CHEMISTRY LETTERS, pp. 2017-2020, 1994.

# Generation of Acyl Radicals from 1-Oxidoalkylidenechromium(0) Complexes by Treatment with Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II) and Their Reactions with Olefins

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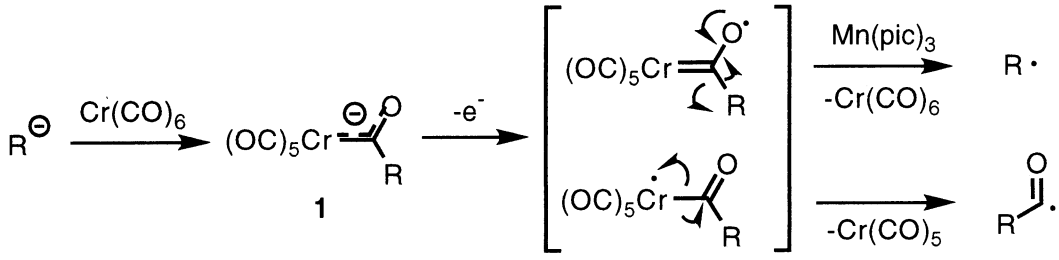
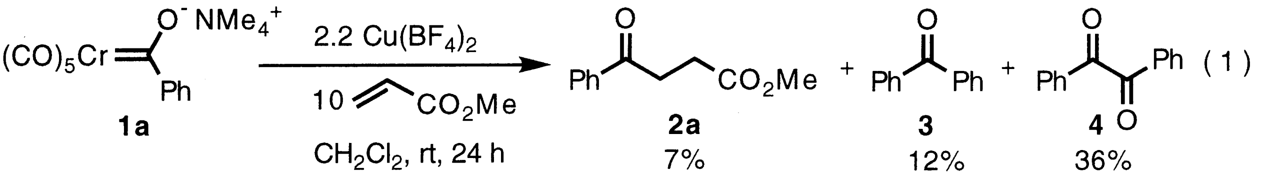
Tetramethylammonium pentacarbonyl(1-oxidoalkylidene)chromium(0) complexes are oxidized with bis(2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II) to generate acyl radicals which react with electron-deficient olefins, giving intermolecular addition products.

Recently, we reported that tetramethylammonium pentacarbonyl(1-oxidoalkylidene)chromium(0) complexes **1** are good precurser for alkyl radicals by treatment with manganese(III) 2-pyridinecarboxylate (Mn(pic)$_3$) as an oxidant.[1] In the above reactions, oxygen-centered radicals initially generated are converted to carbon-centered radicals by eliminating Cr(CO)$_6$. There is another possible fashion of the fragmentation of chromium unit that Cr(CO)$_5$ was released by the homolytic scission of carbon-chromium bond, giving acyl radicals (Scheme 1). It is expected that each of the fragmentation pathways would be selected by the choice of the oxidant.[2,3] Here we report a new method for oxidative generation of acyl radicals from **1** by using copper(II) salt as an oxidant.



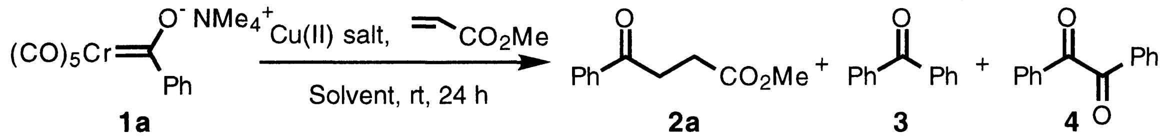
Scheme 1.

