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# Friedel–Crafts Reactions Catalyzed by Rare Earth Metal Trifluoromethanesulfonates

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Rare earth metal trifluoromethanesulfonates (rare earth metal triflates, RE(OTf)$_3$) were found to be efficient catalysts for Friedel–Crafts acylation and alkylation. In the presence of a catalytic amount of RE(OTf)$_3$, acylation of aromatic compounds having electron-donating substituents such as anisole, thioanisole, and mesitylene with acid anhydrides proceeded smoothly to afford the corresponding aromatic ketones in high yields. Although RE(OTf)$_3$ alone is not effective for acylation of less reactive aromatics such as toluene, the combination of RE(OTf)$_3$ and lithium perchlorate (LiClO$_4$) enhanced the catalytic activity dramatically. Friedel–Crafts acylation reactions using rare earth metal perfluoroalkanesulfonates were also successfully performed in supercritical carbon dioxide (scCO$_2$). Moreover, in the presence of a catalytic amount of RE(OTf)$_3$, aromatic compounds reacted with benzyl chloride smoothly to afford the corresponding alkylation products in high yields. In these reactions, RE(OTf)$_3$ could be easily recovered after the reactions were completed and could be reused without loss of activity.

Friedel–Crafts acylation and alkylation are among the most fundamental and useful reactions for introducing functional substituents to aromatic rings,[1] and are often applied to industrial production of pharmaceuticals and agricultural chemicals, plastics, liquid crystals and so on.[2] These reactions were originally performed using more than stoichiometric amounts of Lewis acids such as aluminum trichloride (AlCl$_3$), because the Lewis acids are consumed by coordination with the produced aromatic ketones. A large amount of AlCl$_3$ and its waste after aqueous work-up procedures often cause serious environmental problems. In order to address these issues, there have been several efforts to perform reactions using catalytic amounts of acidic promoters,[3] or to recycle catalysts using metal oxides, etc.[4,5] In most cases, however, substrates are limited to activated benzenes and the development of truly efficient catalysts is strongly in demand.

Recently, we have found that rare earth metal trifluoromethanesulfonates (rare earth metal triflate, RE(OTf)$_3$) work efficiently as Lewis acids even in aqueous media or in the presence of amines, and that a catalytic amount of RE(OTf)$_3$ allows to proceed several synthetically useful reactions such as aldol,[6] Michael,[7] allylation,[8] Mannich,[9] Diels–Alder reactions,[10] etc.[11] It has also been demonstrated in these reactions that a small amount of RE(OTf)$_3$ is enough to complete the reactions, and that the catalyst can be easily recovered from the reaction mixture and can be reused. A key to accomplish the catalytic processes was ascribed to the equilibrium between the Lewis acids and Lewis bases such as water, carbonyl compounds, amines, etc. Based on this consideration, similar equilibrium is expected between Lewis acids and aromatic ketones, and we decided to examine RE(OTf)$_3$-catalyzed Friedel–Crafts acylation. It was found that the acylation proceeded smoothly using a catalytic amount of RE(OTf)$_3$ which was easily recovered and reused.[12] Moreover, in the course of our investigations on the RE(OTf)$_3$-catalyzed Friedel–Crafts acylation, scandium trifluoromethanesulfonate (Sc(OTf)$_3$) was revealed to be the most active catalyst, and the addition of lithium perchlorate (LiClO$_4$) to RE(OTf)$_3$ enhanced the catalytic activities to accomplish the acylation of relatively inactive aromatic compounds such as toluene. In addition, Friedel–Crafts acylation was successfully carried out in supercritical carbon dioxide (scCO$_2$) using rare earth metal perfluoroalkanesulfonates as catalysts. We have also examined Friedel–Crafts alkylation using RE(OTf)$_3$ catalyst.[13—15] In this paper, we report a full account of these results.

## Results and Discussion

**Catalytic Friedel–Crafts Acylation Using RE(OTf)$_3$ as Catalysts.** The reaction of anisole (**1**) with acetic anhydride was chosen as a model, and ytterbium trifluoromethanesulfonate (ytterbium triflate, Yb(OTf)$_3$) was used as a representative RE(OTf)$_3$. Several reaction conditions were examined, and the results are summarized in Table 1. When acetic an-

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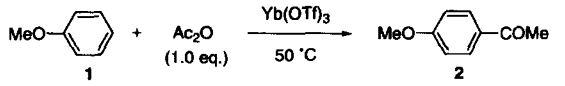
Table 1. $\text{Yb(OTf)}_3$-Catalyzed Friedel–Crafts Acylation of **1**



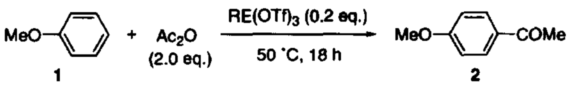
| Entry | $\text{Yb(OTf)}_3$ equiv | Time h | Solvent | Yield[a)] % |
|---|---|---|---|---|
| 1 | 1.0 | 24 | $\text{CS}_2$ | ND[b)] |
| 2 | 1.0 | 24 | $\text{ClCH}_2\text{CH}_2\text{Cl}$ | 8 |
| 3 | 1.0 | 20 | $\text{PhNO}_2$ | 32 |
| 4 | 1.0 | 3 | $\text{(MeCO)}_2\text{O}$ | 53 |
| 5 | 0.2 | 18 | $\text{(MeCO)}_2\text{O}$ | 48 |
| 6 | 1.0 | 24 | MeCN | 52 |
| 7 | 1.0 | 20 | $\text{MeNO}_2$ | 78 |
| 8 | 0.2 | 48 | $\text{MeNO}_2$ | 60 |
| 9[c)] | 0.2 | 18 | $\text{MeNO}_2$ | 99 |
| 10[c)] | 0.05 | 48 | $\text{MeNO}_2$ | 79 |

a) Determined by GLC analyses using an internal standard. b) Not detected. c) Two equiv of $\text{(MeCO)}_2\text{O}$ were used.

