Chromium(II)-Mediated Reactions of Iodonium Tetrafluoroborates with Aldehydes: Umpolung of Reactivity of Diaryl-, Alkenyl(aryl)-, and Alkynyl(aryl)iodonium Tetrafluoroborates

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The method described herein allows us, for the first time, to perform umpolung of reactivity of diaryl-, alkenyl(aryl)-, and alkynyl(aryl)iodonium tetrafluoroborates. The method involves generation of organochromium(III) species via reaction of iodonium salts with anhydrous chromium dichloride, followed by their nucleophilic addition to aldehydes to yield alcohols. In contrast to the reaction of aryl and alkenyl halides with chromium dichloride, these iodonium salts are so active that organochromium(III) could be generated without using a nickel catalyst. Substituent effects of unsymmetrically substituted diaryliodonium salts on the product profiles are in good agreement with the reported mode of decomposition of the intermediate unsymmetrical diaryliodanyl radicals. Alkenyl(mesityl)iodonium tetrafluoroborates undergo exclusive alkenylation of aldehydes with no signs of the formation of an arylation product.

Introduction

Iodonium salts such as diaryl-, alkenyl(aryl)-, and alkynyl(aryl)iodonium salts are known to be versatile agents in organic synthesis.[1] Because of their highly electron-deficient nature and the excellent nucleofugality of the phenyliodonio group, which shows a leaving group ability about 10^6 times greater than triflate,[2] these iodonium salts serve as the highly activated species of halides in nucleophilic substitution reactions. For instance, diaryliodonium salts transfer the aryl group to a variety of organic substrates including carbon, nitrogen, phosphorus, and group 16 element-centered nucleophiles under mild conditions.[1] Alkenyl(aryl)iodonium salts also undergo nucleophilic vinylic substitutions with a number of nucleophiles such as organocuprates, sulfinates, thiolates, nitrites, halides, cyanides, azides, phosphines, and enolates.[3] Similarly, reaction of alkynyl(aryl)iodonium salts with nucleophiles affords substituted alkynes. Although a stepwise pathway including Michael addition followed by carbene rearrangement has been established, the alkynyliodonium salts formally act as alkynyl cation synthons in these reactions.[1] No strategy is available, however, for using these iodonium salts as an anion-equivalent species that can react with electrophiles such as carbonyl compounds. An efficient method for this purpose remains to be established.

Chromium-mediated coupling of organic halides with aldehydes, reported by Nozaki, Hiyama, and co-workers in 1977, is a useful method for carbon−carbon bond formation because of its excellent chemoselectivity for aldehydes as well as its compatibility with other functional groups, e.g., esters, amides, nitriles, ketones, alcohols, and various alcohol protecting groups.[4] The reaction involves intermediacy of organochromium(III) species, which act as carbanion equivalents.[5] Takai and Kishi independently demonstrated that the reaction of aryl and alkenyl halides (I and Br) with $CrCl_2$ requires a catalytic amount of nickel salts for efficient generation of the nucleophilic organochromium(III) intermediates.[6] This reaction is believed to proceed via oxidative addition

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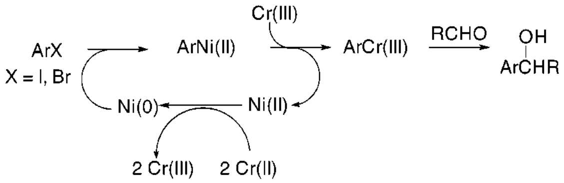
Table 1. Chromium-Mediated Arylation of Aldehydes 2 with Diaryliodonium Salts 1[a]

	iodonium salt			aldehyde		CrCl$_2$[b]	NiCl$_2$[b]	conditions	product (10^2 mol)[b]		
entry	**1**	Ar	mol[b]	**2**	R	(mol)	(mol)	*T*/°C, time/h	**3**[c]	ArI[d]	ArH[d]
1	**1a**	Ph	0.5	**2a**	Ph	4	0.02	25, 5	**3a** (57)	2	33
2	**1a**		0.5	**2a**		4	0.02[e]	25, 24	**3a** (59)	24	17
3	**1a**		0.5	**2a**		4	0.02[f]	25, 5	**3a** (48)	5	39
4	**1a**		1	**2a**		4	0	25, 5	**3a** (69)	84	34
5	**1a**		2	**2a**		4	0	25, 5	**3a** (72)	168	140
6	**1a**		1	**2a**		4	0.02	25, 5	**3a** (87)	35	44
7	**1a**		1.5	**2a**		6	0.03	25, 5	**3a** (92)	24	153
8	**1a**		2	**2a**		8	0.04	0, 5	**3a** (62)	200	40
9	**1a**		2	**2a**		8	0.04	0, 24	**3a** (86)	200	44
10	**1a**		1	**2b**	*p*-ClC$_6$H$_4$	4	0.02	25, 5	**3b** (82)	49	42
11	**1a**		1	**2c**	*p*-MeC$_6$H$_4$	4	0.02	25, 5	**3c** (78)	66	34
12	**1a**		1	**2d**	*p*-MeOC$_6$H$_4$	4	0.02	25, 5	**3d** (72)	−	−
13	**1a**		1	**2e**	*o*-MeC$_6$H$_4$	4	0.02	25, 5	**3e** (79)	−	−
14	**1a**		1.5	**2f**	*n*-C$_{10}$H$_{21}$	6	0.03	25, 5	**3f** (82)	64	30
15	**1a**		1	**2g**	Me$_2$CH	4	0.02	25, 5	**3g** (74)	−	−
16	**1a**		1	**2h**	*t*-Bu	4	0.02	25, 5	**3h** (0)[g]	47	−
17	**1a**		1.5	**2i**	*E*-MeCH=CH	6	0.03	25, 5	**3i** (71)	−	−
18	**1a**		2	**2j**	*E*-PhCH=CH	4	0	25, 5	**3j** (56)	−	−
19	**1b**	*p*-ClC$_6$H$_4$	1.5	**2a**		6	0.03	25, 5	**3b** (79)	36	−
20	**1c**	*p*-MeC$_6$H$_4$	1	**2a**		4	0.02	25, 5	**3c** (72)	73	41

[a] Reactions were carried out using 0.3 mmol of an aldehyde in DMF under Ar. [b] Molar ratios per mol of an aldehyde. [c] Isolated yields. [d] GC yields. −: not determined. [e] Reactions were carried out in DMSO under Ar. [f] Reactions were carried out in the presence of excess amounts of 1,1-diphenylethylene. [g] Benzhydrol (**3a**) (10%) and benzophenone (8%) were obtained.

Scheme 1



of a halide to Ni(0) generated by reduction of Ni(II) with 2 molar equiv of CrCl$_2$, followed by transmetalation reaction with Cr(III), yielding organochromium(III) (Scheme 1).

We report herein, for the first time, chromium(II)-mediated reactivity umpolung of aryl-, alkenyl-, and alkynyliodonium tetrafluoroborates, which involves intermediacy of organochromium(III) followed by nucleophilic addition to aldehydes to yield alcohols.[7] Because of its moderate reducing power as a single-electron-transfer agent,[8] commercially available anhydrous CrCl$_2$ was used for reduction of these iodonium salts.[9]

Results and Discussion

Reaction of Diaryliodonium Salts: Chromium-Mediated Arylation of Aldehydes. The results of reactions of diaryliodonium tetrafluoroborates **1** with CrCl$_2$ in the presence of an aldehyde are summarized in Table 1. Our initial results (Table 1, entry 1) indicated that generation of the phenylchromium(III) species could be achieved by using diphenyliodonium tetrafluoroborate (**1a**) under conventional conditions, i.e., CrCl$_2$ and a catalytic amount of NiCl$_2$ in DMF at room temperature for 5 h; thus, in the presence of benzaldehyde (**2a**), reaction of the iodonium salt **1a** (0.5 equiv) afforded benzhydrol (**3a**) as a product of an addition reaction of the resulting phenylchromium(III) intermediate in 57% yield, in addition to benzene (33%). When DMSO was used as a solvent, a similar yield (59%) of **3a** was obtained along with the formation of iodobenzene (24%) and benzene (17%).

Significantly, in marked contrast to the reaction of aryl halides with CrCl$_2$, we found that the iodonium salt **1a** is so active that phenylchromium(III) could be generated from **1a** without using a nickel catalyst.[10] Thus, reaction of **1a** (1 equiv) with benzaldehyde (**2a**) using CrCl$_2$ (4 equiv) at room temperature afforded benzhydrol (**3a**) in 69% yield (Table 1, entry 4). One of the byproducts of this reaction was found to be a large amount (84%) of iodobenzene that is incapable of generating phenylchromium(III) without a Ni catalyst under these conditions.[6] Use of a catalytic amount of NiCl$_2$ as an additive made it possible to use both of the phenyl moieties in **1a**, which resulted in a much improved yield of **3a** (87%) and a decreased amount (35%) of iodobenzene (Table 1, entry 6). At 0 °C, however, the nickel catalyst no longer effectively activates iodobenzene (Table 1, entries 8 and 9). Use of **1a** (1.5 equiv)/ CrCl$_2$ (6 equiv)/NiCl$_2$ (0.03 equiv) at room temperature afforded a 92% yield of **3a**, but with formation of a large amount of benzene. The original reactions between aryl halides and aldehydes require 2 molar equiv of the halides for an efficient coupling;[6] therefore, this result probably indicates a competing side reaction, i.e., reductive dehalogenation of aryl halides leading to arenes.

In general, the reaction was carried out by adding a solution of an aldehyde **2** and diphenyliodonium salt **1a** in DMF to a solution of CrCl$_2$ doped with NiCl$_2$ in DMF at room temperature under argon. As shown in Table 1, the phenylchromium(III) generated from **1a** readily undergoes additions to aromatic aldehydes **2b**−**e** with electron-withdrawing and -donating substituents as well as aliphatic aldehydes **2f**,**g** to give the alcohols **3** in good yields. With α,β-unsaturated aldehydes, selective 1,2-

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(7) A part of this work has been reported in a preliminary form: Chen, D.-W.; Takai, K.; Ochiai, M. *Tetrahedron Lett.* **1997**, *38*, 8211.

(8) Hanson, J. R. *Synthesis* **1974**, 1.

(9) Reduction of diphenyliodonium chloride with CrCl$_2$ in water has been reported to give benzene. See: Beringer, F. M.; Bodlaender, P. *J. Org. Chem.* **1969**, *34*, 1981.

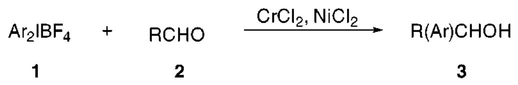
(10) It has been documented that, in some cases, commercially available CrCl$_2$ contains nickel salts as an impurity.[6b,c] The chromium reagent used in our studies was purchased from Kishida Chemical Co. and was not efficient in converting iodobenzene to phenylchromium(III).