Firstly oxidation of tetramethylammonium pentacarbonyl(oxidophenylmethylidene)chromium(0) **1a** was examined with Cu(BF$_4$)$_2$ in the presence of methyl acrylate as a radical acceptor. When **1a** and 10 molar amounts of methyl acrylate in CH$_2$Cl$_2$ were treated with 2.2 molar amounts of Cu(BF$_4$)$_2$, methyl 4-oxo-4-phenylbutyrate **2a** was obtained in 7% yield along with benzophenone **3** and benzil **4** in 12% and 36% yield, respectively (eq. 1). This indicated that benzoyl radical was initially generated by the oxidation with Cu(BF$_4$)$_2$.



Optimization of the reaction conditions was carried out in order to increase the yield of the intermolecular addition product **2a** (Table 1). As shown in entry 1-4, the production of benzophenone **3** or benzil **4** was completely suppressed by using acetonitrile as solvent. Various kind of Cu(II) salts were employed in acetonitrile (entry 4-10) and bis(2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II) ($\mathrm{Cu(dpm)_2}$) was found to give **2a** in good yield (73%). Noteworthy was that in the case of $\mathrm{Cu(dpm)_2}$ only 1.1 molar amounts of the oxidant and 1.5 molar amounts of methyl acrylate are neccessary to accomplish the reaction.

Table 1. Oxidation of Chromium Complex **1a** with Various Cu(II) Salt in the Presence of Methyl Acrylate



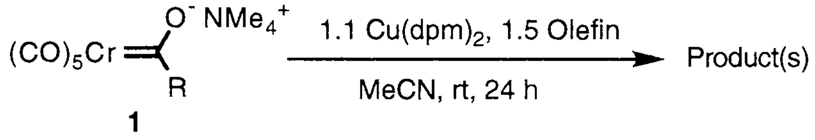
| Entry | Cu(II) salt (equiv.) | Equiv. of methyl acrylate | Solvent | Yield / % | | |
|---|---|---|---|---|---|---|
| | | | | **2a** | **3** | **4** |
| 1 | $\mathrm{Cu(BF_4)_2}$ (2.2) | 10 | $\mathrm{CH_2Cl_2}$ | 7 | 12 | 36 |
| 2 | $\mathrm{Cu(BF_4)_2}$ (2.2) | 10 | THF-HMPA | 2 | 3 | 3 |
| 3 | $\mathrm{Cu(BF_4)_2}$ (2.2) | 10 | DMF | 14 | 0 | 15 |
| 4 | $\mathrm{Cu(BF_4)_2}$ (2.2) | 10 | MeCN | 24 | 0 | 0 |
| 5 | $\mathrm{CuCl_2}$ (2.2) | 10 | MeCN | 0 | 0 | 0 |
| 6 | $\mathrm{Cu(OTf)_2}$ (2.2) | 10 | MeCN | 4 | 0 | 0 |
| 7 | $\mathrm{Cu(acac)_2}^{a)}$ (2.2) | 10 | MeCN | 68 | 0 | 0 |
| 8 | $\mathrm{Cu(acac)_2}^{a)}$ (2.2) | 1.5 | MeCN | 35 | 0 | 0 |
| 9 | $\mathrm{Cu(hfa)_2}^{a)}$ (2.2) | 1.5 | MeCN | 0 | 0 | 0 |
| 10 | $\mathrm{Cu(dpm)_2}^{a)}$ (1.1) | 1.5 | MeCN | 73 | 0 | 0 |