hydride, acetonitrile, or nitromethane was used as a solvent (entries 4—10), the reaction mixture became homogeneous and the acylation reaction proceeded smoothly. Nitromethane gave the highest yield of 4-methoxyacetophenone (**2**) (Entries 7—10). On the other hand, in carbon disulfide, dichloroethane, or nitrobenzene (Entries 1—3), the reaction mixture was heterogeneous and the yield of **2** was low. It should be noted that the acylation proceeded quantitatively by using a catalytic amount of $\text{Yb(OTf)}_3$ (0.2 equiv, Entry 9). Even when 0.05 equiv of the catalyst was employed, **2** was obtained in 79% yield (Entry 10).

Other $\text{RE(OTf)}_3$ were then examined as a catalyst in the reaction of **1** with acetic anhydride (Table 2). Each $\text{RE(OTf)}_3$ was prepared by the reaction of the corresponding rare earth metal oxide with trifluoromethanesulfonic acid in an aqueous solution.[16] All the $\text{RE(OTf)}_3$ listed were effective to catalyze the acylation of **1**. Especially, when scandium trifluoromethanesulfonate (scandium triflate, $\text{Sc(OTf)}_3$)[10b,11b] or $\text{Yb(OTf)}_3$ was used as a catalyst, the acylation product **2** was obtained quantitatively. On the other hand, in the case of lanthanum trifluoromethanesulfonate (lanthanum triflate, $\text{La(OTf)}_3$), the yield of **2** was relatively low. The yields shown in Table 2 reflect the catalytic activities of the respective $\text{RE(OTf)}_3$.

Table 2. Effect of Rare Earth Metal Triflates ($\text{RE(OTf)}_3$)



| RE | Yield/%[a)] | RE | Yield/%[a)] |
|---|---|---|---|
| Sc | 99 | Gd | 77 |
| Y | 69 | Dy | 85 |
| La | 41 | Ho | 79 |
| Pr | 87 | Er | 78 |
| Nd | 79 | Tm | 84 |
| Sm | 80 | Yb | 99 |
| Eu | 78 | Lu | 81 |

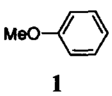
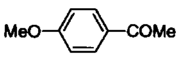
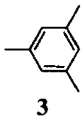
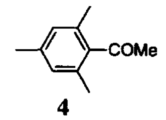
a) Determined by GLC analyses using an internal standard.

The difference of the catalytic activity between $\text{Yb(OTf)}_3$ and $\text{Sc(OTf)}_3$ is clearly shown in Table 3. When the acylation of **1** was performed in a short reaction time (4 h), $\text{Sc(OTf)}_3$ gave a higher yield of **2** than $\text{Yb(OTf)}_3$ did. In the case of the acylation of mesitylene (**3**), the use of $\text{Sc(OTf)}_3$ also resulted in a much higher yield of aromatic ketone **4** in a shorter reaction time (73%, 1 h) than that of $\text{Yb(OTf)}_3$ (16%, 18 h). These results show that $\text{Sc(OTf)}_3$ is the most active Friedel–Crafts catalyst among $\text{RE(OTf)}_3$. In the periodic table, scandium lies above yttrium and lanthanides and its chemical behavior is known to be intermediate between aluminum and lanthanides.[17] Scandium oxide is more basic than aluminum oxide and more acidic than lanthanide oxides.[17] In addition, its ionic radius is the smallest among rare earths, and thus, it would be reasonable to conclude that $\text{Sc(OTf)}_3$ is the strongest Lewis acid among rare earth metal triflates.[8,10b,11b] The effect of the amounts of $\text{Sc(OTf)}_3$ in the acetylation of **1** is summarized in Table 4. The reaction proceeded smoothly in a few hours using a catalytic amount of $\text{Sc(OTf)}_3$, and 6200% yield of acetylation product **2** (based on the catalyst) was obtained when 0.01 equiv of $\text{Sc(OTf)}_3$ was employed (Entry 3).

Reusability of the catalyst is one of the main advantages of using $\text{RE(OTf)}_3$ as a Friedel–Crafts catalyst. $\text{RE(OTf)}_3$ could be easily recovered from the reaction mixture by simple extraction. The catalyst was soluble in the aqueous layer rather than in the organic layer, and was recovered by removing water to give a crystalline residue, which could be reused without further purification (see, Experimental). Efficiency of the recovery and catalytic activity of reused $\text{RE(OTf)}_3$

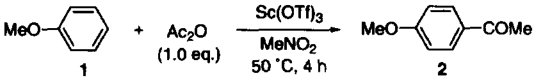
Table 3. Catalytic Activity of $\text{Yb(OTf)}_3$ and $\text{Sc(OTf)}_3$

$$\text{Ar-H} + \underset{(2\ \text{eq.})}{\text{Ac}_2\text{O}} \xrightarrow[\text{MeNO}_2,\ 50\ ^\circ\text{C}]{\text{Catalyst (0.2 eq.)}} \text{Ar-COMe}$$

| Ar–H | Catalyst | Product | Time/h | Yield/%[a)] |
|---|---|---|---|---|
| <br>**1** | $\text{Yb(OTf)}_3$ | <br>**2** | 4 | 55 |
| | $\text{Sc(OTf)}_3$ | | 4 | 89 |
| <br>**3** | $\text{Yb(OTf)}_3$ | <br>**4** | 18 | 55 |
| | $\text{Sc(OTf)}_3$ | | 1 | 89 |

a) Determined by GLC analyses using an internal standard.

