenyl halides as a key compound: Nickel-catalyzed cross coupling reactions with Grignard compounds (Kumada-Tamao-Corriu reaction),[23] and palladium-catalyzed coupling reactions with organostannane compounds (Migita-Stille reaction),[24] or organoboron compounds (Suzuki-Miyaura reaction).[25] Because these coupling reactions, especially the palladium-catalyzed reactions, proceed under mild conditions, they have also been used for intramolecular cyclization.

One stereoselective preparation of iodoalkenes under mild conditions is the haloolefination using haloform and chromium(II) chloride.[26] Chromium(II) chloride reduces two of the three halogens of haloform to form geminal dichromium reagents eq. [16]. Since chromium(II) is a one-electron reductant, four equivalents of chromium(II) are required based on the haloform.

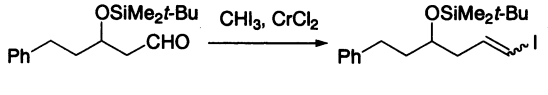


[16]



[17]

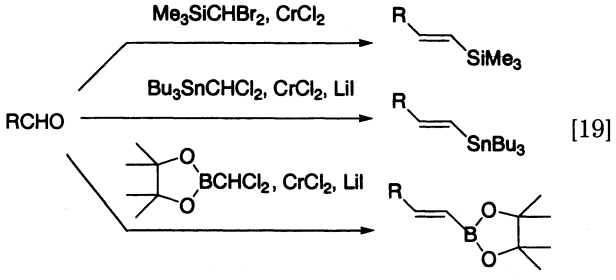
The geminal dichromium reagents prepared from iodoform with chromium(II) chloride react with an aldehyde to give an iodoalkene with one-carbon extension eq. [17].[26] The haloform-chromium(II) chloride reagent produces *E* isomers of alkenyl halides selectively in an *E/Z* ratio of 83:17 to 95:5 eq. [18]. Use of a dioxane-tetrahydrofuran solvent mixture decreases the reaction rate, but considerably improves the *E/Z* ratio.[27]



THF	0 °C, 4 h	73% (*E* / *Z* = 4 / 1)
dioxane	r.t., 4 d	40% (*E* / *Z* = 22 / 1)
dioxane, THF (6:1)	r.t., 8 h	69% (*E* / *Z* = 13 / 1)

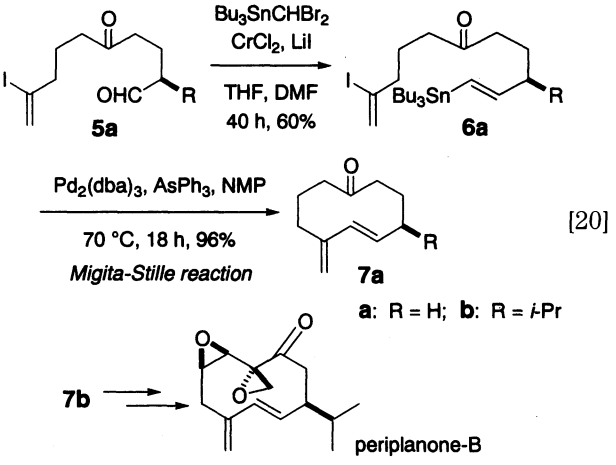
[18]

The geminal dichromium species can be prepared from alkyl-, trimethylsilyl-, triallkylstannyl-, and dioxaborolanyl-substituted geminal dihalomathanes, and the method can be applied to the synthesis of 1,2-disubstituted olefins,[28] alkenylsilanes,[29] alkenylstannanes,[30] and alkenylboronates[31] with high *E*-selectivities eq. [19].



