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Chinese Chemical Letters 23 (2012) 73–76

CHINESE CHEMICAL LETTERS

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Rare earth metal triflates catalyzed electrophilic nitration using N_2O_5

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Received 13 July 2011
Available online 8 November 2011

Abstract

A mild, efficient and eco-friendly process for the electrophilic nitration is described using N_2O_5 as a green nitrating agent in the presence of rare earth metal triflates [RE(OTf)$_3$] under mild conditions.

Keywords: Nitration; Rare earth metal triflates; N_2O_5; Catalysis

Nitration of aromatic substrates is one of the widely studied organic reactions as nitro aromatic compounds are industrially important intermediates during the synthesis of dyes, plastics and pharmaceuticals [1]. Despite this, industry still largely relies upon the early technology involving a mixture of nitric acid and sulfuric acid. Mixed acid nitration systems, however, have many disadvantages like low selectivity, poly-nitration, oxidized products formation and generation of environmentally hazardous waste [2]. The obvious disadvantages of the commercial manufacturing process currently used has led to a substantial effort to develop viable alternatives, by using solid acid catalysts of, *e.g.* MoO_3/SiO_2 [3,4], SO_4^{2-}/SiO_2 [5], zeolite-based solid acid catalysts [6–11]; other sources of NO_2^+, such as nitronium salts in organic media [12], metal nitrates of zinc [13], N_2O_4 [14,15] and N_2O_5 [16–19]; organic nitrating agents of, *e.g.* acetyl nitrates [7,10] and alkyl nitrates [14], other acids replacing sulfuric acid [20], *etc.* However, these are associated with the problem of leaching of acid form the support during reaction and even calcination, require higher diluted conditions, long reaction time and high reaction temperature, and poor selectivity towards some aromatic compounds.

Rare earth metal triflates [RE(OTf)$_3$] are currently frequently used as potent environmentally benign Lewis acids, and it was found that rare earth metal triflates (1–10 mol%) can catalyze the nitration of a range of simple aromatic compounds using nitric acid, the only by-product is water and the catalyst can be readily recycled by simple evaporation [21]. Nevertheless, these nitrations require a long reaction time (12–18 h) at the reflux temperature.

In our efforts to develop a mild, efficient and eco-friendly process for electrophilic aromatic nitration, we attempted nitration of aromatic compounds using a highly active and green nitrating agent, dinitrogen pentoxide (N_2O_5), in the presence of RE(OTf)$_3$ under mild conditions. The results are presented in this letter.

In our initial study, nitration of toluene using N_2O_5 in the presence of a catalytic amounts of various RE(OTf)$_3$ (5–10 mol%) was examined (Scheme 1), the results are also compared with blank reaction (without catalyst), and the orientation of this nitration has been elucidated in Table 1. As can be seen from Table 1, the nitration of toluene indeed

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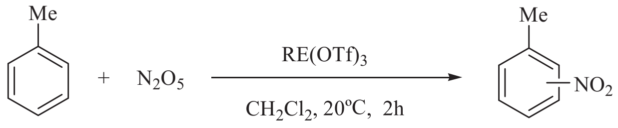
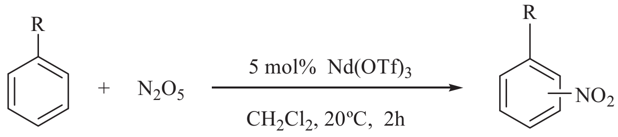
doi:10.1016/j.cclet.2011.09.021



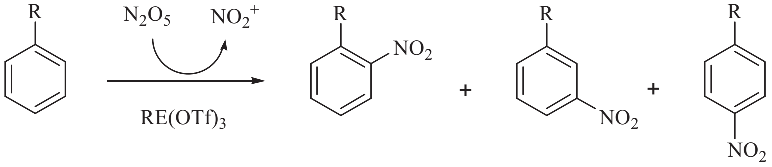
RE=Y, La, Pr, Nd, Sm, Eu, Gd,Tb, Dy, Ho, Er, Tm, Yb, Lu

Scheme 1. Nitration of toluene using N_2O_5 catalyzed by RE(OTf)$_3$.



R=H, F, Cl, Br, Et, ^{i}Pr, ^{t}Bu,

Scheme 2. Nitration of various aromatics using N_2O_5 catalyzed by Nd(OTf)$_3$.



Scheme 3. A possible mechanism for electrophilic nitration.

carried out under mild conditions (20 °C) for 1 h to give the mono-nitrotoluene in good yield and the catalyst loading is of a catalytic amounts (5–10 mol%). A variety of RE(OTf)$_3$ in general gave the similar orientation, and Nd(OTf)$_3$ (5 mol%) shows the highest activity for catalytic nitration (entry 5). Therefore, Nd(OTf)$_3$ was selected as a general Lewis acid catalyst for nitration.

