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Addition Reactions of Cation Radicals of Nitroalkanes to Olefinic Compounds by the Use of Manganese(III) 2-Pyridinecarboxylate

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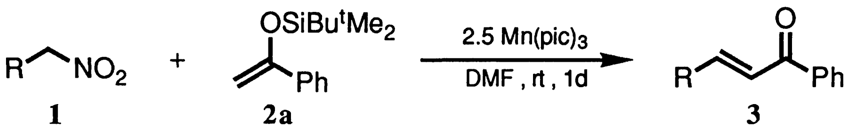
Silyl derivatives of *aci*-nitroalkanes react with olefins such as silyl enol ether, vinyl sulfide, and enamine by oxidation with manganese(III) 2-pyridinecarboxylate to give the intermolecular addition products selectively.

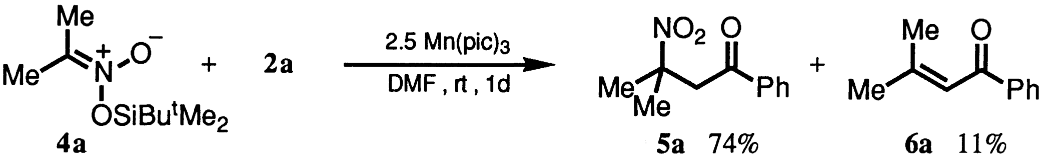
A recent disclosure from this laboratory[1)] reported an efficient method for intermolecular addition reaction of radical species to olefins in which radical species were generated from β-keto carboxylic acids oxidatively by the use of manganese(III) 2-pyridinecarboxylate (Mn(pic)$_3$). These findings prompted us to study on the generation of cation radical species from nitroalkanes[2)] and their addition reactions to olefinic compounds using Mn(pic)$_3$ as an oxidant.

Nitroalkanes **1** were treated with 2.5 molar amounts of Mn(pic)$_3$ in the presence of α-*t*-butyldimethylsiloxystylene (**2a**), but the oxidation of nitroalkanes hardly proceeded. Only in the case of phenylnitromethane, the addition product **3** was obtained in low yield.



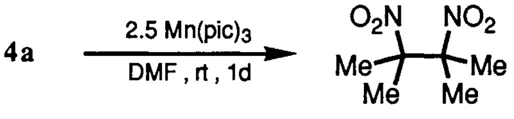
R = Me No Reaction
R = Ph 14%

To facilitate the oxidation of nitroalkanes, silyl derivatives of *aci*-nitroalkanes[3)] **4** were employed instead of nitroalkanes because the silyl derivatives showed lower oxidation potential than the corresponding nitroalkanes.[4)] When a mixture of *t*-butyldimethylsilyl derivative of 2-*aci*-nitropropane **4a** and 1.5 molar amounts of **2a** in DMF was treated with 2.5 molar amounts of Mn(pic)$_3$, the corresponding addition product **5a** and the enone **6a** which was the elimination product of HNO$_2$ from **5a** were obtained in 85% total yield.



4a **5a** 74% **6a** 11%

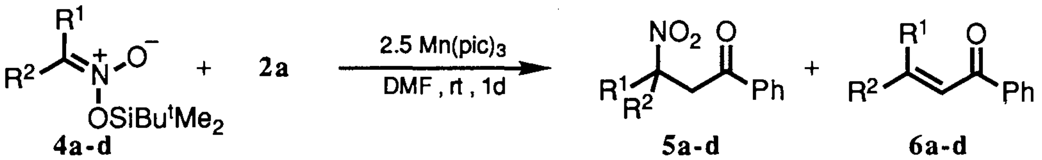
The reaction was also examined by employing various other Mn(III) compounds such as Mn(III) acetate, and acetylacetonato Mn(III), and Mn(pic)$_3$ was found to afford the addition products **5a** and **6a** in good yields without accompanying the self-coupling products of the substrates **4a** and **2a**. It was also noted that the treatment of *aci*-nitro derivative **4a** alone with Mn(pic)$_3$ in DMF under the similar reaction conditions gave the self-coupling product **7** in 10% yield.



