© 1997 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 70, 1421—1426 (1997)

Scandium(III) Perfluorooctanesulfonate [Sc(OPf)$_3$]: A Novel Catalyst for the Hetero Diels–Alder Reaction of Aldehydes with Non-Activated Dienes

Takeshi Hanamoto, Yuichi Sugimoto, Yong Zhi Jin, and Junji Inanaga*

Institute for Fundamental Research of Organic Chemistry (IFOC), Kyushu University, Hakozaki, Fukuoka 812-81

(Received February 7, 1997)

Scandium(III) perfluorooctanesulfonate [scandium(III) perflate, Sc(OPf)$_3$] was prepared from either scandium(III) chloride or oxide and perfluorooctanesulfonic acid. The perflate thus obtained acts as a novel Lewis acid catalyst for the intermolecular hetero Diels–Alder reaction of aldehydes with non-activated dienes under mild conditions. The characteristic features of the catalyst include (i) low hygroscopicity, (ii) ease of handling, and (iii) robustness for the recycling use.

The hetero Diels–Alder reaction is of current interest because it can provide six-membered heterocyclic compounds in one step.[1)] Thus it has frequently been applied to natural product synthesis.[2)] Although many examples of Lewis acid-promoted hetero Diels–Alder reaction of heterodiene with dienophile have been accumulated,[3)] only a limited number of reactions with the opposite combination, diene-hetero-dienophile, have so far been reported.[4)] To our knowledge, there has been no report on the Lewis acid-catalyzed hetero Diels–Alder reaction of non-activated aldehydes with simple alkyl-substituted 1,3-dienes which affords the desired cycloadducts in satisfactory yields under mild conditions.[5)]

Since Forsberg et al. first utilized ytterbium(III) trifluoromethanesulfonate [Yb(OTf)$_3$] as an effective Lewis acid catalyst in organic synthesis, a number of reactions have been found to proceed smoothly by the catalysis of rare earth-(III) triflates [RE(OTf)$_3$].[3b,3c,6,7)] Recently we also reported the Yb(OTf)$_3$-catalyzed glycosylation of 1-*O*-methoxyacetyl sugars and that of 1-hydroxy sugars with alcohols and thiols.[8,9)] During the course of our studies on the development of trivalent lanthanide-catalyzed organic reactions, we prepared a series of rare earth(III) perfluorooctanesulfonates [RE(OPf)$_3$] as novel Lewis acids and found that Sc(OPf)$_3$ can be an excellent catalyst for the hetero Diels–Alder reaction of aldehydes with non-activated dienes such as 2,3-dimethyl-1,3-butadiene and isoprene.[10,11)]

Results and Discussion

Preparation of Scandium(III) Perflate. A series of RE(OPf)$_3$ have been prepared from either rare earth chlorides (method A) or oxides (method B)[6a)] by stirring them with heptadecafluorooctanesulfonic acid. The resulting gelatin-like solid was collected, washed, and dried at 120 °C for 15 h in vacuo. Table 1 shows the yields of RE(OPf)$_3$ complexes prepared and the method employed.

Table 1. Synthesis of RE(OPf)$_3$

Entry	RE	Yield(%)	Method[a)]
1	Sc	81	A
2	Y	97	B
3	La	69	B
4	Ce	56	A
5	Pr	63	B
6	Nd	94	B
7	Sm	91	B
8	Eu	91	B
9	Gd	97	B
10	Tb	69	B
11	Dy	97	B
12	Ho	97	B
13	Er	88	B
14	Tm	94	B
15	Yb	94	B
16	Lu	94	B

a) See the text.

The characterization of RE(OPf)$_3$ thus prepared was attempted with the following four spectroscopic methods: (1) fast atom bombardment mass spectrometry (FAB MS), (2) laser desorption/ionization time-of-flight mass spectrometry (LDI-TOF MS), (3) inductively coupled plasma spectrometry (ICP), and (4) infrared absorption spectroscopy (IR). Neither FAB nor LDI-TOF MS methods were found to be effective for the analysis of these complexes because they decomposed during the measurement. However, the ICP spectrum of the Sc salt showed the content of Sc as 2.9%, supporting the expected metal-ligand ratio (Sc/OPf=1:3). No characteristic change was observed in the FT-IR spectrum of Sc(OPf)$_3$ when it was compared with that of PfOH, which indicates that the ligand OPf$^-$ ion is extremely weakly coordinating to the metal ion, as expected from the same tendency of other salts with superacid residues like perchlorate (ClO$_4^-$), tetraphenylborate (BPh$_4^-$), and hexafluorophosphate (PF$_6^-$)

ions.

Catalytic Hetero Diels–Alder Reaction Using Scandium Perflate. The reaction of benzaldehyde with 2,3-dimethyl-1,3-butadiene was adopted for the evaluation of solvents and catalysts. Table 2 shows the effect of solvents on the Sc(OPf)$_3$-catalyzed reaction under the controlled conditions. The corresponding [4+2] adducts were obtained in quantitative yield where hexane was used as a solvent. On the other hand, almost no reaction took place in THF, which suggests that basic polar solvents seriously deactivate the catalyst through their coordination.

