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Lanthanide Trifluoromethanesulfonates as Reusable Catalysts. Michael and Diels-Alder Reactions

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Key Words: Michael reaction; Diels-Alder reaction; lanthanide triflate; reusable catalyst

Abstract: *The Michael reaction of silyl enolates with α,β-unsaturated ketones and the Diels-Alder reaction of carbonyl containing dienophiles are catalyzed by a catalytic amount of lanthanide trifluoromethanesulfonate to give the corresponding adducts in high yields. In both reactions, the catalyst can be recovered and reused.*

Recently we have found that lanthanide trifluoromethanesulfonates (lanthanide triflates) are quite effective in the aldol-type reactions of silyl enolates with aldehydes or acetals in both aqueous[1a)] and organic solvents.[1b)] While the reactions smoothly proceed under extremely mild conditions to afford the corresponding adducts in high yields, the catalysts can be easily recovered after the reactions are completed and can be reused. These unique characteristic features prompted us to investigate further possibilities as catalysts in other Lewis acid-mediated important synthetic reactions. In this paper, we would like to describe that lanthanide triflates also work well in the Michael reaction of silyl enolates with α,β-unsaturated ketones and some Diels-Alder reactions.

Michael reaction of silyl enol ethers or ketene silyl acetals with α,β-unsaturated carbonyl compounds is among the most important carbon-carbon bond forming processes in organic synthesis. After the first reports using a stoichiometric amount of Lewis acid,[2)] several efficient catalysts have been developed,[3)] however, they could not recovered after the reactions were completed.

We found that lanthanide triflates acted quite well as reusable catalysts in the Michael reaction of silyl enolates with α,β-unsaturated ketones. Several examples are listed in Table 1. In every case, the reactions smoothly proceed in the presence of a catalytic amount of lanthanide triflate under extremely mild conditions to give the corresponding 1,5-dicarbonyl compounds in good yields after acid work up. Silyl enolates derived from ketones, thioesters, and esters are applicable, and no 1,2-addition products are obtained. Every lanthanide triflate screened ($Ln(OTf)_3$: Ln=La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Ef, Tm, Yb, Lu) works well and can be reused. It is noteworthy to refer that the yields of 1st run are almost comparable to those of 2nd run (Table 1). The reaction smoothly proceeded even in the presence of 1 mol% of the catalyst. Furthermore, the product can be isolated as a synthetically valuable silyl enol ether when the crude adduct is worked up without acid. To our knowledge, the present reaction is a first example of the lanthanide-catalyzed Michael reaction of enolate components with α,β-unsaturated carbonyl compounds.

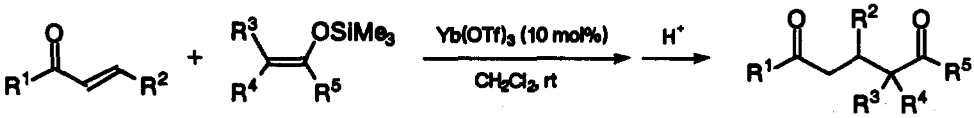
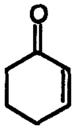
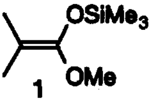
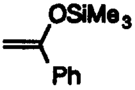
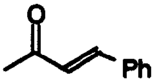
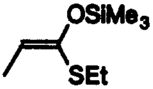
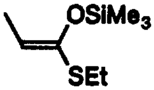
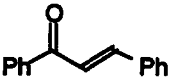
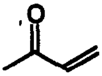
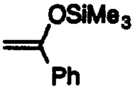
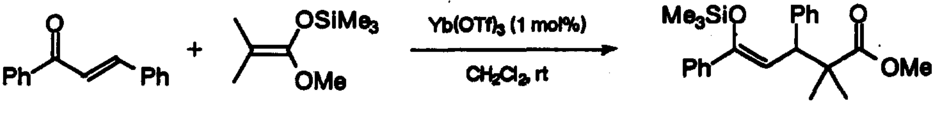


Table 1. Lanthanide Catalyzed Michael Reaction

Entry	α,β-Unsaturated Ketone	Silyl Enolate	1st run Yield / % (syn/anti)[a]	2nd run Yield / % (syn/anti)[a]
1		 1	92	95
2			75	74
3		1	85	85
4			87 (49 / 51)	87 (49 / 51)
5			82 (39 / 61)	78 (38 / 62)
6		1	92 [b]	93
7		1	66	65
8			60	63

a) Determined by ^{13}C NMR.[8]

b) 94% yield when 1 mol% of Yb(OTf)3 was used.

