Scandium(III) Trifluoromethanesulfonate Catalyzed Aromatic Nitration with Inorganic Nitrates and Acetic Anhydride

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The rare earth metal(III) trifluoromethanesulfonate (rare earth metal(III) triflate, RE(OTf)$_3$) was found to be an efficient catalyst for aromatic nitration with carboxylic anhydride–inorganic nitrate as the nitrating agent. In the presence of a catalytic amount of RE(OTf)$_3$, the nitration of substituted benzenes proceeded to afford the corresponding nitrobenzenes. Especially, scandium(III) trifluoromethanesulfonate (scandium(III) triflate, Sc(OTf)$_3$) is the most active catalyst among our tested Lewis acids. It was also found that acetic anhydride–Al(NO$_3$)·9H$_2$O is the most active nitrating agent in this system.

Key words scandium(III) trifluoromethanesulfonate; aromatic nitration; acetyl nitrate; acetic anhydride; aluminum(III) nitrate

Nitration of aromatic compounds is one of the most fundamental and useful reactions for introducing the nitrogen atom directly into aromatic rings.[1—4] This reaction generally requires the use of a potent mixture of concentrated or fuming nitric acid with sulfuric acid, a large amount of acid and its waste after the aqueous work-up procedures often cause serious environmental problems. In order to these issues, there have been some efforts to perform reactions in the absence of sulfric acid.[5—26] For the solution of this problem, we focused on acyl nitrates, which are known as active nitrating agent.[27—36] Acyl nitrates are generally produced *in situ* by the reaction of an excess of concentrated or fuming nitric acid and carboxylic anhydride, or the reaction of silver nitrate and acid chloride. Another method for the generation of acyl nitrates is the reaction of inorganic nitrates and carboxylic anhydride, whereas, in most cases, the nitration by this method is limited to activated substrates.[37] Crivello reported that the acyl nitrates generated from the mixture of ammonium nitrate and trifluoroacetic anhydride and aromatic nitration smoothly proceeded, however, the reaction of ammonium nitrate with acetic anhydride did not produce nitration products.[38]

It is known that rare earth metal(III) trifluoromethanesulfonates (rare earth metal(III) triflates, RE(OTf)$_3$) have a high Lewis acidity compared to the corresponding rare earth metal(III) halides, and are stable in water. In this decade, there have been many reports that RE(OTf)$_3$ as a Lewis acid catalyst has been successfully applied to several synthetic reactions.[39—45] Recently, we have developed RE(OTf)$_3$ catalyzed Friedel–Crafts reactions[46—49] and benzyl-etherification,[50] and these reactions proceed smoothly using small amounts of RE(OTf)$_3$. During the course of our investigations about Friedel–Crafts acylation, we found that acetyl perchlorate, the mixed anhydride of acetic acid and perchloric acid, which acts as an active acylating agent is generated from acetic anhydride and lithium perchlorate in the presence of RE(OTf)$_3$.[46—49] Based on this consideration, the efficient generation of acyl nitrate is expected between an inorganic nitrate and carboxylic anhydride in the presence of RE(OTf)$_3$, and we tried to examine the nitration of aromatic compounds using the RE(OTf)$_3$–carboxylic anhydride–inorganic nitrate system.

Results and Discussion

In the first place, the catalytic activity of Lewis acids was examined for the nitration of *m*-xylene using the acetic anhydride–lithium nitrate system. These results are summarized in Table 1. The nitration of *m*-xylene was carried out in a solution containing 0.3 molar equivalent of Lewis acid, 5.0 molar equivalent of acetic anhydride, and 1.0 molar equivalent of lithium nitrate (LiNO$_3$) at room temperature. 1,3-Dimethyl-2-nitrobenzene (**1**) and 1,3-dimethyl-4-nitrobenzene (**2**) as nitration products were obtained. No di-nitrated products were observed. While it is assumed that the acetylation proceeds in addition to nitration under this condition, acetylation products were not obtained. In the absence of Lewis acids, *m*-xylene was not converted (Entry 1). When conventional Lewis acids such as AlCl$_3$, FeCl$_3$, SnCl$_4$, and BF$_3$·Et$_2$O were examined, the product yields were poor (Entries 2—5). The reaction was next performed using rare earth metal(III) compounds as the Lewis acid catalyst. While ScCl$_3$ or YbCl$_3$ was not effective (Entries 6, 7), RE(OTf)$_3$ was effective (Entries 8, 10). Especially, when a 0.3 molar equivalent of Sc(OTf)$_3$ was used as the catalyst, the nitration of *m*-xylene smoothly proceeded at room temperature and a 74% yield of nitration products was obtained (Entry 8). On the other hand, in the case of no addition of acetic anhydride, the nitration with LiNO$_3$ in the presence of Sc(OTf)$_3$ did not proceed (Entry 9). It is presumed that a highly reactive nitrating agent such as acyl nitrate is generated *in situ* by the reaction of LiNO$_3$ and acetic anhydride in the presence of Sc(OTf)$_3$ as a Lewis acid. It should be noted that this nitration does not require strong acid condition. Table 1 also shows the difference in reactivity between the monobasic acid anhydride and dibasic acid anhydride. For example, the dibasic acid anhydride such as succinic or phthalic anhydride produced no nitration product (Entries 11, 12). On the other hand, the monobasic acid anhydrides are effective, and especially, acetic anhydride gave a good yield (Entries 8, 13).