Next, the catalytic activity of sixteen RE(OPf)$_3$ complexes was examined for the standard hetero Diels–Alder reaction. The results are shown in Fig. 1. While yttrium and all lanthanoid complexes did not show notable activities, Sc(OPf)$_3$ exhibited an exceptionally high catalytic activity for the reaction.[12] This would be ascribed to the higher Lewis acidity of Sc(OPf)$_3$ than those of other RE(OPf)$_3$, which does not conflict the reported pK_a values of the coordinating water molecule to rare earth 3+ ions: Sc^{3+} (pK_a = 4.93) vs. other RE^{3+} ions (pK_a = 9.03—7.94).[13]

The catalytic activity of other rare earth metal salts with different ligands has also been tested. As shown in Table 3, the catalytic activity of the perflates is higher than that of the corresponding triflates[11] or chlorides. Since the acidity of perfluorooctanesulfonic acid is thought to be almost equal to that of triflic acid, the higher catalytic activity of RE(OPf)$_3$ over that of RE(OTf)$_3$ may partly be attributed to the water-repellent nature of the perfluoroalkane chain of the former which refuses the approach of water molecules to the central metal cation, thus maintaining its high Lewis acidity. In fact, RE(OPf)$_3$ was found to be much less hygroscopic than RE(OTf)$_3$.[14] Perfluorooctanesulfonic acid[15] itself can promote the reaction, but it was found to be less effective than Sc(OPf)$_3$. Lanthanide shift reagents for NMR measurement such as tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) europium [Eu(fod)$_3$] and tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato] europium [Eu(hfc)$_3$] are totally inactive for the present reaction.

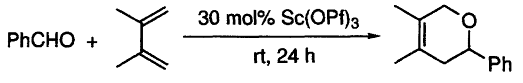


Table 2. Effect of Solvent

Entry	Solvent	Yield(%)[a]
1	Hexane	99
2	Cyclohexane	92
3	Benzene	95
4	Toluene	92
5	CH_2Cl_2	32
6	Ether	59
7	THF	7
8	CH_3CN	27
9	CH_3NO_2	8

a) Isolated yield.

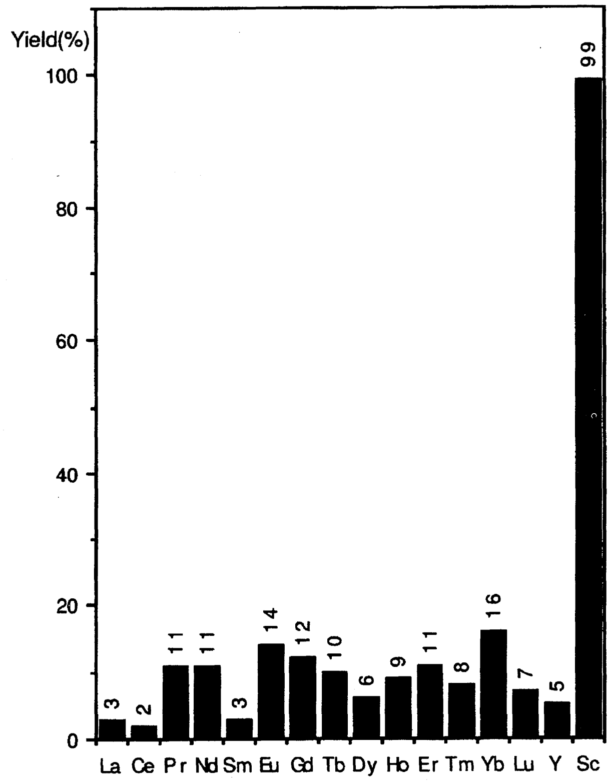


Fig. 1. Effect of rare earth metal ion for the RE(OPf)$_3$-catalyzed hetero Diels–Alder reaction of benzaldehyde with 2,3-dimethyl-1,3-butadiene.

Table 3. Effect of Catalyst for the Hetero Diels–Alder Reaction of Benzaldehyde with 2,3-Dimethyl-1,3-butadiene[a]

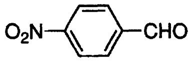
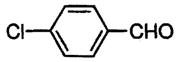
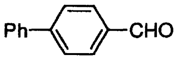
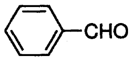
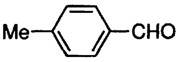
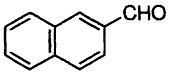
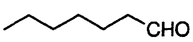
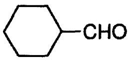
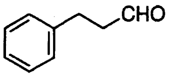
Entry	Catalyst	Yield(%)[b]
1	Yb(OTf)$_3$	—[c]
2	Yb(OPf)$_3$	16
3	$ScCl_3$	Trace
4	Sc(OTf)$_3$	35
5	Sc(OPf)$_3$	99
6	TfOH	59
7	PfOH	61
8	Eu(fod)$_3$	—[c]

a) All reactions were carried out with 30 mol% of the catalyst in hexane at room temperature for 24 h. b) Isolated yield. c) Not detected.

By using the most effective catalyst, Sc(OPf)$_3$, the hetero-Diels–Alder reaction of a variety of aldehydes with 2,3-dimethyl-1,3-butadiene (Table 4) and with isoprene (Table 5) were examined. Both aromatic and aliphatic aldehydes reacted with either diene; the corresponding trisubstituted and disubstituted 5,6-dihydro-2*H*-pyrans were obtained in good yields under mild conditions. The latter reaction proceeded in a highly regioselective manner to give dihydropyran derivatives with methyl substituent at C-4 position as a predominant isomer, as can be expected from the favorable HOMO-LUMO interaction of isoprene and aldehydes.

