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# SYNTHESIS OF CARBONYL COMPOUNDS USING ORGANOMANGANESE PENTACARBONYL COMPLEXES.[1]

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This manuscript is dedicated to George H. Büchi on the occasion of his 65th birthday.

**Abstract** Sequential insertion of carbon monoxide and either strained or electron-deficient alkenes into alkylmanganese pentacarbonyl complexes at pressures of 6 kbar provides manganacycles in a regioselective and stereoselective fashion. The manganacycles can be transformed into carbonyl compounds under photolytic conditions.

The insertion of transition metal-carbon bonds into carbon-carbon or carbon-oxygen multiple bonds is a key reaction in many processes involving heterogeneous and homogeneous transition metal catalysts.[2-4] The prototypic example of this process is the migratory insertion of alkylmanganese pentacarbonyl complexes which has been extensively studied.[5-9] For example, Booth and coworkers have demonstrated that terminal alkynes and strained alkenes reacted with activated manganese complexes such as methylmanganese pentacarbonyl (**1**, $R^1$=Me) at atmospheric pressure to furnish complex **2** (R'=Me) in modest yield resulting from a sequential insertion of carbon monoxide and the alkyne moiety (Scheme).[8] However, these same authors also reported that the sequential insertion process was not a general one since if either the alkylmanganese or alkene component was deactivated the process failed to occur.

In this Communication, we report that alkylmanganese pentacarbonyl complexes (**1**) react regio- and stereoselectively with either strained or electron-deficient alkenes at pressures of 6 kbar to produce manganacycle **3** in good yield. The resulting manganese complex is a versatile intermediate for the synthesis of carbonyl compounds as indicated in the Scheme. This approach to the synthesis of highly functionalized ketones occurs with formation of two new carbon-carbon bonds and the introduction of one molecule of carbon monoxide.

**Scheme**

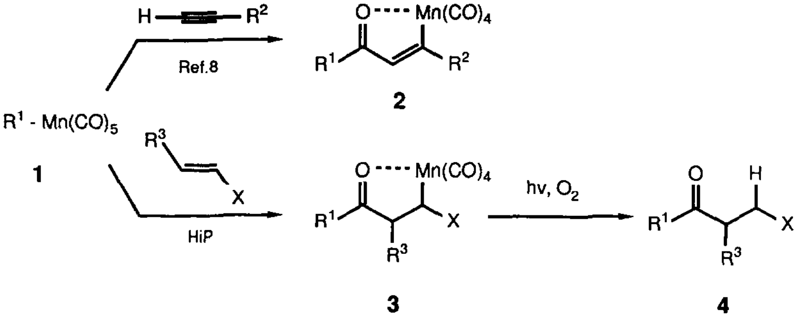
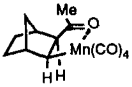
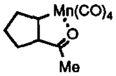
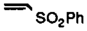
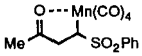
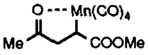
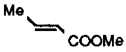
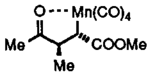
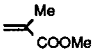
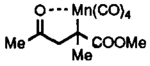
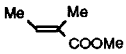
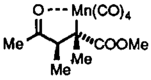
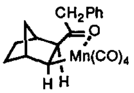
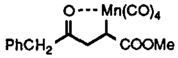
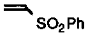
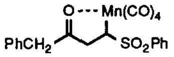
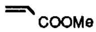
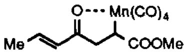
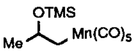
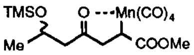
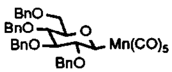
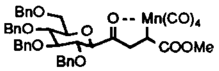


Table 1. Formation of Manganacycle **3** at 6 kbar.

| Entry | Alkylmanganese Complex | Alkene | Manganacycle 3 | Yield (%)[a,b] |
|---|---|---|---|---|
| 1 | Me - $Mn(CO)_5$ |  |  | 90[c] |
| 2 | " |  |  | 30 (90[d]) |
| 3 | " |  |  | 92 |
| 4 | " |  |  | 85 |
| 5 | " |  |  | 60 |
| 6 | " |  |  | 60 |
| 7 | " |  |  | 20 |
| 8 | $PhCH_2$ - $Mn(CO)_5$ |  |  | 85 |
| 9 | " |  |  | 88 |
| 10 | " |  |  | 90 |
| 11 |  |  |  | 70 |
| 12 |  |  |  | 80[e] |
| 13 |  |  |  | 75[f] |

a. Yield of isolated product after chromatographic purification. b. Adducts characterized by IR, $^1H$ NMR, $^{13}C$ NMR, MS, and elemental analysis. c. This adduct can be obtained in 80% yield by reaction of methylmanganese pentacarbonyl and norbornylene in THF at 1 atm. pressure for 7 days. d. Yield based upon consumed starting material. e. Product isolated as ~1:1 mixture of diastereomers. f. See reference 1b.

