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The Addition Reaction of β-Keto Carboxylic Acids to Olefinic Compounds by the Use of Mn(III) Tris(2-pyridinecarboxylate) as an Oxidant

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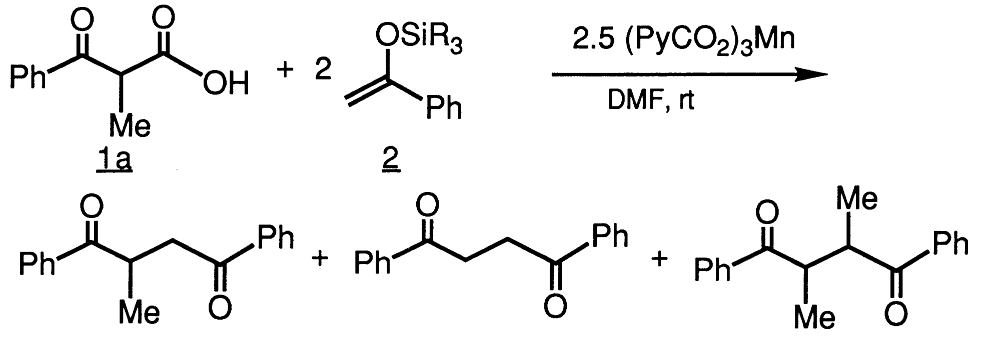
Intermolecular addition reactions of radical species generated from β-keto carboxylic acids to olefinic compounds such as a silyl enol ether, a ketene dithioacetal and an enamine proceed selectively by the use of manganese(III) tris(2-pyridinecarboxylate) as an oxidant.

Radical species have found a limited use in organic synthesis because of the difficulty in controlling reaction pathways mainly due to their high reactivity and the tendency toward the self-coupling. Recently, addition reactions of radical species to olefinic groups afford a significant synthetic tool for constructing carbon skeletons,[1-5] but, in general, control of the reactions of radical species has been still difficult especially in the case of intermolecular reactions.

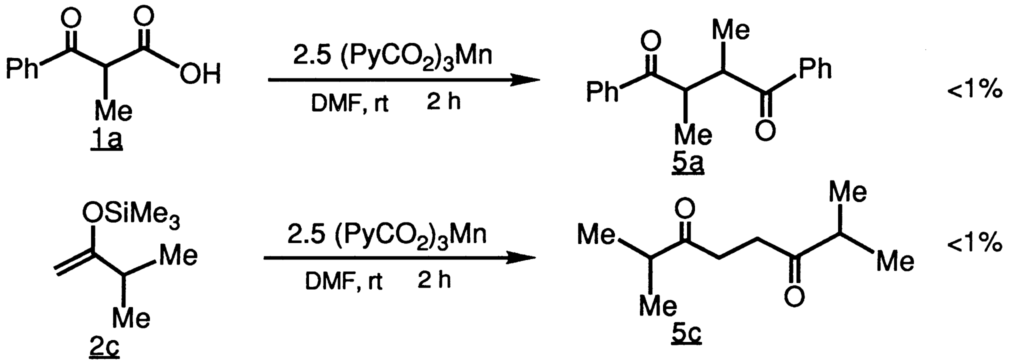
In order to realize good selectivity in radical addition reactions, radical species should be generated in the close proximity to a radical acceptor. When the radical generation is facilitated by the interactions of both of a radical source and an acceptor to metallic center, the addition reaction would proceed in highly selective manner. Such a possibility has been suggested in the reactions of β-keto acids and olefins by the use of manganese(III) acetate, in which the presence of radical acceptors accelerates the generation of radical species.[4b,5b] We had an interest in developing the selective intermolecular radical reaction by the aid of metallic compound. And the generation of radical species from β-keto carboxylic acids and the addition reaction to silyl enol ethers were investigated using various metallic compounds as oxidants.

The reaction of 2-methyl-3-oxo-3-phenylpropionic acid (1a) with 2 equiv. of 1-phenyl-1-trimethylsiloxyethene (2a) was examined in the presence of 2.5 equiv. of various metal oxidants such as manganese(III), cobalt(III), cerium(IV), copper(II), and iron(III) compounds. Among various metal compounds, Mn(III) tris(2-pyridinecarboxylate)[6] (Mn(pic)$_3$) was found to afford the addition product 3a particularly in high selectivity. When the reaction was carried out in N,N-dimethylformamide (DMF) at room temperature, the addition product 3a was obtained in 72% yield with the self-coupling product 4a (47% to 3a). Furthermore, when the t-butyldimethylsilyl enol ether 2b was used instead of the trimethylsilyl enol ether 2a, formation of the self-coupling product 4a was suppressed and the addition product 3a was obtained selectively in 68% yield.

