



Zeolite-Assisted Regioselective Nitration of Toluene in Acetonitrile with Nitric Acid/Acetic Anhydride

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p-Nitrotoluene widely used pharmaceutical and dyestuff intermediates was selectively prepared with nitric acid under the promotion of acetic anhydride in the presence of zeolite catalysts. The ratio of *o*-nitrotoluene isomer to *p*-nitrotoluene could reach 0.553 in a moderate total yield of 62.8 % when the reaction was carried out in acetonitrile with 1.89 mmol toluene, 5.67 mmol nitric acid, 5.67 mmol acetic anhydride and 0.13 g HBEA-280 at reflux temperature. The zeolite catalyst has a strong influence on the reaction and could be easily regenerated.

Keywords: Toluene, Nitrotoluene, Nitric acid, Acetic anhydride, Zeolite.

INTRODUCTION

Aromatic nitro compounds are important starting materials for the manufacture of various industrial products such as pharmaceuticals, dyes and plastics¹⁻⁶. Industrially nitration is mainly carried out by a mixed-acid process. In this process a mixture of conc. nitric acid and sulfuric acid is used for nitration of toluene⁷. However, this traditional process suffers serious disadvantages, including low selectivity for the desired product and the requirement for large quantities of mineral or Lewis acids as activators. Such conditions lead to excessive acid waste which is environmentally unfriendly and expensive to treat. These disadvantages have encouraged extensive efforts to develop alternative methodologies to replace conventional nitration process. A lot of efforts have been directed to search for reusable and environmentally friendly catalysts⁸⁻¹⁰ and many progresses have been achieved¹¹⁻¹³.

Recently many reagents and catalysts such as acetyl nitrate, trimethylsilyl nitrate, benzoyl nitrate¹⁴, nitrogen oxide¹⁵, sulfuric acid supported on silica¹⁶, clay-supported metal nitrates¹⁷⁻¹⁹ have been introduced for the nitration of aromatic compounds. Three isomers of nitrotoluene can be formed in the toluene mononitration process. *p*-Nitrotoluene isomer is highly desirable over the *ortho*- and *meta*- isomers because of its high commercial value. In the present paper, we wish to report the nitration of toluene with nitric acid and acetic anhydride in organic solvent over zeolite catalyst, where the regio-selection of nitration can be improved and in certain cases the isomer ratio of nitration products can be reversed.

EXPERIMENTAL

¹H NMR spectra were determined in CDCl₃ on a Bruker 400 MHz spectrometer. GC 2041-C (WONDACAP-1 df = 1.5 μm 0.53 mm I.D. × 30 m) was utilized to determine product isomer composition. IR measurements were made on a Hitachi IR meter 260-10 for KBr pellets and only characteristic peaks were recorded. Melting points were determined on a WRS-2 apparatus and uncorrected.

General procedure

Typical experimental procedure for the zeolite cation-exchange: The standard procedure for cation-exchange involved stirring a supplied commercial zeolite (5 g) in a refluxing aqueous solution of the corresponding metal chloride (2 mol/L, 100 mL) for 24 h. The solid was filtrated, washed with deionized water until halide-free and dried at 110 °C for 3 h and then calcined in air at 550 °C for 6 h.

General procedure for the nitration with nitric acid and acetic anhydride: Quantities are recorded in the footnotes to the appropriate tables. All reactions were carried out in a 100 mL three-necked round bottomed flask equipped with a water condenser and a magnetic stirrer. In a typical experiment, a mixture of zeolite Hβ-25 (Si/Al = 25, 0.03 g), toluene (0.2 mL, 1.89 mmol), acetic anhydride (0.53 mL, 5.6 mmol), nitric acid (95 %, 0.23 mL, 5.6 mmol) in acetonitrile (5 mL) was heated under reflux for 12 h. When the reaction was over, the zeolite was removed by filtration and the filter liquor was washed with NaHCO₃ (10 mL × 3) and water (10 mL × 3).

The organic layer was separated, nitrobenzene (0.0580 g) was added as a GC standard. The mixture was analyzed by gas chromatography and the yields of mononitration product was calculated. The zeolite was recovered by washing and calcination.

