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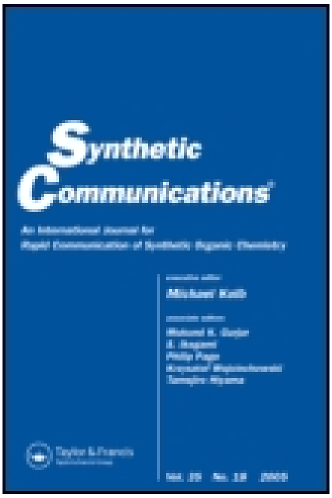

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Acid-Catalyzed Regioselective Nitration of o-Xylene to 4-Nitro-o-xylene with Nitrogen Dioxide: Brønsted Acid Versus Lewis Acid

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Accepted author version posted online: 04 Apr 2014.Published online: 09 Jun 2014.

To cite this article: Bo Tang, Songbo Wei & Xinhua Peng (2014) Acid-Catalyzed Regioselective Nitration of o-Xylene to 4-Nitro-o-xylene with Nitrogen Dioxide: Brønsted Acid Versus Lewis Acid, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 44:14, 2057-2065, DOI: 10.1080/00397911.2013.873468

To link to this article: http://dx.doi.org/10.1080/00397911.2013.873468

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Synthetic Communications®, 44: 2057–2065, 2014
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ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2013.873468

ACID-CATALYZED REGIOSELECTIVE NITRATION OF *O*-XYLENE TO 4-NITRO-*O*-XYLENE WITH NITROGEN DIOXIDE: BRØNSTED ACID VERSUS LEWIS ACID

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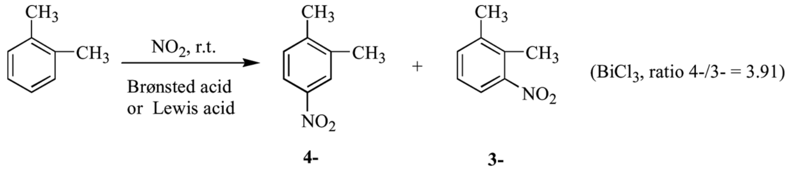
GRAPHICAL ABSTRACT



Brønsted acid: TsOH, CH_3SO_3H, H_2SO_4, CF_3COOH; Lewis acid: $AlCl_3$, $SbCl_3$, $BiCl_3$, $FeCl_3$

Abstract *Nitration of* o-*xylene with nitrogen dioxide imparts remarkable selectivity to 4-nitro-*o-*xylene. The addition of Brønsted acids and Lewis acids can effectively improve the selectivity for 4-nitro-*o-*xylene and/or yield, and the Lewis acids present a better influence on the reactions than Brønsted acids do. A 71% yield of mononitro-*o-*xylene with high selectivity for 4-nitro-*o-*xylene (ratio 4-/3- = 3.91) has been achieved by the assistance of bismuth trichloride under solvent-free conditions.*

Keywords Acid catalysis; nitration; nitrogen dioxide; 4-nitro-*o*-xylene; regioselective

INTRODUCTION

It is well known that 1,2-disubstituted benzenes often pose even more complicated problems in regioselective nitrations than monosubstituted benzenes do.[1] As in the mononitration of *o*-xylene, resulting from the interaction of *ortho-para* directing effects of the two adjacent methyl groups, the nitro group could be introduced into any one of the four nonsubstituted positions on the aromatic ring. Consequently, an equal amount of 4-nitro-*o*-xylene and 3-nitro-*o*-xylene should be formed theoretically during the mononitration of *o*-xylene, which makes it extremely difficult to realize regioselective nitration of *o*-xylene to the commercially more desirable 4-nitro-*o*-xylene isomer. When *o*-xylene was nitrated by the classic methodology based on nitric acid–sulfuric acid,[2,1c] a

Received September 14, 2013.

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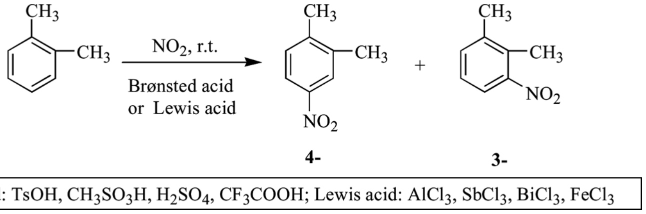
mixture of 4-nitro-*o*-xylene (39–42%) and 3-nitro-*o*-xylene (58–61%) were obtained with relatively poor selectivity for 4-nitro-*o*-xylene. Moreover, the mixed acid nitration cannot avoid the production of large amounts of waste acid and water.