The catalyst can be recovered quantitatively by filtration and reused, after being dried, without serious loss of the catalytic activity. For example, in the Sc(OPf)$_3$-catalyzed

Table 4. $Sc(OPf)_3$ Catalyzed Hetero Diels–Alder Reaction of 2,3-Dimethyl-1,3-butadiene with Various Aldehydes[a)]

Entry	RCHO	Yield(%)[b,c)]
1		98
2		96
3		96 (52 h)
4		99
5		93
6		41 (52 h)
7		78 (96 h)
8		76
9		84
10		68 (48 h)

a) All reactions were carried out with 30 mol% of $Sc(OPf)_3$ in hexane at room temperature for 24 h unless otherwise noted. b) Isolated yield. c) Reaction time in parenthesis.

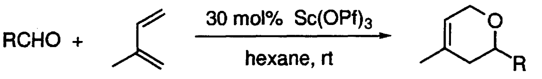
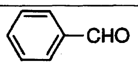
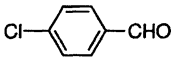
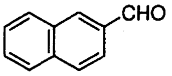
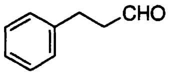


Table 5. $Sc(OPf)_3$ Catalyzed Hetero Diels–Alder Reaction of Isoprene with Various Aldehydes[a)]

Entry	RCHO	Yield(%)[b,c)]
1		90
2		99
3		75 (96 h)
4		35 (48 h)

a) All reactions were carried out with 30 mol% of $Sc(OPf)_3$ in hexane at room temperature for 24 h unless otherwise noted. b) Isolated yield. c) Reaction time in parenthesis.

reaction of benzaldehyde with 2,3-dimethyl-1,3-butadiene, the product was obtained in 99% yield in the first run and 93% in the second run, respectively.[16)]

Conclusion

Scandium(III) perflate [$Sc(OPf)_3$] is demonstrated to be a new and highly effective catalyst for the hetero Diels–Alder reaction of aldehydes and non-activated dienes. The catalyst is easy to prepare, stable and storable, and reusable, which make the practical use attractive. Further study on the application of the catalyst to other reactions which can potentially be promoted by Lewis acids is under way in this laboratory.

Experimental

General. Melting points were measured with a Yanagimoto micro melting point apparatus MP-S3 and are uncorrected. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8600 spectrometer. ^1H NMR and ^{13}C NMR spectra were measured on JEOL JNM-EX 400. Chemical shifts were given by δ relative to that of internal Me_4Si (TMS). Mass spectra were obtained with Shimadzu GCMS QP-5000. Fast atom bombardment mass spectra (FABMS) and laser desorption/ionization time-of-flight mass spectra (LDI-TOF MS) were obtained with Shimadzu/Kratos CONCEPT 1S or JEOL JMS-DX 303 and Shimadzu KOMPACT MALDI III, respectively. Inductively coupled plasma (ICP) spectra were measured on a Hitachi IPC emission spectrochemical analyzer P-4000H apparatus. Elemental analyses were performed on a Yanagimoto MT3 CHN corder or at the service center of the elementary analysis of organic compounds, Kyushu University. Analytical thin layer chromatography (TLC) was performed on a silica gel plate (Merck, Kieselgel 60 F254, 20 × 20 cm, 0.25 mm). All solvents were purified before use: Ether and tetrahydrofuran (THF) were dried over sodium benzophenone ketyl radical; dichloromethane (CH_2Cl_2), 1,2-dichloroethane ($ClCH_2CH_2Cl$), and cyclohexane were distilled from calcium hydride (CaH_2); benzene, toluene, and hexane were dried over sodium metal; acetonitrile (CH_3CN) was distilled from P_2O_5 and then from K_2CO_3; nitromethane (CH_3NO_2) was dried over $CaSO_4$. All reactions were carried out under an atmosphere of argon or nitrogen. Commercially available compounds were purchased and used without further purification: Rare earth oxides [Shin-Etsu Chemical Co., Ltd. (kindly supplied) or Kishida Chemical Co., Ltd.]; rare earth chlorides (Mitsuwa Chemical Co., Ltd.); perfluorooctanesulfonic acid (Tokyo Kasei Chemical Industry Co., Ltd.).

Typical Procedure for the Preparation of RE(OPf)$_3$ (RE=Sc, Y, La∼Lu): Sc(OPf)$_3$. (Method A). To a solution of heptadecafluorooctanesulfonic acid (PfOH, 7.5 g, 15.0 mmol) in water (45 mL) was added a solution of $ScCl_3 \cdot 6H_2O$ (1.3 g, 5.0 mmol) in H_2O (5 mL) and the mixture was stirred for 19 h at room temperature. The aqueous layer was decanted and the residual solid was washed with water (ca. 1.5 L) until the aqueous layer became neutral to pH test paper. The pale pink gelatin-like solid was dried at 120 °C for 15 h in vacuo to give a solid (6.2 g, 81%), which does not have a clear melting point up to 475 °C, but shrinks considerably around 300 °C. MS (LDI-TOF, negative, linear flight mode, 6 kV): 2046 $\{[Sc(OPf)_4+5]^-\}$. ·ICP: Found: Sc, 2.9%. Calcd for $C_{24}O_9F_{51}S_3Sc$: Sc, 2.9%. Anal. Found: C, 18.36; H, 0.29%. Calcd for $C_{24}O_9F_{51}S_3Sc \cdot H_2O$: C, 18.47; H, 0.13%. This was dried again for 5 min by heat-gun under vacuum just before use.