Table 2. Product Distribution in Arylation of 2a with Unsymmetrical Diaryliodonium Salts 4[a]

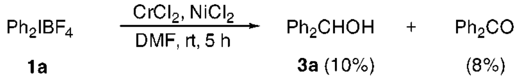
		product (yield/%), ratio								
entry	4	**3a**[b]	**3**[b]	ratio[c]	PhH[d]	ArH[d]	ratio[e]	ArI[d]	PhI[d]	ratio[f]
1	**4a**	**3a** (60)	**3d** (20)	75:25	PhH (4)	PhOMe (6)	71:29	*p*-$MeOC_6H_4I$ (69)	PhI (16)	81:19
2	**4a**[g]	**3a** (46)	**3d** (15)	75:25	PhH (5)	PhOMe (3)	74:26	*p*-$MeOC_6H_4I$ (74)	PhI (15)	83:17
3	**4b**	**3a** (56)	**3k** (0)	100:0	PhH (15)	1,3,5-$Me_3C_6H_3$ (7)	92:8	2,4,6-$Me_3C_6H_2I$ (81)	PhI (19)	81:19
4	**4c**	**3a** (42)	**3c** (24)	64:36	PhH (3)	PhMe (15)	54:46	*p*-MeC_6H_4I (58)	PhI (23)	72:28
5	**4d**	**3a** (26)	**3b** (31)	46:54	PhH (17)	PhCl (21)	45:55	*p*-ClC_6H_4I (26)	PhI (44)	37:63

[a] Reaction conditions: **2a**/**4** (1 molar equiv)/$CrCl_2$(4 molar equiv)/DMF/25 °C/5 h/Ar. [b] Isolated yields. [c] Ratios of **3a**:**3b**−**d**,**k**,**l**. [d] GC yields. [e] Ratios of (**3a** + PhH):(**3b**−**d**,**k**,**l** + ArH). [f] Ratios of ArI:PhI. [g] Reactions were carried out at 0 °C for 24 h.

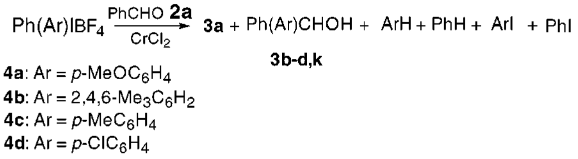
Scheme 2



Scheme 3



Scheme 4



addition to the carbonyl groups was observed; for example, (*E*)-crotonaldehyde (**2i**) afforded the benzyl alcohol **3i** selectively in 71% yield (Table 1, entry 17). Cinnamaldehyde (**2j**), however, gave poor results (less than 10% yield of **3j**) under our standard conditions, probably because of its high propensity to undergo reductive coupling with $CrCl_2$ in DMF yielding glycols.[11] This problem was overcome by adding **2j** into the reaction system containing pregenerated phenylchromium(III) in the absence of an excess Cr(II), and an acceptable yield of **3j** was achieved via the exclusive 1,2-addition (Table 1, entry 18). Substituted phenylchromium species with *p*-chloro and *p*-methyl groups could also be generated from diaryliodonium salts **1b**,**c** and reacted with **2a** affording addition products in good yields (Table 1, entries 19 and 20).

The sterically demanding compounds, pivalaldehyde (**2h**), did not react with phenylchromium(III) under our conditions. In this reaction, small amounts of benzhydrol (**3a**) (10%) and benzophenone (8%) were isolated. These products were proved to be derived from the reaction of phenylchromium(III) with DMF, because the reaction shown in Scheme 3 resulted in formation of the same product mixture in comparable yields in the absence of an aldehyde. DMF has been shown to be a solvent of choice in chromium-mediated coupling of alkenyl and aryl halides with aldehydes because of the high solubility of $CrCl_2$.[6] These results might suggest, however, that DMF itself can act as an electrophile toward phenylchromium(III).[12] In fact, it has been shown that DMF is a good ligand to octahedral chromium(III),[14] which, by activating DMF, would facilitate its reaction with phenylchromium(III).

No reaction of phenylchromium(III) with 3-pentanone and *N*-(benzenesulfonyl)benzaldimine was observed under our conditions. The reaction with hexanoyl chloride afforded the desired 1-phenylhexan-1-one (23%) accompanied by the formation of benzhydrol (**3a**) (8%), benzophenone (4%), and *N*,*N*-dimethylhexanamide (9%).

To investigate the electronic and steric effects of substituents on the aromatic rings of diaryliodonium salts and to gain some insight into the mechanism of this reaction (see below), we analyzed in detail (see Table 2) product compositions for the chromium-mediated coupling of unsymmetrically substituted aryl(phenyl)iodonium salts **4** with benzaldehyde (**2a**) in the absence of Ni catalyst (Scheme 4).

Reaction of *p*-methoxyphenyl(phenyl)iodonium salt **4a** gave rise to the phenylation product **3a** as a major product (60%) and the substituted benzhydrol **3d** as a minor product (20%), accompanied by the formation of dehalogenated arenes (PhH, 4%; PhOMe 6%) and iodoarenes (*p*-$MeOC_6H_4I$, 69%; PhI, 16%) (Table 2, entry 1). Use of *p*-methylphenyliodonium salt **4c** gave similar results, but with reduced selectivity. Interestingly, mesityl(phenyl)iodonium salt **4b** gave benzhydrol (**3a**) selectively with no sign of the formation of substituted **3k** (Ar = 2,4,6-$Me_3C_6H_2$). We have no evidence for the formation of mesitylchromium(III) in this reaction, but, even if it is formed,[15] severe steric congestion derived from the vicinal methyl groups of mesitylchromium(III) would probably inhibit the addition reaction to benzaldehyde (**2a**).[16] Thus, the electron-donating methoxy or methyl group afforded a larger amount of benzhydrol (**3a**) than substituted benzhydrols. On the other hand, introduction of an electron-withdrawing *p*-chloro group reversed the major reaction course, with the substituted **3b** predominating. These substituent effects on the product profiles are in good agreement with the reported mode of decomposition of unsymmetrical diaryliodanyl radicals (see below).[17]

Reaction of Alkenyl(aryl)iodonium Salts: Chromium-Mediated Alkenylation of Aldehydes. Alkenyl-

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[11] This reductive coupling of cinnamaldehyde (**2j**) by the reaction with $CrCl_2$ in DMF is fast (within 5 min at 25 °C) and gives a stereoisomeric mixture of pinacol-type dimers via the ketyl radical anion in good yields. For pinacol coupling of aldehydes with Cr(II), see: (a) Ho, T.-L. *Synthesis* **1979**, 1. (b) Conant, J. B.; Cutter, H. B. *J. Am. Chem. Soc.* **1926**, *48*, 1016. (c) Davis, D. D.; Bigelow, W. B. *J. Am. Chem. Soc.* **1970**, *92*, 5127.

[12] In this reaction, benzaldehyde (**2a**) is probably produced in situ by nucleophilic attack of phenylchromium intermediate to DMF followed by extrusion of dimethylamine. Reaction of phenylchromium(III) with benzaldehyde (**2a**) gives chromium alkoxide of benzhydrol (**3a**). β-Hydrogen abstraction from this chromium alkoxide intermediate will produce benzophenone, as was reported by Yamamoto.[13]

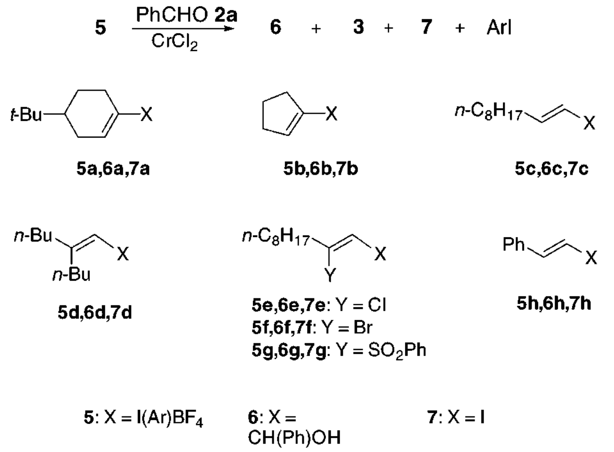
[13] Ito, T.; Ono, T.; Maruyama, K.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2212.

[14] (a) Daly, J. J.; Sneeden, R. P. A.; Zeiss, H. H. *J. Am. Soc. Chem.* **1966**, *88*, 4287. (b) Hiyama, T.; Kimaru, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 1037.

[15] The observed formation both of mesitylene and iodobenzene in this reaction suggests the intervention of mesitylchromium(III).

[16] Lack of formation of the substituted benzhydrol **3k** may reflect the lifetime of the transient mesitylchromium(III). See: Hodgson, D. M.; Wells, C. *Tetrahedron Lett.* **1994**, *35*, 1601.

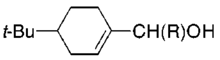
Scheme 5



(aryl)iodonium salts **5** were also reduced at room temperature with $CrCl_2$ in DMF without using $NiCl_2$. Alkenylation yielding allyl alcohols **6** and arylation yielding benzhydrols **3** compete each other in the reaction with benzaldehyde (**2a**) (Scheme 5); thus, treatment of an equivalent amount of 4-*tert*-butylcyclohexenyl(phenyl)-iodonium tetrafluoroborate (**5aa**; Ar = Ph) with **2a** in the presence of $CrCl_2$ afforded a mixture of the alkenylation product, allyl alcohol **6a**, and the arylation product, benzhydrol (**3a**), in a ratio of 45:55 in good yield (Table 3, entry 1). Iodobenzene and cyclohexenyl iodide **7a** were also obtained in a comparable ratio. Introduction of a *p*-methoxy substituent into the phenyl group of **5aa** increased the selectivity for alkenylation of **2a**, and the allyl alcohol **6a** was obtained as a major product in 48% yield, with a 75:25 ratio of alkenylation to arylation. Use of 4-*tert*-butylcyclohexenyl(mesityl)iodonium tetrafluoroborate (**5ac**; Ar = 2,4,6-$Me_3C_6H_2$) gave the alkenylation product **6a** selectively with no sign of the formation of the arylation product **3k** (Table 3, entry 3). These results are in good agreement with the substituent effects shown in Table 2.

Compared to the results obtained with cyclohexenyliodonium salts **5a**, those obtained in the reaction of cyclopentenyliodonium tetrafluoroborates **5ba** and **5bc** with benzaldehyde (**2a**) were poor, probably due to the difference in stability between cyclohexenyl and cyclopentenyl radicals. Acyclic alkenyliodonium salt does not seem to be a suitable substrate for this chromium-mediated coupling with **2a**. (*E*)-1-Decenyl(phenyl)iodonium salt **5ca** afforded a mixture of the allyl alcohol **6c** and benzhydrol (**3a**) with a 24:76 ratio in 34% yield (Table 3, entry 7). Furthermore, no alkenylation products were obtained in the reaction of (*Z*)-2-halo-1-decenyl-(phenyl)iodonium salts **5ea** and **5fa**, and the reactions afforded a large amount of 1-decyne in 31−69% yield through syn *β*-elimination.