7 10%

These findings mean that the oxidation of the silyl derivative of *aci*-nitroalkane **4a** is accelerated in the presence of the silyl enol ether **2a**[5] and the radical species generated from **4a** reacts selectively with the silyl enol ether **2a**. The high selectivity in this intermolecular addition reaction would be attributable to the cage-trapping of the radical species with the coordinated olefin within the coordination sphere, since **4a** does not react appreciably with Mn(pic)$_3$ in the absence of a silyl enol ether.

Reactions of *t*-butyldimethylsilyl derivatives of various *aci*-nitroalkanes **4a-d** and the silyl enol ether **2a** were investigated and the results are summarized below. In all cases, none of the self-coupling product of **4a-d** or **2a** was detected.

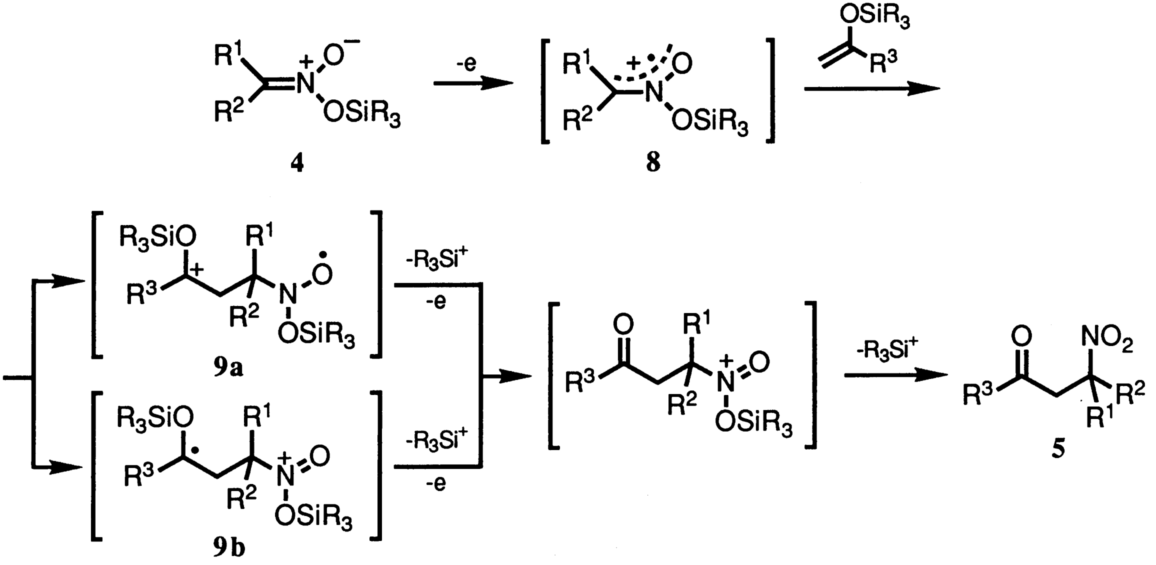


4a-d **5a-d** **6a-d**

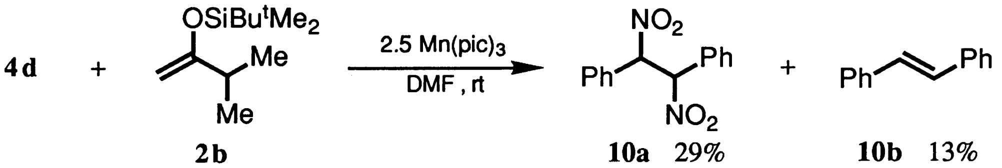
4	R^1	R^2	Yield / % 5	6
4a	Me	Me	74	11
4b	Me	H	–	69
4c	Ph	Me	30	–
4d	Ph	H	–	70

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 α-*t*-butyldimethylsiloxystylene (**2a**, 173 mg, 0.74 mmol) and a DMF (2 ml) solution of **4a** (87 mg, 0.43 mmol) at room temperature under an argon atmosphere. After stirring for 24 h, the reaction mixture was quenched with pH 7 buffer. Products were purified by TLC to afford the desired products **5a** (67 mg, 74% yield) and **6a** (7 mg, 11% yield).

