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Free-Radical Coupling of Alkyl and Aryl Halides with Electron-Deficient Alkenes Mediated by Chromium(II) Complexes[1]

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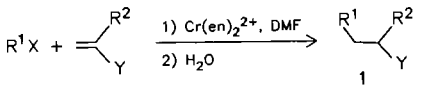
Free radicals generated from organic halides and (ethylenediamine)chromium(II) complexes in DMF are trapped by electron-deficient olefins. The coupling reactions of alkyl halides, described in Part I[1], are extended and, in addition, aryl halides are shown to be efficient radical precursors to yield coupling products in good yield.

The reduction of alkyl and aryl halides by ethylenediamine complexes of chromium(II) [$Cr(en)_2^{2+}$] to the corresponding alkanes and arenes has been known for a long time to be a free-radical process[2,3]. Recently, chromium(II) salts have been used in intramolecular free-radical C–C bond-forming reactions[4,5]. Thus, ω-alkyn-1-yl halides undergo regioselectively free-radical cyclizations when reduced with ethylenediamine complexes of chromium(II) chloride to give substituted methylenecycloalkanes[4]. Similarly, Lübbers and Schäfer have reported that Cr^{II} salts can be used to prepare substituted tetrahydrofurans by radical cyclization of the appropriate alkenyl halides[5].

Intermolecular free-radical C–C bond-forming addition reactions have become valuable and general methods in organic synthesis[6–12]. We have recently reported that $Cr(en)_2^{2+}$ complexes can mediate the coupling reaction of alkyl halides with electron-deficient alkenes[1]. In continuation of our efforts in this area, we report in this paper further coupling reactions of alkyl and, in addition, aryl halides with alkenes.

Diethyl vinyl phosphonate and phenyl vinyl sulfone have been found to be suitable traps for alkyl radicals generated by the reduction of alkyl halides with $Cr(en)_2^{2+}$ complexes. Thus, *tert*-butyl bromide (1 equiv.) readily reacts with phenyl vinyl sulfone (4 equiv.) in the presence of $Cr(en)_2^{2+}$ (2.2 equiv.) to give the coupling product **1** ($R^1 = tBu$, $R^2 = H$, $Y = SO_2Ph$) in 78% yield (Scheme 1).

Scheme 1



R^1 = prim., sek., tert., alkyl, aryl
R^2 = H, CH_3
X = Br, I
Y = CN, CO_2CH_3, SO_2Ph, $PO(OEt)_2$

The reaction has been carried out in dry dimethylformamide (DMF) with commercially available anhydrous chromium(II) chloride. Similarly, diethyl vinyl phosphonate reacts with alkyl halides in the presence of $Cr(en)_2^{2+}$ to give the coupling products **1**. The reactions proceed smoothly and cleanly to afford good yields of the products. The results are summarized in Table 1. Since both vinyl sulfone and vinyl phosphonate are very effective in trapping the alkyl radicals only a fourfold molar excess of olefin is needed to accomplish the reaction, whereas normally we have worked with a tenfold excess. The efficiency of these alkenes in trapping alkyl radicals has recently been described[13,14].

Table 1. Reactions of alkyl bromides (R^1Br) with alkenes ($H_2C{=}CHY$) mediated by chromium(II) complexes in DMF

Entry no.	R^1	Y	Time [hr]	Yield (%)
1	$(CH_3)_3C$	SO_2Ph	4	78[a]
2	$(CH_3)_3C$	$PO(OEt)_2$	4	82[a]
3	1-adamantyl	$PO(OEt)_2$	10	84[a]

[a] Isolated yields of pure (>96% by GC) products.

Our work has been extended to coupling reactions of aryl halides with electron-deficient alkenes. Thus, phenyl iodide reacts with methyl methacrylate in the presence of $Cr(en)_2^{2+}$ to give, after hydrolysis, product **1** ($R^1 = Ph$, $R^2 = CH_3$, $Y = CO_2CH_3$) in good yield (Scheme 1). Other aryl halides as well as other alkenes react under similar reaction conditions to afford the corresponding coupling products in moderate to good yields. The results are presented in Table 2. It is worth mentioning that 1-iodo-4-nitrobenzene fails to react with methyl methacrylate in the presence of the Cr^{II} complex. Stirring of 1-iodo-4-nitrobenzene, methyl methacrylate and $Cr(en)_2^{2+}$ for 24 h at 80°C results mostly in unreacted starting material. Neither coupling products nor the reduction product nitrobenzene have been detected.

