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Communication

Scandium perfluoroalkanesulfonate-catalyzed Diels–Alder reactions in an organic solvent

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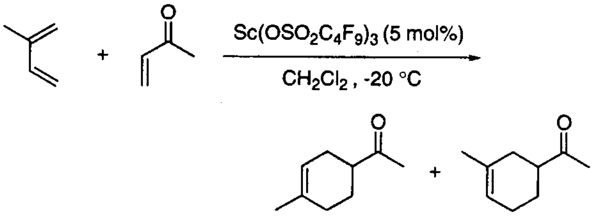
This paper is dedicated to Professor Jean Normant on the occasion of his 65th birthday

Abstract

Scandium perfluoroalkanesulfonate-catalyzed Diels–Alder reactions proceeded smoothly in dry dichloromethane in the presence of molecular sieves (MS) 5 Å. It was found that water interfered with the reactions, contrary to most rare earth-catalyzed reactions that proceed smoothly in aqueous media. Among scandium perfluoroalkanesulfonates tested, scandium triflate ($Sc(OTf)_3$), scandium pentafluoroethanesulfonate ($Sc(OSO_2C_2F_5)_3$), and scandium nonafluorobutanesulfonate ($Sc(OSO_2C_4F_9)_3$) gave the highest yields and selectivities. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Scandium perfluoroalkanesulfonates; Diels–Alder reactions; Rare earth metal triflates

Diels–Alder reaction is one of the most fundamental and important carbon–carbon bond-forming reactions in organic synthesis, and provides a powerful method for the preparation of many cyclic compounds. The reaction is accelerated by a Lewis acid, and high yield and selectivity were obtained under mild conditions [1]. In 1993, we reported that scandium trifluoromethanesulfonate (scandium triflate, $Sc(OTf)_3$) was an effective catalyst for Diels–Alder reaction in dichloromethane [2]. Since we had already found that rare earth metal triflates including $Sc(OTf)_3$ were stable Lewis acids in water and several useful synthetic reactions were shown to proceed smoothly in aqueous solvents [3], it was thought that $Sc(OTf)_3$-catalyzed Diels–Alder reactions might also proceed smoothly in aqueous media. However, it turned out that water interfered with the Diels–Alder reactions. In this paper, we summarize scandium perfluoroalkanesulfonate-catalyzed Diels–Alder reaction, and the effects of water and anions of the scandium salts in this reaction are discussed.



(1)

We first examined the Diels–Alder reaction of methyl vinyl ketone (MVK) with isoprene in the presence of $Sc(OSO_2C_4F_9)_3$ (Eq. (1)).We set up three types of reaction conditions: (i) use of standard $Sc(OSO_2C_4F_9)_3$ that was prepared according to a literature method and stored in a desiccator for a month; (ii) use of dry $Sc(OSO_2C_4F_9)_3$, which was prepared from standard $Sc(OSO_2C_4F_9)_3$ by drying at 200°C/0.5 mmHg for 24 h just before use; (iii) use of dry $Sc(OSO_2C_4F_9)_3$ with molecular sieves (MS) 5 Å. The reactions were carried out in dry dichloromethane using 5 mol% of the scandium catalyst, and the results are summarized in Table 1 and Fig. 1. Unexpectedly, it was found that the reaction proceeded sluggishly in 3 h using standard $Sc(OSO_2C_4F_9)_3$ (condition (i)). While the desired Diels–Alder adduct was obtained in 60% yield in 3 h using dry $Sc(OSO_2C_4F_9)_3$ (condition (ii)), the yield was im-

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Table 1
Effect of the conditioning of the scandium catalyst [a]

Time	Condition (i), yield (%) [b,c]	Condition (ii), yield (%) [b,c]	Condition (iii), yield (%) [b,c]
10 min	0	7	48
30 min	0	38	76
1 h	0	54	91
3 h	4	60	94

[a] See text.

