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The First Examples of Carbon Monoxide Trapping in a Manganese(III)-Induced Oxidation System

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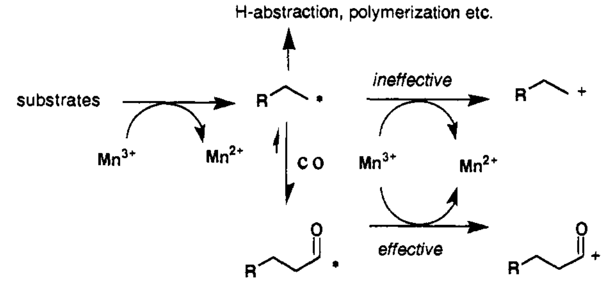
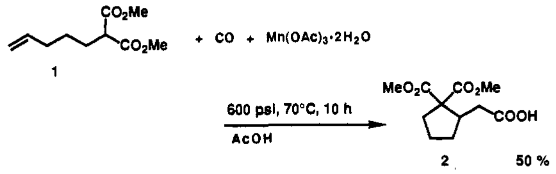
The manganese(III)-induced oxidative addition of carbonyl compounds to alkenes[1] has attracted renewed attention in recent years. The work of Corey,[2a] Fristad,[2b] Snider,[2c] and their coworkers is noteworthy, since they have expanded the synthetic scope of this chemistry to include intramolecular cyclization processes. It is presumed that the reaction begins with a one-electron oxidation to produce a free radical, which adds to an alkene. The free-radical process is probably terminated via a one-electron oxidation. However, the relatively inefficient oxidation step permits hydrogen transfer and polymerization to compete. Copper(II) salts have been frequently used to assist in the termination step,[1c,3] resulting in effective oxidation to give olefins as the final products.[4,5]

In conjunction with our research program concerning the development of new carbonylation systems, we were intrigued with the possibility of achieving carbonylation in a manganese-induced oxidation system. At the start of this work, we were uncertain if Mn^{3+} would oxidize carbon monoxide more rapidly than the enol substrate, giving carbon dioxide and manganese(II) acetate and/or manganese(0) carbonyl. We were pleased to find that this oxidation of CO did not hinder the desired reaction, and we report herein the first carbon monoxide trapping reaction in a Mn^{3+}-induced oxidation system.

The first substrate we examined for the carbonylation was dimethyl (4-pentenyl)malonate (**1**). The cyclization and oxidation of **1** with $Mn(OAc)_3$ has been pursued by Snider and co-workers.[6a] They reported that, in the absence of a cupric salt, 5-exo cyclization products were obtained in very low yields. This is primarily due to the very slow oxidation of the resulting primary radical (cyclopentylmethyl radical) by Mn^{3+}, which allows time for abstraction of hydrogen atoms from solvent and/or starting substrate or undesirable polymerization.[6a] We believed that if the intermediate radical in the Mn^{3+} system trapped carbon monoxide,[7] the termination step should occur smoothly by oxidation to an acyl cation as outlined in Scheme I. As anticipated, the reaction of **1** with manganese triacetate (2.5 mol equiv) in acetic acid under 600 psi of carbon monoxide gave the desired carboxylic acid **2** in 50% yield (eq 1).[8]

Scheme I





(1)

We next examined the keto ester **3** and found that it also worked well. Thus, when **3** was treated with manganese triacetate (2.3 mol equiv) and CO under similar reaction conditions, the carboxylic acid **4**, having a six-membered ring enol structure, was obtained in 55% yield (eq 2).[9,10] Careful examination of the crude NMR suggested the presence of trace quantities of the aromatic product **5**, which is presumably produced by the further oxidation of **4**.[11]

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(8) The reaction proceeded to some extent even under atmospheric pressure of CO, but polymerization became competitive under such conditions, as observed previously by Snider et al.[6a] On the other hand, higher CO pressures (1000 psi) did not necessarily improve the yield.