Main side reactions observed involve reduction of the aryl halides to arenes and the formation of double addition products, especially with acrylonitrile and methyl acrylate. The former side reaction can be suppressed to a large extent by applying higher proportions of

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the trapping alkenes. Aryl radicals are well established to add to electron-poor alkenes at an extremely high rate[15].

Table 2. Reactions of aryl halides (ArX) with alkenes ($CH_2=CR^2Y$) mediated by chromium(II) complexes in DMF

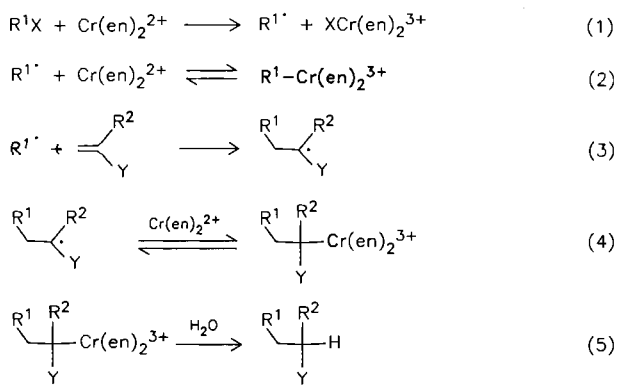
Entry no.	Ar	X	R^2	Y	Time [hr]	Yield[a,b] (%)
1	C_6H_5	I	CH_3	CO_2CH_3	18	75
2	4-$H_3CC_6H_4$	I	CH_3	CO_2CH_3	14	78
3	4-$H_3CC_6H_4$	Br	CH_3	CO_2CH_3	35	36[c,d]
4	4-$H_3COC_6H_4$	I	CH_3	CO_2CH_3	12	64
5	4-ClC_6H_4	I	CH_3	CO_2CH_3	16	65
6	1-naphthyl	I	CH_3	CO_2CH_3	16	58
7	2-thienyl	I	CH_3	CO_2CH_3	18	52
8	4-$H_3CC_6H_4$	I	H	$PO(OEt)_2$	16	55
9	4-$H_3COC_6H_4$	I	H	$PO(OEt)_2$	14	65
10	4-$H_3COC_6H_4$	Br	H	$PO(OEt)_2$	22	30[c,d]
11	4-ClC_6H_4	I	H	$PO(OEt)_2$	16	60
12	C_6H_5	I	H	$PO(OEt)_2$	24	50[c]
13	C_6H_5	I	H	CO_2CH_3	22	52[c]
14	4-$H_3CC_6H_4$	I	H	CO_2CH_3	18	48[c]
15	1-naphthyl	I	H	CO_2CH_3	16	42[c]
16	1-naphthyl	I	H	CN	14	35[c]
17	4-$O_2NC_6H_4$	I	CH_3	CO_2CH_3	24	0[e]

[a] Isolated yields of pure (>96% by GC) products unless otherwise mentioned; all isolated products were fully characterized by MS and ^1H and ^{13}C NMR. – [b] Reduced arenes were detected in ca. 10–15% (GC). – [c] GC yields using *n*-decane as internal standard. – [d] Reduced arenes were detected in ca. 30% yield (GC). – [e] Neither coupling product nor nitrobenzene were detected.

Aryl iodides can be replaced by aryl bromides as radical precursors in the above reaction. However, their reactions are slower, and even after prolonged reaction times unreacted aryl bromide remains. The slow reduction of aryl bromides observed in dry DMF contrasts with their rapid reduction in aqueous DMF reported by Kochi and Powers[2].

The reaction is believed to proceed by a free-radical mechanism. The formation of product **1** is consistent with the mechanism given in Scheme 2. The reaction involves a regioselective addition of the radical R^1 to the alkene followed by trapping of the adduct radical by another equivalent of chromium(II).

Scheme 2



The results of this work are in good agreement with prior work on the coupling of alkyl and aryl halides with electron-deficient alkenes[6,15]. The use of chromium(II) for radical generation gives results comparable to those obtained with alkylmercury compounds and tributyltin hydride as well as the coupling of aryldiazonium salts with electron-deficient alkenes mediated by titanium salts, thus extending the present methodology.

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Experimental

Analytical Instruments: ^1H and ^{13}C NMR (internal standard TMS): Varian XL 200. – GLC: Varian 3700 with CDS 111 data system. – MS: HP-5971 MSD, coupled with HP-5980 gas chromatograph.

Materials: Anhydrous chromium(II) chloride, alkyl halides, aryl halides and alkenes were purchased from Aldrich. DMF was dried as described in ref.[16].