The results of chromium-mediated alkenylations of various aldehydes **2** using 2 equiv of alkenyl(mesityl)-iodonium salts **5** are summarized in Table 4. The cyclohexenylchromium(III) generated from **5ac** readily undergoes addition to aromatic aldehydes **2a**−**c** as well as aliphatic aldehydes **2g**,**i**,**k**, yielding the allyl alcohols **6** in good yields (Table 4, entries 1−6). (*E*)-Crotonaldehyde (**2i**) underwent selective 1,2-addition to the carbonyl group and, after quenching of the reaction mixture with an aqueous $NaHCO_3$ solution, afforded the allyl alcohol **6l** selectively in 67% yield (Table 4, entry 5). When the reaction mixture was quenched with water, formation of a considerable amount of the conjugated dienyl alcohol **8** (16%) was observed in addition to the allyl alcohol **6l** (55%). The alcohol **8** would be a thermodynamic product, formed by acid-catalyzed rearrangement of the allyl alcohol **6l** during workup using water (Scheme 6). It has been shown that an aqueous solution of $CrCl_3$ is moderately acidic.[18] (*E*)-Styryl(mesityl)iodonium tetrafluoroborate (**5hc**) gave the alkenylation product **3j** in low yield (15%) and (*E*)-*β*-chlorostyrene as a major product (49%).



6i: R = *p*-ClC_6H_4
6j: R = *p*-MeC_6H_4
6k: R = Me_2CH
6l: R = *E*-MeCH=CH
6m: R = *n*-C_9H_{19}

Reaction of Alkynyl(aryl)iodonium Salts: Chromium-Mediated Alkynylation of Aldehydes. 1-Alkynyl iodides are reduced with $CrCl_2$ in DMF to give alkynylchromium(III), which adds to aldehydes to yield propargyl alcohols.[19] The results of alkynylation of benzaldehyde (**2a**) with 1-decynyl(phenyl)iodonium tetrafluoroborate (**9**) are summarized in Table 5. Reaction of an equivalent amount of the alkynyliodonium salt **9** with **2a** in the presence of $CrCl_2$ and $NiCl_2$ in DMF at 25 °C afforded the alkynylation product, propargyl alcohol **10**, in 29% yield along with the formation of a small amount of alkynyl ketone **11** (5%) (Scheme 7; Table 5, entry 1).[13] Use of 2 equiv of **9** increased the yield of **10** (59−63%, Table 5, entries 2 and 3). Interestingly, this alkynylation of **2a** appears to be highly selective in the sense that we did not observe phenylation of **2a** to yield **3**. This observation is in a good agreement with formation of a large amount of iodobenzene.

DMSO as a solvent gave comparable results; however, other solvents such as THF, PhH, CH_2Cl_2, and MeOH afforded no evidence of alkynylation (Table 5, entries 5−8). MeOH resulted in exclusive reduction, affording 1-decyne (**12**) in 85% yield.[20] When the reaction was carried out in CH_2Cl_2, extensive halogen exchange was observed: that is, 1-chlorodecyne (**13**) was obtained selectively in 80% yield along with iodobenzene (83%). PhH as a solvent gave similar results. Such halogen exchanges have been observed in the reaction of primary alkyl iodides with $CrCl_2$ in DMF that results in the formation of alkyl chlorides.[21b,22]

Reaction Mechanism. A. Diaryliodonium Salt. As illustrated in Scheme 8, the reaction mechanism for the

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(17) Generation of diaryliodanyl radicals has been well documented. (a) In nucleophilic substitutions: Tanner, D. D.; Reed, D. W.; Setiloane, B. P. *J. Am. Chem. Soc.* **1982**, *104*, 3917. Singh, P. R.; Khanna, R. K. *Tetrahedron Lett.* **1982**, *23*, 5355. Beringer, F. M.; Falk, R. A. *J. Chem. Soc.* **1964**, 4442. (b) Under photochemical conditions: Crivello, J. V. *Adv. Polym. Sci.* **1984**, *62*, 1. Crivello, J. V. *Annu. Rev. Mater. Sci.* **1983**, *13*, 173. Kampmeier, J. A.; Nalli, T. W. *J. Org. Chem.* **1994**, *59*, 1381. Kampmeier, J. A.; Nalli, T. W. *J. Org. Chem.* **1993**, *58*, 943. (c) In electrochemical reductions: Mubarak, M. S.; Peters, D. G. *J. Org. Chem.* **1985**, *50*, 673.

(18) Yamada, Y. *Haiikagoubutu no Kagaku*; Kagakudojin: Tokyo, 1980.

(19) Takai, K.; Kuroda, T.; Nakatsukasa, S.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1985**, *26*, 5585.

(20) Reaction of phenylchromium(III) with methanol proceeds at room temperature and gives benzene. See ref 13.

(21) (a) Crandall, J. K.; Michaely, W. J. *J. Org. Chem.* **1984**, *49*, 4244. (b) Takai, K.; Nitta, K.; Fujimura, O.; Utimoto, K. *J. Org. Chem.* **1989**, *54*, 4732.

(22) Takai, K.; Matsukawa, N.; Takahashi, A.; Fujii, T. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 152.

Table 3. Chromium-Mediated Coupling of Benzaldehyde 2a with Alkenyl(aryl)Iodonium Salts 5[a]

	iodonium salt		product (yield/%), ratio					
entry	**5**	Ar	**6**[b]	**3**[b]	ratio[c]	ArI[d]	**7**[d]	ratio[e]
1	**5aa**	Ph	**6a** (35)	**3a** (43)	45:55	PhI (39)	**7a** (61)[b]	39:61
2	**5ab**	*p*-$MeOC_6H_4$	**6a** (48)	**3d** (16)	75:25	*p*-$MeOC_6H_4I$ (58)[b]	**7a** (23)[b]	72:28
3	**5ac**	2,4,6-$Me_3C_6H_2$	**6a** (62)	**3k** (0)	100:0	2,4,6-$Me_3C_6H_2I$(72)[b]	**7a** (11)[b]	87:13
4	**5ba**	Ph	**6b** (0)	**3a** (49)	0:100	PhI(3)	**7b** (13)	19:81
5	**5bc**[f]	2,4,6-$Me_3C_6H_2$	**6b** (8)	**3k** (0)	100:0	2,4,6-$Me_3C_6H_2I$ (35)	**7b** (22)	61:39
6	**5ca**[f]	Ph	**6c**[g] (8)	**3a** (26)	24:76	PhI (18)	**7c** (63)[b]	22:78
7	**5cc**[f]	2,4,6-$Me_3C_6H_2$	**6c**[g] (23)	**3k** (0)	100:0	2,4,6-$Me_3C_6H_2I$ (64)[b]	**7c** (36)[b]	64:36
8	**5dc**[f]	2,4,6-$Me_3C_6H_2$	**6d** (12)	**3k** (0)	100:0	2,4,6-$Me_3C_6H_2I$ (66)	**7d** (34)	66:34
9	**5ea**[f]	Ph	**6e**[g] (0)	**3a** (9)	0:100	PhI (84)	**7e** (15)	85:15
10	**5fa**[f]	Ph	**6f**[g] (0)	**3a** (6)	0:100	PhI (76)	**7f** (13)	85:15
11	**5ga**[f]	Ph	**6g**[g] (12)	**3a** (trace)	100:0	PhI (74)	**7g** (0)	91:9

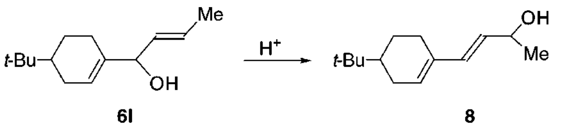
[a] Reaction conditions: **2a**/**5** (1 molar equiv)/$CrCl_2$(4 molar equiv)/DMF/25 °C/5 h/Ar. [b] Isolated yields. [c] Ratios of **6**:**3**. [d] GC or ^1H NMR yields. [e] Ratios of ArI:**7**. [f] 2 equiv of $CrCl_2$ was used. [g] Formation of 1-decyne (**12**) was observed: entry 6, 5%; entry 7, 7%; entry 9, 31%; entry 10, 69%; entry 11, 22%.

Table 4. Chromium-Mediated Alkenylation of Aldehydes 2 with Alkenyl(mesityl)iodonium Salts 5[a]

entry	**5**	**2** (R)	**6**	yield[b]/%
1	**5ac**	**2a** (Ph)	**6a**	81
2	**5ac**	**2b** (*p*-ClC_6H_4)	**6i**	77
3	**5ac**	**2c** (*p*-MeC_6H_4)	**6j**	72
4	**5ac**	**2g** (Me_2CH)	**6k**	70
5	**5ac**	**2i** (*E*-MeCH═CH)[c]	**6l**	67
6	**5ac**	**2k** (*n*-C_9H_{19})	**6m**	72
7	**5bc**	**2a** (Ph)	**6b**	21
8	**5cc**	**2a** (Ph)	**6c**	40
9	**5dc**	**2a** (Ph)	**6d**	27
10	**5hc**	**2a** (Ph)[d]	**3j**	15[e]

[a] Reaction conditions: **2**/**5** (2 molar equiv)/$CrCl_2$(4 molar equiv)/DMF/25 °C/5 h/Ar. [b] Isolated yields. [c] The reaction mixture was quenched with an aqueous $NaHCO_3$ solution. [d] Reaction conditions: **2a**/**5hc** (1 molar equiv)/$CrCl_2$(2 molar equiv)/DMF/25 °C/5 h/Ar. [e] (*E*)-*β*-Chlorostyrene was obtained in 49% yield.

Scheme 6



Cr-mediated coupling of diaryliodonium salts **1** with aldehyde **2** might be assumed to involve reduction of the hypervalent iodine generating the [9-I-2][23] iodanyl radical **14** via a single-electron transfer from Cr(II).[17] Unimolecular decomposition of the iodanyl radical **14** will produce both aryl radical and aryl iodide. Further reduction of the aryl radical with Cr(II) generates arylchromium(III), which reacts with aldehydes **2** yielding the alcohol **3**. The arylchromium(III) is also produced from the aryl iodide, when Ni catalyst is present;[6] in fact, formation of a large amount of iodobenzene was observed in the reaction of diphenyliodonium salt **1a** with benzaldehyde (**2a**) without using a nickel catalyst, whereas a reduced amount of iodobenzene along with an increased yield of **3a** was produced in the presence of Ni(II) (compare entries 4 and 6 in Table 1).

Several experimental observations are in line with this proposed mechanism. It has been well established that unsymmetrically substituted [9-I-2] aryl(phenyl)iodanyl radicals **15** would decompose by two paths, one leading to phenyl radical and iodoarene and the other to aryl radical and iodobenzene. It has also been established that the decomposition of the divalent radicals **15** favors cleavage of the Ar−I bond if the aryl groups have electron-withdrawing substituents but cleavage of the Ph−I bond if the aryl groups have electron-donating substituents (Scheme 9).[17] The relative ratios of rate constants k_2/k_1 were calculated from the relative yields of iodoarenes shown in Table 2 and compared with the reported values (Table 6). The relative rates of aryl radical departure k_2/k_1 obtained for the chromium-mediated reaction of phenyl(tolyl)- **4c** and anisyl(phenyl)-iodonium salts **4a** are in good agreement with the reported values of decomposition of unsymmetrical diaryliodanyl radicals **15** generated by single-electron transfer from sodium phenoxide or di-*tert*-butyl nitroxide.[17a] The selectivity observed may be attributable to the differences in bond dissociation energies of aryl carbon−iodine bonds.[24] These results would suggest the involvement of the [9-I-2] iodanyl radical **15** in this chromium-mediated coupling.