Several reaction conditions were examined, and the results are summarized in Table 2. This table shows that the yields of the products are dependent on the solubility of the inor-

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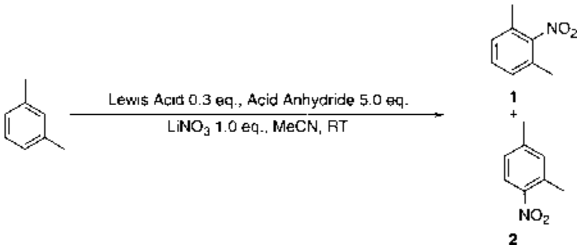
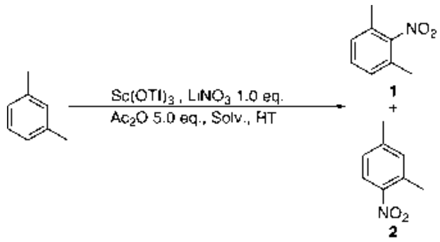
Table 1. Lewis Acid Catalyzed Nitration with $LiNO_3$ and Acid Anhydride



Entry	Lewis acid	Acid anhydride	Time/h	Yield/%[a)	Selectivity/%[b)	
				1+**2**	**1**	**2**
1	None	Acetic anhydride	24	N.D.[c)		
2	$AlCl_3$	Acetic anhydride	5	Trace		
3	$FeCl_3$	Acetic anhydride	24	15	20	80
4	$SnCl_4$	Acetic anhydride	24	23	13	87
5	$BF_3\cdot Et_2O$	Acetic anhydride	24	17	24	76
6	$ScCl_3$	Acetic anhydride	24	Trace		
7	$YbCl_3$	Acetic anhydride	24	Trace		
8	$Sc(OTf)_3$	Acetic anhydride	2	74	16	84
9	$Sc(OTf)_3$	None	24	N.D.[c)		
10	$Yb(OTf)_3$	Acetic anhydride	2	44	19	81
11	$Sc(OTf)_3$	Succinic anhydride	2	N.D.[c)		
12	$Sc(OTf)_3$	Phthalic anhydride	2	N.D.[c)		
13	$Sc(OTf)_3$	Benzoic anhydride	2	32	12	88

a) Isolated yield. *b*) Ratio of **1** and **2** was determined by ^{1}H-NMR. *c*) Not detected.

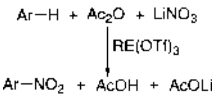
Table 2. Nitration of *m*-Xylene by $Sc(OTf)_3$–$LiNO_3$–Acetic Anhydride



Entry	$Sc(OTf)_3$	Solv.	Time	Yield/%[a)	Selectivity/%[b)	
	eq		h	**1**+**2**	**1**	**2**
1	0.3	MeCN	2	74 (247)	20	80
2	0.3	$MeNO_2$	2	51 (170)	12	88
3	0.3	$C_2H_4Cl_2$	2	62 (207)	11	89
4	0.3	MeCN	24	85 (283)	18	82
5	0.3	MeCN	48	82 (273)	17	83
6	0.1	MeCN	24	32 (320)	25	75

a) Isolated yield. The numbers in parentheses are yields based on $Sc(OTf)_3$. *b*) Ratio of **1** and **2** was determined by ^{1}H-NMR.

ganic nitrate in the reaction media employed. For example, the nitration in acetonitrile was a homogeneous reaction and the yield of the nitration products was 74% (Entry 1). On the other hand, in nitromethane or dichloroethane (Entries 2, 3), the reaction mixture was heterogeneous and the yield was relatively low. This table also shows the effect of the amount of catalyst and reaction time. For the nitration with a 0.3 molar equivalent of $Sc(OTf)_3$ in acetonitrile for 24 h, the nitration products were obtained in an 85% yield (Entry 4). The yield was not further increased when the reaction time was extended to 48 h (Entry 5). When a 0.1 molar equivalent of $Sc(OTf)_3$ was used, the yield was only 32% (Entry 6). We considered that this low catalytic activity of $Sc(OTf)_3$ was due to the basicity of lithium acetate which was generated as a co-product in the reaction system (Chart 1).



$$\mathrm{Ar{-}H + Ac_2O + LiNO_3 \xrightarrow{RE(OTf)_3} Ar{-}NO_2 + AcOH + AcOLi}$$

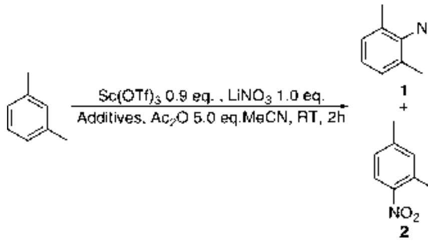
Chart 1. Possible Equation of Nitration of Aromatics by Using $RE(OTf)_3$–Ac_2O–$LiNO_3$

For the study of the negative effect of the co-products, we examined the addition of co-products to this nitration system (Table 3). This table clearly shows that lithium acetate interferes with the $Sc(OTf)_3$-catalyzed nitration. While the nitration reaction proceeded with no addition of lithium acetate or acetic acid (Entry 4), the reaction did not proceed in the presence of lithium acetate (Entries 1, 2). Based on this evidence, it is concluded that the Lewis acidity of $Sc(OTf)_3$ decreased due to the basicity of lithium acetate and the reaction did not proceed.