Table 4. Effect of the Amounts of $\text{Sc(OTf)}_3$

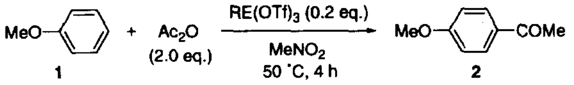


| Entry | $\text{Sc(OTf)}_3$/equiv | Yield/%[a)] |
|---|---|---|
| 1 | 0.2 | 89 (445) |
| 2 | 0.05 | 76 (1520) |
| 3 | 0.01 | 62 (6200) |

a) Determined by GLC analyses using an internal standard. The number in parentheses is the yield based on $\text{Sc(OTf)}_3$.

were examined in the reaction of **1** with acetic anhydride using $Yb(OTf)_3$ and $Sc(OTf)_3$ as representative $RE(OTf)_3$. As shown in Table 5, more than 90% of $Yb(OTf)_3$ and $Sc(OTf)_3$ were easily recovered, and the yields of acylation product **2** in the second and third uses were almost the same as those in the first use.

Table 5. Reuse of $RE(OTf)_3$ in the Acetylation of **1**



| $RE(OTf)_3$ | No. of times used | Yield[a] % | Recovery of $RE(OTf)_3$/% |
|---|---|---|---|
| $Sc(OTf)_3$[b] | 1 | 89 | 94 |
| | 2 | 93 | 90 |
| | 3 | 91 | 92 |
| $Yb(OTf)_3$[c] | 1 | 70 | 93 |
| | 2 | 69 | 90 |
| | 3 | 71 | 92 |

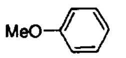
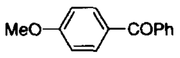
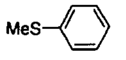
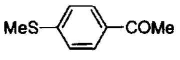
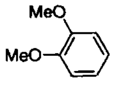
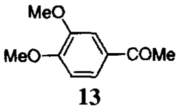
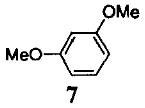
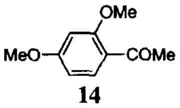
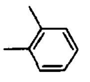
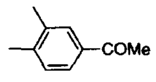
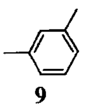
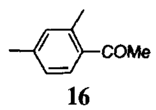
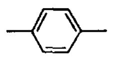
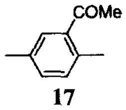
a) Determined by GLC analyses using an internal standard. b) One equiv of $Ac_2O$ was used. c) Two equiv of $Ac_2O$ were used.

Several substituted benzenes were subjected to the $Yb(OTf)_3$ or $Sc(OTf)_3$-catalyzed acylation using acetic anhydride, acetyl chloride, benzoic anhydride, or benzoyl chloride as an acylating agent. The results are summarized in Table 6. Although the acylation of benzene or toluene did not proceed, introduction of electron-donating groups such as methoxy, methylthio, and dimethylamino groups was effective to promote the acylation. For example, acetylation of thioanisole (**5**), *o*- or *m*-dimethoxybenzene (**6** or **7**) proceeded smoothly to afford a single acetylation product in an excellent yield. In the cases of introducing two methyl groups to the benzene ring (xylenes), the acetylation adducts were obtained in lower yields. While acetyl chloride was effective for the reaction, 5—10% lower yields were observed. As for benzoylation, both benzoic anhydride and benzoyl chloride were successfully used as benzoylating agents. Anisole (**1**) reacted smoothly in the presence of a catalytic amount of $Sc(OTf)_3$ to give 4-methoxybenzophenone (**11**) in high yields (Entries 1 and 2). In each reaction, no formation of other isomers was observed (checked by GLC).

We then performed acylation of 2-methoxynaphthalene (**18**) using $RE(OTf)_3$. Two products, 1-acetyl-2-methoxynaphthalene (**19**) and 6-acetyl-2-methoxynaphthalene (**20**), were obtained in the reaction of **18** with acetic anhydride

Table 6. $RE(OTf)_3$-Catalyzed Friedel–Crafts Acylation

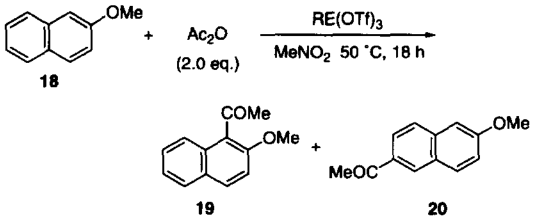
$$\text{Ar-H} + \text{Acylating Agent} \xrightarrow[\text{MeNO}_2,\ 50\ ^\circ\text{C}]{\text{RE(OTf)}_3\ (0.2\ \text{eq.})} \text{Ar-COMe}$$

| Entry | Ar–H | $RE(OTf)_3$ | Acylating agent | Time/h | Product | Yield/%[a] |
|---|---|---|---|---|---|---|
| 1 | <br>**1** | $Sc(OTf)_3$ | PhCOCl | 18 | <br>**11** | 79 |
| 2 | | $Sc(OTf)_3$ | $(PhCO)_2O$ | 18 | | 90 |
| 3 | <br>**5** | $Yb(OTf)_3$ | $Ac_2O$ | 42 | <br>**12** | 83 |
| 4 | | $Sc(OTf)_3$ | $Ac_2O$ | 1 | | 97 |
| 5 | <br>**6** | $Sc(OTf)_3$ | $Ac_2O$ | 1 | <br>**13** | 99 |
| 6 | <br>**7** | $Sc(OTf)_3$ | $Ac_2O$ | 1 | <br>**14** | 89 |
| 7 | <br>**8** | $Yb(OTf)_3$ | $Ac_2O$ | 18 | <br>**15** | 22 |
| 8 | | $Sc(OTf)_3$ | $Ac_2O$ | 1 | | 14 |
| 9 | <br>**9** | $Yb(OTf)_3$ | $Ac_2O$ | 18 | <br>**16** | 25 |
| 10 | | $Sc(OTf)_3$ | $Ac_2O$ | 1 | | 11 |
| 11 | <br>**10** | $Yb(OTf)_3$ | $Ac_2O$ | 18 | <br>**17** | 2 |
| 12 | | $Sc(OTf)_3$ | $Ac_2O$ | 1 | | 1 |

a) Determined by GLC analyses using an internal standard.