RESULTS AND DISCUSSION

Toluene can form three isomers of nitrotoluene in the mononitration process (**Scheme-I**). *o*-Nitrotoluene **2** and *p*-nitrotoluene **4** are useful intermediates in the manufacture of pigments, pesticides and dyestuffs. The latter compound is greater market demand than the former. We attempted to vary the solvents in order to increase the ratio of **4**.

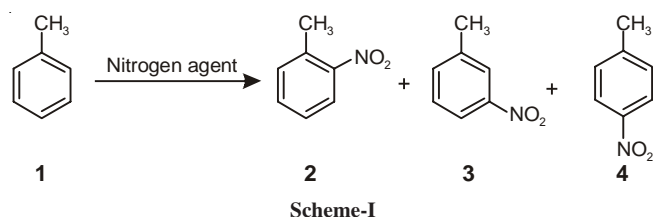


Table-1 shows the effect of various solvent on the nitration reaction of toluene. The solvents influence is an important parameter for the determination of yield of the product. The yield of various solvents are in the following order: acetonitrile > dichloromethane > hexane. Among the four different polarity solvent used, acetonitrile with a high dielectric constant exhibited the best yield, while *n*-hexane gave highest selectivity of *p*-nitrotoluene for its low polarity.

To further improve the selectivity of *p*-nitrotoluene, zeolite was used as catalyst for it was very attractive to make the positive contributions to the positional selectivity in the novel nitration process. Zeolite BEA was used as catalyst because preliminary screening suggested that it was quite active. And ZSM-5, a medium-pore zeolite, was included for comparison. Additionally, cation-exchanged zeolites were undertaken in order to find a best catalyst to improve *p*-selectivity. The result was shown in Table-2.

ZSM-5 gave lower *para* selectivity which probably reflect more restricted diffusion through the pores, allowing greater opportunity for competition from reaction at the external surface of the solid. With the Si/Al ratio increasing of HBEA, a high ratio of formation of *p*-nitrotoluene was favored. It may be due to the dealumination would modify the distribution of the size and shape of pores in the zeolite. Interestingly, the yield and selectivity were both significantly lower when the cation associated with zeolite. The highest yield was reached when LaZSM-5 was used. It may be that rare earth cation-exchanged zeolite would display both Lewis and Brønsted types of acidity due to high charge density which generated acidic hydroxyl groups inside the zeolite cavities.

The temperature effect on the nitration of toluene in the solvent of choice (acetonitrile) was also carefully investigated. The results are shown in Table-3.

The effect of the amount of zeolite for the nitration reaction was then investigated at the optimal temperature discovered above. The results are shown in Table-4. Increasing the amount of catalyst favored the reaction further toward the 2:4 ratio up to 0.553, while the yield was decreased. More products may be adsorbed in the catalyst.

TABLE-1
NITRATION OF TOLUENE BY NITRIC ACID IN VARIOUS SOLVENTS^a

Entry	Reaction condition	Solvent	Conversion (%) ^b	Yield (%) ^c	Temperature (°C)	Isomer proportion (%) ^d			2:4 Ratio
						2	3	4	
1	HNO ₃ (65 %)	-	18.3	8.81	RT	58.7	6.40	34.9	1.68
2	HNO ₃ (95 %)	-	77.2	67.4	RT	55.6	3.70	40.7	1.37
3	HNO ₃ (95 %)	Acetonitrile	77.0	73.1	Reflux	60.8	4.80	34.4	1.77
4	HNO ₃ (95 %)	Dichloromethane	57.6	90.5	Reflux	57.4	2.60	40.0	1.44
5	HNO ₃ (95 %)	Hexane	82.5	46.8	Reflux	53.6	4.10	42.3	1.27
6	HNO ₃ (95%)	Acetic anhydride	79.8	63.8	90°	58.0	3.80	38.2	1.52