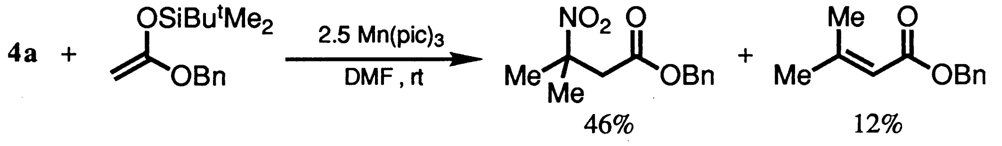
The reaction is considered to proceed through the following mechanism. A silyl derivative of *aci*-nitroalkane **4** is oxidized to the cation radical **8** with Mn(pic)$_3$, which then adds to a silyl enol ether. The resulting radical **9** is further oxidized with Mn(pic)$_3$ to give the corresponding addition product **5**.

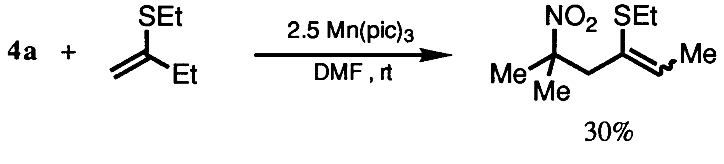


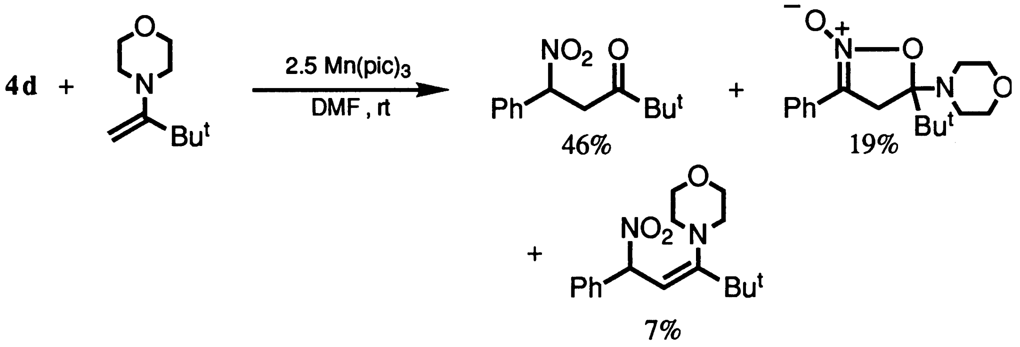
Generation of the intermediate **9** would be suggested by the reaction of **4d** and an aliphatic silyl enol ether **2b**, which gave only the self-coupling products **10a** and **10b**. Thus the presence of **2b** accelerated the oxidation of **4d**, however, **2b** could not react with the cation radical **8** due to the low radical and cation stability of the intermediate **9**.



Silyl derivatives of *aci*-nitroalkanes **4** are generally employed as nucleophiles in the carbon-carbon bond forming reactions.$^{6)}$ On the other hand, **4** exhibited the electrophilic nature by the one electron oxidation and reacted preferably with nucleophilic acceptors. Various electron rich olefinic compounds such as ketene silyl acetal, vinyl sulfide, and enamine, reacted with **4a** as the radical acceptors to yield the corresponding addition products in moderate yields.







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References

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3) E. W. Colvin, A. K. Beck, B. Bastani, D. Seebach, Y. Kai, and J. D. Dunitz, *Helv. Chim. Acta*, **63**, 697 (1980).

4) By the cyclic voltammogram measurements, *t*-butyldimethylsilyl derivative of *aci*-nitroethane exhibits an oxidation peak at about 2.1 V (Ag/Ag^+ *vs.* SCE, CH_3CN, irreversible). But nitroethane itself does not show an oxidation peak at lower than 3.0 V.

5) In the presence of the silyl enol ether, the reaction was accompanied by a slow color change of $Mn(pic)_3$ from dark red to white. On the other hand, in the absence of it, the color of reaction mixture did not change under the same reaction conditions. These observations also indicate that silyl derivative of *aci*-nitroalkane is hardly oxidized by $Mn(pic)_3$ without silyl enol ether.

6) D. Seebach, A. K. Beck, T. Mukhopadhyay, and E. Thomas, *Helv. Chim. Acta*, **65**, 1101 (1982) and references cited therein.

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