3,4-Dimethyl-6-phenyl-5,6-dihydro-2*H*-pyran:[5,17)] To a suspension of $Sc(OPf)_3$ (93 mg, 0.06 mmol) in hexane (2 mL) were successively added benzaldehyde (20.5 μL, 0.20 mmol) and 2,3-dimethyl-1,3-butadiene (46.0 μL, 0.40 mmol), and the mixture was stirred for 20 h at room temperature. After the catalyst was filtered off, the filtrate was concentrated and purified by preparative TLC on silica gel to give 37.2 mg (99%) of the title compound as an oil: IR (neat) 2916, 2810, 1450, 1383, 1103, 758, 712, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 7.25—7.39 (m, 5H), 4.54 (dd, 1H, J = 10.5, 3.7 Hz), 4.21 (d, 1H, J = 15.6 Hz), 4.11 (d, 1H, J = 15.1 Hz), 2.30 (dd, 1H, J = 16.6, 11.7 Hz), 2.08 (d, 1H, J = 16.6 Hz), 1.69 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (CDCl$_3$) δ = 142.64, 128.33, 127.37, 125.83, 124.53, 123.84, 76.32, 70.31, 38.54, 18.33, 13.83. CIMS (2-methylpropane) m/z (rel intensity) 189 (M$^+$+1; 17), 188 (M$^+$; 18), 187 (M$^+$−1; 9), 171 (39), 131 (10), 105 (49), 82 (100), 67 (67). Found: C, 82.85; H, 8.40%. Calcd for $C_{13}H_{16}O$: C, 82.92; H, 8.58%. CA Registry No. 36681-67-1.

3,4-Dimethyl-6-(4-nitrophenyl)-5,6-dihydro-2*H*-pyran: A solid (98%); mp 53.2—54.5 °C IR (KBr) 2921, 2846, 1604, 1516, 1489, 1343, 1239, 1105, 853, 829, 755, 717, 691, 607 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 8.21 (d, 2H, J = 8.8 Hz), 7.54 (d, 2H, J = 8.8 Hz), 4.65 (dd, 1H, J = 10.3, 3.9 Hz), 4.22 (d, 1H, J = 16.1 Hz), 4.14 (d, 1H, J = 15.6 Hz), 2.15—2.25 (m, 1H), 2.13 (d, 1H, J = 16.6 Hz), 1.70 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (CDCl$_3$) δ = 150.22, 147.16, 126.42, 124.76, 123.64, 123.33, 75.20, 70.17, 38.46, 18.36, 13.88. CIMS (2-methylpropane) m/z (rel intensity) 235 (M$^+$+2; 16), 234 (M$^+$+1; 100), 233 (M$^+$; 1), 83 (49), 82 (11). HRMS Found: m/z 233.1046. Calcd for $C_{13}H_{15}NO_3$: M$^+$, 233.1052.

6-(4-Chlorophenyl)-3,4-dimethyl-5,6-dihydro-2*H*-pyran:[5,17a] An oil (96%); IR (neat) 2917, 2858, 2822, 1599, 1491, 1449, 1405, 1384, 1237, 1090, 1062, 1015, 884, 821, 727, 612 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 7.31 (s, 4H), 4.51 (dd, 1H, J = 10.5, 3.7 Hz), 4.19 (d, 1H, J = 15.6 Hz), 2.15—2.30 (m, 1H), 2.07 (d, 1H, J = 16.6 Hz), 1.68 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (CDCl$_3$) δ = 141.21, 132.98, 128.44, 127.16, 124.57, 123.60, 75.52, 70.22, 38.47, 18.31, 13.82. CIMS (2-methylpropane) m/z (rel intensity) 225 (M$^+$+2; 6), 224 (M$^+$+1; 6), 223 (M$^+$; 21), 222 (M$^+$−1; 11), 221 (M$^+$−2; 5), 205 (34), 141 (20), 111 (23), 82 (100), 67 (26). CA Registry No. 36681-68-2.

6-(4-Biphenylyl)-3,4-dimethyl-5,6-dihydro-2*H*-pyran: A solid (96%); mp 59.5—61.7 °C; IR (KBr) 2901, 2826, 1599, 1566, 1485, 1466, 1383, 1371, 1338, 1099, 831, 764, 731, 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 7.54—7.59 (m, 4H), 7.41—7.45 (m, 4H), 7.33 (t, 1H, J = 7.3 Hz), 4.59 (dd, 1H, J = 10.7, 3.4 Hz), 4.23 (d, 1H, J = 15.1 Hz), 4.13 (d, 1H, J = 15.1 Hz), 2.35 (dd, 1H, J = 16.6, 10.7 Hz), 2.12 (d, 1H, J = 16.6 Hz), 1.70 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (CDCl$_3$) δ = 141.69, 141.01, 140.31, 128.70, 127.15, 127.09, 126.27, 124.57, 123.80, 76.07, 70.31, 38.47, 18.35, 13.85. CIMS (2-methylpropane) m/z (rel intensity) 266 (M$^+$+2; 11), 265 (M$^+$+1; 51), 264 (M$^+$; 14), 247 (36), 182 (100), 111 (47), 82 (20), 67 (17). HRMS Found: m/z 264.1515. Calcd for $C_{19}H_{20}O$: M$^+$, 264.1514.