Various of alkyl nitrates[3] assisted by acid catalysts have also been used to nitrate *o*-xylene with a isomer distribution of ratio 4-/3- (4-nitro-*o*-xylene/3-nitro-*o*-xylene) = 0.67–1.27, but the selectivity for 4-nitro-*o*-xylene is still not satisfactory. *o*-Xylene has also been nitrated by nitroxyl salts[4] with even worse selectivity (ratio 4-/3- = 0.25–0.61). Zolfigol has developed two novel nitration systems of nitrate salts ($NaNO_3$/silica sulfuric acid–SiO_2[5] and [Msim]NO_3[6]) that selectively nitrate *o*-xylene to 4-nitro-*o*-xylene with good yields of 85% and 89%, respectively. Unfortunately very large quantities of the silica sulfuric acid–SiO_2 were required and the preparation of [Msim]NO_3 needs highly corrosive chlorosulfonic acid and nitric acid (100%). Researchers have also focused on nitration of *o*-xylene with different concentrations of nitric acid (30–100%) in the presence of numerous solid acid catalysts (zeollite H-β,[7] zeollite-β,[8] UDCaT-8,[9] $MoO_3/TiO_2/SiO_2$,[10] $MoO_3/TiO_2/ZrO_2$,[11] $Al(H_2PO_4)_3$,[12] Zn^{2+} or Fe^{3+} modified montmorillonite,[13] and TiO_2-$[Ti_4H_{11}(PO_4)_9]\cdot 4H_2O$[14]), which still have more or less the same problems: requirement of high temperature, poor conversion of *o*-xylene, complicated preparative process of catalyst, and/or relatively low ratio of 4-/3-.

In recent years, nitrogen dioxide treated as a nonacidic nitration agent for the preparative aromatic nitration has received a great deal of attention,[15] generally accompanied by superior regioselectivity relative to traditional nitration methods. An extremely high selectivity for 4-nitro-*o*-xylene (ratio 4-/3- = 8.09) has been obtained by irradiating the dichloromethane solution of *o*-xylene and nitrogen dioxide with $\lambda_{exc} > 415$ nm at −78 °C; however, the conversion of *o*-xylene is pitifully low (2%) even after 6 h.[16] Nitration of *o*-xylene with NO_2/O_2 system in the presence of mercury(II) acetate and acetic acid can also give a relatively high selectivity for 4-nitro-*o*-xylene (ratio 4-/3- = 4.56).[17] The replacement of molecular oxygen with air reduced the ratio 4-/3- sharply to 3.17, indicating that in pursuit of greater selectivity for 4-nitro-*o*-xylene molecular oxygen is indispensable and brings inconvenience in the experimental operation. Apart from this, the extremely toxic mercury(II) acetate and acetic acid as solvent are environmentally unfriendly. Therefore, in an attempt to develop a method that would realize highly regioselective nitration of *o*-xylene to 4-nitro-*o*-xylene, the nitrogen dioxide was considered to be a preferable nitration agent. In addition, to avoid the mentioned drawbacks as much as possible, the exploration of effective, inexpensive, and low-toxicity catalysts is a major task. Eventually, the reactions of *o*-xylene and nitrogen dioxide in the absence and presence of Brønsted acids and Lewis acids were investigated. We now describe the entire results of nitration of *o*-xylene with nitrogen dioxide.

RESULTS AND DISCUSSION

To discover the intrinsic performance of nitration of *o*-xylene with nitrogen dioxide and the influence of circumstantial factors such as reagent/substrate ratio and temperature on the reactions, comparative experiments was initially carried out in the absence of Brønsted acids and Lewis acids compared with Scheme 1. The results are shown in Table 1.



Scheme 1. Acid-catalyzed nitration of *o*-xylene with nitrogen dioxide.

As can be seen from Table 1, nitrogen dioxide exhibited a remarkable selectivity for 4-nitro-*o*-xylene with a 4-/3- ratio readily greater than 2 in the nitration of *o*-xylene, and the circumstantial factors had a significant effect on the reactions. Both conversion and 4-/3- ratio increased with the ratio of nitrogen dioxide to *o*-xylene. However, when a large excess of nitrogen dioxide was used, there appears to be a decreased yield of both 4-nitro-*o*-xylene and 3-nitro-*o*-xylene despite the increased conversion (compare entries 4 and 5 in Table 1). This is presumably because the side reactions leading to the production of other nonring aromatic nitration substances (aldehydes, phenols, alcohols, nitric acid esters, alkyl nitro compounds)[18,15c] become more pronounced. Therefore, there is a balance that should be struck between the selectivity for 4-nitro-*o*-xylene and the yield to determine the appropriate amount of nitrogen dioxide used.