Various inorganic nitrates were then examined for the nitration of *m*-xylene with acetic anhydride and $Sc(OTf)_3$, and these results are summarized in Table 4. The amount of nitronium ion in the inorganic nitrate was equivalent to that of the *m*-xylene. All the inorganic nitrates were effective and the corresponding nitrated products were obtained. Especially, the inorganic nitrates of group 3 or 13 in the periodic table were effective and the nitration products were obtained in good yield (Entries 7—9, 20, 21). The inorganic nitrate of Zr, Cr, Fe, or Bi was also effective (Entries 10, 11, 13, 23). However, alkaline or alkaline earth metal nitrate has a low nitration activity, and the yields of products were very poor (Entries 1—6).

The difference in activity of the nitration of benzene using

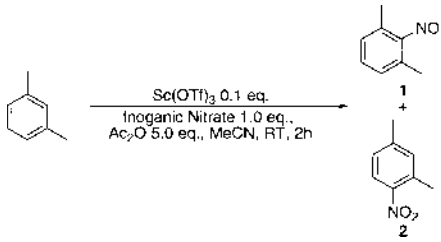
Table 3. Negative Effect of Co-Product



Entry	Additives	Yield/%[a]	Selectivity/%[b]	
		1+**2**	**1**	**2**
1	AcOLi 0.9 eq. AcOH 0.9 eq.	N.D.[c]		
2	AcOH 0.9 eq.	N.D.[c]		
3	AcOH 0.9 eq.	52	17	83
4	None	74	20	80

a) Isolated yield. *b*) Ratio of **1** and **2** were determined by ^{1}H-NMR. *c*) Not detected.

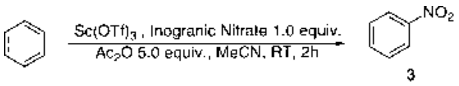
Table 4. Effect of Nitric Acid Salt on Nitration of *m*-Xylene



Entry	Inorganic nitrate	Yield/%[a]	Selectivity/%[b]	
		1+**2**	**1**	**2**
1	$LiNO_3$	14	29	71
2	$NaNO_3$	25	16	84
3	KNO_3	25	16	84
4	$Mg(NO_3)_2 \cdot 6H_2O$	4	25	75
5	$Ca(NO_2)_2 \cdot 4H_2O$	20	15	85
6	$Ba(NO_3)_2$	22	14	86
7	$Sc(NO_3)_3 \cdot 4H_2O$	95	17	83
8	$Y(NO_3)_3 \cdot 6H_2O$	71	17	83
9	$Yb(NO_3)_3 \cdot 3H_2O$	84	18	82
10	$ZrO(NO_3)_2 \cdot 2H_2O$	82	17	83
11	$Cr(NO_3)_3 \cdot 3H_2O$	88	16	84
12	$Mn(NO_3)_2 \cdot 6H_2O$	30	17	83
13	$Fe(NO_3)_3 \cdot 9H_2O$	90	17	83
14[c]	$Co(NO_3)_2 \cdot 6H_2O$	48	17	83
15[c]	$Ni(NO_3)_2 \cdot 6H_2O$	10	30	70
16	$Rh(NO_3)_3$	24	17	83
17	$Cu(NO_3)_2 \cdot 3H_2O$	32	16	84
18[c]	$AgNO_3$	50	16	84
19[c]	$Zn(NO_3)_2 \cdot 6H_2O$	8	12	82
20	$Al(NO_3)_3 \cdot 9H_2O$	92	16	84
21	$In(NO_3)_3 \cdot 3H_2O$	75	17	83
22	$Pb(NO_3)_2$	50	18	82
23	$Bi(NO_3)_3 \cdot 5H_2O$	77	17	83
24	NH_4NO_3	21	14	86

a) Isolated yield. *b*) Ratio of **1** and **2** was determined by ^{1}H-NMR. *c*) 0.3 eq of $Sc(OTf)_3$ was used.

