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# Generation of Alkyl Radicals from 1-Oxidoalkylidenechromium(0) Complexes by Oxidation with Manganese(III) 2-Pyridinecarboxylate and Their Reactions with Olefins

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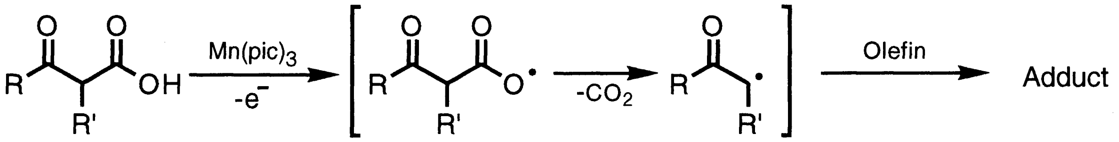
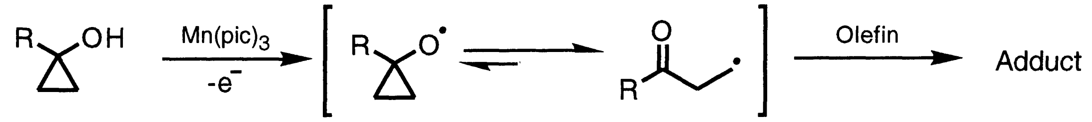
Tetramethylammonium pentacarbonyl(1-oxidoalkylidene)chromium(0) complexes, prepared from the corresponding carbanion and hexacarbonylchromium(0), are oxidized with manganese(III) 2-pyridinecarboxylate to generate carbon-centered radicals which react with various olefins giving the intermolecular addition products.

Reductive generation of alkyl radicals has been widely studied using tin hydride, low-valent metallic compounds etc. as reducing reagents, and the radicals thus generated are applied frequently to construction of carbon skeletons, particularly by the intramolecular reactions.[1)] Although one-electron oxidation of carbanions has been considered to be one of the representative methods for generation of alkyl radicals since the discovery of the Kolbe electrolysis,[2)] this method has found serious limitation on the substrates.[3)] By using manganese(III) 2-pyridinecarboxylate (Mn(pic)$_3$) as an oxidant, our laboratory reported a method for generation of α-keto and β-keto radicals from β-keto carboxylic acids (Eq. 1)[4)] and cyclopropanols (Eq. 2)[5-7)] respectively and their intermolecular and intramolecular reactions with various olefins. In these reactions, the oxygen-centered radicals initially generated are converted to the carbon-centered radicals by fragmentation reactions.

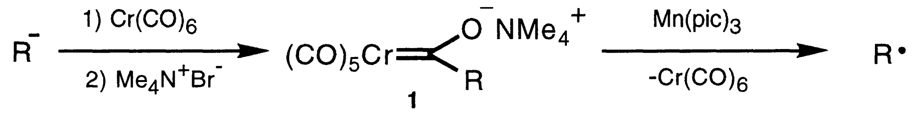


(1)



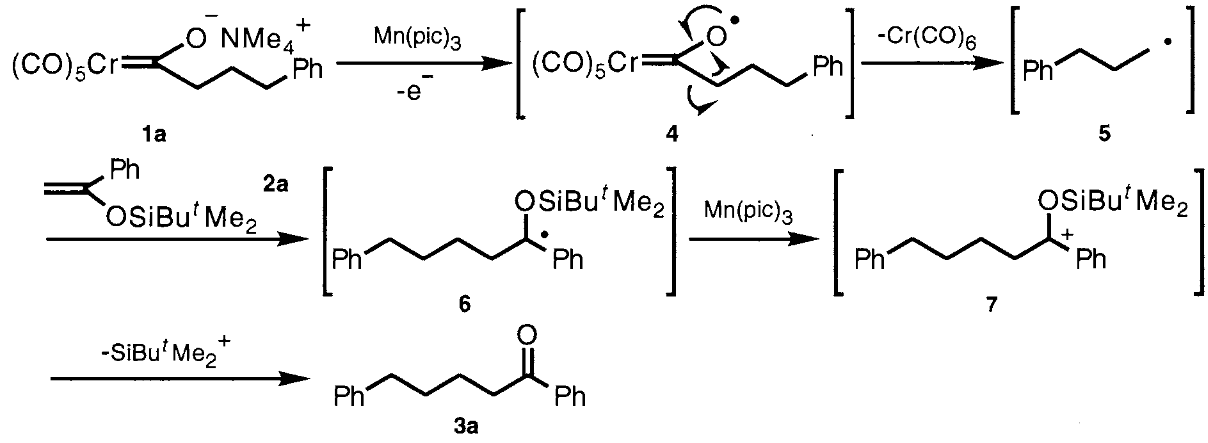
(2)

Here we report a new method for oxidative generation of alkyl radicals from the corresponding carbanions via pentacarbonyl(1-oxidoalkylidene)chromium(0) complexes **1**. The chromium(0) complexes **1** are easily prepared from hexacarbonylchromium(0) and carbanions such as alkyllithium[8)] and are supposed to be oxidized with Mn(pic)$_3$, giving carbon-centered radicals by the elimination of chromium component (Eq. 3).