[b] Yield into 3 (and 4)-methyl-1-acetylcyclohex-3-ene was determined by GC analysis.

[c] Ratio of isomers was not determined.

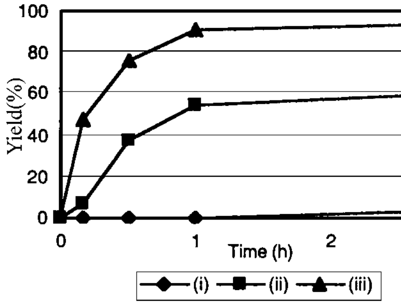

Fig. 1.

proved to 94% using dry $Sc(OSO_2C_4F_9)_3$ with MS 5 Å (condition (iii)). These results suggested that water interferes with the Diels–Alder reaction. It is noteworthy that this suppressive effect of water is contrary to that in most rare earth metal triflate-catalyzed reactions, which proceed smoothly in the presence of water [3]. We then examined the length of perfluoroalkyl chains of scandium salts[1] in the model Diels–Alder reaction (Table 2, Fig. 2). All reactions were carried out using 5 mol% of scandium salts with MS 5 Å. Scandium triflate ($Sc(OTf)_3$), scandium pentafluoroethanesulfonate ($Sc(OSO_2C_2F_5)_3$), and scandium nonafluorobutanesulfonate ($Sc(OSO_2C_4F_9)_3$) worked well to afford the desired Diels–Alder adduct in excellent yields in 1 h. Almost the same activity was observed among these three scandium salts. On the other hand, a slight decrease of the activity was observed when scandium tridecafluorohexanesulfonate ($Sc(OSO_2C_6F_{13})_3$) was used, and less activity was obtained using scandium heptadecafluorooctanesulfonate ($Sc(OSO_2C_8F_{17})_3$. Longer perfluoroalkanesulfonates gave lower yields probably due to bulkiness of the counter anions albeit the longer perfluoroalkyl groups induce high Lewis acidity of the scandium.

Table 2
Effect of scandium salts ($Sc(OSO_2C_nF_{2n+1})_3$) [a,b]

Time	$n = 1$, yield (%)	$n = 2$, yield (%)	$n = 4$, yield (%)	$n = 6$, yield (%)	$n = 8$, yield (%)
10 min	52	45	48	23	4
30 mm	80	76	76	54	21
1 h	88	87	91	77	38
3 h	92	92	94	87	69

[a] Yield into 3 (and 4)-methyl-1-acetylcyclohex-3-ene was determined by GC analysis. See also text.

[b] Ratio of isomers was not determined.

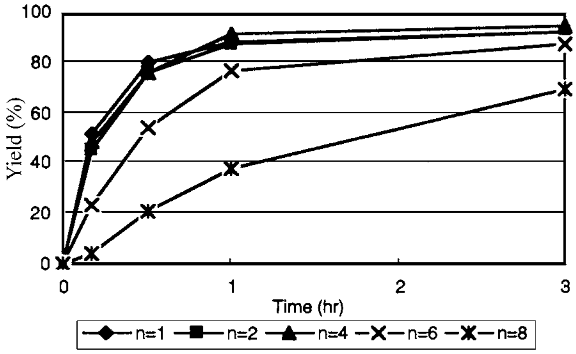

Fig. 2.

Several examples of the Diels–Alder reactions using $Sc(OSO_2C_4F_9)_3$ as a catalyst are shown in Table 3. 3-Acyl-1,3-oxazolidin-2-one, MVK, and maleic anhydride smoothly reacted with dienes such as cyclopentadiene, 1,3-cyclohexadiene, and isoprene to afford the corresponding Diels–Alder adducts in high yields with high diastereoselectivity. It is noted that less reactive dimethyl fumarate and dimethyl acetylenedicarboxylate reacted with cyclopentadiene to afford the desired Diels–Alder adducts in high yields, respectively.