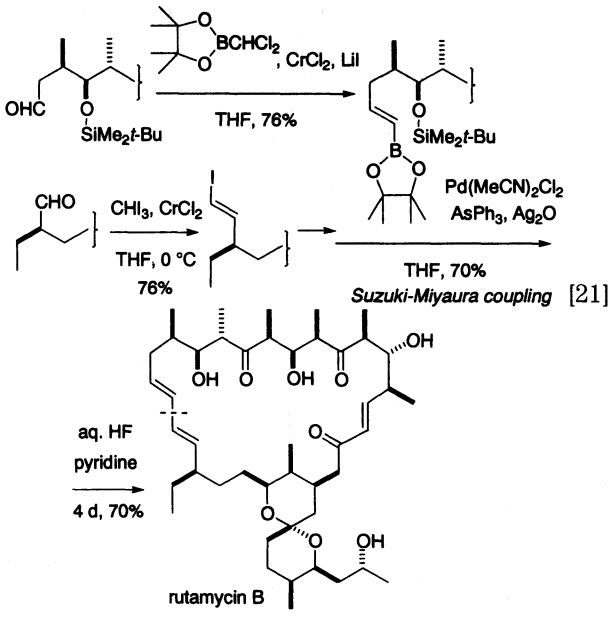
[19]

Hodgson showed that a medium-sized ring could be obtained by the Migita-Stille reaction eq. [20].[32] One of the key conditions was the concentration of the substrate; 82% yield of **7a** was obtained at 0.04 M and the yield increased to 96% at 0.009 M. The starting (*E*)-alkenylstannane **6a** was prepared by treatment of keto aldehyde **5a** with a geminal dichromium reagent derived from $Bu_3SnCHBr_2$, LiI and $CrCl_2$.[30] It is important to note that only an aldehyde group was transferred to an alkenylstannane without affecting the coexisting ketone.



[20]

In 1998, White synthesized rutamycin B by a palladium catalyzed intramolecular Suzuki-Miyaura reaction eq. [21].[33] Both functional groups for the coupling reaction, alkenyl iodide and boronate moieties, were prepared with the corresponding geminal dichromium reagents under mild conditions.



[21]

Coupling reactions between alkynyl iodides and aldehydes with chromium(II). Nucleophilic addition of an alkynylmetal compound to a carbonyl group has been widely employed in carbon-chain extension reactions. Unfortunately, alkynyllithium and -magnesium compounds add to both aldehyde and ketone groups indiscriminately. In contrast, alkynylchromium compounds, which are generated by reduction of alkynyl halides with chromium(II) chloride in DMF, add selectively to an aldehyde moiety without affecting the coexisting ketone group of the substrate (Table I).[34] In addition, potential problems such as epimerization and dehydration associated with enolization do not occur.[35]

Table I

PhCHO + PhCOMe → BuC≡CCHPh (OH) (**A**) + BuC≡CCMePh (OH) (**B**)

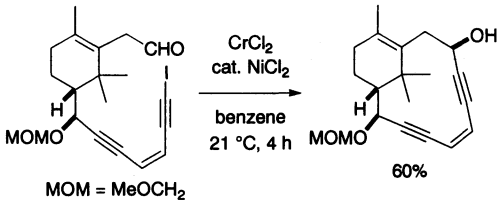
Reagents	Solvents	Temp / °C	Time / h	Yields/% **A**	**B**
BuC≡CLi	THF	0	0.5	53	45
BuC≡CMgBr	THF	0	0.25	53	43
BuC≡Cl + $CrCl_2$	DMF	25	2	82	< 3[a]

a) Recovery of PhCOMe: 92%.

The chromium(II) reagent prepared from $CrCl_3$ and $LiAlH_4$ is also effective for the reaction. Although reactions between simple halo alkynes and aldehydes proceed without a catalytic amount of nickel(II) chloride,[34] the chromium(II) chloride-nickel(II) chloride system is used for highly oxygenated substrates,[35),36] and

for intramolecular cyclizations.[37] The amount of nickel(II) chloride used for iodoacetylene addition to carbonyl groups is smaller (0.01–0.1% w/w) than that for iodoalkenes.