It was of interest to know the effects of various reaction temperatures on the reactions. Lowering the reaction temperature significantly retards the rate of reaction, and the conversion of *o*-xylene was diminished to only 53.3% even over a 24-h period (entry 7 in Table 1). Also, surprisingly at lower temperature the ratio of 4-/3- did not appear to be increased but reduced (compare entries 4 and 7 in Table 1), suggesting that there is no major advantages to be gained from carrying out the reactions at low temperature. Elevating the reaction temperature to 50 °C gave a slightly greater conversion but with a dramatic decrease of the ratio 4-/3- to 2.25 (compare entries 4 and 6 in Table 1).

Table 1. Nitration of *o*-xylene with NO_2 under several conditions[a]

Entry	Temperature (°C)	NO_2/*o*-xylene molar ratio	Conversion[b] (%)	Product yield (%)[c] 3-	4-	4-/3-
1	rt	1	63.2	2.9	6.2	2.11
2	rt	2	71.1	5.8	17.0	2.94
3	rt	3	76.3	6.6	21.0	3.16
4	rt	4	80.3	8.2	26.3	3.19
5	rt	5	85.4	6.4	22.3	3.48
6	50	4	86.6	10.5	23.5	2.25
7[d]	0	4	53.3	4.9	12.3	2.51

[a] All reactions were carried out with 5.0 mmol of *o*-xylene for 12 h, unless otherwise noted.
[b] Based on *o*-xylene and determined by calibrated quantitative GC analysis using an internal standard.
[c] Absolute yield (internal standard) based on *o*-xylene.
[d] Reaction time 24 h.

Therefore, it is clear from the results in Table 1 that it is preferable to nitrate *o*-xylene with nitrogen dioxide of 3–4 equivalent amounts at room temperature in view of regioselecive nitration of *o*-xylene to 4-nitro-*o*-xylene with good selectivity and yield.

On the basis of the optimum conditions mentioned previously, a range of different Brønsted acids was primarily tested for efficacy at catalyzing the reaction according to Scheme 1. The representative results are recorded in Table 2. The results given in Table 2 show that adding Brønsted acids to the reaction mixture generally causes the decrease of the 4-/3- ratio in different degrees except for trifluoroacetic acid (entries 1–5 in Table 2). Therefore, prior to other Brønsted acids trifluoroacetic acid was selected for further investigation to improve the conversion and yield. However, only a little benefit was obtained by varying the amount of trifluoroacetic acid and nitrogen dioxide, and more often with a slight decrease of 4-/3- ratio (entries 5–8 in Table 2). Even though a greater selectivity (ratio 4-/3- = 3.51) has been received when less trifluoroacetic acid was added (entry 6 in Table 2), the conversion and yield declined to the lowest amounts. It suggests that trifluoroacetic acid can offer a relatively good selectivity for 4-nitro-*o*-xylene but has limited improvement in the conversion and yield. In contrast, sulfuric acid exhibited a distinguishing effect. Even though a small amount of sulfuric acid was added, the ratio of 4-/3- decreased remarkably. With the increase of the added amount of sulfuric acid, the ratio of 4-/3- fell more significantly than with trifluoroacetic acid. Fortunately, sulfuric acid at least can provide good conversion and yield. The addition of equivalent sulfuric acid (relative to *o*-xylene) readily ensures the complete consumption of *o*-xylene with ca. 80% yield of mononitro-*o*-xylene (entry 12 in Table 2). Therefore, sulfuric acid allowed a rapid reaction with good yield of mononitro-*o*-xylene accompanied by the cost of remarkably dropped selectivity for 4-nitro-*o*-xylene. From a mechanistic perspective, the distinctive manifestation

Table 2. Nitration of *o*-xylene with NO_2 in the presence of Brønsted acids[a]