The results summarized in Table 1 indicate that at pressures of 6 kbar[10] alkylmanganese pentacarbonyl complexes (**1**) reacted regioselectively with structurally diverse alkenes to furnish manganacycles **3**. The manganacycles displayed remarkable stability and were not susceptible to either multiple insertion processes or β-elimination.[11]

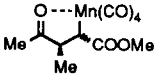
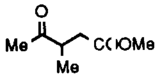
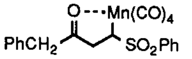
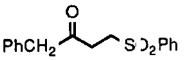
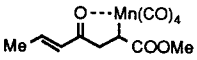
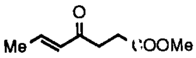
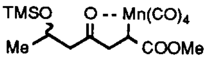
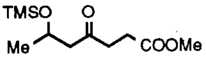
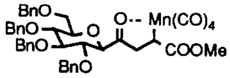
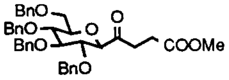
Several features of the results in Table 1 should be noted. Methylmanganese pentacarbonyl (**1**, R=Me) is more reactive than the corresponding benzyl complex (**1**, R=$CH_2Ph$) with regard to migratory insertion[5b,9b,9i], and in analogy with the report of Booth[8], the very reactive methyl complex reacted with norbornylene (entry 1) at atmospheric pressure to yield the corresponding adduct. On the other hand, the benzyl complex produced an adduct with norbonylene only under high pressure reaction conditions (entry 8). These results demonstrate that the high pressure conditions are essential if manganacycles (**3**) are to be prepared from less reactive alkylmanganese complexes such as benzyl- and allylmanganese pentacarbonyl. Similarly, adduct formation with β-silyloxy manganese complex **5**[13] and β-glucosyl complex **6**[1b] necessitated application of high pressure conditions .

A single manganacycle was obtained in all cases indicating that addition of the alkene occurred in a highly regio- and stereoselective manner. The regiochemical assignment was confirmed by subsequent transformations of the adducts (*vide infra*) and by X-ray analysis of the adduct from benzylmanganese pentacarbonyl and phenyl vinyl sulfone (entry 10).[12]

Methyl acrylate and phenyl vinyl sulfone functioned as the alkene component in the sequential insertion reaction to furnish the respective manganacycles (entries 3, 4, 9-13) in good yield. Mono-substituted acrylate esters also gave adducts albeit in slightly reduced yields; however, methyl tiglate (entry 7) yielded only 20% of the manganacycle under these conditions. Cyclohexene, styrene, ethyl vinyl ether, and methyl vinyl ketone failed to give manganacycles under the reaction conditions.

Photolysis of the manganacycles in acetonitrile at 350 nm followed by exposure of the reaction mixture to oxygen resulted in expulsion of manganese and formation of the corresponding ketone **4** in good yield. Table 2 summarizes representative examples of the process.

**Table 2.** Photodemetalation of Manganacycles.

| Entry | Manganacycle | Product | Yield (%) |
|---|---|---|---|
| 1 |  |  | 75 |
| 2 |  |  | 65 |
| 3 |  |  | 65 |
| 4 |  |  | 80 |
| 5 |  |  | 70 |

The mechanism of the photodemetalation reaction has not yet been completely elucidated, however, preliminary experiments have demonstrated that the process does not proceed by a pathway in which homolytic rupture of the carbon-metal bond produces an alkyl radical. The strict requirement of oxygen subsequent to photolysis suggests that a more complex process is functioning in this case.[14]

The two step sequence of manganacycle formation by sequential insertion of an alkene into alkylmanganese pentacarbonyl complexes and subsequent demetalation produces functionalized ketones in a highly regio- and stereoselective manner. Applications of this methodology to total synthesis will be reported in due course.

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12. Crystal Data: $C_{14}H_9MnO_5$, ($\underline{4}$) monoclinic, $\underline{P}2_1/\underline{c}$, $\underline{a}$ = 7.558(1), $\underline{b}$ = 14.803(3), $\underline{c}$ = 12.889(3) Å, $\underline{b}$ = 98,84(2) °, $\underline{V}$ = 1425.9(5) Å$^3$, $\underline{Z}$ = 4, $\underline{R}_F$ = 4.75%, $\underline{R}_{WF}$ = 5.09%.

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