(3)

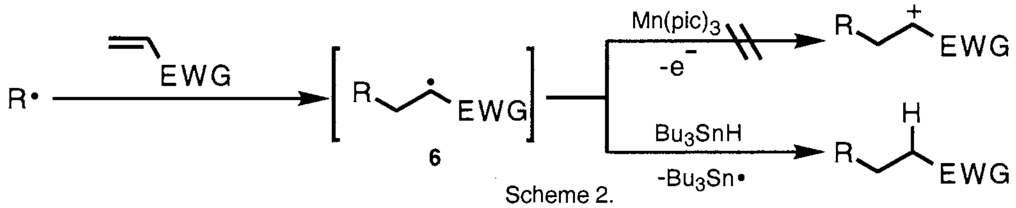
The possibility of this hypothesis was firstly examined by the oxidation of tetramethylammonium pentacarbonyl(1-oxido-4-phenylbutylidene)chromium(0) (**1a**)[9] with Mn(pic)$_3$ in the presence of α-(*t*-butyldimethylsiloxy)styrene (**2a**) as a radical acceptor. When **1a** and 3 molar amounts of **2a** in DMF were treated with 2.5 molar amounts of Mn(pic)$_3$, the reaction proceeded smoothly (0 °C, 1 h) and the addition product **3a** was obtained in good yield (74%) without any formation of the self-coupling products.[10] This reaction is considered to proceed in the pathway shown in Scheme 1. The chromium complex **1a** is oxidized by Mn(pic)$_3$ to generate the oxygen-centered radical **4**, which cleaves into 3-phenylpropyl radical **5** and Cr(CO)$_6$. The resulting alkyl radical **5** reacts with the silyl enol ether **2a** to give a radical intermediate **6**, which is further oxidized with Mn(pic)$_3$ to afford the addition product **3a.**



Scheme 1.

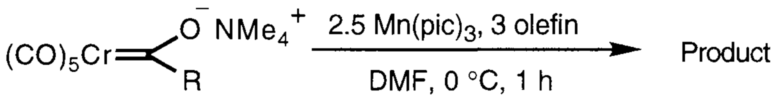
This method exhibits a wide generality for the generation of alkyl radicals and for the reaction with electron rich olefins as shown in Table 1. The 4-phenylbutylidene complex **1a** could react with some other electron rich olefins such as **2b**, **2c**, and **2d**, and 3-phenylpropyl group is introduced to these olefinic compounds, giving the adducts such as **3b**, **3c**, and **3d** in moderate yield. Furthermore, a secondary and a tertiary alkyl radicals could be generated from **1c** and **1d** in addition to the primary alkyl radicals from **1a** and **1b**.

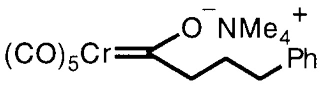
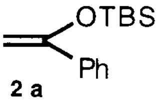
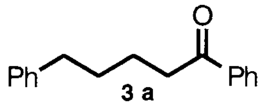
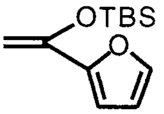
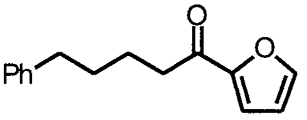
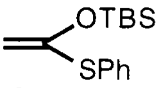
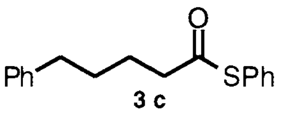
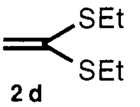
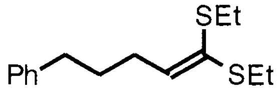
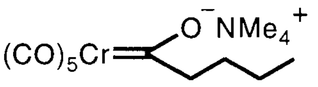
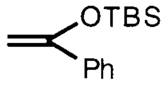
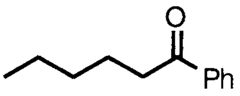
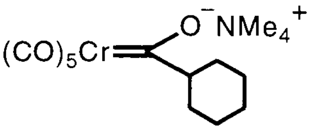
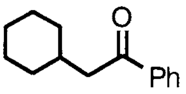
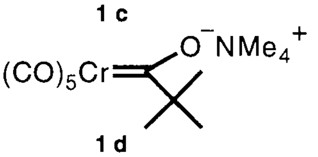
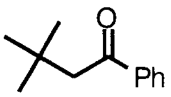
By considering the nucleophilic character of alkyl radicals, the radicals generated from these chromium complexes **1** was supposed to react with electron deficient olefins as well as electron rich olefins. In the reaction with electron deficient olefins, the radical intermediates **6** formed by the addition of alkyl radicals to electron deficient olefins seemed difficult to be oxidized to the cations due to an electron withdrawing group on the radical carbon (Scheme 2).[6] Accordingly, the reaction of **1a** with acrylonitrile **2d** was tried in the presence of various radical trapping reagents as shown in Table 2, and tributylstannane was found to be most suitable. These reaction conditions were available for the reaction of **1a** with other electron deficient olefins such as **2e**, **2f**, and **2g** to afford the addition products **3i**, **3j**, and **3k** (Table 2).[10]



Scheme 2.