A Hammett plot of $\log(k_2/k_1)$ vs σ is linear with $\rho = 2.04$ and correlation coefficient = 0.99. In the unimolecular decomposition of the [9-I-2] intermediate **15** to yield aryl radicals, involvement of a polar transition state **16** has been proposed (Scheme 10).[17a,25] This partial charge separation predicts a decomposition pathway favoring cleavage of the Ar−I bond when the aryl groups have electron-withdrawing substituents, which is in a good agreement both with the observed departure aptitudes k_2/k_1 of the chromium-mediated reaction of **4** and with the positive ρ value of the Hammett plots.

Both the formyl and methyl groups of DMF act as a good hydrogen atom donor toward carbon- and oxygen-centered radicals ($Ph^\bullet$, $HO^\bullet$, and *t*-$BuO^\bullet$).[26] Formation of a considerable amount of the reduced arenes as byproducts (Table 1) might partly involve the intervention of aryl radicals, which will abstract hydrogen from the solvent DMF; when Cr-mediated coupling of **1a** with **2a** was performed in DMF-d_7, GC−MS analysis showed a 20% deuterium incorporation in the byproduct benzene. This hydrogen abstraction from DMF by aryl radicals would compete with the reduction by Cr(II) that yields the arylchromium(III).

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(23) For nomenclature, see: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

(24) The bond dissociation energies of aryl carbon−iodine bond in homolysis follow the order: PhI < *p*-MeC_6H_4I < *p*-$MeOC_6H_4I$.[17a,25]

(25) (a) Danen, W. C.; Saunders: D. G. *J. Am. Chem. Soc.* **1969**, *91*, 5924. (b) Davis, W. H.; Gleaton, J. H.; Pryor, W. A. *J. Org. Chem.* **1977**, *42*, 7.

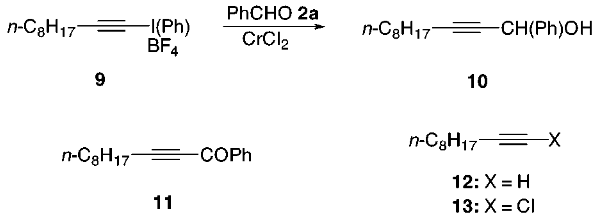
(26) (a) Gardini, G. P.; Minisci, F.; Palla, G.; Arnone, A.; Galli, R. *Tetrahedron Lett.* **1971**, 59. (b) Doyle, M. P.; Dellaria, J. F.; Siegfried, B.; Bishop, S. W. *J. Org. Chem.* **1977**, *42*, 3494.

Table 5. Chromium-Mediated Alkynylation of Aldehyde 2a with Alkynyliodonium Salt 9[a]

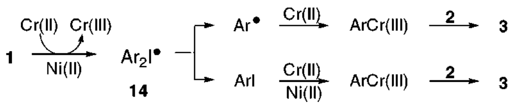
						product (10^2 mol)[b]				
entry	**9**[b] (mol)	$CrCl_2$[b] (mol)	$NiCl_2$[b] (mol)	solvent	conditions time/h	**10**[c]	**11**[c]	**12**[d]	**13**[d]	PhI[d]
1	1	2	0.01	DMF	5	29	5	29	12	100
2	2	4	0	DMF	5	63	6	31	0	184
3	2	4	0.02	DMF	5	59	4	80	0	186
4	1	2	0.01	DMSO	5	17	0	42	3	89
5	1	2	0.01	THF	5	0	0	32	12	75
6	1	2	0.01	PhH	30	0	0	8	50	80
7	1	2	0.01	CH_2Cl_2	30	0	0	3	80	83
8	1	2	0.01	MeOH	30	0	0	85	02	86

[a] Reactions were carried out using 0.3 mmol of benzaldehyde (**2a**) in DMF at 25 °C under Ar. [b] Molar ratios per mol of **2a**. [c] Isolated yields. [d] GC yields.

Scheme 7



Scheme 8



Scheme 9

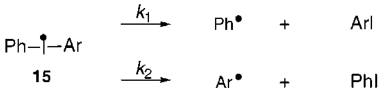
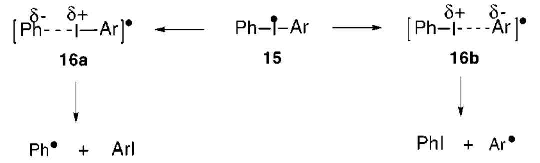


Table 6. Relative Ratios of Rate Constants k_2/k_1 for Decomposition of 15

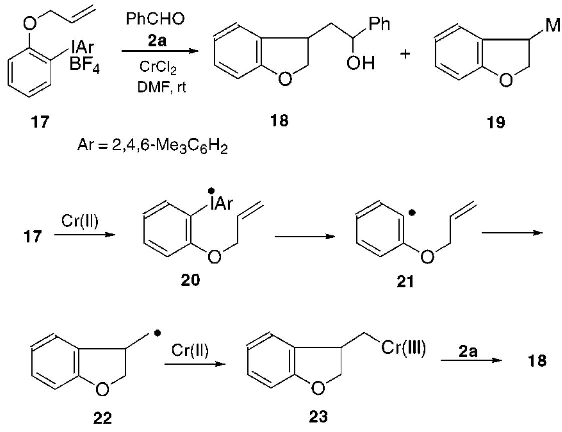
reagent	conditions	*p*-MeO	*p*-Me	*p*-Cl
Cr(II)[a]	DMF/25 °C	0.24	0.39	2.42
PhONa[b]	H_2O/60 °C	0.093	0.30	—[c]
t-$Bu_2NO^{\bullet}$[b]	$h\nu$/H_2O/60 °C	0.10	0.34	—[c]
Ph_3P[d]	$h\nu$/acetone/25 °C	0.61	0.85	—[c]

[a] This work. [b] Reference 17a. [c] —: not determined. [d] Reference 17b.

Scheme 10



Scheme 11



Use of a radical inhibitor 1,1-diphenylethylene, being an efficient phenyl radical trap,[27] showed negligible effects on the product profiles for the coupling of **1a** with **2a** (compare Table 1, entries 1 and 3), which suggests that the rate of reduction of phenyl radical with Cr(II) is faster than that of intermolecular addition to the double bond of 1,1-diphenylethylene. Intervention of aryl radicals was firmly established by the following intramolecular radical trapping method (Scheme 11).[28] Exposure of (*o*-allyloxyphenyl)mesityliodonium salt **17** to $CrCl_2$ (3 equiv) in the presence of benzaldehyde (**2a**) (1 equiv) at room temperature in DMF afforded a diastereomeric mixture of the cyclized alcohol **18** (16%) in a ratio of 3:1 and the cyclized reduced product, 3-methyl-2,3-dihydrobenzofuran (**19**) (9%).[21] Increased amounts (24%) of **19** were obtained when the reaction was carried out in DMF–H_2O (4:1). Use of 5 equiv of **2a** in DMF afforded the dihydrobenzofuran **18** in 47% yield.[29]

Dihydrobenzofuran **18** can be produced via intramolecular 5-exo cyclization of the aryl radical **21**, derived from the selective collapse of iodanyl radical **20**. Association of the cyclized alkyl radical **22** with Cr(II) followed by the reaction with benzaldehyde (**2a**) gives **18**. The aryl radical **21** undergoes 5-exo cyclization with the first-order rate constant of 5.3 × 10^9 s^{-1} at 25 °C.[30] The fact that there is no formation of the uncyclized products derived from the radical **21** clearly indicates that the association of the radical **21** with Cr(II) yielding the corresponding arylchromium(III) species will not be able to compete with this rapid 5-exo cyclization.[31]

B. Alkenyl(aryl)iodonium Salt. The chromium-mediated alkenylation of an aldehyde **2** with alkenyl(aryl)iodonium salts **5** competes with the arylation. This

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(27) (a) Barton, D. H. R.; Finet, J.-P.; Giannotti, C.; Halley, F. *J. Chem. Soc., Perkin Trans. 1* **1987**, 241. (b) Lubinkowski, J. J.; Knapczyk, J. W.; Calderon, J. L.; Petit, L. R.; McEwen, W. E. *J. Org. Chem.* **1975**, *40*, 3010. (c) Lubinkowski, J. J.; Arrieche, C. G.; McEwen, W. E. *J. Org. Chem.* **1980**, *45*, 2076. (d) Weldon, D.; Holland, S.; Scaiano, J. C. *J. Org. Chem.* **1996**, *61*, 8544.

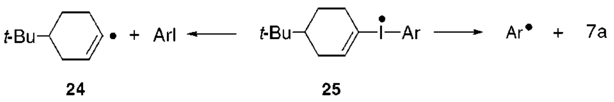
(28) (a) Meijs, G. F.; Beckwith, A. L. J. *J. Am. Chem. Soc.* **1986**, *108*, 5890. (b) Molander, G. A.; Harring, L. S. *J. Org. Chem.* **1990**, *55*, 6171. (c) Curran, D. P.; Totleben, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 6050.

(29) No formation of dihydrobenzofurans was observed in the attempted radical cyclizations of **17** using tetrathiafulvalene as an electron donor. See: Lampard, C.; Murphy, J. A.; Lewis, N. *J. Chem. Soc., Chem. Commun.* **1993**, 295.

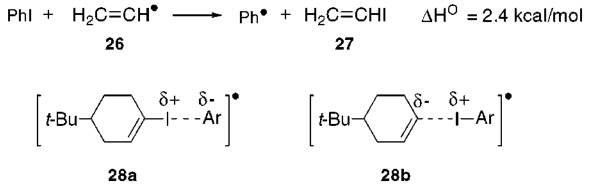
(30) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925.

(31) The rate constant for association of 5-hexenyl radical with Cr(II) is evaluated to be 4 ×10^7 M^{-1} s^{-1} at 25 °C in DMF–H_2O. See: Kochi, J. K.; Powers, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 137.

Scheme 12



Scheme 13

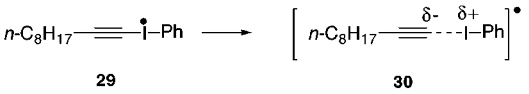


reaction also involves intervention of the [9-I-2] iodanyl radical via a single-electron transfer form Cr(II) analogous to the reaction with diaryliodonium salts **1**. As illustrated in Scheme 12, decomposition of the iodanyl radical **25** derived from **5a** could produce both the cyclohexenyl radical **24** and an aryl radical. The former will result in formation of allyl alcohols **6** via the reaction with aldehydes whereas the latter will yield the alcohols **3**.