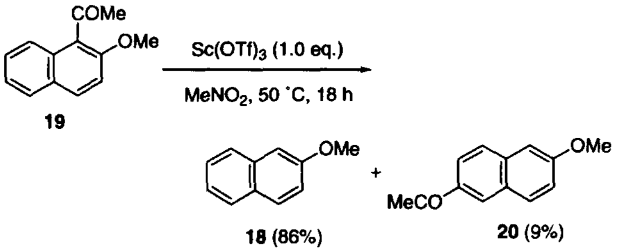
(Table 7). It was found that the ratio of **19** to **20**, namely the regioselectivity of the acylation, depended on the amounts of the catalyst.[18] When less than 1.0 equiv of Sc(OTf)$_3$ or Yb(OTf)$_3$ was used, 1,2-isomer **19** was dominantly obtained (Entries 1—3 and 5). On the other hand, the selectivity dramatically changed and 2,6-isomer **20** became the major product when 1.0 equiv of Yb(OTf)$_3$ or Sc(OTf)$_3$ was used (Entries 4 and 6—8). For the study of the reaction pathway, **19** was treated in the presence of an equimolar amount of Sc(OTf)$_3$ at 50 °C, and it was revealed that two products, **18** and **20**, were obtained, although **19** was not observed (Scheme 1).[19] This result showed that deacetylation of **19** and migration of the acetyl group to the 6-position of **20** occurred under the influence of 1.0 equiv of RE(OTf)$_3$.[19,20] Miura et al. reported that the 1-position of **18** was the most reactive towards electrophilic substitution based on the semi-empirical MO calculations.[3i] The MO calculation of benzoyl substituted 2-methoxynaphthalene also indicated that 2,6-isomer **20** was the most stable.[18] From these investigations, we assume a possible pathway of the acylation of **18** using RE(OTf)$_3$ as follows. In the presence of Sc(OTf)$_3$, **18** reacts with acetic anhydride to form **19** first. Adduct **19** would be stabilized by bidentate chelation of RE(OTf)$_3$ shown in Scheme 2, and in the presence of a smaller amount of RE(OTf)$_3$, the reaction stops at this stage. On the other hand, in the presence of a large amount of RE(OTf)$_3$, the migration of the acetyl group occurs to yield **20**.

Table 7. RE(OTf)$_3$-Catalyzed Acetylation of **18**

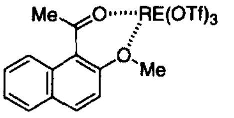


| Entry | RE(OTf)$_3$ (equiv) | Yield/%[a] | (**19** : **20**) |
|---|---|---|---|
| 1 | Yb(OTf)$_3$ (0.2) | 76 | (88 : 12) |
| 2 | Yb(OTf)$_3$ (0.5) | 78 | (85 : 15) |
| 3 | Yb(OTf)$_3$ (0.75) | 63 | (70 : 30) |
| 4 | Yb(OTf)$_3$ (1.0) | 51 | (8 : 92) |
| 5 | Sc(OTf)$_3$ (0.2) | 86 | (85 : 15) |
| 6 | Sc(OTf)$_3$ (1.0) | 77 | (5 : 95) |
| 7[b] | Sc(OTf)$_3$ (1.0) | 57 | (9 : 91) |
| 8[c] | Sc(OTf)$_3$ (1.0) | 10 | (3 : 97) |

a) Determined by GLC analyses using an internal standard.
b) 4 h. c) 2 h.



Scheme 1. Reaction of **19** in the presence of Sc(OTf)$_3$.



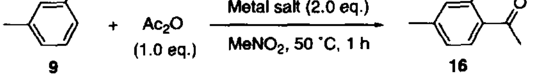
Scheme 2. A Possible stable complex of **21** and RE(OTf)$_3$.

**Catalytic Friedel–Crafts Acylation Using a RE(OTf)$_3$–LiClO$_4$ System.** In the previous section, it has been demonstrated that a catalytic amount of RE(OTf)$_3$ effectively promoted Friedel–Crafts acylation, and that the catalyst was easily recovered and reused. On the other hand, it was also found that this catalytic system worked well in the acylation of aromatic compounds having electron-donating substituents. For example, while the acylation of anisole, mesitylene, and xylenes proceeded, benzene or toluene did not react under the same conditions (see Table 6).

To enhance the reactivity of the acylation, we focused on the acylating agent. Olah et al. reported that an ionic species such as CH$_3$CO$^+$SbF$_6^-$, CH$_3$CO$^+$PF$_6^-$, CH$_3$CO$^+$BF$_4^-$, and CH$_3$CO$^+$AsF$_6^-$, was an active acylating agent, in which the acylium cation was stabilized by the weakly basic counter anion.[21] It was also known that acetyl perchlorate, CH$_3$CO$^+$ClO$_4^-$, generated in situ by the reaction of carboxylic acid or carboxylic anhydride with perchloric acid in aqueous media, had high reactivity in acylation of aromatic compounds.[22] Recently, our group reported that lithium perchlorate (LiClO$_4$) formed a stable acylium cation when mixed with an acylating agent in the presence of an antimony or a hafnium compound.[23] It was expected that an acylium cationic species such as acyl perchlorate generated in the presence of RE(OTf)$_3$ would react with aromatic compounds to afford the corresponding aromatic ketones. Thus, we attempted to generate the active acylium cation species in the presence of RE(OTf)$_3$.