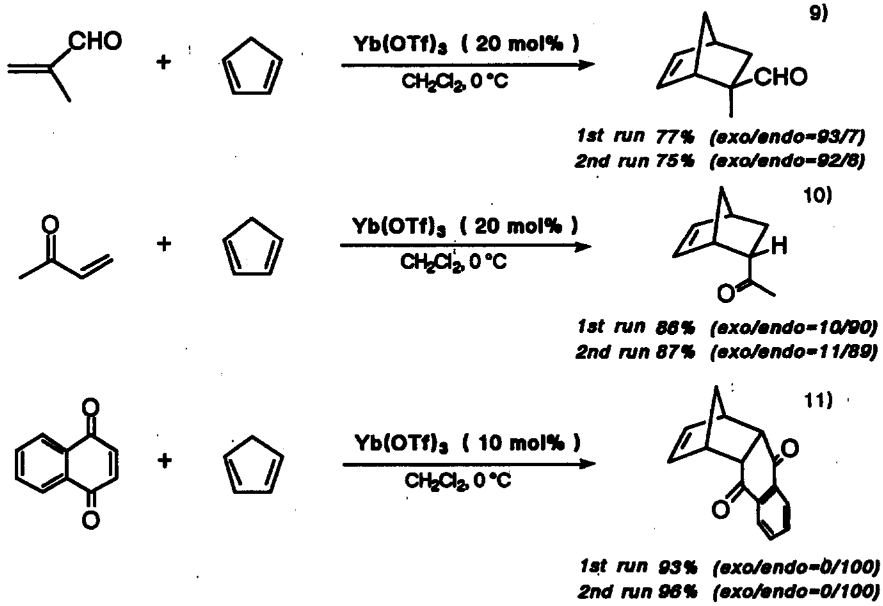


89% yield

A typical experimental procedure is described for the reaction of the ketene silyl acetal derived from methyl isobutyrate 1 with chalcone; to a suspension of Yb(OTf)$_3$ (0.04 mmol, 10 mol%)[4] in dichloromethane (1.5 ml) was added a mixture of 1 (0.6 mmol) and chalcone (0.4 mmol) in dichloromethane (1 ml) at r.t. The mixture was stirred for 12 h at this temperature and then water was added and the product was extracted with dichloromethane. Treatment of the crude product with THF:1N HCl (20:1) for 0.5 h at 0 °C and purification by silica gel column chromatography gave the corresponding 1,5-dicarbonyl compound (92%). Yb(OTf)$_3$ could be almost quantitatively recovered from the aqueous layer and could be reused[5] (2nd use; 93%). When the crude product was directly purified, the corresponding silyl enol ether could be obtained in 89% yield.

Next, we examined the function of lanthanide triflates as catalysts in the Diels-Alder reaction. Although many Diels-Alder reactions have been carried out in higher reaction temperatures without necessity of catalysts, heat sensitive compounds in complex and multistep synthesis can not be employed. While Lewis acid catalysts make the reactions possible to proceed at room temperature with satisfactory yields, they are often accompanied by diene polymerization and excess amounts of the catalyst are often needed to catalyze carbonyl containing dienophiles.[6]

We found that the lanthanide triflate is also an efficient catalyst in the Diels-Alder reaction of carbonyl containing dienophiles with cyclopentadiene.[7] Some examples are shown below, and in every case the reactions smoothly proceeded to give the corresponding adducts in high yields. It should be noted that a catalytic amount of Yb(OTf)$_3$ is enough to promote the reactions and that the catalyst can be easily recovered and reused.



1st run 77% (exo/endo=93/7)
2nd run 75% (exo/endo=92/8)

1st run 88% (exo/endo=10/90)
2nd run 87% (exo/endo=11/89)

1st run 93% (exo/endo=0/100)
2nd run 96% (exo/endo=0/100)

Lanthanide Catalyzed Diels-Alder Reaction

In summary, lanthanide triflates have found to be efficient reusable catalysts in not only aldol but also Michael and Diels-Alder reactions. These lanthanide catalysts are expected to have potential abilities as mild Lewis acid catalysts to solve even environmental problems in industrial processes, and further progress according to this line is now under investigations in our laboratory.

References and notes

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3) For example, a) Kobayashi, S.; Murakami, M.; Mukaiyama, T. *Chem. Lett.* **1985**, 953. b) Mukaiyama, T.; Tamura, M.; Kobayashi, S. *ibid.* **1987**, 743. c) Iwasawa, N.; Mukaiyama, T. *ibid.* **1987**, 463. d) Mukaiyama, T.; Kobayashi, S.; Tamura, M.; Sagawa, Y. *ibid.* **1987**, 491. e) Kawai, M.; Onaka, M.; Izumi, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1203. f) Minowa, N.; Mukaiyama, T. *Chem. Lett.* **1987**, 1719. g) Ohki, H.; Wada, M.; Akiba, K. *Tetrahedron Lett.* **1988**, *29*, 4719. h) Kobayashi, S.; Tamura, M.; Mukaiyama, T. *Chem. Lett.* **1988**, 91. i) Mukaiyama, T.; Hara, R. *ibid.* **1989**, 1171. j) Sato, T.; Wakahara, Y.; Otera, J.; Nozaki, H. *Tetrahedron Lett.* **1990**, *31*, 1581.

4) $Yb(OTf)_3$ was dried at 200 °C / 1 mmHg for 6 h before use. For the preparation of $Yb(OTf)_3$, see Forsberg, J. H.; Spaziano, V. T.; Balasubramanian, T. M.; Liu, G. K.; Kinsley, S. A.; Duckworth, C. A.; Poteruca, J. J.; Brown, P. S.; Miller, J. L. *J. Org. Chem.* **1987**, *52*, 1017.

5) After removal of water under reduced pressure, recovered $Yb(OTf)_3$ was dried at 200 °C / 1 mmHg for 6 h before 2nd use.

6) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: Oxford. 1990.

7) Concerning hetero-Diels-Alder reactions using lanthanide catalysis including NMR shift reagents, several examples were already reported. a) Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* **1983**, *105*, 3716. b) Bednarski, M.; Maring, C.; Danishefsky, S. *Tetrahedron Lett.*. **1983**, *24*, 3451. c) Danishefsky, S. J.; DeNinno, M. P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 15. See also, Molander, G. A. *Chem. Rev.* **1992**, *92*, 29, and references cited therein.

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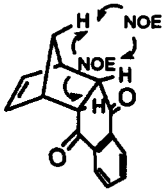
11) Only one isomer was obtained. Endo selectivity was confirmed by the observation of NOE. Cf. Suzuki, T.; Yamashita, Y.; Mukai, T.; Miyashi, T. *Tetrahedron Lett.* **1988**, *29*, 1405.



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