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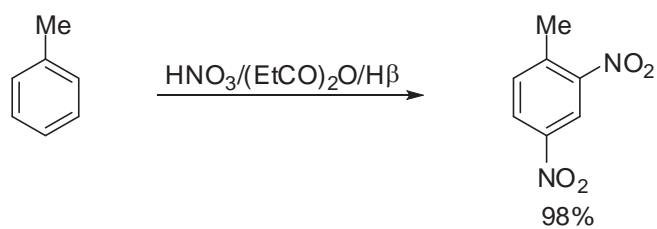
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## Highly regioselective dinitration of toluene over reusable zeolite H $\beta$

Keith Smith, Mohammad Hayal Alotaibi, Gamal A. El-Hiti

### Graphical abstract



### Highlights

Nitration of toluene gave 2,4-DNT in 98%.

Highly selective process.

Zeolite reused.

# Highly regioselective dinitration of toluene over reusable zeolite H $\beta$

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## ABSTRACT

A nitration system comprising nitric acid, propanoic anhydride and zeolite H $\beta$  has been developed for dinitration of toluene to give 2,4-dinitrotoluene in 98% yield, with a 2,4-:2,6-dinitotouene ratio of over 120. This represents the most selective quantitative method for 2,4-dinitration of toluene; the catalyst is re-usable, solvent is not needed and an aqueous work-up is not required.

*Key word:* Nitration, Acidic zeolite catalysis, Propanoyl nitrate, Mono-substituted benzenes, Zeolite H $\beta$ , Regioselectivity

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## 1. Introduction

The synthesis of valuable chemicals frequently involves electrophilic aromatic substitution reactions. However, the commercial syntheses of these compounds commonly suffer serious disadvantages, including: a requirement for large quantities of mineral or Lewis acids as activators, which on work-up may generate large quantities of corrosive and toxic waste by-products; the use of stoichiometric quantities of toxic reagents; poor yields; or production of mixtures of regioisomers with low selectivity [1–4].

Major efforts are therefore being made to develop clean and environmentally benign processes, particularly for the regioselective production of *para*-substituted products. It is well recognized that zeolite catalysts can play an important role through their abilities to act as recyclable heterogeneous catalysts that can enhance product selectivities [5–11]. We have investigated the use of zeolites in electrophilic substitution of aromatic compounds [12–14] and have shown that they can be used successfully in

cleaner *para*-regioselective reactions including nitration [15–22], alkylation [23], acylation [24,25], halogenation [26,27] and methanesulfonylation [28] reactions.

2,4-Dinitrotoluene (2,4-DNT) is a crucial intermediate for the production of many industrially important chemicals, including polyurethanes, explosives, dyes, pharmaceuticals, agrochemicals and fragrances [29,30]. Unfortunately, dinitration of toluene with mixed acids produces 2,4- and 2,6-dinitrotoluenes in a ratio of only 4:1. There have been several attempts to improve the process by use of solid catalysts [31–36]. For example, the 2,4-:2,6-dinitrotoluene ratio can be improved to 9:1 (in 85% yield) when nitration is carried out over claycop, using nitric acid and acetic anhydride [29,30], but the method requires a large excess of nitric acid and the use of carbon tetrachloride as a solvent. A better ratio (14:1) was reported using nitric acid over a zeolite  $\beta$  catalyst [37].

We have previously investigated the dinitration of toluene with nitric acid and trifluoroacetic anhydride (TFAA) over zeolite H $\beta$ , which gave a 92% yield of 2,4-DNT with a 2,4-:2,6-dinitrotoluene (2,6-DNT) ratio of 25 [21]. Even greater selectivity (70:1; in 96% yield) was obtained when the reaction was conducted in two stages, with trifluoroacetic anhydride added only in the second stage [21]. However, trifluoroacetic anhydride's volatility, toxicity and cost may render it unattractive for commercial processes. We have therefore sought to find a more attractive alternative [38].

