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Scandium Trifluoromethanesulfonate ($Sc(OTf)_3$). A Novel Reusable Catalyst in the Diels-Alder Reaction

Shū KOBAYASHI *, Iwao HACHIYA, Mitsuharu ARAKI, and Haruro ISHITANI

Department of Applied Chemistry, Faculty of Science,
Science University of Tokyo (SUT), Kagurazaka, Shinjuku-ku, Tokyo 162

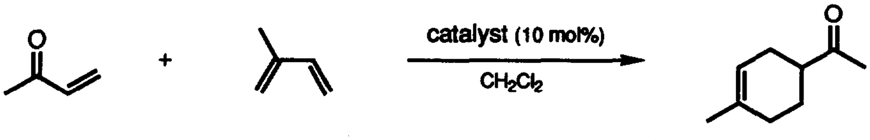
Abstract: *Scandium trifluoromethanesulfonate ($Sc(OTf)_3$) is found to be quite effective as a Lewis acid catalyst in the Diels-Alder reaction. The novel catalyst is available in both aqueous and organic media, is easily recovered from aqueous layer after the reaction is completed, and can be reused.*

Although element scandium (Sc) is in group 3 and lies above La and Y, its radius is appreciably smaller than those of any other rare earth elements and the chemical behavior of scandium is known to be intermediate between that of aluminum and that of lanthanides.1) Scandium has been uncommon probably due to the lack of rich sources and to difficulties in separation, and use in organic synthesis is rather limited though unique characteristics might be expected. In the course of our investigations to search for novel Lewis acid catalysts, especially metal trifluoromethanesulfonates (triflates),2) which can efficiently catalyze fundamental and important carbon-carbon bond forming reactions, we focused on element scandium. In this communication, we would like to report a novel catalyst, scandium trifluoromethanesulfonate (scandium triflate, $Sc(OTf)_3$), for the Diels-Alder reaction.

$Sc(OTf)_3$ is prepared from the corresponding oxide (Sc_2O_3) and trifluoromethanesulfonic acid (TfOH);3) 1.5 eq. of Sc_2O_3 was added to an aqueous solution of TfOH (ca. 50% v/v), and the mixture was heated at 100 °C for 1 h. After filtration to remove the unreacted oxide, water was evaporated under reduced pressure. The resulting white powder was dried by heating *in vacuo* at 200 °C.

$$Sc_2O_3 \quad + \quad \underset{\text{(ca 50\% TfOH/}H_2O\text{)}}{6\ \text{TfOH}} \quad \longrightarrow \quad 2\ Sc(OTf)_3 \quad + \quad H_2O$$

$Sc(OTf)_3$ thus prepared was first tested as a Lewis acid catalyst in the Diels-Alder reaction4) of MVK with isoprene. $Y(OTf)_3$ or $Ln(OTf)_3$ is known to be effective in some Diels-Alder reactions,5,6) however, only a trace amount of corresponding adduct **1** was obtained in the above reaction. On the other hand, the reaction quite smoothly proceeded to give **1** in the presence of 10 mol% of $Sc(OTf)_3$ (Table 1).



1

Table 1. Effect of Catalyst

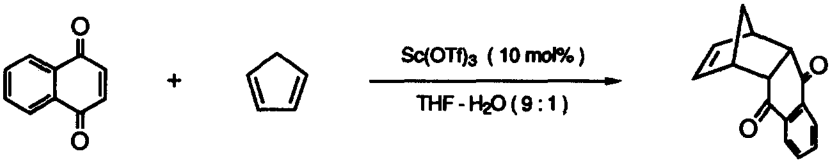
Entry	Catalyst	Conditions	Yield / %
1	$Sc(OTf)_3$	0 °C, 13h	91[a]
2	$Y(OTf)_3$	0 °C, 24 h	trace
3	$Yb(OTf)_3$	0 °C, 24 h	trace

a) Containing 6.7% of regioisomer.

Several examples of the Diels-Alder reaction is shown in Table 2. 3-Acyl-1,3-oxazolidin-2-ones, MVK, or naphtoquinone smoothly reacts with dienes such as cyclopentadiene, 1,3-cyclohexadiene, isoprene, or 2,3-dimethylbutadiene, to afford the corresponding Diels-Alder adducts in high yields with endo selectivities. Moreover, $Sc(OTf)_3$ is quite effective and use of even 1 mol% of $Sc(OTf)_3$ is enough to complete the reaction.