The starting 1-iodo-1-alkynes can be prepared from 1-alkynes with iodine and morpholine in excellent yields under mild conditions.[36] Thus, the reaction is suitable for intramolecular cyclization. Nine-, ten-, and twelve-membered rings are prepared by intramolecular cyclization with chromium(II) chloride and a catalytic amount of nickel(II) chloride. Notably, this method has been used to synthesize endiynes, and one diastereomer was produced probably due to the ring strain eq. [22].[38]



[22]

As describe above, several chromium(II)-mediated synthetic reactions have been proposed by the authors and others. Due to the advantages over the corresponding organolithium and -magnesium reagents, these reactions have been employed in a number of excellent syntheses, demonstrating further usefulness of the reactions.[39]

References

1) Barton, D. H. R., Basu, N. K., Hesse, R. H., Morehouse, F. S., and Pechet, M. M. (1966) J. Am. Chem. Soc. **88**(12), 3016-3021.
2) Cole, W., and Julian, P. L. (1954) J. Org. Chem. **19**(2), 131-138.
3) Anet, F. A. L., and Leblanc, E. (1957) J. Am. Chem. Soc. **79**(10), 2649-2650; Kauffmann, T., Abeln, R., and Wingbermühle, D. (1984) Angew. Chem., Int. Ed. Engl. **23**(9), 729-730.
4) Nozaki, H., Aratani, T., and Noyori, R. (1967) Tetrahedron **23**(9), 3645-3650.
5) Moore, W. R., and Ward, H. R. (1960) J. Org. Chem. **25**(11), 2073; Skattebøl, L. (1961) Tetrahedron Lett. (5), 167-172.
6) Okude, Y., Hirano, S., Hiyama, T., and Nozaki, H. (1977) J. Am. Chem. Soc. **99**(9), 3179-3181.
7) Okude, Y., Hiyama, T., and Nozaki, H. (1977) Tetrahedron Lett. (43), 3829-3830.
8) Buse, C. T., and Heathcock, C. H. (1978) Tetrahedron Lett. (19), 1685-1688; Hiyama, T., Kimura, K., and Nozaki, H. (1981) Tetrahedron Lett. **22**(11), 1037-1040.
9) Khan, S. I., and Bau, R. (1983) Organometallics **2**(12), 1896-1897; Daly, J. J., Sneeden, R. P. A., and Zeiss, H. H. (1966) J. Am. Chem. Soc. **88**(18), 4287-4288.
10) Still, W. C., and Mobilio, D. (1983) J. Org. Chem. **48**(24), 4785-4786.
11) Fürstner, A., and Shi, N. (1996) J. Am. Chem. Soc. **118**(49), 12349-12357.
12) Chen, C., Tagami, K., and Kishi, Y. (1995) J. Org. Chem. **60**(17), 5386-5387.
13) Bandini, M., Cozzi, P. G., Melchiorre, P., and Umani-Ronchi, A. (1999) Angew. Chem. Int. Ed. **38**(22), 3357-3359.
14) Castro, C. E., and Kray, W. C., Jr. (1963) J. Am. Chem. Soc. **85**(18), 2768-2773.
15) Takai, K., Matsukawa, N., Takahashi, A., and Fujii, T. (1998) Angew. Chem. Int. Ed. **37**(1/2), 152-155.
16) Takai, K., Kimura, K., Kuroda, T., Hiyama, T., and Nozaki, H. (1983) Tetrahedron Lett. **24**(47), 5281-5284.
17) Takai, K., Tagashira, M., Kuroda, T., Oshima, K., Utimoto, K., and Nozaki, H. (1986) J. Am. Chem. Soc. **108**(19), 6048-6050.
18) Jin, H., Uenishi, J.-i., Christ, W. J., and Kishi, Y. (1986) J. Am. Chem. Soc. **108**(18), 5644-5646.
19) Armstrong, R. W., Beau, J.-M., Cheon, S. H., Christ, W. J., Fujioka, H., Ham, W.-H., Hawkins, L. D., Jin, H., Kang, S. H., Kishi, Y., Martinelli, M. J., Mcwhorter, W. W., Jr., Mizuno, M., Nakata, M., Stutz, A. E., Talamas, F. X., Taniguchi, M., Tino, J. A., Ueda, K., Uenishi, J.-i., White, J. B., and Yonaga, M. (1989) J. Am. Chem. Soc. **111**(19), 7525-7530.
20) Schreiber, S. L., and Meyers, H. V. (1988) J. Am. Chem. Soc. **110**(15), 5198-5200.
21) Aoyagi, S., Wang, T.-C., and Kibayashi, C. (1993) J. Am. Chem. Soc. **115**(24), 11393-11409.
22) Nicolaou, K. C., Theodorakis, E. A., Rutjes, F. P. I. T., Sato, M., Tiebes, J., Xiao, X.-Y., Hwang, C.-K., Duggan, M. E., Yang, Z., Couladouros, E. A., Sato, F., Shin, J., He, H.-M., and Bleckman, T. (1995) J. Am. Chem. Soc. **117**(41), 10239-10251.
23) Tamao, K., Sumitani, K., and Kumada, M. (1972) J. Am. Chem. Soc. **94**(12), 4374-4376; Corriu, R. J., and Masse, J. P. (1972) J. Chem. Soc., Chem. Commun. (3), 144.
24) Kosugi, M., Sasazawa, K., Shimizu, Y., and Migita, T. (1977) Chem. Lett. (3), 301-302; Stille, J. K. (1986) Angew. Chem., Int. Ed. Engl. **25**(6), 508-524.
25) Miyaura, N., and Suzuki, A. (1995) Chem. Rev. **95**(7), 2457-2483.
26) Takai, K., Nitta, K., and Utimoto, K. (1986) J. Am. Chem. Soc. **108**(23), 7408-7410.
27) Evans, D. A., and Black, W. C. (1993) J. Am. Chem. Soc. **115**(11), 4497-4513.
28) Okazoe, T., Takai, K., and Utimoto, K. (1987) J. Am. Chem. Soc. **109**(3), 951-953.
29) Takai, K., Kataoka, Y., Okazoe, T., and Utimoto, K. (1987) Tetrahedron Lett. **28**(13), 1443-1446.
30) Hodgson, D. M. (1992) Tetrahedron Lett. **33**(38), 5603-5604; Hodgson, D. M., Foley, A. M., and Lovell, P. J. (1998) Tetrahedron. Lett. **39**(35), 6419-6420.