## **2. Experimental**

### *2.1 Materials*

Commercial H $\beta$  zeolite was purchased from Zeolyst International and was freshly calcined at 450 °C for a minimum of 6 h prior to use. Toluene was purchased from Fisher Scientific and nitric acid (100%) was purchased from BDH Laboratory Supplies. Other

chemicals were purchased from Aldrich Chemical Company and used without further purification except for toluene and propanoic anhydride, which were distilled.

## *2.2 Analysis and characterisation of the products*

All GC analyses were carried out on a PU 4400 Gas Chromatograph (Philips) using a capillary ZB Carbowax column (30 m, 0.32 mm ID). The GC conditions used for analysis were: 35 °C for 0.5 min, ramped to 240 °C at 20 °C/min and held for 15 min. The injection temperature was 300 °C and the detection temperature 300 °C. Hexadecane was added as an internal standard to allow quantification. All of the expected products from nitration of toluene were purchased from Aldrich Chemical Company and used to determine retention times and response factors relative to hexadecane (average from four injections) for each product.

<sup>1</sup>H NMR Spectroscopy was the method of analysis for substrates other than toluene; the calculated mass balances were consistent with the total weights of products obtained.

## *2.3. Typical experimental procedure for the double nitration of toluene using nitric acid, propanoic anhydride and zeolite H $\beta$ catalyst*

Propanoic anhydride (16.90 g, 130 mmol) was added to a stirring mixture of nitric acid (7.65 g, 100%, 120 mmol) and H $\beta$  (2.0 g, SiO<sub>2</sub>: Al<sub>2</sub>O<sub>3</sub> = 25) at 0 °C and the mixture was stirred for 5 min at constant temperature. Toluene (3.22 g, 35 mmol) was then added dropwise and the mixture was allowed to warm to room temperature. The flask was equipped with a water condenser fitted with a calcium chloride guard tube and was stirred at 50 °C for 4 h. The reaction mixture was cooled to room temperature and analytical grade acetone (30 mL) was then added and the mixture was stirred for 5 min. The zeolite was removed by suction

filtration and washed with copious amounts of acetone. The mother liquors were combined, hexadecane (1.00 g) was added and the mixture was subjected to GC analysis.

#### 2.4 Purification of 2,4-dinitrotoluene (2,4-DNT)

The isolation procedure is for a reaction that did not have hexadecane added. At the end of the reaction, the mixture was allowed to cool to room temperature and the catalyst was removed by filtration and washed with analytical grade acetone ( $3 \times 10$  mL). Water (30 mL) and DCM (30 mL) were added to the combined filtrate and washings and the layers were separated. The aqueous layer was extracted with DCM (20 mL) and the organic layers were combined. The organic extract was washed with aq. saturated  $\text{NaHCO}_3$  solution (30 mL) followed by water (30 mL), dried ( $\text{MgSO}_4$ ) and evaporated to constant weight under reduced pressure to give the crude product (6.34 g). The crude product was recrystallized from analytical grade acetone to give pure 2,4-dinitrotoluene (5.99 g, 94%; >99% purity by GC).

### 3. Results and Discussion

Zeolite  $\beta$  shows high *para*-selectivity in mono-nitration of toluene with acetyl nitrate [22]. The high *para*-selectivity has been attributed to steric hindrance of the surface-bound acetyl nitrate complex [39,40]. Therefore, we first attempted direct dinitration of toluene over zeolite H $\beta$  ( $\text{SiO}_2:\text{Al}_2\text{O}_3 = 25$ ) with  $\text{HNO}_3$  and acetic anhydride, which generates acetyl nitrate *in situ*. However, although we varied the stoichiometry, amount of zeolite, reaction temperature and reaction time, the maximum yield of 2,4-DNT obtained was 89%, though with only trace amounts of 2,6-DNT, along with 9% of 4-nitrotoluene (4-NT) and ca. 2% of 3-nitrotoluene (3-NT). Although the reaction was highly selective we were unable to cause the reaction to go to completion. It was thought that nitration of toluene using propanoyl