Table 5. Effect of Nitric Acid Salt on Ntiration of Benzene



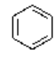
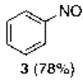
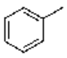
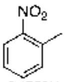
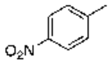
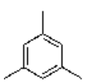
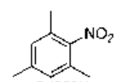
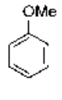
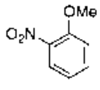
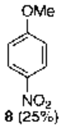
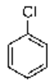
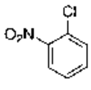
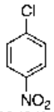
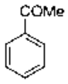
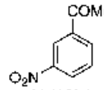
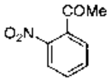
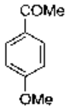
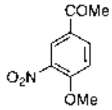
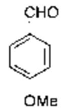
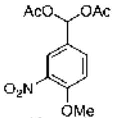
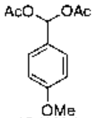
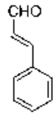
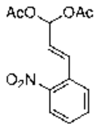
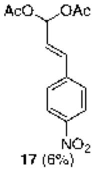
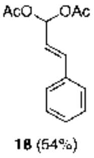
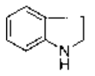
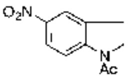
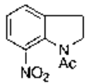
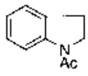
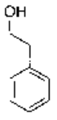
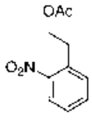
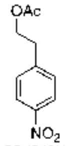
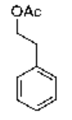
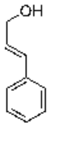
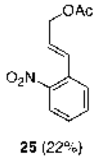
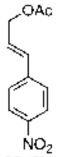
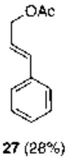
Entry	Inorganic nitrate	$Sc(OTf)_3$	Yield/%[a]
1	$In(NO_3) \cdot 3H_2O$	0.1	63
2	$In(NO_3) \cdot 3H_2O$	None	32
3	$Bi(NO_3)_2 \cdot 5H_2O$	0.1	56
4	$Bi(NO_3)_2 \cdot 5H_2O$	None	32
5	$ZrO(NO_3)_2 \cdot 2H_2O$	0.1	61
6	$ZrO(NO_3)_2 \cdot 2H_2O$	None	41
7	$Cr(NO_3)_3 \cdot 3H_2O$	0.1	67
8	$Cr(NO_3)_3 \cdot 3H_2O$	None	N.D.[b]
9	$Fe(NO_3)_3 \cdot 9H_2O$	0.1	70
10	$Fe(NO_3)_3 \cdot 9H_2O$	None	N.D.[b]
11	$Al(NO_3)_3 \cdot 9H_2O$	0.1	78
12	$Al(NO_3)_3 \cdot 9H_2O$	None	N.D.[b]
13	$Sc(NO_2)_3 \cdot 4H_2O$	0.1	81
14	$Sc(NO_2)_3 \cdot 4H_2O$	None	66
15[c]	$Sc(NO_2)_3 \cdot 4H_2O$	None	N.D.[b]

a) Isolated yield. *b*) Not detected. *c*) No Ac_2O was used.

the $Sc(OTf)_3$–acetic anhydride–inorganic nitrate system is shown in Table 5. The inorganic nitrates of In, Bi, Zr, Cr, Fe, Al, and Sc were examined. These inorganic nitrates are also effective for the nitration of benzene. In the case of the In, Bi, Zr, or Sc salt, while the yields were low to moderate, the nitration proceeded in the absence of $Sc(OTf)_3$ (Entries 2, 4, 6, 14). In the case of the Cr, Fe, or Al salt, the reaction did not proceed in the absence of $Sc(OTf)_3$ (Entries 8, 10, 12). On the other hand, the yield of nitrobenzene (**3**) increased with the addition of $Sc(OTf)_3$ in every case. The reaction with $Sc(NO_3)_3 \cdot 4H_2O$ in the absence of acetic anhydride and $Sc(OTf)_3$ gave no nitrated products (Entry 15). Especially, when the inorganic nitrate of Al or Sc was used with $Sc(OTf)_3$ and acetic anhydride, **5** was obtained in good yield (Entries 11, 13). We realized that $Al(NO_3)_3 \cdot 9H_2O$ is the most reactive inorganic nitrate in this system.

The nitration of several kinds of aromatic compounds was examined (Table 6). Although the reaction conditions were not yet optimized, every reaction proceeded at room temperature and corresponding mono-nitrated products were obtained. While oxidation as a side reaction often occurs under the conventional nitration conditions, no oxidation products were observed in this reaction. The nitration of benzene and a substituted benzene having an electron-donating group such as anisole or alkylated benzenes proceeded in good yield (Entries 1—4). On the other hand, the introduction of an electron-withdrawing group such as a halogen or acetyl group was ineffective for this nitration. While the nitration of benzene produced a 78% yield of **3**, the reaction of chlorobenzene gave a poor yield (Entry 5). For the acetyl group, although acetophenone gave a lower yield than chlorobenzene did, the yield improved by the introduction of a methoxy group and an 81% yield of nitration products was obtained (Entries 6, 7). Interestingly, the reaction of 4-methoxyacetophenone gave not only 3-nitro-4-methoxyacetophenone (**13**) as expected but also 4-methoxynitrobenzene (**8**) (Entry 7). However, neither 2-methoxynitrobenzene (**7**) nor anisole was observed in this reaction. From these results, it is presumed that **8** is obtained not by the nitration of anisole as a de-acetylation product but by an ipso attack of the nitronium ion.[51] The reaction of 4-methoxybenzaldehyde also proceeded, and a 64% yield of (4-methoxy-3-nitro-

Table 6. Nitration by $\mathrm{Sc(OTf)_3}$–$\mathrm{MNO_3}$–$\mathrm{Ac_2O}$

Entry	Condition$^{a)}$	Ar-H	Ar-NO$_2$$^{b)}$		
1	A		 **3** (78%)		
2	A		 **4** (52%)	 **5** (35%)	
3	B		 **6** (88%)		
4	A		 **7** (56%)	 **8** (25%)	
5	A		 **9** (11%)	 **10** (34%)	
6$^{c)}$	A		 **11** (12%)	 **12** (6%)	
7	B		 **13** (67%)	**8** (14%)	
8$^{d)}$	B		 **14** (64%)	 **15** (19%)	
9$^{e)}$	B		 **16** (28%)	 **17** (6%)	 **18** (54%)
10	B		 **19** (26%)	 **20** (3%)	 **21** (68%)
11	B		 **22** (13%)	 **23** (21%)	 **24** (63%)
12$^{d)}$	B		 **25** (22%)	 **26** (5%)	 **27** (28%)
13$^{d)}$	B	**27**	**25** (28%)	**26** (7%)	

a) Condition A; $\mathrm{Sc(OTf)_3}$ 0.1 eq., $\mathrm{Al(NO_3)_3 \cdot 9H_2O}$ 1.0 eq., room temperature, 2 h. Condition B; $\mathrm{Sc(OTf)_3}$ 0.3 eq., $\mathrm{LiNO_3}$ 1.0 eq., room temperature, 5 h. *b*) The numbers in parentheses are isolated yields. *c*) Reaction time was 24 h. *d*) Reaction time was 4 h. *e*) Reaction time was 3 h.