31) Takai, K., Shinomiya, N., Yoshida, N., Kaihara, H., Moriwake, T., and Utimoto, K. (1995) Synlett (9), 963-964.
32) Hodgson, D. M., Foley, A. M., Boulton, L. T., Lovell, P. J., and Maw, G. N. (1999) J. Chem. Soc., Perkin Trans. **1** (20), 2911-2922.
33) White, J. D., Tiller, T., Ohba, Y., Porter, W. J., Jackson, R. W., Wang, S., and Hanselmann, R. (1998) Chem. Commun. (1), 79-80.
34) Takai, K., Kuroda, T., Nakatsukasa, S., Oshima, K., and Nozaki, H. (1985) Tetrahedron Lett. **26**(45), 5585-5588.
35) Aicher, T. D. and Kishi, Y. (1987) Tetrahedron Lett. **28**(30), 3463-3466.
36) Wang, Y., Babirad, S. A., and Kishi, Y. (1992) J. Org. Chem. **57**(2), 468-481.
37) Crévisy, C., and Beau, J.-M. (1991) Tetrahedron Lett. **32**(27), 3171-3174; Nicolaou, K. C., Liu, A., Zeng, Z., and McComb, S. (1992) J. Am. Chem. Soc. **114**(24), 9279-9282.
38) Lu, Y.-F., Harwig, C. W., and Fallis, A. G. (1993) J. Org. Chem. **58**(16), 4202-4204.
39) Hiyama, T. (1981) J. Synth. Org. Chem., Jpn. **39**(1), 81-85; Takai, K., and Utimoto, K. (1988) J. Synth. Org. Chem., Jpn. **46**(1), 66-77; Saccomano, N. A. (1991) In Comprehensive Organic Synthesis (eds. Trost, B. M., and Fleming, I.). vol. 1, Pergamon Press, New York, pp. 173-209; Hodgson, D. M. (1994) J. Organomet. Chem. **476**(1), 1-5; Avalos, M., Babiano, R., Cintas, P., Jiménez, J. L., and Palacios, J. C. (1999) Chem. Soc. Rev. **28**(3), 169-177; Fürstner, A. (1999) Chem. Rev. **99**(4), 991-1046; Wessjohann, L. A., and Scheid, G. (1999) Synthesis (1), 1-36.