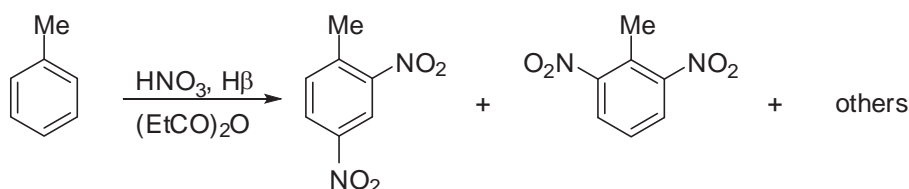


nitrate as nitrating reagent instead of acetyl nitrate could enhance the production of 2,4-DNT as a result of both additional steric hindrance of the surface-bound reagent, which could lead to even greater selectivity, and its lower volatility, which might reduce losses of reagent during the reaction period. Therefore, we decided to try the use of propanoic anhydride and nitric acid, which should generate the propanoyl nitrate *in situ* (Scheme 1). We now report success with this system.



**Scheme 1.** Generation of propanoyl nitrate.

Initially we attempted a single step double nitration of toluene (Scheme 2) using toluene (35 mmol), propanoic anhydride (70 mmol) and nitric acid (100%, 70 mmol) in the presence of zeolite H $\beta$  (2.0 g), but even for a reaction carried out at 50 °C for 4 h the yield of dinitrotoluenes (DNTs) was only 57%, with a 61:1 ratio of 2,4-:2,6-isomers. However, when the amounts of nitric acid and propanoic anhydride were increased to 120 mmol each under identical conditions the reaction gave 94% of DNTs, with a 85:1 ratio of 2,4-:2,6-isomers, along with around 5% of 4-NT and 1% of 3-NT.



**Scheme 2.** Nitration of toluene over a  $\text{HNO}_3/(\text{EtCO})_2\text{O}/\text{H}\beta$  system.

To try to improve the yield and selectivity even further we investigated the effect of an even larger excess of propanoic anhydride. Just increasing the amount of anhydride to 130 mmol caused the reaction to go to completion, producing dinitrotoluenes in almost

quantitative yield (98% 2,4-dinitrotoluene and 0.8% 2,6-dinitrotoluene) with a 2,4-:2,6-ratio of over 120:1. Pure 2,4-DNT was isolated in 94% yield by simply filtering, washing the zeolite with solvent, concentrating the mother liquor, and recrystallization from diethyl ether. (For large scale work solvent extraction of the zeolite would probably be unnecessary, since residual product could be removed from the zeolite under reduced pressure, but to ensure that all products were accounted for, in this work the zeolite was fully extracted).

In order to check whether the period of 4 hours used in reactions thus far was required, various reaction times were attempted (Table 1). As can be seen from Table 1 the yield of 2,4-dinitrotoluene increased with increasing reaction time. The yield of dinitrotoluenes was 82% even after 5 min; at that point the 2,4-:2,6-DNT ratio was around 74 and already there was virtually no residual 2-nitrotoluene, suggesting that it reacted rapidly to give dinitrotoluenes. The 4-nitrotoluene evidently reacted more slowly, so that the yield of DNTs and the selectivity for 2,4-DNT both rose over time after the first few minutes. It is not clear whether the apparent small reduction in the amount of 2,6-DNT over time was real, as a result of its further reaction (perhaps to produce 2,4,6-trinitrotoluene, which would not have been detected by the GC system used) or whether the results reflect experimental error in the measurement, with all yields of 2,6-DNT being essentially the same at  $0.9 \pm 0.2\%$ . Similarly, it is not clear whether the small reduction in quantity of 3-nitrotoluene over time is real, caused by its conversion into one or more trace dinitrotoluenes, or reflects experimental variation in measurement. However, it is clear that for the reaction to be complete a 4 hours reaction period was necessary.