We first performed the reaction of *m*-xylene with acetic anhydride in the presence of Sc(OTf)$_3$ (0.2 equiv) and an alkali or alkaline earth metal salt (2.0 equiv). The results are shown in Table 8. Without the metal salt, acylation product **16** was obtained only in 12% yield (Entry 1). On the other hand, the acylation was accelerated by adding LiClO$_4$ and the yield was improved to 50% (Entry 2), while sodium

Table 8. Effect of Metal Salts



| Entry | Metal salt | Yield/%[a] |
|---|---|---|
| 1 | None | 12 |
| 2 | LiClO$_4$ | 50 |
| 3 | NaClO$_4$ | 11 |
| 4 | Mg(ClO$_4$)$_2$ | ND[b] |
| 5 | LiOTf | 2 |
| 6 | LiBF$_4$ | 11 |

a) Determined by GLC analyses using an internal standard.
b) Not detected.

or magnesium perchlorate was not effective (Entries 3 and 4). In the absence of $Sc(OTf)_3$, $LiClO_4$ was not soluble in the reaction mixture and no acylation product was obtained. When $Sc(OTf)_3$ was added to a suspension of $LiClO_4$, acetic anhydride, and *m*-xylene (**9**) in nitromethane, the suspension changed to a dark-red homogeneous solution and the acylation reaction began to proceed.

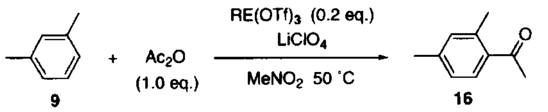
The acceleration effect on the acylation of the above-mentioned $RE(OTf)_3$–$LiClO_4$ system strongly depends on the amount of $LiClO_4$ as summarized in Table 9. $Sc(OTf)_3$ or $Yb(OTf)_3$ was used as a representative $RE(OTf)_3$, and the reaction of **9** with acetic anhydride was studied. The yields were increased in accordance with the amount of $LiClO_4$ in both cases. In the absence of $LiClO_4$, $Sc(OTf)_3$ catalyzed the acylation of **9** to afford **16** in only 12% yield. On the other hand, when $Sc(OTf)_3$ was combined with 10 equiv of $LiClO_4$, the yield was improved to 89%.

The effect of the amounts of $Sc(OTf)_3$ on the $Sc(OTf)_3$–$LiClO_4$ system is summarized in Table 10. The reaction proceeded smoothly by using a catalytic amount of $Sc(OTf)_3$ and a 3000% yield of the product **16** (based on catalyst) was obtained when 0.01 equiv of $Sc(OTf)_3$ was employed (Entry 3).

Several kinds of substituted benzenes were subjected to the $Sc(OTf)_3$–$LiClO_4$-catalyzed acylation, and the results are summarized in Table 11. Each acylation reaction in the table gave a single acylation product and no formation of other isomers was detected by GLC. Acetylation of thioanisole (**5**) and anisole (**1**) resulted in excellent yields of the products (Entries 1 and 2). Mesitylene (**3**) and xylenes (**8**—**10**) were transformed to 2,4,6-trimethylacetophenone (**4**) and dimethylacetophenones (**17**—**19**) in moderate yields, respectively (Entries 3—6). It should be noted that toluene (**21**) was acylated by the $Sc(OTf)_3$–$LiClO_4$ system to give 4-methylacetophenone (**22**) in 48% yield (Entry 7), while the acylation of toluene did not proceed without the addition of $LiClO_4$. Furthermore, recovery and reuse of the $RE(OTf)_3$–$LiClO_4$ system were successfully performed. As shown in Table 12, the yields of **16** in the second and third uses of the catalyst system were almost the same as that in the first use.

**Friedel–Crafts Acylation in Supercritical Carbon Dioxide.** Supercritical carbon dioxide ($scCO_2$) is regarded as a desirable substitute for some toxic organic solvents leading to benign chemical reactions.[24] Quite recently, we have found that Diels–Alder reactions of carbonyl dienophiles with dienes and aza Diels–Alder reactions of imines with dienes proceeded smoothly using scandium tris (heptadecafluorooctanesulfonate) ($Sc(OSO_2C_8F_{17})_3$) as a Lewis acid catalyst in $scCO_2$.[25] The length of perfluorocarbon chains of

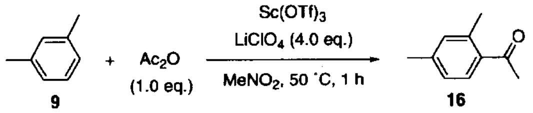
Table 9. Acceleration of the Acylation by $LiClO_4$



| RE = Sc[a)] | | RE = Yb[b)] | |
|---|---|---|---|
| $LiClO_4$ | Yield[c)] | $LiClO_4$ | Yield[c)] |
| equiv | % | equiv | % |
| None | 12 | none | ND[d)] |
| 0.4 | 22 | 0.4 | 8 |
| 0.8 | 28 | 0.8 | 17 |
| 1.0 | 36 | 1.0 | 22 |
| 2.0 | 51 | 2.0 | 38 |
| 4.0 | 61 | 4.0 | 67 |
| 6.0 | 82 | 6.0 | 83 |
| 8.0 | 88 | | |
| 10.0 | 89 | | |

a) 1 h. b) 4 h. c) Determined by GLC analyses using an internal standard. d) Not detected.