Entry	Additives (mol%)[b]		NO_2/*o*-xylene molar ratio	Conversion (%)	Product yield (%)		4-/3-
					3-	4-	
1	—		4	80.3	8.2	26.3	3.19
2	TsOH	50	4	71.4	5.8	15.6	2.70
3	CH_3SO_3H	50	4	96.2	10.0	26.9	2.69
4	H_2SO_4	50	4	88.7	12.9	34.6	2.68
5	CF_3COOH	50	4	81.7	10.1	34.7	3.43
6	CF_3COOH	10	4	79.8	9.3	32.6	3.51
7	CF_3COOH	100	4	84.3	11.8	33.8	2.86
8	CF_3COOH	100	3	83.9	12.4	34.7	2.78
9	H_2SO_4	10	4	87.6	10.0	30.0	3.00
10	H_2SO_4	100	4	99.7	26.2	51.2	1.95
11	H_2SO_4	100	3	99.8	27.9	50.2	1.80
12	H_2SO_4	100	2	100.0	32.2	48.6	1.51

[a] All reactions were carried out with 5.0 mmol of *o*-xylene at room temperature for 12 h, unless otherwise noted. The definitions of conversion and product yield are consistent with Table 1.

[b] Relative to *o*-xylene.

between trifluoroacetic acid and sulfuric acid is probably because the different interaction of Brønsted acids and nitrogen dioxide, which may result in the generation of different reactive intermediates (e.g., NO^+, NO_2^+, etc.) derived from the ionic dissociation of dinitrogen tetroxide. Induced by trifluoroacetic acid, nitrosonium (NO^+) is preferable to form and the more *para*-selective nitrosation would principally take place rather than nitration,[19] which is why the ratio of 4-/3- can still maintain a relatively high magnitude with the addition of trifluoroacetic acid to the mixture of *o*-xylene and nitrogen dioxide. With respect to sulfuric acid, nitronium (NO_2^+) is favored to be produced,[20] and therefore the conventional nitration with the characteristics of fast reaction rate and poor selectivity would occupy a dominant part, especially with the increase of the quantity of added sulfuric acid. This is consistent with the results given by sulfuric acid. The remaining *p*-toluene sulfonic acid and methanesulfonic acid gave a poor conversion of *o*-xylene and/or a poor yield of nitration product in addition to worse selectivity for 4-nitro-*o*-xylene, otherwise having no particular advantages for the selective nitration of *o*-xylene to 4-nitro-*o*-xylene. Therefore, it was not considered worthwhile to conduct a detailed study of two of them.

In an attempt to seek an even more effective catalyst, several Lewis acids were investigated for this purpose (Scheme 1). Table 3 records the results of reactions in the presence of Lewis acids. It is especially noteworthy that the addition of nitrogen dioxide to the mixture of *o*-xylene and Lewis acids assigned to aluminum trichloride or antimony trichloride instantly causes a lump of sticky solid, unable to be stirred. In the case of the two mentioned Lewis acids, dichloromethane has to be added beforehand as solvent (entries 2 and 3 in Table 3). Unexpectedly, both of them led to a sharp decrease of ratio 4-/3- and had no obviously beneficial effect on the conversion and yield (compare entries 1–4 in Table 3), suggesting that it was not considered worthwhile to conduct a detailed study of aluminum trichloride or antimony trichloride. Because the reactions involving bismuth trichloride and ferric trichloride were capable of being carried out under solvent-free conditions, it is

Table 3. Nitration of *o*-xylene with NO_2 in the presence of Lewis acids[a]

Entry	Additives (mol%)[b]		NO_2/*o*-xylene molar ratio	Time (h)	Conversion (%)	Products yield (%)		4-/3-
						3-	4-	
1	—		4	12	80.3	8.2	26.3	3.19
2[c]	$AlCl_3$	25	4	12	76.4	12.0	24.5	2.04
3[c]	$SbCl_3$	25	4	12	63.8	9.7	25.5	2.64
4[c]	$BiCl_3$	25	4	12	78.1	9.5	34.0	3.58
5	$BiCl_3$	25	4	12	83.3	10.4	38.6	3.73
6	$FeCl_3$	25	4	12	81.3	10.5	35.61	3.40
7	$BiCl_3$	25	4	24	92.6	11.5	43.1	3.75
8	$BiCl_3$	25	3	24	95.2	13.5	51.3	3.81
9	$BiCl_3$	50	3	24	100.0	14.5	56.8	3.91

[a] All reactions were carried out with 5.0 mmol of *o*-xylene at room temperature, unless otherwise noted. The definitions of conversion and product yield is consistent with Table 1.