A typical experimental procedure is described for the reaction of MVK with isoprene: to a suspension of $Sc(OSO_2C_4F_9)_3$ (62.2 mg, 0.066 mmol), naphthalene (82.6 mg, 0.644 mmol; internal standard), and MS 5 Å (100 mg) in dichloromethane (3 ml) were added MVK (93.4 mg, 1.33 mmol) and isoprene (385 µl, 3.85 mmol). After the mixture was stirred at −20°C for 3 h, $NaHCO_3$ aq. was added to quench the reaction. After a usual work-up, the yield and stereoselectivity were determined by GC analysis.

In summary, Diels–Alder reactions proceeded smoothly in the presence of a catalytic amount of scandium perfluoroalkanesulfonate. Contrary to other rare earth-catalyzed reactions, water interfered with the reactions, and the desired adducts were most effectively

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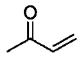
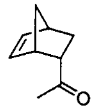
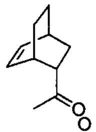
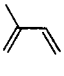
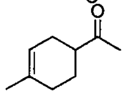
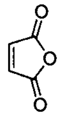
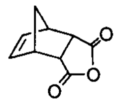
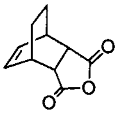
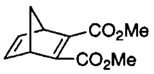
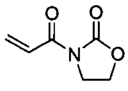
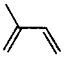
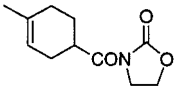
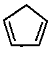
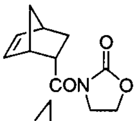
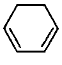
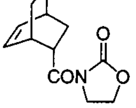
[1] We used five scandium catalysts, $Sc(OTf)_3$, $Sc(OSO_2C_2F_5)_3$, $Sc(OSO_2C_4F_9)_3$, $Sc(OSO_2C_6F_{13})_3$, $Sc(OSO_2C_8F_{17})_3$, which were readily prepared from Sc_2O_3 and the corresponding acids (TfOH, $C_2F_5SO_3H$, $C_4F_9SO_3H$, $C_6F_{13}SO_3H$) or $ScCl_3$ and the corresponding acid ($C_8F_{17}SO_3H$).

Table 3
$Sc(OSO_2C_4F_9)_3$-catalyzed Diels–Alder reactions

Entry	Dienophile	Diene	Major Product	Yield / %	Isomers
$1^{a,d}$				quant.	98 / 2^{f}
$2^{a,d}$				88	>99 / $<1^{f}$
$3^{a,d}$				89	96 / 4^{g}
$4^{a,e}$				85	>99 / $<1^{f}$
$5^{b,e}$				77	>99 / $<1^{f}$
$6^{a,e}$				73	—
$7^{c,d}$				96	>99 / $<1^{g}$
$8^{c,e}$				90	>99 / $<1^{f}$
$9^{c,e}$				88	>99 / $<1^{f}$

Reaction conditions; $Sc(OSO_2C_4F_9)_3$ 5 mol% with MS5A,
a) CH_2Cl_2, -20 °C, b) CH_2Cl_2, 0 °C, c)CH_2Cl_2 : CH_3CN = 1: 1, r.t.
d)Yield and ratio of isomers were determined by GC analysis.
e) Isolated yield. Ratio of isomers was determined by ^{1}H- NMR. f) endo/exo isomers. g) 1,4/1,3 isomers.

obtained by using a catalytic amount of $Sc(OTf)_3$, $Sc(OSO_2C_2F_5)_3$, or $Sc(OSO_2C_4F_9)_3$ in dichloromethane with MS 5 Å. This suppressive effect of water is mechanistically interesting because (i) it is reported that some Diels–Alder reactions are accelerated by water [5]; (ii) many other $Sc(OTf)_3$-catalyzed reactions proceed smoothly in water. The mechanistic aspects, especially the effect of water in these reactions, are now under investigation [6].

Acknowledgements

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