Table 1
Nitration of toluene using N_2O_5 in the presence of rare earth metal triflates.[a]

Entry	Catalyst	Yield (%)[c]	Product isomers (%)[d]			o/p[d]
			Ortho	Meta	Para	
1	None	64	56.4	3.0	40.6	1.38
2	Y(OTf)$_3$	80	56.9	2.3	40.8	1.39
3	La(OTf)$_3$	93	55.4	2.6	42.0	1.32
4[b]	Pr(OTf)$_3$	95	55.8	2.7	41.5	1.34
5[b]	Nd(OTf)$_3$	100	57.6	2.1	40.3	1.42
6	Sm(OTf)$_3$	94	54.9	2.6	42.5	1.29
7[b]	Eu(OTf)$_3$	94	56.6	2.3	41.1	1.38
8	Gd(OTf)$_3$	96	55.4	2.7	41.9	1.32
9	Tb(OTf)$_3$	92	55.5	2.8	41.7	1.33
10	Dy(OTf)$_3$	91	55.2	2.8	42.0	1.31
11	Ho(OTf)$_3$	78	57.1	2.3	40.6	1.40
12	Er(OTf)$_3$	87	55.5	2.7	41.8	1.32
13	Tm(OTf)$_3$	87	56.2	2.6	41.2	1.36
14	Yb(OTf)$_3$	82	57.1	2.1	40.8	1.39
15	Lu(OTf)$_3$	89	55.8	2.7	41.5	1.34

[a] *Reaction conditions*: toluene (5.0 mmol), N_2O_5/CH_2Cl_2 (5.0 mmol/5.0 mL), RE(OTf)$_3$ (10 mol%), 1 h, 20 °C.

[b] The catalyst amount is 5 mol%.

[c] Yields are GC yields.

[d] Determined by original GC data.

Table 2
Nitration of various aromatics using N_2O_5 catalyzed by $Nd(OTf)_3$.[a]

Entry	R	Yield (%)[b]	Product isomers (%)[c]			*o*/*p*[c]
			Ortho	Meta	Para	
1	F	97	32.4	–	67.6	0.48
2	Cl	92	44.0	–	56.0	0.78
3	Br	84	45.2	–	54.8	0.82
4	H	100	–	–	–	–
5	Et	100	43.9	3.0	52.7	0.83
6	^{i}Pr	98	24.8	4.1	70.2	0.35
7	^{t}Bu	100	13.1	6.2	80.4	0.16

[a] *Reaction conditions*: substrate (5.0 mmol), N_2O_5/CH_2Cl_2 (5.0 mmol/5.0 mL), $Nd(OTf)_3$ (5 mol%), 1 h, 20 °C. All products are known and identified by comparison using GC with authentic samples.

[b] Yields are GC yields.

[c] Determined by GC data.

By means of the optimized reaction conditions, extended investigation on a variety of other aromatic compounds was studied (Scheme 2). The results were summarized in Table 2. High yields were obtained in most of the cases with 5 mol% catalyst loading under mild conditions. For the nitration of halogen benzene mono-nitro products were gained in moderate yield (Table 2, entries 1–3), and nitration of alkyl benzenes gave totally conversion and para-selectivity. Dinitration was not observed in all reactions.

A probable mechanism for electrophilic aromatic nitration (Scheme 3): Numerous papers have reported that high nitration conversion can be obtained with strong acidic catalyst, and $RE(OTf)_3$ is well-known as an efficient and strong Lewis acid catalyst, which can promote the formation of electrophilic nitronium ions (NO_2^+) from N_2O_5, then aromatics are rapidly nitrated with this strong electrophile. Thus, this reaction may be related to a normal electrophilic aromatic substitution mechanism involving the nitronium ion via N_2O_5 over Lewis catalyst.

In conclusion, we have developed a mild, efficient and eco-friendly process for the nitration of simple aromatic compounds. This method is conducted under mild conditions and is suitable for scale-up, and the combination of $RE(OTf)_3$ and N_2O_5 seems to be a new direction for environmental chemistry in nitration.

1. Experimental

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification; N_2O_5 was prepared with Ref. [17]. All products are known and identified by comparison using GC with authentic samples.

1.1. General procedure

To a cooled (0 °C) vigorously stirred mixture of the RE(OTf) (5 mol%) and toluene (5 mmol) was added a solution of N_2O_5 (5 mmol) and CH_2Cl_2 (5 mL). The reaction was carried out at 20 °C for 1 h, then the catalyst was filtered off and washed with some CH_2Cl_2, which was added to the filtrate. The CH_2Cl_2 solution was washed with a few portions of saturated $NaHCO_3$ solution, then several times with water, dried with $MgSO_4$, and examined by GC.

Acknowledgment

We are grateful for the financial support from the National Nature Science Foundation of China Academy of Engineering Physics (No. 10976014) and Nature Science Foundation of Jiangsu Province (No. BK2011697).

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