3,4-Dimethyl-6-(4-methylphenyl)-5,6-dihydro-2*H*-pyran: An oil (93%); IR (neat) 2980, 2918, 2857, 1516, 1447, 1383, 1237, 1102, 1063, 1021, 885, 813, 724, 566 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 7.26 (d, 2H, J = 7.8 Hz), 7.15 (d, 2H, J = 7.8 Hz), 4.51 (dd, 1H, J = 10.7, 3.4 Hz), 4.20 (d, 1H, J = 15.6 Hz), 4.09 (d, 1H, J = 15.6 Hz), 2.34 (s, 3H), 2.25—2.35 (m, 1H), 2.06 (d, 1H, J = 16.6 Hz), 1.68 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (CDCl$_3$) δ = 139.74, 137.07, 129.09, 125.87, 124.59, 123.97, 76.28, 70.39, 38.60, 21.21, 18.43, 13.93. CIMS (2-methylpropane) m/z (rel intensity) 204 (M$^+$+2; 11), 203 (M$^+$+1; 71), 202 (M$^+$; 13), 201 (M$^+$−1; 13), 185 (53), 121 (100), 119 (47), 111 (40), 83 (10), 82 (18). HRMS Found: m/z 202.1313. Calcd for $C_{14}H_{18}O$: M$^+$, 202.1357.

3,4-Dimethyl-6-(4-methoxyphenyl)-5,6-dihydro-2*H*-pyran:[5,17a] An oil (41%); IR (neat) 2914, 2833, 1614, 1514, 1464, 1382, 1371, 1303, 1249, 1173, 1101, 1038, 828, 645 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 7.30 (d, 2H, J = 8.3 Hz), 6.88 (d, 2H, J = 8.8 Hz), 4.49 (dd, 1H, J = 10.5, 3.7 Hz), 4.20 (d, 1H, J = 15.1 Hz), 4.08 (d, 1H, J = 15.1 Hz), 3.80 (s, 3H), 2.25—2.40 (m, 1H), 2.05 (d, 1H, J = 16.6 Hz), 1.69 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (CDCl$_3$) δ = 158.93, 134.83, 127.16, 124.51, 123.87, 113.74, 75.96, 70.33, 55.27, 38.41, 18.35, 13.83. CIMS (2-methylpropane) m/z (rel intensity) 220 (M$^+$+2; 12), 219 (M$^+$+1; 87), 218 (M$^+$; 17), 217 (M$^+$−1; 10), 201 (62), 135 (100), 121 (62), 111 (58), 82 (29), 67 (21). CA Registry No. 36681-71-7.

3,4-Dimethyl-6-(2-naphthyl)-5,6-dihydro-2*H*-pyran: An oil (78%); IR (neat) 2920, 2820, 1601, 1508, 1447, 1383, 1338, 1103, 853, 818, 745, 478 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 7.80—7.84 (m, 4H), 7.42—7.51 (m, 3H), 4.71 (dd, 1H, J = 10.7, 3.4 Hz), 4.26 (d, 1H, J = 16.1 Hz), 4.16 (d, 1H, J = 15.1 Hz), 2.38 (dd, 1H, J = 15.6, 10.7 Hz), 2.17 (d, 1H, J = 15.6 Hz), 1.71 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (CDCl$_3$) δ = 140.09, 133.33, 132.85, 128.02, 127.97, 127.60, 125.94, 125.63, 124.55, 124.29, 124.15, 123.82, 76.31, 70.31, 38.54, 18.35, 13.87. CIMS (2-methylpropane) m/z (rel intensity) 240 (M$^+$+2; 18), 239 (M$^+$+1; 70), 238 (M$^+$; 42), 237 (M$^+$−1; 9), 221 (60), 181 (16), 156 (100), 141 (20), 111 (72), 83 (24), 67 (16). Found C, 85.65; H, 7.58%. Calcd for $C_{17}H_{18}O$: C, 85.66; H, 7.63%.

3,4-Dimethyl-6-hexyl-5,6-dihydro-2*H*-pyran: An oil (76%); IR (neat) 2926, 2856, 1458, 1381, 1103 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 4.01 (d, 1H, J = 16.1 Hz), 3.93 (d, 1H, J = 15.6 Hz), 3.41—3.48 (m, 1H), 1.94 (dd, 1H, J = 15.6, 12.2 Hz), 1.80 (d, 1H, J = 15.6 Hz), 1.63 (s, 3H), 1.53 (s, 3H), 1.40—1.46 (m, 2H), 1.25—1.33 (m, 8H), 0.88 (t, 3H, J = 6.8 Hz); ^{13}C NMR (CDCl$_3$) δ = 124.38, 123.54, 74.28, 69.81, 36.71, 35.91, 31.83, 29.38, 25.45, 22.61, 18.36, 14.07, 13.87. CIMS (2-methylpropane) m/z (rel intensity) 197 (M$^+$+1; 15), 196 (M$^+$; 16), 157 (5), 113 (10), 83 (100), 67 (11). Found: C, 79:51; H, 12.26%. Calcd for $C_{13}H_{24}O$: C, 79.51; H, 12.34%.