Table 10. Effect of the Amounts of $Sc(OTf)_3$

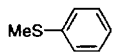
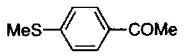
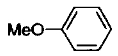
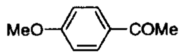
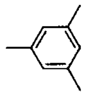
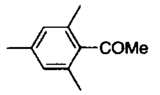
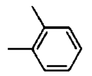
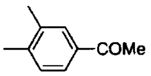
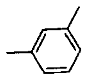
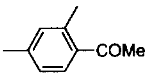
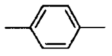
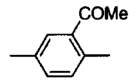
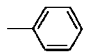
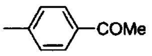


| Entry | $Sc(OTf)_3$/equiv | Yield/%[a)] | Turnover |
|---|---|---|---|
| 1 | 0.2 | 61 | 3 |
| 2 | 0.1 | 59 | 6 |
| 3 | 0.01 | 30 | 30 |

a) Determined by GLC analyses using an internal standard.

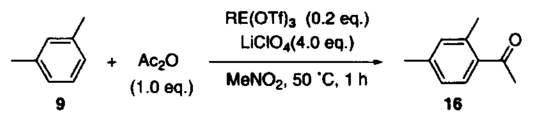
Table 11. $RE(OTf)_3$-Catalyzed Acylation in $LiClO_4$–$MeNO_2$

$$\underset{}{\text{Ar-H}} + \underset{(1.0\ \text{eq.})}{Ac_2O} \xrightarrow[\text{MeNO}_2,\ 50\ ^\circ\text{C},\ 1\ \text{h}]{\text{Sc(OTf)}_3\ (0.2\ \text{eq.})\ \ \text{LiClO}_4\ (4.0\ \text{eq.})} \text{Ar-COMe}$$

| Entry | Ar–H | Product | Yield/%[a)] |
|---|---|---|---|
| 1 | <br>**5** | <br>**12** | 97 |
| 2 | <br>**1** | <br>**2** | 96 |
| 3 | <br>**3** | <br>**4** | 93 |
| 4 | <br>**8** | <br>**15** | 55 |
| 5 | <br>**9** | <br>**16** | 61 |
| 6 | <br>**10** | <br>**17** | 16 |
| 7[b)] | <br>**21** | <br>**22** | 47 |

a) Determined by GLC analyses using an internal standard.
b) 20 h.

Table 12. Catalytic Activity of Recovered RE(OTf)$_3$–LiClO$_4$

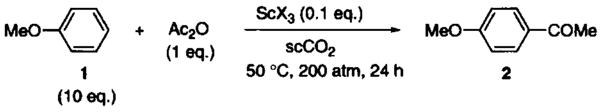


| RE | Number of times used | Yield[a)] % | Recovry of catalyst/% |
|---|---|---|---|
| Sc | 1 | 61 | 96 |
| | 2 | 55 | 94 |
| | 3 | 53 | 87 |
| Yb[b)] | 1 | 68 | 95 |
| | 2 | 73 | 99 |
| | 3 | 70 | 91 |

a) Determined by GLC analyses using an internal standard.
b) LiClO$_4$ (10.0 equiv) was used and the reaction time was 4 h.

the scandium catalyst was an essential factor for the catalytic activity in scCO$_2$. We decided to examine Friedel–Crafts acylation in scCO$_2$ using the scandium catalyst. The effect of the scandium catalysts in the reaction of anisole (**1**) with acetic anhydride in scCO$_2$ (50 °C, 200 atm) is shown in Table 13. Different from the Diels–Alder reactions, scandium tris(nonafluorobutanesulfonate) (Sc(OSO$_2$C$_4$F$_9$)$_3$) gave the best results. Several aromatics were subjected to the Sc(OSO$_2$C$_4$F$_9$)$_3$-catalyzed Friedel–Crafts acylation in scCO$_2$, and the results are summarized in Table 14. In all cases, the ampoule method was used to prevent neat reactions.[26] Activated benzens such as **1** and mesitylene (**3**) reacted smoothly in the presence of a catalytic amount of Sc(OSO$_2$C$_4$F$_9$)$_3$ to afford the corresponding aromatic ketones in high yields, while lower yields were obtained in the acylation of *m*-xylene. Although remarkable improvement of the catalytic activity was not observed in scCO$_2$ under the reaction conditions, it should be noted that practical catalysis has been achieved in Friedel–Crafts acylation in the enviromentally friendly solvent system.

Table 13. Effect of Perfluoroalkyl Chains in Scandium Perfluoroalkanesulfonates

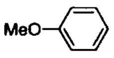
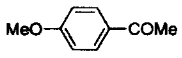
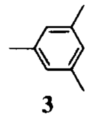
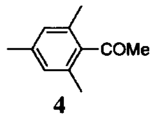
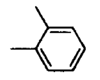
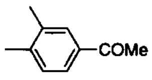
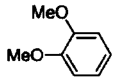
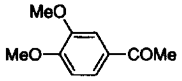
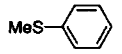
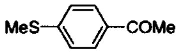


| Entry | ScX$_3$ | Yield/%[a)] |
|---|---|---|
| 1 | Sc(OSO$_2$CF$_3$)$_3$ | 70 |
| 2 | Sc(OSO$_2$C$_4$F$_9$)$_3$ | 80 |
| 3 | Sc(OSO$_2$C$_8$F$_{17}$)$_3$ | 63 |

a) Determined by GLC analyses using an internal standard.
b) When 1 equiv of **1** and 2 equiv of acetic anhydride were used, **2** was obtained in 58% yield.