**Table 1**

Effect of reaction time in dinitration of toluene with  $\text{HNO}_3/(\text{EtCO})_2\text{O}/\text{H}\beta$  system according to Scheme 2.<sup>a</sup>

Time (min)	Yields of products <sup>b</sup>				2,4-:2,6-ratio <sup>c</sup>	Mass balance (%) <sup>d</sup>
	3-NT	4-NT	2,4-DNT	2,6-DNT		
5	1.1	15	81	1.1	74	98.2
15	1.0	13	82	1.0	82	97.0
30	1.1	11	84	1.1	76	97.2
60	0.9	8.0	91	0.7	130	100.6
120	0.8	4.8	93	0.9	103	99.5
240	0.4	0.8	98	0.8	123	100.0

<sup>a</sup> Propanoic anhydride (16.90 g, 130 mmol) was added to a stirring mixture of nitric acid (7.65 g, 100%, 120 mmol) and  $\text{H}\beta$  (2.00 g) at 0 °C and the mixture was stirred for 5 min. Toluene (3.22 g, 35 mmol) was added dropwise and the mixture was allowed to warm to room temperature. The mixture was then stirred at 50 °C under a calcium chloride guard tube for the time indicated.

<sup>b</sup> By quantitative GC. Recorded to the nearest 1% (above 10%) or 0.1% (below 10%).

<sup>c</sup> Ratio calculated directly from GC data and not from the rounded figures in the Table.

<sup>d</sup> Sum total of the calculated yields of the identified compounds.

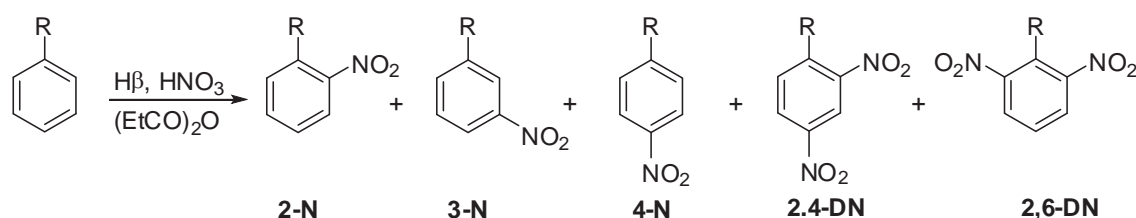
In order to check on the possibility of reuse of the zeolite, it was recovered following extraction of the products and was regenerated by heating overnight in air at 450 °C. Nitration reactions were then conducted under identical conditions using the recovered zeolite. The reaction was repeated seven times using the same batch of catalyst, but later reactions were scaled down somewhat due to small losses of zeolite during recovery. The results showed that under the standard conditions there was only a slight decrease (to 94%) in the yield of 2,4-dinitrotoluene even after using the same zeolite seven times under identical conditions, and the selectivity was virtually the same.

Reactions were also conducted in various solvents (cyclohexane, chloroform, 1,2-dichloroethane, propanoic acid or excess propanoic anhydride). However, use of solvent invariably brought about a decrease in yield of DNTs, presumably as a result of the lower concentrations of reacting species, and in all cases except for propanoic anhydride the 2,4-:2,6-DNT ratio was also somewhat lower, consistent with the reduced

extent of reaction of 4-nitrotoluene. Therefore, the addition of solvent to the nitration system has no advantages on either selectivity or yield and is not necessary.

After the success in producing a high yield of 2,4-dinitrotoluene selectively, attention was turned to nitration of various other mono-substituted benzenes using the same system (Scheme 3).