6-Cyclohexyl-3,4-dimethyl-5,6-dihydro-2*H*-pyran:[18] An oil (84%); IR (neat) 2922, 2853, 1448, 1385, 1109 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 3.99 (d, 1H, J = 15.9 Hz), 3.93 (d, 1H, J = 15.6 Hz), 3.19 (ddd, 1H, J = 10.7, 6.8, 3.4 Hz), 1.93—2.04 (m, 2H), 1.67—1.78 (m, 4H), 1.63 (s, 3H), 1.52 (s, 3H), 1.34—1.43 (m, 1H), 1.13—1.31 (m, 4H), 0.93—1.06 (m, 2H); ^{13}C NMR (CDCl$_3$) δ = 124.48, 123.65, 78.63, 70.12, 42.71, 33.79, 29.14, 28.43, 26.64, 26.20, 26.07, 18.46, 13.82. CIMS (2-methylpropane) m/z (rel intensity) 195 (M$^+$+1; 14), 194 (M$^+$; 22), 193 (M$^+$−1; 11), 177 (13), 111 (53), 83 (100), 67 (14). Found: C, 80.43; H, 11.27%. Calcd for $C_{13}H_{22}O$: C, 80.33; H, 11.43%. CA Registry No. 96482-08-5.

3,4-Dimethyl-6-(2-phenylethyl)-5,6-dihydro-2*H*-pyran: An oil (68%); IR (neat) 2878, 2818, 2859, 1496, 1454, 1386, 1108, 748, 699, 668 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 7.16—7.30 (m, 5H), 4.02 (d, 1H, J = 16.6 Hz), 3.96 (d, 1H, J = 15.1 Hz), 3.42—3.48 (m, 1H), 2.76—2.84 (m, 1H), 2.65—2.74 (m, 1H), 1.96—2.03 (m, 1H), 1.72—1.95 (m, 3H), 1.63 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (CDCl$_3$) δ = 142.32, 128.58, 128.40, 125.78, 124.52, 123.53, 73.28, 69.84, 37.51, 36.76, 31.80, 18.40, 13.95. CIMS (2-methylpropane) m/z (rel intensity) 218 (M$^+$+2; 13), 217 (M$^+$+1; 100), 216 (M$^+$; 4), 199 (17), 198 (14), 135 (13), 133 (10), 117 (17), 110 (10), 91 (11), 83 (85). Found: C, 83.55; H, 9.55%. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32%.

4-Methyl-6-phenyl-5,6-dihydro-2*H*-pyran:[19] An oil (90%); IR (neat) 2964, 2822, 1450, 1381, 1163, 1121, 1036, 754, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 7.33—7.40 (m, 4H), 7.27—7.29 (m, 1H), 5.45—5.55 (m, 1H), 4.53 (dd, 1H, J = 10.3, 3.4 Hz), 4.25—4.40 (m, 2H), 2.25—2.38 (m, 1H), 2.11 (d, 1H, J = 16.6 Hz), 1.75 (s, 3H); ^{13}C NMR (CDCl$_3$) δ = 142.60, 132.05, 128.37, 127.44, 125.87, 119.79, 75.81, 66.47, 37.68, 22.90. CIMS (2-methylpropane) *m/z* (rel intensity) 175 (M^++1; 13), 174 (M^+; 8), 173 (M^+-1; 9), 157 (33), 131 (5), 105 (100), 68 (72). Found: C, 82.61; H, 7.93%. Calcd for $C_{12}H_{14}O$: C, 82.70; H, 8.11%. CA Registry No. 60335-71-9.

6-(4-Chlorophenyl)-4-methyl-5,6-dihydro-2*H*-pyran: An oil (99%); IR (neat) 2930, 2910, 2823, 1492, 1381, 1373, 1120, 1087, 1040, 825, 782, 668 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 7.32$ (s, 4H), 5.50 (s, 1H), 4.50 (dd, 1H, $J = 10.7$, 3.9 Hz), 4.31 (d, 1H, $J = 2.4$ Hz), 4.30 (d, 1H, $J = 2.0$ Hz), 2.15—2.30 (m, 1H), 2.09 (d, 1H, $J = 17.1$ Hz), 1.75 (s, 3H); ^{13}C NMR ($CDCl_3$) $\delta = 141.27$, 133.15, 131.89, 128.58, 127.32, 119.89, 75.13, 66.51, 37.26, 22.99. CIMS (2-methylpropane) *m/z* (rel intensity) 211 (M^++3; 24), 210 (M^++2; 14), 209 (M^++1; 72), 208 (M^+; 11), 193 (33), 191 (100), 143 (25), 141 (90), 139 (57), 97 (37), 69 (59), 68 (35). Found: C, 68.97; H, 6.41%. Calcd for $C_{12}H_{13}ClO$: C, 69.07; H, 6.28%.