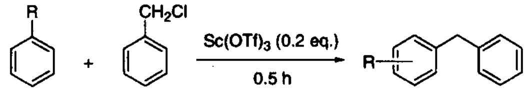
Table 14. Sc(OSO$_2$C$_4$F$_9$)$_3$-Catalyzed Acetylation of Aromatics in scCO$_2$

$$\underset{(10\ \text{eq.})}{\text{Ar-H}} + \underset{(1\ \text{eq.})}{\text{Ac}_2\text{O}} \xrightarrow[\text{scCO}_2,\ 50\ ^\circ\text{C, 200 atm, 24 h}]{\text{Sc(OSO}_2\text{C}_4\text{F}_9)_3\ (0.1\ \text{eq.})} \text{Ar-COMe}$$

| Entry | Ar–H | Product | Yield/%[a)] |
|---|---|---|---|
| 1 |  **1** |  **2** | 80 |
| 2 |  **3** |  **4** | 83 |
| 3 |  **8** |  **15** | 19 |
| 4 |  **6** |  **13** | 74 |
| 5 |  **5** |  **12** | 37 |

a) Determined by GLC analyses using an internal standard.

Table 15. Sc(OTf)$_3$-Catalyzed Benzylation



| Entry | R | Sc(OTf)$_3$ equiv | Temp °C | Yield[a)] % |
|---|---|---|---|---|
| 1[b)] | H | 0.2 | 75 | 76 (380) |
| 2 | H | 0.2 | 75 | 38 (190) |
| 3 | Me | 0.2 | 100 | 99 (495)[c)] |
| 4 | Me | 0.1 | 100 | 98 (980) |
| 5 | Me | 0.05 | 100 | 93 (1980) |
| 6 | Me | 0.01 | 100 | 93 (9300) |
| 7 | Me | 0.001 | 100 | 39 (39000) |

a) Yields based on benzyl chloride were determined by GLC analyses using an internal standard. The numbers in parentheses are yields based on Sc(OTf)$_3$. b) 18 h. c) The ratio of *o*:*m*:*p* was 43:3:54. The distribution of isomers was determined by $^{13}$C NMR and GLC analysis by comparing with those of authentic samples.

**RE(OTf)$_3$-Catalyzed Friedel–Crafts Alkylation.** RE(OTf)$_3$ was also found to be an excellent catalyst in Friedel–Crafts alkylation. The Sc(OTf)$_3$-catalyzed alkylation of benzene and toluene with benzyl chloride was performed and the results are summarized in Table 15. As might be expected, the methyl substituent facilitated the reaction and benzylation of toluene completed within 30 min at 100 °C (Entries 3—7), while benzylation of benzene proceeded incompletely in 18 h at 75 °C (Entry 1). The effect of the amounts of Sc(OTf)$_3$ is also shown in Table 15, and a 39,000% yield of the product (based on the catalyst) was attained in benzylation of toluene when 0.001 equiv of Sc(OTf)$_3$ was employed (Entry 7).

## Conclusion

We have developed RE(OTf)$_3$-catalyzed Friedel–Crafts acylation and alkylation, which were found to have several advantageous features compared to reactions promoted by conventional Lewis acids. (1) The Friedel–Crafts acylation proceeded smoothly using a catalytic amount of RE(OTf)$_3$. (2) Sc(OTf)$_3$ is the most active catalyst among RE(OTf)$_3$. (3) RE(OTf)$_3$ is easily recovered and reused without loss of activity. (4) The addition of LiClO$_4$ is quite effective to accelerate the RE(OTf)$_3$-catalyzed Friedel–Crafts acylation. (5) RE(OTf)$_3$-LiClO$_4$ as a catalyst system can be also easily recovered and reused in Friedel–Crafts acylation without loss of activity. (6) Regioselectivity in the acylation of 2-methoxynaphthalene is dramatically changed by the amounts of RE(OTf)$_3$. (7) RE(OTf)$_3$-catalyzed Friedel–Crafts acylation is successfully performed in scCO$_2$. (8) RE(OTf)$_3$ is also shown to be an excellent catalyst in Friedel–Crafts alkylation.

## Experimental

$^1$H and $^{13}$C NMR spectra were recorded on a JEOL JNR-EX400 spectrometer. GC-MS spectra were measured on a Shimadzu QP-1000 spectrometer. IR spectra were recorded on a Shimadzu IR-460. Gas chromatography analyses were carried out with a Shimadzu GC-17A using a capillary column (TC-1701, GL-Science Inc., 0.25 mm, 30 m), and FID was used as a detector. Silica-gel column chromatography was performed using Merck Kieselgel 60 (70—230 mesh).

RE(OTf)$_3$ were prepared from the corresponding rare earth metal oxides (Soekawa Rikagaku Co., Ltd.) and trifluoromethanesulfonic acid (Kanto Kagaku Co., Ltd.) in water according to the literature.[16] All reagents used in this work are commercially available and were not purified before use unless otherwise noted.

**A Typical Procedure of RE(OTf)$_3$-Catalyzed Friedel–Crafts Acylation.** A mixture of Yb(OTf)$_3$ (620 mg, 1 mmol), anisole (**1**, 540 μl, 5 mmol), and acetic anhydride (940 μl, 10 mmol) in nitromethane (5 ml) was stirred at 50 °C for 4 h. After dilution with water (10 ml), the mixture was extracted with chloroform. The acylation product, 4-methoxyacetophenone (**2**), was dissolved in the chloroform layer and the yield (70 %) was determined by GLC using an internal standard method. The aqueous layer was concentrated in vacuo to give a crystalline residue, which was finally heated at 190 °C for 4 h in vacuo to afford 576.6 mg (93%) of Yb(OTf)$_3$ as colorless crystals. The recovered Yb(OTf)$_3$ was reused in the next acylation reaction. All the products of the acylation of aromatic compounds listed in Tables 1—14 are known compounds and were identified by comparison of their spectra data and retention time in GLC with those of authentic samples. Commercially available authentic samples: 4-methoxyacetophenone (**2**) and 3,4-dimethoxyacetophenone (**13**) (from Kanto Kagaku Co., Ltd.), 2,4,6-trimethylacetophenone (**4**), 4-methoxybenzophenone (**11**), 2,4-dimethoxyacetophenone (**14**), 2,4-dimethylacetophenone (**16**), and 2,5-dimethylacetophenone (**17**) (from Tokyo Chemical Industry Co., Ltd.), 3,4-dimethylacetophenone (**15**) and 6-acetyl-2-methoxynaphthalene (**20**) (from Aldrich Chemical Co., Inc.). Authentic samples of other products, **12**[27] and **19**[28] were prepared by the acylation using AlCl$_3$ as a catalyst according to the procedures described in the literature.