Several mono-substituted benzenes, including ones that are activated (anisole, phenetole), moderately activated (ethylbenzene, propylbenzene), and moderately deactivated (fluorobenzene, chlorobenzene, bromobenzene), were subjected to the nitrating system under the same conditions as those optimized for toluene. Reactions were worked up and product compositions determined by proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectroscopy (since all expected products were not to hand for use as GC standards). The calculated mass balances were consistent with the total weights of products obtained (Table 2).



**Scheme 3.** Nitration of mono-substituted benzenes with a  $\text{HNO}_3/(\text{EtCO})_2\text{O}/\text{H}\beta$  system.

In no case other than toluene was there evidence of a significant quantity of 3-nitro compounds, presumably because they were converted into trace quantities of dinitro derivatives. All reactions appeared to be extremely selective for formation of 2,4-dinitro isomer or 4-mononitro derivative. Highly active anisole and phenetole produced excellent yields of the corresponding 2,4-dinitro derivatives (97 and 96%, respectively). 2,6-Dinitroanisole and 2,6-dinitrophenetole were produced in very low yields (1%) along with small quantities of other nitrated products.

**Table 2**Nitration of mono-substituted benzenes according to Scheme 3.<sup>a</sup>

Entry	R	Yield (%) <sup>b</sup>					Mass balance (%) <sup>c</sup>
		2-N	3-N	4-N	2,4-DN	2,6-DN	
1	OMe	trace	trace	trace	97	1	98 <sup>d</sup>
2	OEt	trace	trace	trace	96	1	97 <sup>d</sup>
3	Me	—	0.4	0.8	98	0.8	100 <sup>e</sup>
4	Et	7	trace	17	73	trace	97
5	Pr	5 (3) <sup>f</sup>	trace	31 (7) <sup>f</sup>	61 (89) <sup>f</sup>	trace	97 (99) <sup>f</sup>
6	F	7	trace	85	5	—	97
7	Cl	2	—	92	2	2	98
8	Br	2	—	92	2	2	98

<sup>a</sup> Propanoic anhydride (16.90 g, 130 mmol) was added to a stirring mixture of nitric acid (7.65 g, 100%, 120 mmol) and zeolite H $\beta$  (2.00 g) at 0 °C and the mixture was stirred for 5 min. Substituted benzene (35 mmol) was added dropwise and the mixture was allowed to warm to room temperature then stirred at 50 °C for 4 h under a calcium chloride guard tube. (The order of addition was found not to be important for halobenzenes, but it was important for the more reactive substrates.) The mixture was allowed to cool to room temperature and the catalyst was removed by filtration and washed with acetone (3  $\times$  10 mL). Water (30 mL) and DCM (30 mL) were added to the combined filtrate and washings and the layers were separated. The aqueous layer was extracted with DCM (20 mL) and the organic layers were combined. The combined organic extract was washed with aq. saturated NaHCO<sub>3</sub> solution (30 mL) and water (30 mL), dried (MgSO<sub>4</sub>) and evaporated under reduced pressure to give the crude product.

<sup>b</sup> By weight of products and their <sup>1</sup>H NMR spectra.

<sup>c</sup> The sum of the calculated percentage yields of nitro products based on weight of products and their <sup>1</sup>H NMR spectra.

<sup>d</sup> Traces of other dinitro compounds, possibly arising from 3-nitro derivative were also seen.

<sup>e</sup> Yields of isomers calculated by use of quantitative GC.

<sup>f</sup> When 4.00 g of H $\beta$  was used.

With ethylbenzene and propylbenzene, significant amounts (17–31%) of 4-nitro-1-alkylbenzenes remained after 4 hours, although relatively high yields of 2,4-dinitro-1-alkylbenzenes (61–73%) were obtained. The yield of 2,4-dinitrophenylpropane increased to 89% under similar reaction conditions when the amount of zeolite used was doubled to 4 g. However, toluene gave a very high yield of 2,4-DNT even with 2 g of zeolite, so it seems that longer-chain alkylbenzenes react more slowly, presumably because of more difficult diffusion through the pores and/or more restricted transition states within the pores of the zeolite.