phenyl)methanediol diacetate (**14**) and 19% yield of (4-methoxyphenyl)methanediol diacetate (**15**) were obtained (Entry 8). For the cinnamaldehyde, (*E*)-3-(2-nitrophenyl)-2-propene-1,1-diol diacetate (**16**), (*E*)-3-(4-nitrophenyl)-2-propene-1,1-diol diacetate (**17**), and (*E*)-3-phenyl-2-propene-1,1-diol diacetate (**17**) were obtained (Entry 9). Although it is well known that the aldehyde group is easily oxidized, no oxidation products were observed in Entries 8 and 9. These results show that the aldehyde group is first converted to an acylal group and then nitration occurred. For the reaction of indoline, the acetylation of the NH group and nitration of the aromatic ring proceeded, and *N*-acetylnitroindolines were obtained (Entry 10). The nitration of an aromatic substituted aliphatic alcohols was also examined (Entries 11, 12). It is known that the nitration of an aromatic substituted aliphatic alcohol produces the *O*-nitration product.[52—55] While the reaction with phenethyl alcohol yielded 13% of 2-(2-nitrophenyl)ethyl acetate (**22**), 21% of 2-(4-nitrophenyl)ethyl acetate (**23**), and 63% of 2-phenylethyl acetate (**24**), the *O*-nitration products was not observed. For the cinnamyl alcohol, (*E*)-2-nitrocinnamyl acetate (**25**) and (*E*)-4-nitrocinnamyl acetate (**26**) were obtained. These results show that the *O*- and *N*-acetylations first proceed and then the aromatic nitration occurrs.

Conclusion

We have developed the $\mathrm{RE(OTf)_3}$ catalyzed aromatic nitration using carboxylic anhydride–inorganic nitrate as the nitrating agent which was found to be have the following specific features:

1) The aromatic nitration with carboxylic anhydride–metal nitrate as the nitrating agent smoothly proceeds using a catalytic amount of $\mathrm{RE(OTf)_3}$.
2) The nitration does not require a strong acid condition.
3) $\mathrm{Sc(OTf)_3}$ is the most active catalyst among the author's tested Lewis acids.
4) Acetic anhydride–$\mathrm{Al(NO_3) \cdot 9H_2O}$ is the most active nitrating.
5) The *O*- and *N*-nitrations do not proceed.

Experimental

Melting points were measured with a Yanagimoto micro melting point apparatus. The IR spectra were recorded on a JASCO FT/IR-350. The ^{1}H-NMR spectra (tetramethylsilane (TMS) as an internal standard) were recorded on a Varian VXR-500 spectrometer. Chemical shifts are given in ppm. The Mass spectra were measured on a VG-70SE spectrometer. Elemental analyses were carried out using Yanaco MT-5. For the thin-layer chromatography (TLC) analyses throughout this study, Merck precoated TLC plates (silica gel 60 F_{254}) were used. Silica-gel column chromatography was performed using Merck Kieselgel 60 (70—230 mesh).

All of the $\mathrm{RE(OTf)_3}$ were prepared from the corresponding rare earth metal(III) oxide (Soekawa Chemicals Co., Ltd.) and trifluoromethanesulfonic acid (Kanto Chemicals Co., Ltd.) in water according to the literature method.[56,57] Acetic anhydride and acetonitrile were dried by distillation from calcium hydride. All reagents used in this study were commercially available.

Typical Experimental Procedure for the $\mathrm{RE(OTf)_3}$-Catalyzed Nitration with $\mathrm{LiNO_3}$ and Acetic Anhydride A typical experimental procedure is described for the $\mathrm{Sc(OTf)_3}$-catalyzed nitration of *m*-xylene (Table 1, Entry 10). $\mathrm{Sc(OTf)_3}$ was prepared from the scandium(III) oxide and trifluoromethanesulfonic acid.[56,57] A mixture of $\mathrm{Sc(OTf)_3}$ (451 mg, 0.92 mmol), *m*-xylene (320 mg, 3.0 mmol), acetic anhydride (1.4 ml, 15 mmol), and $\mathrm{LiNO_3}$ (210 mg, 3.0 mmol, the amounts of nitronium ion are equivalent to *m*-xylene) in acetonitrile (5 ml) was stirred at room temperature. The progress of the reaction was monitored by TLC. After 2 h, the reaction mixture was quenched by the addition of aqueous NaOH. The organic layer was extracted with ether, washed with brine, and dried over anhydrous $MgSO_4$. After removal of the solvents, the crude products were purified by column chromatography on silica-gel using ethyl acetate–*n*-hexane (1 : 40) to afford a mixture of nitrated products **1** and **2** as a yellow oil (74% yield). The isomer ratio of the products determined by ^{1}H-NMR was **1** : **2** = 16 : 84.

Spectral data and mps of the new compounds as well as those of the less common compounds are shown below.