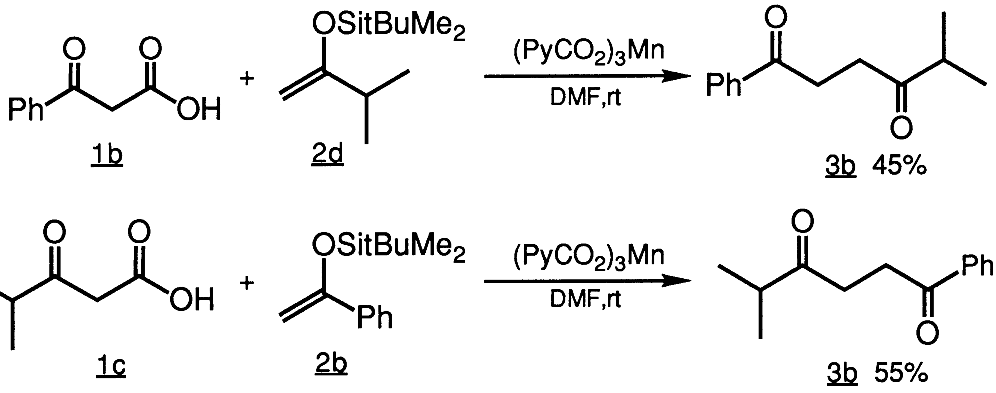


2a (R_3=Me_3) 3a 70% 4a 47% to 3a 5a Undetected
2b (R_3=t-$BuMe_2$) 3a 68% 4a Undetected 5a Undetected

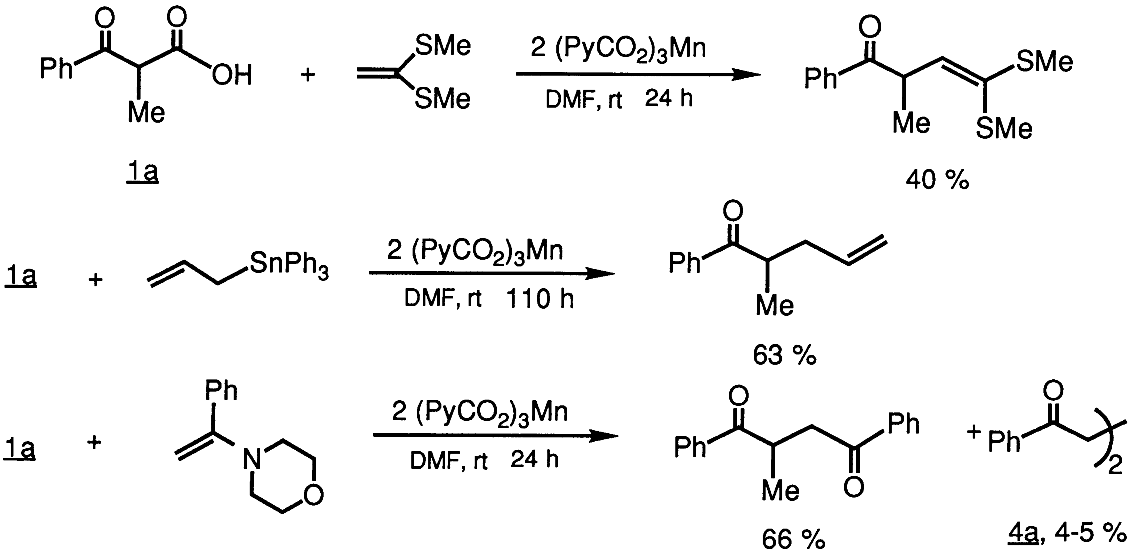
Each of the β-keto acid 1a and the silyl enol ether 2c was treated independently with $Mn(pic)_3$ in DMF at room temperature for 2 h, but a trace amount of the expected self-coupling products 5a and 5c were detected with GC analysis (in less than 1% yield). These results mean that the generation of radical species from the β-keto carboxylic acid 1a does not proceed only with $Mn(pic)_3$, but is supposed to be facilitated by the interaction of the both reactants 1a and 2c with $Mn(pic)_3$. Therefore, the high selectivity of the present intermolecular addition reaction is mainly due to the above characteristics of $Mn(pic)_3$.