(9) Typical procedure: deaerated acetic acid (10 mL), $Mn(OAc)_3 \cdot 2H_2O$ (0.807 g, 3 mmol), and **3** (0.204 g, 1.29 mmol) were placed in a 50-mL stainless steel autoclave containing a glass liner. The autoclave was then pressurized with 600 psi of carbon monoxide and heated with stirring at 70 °C for 13 h. After excess CO was discharged at room temperature, the reaction mixture was filtered through Celite. The filtrate was diluted with ether and washed twice with water, and then the water layer was extracted with ether (three times). The combined organic extracts were dried over $MgSO_4$. Filtration and solvent removal gave an oil, which was purified by flash chromatography (hexane/AcOEt/EtOH = 8/2/1), affording 152 mg of crystallized **4** (55% yield). To confirm the six-membered ring structure, conversion of **4** to the corresponding ethyl ester was made. Its spectral data were identical with those reported by Posner et al., see: Posner, G. H.; Shulman-Roskes, E. M. *J. Org. Chem.* **1989**, *54*, 3514. We are grateful to one referee for calling our attention to this paper, as well as for his suggestion of the correct structure.

(10) The formation of salicylate esters in the oxidation of related keto esters with Mn(III) and Cu(II) has been reported by two groups: (a) Peterson, J. R.; Egler, R. S.; Horsley, D. B.; Winter, T. J. *Tetrahedron Lett.* **1987**, *28*, 6109. (b) Snider, B. B; Patricia, J. J. *J. Org. Chem.* **1989**, *54*, 38. The preferential occurrence of six-membered ring cyclization for α-keto radicals (with a carbonyl group inside the ring) has been discussed in terms of stereoelectronic effect by Curran et al., see: (c) Curran, D. P.; Chang, C.-T. *J. Org. Chem.* **1989**, *54*, 3140.

(11) This was ascertained by a separate experiment with isolated **4**: treatment of **4** with 4 equiv of Mn(III) in acetic acid yielded **5** (42 °C, 10 h, 17% yield).

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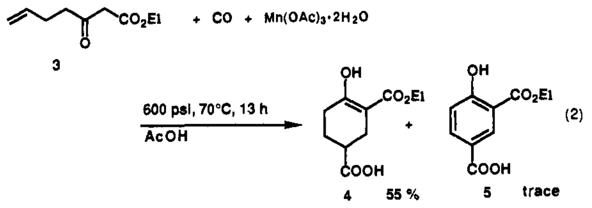
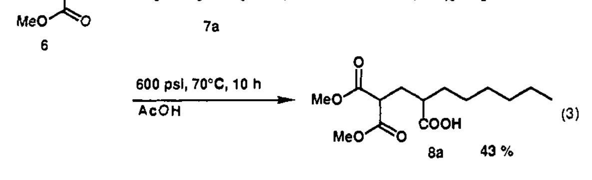
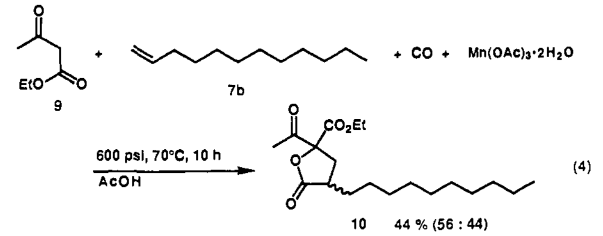


3 4 55 % 5 trace (2)

The intermolecular alkene-addition/carbonylation reaction was also examined with dimethyl malonate (**6**) and 1-octene (**7a**) as the starting substrates (molar ratio, **6**/**7a**/Mn(III) = 2/1/2.4). The expected carboxylic acid **8a** was obtained in 43% yield (based on **7a**) after purification by flash chromatography (eq 3). Thus, the addition to a terminal alkene and subsequent CO–trapping had been realized.[12] The reaction of ethyl acetoacetate (**9**) and 1-dodecene (**7b**) was also examined. When **9** and **7b** were subjected to the intermolecular addition/carbonylation sequence, the carbonylated product was obtained as a five-membered ring lactone **10** (44%, diastereomeric ratio = 56:44) (eq 4).[13] This is produced by a second oxidative cyclization of the initially formed carboxylic acid.[14]