It is known that a combination of the simple vinyl radical **26** and iodobenzene is more stable than that of phenyl radical with vinyl iodide **27** (Scheme 13).[3a,32] The stabilization energy ($SE^\circ = -6.16$ kcal/mol) of the vinyl radical **26** is larger than that of the phenyl radical (-10.27 kcal/mol).[33] These thermochemical data would predict a larger extent of alkenylation than phenylation in the reaction of **5aa** and **5ca** with benzaldehyde (**2a**), which is contrary to the results shown in Table 3, entries 1 and 6. The polar transition state **28** (Ar = Ph) with partial charge separation, as was discussed for decomposition of the unsymmetrical diaryliodanyl radicals **15**, explains the selectivity for cleavage of phenyl−iodine over vinyl−iodine bonds of **25** (Ar = Ph). The polar transition state **28a** (Ar = Ph) might be energetically more favorable than the alternative **28b** (Ar = Ph) because the negative charge developed will be more effectively stabilized by the phenyl group than by the vinyl group. The fact that phenyl carbanion is slightly more stable than ethenyl carbanion is compatible with this hypothesis,[34] since replacement of an α-hydrogen of a carbanion with an alkyl group is known to decrease the stability. When electron-donating groups were introduced to the aryl moiety of **5a**, the energy of the transition state **28a** will be increased, and therefore, cleavage of the vinyl−iodine bond of **25** leading to the formation of allyl alcohol **6a** becomes more favored. The results in Table 3 (entries 2 and 3) probably reflect this substituent effect.

Extensive cleavage of phenyl−iodine over vinyl−iodine bonds was observed in the reaction of (*E*)-1-decenyl(phenyl)iodonium salt **5ca**, whereas β-halo **5ea** and **5fa** and β-benzenesulfonyl derivatives **5ga** showed reversed selectivity (Table 3, entries 6 and 9−11). These electron-withdrawing β-substituents stabilize the negative charge developed at the vinylic carbon in the polar transition state, which in turn results in predominant cleavage of the vinyl−iodine bond. Formation of a large amount of 1-decyne in the reaction of **5ea**, **5fa**, and **5ga** is probably due to the facile concerted or stepwise syn β-elimination of the corresponding iodanyl radicals.

Scheme 14



C. Alkynyl(aryl)iodonium Salt. Reaction of 1-decynyl(phenyl)iodonium salt **9** with benzaldehyde (**2a**) showed high selectivity for alkynylation yielding the propargyl alcohol **10**. No formation of benzhydrol (**3a**) was observed (Table 5). Formation of a large amount of iodobenzene also suggests the selective cleavage of alkynyl−iodine bond of **9**. Intervention of the polar transition state **30** generating an alkynyl radical may be compatible with these experimental results. The selective generation of 1-decynyl radical from **29** (Scheme 14), however, seems to be very difficult, because it has been shown that an alkynyl radical is a highly energetic species, with a stabilization energy of $SE^\circ = -15.57$ kcal/mol for $HC{\equiv}C^\bullet$.[33,35]

When Cr-mediated coupling of **9** with **2a** was performed in DMF-d_7, GC−MS analysis showed only 7% deuterium incorporation in the byproduct 1-decyne (**12**), while in MeOD the reaction revealed 98% deuterium incorporation at the terminal position. These results may constitute an evidence for the generation of 1-decynylchromium(III) but not for the intervention of 1-decynyl radical. Alkynyl radicals might selectively abstract the α-hydrogen of MeOD because the dissociation energy (94.55 kcal/mol) of the C−H bond of methanol is smaller than that of the O−H bond (103 kcal/mol).[36] It has been reported that photochemical decomposition of (3,3-dimethyl-1-butynyl)(phenyl)iodonium tosylate in ethanol generates, via a single-electron transfer, the corresponding 9-I-2 iodanyl radical, which undergoes cleavage of the phenyl−iodine bond with high selectivity and affords a mixture of 3,3-dimethyl-1-iodo-1-butyne and iodobenzene in a ratio of 84:16.[37,38] This selectivity is quite different from those shown in Table 5. Therefore, it seems reasonable to assume that generation and decomposition of 9-I-2 iodanyl radical **29** to produce 1-decynyl radical is not a significant process in the reaction of 1-decynyliodonium salt **9** with $CrCl_2$.

It has been generally accepted that one of the most common modes of the reactions of alkynyliodonium salts with nucleophiles involves the Michael addition to the electron-deficient β-acetylenic carbon atom to generate alkylidenecarbenes via reductive elimination of the hyperleaving group.[11,40] This Michael−carbene pathway might account for the predominant formation of the propargyl alcohol **10** and iodobenzene.[41]

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[38] Similar selectivity for decomposition of 1-decynyl(phenyl)iodonium salt **9** was observed in the reduction with tetrakis(dimethylamino)ethylene,[39] which gave a mixture of 1-iodo-1-decyne (58%), iodobenzene (13%), 1-decyne (**12**) (37%), and benzene (46%). The reduction with triethylamine afforded a similar ratio of the products. These reactions probably involve the intervention of 9-I-2 iodanyl radical **29**.

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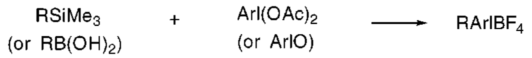
Scheme 15



$RSiMe_3$ (or $RB(OH)_2$) + $ArI(OAc)_2$ (or $ArIO$) $\longrightarrow$ $RArIBF_4$

Synthesis of Iodonium Salts. BF_3-Catalyzed silicon−iodine(III) exchange reaction of organosilanes with (diacetoxyiodo)arenes or iodosylarenes constitutes a general method for synthesis of alkenyl(aryl)iodonium salts (Scheme 15).[3a,42] This reaction proceeds under mild conditions and in a stereospecific manner with retention of configuration of organosilanes. Thus, 4-*tert*-butylcyclohexenyl(aryl)iodonium tetrafluoroborates **5aa**−**5ac** were prepared from 4-*tert*-butyl-1-(trimethylsilyl)cyclohexene by reaction with iodosylarenes in the presence of $BF_3{\cdot}Et_2O$.[2,43] Similarly, reaction of 1-(trimethylsilyl)-cyclopentene, (*E*)-1-(trimethylsilyl)decene, and 2-butyl-1-(trimethylsilyl)hexene afforded 1-cyclopentenyliodonium salts **5ba** and **5bc**, (*E*)-1-decenyliodonium salts **5ca** and **5cc**, and 2-butyl-1-hexenyliodonium salt **5dc**, respectively. BF_3-Catalyzed borane−iodine(III) exchange of organoboronic acids with (diacetoxyiodo)arenes is an efficient alternative for the synthesis of iodonium salts;[44] (*E*)-β-styryl(mesityl)iodonium tetrafluoroborate (**5hc**) was obtained by the reaction of (*E*)-β-styrylboronic acid with 2,4,6-trimethyl(diacetoxyiodo)benzene in the presence of $BF_3{\cdot}Et_2O$. Symmetrical **1c** and unsymmetrical diaryliodonium salts **4c** and **4d** were prepared by the borane−iodine(III) exchange reaction. Similarly, reaction of *o*-allyloxyphenylboronic acid[45] with 2,4,6-trimethyl(diacetoxyiodo)benzene afforded the (*o*-allyloxyphenyl)-mesityliodonium salt **17**.

Conclusions

We have demonstrated that diaryliodonium salts react with $CrCl_2$ in DMF at room temperature to generate arylchromiun(III) species, which efficiently add to a variety of aldehydes to produce alcohols in good yields. In marked contrast to the reaction of aryl halides with $CrCl_2$, the activation of diaryliodonium salts by a nickel catalyst is not required in this reaction, probably because of the highly electron-deficient nature of these salts. Addition of a catalytic amount of $NiCl_2$ makes possible the use of both aryl moieties of diaryliodonium salts. Studies on substituent effects in the reaction of unsymmetrical diaryliodonium salts and intramolecular radical trapping experiments revealed that the Cr-mediated coupling of diaryliodonium salts with aldehydes would involve (1) reduction of the hypervalent iodine to generate iodanyl radical via a single-electron transfer, (2) unimolecular decomposition of the iodanyl radical via a polar transition state to produce both aryl radical and aryl iodide, and (3) association of the aryl radical with $CrCl_2$ to generate arylchromium(III), which reacts with aldehydes to give alcohols. The aryl iodide produced in situ also generates arylchromium(III) when a Ni catalyst is present.

In the Cr-mediated coupling of alkenyl(phenyl)iodonium salts with aldehydes, alkenylation and phenylation compete with each other; however, use of alkenyl(mesityl)iodonium salts gives the alkenylation product exclusively. Similarly, alkynyl(phenyl)iodonium salts selectively undergo alkynylation of aldehydes. This method of using aryl-, alkenyl-, and alkynyliodonium salts as their anion equivalents in the reaction with aldehydes represents the first example of reactivity umpolung of iodonium salts.

Experimental Section

General Methods. For general experimental details, see ref 2. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (Merck, silica gel F-254). Kieselgel 60 (Merck, 230−400 mesh) was used for flash chromatography. Anhydrous chromium dichloride was purchased form Kishida Chemical Co. The color should be gray. Any green color means low purity. Handling of this reagent must be carried out in drybox under nitrogen.

Synthesis of Iodonium Tetrafluoroborates via Silicon−Iodine(III) Exchange. A Representative Example. (4-*tert*-Butyl-1-cyclohexenyl)(2,4,6-trimethylphenyl)iodonium Tetrafluoroborate (5ac). To a stirred solution of iodosylmesitylene[46] (1.05 g, 4.0 mmol) and 4-*tert*-butyl-1-(trimethylsilyl)cyclohexene (840 mg, 4.0 mmol) in dichloromethane (30 mL) was added $BF_3{\cdot}Et_2O$ (570 mg, 4.0 mmol) at 0 °C in nitrogen, and the mixture was stirred for 1 h at 0 °C and for 17 h at room temperature. After addition of a saturated aqueous sodium tetrafluoroborate (80 mmol) solution, the mixture was stirred for 30 min. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was concentrated under aspirator vacuum to give an oil, which was washed several times with hexane−diethyl ether by decantation at −78 °C. Recrystallization from hexane−dichloromethane gave the vinyliodonium salt **5ac** (707 mg, 38%) as a colorless powder: mp 113−114 °C; IR ($CHCl_3$) 1217, 1029, 774, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.13 (s, 2H), 6.73 (m, 1H), 2.61 (s, 6H), 2.60−2.10 (m, 3H), 2.38 (s, 3H), 2.00−1.88 (m, 1H), 1.70−1.30 (m, 3H), 0.84 (s, 9H); FAB MS *m/z* 383 $[(M - BF_4)^+]$. Anal. Calcd for $C_{19}H_{28}BF_4I$: C, 48.54; H, 6.00. Found: C, 48.28; H, 5.92.

(1-Cyclopentenyl)(2,4,6-trimethylphenyl)iodonium tetrafluoroborate (5bc): 25%; pale brown crystals; mp 110−111 °C (recrystallized from hexane-dichloromethane); IR ($CHCl_3$) 1216, 1063, 1024, 765, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.12 (s, 2H), 6.70 (br s, 1H), 2.75−2.55 (4H), 2.62 (s, 6H), 2.37 (s, 3H), 2.05 (quint, J = 7.5 Hz, 2H); HRMS (FAB) calcd for $C_{14}H_{18}I$ $[(M - BF_4)^+]$ 313.0453, found 313.0432.