4-Methoxy-3-nitroacetophenone (**13**)[58]: mp 92—94 °C (ethyl acetate); IR (KBr) 1680, 1535, 1275, 1240 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.61 (s, 3H), 4.04 (s, 3H), 7.17 (d, 1H, *J*=8.5 Hz), 8.18 (dd, 1H, *J*=8.5, 2.5 Hz), 8.43 (d, 1H, *J*=2.5 Hz). *Anal.* Calcd for $C_9H_9NO_4$: C, 55.38; H, 4.65; N, 7.18%. Found: C, 55.10; H, 4.84; N, 7.15%.

(4-Methoxy-3-nitrophenyl)-methanediol Diacetate (**14**): mp 69—72 °C (ethyl acetate); IR (KBr) 1740, 1535, 1350, 1245 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.14 (s, 6H), 3.99 (s, 3H), 7.12 (d, 1H, *J*=8.5 Hz), 7.63 (s, 1H), 7.69 (dd, 1H, *J*=8.5, 2.0 Hz), 8.04 (d, 1H, *J*=2.0 Hz). *Anal.* Calcd for $C_{12}H_{13}NO_7$: C, 50.88; H, 4.63; N, 4.95%. Found: C, 50.92; H, 4.70; N, 5.00%.

(4-Methoxyphenyl)-methanediol Diacetate (**15**)[59]: mp 60—63 °C (ethyl acetate); IR (KBr) 1750, 1545 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.09 (s, 6H), 3.80 (s, 3H), 6.89 (d, 2H, *J*=8.5 Hz), 7.45 (d, 2H, *J*=8.5 Hz), 7.62 (s, 1H). *Anal.* Calcd for $C_{12}H_{13}NO_7$: C, 50.88; H, 4.63; N, 4.95%. Found: C, 50.92; H, 4.70; N, 5.00%.

(*E*)-3-(2-Nitrophenyl)-2-propene-1,1-diol Diacetate (**16**)[60]: mp 75—80 °C (ethyl acetate); IR (KBr) 1760, 1530, 1350, 1240, 1200, 1100, 1070, 1010 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.15 (s, 6H), 6.19 (dd, 1H, *J*=16.0, 5.5 Hz), 7.34 (d, 1H, *J*=5.5 Hz), 7.38 (d, 1H, *J*=16.0 Hz), 7.4—7.7 (m, 3H), 8.0 (d, 1H, *J*=7.5 Hz).

(*E*)-3-(4-Nitrophenyl)-2-propene-1,1-diol Diacetate (**17**)[61] mp 105—109 °C (ether–*n*-hexane); IR (KBr) 1760, 1530, 1350, 1240, 1200, 1100, 1070, 1010 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.15 (s, 6H), 6.37 (dd, 1H, *J*=16.0, 5.5 Hz), 6.93 (d, 1H, *J*=16.0 Hz), 7.33 (d, 1H, *J*=6.5 Hz), 7.57 (d, 2H, *J*=8.5 Hz), 8.21 (d, 2H, *J*=8.5 Hz).

(*E*)-3-Phenyl-2-propene-1,1-diol Diacetate (**18**)[32]: mp 81—84 °C (ethyl acetate); IR (KBr) 1760, 1680, 1625, 1490, 1455, 1375, 1245, 1195, 1130, 1060, 1000, 940, 750, 690 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.11 (s, 6H), 6.19 (dd, 1H, *J*=16.5, 6.4 Hz), 6.90 (d, 1H, *J*=16.5 Hz), 7.1—7.6 (m, 6H), 7.57 (d, 2H, *J*=8.5 Hz), 8.21 (d, 2H, *J*=8.5 Hz).

1-Acetyl-7-nitroindoline (**20**)[62]: IR (KBr) 1670, 1520, 1400, 1320 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.27 (s, 3H), 3.23 (t, 2H, *J*=8.0 Hz), 4.24 (t, 2H, *J*=8.0 Hz), 7.14 (dd, 1H, *J*=8.0, 8.0 Hz), 7.42 (ddd, 1H, *J*=8.0, 1.5, 1.5 Hz), 7.62 (dd, 1H, *J*=8.0, 1.5 Hz).

2-(2-Nitrophenyl)ethyl Acetate (**22**)[63]: Yellow oil; IR (neat) 1720, 1520, 1350, 1240 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.03 (s, 3H), 3.26 (td, 2H, *J*=8.0, 1.5 Hz), 4.36 (t, 2H, *J*=8.0 Hz), 7.40 (m, 2H), 7.41 (ddd, 1H, *J*=8.0, 8.0, 1.5 Hz), 7.94 (dd, 1H, *J*=8.0, 1.5 Hz).

2-(4-Nitrophenyl)ethyl Acetate (**23**)[64]: Yellow oil; IR (neat) 1720, 1520, 1350, 1240 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.04 (s, 3H), 3.06 (td, 2H, *J*=8.0, 1.5 Hz), 4.33 (td, 2H, *J*=8.0, 1.5 Hz), 7.40 (dd, 2H, *J*=8.0, 1.5 Hz), 8.18 (dd, 2H, *J*=8.0, 1.5 Hz).