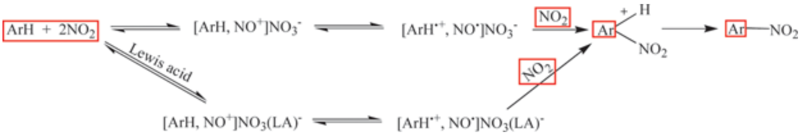
[b] Relative to *o*-xylene.

[c] Dichloromethane (3 mL) was added as solvent.

necessary to ascertain the effect of added dichloromethane. Therefore, the control experiments in the presence and absence of dichloromethane (entries 4 and 5 in Table 3) were carried out in which bismuth trichloride was chosen as a representative Lewis acid, under otherwise identical conditions. It is apparent that at least in terms of bismuth trichloride the existence of solvent is really disadvantageous to the reactions in all aspects, presumably because the dilution of reaction mixture with dichloromethane is not beneficial to the selectivity for 4-nitro-*o*-xylene and conversion of *o*-xylene.[21] Accordingly, to obtain better results from the reactions involving bismuth trichloride and ferric trichloride, optimization procedures were uniformly performed under solvent-free conditions. It appears that the former presented a little more beneficial effect on the reactions than the latter did (compare entries 5 and 6 in Table 3). Consequently, bismuth trichloride was ultimately selected for further investigation, uniformly under solvent-free conditions. In consideration of the incomplete transformation of *o*-xylene, initially the reaction time was prolonged. As expected, the conversion of *o*-xylene increased successfully but just to a certain level (entry 7 in Table 3). Thus it was next of interest to vary the amount of bismuth trichloride and nitrogen dioxide. Fortunately, *o*-xylene was eventually consumed completely (entry 9 in Table 3). The greater selectivity for 4-nitro-*o*-xylene (ratio 4-/3- = 3.91) and a good yield of mononitro-*o*-xylene (71%) were particularly striking.

Explanation of the excellent effect obtained by the addition of Lewis acids, especially bismuth trichloride ($BiCl_3$), should show a deep level of mechanistic insight. The proposed reaction pathway of nitration of *o*-xylene with nitrogen dioxide in the absence and presence of Lewis acid is shown in Scheme 2.[16] In the absence of Lewis acid, the ionic disproportionation of dinitrogen tetroxide induced by the reactive aromatic donor *o*-xylene results in the formation of electron donor–acceptor (EDA) complexes ($[ArH, NO^+]NO_3^-$), followed by charge-transfer (CT) to produce radical pair ($[ArH^{\cdot+}, NO]NO_3^-$) and homolytic coupling of generated cation radical ($ArH^{\cdot+}$) and NO_2 to σ-complexes, which ultimately collapse into nitration products by deprotonation. Therefore the existence of added Lewis acid would stabilize the EDA complexes via coordination to the anionic nitrate moiety, providing additional driving force to shift the disproportionation equilibrium to the right, and simultaneously the nucleophilic attack of nitrate anion (NO_3^-) to cation radical ($ArH^{\cdot+}$) is greatly suppressed. The generation of aromatic nitration products would be eventually promoted by adding Lewis acids. The extraordinarily good selectivity for 4-nitro-*o*-xylene exhibited in the case of bismuth trichloride is possibly due to a larger atomic radius of bismuth ions.

In summary, the addition of Brønsted acids and Lewis acids can effectively improve the selectivity and/or yield in the regioselective nitration of *o*-xylene to 4-nitro-*o*-xylene with nitrogen dioxide. The latter exhibits a superior effect on the



Scheme 2. Proposed reaction pathway of nitration of *o*-xylene with nitrogen dioxide.

reactions. Among the entire range of acid catalysts, bismuth trichloride presents an outstanding degree of selectivity for 4-nitro-*o*-xylene (ratio 4-/3- = 3.91) with the added practical advantages of capably avoiding the need for solvent. The combination of bismuth trichloride with nitrogen dioxide provides a synthetically useful method for the selective synthesis of 4-nitro-*o*-xylene from *o*-xylene.

EXPERIMENTAL

All reagents and solvents used were obtained from commercial sources without any purification unless otherwise noted. Nitrogen dioxide (from Nanjing Shangyuan Industrial Gas Factory, China) was released from compressed steel cylinder and then passed through a preprepared cooling device equipped with condenser (cooling liquid provided by cryostat), cooled to liquid nitrogen dioxide, and stored in the refrigerator while further freezing to solid (stand-by service).