A typical experimental procedure is described for the reaction of MVK with cyclopentadiene: to a dichloromethane suspension (1 ml) of $Sc(OTf)_3$ (0.04 mmol) was added a mixture of MVK (0.4 mmol) and cyclopentadiene (0.12 mmol, freshly distilled before use) in dichloromethane at 0 °C. The mixture was stirred for 12 h at 0 °C and water was added. The aqueous layer was extracted with dichloromethane and the combined organic solvents were dried (Na_2SO_4). After purification by silica gel column chromatography, the desired Diels-Alder adduct was obtained in 96% yield (endo/exo=89/11). The catalyst was recovered from the aqueous layer and could be reused (see below).

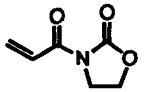
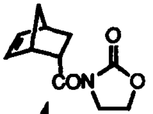
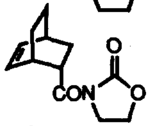
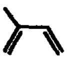
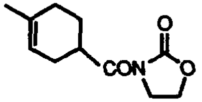
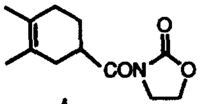
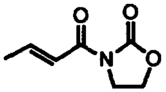
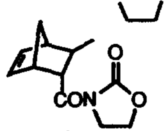
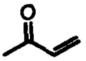
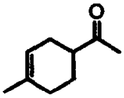
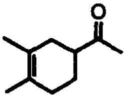
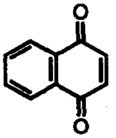
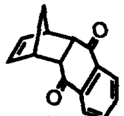
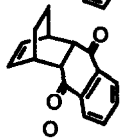
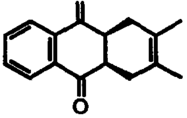
The present Diels-Alder reaction proceeds even in aqueous media.[7] Thus, naphtoquinone reacted with cyclopentadiene in THF-H_2O (9:1) at room temperature to give the corresponding adduct in 93% yield (endo/exo=100/0). While most Lewis acids are decomposed or deactivated under the influence of water, $Sc(OTf)_3$ is stable and can efficiently behave as a Lewis acid even in aqueous solution.[8]



93% yield, endo/exo=100/ 0

Another characteristic feature of $Sc(OTf)_3$ as a Lewis acid catalyst is that it can be easily recovered and reused. After the reaction is completed and the Diels-Alder adduct is extracted with dichloromethane, the aqueous layer is concentrated to remove the water under reduced pressure. $Sc(OTf)_3$ is almost quantitatively recovered and the recovered catalyst is also effective in the Diels-Alder reaction (Table 3). It should be noted that the yields of 2nd and even 3rd runs are comparable to that of 1st run.

Table 2. Sc(OTf)$_3$ Catalyzed Diels-Alder Reaction [a]

Entry	Dienophile	Diene	Major Product	Yield /% [b]	endo / exo [c]
1				95 (quant.	87 / 13 86 / 14) [d]
2				89	100 / 0
3				90	—
4				86	—
5				97	84 / 16
6				96	89 / 11
7				83	>95 / 5
8				91	—
9				88	—
10				83	100 / 0
11				89	94 / 6
12				92	—

a) Reaction conditions; Sc(OTf)$_3$ 10 mol%, CH$_2$Cl$_2$, 0 °C. b) Isolated yield. c) Determined by ^{1}H and/or ^{13}C NMR. d) Sc(OTf)$_3$ 1 mol%.

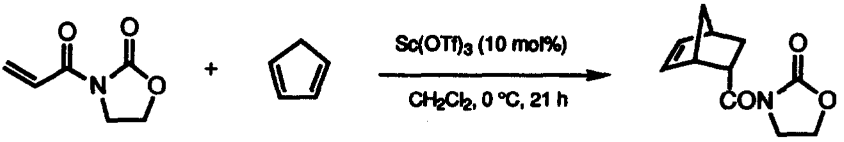


Table 3. Reuse of the catalyst

Run	Yield / %	endo / exo
1st	95	87 / 13
2nd	91	88 / 12
3rd	90	91 / 9

Further investigation to develop synthetic reactions, especially carbon-carbon bond forming reactions, using this novel catalyst is now in progress.

Acknowledgement

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References and Notes

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