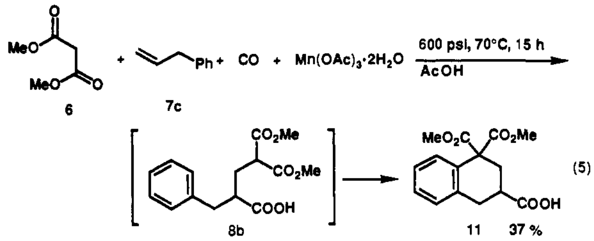


6 7a 8a 43 % (3)



9 7b 10 44 % (56 : 44) (4)

In the reaction with dimethyl malonate (**6**) and allylbenzene (**7c**) in the presence of 4 mol equiv of manganese triacetate, we anticipated that two consecutive processes should occur: (i) the oxidative addition of **6** to **7c** and subsequent carbonylation to give **8b** and (ii) the oxidative addition of **8b** to the internal aromatic ring to produce a fused aromatic compound.[15] When an equimolar amount of **6** and **7c** was heated with manganese triacetate at 70 °C for 15 h, under 600 psi of CO, the expected tetrahydronaphthalene derivative **11** was obtained in 37% yield (eq 5). Therefore the radical obtained from **8b** adds to the aromatic ring in preference to the carboxyl group.



6 7c 8b 11 37 % (5)

In summary, we have demonstrated the first example of carbon monoxide trapping in a Mn^{3+} oxidation system. An inefficient termination step has been bypassed via carbon monoxide trapping. Subsequent efficient termination leads to acyl cations and finally carboxylic acids. The overall transformation involves the oxidative carbonylation of organic compounds.

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Supplementary Material Available: Descriptions of the procedures for carbonylation and spectral data, including IR, ^1H and ^{13}C NMR, and exact mass spectra for **2**, **4**, **8a**, **8b**, **9**, **10**, **11**, and **12** (5 pages). Ordering information is given on any current masthead page.

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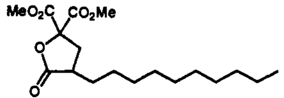
(12) The attempted carbonylation of 2,2-dialkyl-substituted 1-alkenes was unsuccessful, presumably due to the very rapid oxidation of tertiary radicals prior to CO trapping.

(13) This yield was obtained with 3.3 mol equiv of manganese triacetate (**9**/**7b**/Mn(III) = 1/1/1.3). Even with 2 mol equiv of manganese triacetate, the cyclized compound **10** was the major product, suggesting that the oxidation of the initial product is a very rapid process. It should be noted that further cyclization also occurred in the case of dimethyl malonate (**6**). For example, the reaction of 1-dodecene (**7b**) (1.5 mmol) with **6** (1.5 mmol) and manganese triacetae (6 mmol) under similar carbonylation conditions gave the γ-lactone **12** in 30% yield after isolation by HPLC.



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(14) The tertiary α,α′-diketo-substituted radical, generated by the oxidation of the initially produced carboxylic acid, could cyclize reversibly to yield a five-membered ring radical stabilized by two α-oxygen atoms. This radical could be easily oxidized to give **10**. An analogous mechanism has been suggested in a similar lactonization with a Mn(III)/Cu(II) system, see ref 6a.

(15) This step has precedence, see: Citterio, A.; Fancelli, D.; Finzi, C.; Pesce, L. *J. Org. Chem.* **1989**, *54*, 2713. Note that a separate experiment was performed in order to obtain **8b**, see supplementary material.