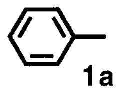
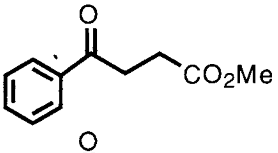
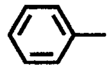
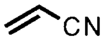
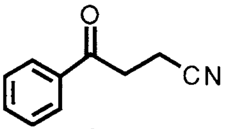
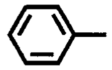
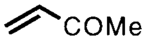
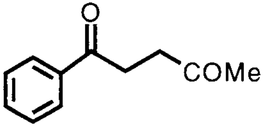
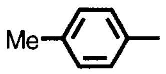
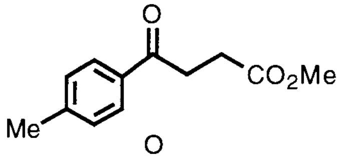
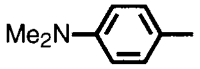
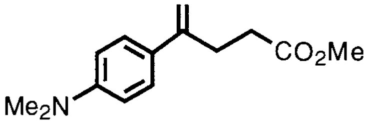
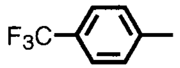
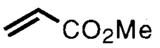
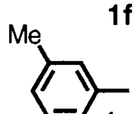
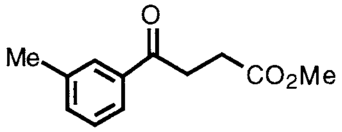
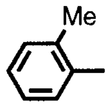
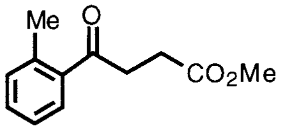
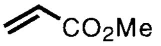
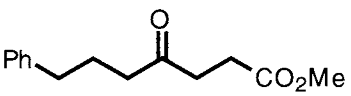
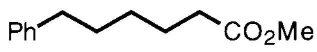
a) acac: 2,4-pentanedionato, hfa: 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato,
dpm: 2,2,6,6-tetramethyl-3,5-haptanedionato

As shown in entry 2 and 3 in Table 2, acryronitrile and methyl vinyl ketone were also available as radical acceptors. Substituents on the phenyl group of the chromium complex strongly influenced the yield of the adducts as shown in entry 4-8. When an electron-donating group such as dimethylamino group is introduced on the *para* position the yield is increased, although the introduction of an electron-withdrawing group or the introduction of a substituent on the *ortho* position conspicuously decreases the yield. Furthermore, an alkyl-substituted chromium complex **1i** can react with methyl acrylate to give acylated adduct **2i** in 27% yield, accompanying with an adduct with alkyl radical **5i** (entry 9).[4]

This reaction is considered to proceed via the pathway shown in Scheme 2. The chromium complex **1** is oxidized by $\mathrm{Cu(dpm)_2}$ to generate benzoyl radical equivalent and $\mathrm{Cr(CO)_5(MeCN)}$ by homolytic scission of the carbon-chromium bond. The resulting benzoyl radical reacts with methyl acrylate to give a radical intermediate **6**. Finally

Table 2. The Reaction of Chromium Complex **1** with Cu(dpm)$_2$ in the Presence of Olefins[5)]

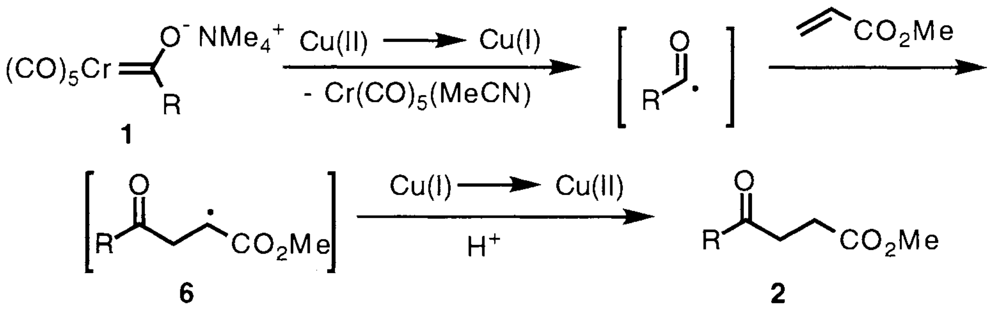


| Entry | R | Olefin | Product(s) (yield / %) | |
|---|---|---|---|---|
| 1 |  **1a** |  |  | **2a**( 73 ) |
| 2 |  **1a** |  |  | **2b**( 58 ) |
| 3 |  **1a** |  |  | **2c**( 46 ) |
| 4 |  **1d** |  |  | **2d**( 72 ) |
| 5 |  **1e** |  |  | **2e**( 76 ) |
| 6 |  **1f** |  | No Product | |
| 7 |  **1g** |  |  | **2g**( 63 ) |
| 8 |  **1h** |  |  | **2h**( 2 ) |
| 9 | PhCH$_2$CH$_2$CH$_2$— **1i** |  |  **2i**( 27 ) |  **5i**( 8 ) |