**1-[4-(Methylthio)phenyl]ethanone (12).** $^1$H NMR (DMSO-$d_6$) $\delta$ = 2.52 (s, 3H), 2.57 (s, 3H), 7.27 (d, 2H, $J$ = 8.30 Hz), 7.87 (d, 2H, $J$ = 8.30 Hz); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 13.8, 26.4, 124.7, 128.6, 133.0, 145.3, 196.8.

**1-Acetyl-2-methoxynapthalene (19).** $^1$H NMR (CDCl$_3$) $\delta$ = 2.64 (s, 3H), 3.94 (s, 3H), 7.25 (d, 1H, $J$ = 8.79 Hz), 7.35 (d, 1H, $J$ = 7.81 Hz), 7.46 (d, 1H, $J$ = 7.81 Hz), 7.77 (dd, 2H, $J$ = 7.81 Hz), 7.86 (d, 1H, $J$ = 7.81 Hz); $^{13}$C NMR (CDCl$_3$) $\delta$ = 32.9, 56.4, 113.0, 123.8, 124.2, 125.0, 127.8, 128.4, 129.0, 130.5, 131.7, 154.3, 205.1.

**2-Acetyl-6-methoxynapthalene (20).** $^1$H NMR (CDCl$_3$) $\delta$ = 2.67 (s, 3H), 3.91 (s, 3H), 7.12 (d, 1H, $J$ = 2.44 Hz), 7.18 (dd, 1H, $J$ = 8.79, 2.44 Hz), 7.72 (d, 1H, $J$ = 8.79 Hz), 7.81 (d, 1H, $J$ = 8.79 Hz), 7.98 (dd, 1H, $J$ = 8.79, 1.95 Hz), 8.35 (d, 1H, $J$ = 1.95 Hz); $^{13}$C NMR (CDCl$_3$) $\delta$ = 26.5, 55.4, 105.7, 119.7, 124.9, 127.1, 127.8, 130.0, 131.1, 132.6, 137.3, 159.7, 197.8.

**Reaction of 1-Acetyl-2-methoxynaphthalene (19) Using an Equimolar Amount of Sc(OTf)$_3$.** A mixture of 1-acetyl-2-methoxynaphthalene (780 mg, 5 mmol) and Sc(OTf)$_3$ (2460 mg, 5 mmol) in nitromethane (5 ml) was stirred at 50 °C for 18 h. After dilution with water (10 ml), the mixture was extracted with chloroform. The chloroform layer was concentrated in vacuo to give a mixture of 1-methoxynaphthalene (86%) and 2-acetyl-6-methoxynaphthalene (9%). The yields were determined by GLC by using an internal standard method.

**A Typical Procedure of RE(OTf)$_3$–LiClO$_4$ System-Catalyzed Friedel–Crafts Acylation.** To a suspension of Sc(OTf)$_3$ (490 mg, 1 mmol), *m*-xylene (610 μl, 5 mmol), and LiClO$_4$ (2130 mg, 20 mmol) in nitromethane (5 ml) was added acetic anhydride (470 μl, 5 mmol); the suspension then changed to a dark-red homogeneous solution. After stirring at 50 °C for 1 h, the reaction mixture was diluted with water (10 ml), and the aqueous layer was extracted with chloroform (10 ml×3). The acylation product, 2,4-dimethylacetophenone, was in the chloroform layer and the yield (61%) was determined by GLC. The aqueous layer was concentrated to give crystalline residues, which were finally heated at 190 °C for 4 h in vacuo to afford a mixture of LiClO$_4$ and Sc(OTf)$_3$ (2510 mg, 96%). The recovered catalyst was reused in the next acylation reaction. All the products are known compounds and were identified by a comparison of their spectra data and retention time in GLC with those of authentic samples.

**A Typical Procedure of RE(OTf)$_3$-Catalyzed Friedel–Crafts Acylation in scCO$_2$.** Under an argon atmosphere, Sc(OSO$_2$C$_4$F$_9$)$_3$ (188 mg, 0.2 mmol) was placed in a 10-ml reactor along with a magnetic bar, and precooled low-pressure CO$_2$ was introduced to the sealed reactor at room temperature. After a mixture of anisole (**1**, 1080 μl, 10 mmol) and acetic anhydride (94 μl, 1.0 mmol) was added through the Feed Line, the reactor was pressurized to 200 atm at 50 °C. After 24 h, the pressure in the reactor was slowly released, the reactor was opened under 0 °C, and H$_2$O (10 ml) was added to the residue. The mixture was extracted with Et$_2$O, and the chemical yield (80%) was determined by GC using an internal standard.

**A Typical Procedure of RE(OTf)$_3$-Catalyzed Friedel–Crafts Alkylation by Benzyl Chloride as an Alkylating Agent.** A mixture of Sc(OTf)$_3$ (490 mg, 1 mmol) and benzyl chloride (633 mg, 5 mmol) in benzene (5 ml) was stirred at 75 °C for 18 h. After dilution with water (10 ml), the mixture was extracted with chloroform. The alkylation product, diphenylmethane, was dissolved in the chloroform layer and the yield was (76%) determined by GLC.

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