General Procedure: All operations were performed under argon. To a green suspension of chromium(II) chloride (1.22 g, 10.0 mmol) in dry DMF (30 ml) was added dropwise a solution of ethylenediamine (1.20 g, 20.0 mmol) in DMF (10 ml). The initially pale blue color of the solution had turned to a deep blue at the end of the reaction. The trapping alkene (40.0 mmol) was added in one portion, then the aryl halide (4.00 mmol) in DMF (10 ml) was added dropwise with continuous stirring. The reaction mixture was heated at 80°C (for reaction times see Tables 1 and 2), during which time the color became brown. The reaction mixture was poured into water (60 ml). The aqueous solution was extracted with diethyl ether (3 × 40 ml). The combined ethereal extracts were washed with water (2 × 30 ml), dried with magnesium sulfate and filtered. Ether was distilled off from the filtrate and the residue was distilled under reduced pressure to give the coupling product. In the case of alkyl halides the reactions were carried out at room temp. by using fourfold excess of the trapping alkene. The following compounds (same sequence as in Tables 1 and 2) were prepared according to the above procedure (yields are given in Tables 1 and 2).

3,3-Dimethylbutyl(phenyl)sulfon: M.p. 58°C (ref.[17] 59–60°C). – ^1H NMR ($CDCl_3$): δ = 7.79 (m, 2H, aromatic H), 7.59 (m, 3H, aromatic H), 3.05 (m, 2H, CH_2), 1.60 (m, 2H, CH_2), 0.87 [s, 9H, $C(CH_3)_3$]. – MS (70 eV), *m/z* (%): 226 (0.5) [M^+], 169 (22) [M^+ – *t*Bu], 143 (87) [$PhSO_2H_2^+$], 57 (100).

Diethyl (3,3-Dimethylbutyl)phosphonate[13]: ^1H NMR ($CDCl_3$): δ = 4.10 (m, 4H, OCH_2), 1.70 (m, 2H, PCH_2), 1.50 (m, 2H, CH_2), 1.33 (t, J = 7 Hz, 6H, CH_3), 0.90 [s, 9H, $C(CH_3)_3$]. – MS (70 eV), *m/z* (%): 221 (1) [M^+ – 1], 207 (45) [M^+ – CH_3], 165 (100) [M^+ – *t*Bu], 138 (85), 57 (19).

Diethyl [2-(1-Adamantyl)ethyl]phosphonate: B.p. 140–145°C/1 Torr. – ^1H NMR ($CDCl_3$): δ = 4.08 (m, 4H, OCH_2), 1.96–1.38 (m, 19H, adamantyl H and 2 CH_2), 1.32 (t, J = 7.0 Hz, 6H, CH_3). – ^{13}C-NMR ($CDCl_3$): δ = 61.4, 61.3 (d, $^3J_{C,P}$ = 5.0 Hz, OCH_2), 41.7, 37.2 (d, $^2J_{C,P}$ = 225.0 Hz, PCH_2), 35.9, 35.8 (d, $^3J_{C,P}$ = 5.0 Hz, CH_2), 36.9, 28.4, 20.3, 17.5 (Ad), 16.4, 16.3 (d, $^4J_{C,P}$ = 5.0 Hz, CH_3). – MS (70 eV), *m/z* (%): 300 (3) [M^+], 165 (100). – $C_{16}H_{29}O_3P$ (300.4): calcd. C 63.96, H 9.75; found C 64.15, H 10.19.

Methyl 2-Methyl-3-phenylpropanoate: B.p. 90–93°C/1 Torr (ref.[18] 247–252°C). – ^1H NMR ($CDCl_3$): δ = 7.24 (m, 5H, aromatic H), 3.63 (s, 3H, OCH_3), 3.05 (m, 1H, CH), 2.70 (m, 2H, CH_2), 1.15 (d, 3H, J = 6.6 Hz, CH_3). – MS (70 eV), *m/z* (%): 178 (18) [M^+], 118 (41), 91 (100).

Methyl 2-Methyl-3-(4-methylphenyl)propanoate: B.p. 96–99°C/1 Torr. – ^1H NMR ($CDCl_3$): δ = 7.02 (s, 4H, aromatic H), 3.56 (s, 3H, OCH_3), 2.95 (m, 1H, CH), 2.63 (m, 2H, CH_2), 2.25 (s, 3H, CH_3),

1.10 (d, 3H, $J = 6.6$ Hz, CH_3). – ^{13}C-NMR ($CDCl_3$): $\delta = 176.6$ (C=O), 136.6, 135.9, 129.4, 129.2 (aromatic C), 51.6 (OCH_3), 41.8 (CH_2), 39.6 (CH), 21.2 (CH_3), 16.9 (CH_3). – MS (70 eV), *m/z* (%): 192 (14) [M^+], 132 (14), 105 (100). – $C_{12}H_{16}O_2$ (192.2): calcd. C 74.97, H 8.38; found C 74.88, H 8.35.