4-Methyl-6-(2-naphthyl)-5,6-dihydro-2*H*-pyran: An oil (75%); IR (neat) 2909, 2822, 1508, 1443, 1381, 1159, 1113, 856, 818, 746, 478 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 7.81$—7.84 (m, 4H), 7.43—7.52 (m, 3H), 5.53 (s, 1H), 4.70 (dd, 1H, $J = 10.5$, 3.7 Hz), 4.37 (s, 2H), 2.30—2.45 (m, 1H), 2.19 (d, 1H, $J = 15.1$ Hz), 1.77 (s, 3H); ^{13}C NMR ($CDCl_3$) $\delta = 140.02$, 133.33, 132.87, 132.01, 128.08, 127.97, 127.62, 125.96, 125.66, 124.37, 124.15, 119.81, 75.79, 66.48, 37.68, 22.92. CIMS (2-methylpropane) *m/z* (rel intensity) 226 (M^++2; 10), 225 (M^++1; 59), 224 (M^+; 34), 207 (38), 181 (15), 157 (100), 141 (28), 97 (38), 69 (19). Found: C, 85.70; H, 7.11%. Calcd for $C_{16}H_{16}O$: C, 85.66; H, 7.20%.

4-Methyl-6-(2-phenylethyl)-5,6-dihydro-2*H*-pyran: An oil (35%); IR (neat) 3025, 2962, 2928, 2854, 1456, 1397, 1261, 1159, 1128, 1045, 1028, 808, 745, 699, 668 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 7.16$—7.30 (m, 5H), 5.41 (s, 1H), 4.19 (d, 1H, $J = 16.6$ Hz), 4.12 (d, 1H, $J = 16.1$ Hz), 3.40—3.48 (m, 1H), 2.78—2.86 (m, 1H), 2.66—2.75 (m, 1H), 1.72—2.05 (m, 4H), 1.68 (s, 3H); ^{13}C NMR ($CDCl_3$) $\delta = 142.30$, 131.87, 128.58, 128.42, 125.82, 119.86, 72.84, 65.96, 37.63, 35.99, 31.84, 23.08. CIMS (2-methylpropane) *m/z* (rel intensity) 204 (M^++2; 10), 203 (M^++1; 69), 202 (M^+; 17), 185 (25), 135 (23), 117 (36), 69 (100). Found: C, 83.24; H, 9.21%. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

The present work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "New Development of Rare Earth Complexes" No. 06241108 and partially for Exploratory Research from the Ministry of Education, Science, Sports, and Culture, and also by the Asahi Glass Foundation. We thank the Shin-Etsu Chemical Co., Ltd. for providing several kinds of rare earth oxides.

References

1) For reviews, see: a) D. L. Boger and S. M. Weinreb, "Hetero Diels–Alder Methodology in Organic Synthesis," Academic, San Diego (1987); b) W. Oppolzer, "Intermolecular Diels–Alder Reactions," in "Comprehensive Organic Synthesis," ed by B. M. Trost, I. Fleming, and L. A. Paquette, Pergamon, Oxford (1991), Vol. 5, p. 315; c) H. B. Kagan and O. Riant, *Chem. Rev.*, **92**, 1007 (1992); d) J. Jurczak and A. Golebiowski, *Chem. Rev.*, **89**, 149 (1989).

2) For example, see: R. R. Schmidt, *Acc. Chem. Res.*, **19**, 250 (1986).

3) a) D. L. Boger, "Heterodiene Additions," in "Comprehensive Organic Synthesis," ed by B. M. Trost, I. Fleming, and L. A. Paquette, Pergamon, Oxford (1991), Vol. 5, p. 451. For some recent examples, see: b) Y. Makioka, T. Shindou, Y. Taniguchi, K. Takaki, and Y. Fujiwara, *Synthesis*, **1995**, 801; c) S. Kobayashi, H. Ishitani, and S. Nagayama, *Synthesis*, **1995**, 1195.

4) S. M. Weinreb, "Heterodienophile Additions to Dienes," in "Comprehensive Organic Synthesis," ed by B. M. Trost, I. Fleming, and L. A. Paquette, Pergamon, Oxford (1991), Vol. 5, p. 434.

5) Ansell et al. reported the *p*-toluenesulfonic acid-catalyzed hetero Diels–Alder reaction of aromatic aldehydes with 2,3-dimethyl-1,3-butadiene. M. F. Ansell and A. A. Charalambides, *J. Chem. Soc., Chem. Commun.*, **1972**, 739.