**6** is reduced by Cu(I) salt to afford a carbaion species, giving the addition product **2** by the protonation.[7)]

Tetramethylammonium pentacarbonyl(1-oxidoalkylidene)chromium(0) complexes **1** was found to be a precursor for both alkyl radicals and acyl radicals, and these two radical species could be generated selectively by the choice of the metallic oxidants, Mn(pic)$_3$[1)] and Cu(dpm)$_2$, respectively. A lot of methods for the generation of acyl radical have been reported and some of them succeeded in the intermolecular addition reaction with olefins.[6)]

However, in most of these cases a large amount of olefin is neccessary to trap the radical species efficiently, while the chromium complex **1** and Cu(dpm)$_2$ system requires a small excess amount of olefins.



Scheme 2.

This work was supported by Takeda Science Foundation and the Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236101 from the Ministry of Education, Science and Culture, Japan.

References

1) K. Narasaka and H. Sakurai, *Chem. Lett.*, **1993**, 1269.

2) Oxidation of the chromium complex **1** with iodine is known to generate an acyl iodide, see; B. C. Söderberg and B. A. Bouden, *Organometallics*, **11**, 2220 (1992).

3) Anodic oxidation of tetraethylammmonium pentacarbonyl(oxidophenylmethylidene)chromium(0) was also reported to yield benzene in 8% yield, see; R. J. Klingler, J. C. Huffman, and J. K. Kochi, *Inorg. Chem.*, **20**, 34 (1981).

4) The reaction of the alkyl substituted chromium complex **1i** with Mn(pic)$_3$ in the presence of Bu$_3$SnH gave only the alkyl radical adduct **5i** in 77% yield.1) On the other hand, the reaction of the phenyl substituted chromium complex **1a** with Mn(pic)$_3$ gave no addition products.3)

5) General procedure was as follows. To a suspension of Cu(dpm)$_2$ (1.1 mmol) and acetonitrile (5 ml) was added an acetonitrile (2 ml) solution of the chromium complex **1** (1 mmol) and olefin (1.5 mmol) at room temperature (ca. 20 °C). After stirring for 24 h, saturated aq. NH$_4$Cl and ether were added and the mixture was stirred for additional 2 h. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic extracts were washed with water and brine, and dried over Na$_2$SO$_4$. PTLC gave the addition product(s).

6) The representative examples of intermolecular addition reaction of acyl radical with olefinic compound, see; R. Schefford and R. Orlinski, *J. Am. Chem. Soc.*, **105**, 7200 (1983); T. Punniyamurthy, B. Bhatia, and J. Iqbal, *J. Org. Chem.*, **59**, 850 (1994); D. L. Boger and R. J. Mathvink, *ibid.*, **54**, 1777 (1989); I. Ryu, K. Kusano, H. Yamazaki, and N. Sonoda, *ibid.*, **56**, 5003 (1991); I. Ryu, H. Yamazaki, K. Kusano, A. Ogawa, and N. Sonoda, *J. Am. Chem. Soc.*, **113**, 8558 (1991); I. Ryu, M. Hasegawa, A. Kurihara, A. Ogawa, S. Tsunoi, and N. Sonoda, *Synlett*, **1993**, 143; and references cited therein.

7) This proposed mechanism indicates that the amount of Cu(II) salt can be reduced to be catalytic. However, when the reaction of **1a** with methyl acrylate was carried out using 50 mol% of Cu(dpm)$_2$, addition product **2a** was obtained in 47% yield.

(Received August 3, 1994)