For the determination of the conversion of substrates and composition of the products, gas chromatographic (GC) analysis was performed on an Agilent 6820 gas chromatograph equipped with a flame ionization detector using a 30-m × 0.32-mm capillary column (Agilent Technologies, SE-54). All products were known and identified by direct comparison with the authentic samples. The products 3- and 4-nitro-*o*-xylenes were isolated by distillation and confirmed by ^{1}H NMR, recorded in $CDCl_3$ on Bruker UX-300 spectrometers using tetramethylsilane (TMS) as an internal reference. The characterized results are consistent with those reported by Shi and Cui,[22] which confirms the formation of 3- and 4-nitro-*o*-xylenes.

3-Nitro-*o*-xylene

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.40 (s, 6H, CH_3), 7.20 (t, 1H, $J = 7.8$ Hz, Ar), 7.38 (d, 1H, $J = 7.3$ Hz, Ar), 7.61 (d, $J = 8.0$ Hz, 1H, Ar).

4-Nitro-*o*-xylene

^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.37 (s, 6H, CH_3), 7.26 (d, 1H, $J = 8.0$ Hz, Ar), 7.95–8.0 (m, 2H, Ar).

General Procedure for the Nitration of *o*-Xylene with NO_2

o-Xylene (0.53 g, 5.0 mmol) was added to a 50-mL single-necked flask. Next the solid nitrogen dioxide stored in the refrigerator was warmed until the appearance of a few drops of liquid, and liquid nitrogen dioxide (0.69 g, 15.0 mmol) was added rapidly. Simultaneously the flask was equipped with condenser (cooling liquid provided by cryostat). The reaction mixture was then stirred at room temperature. After 12 h, the reaction was quenched by the addition of aqueous sodium hydrogen carbonate (5.00 g, 20%). After that *m*-nitro-toluene (internal standard) and dichloromethane (5 mL) were added. The organic phase was separated, and the aqueous phase was extracted twice with dichloromethane (2 × 5 mL). Combined organic layers were washed with water, dried over anhydrous sodium sulfate, filtered off, and evaporated. The samples finally were analyzed by GC.

General Procedure for the Nitration of *o*-Xylene with NO_2 in the Presence of Brønsted Acids

o-Xylene (0.53 g, 5.0 mmol) and sulfuric acid (0.49 g, 4.9 mmol) were added to a 50-mL single-necked flask. Next liquid nitrogen dioxide (0.47 g, 10.2 mmol) was rapidly added into the mixture of *o*-xylene and sulfuric acid. The reaction mixture was then stirred at room temperature for 12 h. The workup was performed by the procedure described previously. Under similar conditions, the nitration of *o*-xylene in the presence of other Brønsted acids was also performed.

General Procedure for the Nitration of *o*-Xylene with NO_2 in the Presence of Lewis Acids

A solution of *o*-xylene (0.52 g, 4.9 mmol) in dichloromethane (3 mL) and antimony trichloride (0.27 g, 1.2 mmol) was added to a 50-mL single-necked flask. Next liquid nitrogen dioxide (0.92 g, 20.0 mmol) was rapidly added into the mixture of *o*-xylene and antimony trichloride, The reaction mixture was then stirred at room temperature. After 12 h, the reaction was quenched by the addition of aqueous sodium hydrogen carbonate (5.00 g, 20%). A large amount of precipitate was produced, which was treated with suction to remove the solid. The solid was washed three times with dichloromethane (3 × 2 mL). After that *m*-nitro-toluene (internal standard) was added to the filtrate. The organic phase was separated and the aqueous phase was extracted twice again with dichloromethane (2 × 5 mL). The combined organic layers were washed with water, dried over anhydrous sodium sulfate, filtered off, and evaporated. The samples finally were analyzed by GC. Under similar conditions, the nitration of *o*-xylene in the presence of other Lewis acids was also performed.

Procedure for the Solvent-Free Nitration of *o*-Xylene with NO_2 in the Presence of $BiCl_3$

o-Xylene (0.53 g, 5.0 mmol) and bismuth trichloride (0.76 g, 2.4 mmol) were added to a 50-mL single-necked flask. Next liquid nitrogen dioxide (0.67 g, 14.5 mmol) was rapidly added into the mixture of *o*-xylene and bismuth trichloride. The reaction mixture was then stirred at room temperature for 24 h. The workup was performed by the procedure of Lewis acids described previously.

SUPPORTING INFORMATION

^{1}H NMR spectrum and GC, as well as analysis parameters (conditions, retention times), can be accessed on the publisher's website.

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