Methyl 2-Methyl-3-(4-methoxyphenyl)propanoate: B.p. 99 to 101 °C/0.8 Torr. – ^{1}H NMR ($CDCl_3$): $\delta = 7.02$ (m, 2H, aromatic H), 6.78 (m, 2H, aromatic H), 3.72 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 2.92 (m, 1H, CH), 2.63 (m, 2H, CH_2), 1.12 (d, $J = 6.8$ Hz, 3H, CH_3). – ^{13}C-NMR ($CDCl_3$): $\delta = 176.5$ (C=O), 158.2, 131.4, 129.9, 113.8 (aromatic C), 55.1, 51.4 (OCH_3), 41.6 (CH), 38.9 (CH_2), 16.4 (CH_3). – MS (70 eV), *m/z* (%): 208 (10) [M^+], 121 (100). – $C_{12}H_{16}O_3$ (208.2): calcd. C 69.21, H 7.73; found C 69.40, H 7.61.

Methyl 3-(4-Chlorophenyl)-2-methylpropanoate: B.p. 109 to 113 °C/0.8 Torr. – ^{1}H NMR ($CDCl_3$): $\delta = 7.06$ (m, 4H, aromatic H), 3.52 (s, 3H, OCH_3), 2.85 (m, 1H, CH), 2.57 (m, 2H, CH_2), 1.05 (d, $J = 6.5$ Hz, 3H, CH_3). – ^{13}C NMR ($CDCl_3$): $\delta = 175.2$ (C=O), 136.9, 131.1, 129.3, 127.5 (aromatic C), 50.6 (OCH_3), 40.3 (CH_2), 38.0 (CH), 15.6 (CH_3). – MS (70 eV), *m/z* (%): 212 (14) [M^+], 152 (20), 125 (100). – $C_{11}H_{13}ClO_2$ (211.7): calcd. C 62.40, H 6.19; found C 62.56, H 6.28.

Methyl 2-Methyl-3-(1-naphthyl)propanoate: B.p. 117 – 120 °C/0.5 Torr. – ^{1}H NMR ($CDCl_3$): $\delta = 7.98$ (m, 1H), 7.72 (m, 2H), 7.33 (m, 4H, aromatic H), 3.55 (s, 3H, OCH_3), 3.52 (m, 1H, CH), 2.95 (m, 2H, CH_2), 1.13 (d, $J = 6.8$ Hz, 3H, CH_3). – ^{13}C NMR ($CDCl_3$): $\delta = 176.6$ (C=O), 135.4, 134.0, 131.9, 128.9, 127.3, 127.2, 126.0, 125.5, 125.3, 123.6 (aromatic C), 51.5 (OCH_3), 40.4 (CH), 36.9 (CH_2), 16.9 (CH_3). – MS (70 eV), *m/z* (%): 228 (22) [M^+], 141 (100). – $C_{15}H_{16}O_2$ (228.3): calcd. C 78.94, H 7.02; found C 78.82, H 7.04.

Methyl 2-Methyl-3-(2-thienyl)propanoate: B.p. 92 – 94 °C/1 Torr. – ^{1}H NMR ($CDCl_3$): $\delta = 7.12$ (dd, $J_{4,5}$ (Thiophen) = 5.1 Hz, $J_{3,5}$ (Thiophen) = 1.1 Hz, 1H, 5-H (Thiophen)), 6.87 (m, 1H, 4-H (Thiophen)), 6.79 (dd, $J_{3,4}$ (Thiophen) = 2.6 Hz, $J_{3,5}$ (Thiophen) = 1.1 Hz, 1H, 3-H (Thiophen)), 3.67 (s, 3H, OCH_3), 3.22 (m, 1H, CH), 2.85 (m, 2H, CH_2), 1.20 (d, $J = 7.0$ Hz, 3H, CH_3). – ^{13}C NMR ($CDCl_3$): $\delta = 176.0$ (C=O), 141.6, 126.8, 125.6, 123.8 (thienyl C), 51.7 (OCH_3), 41.8 (CH), 33.6 (CH_2), 16.8 (CH_3). – MS (70 eV), *m/z* (%): 184 (20) [M^+], 124 (17), 97 (100). – $C_9H_{12}O_2S$ (184.2): calcd. C 58.70, H 6.52; found C 58.18, H 6.26.