(*E*)-2-Nitrocinnamyl Acetate (**25**): Yellow oil; IR (neat) 1740, 1520, 1345, 1230, 1440, 1030, 965, 860, 785, 740, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.13 (s, 3H), 4.78 (dd, 2H, *J*=6.0, 1.5 Hz), 6.27 (dt, 1H, *J*=16.0, 6.0 Hz), 7.14 (dd, 1H, *J*=16.0, 1.5 Hz), 7.43 (ddd, 1H, *J*=8.0, 7.5, 2.0 Hz), 7.5—7.6 (m, 2H), 7.95 (dd, 1H, *J*=8.0, 0.5 Hz).

(*E*)-4-Nitrocinnamyl Acetate (**26**): Yellow oil; IR (neat) 1740, 1520, 1345, 1230, 1440, 1030, 965, 860, 785, 740, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.13 (s, 3H), 4.78 (dd, 2H, *J*=6.0, 1.5 Hz), 6.46 (dt, 1H, *J*=16.0, 6.0 Hz), 7.14 (dd, 1H, *J*=16.0, 1.5 Hz), 7.52 (d, 2H, *J*=8.5 Hz), 8.19 (d, 2H, *J*=8.5 Hz).

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References and Notes

1) Olah G. A., Malhotra R., Narang S. C., "Nitration: Methods and Mechanisms," VCH Publishers Inc., New York, 1989.
2) Olah G. A., "Friedel–Crafts and Related Reactions," Vol. 3, Wiley-Interscience, New York, 1964.
3) "The Chemistry of the Nitro and Nitroso Groups," Vol. II, ed. by Feuer H., in the series of "The Chemistry of Functional Groups," ed. by Patai S., Wiley-Interscience, New York, 1969.
4) "Supplement F: The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives," ed. by Patai S., in the series of "The Chemistry of Functional Groups," ed. by Patai S., Wiley, New York, 1982.
5) Waller F. J., Barrett A. G. M., Braddock D. C., Ramprasad D., *J. Chem. Soc., Chem. Commun.*, **1997**, 613—614 (1997).
6) Ramprasad D., Waller F. J., Barrett A. G. M., Braddock D. C., U.S. Patent 5728901 (1998) [*Chem. Abstr.*, **128**, 204692 (1998)].
7) Waller F. J., Barrett A. G. M., Braddock D. C., Ramprasad D., *Tetrahedron Lett.*, **39**, 1641—1642 (1998).
8) Waller F. J., Barrett A. G. M., Braddock D. C., Ramprasad D., McKinnell R. M., White J. P., Williams D. J., Ducray R., *J. Org. Chem.*, **64**, 2910—2913 (1999).
9) Waller F. J., Ramprasad D., Barrett A. G. M., Braddock D. C., *Chem. Ind.* (*Dekker*), **75**, 289—305 (1998).
10) Waller F. J., Barrett A. G. M., Braddock D. C., McKinnell R. M., Ramprasad D., *J. Chem. Soc.*, *Perkin Trans. 1*, **1999**, 867—872 (1999).
11) Barrett A. G. M., Braddock D. C., Ducray R., McKinnell R. M., Waller F. J., *Synlett*, **2000**, 57—58 (2000).
12) Suzuki H., Murashima T., Kozai I., Mori T., *J. Chem. Soc.*, *Perkin Trans. 1*, **1993**, 1591—1957 (1993).
13) Suzuki H., Mori T., *J. Chem. Soc.*, *Perkin Trans. 2*, **1994**, 479—484 (1994).
14) Suzuki H., Murashima T., *J. Chem. Soc.*, *Perkin Trans. 1*, **1994**, 903—908 (1994).
15) Suzuki H., Yonezawa S., Mori T., Maeda K., *J. Chem. Soc.*, *Perkin Trans. 1*, **1994**, 1367—1639 (1994).
16) Suzuki H., Mori T., Maeda K., *Synthesis*, **1994**, 841—845 (1994).
17) Suzuki H., Mori T., *J. Chem. Soc.*, *Perkin Trans. 2*, **1995**, 41—44 (1995),
18) Suzuki H., Mori T., *J. Chem. Soc.*, *Perkin Trans. 1*, **1995**, 291—293 (1995).
19) Suzuki H., Tatsumi A., Ishibashi T., Mori T., *J. Chem. Soc.*, *Perkin Trans. 1*, **1995**, 339—343 (1995).
20) Suzuki H., Tomaru J., Murashima T., *J. Chem. Soc.*, *Perkin Trans. 1*, **1994**, 2413—2416 (1994).
21) Suzuki H., Yonezawa S., Mori T., *Bull. Chem. Soc. Jpn.*, **68**, 1535—1544 (1995).
22) Suzuki Hit, Tatsumi A., Suzuki Hid, Maeda K., *Synthesis*, **1995**, 1353—1554 (1995).
23) Suzuki H., Mori T., *J. Chem. Soc.*, *Perkin Trans. 2*, **1996**, 677—683 (1996).
24) Suzuki H., Yonezawa S., Nonoyama N., Mori T., *J. Chem. Soc.*, *Perkin Trans. 1*, **1996**, 2385—2389 (1996).
25) Suzuki H., Mori T., *J. Org. Chem.*, **62**, 6498—6502 (1997).
26) Enya T., Suzuki H., Hisamatsu Y., *Bull. Chem. Soc. Jpn.*, **71**, 2221—2228 (1998).
27) For example see: Deans F. B., Eaborn C., *J. Chem. Soc.*, **1957**, 498—499 (1957).
28) For example see: Paul M. A., *J. Am. Chem. Soc.*, **80**, 5329—5332 (1958).
29) For example see: Bordwell F. G., Garbisch E. W., *J. Am. Chem. Soc.*, **82**, 3588—3598 (1960).
30) For example see: Sparks A. K., *J. Org. Chem.*, **31**, 2299—2302 (1966).
31) For example see: Hartshorn S. R., Moodie R. B., Schofield K., *J. Chem. Soc. B*, **1971**, 1256—1261 (1971).
32) For example see: Kurz M. E., Yang L. T. A., Zahora E. P., Adams R. C., *J. Org. Chem.*, **38**, 2271—2281 (1973).
33) For example see: Narang S. C., Thompson M. J., *Aust. J. Chem.*, **28**, 385—389 (1975).
34) For example see: Sifniades S., *J. Org. Chem.*, **40**, 3562—3566 (1975).
35) For example see: Morzycki J. W., Lotowski Z., Stepniowska M., Gryszkiewicz A., Wilczewska A. Z., *Tetrahedron*, **53**, 16161—16168 (1997).
36) For example see: Olah G. A., Malhotra R., Narang S. C., "Nitration: Methods and Mechanisms," VCH Publishers Inc., New York, 1989, pp. 43—45.
37) Olah G. A., Malhotra R., Narang S. C., "Nitration: Methods and Mechanisms," VCH Publishers Inc., New York, 1989, pp. 32—36.
38) Crivello J. V., *J. Org. Chem.*, **46**, 3056—3060 (1981).
39) For example see: Kobayashi S., Hachiya I., Yamanoi Y., *Bull. Chem. Soc. Jpn.*, **67**, 2342—2344 (1994).
40) For example see: Hachiya I., Kobayashi S., *J. Org. Chem.*, **58**, 6958—6966 (1993).
41) For example see: Manabe K., Oyamada H., Sugita K., Kobayashi S., *J. Org. Chem.*, **64**, 8054—8057 (1999).
42) For example see: Kobayashi S., Ishitani H., Hachiya I., Araki M., *Tetrahedron*, **50**, 11623—11633 (1994).