Since the high selectivity was observed in the above reaction, reactions between some β-keto carboxylic acids 1 and t-butyldimethylsilyl ethers 2b,d were examined by employing $Mn(pic)_3$ in DMF. As shown in the following equations, the addition product 3b was obtained selectively in moderate yield.

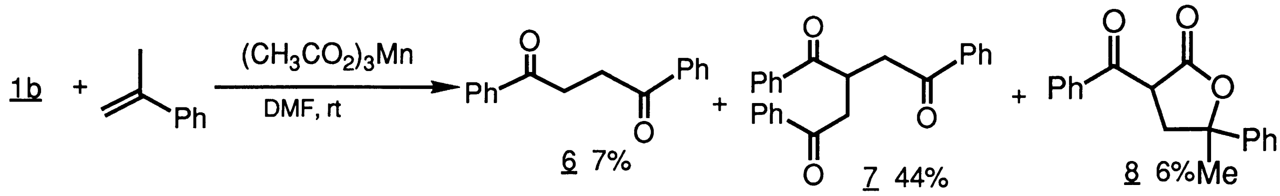


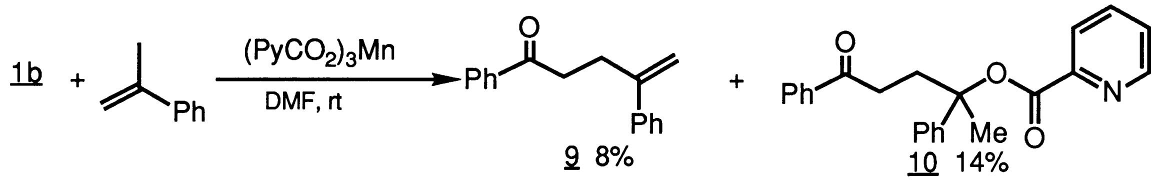
In the most of oxidative radical generation by the use of manganese (III) compounds such as manganese(III) acetate, acetic acid was usually employed as a solvent.[2,4,5a,b] Accordingly, acid sensitive olefins like a silyl enol ether could not be used as a radical acceptor. On the other hand, as the present method using Mn(pic)$_3$ could be widely applied to the other olefinic compounds, such as a ketene dithioacetal, an allyltin and an enamine because the reaction proceed smoothly under nearly neutral conditions such as in DMF. The corresponding addition products were isolated selectively, excepting only in the case of an enamine, where a small amount of self-coupling product 4a was detected.



A typical experimental procedure is as follows: To a DMF suspension (1 ml) of Mn(pic)$_3$ (418 mg, 0.99 mmol) was added a DMF (2 ml) solution of 1-phenyl-1-t-butyldimethylsiloxyethene (2b, 219 mg, 0.93 mmol) and a DMF (2 ml) solution of 2-methyl-3-oxo-3-phenylpropionic acid (1a, 70 mg, 0.39 mmol) with stirring at room temperature under an argon atmosphere. After stirring for 24 h, a reaction mixture was quenched with pH 7 buffer. Products were purified by TLC to afford the desired product 3a (68 mg, 68% yield).

In the above reactions, all the intermolecular addition products were isolated as the adducts of the olefins and the decarboxylated keto acid components. In order to determine whether the generation of radical species occurs with decarboxylation (giving α-keto radical) or without decarboxylation (giving α-radical of β-keto acid),[4b,5a,b] the reaction between 3-oxo-3-phenylpropionic acid 1b and 2-phenylpropene was examined in DMF by using Mn(III) triacetate or Mn(pic)$_3$. When Mn(OAc)$_3$, which oxidized β-keto carboxylic acids to -radicals, was used as an oxidant, the dimer 6 and the trimer 7 of the keto acid 1b and the lactone 8 were obtained.[5b] On the other hand, by employing Mn(pic)$_3$, the adducts 9 and 10 were obtained and the lactone 8 and the trimer 7 were not found. Since the products from the α-radical of the keto acid, 7 and 8, were not isolated in the reaction with Mn(pic)$_3$, the α-keto radical may be generated with Mn(pic)$_3$ via the decarboxylation reaction of the keto acids.





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