^aReaction condition: n(nitric acid) : n(toluene) = 1 : 1, n(nitric acid) : n(acetic anhydride) = 1 : 1, solvent (5 mL), reflux temperature. ^bDetermined by GC, Nitrobenzene was used as an internal standard, ^cCombined yield of **2**, **3** and **4** based on consumed **1**. Nitrobenzene was used as an internal standard, ^dProportion of products was determined by GC. ^eAcetic anhydride was used as solvent

TABLE 2
EFFECT OF ZEOLITE TYPE ON THE NITRATION OF TOLUENE WITH FUME-NITRIC ACID^a

Entry	Catalyst ^b	Reaction condition	Yield (%) ^c	Isomer proportion (%) ^d			2:4 ratio
				2	3	4	
1	HZSM-5	HNO ₃	72.2	62.0	4.30	33.7	1.84
2	HBEA-25	HNO ₃	79.2	47.3	4.80	47.9	0.987
3	HBEA-280	HNO ₃	54.5	37.8	5.40	56.8	0.665
4	CuBEA-25	HNO ₃	68.8	41.5	4.40	54.1	0.767
5	FeBEA-25	HNO ₃	78.0	58.9	4.50	36.6	1.61
6	FeZSM-5	HNO ₃	67.2	62.6	4.10	33.3	1.88
7	CoZSM-5	HNO ₃	48.1	61.7	4.30	34.0	1.81
8	LaZSM-5	HNO ₃	94.4	62.2	4.30	33.5	1.86

^aAll reactions were carried out in acetonitrile (5 mL) with substrate **1** (0.2 mL, 1.89 mmol), nitric acid (0.23 mL, 5.67 mmol), acetic anhydride (0.53 mL, 5.67 mmol) and zeolite catalyst (0.03 g). Acetonitrile was dried over 4 Å molecular sieves before using. ^bZeolites were calcined at 550 °C for 2 h in air prior to use. ^cCombined yield of **2**, **3** and **4** based on consumed **1**. Nitrobenzene was used as an internal standard. ^dProportion of products was determined by GC

TABLE-3
EFFECT OF REACTION TEMPERATURE^a

Entry	Temperature (°C)	Yield (%) ^b	Isomer proportion (%) ^c			2:4 ratio
			2	3	4	
1	0	57.3	57.8	4.30	37.9	1.53
2	20	73.7	52.0	5.10	42.9	1.21
3	40	65.5	45.4	5.30	49.3	0.921
4	60	58.4	41.5	8.10	50.4	0.823
5	80	54.5	37.8	5.40	56.8	0.665

^aAll reactions were carried out in acetonitrile (5 mL) with substrate **1** (0.2 mL, 1.89 mmol), nitric acid (0.23 mL, 5.67 mmol), acetic anhydride (0.53 mL, 5.67 mmol) and HBEA-280 zeolite (0.03 g). Acetonitrile was dried over 4 Å molecular sieves before using. ^bCombined yield of **2**, **3** and **4** based on consumed **1**. Nitrobenzene was used as an internal standard. ^cProportion of products was determined by GC

TABLE-4
EFFECT OF AMOUNT OF HBEA-25^a

Entry	Amount of catalyst	Yield (%) ^b	Isomer proportion (%) ^c			2:4 ratio
			2	3	4	
1	0.03 g	54.5	37.8	5.40	56.8	0.665
2	0.06 g	74.3	43.9	5.30	50.8	0.864
3	0.10 g	67.5	36.2	5.30	58.5	0.619
4	0.13 g	62.8	33.4	6.20	60.4	0.553

^aAll reactions were carried out in acetonitrile (5 mL) using substrate **1** (0.2 mL, 1.89 mmol), nitric acid (0.23 mL, 5.67 mmol) acetic anhydride (0.53 mL, 5.67 mmol) and HBEA-280 zeolite. Acetonitrile was dried over 4 Å molecular sieves before using. ^bCombined yield of **2**, **3** and **4** based on consumed **1**. Nitrobenzene was used as an internal standard. ^cProportion of products was determined by GC

Conclusion

To conclude, we have developed an efficient procedure for the nitration of toluene with nitric acid and acetic anhydride in HBEA-280 zeolite catalyst. Moreover, the solid catalysts could be recovered and reused with the avoidance of toxic waste generated.

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