43) For example see: Xie W., Jin Y., Wang P. G., *Chemtech*, **29**, 23—29 (1999).

44) For example see: Kobayashi S., *Eur. J. Org. Chem.*, **1999**, 15—27 (1999).

45) For example see: Kobayashi S., Manabe K., *Pure Appl. Chem.*, **72**, 1373—1380 (2000).

46) Kawada A., Mitamura S., Kobayashi S., *J. Chem. Soc.*, *Chem. Commun.*, **1993**, 1157—1158 (1993).

47) Kawada A., Mitamura S., Kobayashi S., *Synlett*, **1994**, 545—546 (1994).

48) Kawada A., Mitamura S., Kobayashi S., *J. Chem. Soc.*, *Chem. Commun.*, **1996**, 183—184 (1996).

49) Kawada A., Mitamura S., Matsuo J., Tsuchiya T., Kobayashi S., *Bull. Chem. Soc. Jpn.*, **73**, 2325—2333 (2000).

50) Kawada A., Yasuda K., Abe H., Harayama T., *Chem. Pharm. Bull.*, **50**, 380—383 (2002).

51) Olah G. A., Malhotra R., Narang S. C., "Nitration: Methods and Mechanisms," VCH Publishers Inc., New York, 1989, pp. 158—163.

52) Barbiere J., *Bull. Soc. Chim. Fr.*, **11**, 470—480 (1944).

53) Akashi T., Kawamura K., Shiratsuchi M., Ishihama H., *Chem. Pharm. Bull.*, **34**, 2024—2036 (1986).

54) Shiratsuchi M., Kawamura K., Akashi T., Fujii M., Ishihama H., Uchida Y., *Chem. Pharm. Bull.*, **35**, 632—641 (1987).

55) Benedini F., Bertolini G., Ferrario F., Guindani R., Sala A., *J. Heterocycl. Chem.*, **31**, 1589—1592 (1994).

56) Forsberg J. H., Spaziano V. T., Balasubramanian T. M., Liu G. K., Kinsley S. A., Duckworth C. A., Poteruca J. J., Brown P. S., Miller J. L., *J. Org. Chem.*, **52**, 1017—1021 (1987).

57) Thom K. F., U. S. Patent 3615169 (1971) [*Chem. Abstr.*, **76**, 5436a (1972)].

58) Bunnett J. F., Draper F., Ryason P. R., Noble P., Tonkyn R. G., Zahler R. E., *J. Am. Chem. Soc.*, **75**, 642—645 (1953).

59) Knovenagel E., *Liebig's Annalen der Chemie*, **402**, 111—148 (1913).

60) Davey W., Gwilt J. R., *J. Chem. Soc.*, **1955**, 1384—1385 (1955).

61) Carrara G., Ettorre R., Fava F., Rolland G., Testa E., Vecchi A., *J. Am. Chem. Soc.*, **76**, 4391—4395 (1954).

62) Somei M., Kawasaki T., Ohta T., *Heterocycles*, **27**, 2363—2365 (1988).

63) Perumal P. T., Venugopal M., Velusamy T. P., *Indian J. Chem.*, *Sect. B: Org. Chem. Incl. Med. Chem.*, **35B**, 242—243 (1996).

64) Tsuno Y., Fujio M., Seki Y., Mishima M., Kim S., *Nippon Kagaku Kaishi*, **1977**, 1673—1678 (1977).