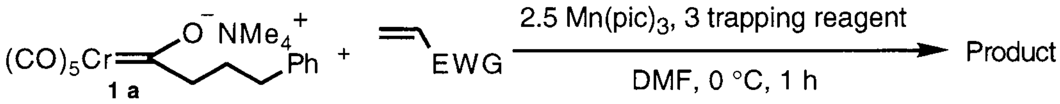
Table 1. The Reactions of Various Chromate(0) Complex with Electron Rich Olefins[10)]

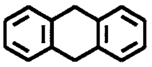
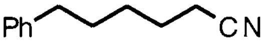
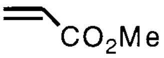
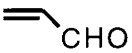


| Chromate(0) Complex | Olefin | Product | Yield / % |
|---|---|---|---|
| <br>**1a** | <br>**2a** | <br>**3a** | 74 |
| **1a** | <br>**2b** | <br>**3b** | 61 |
| **1a** | <br>**2c** | <br>**3c** | 33 |
| **1a** | <br>**2d** | <br>**3d** | 64 |
| <br>**1b** | <br>**2a** | <br>**3e** | 68 |
| <br>**1c** | **2a** | <br>**3f** | 64 |
| <br>**1d** | **2a** | <br>**3g** | 64 |

Direct oxidation of carbanions has been hardly employed for the generation of alkyl radicals partly because of the difficulty to control the intermolecular addition reaction. In fact, treatment of butyllithium directly with Mn(pic)$_3$ in the presence of the silyl enol ether **2a** in THF afforded the addition product **3e** in only 2% yield. Use of the chromium complex **1**, on the other hand, can realize such an efficient control toward the intermolecular addition reaction. Furthermore, this oxidation system expands the utility of tetramethylammonium pentacarbonyl(1-oxidoalkylidene)chromium(0) complexes **1** in organic synthesis, which has been considered only as precursors of Fischer carbene complexes although they are stable and readily prepared.[11)]

Table 2. The Reactions of Chromate Complex **1a** with Electron Deficient Olefins in the Presence of Radical Trapping Reagent[10)]



| Olefin | Trapping reagent | Product | Yield / % |
|---|---|---|---|
| <br>**2d** |  | <br>**3h** | 24 |
| **2d** | $(TMS)_3SiH$ | **3h** | 28 |
| **2d** | $Bu_3SnH$ | **3h** | 68 |
| <br>**2e** | $Bu_3SnH$ | <br>**3i** | 77 |
| <br>**2f** | $Bu_3SnH$ | <br>**3j** | 48 |
| <br>**2g** | $Bu_3SnH$ | <br>**3k** | 47 |

References

1) For recent reviews for the synthetic application of radical reactions, see; B. Giese, "Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds," Pergamon Press, Oxford (1986); C. P. Jasperse, D. P. Curran, and T. L. Fevig, *Chem. Rev.*, **91**, 1237 (1991).

2) H. Kolbe, *Justus Liebigs Ann. Chem.*, **69**, 257 (1849).

3) A few specific oxidation conditions enabled intermolecular reaction, see; Anodic oxidation: H. J. Schäfer, *Angew. Chem., Int. Ed. Engl.*, **20**, 911 (1981); Vitamin $B_{12}$ oxidation: R. Schefford, *Chimia*, **39**, 203 (1985).

4) K. Narasaka, N. Miyoshi, K. Iwakura, and T. Okauchi, *Chem. Lett.*, **1989**, 2169.

5) N. Iwasawa, S. Hayakawa, K. Isobe, and K. Narasaka, *Chem. Lett.*, **1991**, 1193.

6) N. Iwasawa, S. Hayakawa, M. Funahashi, K. Isobe, and K. Narasaka, *Bull. Chem. Soc. Jpn.*, **66**, 819 (1993).

7) N. Iwasawa, M. Funahashi, S. Hayakawa, and K. Narasaka, *Chem. Lett.*, **1993**, 545.

8) E. O. Fischer and A. Maasböl, *Chem. Ber.*, **100**, 2445 (1967).

9) The chromium complexes **1** were prepared from $Cr(CO)_6$ and the corresponding alkyllithium compounds followed by treatment of the intermediate lithium complex with $Me_4NBr$ as described in Ref. 8.

10) The reactions were performed according to the literature in Ref. 6.

11) For other example of the application of **1** in organic synthesis, see; B. C. Söderberg and B. A. Bouden, *Organometallics*, **11**, 2220 (1992).

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