(*E*)-(1-Decenyl)(2,4,6-trimethylphenyl)iodonium tetrafluoroborate (5cc): 42%; colorless amorphous solids; IR ($CHCl_3$) 1216, 1063, 1024, 769, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ

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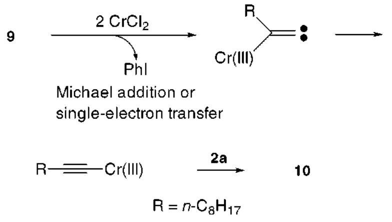
(41) There is no available data on the nucleophilicity of $CrCl_2$ and no evidence supporting this mechanism, but intervention of alkynylchromium(IV) species have been proposed in the reaction of alkynyl iodides with $CrCl_2$.[19] Generation of α-chromium(III) alkylidenecarbenes by the reaction of **9** with 2 molar equiv of $CrCl_2$ via a single-electron transfer is a possible alternative.



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7.13 (s, 2H), 6.56 (d, $J = 13.7$ Hz, 1H), 6.35 (dt, $J = 13.7$, 6.8 Hz 1H), 2.61 (s, 6H), 2.37(s, 3H), 2.25 (q, $J = 6.8$ Hz, 2H), 1.45−1.15 (m, 12H), 0.87 (t, $J = 6.4$ Hz, 3H); HRMS (FAB) calcd for $C_{19}H_{30}I$ [$(M - BF_4)^+$] 385.1392, found 385.1418.

(2-Butyl-1-hexenyl)(2,4,6-trimethylphenyl)iodonium tetrafluoroborate (5dc): 55%; colorless needles; mp 67−68 °C (recrystallized from hexane-dichloromethane); IR ($CHCl_3$) 1215, 780, 741 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.10 (s, 2H), 6.18 (s, 1H), 2.63 (s, 6H), 2.45−2.30 (7H), 1.55−1.20 (m, 8H), 0.97−0.83 (6H); HRMS (FAB) calcd for $C_{19}H_{30}I$ [$(M - BF_4)^+$] 385.1392, found 385.1386. Anal. Calcd for $C_{19}H_{30}BF_4I\cdot{}^1/_2H_2O$: C, 47.42; H, 6.49. Found: C, 47.45; H, 6.26.

(4-*tert*-Butyl-1-cyclohexenyl)phenyliodonium tetrafluoroborate (**5aa**),[2] (4-*tert*-butyl-1-cyclohexenyl)(*p*-methoxyphenyl)iodonium tetrafluoroborate (**5ab**),[3g] (1-cyclopentenyl)phenyliodonium tetrafluoroborate (**5ba**),[3g] and (*E*)−(1-decenyl)phenyliodonium tetrafluoroborate (**5ca**)[3b] were prepared similarly by the silicon−iodine(III) exchange reaction.

Synthesis of Iodonium Tetrafluoroborates via Borane−Iodine(III) Exchange. A Representative Example. (2-(2-Propenyloxy)phenyl)(2,4,6-trimethylphenyl)iodonium Tetrafluoroborate (17). To a stirred mixture of *o*-allyloxyphenyl boronic acid[45] (187 mg, 1.05 mmol) and $BF_3\cdot Et_2O$ (156 mg, 1.10 mmol) in dichloromethane (10 mL) was added a solution of 2,4,6-trimethyl(diacetoxyiodo)benzene[46] (364 mg, 1.0 mmol) in dichloromethane (10 mL) at 0 °C in nitrogen, and the mixture was stirred for 1.5 h at 0 °C. After the addition of a saturated aqueous sodium tetrafluoroborate (20 mmol) solution, the mixture was stirred for 30 min. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was concentrated under aspirator vacuum to give a solid residue, which was washed several times with diethyl ether by decantation at −78 °C. Recrystallization from diethyl ether−dichloromethane gave the vinyliodonium salt **17** (407 mg, 87%) as pale yellow crystals: mp 168−170 °C; IR ($CHCl_3$) 1216, 1024, 759, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.54 (br t, $J = 7.7$ Hz, 1H), 7.17 (s, 2H), 7.16−6.93 (m, 3H), 6.12−5.90 (m, 1H), 5.45−5.33 (2H), 4.77 (d, $J = 7.7$ Hz, 2H), 2.60 (s, 6H), 2.39 (s, 3H); HRMS (FAB) calcd for $C_{18}H_{20}IO$ [$(M - BF_4)^+$] 379.0559, found 379.0544. Anal. Calcd for $C_{18}H_{20}BF_4IO$: C, 46.39; H, 4.33. Found: C, 46.09; H, 4.24.

(4-Methylphenyl)phenyliodonium tetrafluoroborate (4c): 83%; pale brown prisms; mp 128−129 °C (recrystallized from hexane−dichloromethane); IR ($CHCl_3$) 1218, 1067, 1026, 774, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.00 (br d, $J = 7.5$ Hz, 2H), 7.92 (d, $J = 8.5$ Hz, 2H), 7.61 (br t, $J = 7.5$ Hz, 1H), 7.45 (br t, $J = 7.5$ Hz, 2H), 7.27 (d, $J = 8.5$ Hz, 2H), 2.40 (s, 3H); FAB MS *m/z* 295 [$(M - BF_4)^+$]. Anal. Calcd for $C_{13}H_{12}BF_4I$: C, 40.88; H, 3.17. Found: C, 41.02; H, 3.16.

(4-Chlorophenyl)phenyliodonium tetrafluoroborate (4d): 73%; colorless crystals; mp 113−115 °C (recrystallized from hexane−dichloromethane); IR ($CHCl_3$) 1216, 1070, 1028, 759, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.04 (br d, $J = 7.5$ Hz, 2H), 7.98 (br d, $J = 8.8$ Hz, 2H), 7.62 (br t, $J = 7.5$ Hz, 1H), 7.48−7.32 (4H); FAB MS *m/z* 315 [$(M - BF_4)^+$]. Anal. Calcd for $C_{12}H_9BClF_4I$: C, 35.82; H, 2.25. Found C, 35.75; H, 2.34.

(*E*)-(*β*-Styryl)(2,4,6-trimethylphenyl)iodonium tetrafluoroborate (5hc): 59%; pale brown prisms; mp 177−178 °C (recrystallized from hexane-dichloromethane); IR ($CHCl_3$) 1216, 1030, 770, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40−7.10 (9H), 2.66 (s, 6H), 2.39 (s, 3H); FAB MS *m/z* 349 [$(M - BF_4)^+$]. Anal. Calcd for $C_{17}H_{18}BF_4I$: C, 46.83; H, 4.16. Found: C, 46.82; H, 4.12.

Bis(4-methylphenyl)iodonium tetrafluoroborate (**1c**)[47] was prepared similarly in 83% yield by the borane−iodine(III) exchange reaction.

Synthesis of Phenyl(2,4,6-trimethylphenyl)iodonium Tetrafluoroborate (4b). The unsymmetrical diaryliodonium salt **4b** was prepared in 84% yield by Friedel−Crafts-type condensation between (diacetoxyiodo)benzene and mesitylene in acetic acid−acetic anhydride in the presence of sulfuric acid, according to the procedure developed by Beringer.[48] **4b**: colorless needles; mp 209−210 °C (recrystallized from hexane−dichloromethane); IR ($CHCl_3$) 1216, 1075, 1031, 778, 744, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.69 (br d, $J = 7.5$ Hz, 2H), 7.54 (br t, $J = 7.5$ Hz, 1H), 7.42 (br t, $J = 7.5$ Hz, 2H), 7.12 (s, 2H), 2.64 (s, 6H), 2.36 (s, 3H); FAB MS *m/z* 323 [$(M - BF_4)^+$]. Anal. Calcd for $C_{15}H_{16}BF_4I$: C, 43.94; H, 3.93. Found: C, 43.93; H, 3.94.

(4-Methoxyphenyl)phenyliodonium tetrafluoroborate (**4a**)[49] was prepared in a similar manner. Bis(4-chlorophenyl)iodonium tetrafluoroborate (**1b**)[47] was prepared by coupling of chlorobenzene with iodyl sulfate in sulfuric acid.[50] Michael addition of acids to 1-decynyl(phenyl)iodonium tetrafluoroborate (**9**)[51] gave *β*-chloro- **5ea**,[52] *β*-bromo- **5fa**,[52] and *β*-(phenylsulfonyl)vinyliodonium tetrafluoroborates **5ga**[40b] in good yields.

General Procedure for Chromium-Mediated Arylation of Aldehydes 2 with Diaryliodonium Tetrafluoroborates 1. To a stirred emerald green solution of anhydrous $CrCl_2$ (148 mg, 1.2 mmol) and $NiCl_2$ (0.8 mg, 0.006 mmol) in dry DMF (4 mL) was added a solution of an diaryliodonium tetrafluoroborate **1** (0.3 mmol) and an aldehyde **2** (0.3 mmol) in DMF (1 mL) under argon at room temperature, and the solution was stirred for 5 h. The reaction mixture was quenched with water and extracted with diethyl ether. The combined organic extracts were washed with water and brine. The organic layer was filtered and dried over anhydrous sodium sulfate. The yields of arenes and iodoarenes were determined by analytical GC (decane or tetradecane as the internal standard). Purification with preparative TLC (hexane−ethyl acetate) gave pure products **3**. The yields of pure products are given in Table 1.

Diphenylmethanol (3a): colorless prisms; mp 69 °C (recrystallized from dichloromethane−hexane, lit.[53] mp 69 °C); ^1H NMR ($CDCl_3$) δ 7.42−7.2 (m, 10H), 5.85 (s, 1H), 2.25 (s, 1H).

(4-Chlorophenyl)phenylmethanol (3b): colorless needles; mp 59−61 °C (recrystallized from dichloromethane−hexane, lit.[54] mp 59 °C); ^1H NMR ($CDCl_3$) δ 7.40−7.27 (m, 9H), 5.81 (s, 1H), 2.24 (br s, 1H); HRMS calcd for $C_{13}H_{11}ClO$ (M^+) 218.0498, found 218.0501.

(4-Methylpheny)phenylmethanol (3c): colorless needles; mp 52 °C (recrystallized from dichloromethane−hexane, lit.[55] mp 52−53 °C); ^1H NMR ($CDCl_3$) δ 7.40−7.10 (9H), 5.80 (s, 1H), 2.32 (s, 3H), 2.20 (br s, 1H); HRMS calcd for $C_{14}H_{14}O$ (M^+) 198.1045, found 198.1036.

(4-Methoxyphenyl)phenylmethanol (3d):[56] mp 95 °C (recrystallized from dichloromethane−hexane); ^1H NMR ($CDCl_3$) δ 7.40−7.21 (m, 7H), 6.86 (d, $J = 7.8$ Hz, 2H), 5.80 (br s, 1H), 3.78 (s, 3H), 2.20 (br s, 1H); HRMS calcd for $C_{14}H_{14}O_2$ (M^+) 214.0994, found 214.0982.