6) a) J. H. Forsberg, V. T. Spaziano, T. M. Balasubramamian, G. K. Liu, S. A. Kinsley, C. A. Duckworth, J. J. Poteruca, P. S. Brown, and J. L. Miller, *J. Org. Chem.*, **52**, 1107 (1987). For a review, see: b) S. Kobayashi, *Synlett*, **1994**, 689. For other recent reports concerning the $RE(OTf)_3$-catalyzed reactions, see: c) T. Tsuchimoto, K. Tobita, T. Hiyama, and S. Fukuzawa, *Synlett*, **1996**, 557; d) K. Ishihara, M. Kubota, H. Kurihara, and H. Yamamoto, *J. Org. Chem.*, **61**, 4560 (1996); e) S. Kobayashi, M. Morikawa, and H. Ishitani, *Synlett*, **1995**, 1153; f) S. Hosono, W. Kim, H. Sasai, and M. Shibasaki, *J. Org. Chem.*, **60**, 4 (1995); g) K. Ishihara, M. Kubota, H. Kurihara, and H. Yamamoto, *J. Am. Chem. Soc.*, **117**, 4413 (1995); h) S. Fukuzawa, T. Tsuchimoto, and T. Kanai, *Bull. Chem. Soc. Jpn.*, **67**, 2227 (1994); i) H. C. Aspinall, A. F. Browning, N. Greeves, and P. Ravenscroft, *Tetrahedron Lett.*, **35**, 4639 (1994); j) S. Matsubara, M. Yoshioka, and K. Utimoto, *Chem. Lett.*, **1994**, 827; k) M. Chini, P. Crotti, L. Favero, F. Macchia, and M. Pineschi, *Tetrahedron Lett.*, **35**, 433 (1994); l) M. Meguro, N. Asao, and Y. Yamamoto, *J. Chem. Soc., Perkin Trans. 1*, **1994**, 2597; m) S. Kobayashi, I. Hachiya, M. Araki, and H. Ishitani, *Tetrahedron Lett.*, **34**, 3755 (1993); n) S. Kobayashi, M. Araki, and I. Hachiya, *J. Org. Chem.*, **59**, 3758 (1994); o) T. Hanamoto, Y. Sugimoto, Y. Yokoyama, and J. Inanaga, *J. Org. Chem.*, **61**, 4491 (1996).

7) For $RE(NTf_2)_3$-catalyzed reactions, see: a) H. Kobayashi, J. Nie, and T. Sonoda, *Chem. Lett.*, **1995**, 307; b) K. Mikami, O. Kotera, Y. Motoyama, H. Sakaguchi, and M. Maruta, *Synlett*, **1996**, 171. Very recently, polymer-supported $Sc[N(R)Tf](OTf)_2$-type catalyst was prepared and successfully used for the synthesis of a series of quinolines: S. Kobayashi and S. Nagayama, *J..Am. Chem. Soc.*, **118**, 8977 (1996).

8) J. Inanaga, Y. Yokoyama, and T. Hanamoto, *Tetrahedron Lett.*, **34**, 2791 (1993).

9) J. Inanaga, Y. Yokoyama, and T. Hanamoto, *J. Chem. Soc., Chem. Commun.*, **1993**, 1090.

10) A preliminary result was briefly reported: J. Inanaga, Y. Sugimoto, and T. Hanamoto, The Special Issue of *New. J. Chem.*, "Molecular Compounds of the f-Elements," **19**, 707 (1995).

11) In order to evaluate the catalytic activity of $RE(OPf)_3$, the glycosylation of 1-*O*-methoxyacetyl 2,3,4,6-tetra-*O*-benzyl-α-D-glycoside with 1-octanol was carried out with 5 mol % of $RE(OPf)_3$ or $RE(OTf)_3$ in CH_3CN at 53 °C for 10 min. The observed relative catalytic activities follow: $Sc(OPf)_3$ (99%)>$Yb(OPf)_3$ (81%)≈$Sc(OTf)_3$ (80%)>$Yb(OTf)_3$ (40%). Y. Sugimoto, T. Hanamoto, and J. Inanaga, unpublished results.

12) A high catalytic activity of $Sc(OTf)_3$ as Lewis acid has been reported. See Refs. 3c, 6c, 6d, 6m, and 6n.

13) In "Lange's Handbook of Chemistry," 13th ed, ed by J. A. Dean, McGraw-Hill, New York (1985), pp. 5—14.

14) $RE(OTf)_3$ becomes liquid within several hours when it is allowed to stand in the air, whereas $RE(OPf)_3$ does not even after two days. Water-repellent property of the perfluorinated alkane chain $[(-CF_2-CF_2-)_n]$ of $RE(OPf)_3$ may be expected from its low surface tension (ca. 10 $mN\,m^{-1}$) compared with that of water (72

mN m^{-1}).

15) a) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, **1957**, 2640; b) X. Fu, M. He, Q. Lei, and B. Luo, *Synth. Commun.*, **21**, 1273 (1991); c) F. Effenberger, E. Sohn, and G. Epple, *Chem. Ber.*, **116**, 1195 (1983); d) D. Häbich and F. Effenberger, *Synthesis*, **1978**, 755; e) F. Effenberger and G. Epple, *Angew. Chem., Int. Ed. Engl.*, **11**, 300 (1972).

16) For precedents on recycling use of rare earth metal salts as catalysts, see: N. Mine, Y. Fujiwara, and H. Taniguchi, *Chem. Lett.*, **1986**, 357; Refs. 6b and 6o.

17) a) H. Griengl and K. P. Geppert, *Monatsh. Chem.*, **107**, 675 (1976); b) N. A. Romanov, E. A. Kantor, R. A. Karakhanov, and D. L. Rakhmankulov, *Zh. Org. Khim.*, **18**, 455 (1982).

18) J. P. Michael, P. C. Ting, and P. A. Bartlett, *J. Org. Chem.*, **50**, 2416 (1985).

19) a) N. L. J. M. Broekhof and J. J. Hofma, European Patent Appl., 5 pp., EP 325000 A1 890726, Naarden International N. V., Netherlands; b) U. G. Ibatullin, Y. V. Pavlov, and M. G. Safarov, *Khim. Geterotsikl. Soedin.*, **1989**, 1326.