Diethyl [2-(4-Methylphenyl)ethyl]phosphonate: B.p. 137 to 141 °C/1 Torr. – ^{1}H NMR ($CDCl_3$): $\delta = 7.09$ (s, 4H, aromatic H), 4.09 (m, 4H, OCH_2), 2.86 (m, 2H, PCH_2), 2.30 (s, 3H, CH_3), 2.03 (m, 2H, CH_2), 1.32 (t, $J = 7.0$ Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): $\delta = 137.8$, 135.8, 129.3, 128.0 (aromatic C), 61.7, 61.6 (d, $^3J_{C,P} = 5.0$ Hz, OCH_2), 29.1, 26.4 (d, $^2J_{C,P} = 135.0$ Hz, PCH_2), 28.2, 28.1 (d, $^3J_{C,P} = 5.0$ Hz, CH_2), 20.9 (CH_3), 16.5, 16.4 (d, $^4J_{C,P} = 5.0$ Hz, CH_3). – MS (70 eV), *m/z* (%): 256 (42) [M^+], 183 (14), 138 (48), 118 (100). – $C_{13}H_{21}O_3P$ (256.3): calcd. C 60.93, H 8.20; found C 61.09, H 8.23.

Diethyl [2-(4-Methoxyphenyl)ethyl]phosphonate: B.p. 148 to 151 °C/1 Torr. – ^{1}H NMR ($CDCl_3$): $\delta = 6.96$ (m, 4H, aromatic H), 4.08 (m, 4H, OCH_2), 3.74 (s, 3H, CH_3), 2.87 (m, 2H, PCH_2), 2.00 (m, 2H, CH_2), 1.30 (t, $J = 7.0$ Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): $\delta = 158.2$, 133.2, 129.0, 114.0 (aromatic C), 61.6, 61.5 (d, $^3J_{C,P} = 5.0$ Hz, OCH_2), 55.1 (OCH_3), 29.2, 26.5 (d, $^2J_{C,P} = 135.2$ Hz, PCH_2), 27.8, 27.7 (d, $^3J_{C,P} = 5.0$ Hz, CH_2), 16.5, 16.4 (d, $^4J_{C,P} = 5.0$ Hz, CH_3). – MS (70 eV), *m/z* (%): 272 (12) [M^+], 134 (100). – $C_{13}H_{21}O_4P$ (272.3): calcd. C 57.29, H 7.72; found C 57.44, H 7.82.

Diethyl [2-(4-Chlorophenyl)ethyl]phosphonate[19]: B.p. 162 to 165 °C/1 Torr. – ^{1}H NMR ($CDCl_3$): $\delta = 7.19$ (m, 4H, aromatic H), 4.10 (m, 4H, OCH_2), 2.89 (m, 2H, PCH_2), 2.89 (m, 2H, PCH_2), 2.02 (m, 2H, CH_2), 1.32 (t, $J = 7.0$ Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): $\delta = 139.3$, 132.1, 129.5, 128.7 (aromatic C), 61.7, 61.6 (d, $^3J_{C,P} = 5.0$ Hz, OCH_2), 28.9, 26.1 (d, $^2J_{C,P} = 140.0$ Hz, PCH_2), 28.1, 28.0 (d, $^3J_{C,P} = 5.0$ Hz, CH_2), 16.5, 16.4 (d, $^4J_{C,P} = 5.0$ Hz, CH_3). – MS (70 eV), *m/z* (%): 278 (8) [$M^+ + 2$], 276 (23) [M^+], 138 (100), 111 (59). – $C_{12}H_{18}ClO_3P$ (276.7): calcd. C 52.17, H 6.52; found C 51.95, H 6.59.

Dimethyl (2-phenylethyl)phosphonate[20]: MS (70 eV), *m/z* (%): 242 (36) [M^+], 138 (92), 111 (100), 82 (54).

Methyl 3-Phenylpropanoate[21]: ^{1}H NMR ($CDCl_3$): $\delta = 7.16$ (m, 5H, aromatic H), 3.60 (s, 3H, OCH_3), 2.87 (m, 2H, CH_2), 2.53 (m, 2H, CH_2). – MS (70 eV), *m/z* (%): 164 (31) [M^+], 104 (100), 91 (57).

Methyl 3-(4-Methylphenyl)propanoate[22]: MS (70 eV), *m/z* (%): 178 (36) [M^+], 105 (100).

Methyl 3-(1-Naphthyl)propanoate[23]: MS (70 eV), *m/z* (%): 214 (46) [M^+], 154 (45), 141 (100).

3-(1-Naphthyl)propannitrile[24]: MS (70 eV), *m/z* (%): 181 (24) [M^+], 141 (100), 115 (20).

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