Halobenzenes produced very low yields of dinitro compounds (2–5%). Instead, nitration of fluorobenzene, chlorobenzene and bromobenzene gave 1-fluoro-4-nitrobenzene (85%), 1-chloro-4-nitrobenzene (92%) and 1-bromo-4-nitrobenzene (92%), respectively, as the main products. We have not optimized conditions for each substrate but longer reaction times, additional nitrating reagent, more catalyst and/or higher temperature might lead to high yields of 2,4-dinitro derivatives for many substrates. We continue to investigate such reactions.

## 4. Conclusion

Use of a 1:3.4:3.7 ratio of toluene:nitric acid:propanoic anhydride with zeolite H $\beta$  gives 2,4-dinitrotoluene in 98% yield with a 2,4-:2,6- ratio around 123:1. This is easily the most selective quantitative double nitration of toluene ever recorded.

Propanoic anhydride is more attractive than trifluoroacetic anhydride in terms of selectivity, volatility, toxicity and cost. Since propanoic acid can be recovered and the zeolite can be reused several times, the method could be attractive for larger scale syntheses. It also works well for dinitration of activated substrates such as anisole and phenetole. Other alkylbenzenes give dinitro compounds in lower yields but high selectivity, while halobenzenes give mainly *para*-nitro derivatives.

## Acknowledgments

We thank the Saudi Government and Cardiff University for financial support.

## Supplementary data

The supplementary material contains the  $^1\text{H}$  NMR spectra of the crude products from nitration reactions.

## References

- [1] J.H. Clark (Ed.), *Chemistry of Waste Minimisation*, Chapman and Hall, London, 1995.
- [2] R. Taylor, *Electrophilic aromatic substitution*, Wiley, Chichester, 1990.
- [3] G.A. Olah, R. Malhotra, S.C. Narang, *Nitration: methods and mechanisms*, VCH, New York, 1989.
- [4] K. Schofield, *Aromatic nitration*, Cambridge University Press, Cambridge, 1980.
- [5] J.H. Clark, *Acc. Chem. Res.* 35 (2002) 791.
- [6] J.M. Thomas, W.J. Thomas (Eds.), *Principles and Practice of Heterogeneous Catalysis*, VCH, Weinheim, 1997.
- [7] J.H. Clark (Ed.), *Catalysis of Organic Reactions using Supported Inorganic Reagents*, VCH, New York, 1994.
- [8] L. Delaude, P. Laszlo, K. Smith, *Acc. Chem. Res.* 26 (1993) 607.
- [9] K. Smith, in: Z. Yoshida, Y. Ohshiro (Eds.), *New aspects of organic synthesis II*, Kadonsha, Tokyo and VCH, Weinheim, 1992, pp. 43.
- [10] M. Butters, in: K. Smith (Ed.), *Solid supports and catalysts in organic synthesis*, Ellis Harwood, Chichester, 1992, pp. 130–170.
- [11] K. Smith, in: M.G. Scaros, M.L. Prunier (Eds.), *Catalysis of organic reactions*, Marcel Dekker, New York, 1991, pp. 91.
- [12] K. Smith, G.A. El-Hiti, *Green. Chem.* 13 (2011) 1579.
- [13] K. Smith, G.A. El-Hiti, *Curr. Org. Chem.* 10 (2006) 1603.
- [14] K. Smith, G.A. El-Hiti, *Curr. Org. Synth.* 1 (2004) 253.
- [15] K. Smith, A.K.H. Al-Khalaf, G.A. El-Hiti, S. Pattisson *Green. Chem.* 14 (2012) 1103.
- [16] K. Smith, M.D. Ajarim, G.A. El-Hiti, *Catal. Lett.* 134 (2010) 270.