(2-Methylphenyl)phenylmethanol (3e): colorless prisms; mp 95 °C (recrystallized from dichloromethane−hexane, lit.[57] mp 95 °C); ^1H NMR ($CDCl_3$) δ 7.56−7.49 (m, 1H), 7.37−7.09 (m, 8H), 6.00 (br s, 1H), 2.25 (s, 3H), 2.13 (1H); HRMS calcd for $C_{14}H_{14}O$ (M^+) 198.1045, found 198.1042.

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1-Phenyl-1-undecanol (3f):[58] colorless oil; ^{1}H NMR (CDCl$_3$) δ 7.36−7.26 (m, 5H), 4.66 (t, J = 6.8 Hz, 1H), 1.85−1.70 (m, 3H), 1.25 (m, 16H), 0.88 (t, J = 6.5 Hz, 3H); HRMS calcd for $C_{17}H_{28}O$ (M^+) 248.2140, found 248.2130.

2-Methyl-1-phenyl-1-propanol (3g):[59] colorless oil; ^{1}H NMR (CDCl$_3$) δ 7.40−7.20 (m, 5H), 4.36 (d, J = 6.6 Hz, 1H), 1.96 (octet, J = 6.6 Hz, 1H), 1.88 (br s, 1H), 1.00 (d, J = 6.6 Hz, 3H), 0.80 (d, J = 6.6 Hz, 3H); HRMS calcd for $C_{10}H_{14}O$ (M^+) 150.1045, found 150.1038.

(*E*)-1-Phenyl-2-buten-1-ol (3i):[60] colorless oil; ^{1}H NMR (CDCl$_3$) δ 7.41−7.20 (m, 5H), 5.88−5.60 (m, 2H), 5.15 (d, J = 5.1 Hz, 1H), 1.87 (br s, 1H), 1.72 (d, J = 5.1 Hz, 3H); HRMS calcd for $C_{10}H_{12}O$ (M^+) 148.0888, found 148.0892.

(*E*)-1,3-Diphenyl-2-propen-1-ol (3j):[61] colorless oil; ^{1}H NMR (CDCl$_3$) δ 7.48−7.19 (m, 10H), 6.69 (d, J = 16 Hz, 1H), 6.38 (dd, J = 16, 6.4 Hz, 1H), 5.38 (d, J = 6.4 Hz, 1H), 2.1 (br s, 1H); HRMS calcd for $C_{15}H_{14}O$ (M^+) 210.1045, found 210.0974.

Chromium-Mediated Coupling of Hexanoyl Chloride with Diphenyliodonium Tetrafluoroborate (1a). To a stirred solution of CrCl$_2$ (83 mg, 0.67 mmol) doped with NiCl$_2$ (0.5 mol %) in dry DMF (2 mL) was added a solution of diphenyliodonium tetrafluoroborate (**1a**) (62 mg, 0.17 mmol) and hexanoyl chloride (23 mg, 0.17 mmol) in DMF (0.5 mL) under argon at room temperature, and the solution was stirred for 5 h. The reaction mixture was quenched with water and extracted with diethyl ether. The combined organic extracts were washed with water and brine. The organic layer was filtered, dried over anhydrous sodium sulfate, and concentrated to give an oil, which was purified by preparative TLC (hexane−ethyl acetate (10:1)) to give hexanophenone (6.7 mg, 23%), benzophenone (1.3 mg, 4%), benzhydrol (**3a**) (2.4 mg, 8%), and *N*,*N*-dimethylhexanamide (2.2 mg, 9%). Hexanophenone: colorless oil; ^{1}H NMR (CDCl$_3$) δ 7.96 (d, J = 7 Hz, 2H), 7.60−7.40 (m, 3H), 2.97 (t, J = 7.6 Hz, 2H), 1.75 (m, 2H), 1.36 (m, 4H), 0.91 (t, J = 6.6 Hz, 3H). *N*,*N*-Dimethylhexanamide: colorless oil; ^{1}H NMR (CDCl$_3$) δ 3.01 (s, 3H), 2.94 (s, 3H), 2.31 (t, J = 7.3 Hz, 2H), 1.63 (m, 2H), 1.32 (m, 4H), 0.90 (t, J = 6.5 Hz, 3H).

Representative Procedure for Chromium-Mediated Coupling of Aldehydes 2 with Alkenyl(aryl)iodonium Tetrafluoroborates 5 (Table 3, Entry 1). To a stirred emerald green solution of anhydrous CrCl$_2$ (47 mg, 0.38 mmol) in dry DMF (1 mL) was added a solution of 4-*tert*-butylcyclohexenyl(phenyl)iodonium tetrafluoroborate (**5aa**) (46 mg, 0.09 mmol) and benzaldehyde (**2a**) (10 mg, 0.09 mmol) in DMF (0.3 mL) under argon at room temperature, and the solution was stirred for 5 h. The reaction mixture was quenched with water and extracted with diethyl ether. The combined organic extracts were washed with water and brine. The organic layer was filtered and dried over anhydrous sodium sulfate. The yield (39%) of iodobenzene was determined by analytical GC (tetradecane as the internal standard). Purification with preparative TLC (hexane−ethyl acetate (10:1)) gave a diastereomeric mixture (6:4) of 4-*tert*-butyl-1-(hydroxy(phenyl)-methyl)-1-cyclohexene (**6a**) (8.1 mg, 35%) as a colorless oil, benzhydrol (**3a**) (7.4 mg, 43%), and 4-*tert*-butyl-1-iodo-1-cyclohexene (**7a**) (15.1 mg, 61%). **6a**:[62] IR (CHCl$_3$) 3575, 1360 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.40−7.26 (m, 5H), 5.89−5.84 (m, 1H), 5.14 (s, 0.4H), 5.09 (s, 0.6H), 2.26−2.0 (m, 1H), 1.95−1.70 (m, 4H), 1.56 (s, 1H), 1.34−1.0 (m, 2H), 0.85 (s, 9H); MS *m*/*z* (relative intensity) 244 (100, M^+), 187 (15), 105 (98); HRMS calcd for $C_{17}H_{24}O$ (M^+) 244.1827, found 244.1810. **7a**:[63] ^{1}H NMR (CDCl$_3$) δ 6.37−6.28 (m, 1H), 2.60−2.48 (m, 2H) 2.2−1.2 (m, 5H), 0.85 (s, 9H).

1-(Hydroxy(phenyl)methyl)-1-cyclopentene (6b):[64] colorless oil; ^{1}H NMR (CDCl$_3$) δ 7.40−7.24 (m, 5H), 5.69 (br s, 1H), 5.33 (s, 1H), 2.40−2.15 (m, 5H), 1.98−1.78 (m, 2H).

(*E*)-1-Phenyl-2-undecen-1-ol (6c): ^{1}H NMR (CDCl$_3$) δ 7.44−7.20 (m, 5H), 5.78 (dt, J = 15.0, 6.9 Hz, 1H), 5.66 (dd, J = 15.0, 6.2 Hz, 1H), 5.18 (d, J = 6.2 Hz, 1H), 2.12−2.0 (m, 2H), 1.90−1.80 (1H), 1.45−1.20 (12H), 0.88 (t, J = 6.6 Hz, 3H); MS *m*/*z* (relative intensity) 246 (53, M^+), 133 (100), 120 (76), 105 (58); HRMS calcd for $C_{17}H_{26}O$ (M^+) 246.1984, found 246.1952. The alcohol **6c** was contaminated with a small amount of impurities.

3-Butyl-1-phenyl-2-hepten-1-ol (6d): colorless oil; IR (CHCl$_3$) 3600, 1660 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.41−7.21 (m, 5H), 5.49 (d, J = 8.6 Hz, 1H), 5.39 (d, J = 8.6 Hz, 1H), 2.25−2.10 (m, 2H), 2.10−1.95 (m, 2H), 1.70 (s, 1H), 1.52−1.17 (m, 8H), 0.92 (t, J = 6.6 Hz, 3H), 0.89 (t, J = 6.6 Hz, 3H); MS *m*/*z* (relative intensity) 246 (6, M^+),189 (100), 129 (11); HRMS calcd for $C_{17}H_{26}O$ (M^+) 246.1984, found 246.1983.

(*Z*)-1-Phenyl-3-phenylsulfonyl-2-uncecen-1-ol (6g): colorless oil; IR (CHCl$_3$) 3590, 1305, 1152, 780, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.9−7.8 (m, 2H), 7.65−7.48 (m, 3H), 7.38 (5H), 7.08 (d, J = 7.5 Hz, 1H), 5.45 (d, J = 7.5 Hz, 1H), 2.41−2.2 (m, 2H), 2.10 (br s, 1H), 1.45−1.0 (12H), 0.87 (t, J = 6.6 Hz, 3H); MS *m*/*z* (relative intensity) 386 (2, M^+), 281 (70), 245 (100), 143 (90), 107 (100), 79 (80); HRMS calcd. for $C_{23}H_{30}O_3S$ (M^+) 386.1916, found 386.1943.

4-*tert*-Butyl-1-(hydroxy(4-chlorophenyl)methyl)-1-cyclohexene (6i): a 6:4 mixture of diastereoisomers; colorless oil; IR (CHCl$_3$) 3600, 1380, 1100 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.29 (s, 4H), 5.84 (m, 1H), 5.10 (s, 0.4H), 5.07 (s, 0.6H), 2.23−1.95 (m, 1H), 1.95−1.70 (m, 5H), 1.34−1.0 (m, 2H), 0.85 (s, 9H); MS *m*/*z* (relative intensity) 278 (55, M^+), 203 (49), 139 (100); HRMS calcd for $C_{17}H_{23}ClO$ (M^+) 278.1437, found 278.1424.

4-*tert*-Butyl-1-(hydroxy(4-methylphenyl)methyl)-1-cyclohexene (6j): a 6:4 mixture of diastereoisomers; colorless oil; IR (CHCl$_3$) 3600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.25−7.10 (4H), 5.84 (m, 1H), 5.07 (s, 0.4H), 5.04 (s, 0.6H), 2.34 (s, 3H), 2.22−1.98 (m, 1H), 1.95−1.70 (m, 5H), 1.34−1.0 (m, 2H), 0.85 (s, 9H); MS *m*/*z* (relative intensity) 258 (55, M^+), 243 (51), 134 (40), 119 (100); HRMS calcd for $C_{18}H_{26}O$ (M^+) 258.1984, found 258.1978.

4-*tert*-Butyl-1-(1-hydroxy-2-methylpropyl)-1-cyclohexene (6k): a 6:4 mixture of diastereoisomers; colorless oil; IR (CHCl$_3$) 3600, 1370, 1005 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.76−5.58 (1H), 3.63 (d, J = 6.8 Hz, a minor isomer), 3.57 (d, J = 7.5 Hz, a major isomer), 2.30−1.04 (m, 9H), 1.0 (d, J = 6.8 Hz, a major isomer), 0.95 (d, J = 6.8 Hz, a minor isomer), 0.89 (s, 9H), 0.83 (d, J = 6.8 Hz, a minor isomer), 0.80 (d, J = 6.8 Hz, a major isomer); MS *m*/*z* (relative intensity) 210 (7, M^+), 192 (37), 167 (100), 135 (95); HRMS calcd for $C_{14}H_{26}O$ (M^+) 210.1984, found 210.1975.

(*E*)-4-*tert*-Butyl-1-(1-hydroxy-2-butenyl)-1-cyclohexene (6l): colorless oil; IR (CHCl$_3$) 3600, 1370, 980 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.80−5.43 (m, 3H), 4.45 (d, J = 6.8 Hz,1H), 2.22−1.75 (m, 5H), 1.72 (d, J = 6.5 Hz, 3H), 1.34−1.0 (m, 2H), 0.87 (s, 9H); MS *m*/*z* (relative intensity) 208 (78, M^+), 193 (60), 151 (93), 133 (98), 91 (96), 69 (100); HRMS calcd for $C_{14}H_{24}O$ (M^+) 208.1827, found 208.1834.

4-*tert*-Butyl-1-(1-hydroxydecanyl)-1-cyclohexene (6m): colorless oil; IR (CHCl$_3$) 1380 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.63 (m, 1H), 3.97 (t, J = 6 Hz, 1H), 2.30−1.10 (m, 24H), 0.87 (12H); MS *m*/*z* (relative intensity) 294 (27, M^+), 167 (100), 149 (57), 123 (25), 93 (31); HRMS calcd for $C_{20}H_{38}O$ (M^+) 294.2923, found 294.2922.

(*E*)-1-Iodo-1-decene (7c):[3b] ^{1}H NMR (CDCl$_3$) δ 6.51 (dt, J = 14.4, 7.1 Hz, 1H), 5.97 (d, J = 14.4 Hz, 1H), 2.05 (q, J = 7.1 Hz, 2H), 1.50−1.15 (m, 12H), 0.88 (t, J = 6.6 Hz, 3H).

1-Iodo-2-butyl-1-hexene (7d): ^{1}H NMR (CDCl$_3$) δ 5.85 (s, 1H), 2.25−2.12 (m, 4H), 1.50−1.20 (m, 8H), 0.95 (t, J = 6.6 Hz, 3H), 0.90 (t, J = 6.6 Hz, 3H).

(*Z*)-2-Chloro-1-iodo-1-decene (7e):[3e] ^{1}H NMR (CDCl$_3$) δ 6.41 (s, 1H), 2.49 (t, J = 7.3 Hz, 2H), 1.64−1.19 (m, 12H), 0.88 (t, J = 6.5 Hz, 3H).

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(*Z*)-2-Bromo-1-iodo-1-decene (7f):[3e] ^{1}H NMR ($CDCl_3$) δ 6.82 (s, 1H), 2.57 (t, $J = 7.3$ Hz, 2H), 1.64−1.20 (m, 12H), 0.88 (t, $J = 6.6$ Hz, 3H).

(*E*)-4-*tert*-Butyl-1-(3-hydroxy-1-butenyl)-1-cyclohexene (8): colorless oil; IR ($CHCl_3$) 2940, 1370 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.20 (d, $J = 16$ Hz, 1H), 5.76 (m, 1H), 5.58 (dd, $J = 16$, 6.6 Hz, 1H), 4.35 (m, 1H), 2.40−1.80 (m, 5H), 1.4−1.05 (m, 2H), 1.30 (d, $J = 6.4$ Hz, 3H), 0.88 (s, 9H); MS *m*/*z* (relative intensity) 208 (19, M$^+$), 190 (40), 133 (100); HRMS calcd for $C_{14}H_{24}O$ (M$^+$) 208.1827, found 208.1823.

Representative Procedure for Chromium-Mediated Coupling of Aldehyde 2a with 1-Decynyl(phenyl)iodonium Tetrafluoroborate (9) (Table 5, Entry 2). To a stirred emerald green solution of $CrCl_2$ (148 mg, 1.2 mmol) in dry DMF (3 mL) was added a solution of 1-decynyliodonium tetrafluoroborate **9** (256 mg, 0.6 mmol) and benzaldehyde (**2a**) (32 mg, 0.3 mmol) in DMF (1 mL) under argon at room temperature, and the solution was stirred for 5 h. The reaction mixture was quenched with water and extracted with diethyl ether. The combined organic extracts were washed with water and brine. The organic layer was filtered and dried over anhydrous sodium sulfate. The yield (31%) of 1-decyne (**12**) was determined by analytical GC (tetradecane as the internal standard). Purification with preparative TLC (hexane−ethyl acetate (10:1)) gave 1-phenyl-2-undecyn-1-ol (**10**) (46 mg, 63%) and 1-phenyl-2-undecyn-1-one (**11**) (4.5 mg, 6%). **10**: colorless oil; IR ($CHCl_3$) 3575, 2200, 1640, 1270 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.60−7.50 (m, 2H), 7.45−7.25 (m, 3H), 5.48 (br s, 1H), 2.28 (dt, $J = 1.5$, 7.5 Hz, 2H), 2.11 (1H) 1.65−1.16 (m, 12H), 0.90 (t, $J = 6.5$ Hz, 3H); MS *m*/*z* (relative intensity) 244 (100, M$^+$), 145 (66), 105 (71), 77 (56); HRMS calcd for $C_{17}H_{24}O$ (M$^+$) 244.1827, found 244.1813. **11**: colorless oil; IR ($CHCl_3$) 2190, 1635, 1265 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.14 (br d, $J = 7.3$ Hz, 2H), 7.61 (br t, $J = 7.3$ Hz, 1H), 7.48 (br t, $J = 7.3$ Hz, 2H), 2.51 (t, $J = 7.0$ Hz, 2H), 1.80−1.20 (m, 12H), 0.89 (t, $J = 6.8$ Hz, 3H); MS *m*/*z* (relative intensity) 242 (3, M$^+$), 200 (26), 157 (30), 105 (100), 77 (40); HRMS calcd for $C_{17}H_{22}O$ (M$^+$) 242.1671, found 242.1707.

GC−MS Analysis of Byproduct Benzene in the Reaction of Aldehyde 2a with Diphenyliodonium Salt 1a in DMF-*d*$_7$. To a stirred solution of anhydrous $CrCl_2$ (48 mg, 0.39 mmol) doped with $NiCl_2$ (0.5 mol %) in dry DMF-*d*$_7$ (99.5% D, 0.5 mL) was added a solution of diphenyliodonium tetrafluoroborate (**1a**) (36 mg, 0.098 mmol) and aldehyde **2a** (10 mg, 0.098 mmol) in DMF- -*d*$_7$ (0.5 mL) under argon at room temperature, and the solution was stirred for 5 h. The reaction mixture was quenched with water and extracted with diethyl ether. The combined organic extracts were washed with water and brine. The organic layer was filtered and dried over anhydrous sodium sulfate. GC−MS analysis of byproduct benzene was carried out using an FFS ULBON HR-1 capillary column (0.25 mm × 50 m, 50 °C). The abundances at *m*/*z* of 78 and 79 were analyzed. The percentage of deuterium isotopic composition of benzene-*d*$_1$ was found to be 20%.

Chromium-Mediated Reaction of Aldehyde 2a with (*o*-Allyloxyphenyl)mesityliodonium Salt 17. To a stirred solution of $CrCl_2$ (45 mg, 0.36 mmol) in DMF (1.5 mL) was added a solution of (*o*-allyloxyphenyl)mesityliodonium salt **17** (43 mg, 0.09 mmol) and benzaldehyde (**2a**) (10 mg, 0.09 mmol) in DMF (1 mL) under argon at room temperature, and the solution was stirred for 12 h. The reaction mixture was quenched with water and extracted with diethyl ether. The combined organic extracts were washed with water and brine. The organic layer was filtered, dried over anhydrous sodium sulfate, and concentrated to give an oil, which was purified by preparative TLC (hexane−ethyl acetate (5:1)) to give a diastereomeric mixture (3:1) of the cyclized alcohol **18** (3.4 mg, 16%), 3-methyl-2,3-dihydrobenzofuran (**19**) (1.1 mg, 9%),[28a] iodomesitylene (14.1 mg, 63%%), and *o*-(allyloxy)iodobenzene (2 mg, 8%). 3-(2-Hydroxy-2-phenylethyl)-2,3-dihydrobenzofuran (**18**): colorless oil; IR ($CDCl_3$) 3575, 1595, 1480, 1010 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40−7.26 (m, 5H), 7.22−7.09 (2H), 6.88−6.85 (1H), 6.81−6.77 (1H), 4.87 (dd, $J = 8.8$, 4.9 Hz, 0.75H), 4.82 (dd, $J = 8.3$, 4.4 Hz, 0.25H), 4.69 (t, $J = 8.8$ Hz, 0.75H), 4.60 (t, $J = 8.8$ Hz, 0.25H), 4.30−4.23 (1H), 3.72−3.63 (m, 0.25H), 3.63−3.54 (m, 0.75H), 2.36−1.92 (2H); ^{13}C NMR ($CDCl_3$) δ; 159.82, 144.34, 130.51, 128.72, 128.26, 128.20, 127.96, 127.91, 125.74, 125.68, 124.36, 124.12, 120.48, 120.34, 109.61, 109.53, 77.67, 76.85, 73.48, 72.75, 44.07, 39.74, 38.66; MS *m*/*z* (relative intensity) 240 (50, M$^+$), 209 (78), 119 (88), 91 (100), 77 (52); HRMS calcd for $C_{16}H_{16}O_2$ (M$^+$) 240.1150, found 240.1132. **19**:[28a] ^{1}H NMR ($CDCl_3$) δ 7.20−7.08 (2H), 6.87 (t, $J = 7.1$ Hz, 1H), 6.79 (d, $J = 7.9$ Hz, 1H), 4.68 (t, $J = 8.5$ Hz, 1H), 4.07 (t, $J = 8.5$ Hz, 1H), 3.65−3.45 (m, 1H), 1.33 (d, $J = 6.8$ Hz, 3H).

GC-MS Analysis of 1-Decyne (12) in the Reaction of Aldehyde 2a with 1-Decynyl(phenyl)iodonium Salt 9 in MeOD. To a stirred suspension of $CrCl_2$ (74 mg, 0.6 mmol) doped with $NiCl_2$ (0.5 mol %) in dry MeOD (1 mL) was added a solution of 1-decynyliodonium tetrafluoroborate **9** (128 mg, 0.3 mmol) and benzaldehyde (**2a**) (32 mg, 0.3 mmol) in MeOD (2 mL) under argon at room temperature, and the solution was stirred for 30 h. The reaction mixture was quenched with water and extracted with diethyl ether. The combined organic extracts were washed with water and brine. The organic layer was filtered and dried over anhydrous sodium sulfate. GC−MS analysis of 1-decyne (**12**) was carried out using an FFS ULBON HR-17 capillary column (0.25 mm × 50 m, 60−150 °C, 20 °C/min). The abundances at *m*/*z* of 109 and 110 were analyzed. The percentage of deuterium isotopic composition of 1-decyne-*1-d* was found to be 98%.

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