- [17] K. Smith, M.D. Ajarim, G.A. El-Hiti, C. Peters, *Topics Catal.* 52 (2009) 1696.
- [18] K. Smith, S. Almeer, S.J. Black, C. Peters, *J. Mater. Chem.* 12 (2002) 3285.
- [19] K. Smith, S. Almeer, C. Peters, *Chem. Commun.* (2001) 2748.
- [20] K. Smith, S. Almeer, S.J. Black, *Chem. Commun.* (2000) 1571.
- [21] K. Smith, T. Gibbins, R.W. Millar, R.P. Claridge, *J. Chem. Soc. Perkin Trans. 1* (2000) 2753.
- [22] K. Smith, A. Musson, G.A. DeBoos, *J. Org. Chem.* 63 (1998) 8448.
- [23] K. Smith, S.D. Roberts, G.A. El-Hiti, *Org. Biomol. Chem.* 1 (2003) 1552.
- [24] K. Smith, G.A. El-Hiti, A.J. Jayne, M. Butters, *Org. Biomol. Chem.* 1 (2003) 2321.
- [25] K. Smith, G.A. El-Hiti, A.J. Jayne, M. Butters, *Org. Biomol. Chem.* 1 (2003) 1560.
- [26] K. Smith, G.A. El-Hiti, M.E.W. Hammond, D. Bahzad, Z. Li, C. Siquet, *J. Chem. Soc. Perkin Trans. 1* (2000) 2745.
- [27] K. Smith, P. He, A. Taylor, *Green. Chem.* 1 (1999) 35.
- [28] K. Smith, G.M. Ewart, G.A. El-Hiti, K.R. Randles, *Org. Biomol. Chem.* 2 (2004) 3150.
- [29] B. Gigante, A. Prazeres, M. Marcelo-Curto, A. Cornelis, P. Laszlo, *J. Org. Chem.* 60 (1995) 3445.
- [30] B. Carvalheiro, P. Laszlo, A. Cornelis, M. Marcelo-Curto, *PCT Int. Appl. WO* 1994/019310, 1994.
- [31] D.B. Akolekar, G. Lemay, A. Sayari, S. Kaliaguine, *Res. Chem. Intermed.* 21 (1995) 7.
- [32] A.B. Quakenbush, B.T. Pennington, in: L.F. Albright, R.V.C. Carr, R.J. Schmitt (Eds.), *Nitration: Recent Laboratory and Industrial Developments*, ACS Symposium Series, 1996, vol 623, pp. 214
- [33] N.L. Lancaster, R.B. Moodie, P.B. Sandall, *J. Chem. Soc. Perkin Trans. 2* (1997) 847.



- [34] A. Kogelbauer, D. Vassena, R. Prins, J.N. Armor, *Catal. Today* 55 (2000) 151.
- [35] D. Vassena, A. Kogelbauer, R. Prins, *Catal. Today* 60 (2000) 275.
- [36] W.-B. Yi, C. Cai, *Synth. Commun.* 36 (2006) 2957.
- [37] A. Kogelbauer, D. Vassena, R. Prins, J. Armor, Abstracts from EuropaCat-IV, Rimini, p 222 (1999).
- [38] K. Smith, G. El-Hiti, M. Alotaibi, *PCT Int. Appl. WO* 2012/049513 A1, 2012.
- [39] S. Bernasconi, G.D. Pirngruber, A. Kogelbauer, R. Prins, *J. Catal.* 219 (2003) 231.
- [40] S. Bernasconi, G.D. Pirngruber, R. Prins, *J. Catal.* 224 (2004) 297.

## **List of Figure Captions**

**Scheme 1.** Generation of propanoyl nitrate.

**Scheme 2.** Nitration of toluene over a  $\text{HNO}_3/(\text{EtCO})_2\text{O}/\text{H}\beta$  system.

**Scheme 3.** Nitration of mono-substituted benzenes with a  $\text{HNO}_3/(\text{EtCO})_2\text{O}/\text{H}\beta$  system.

**Table 1**

Effect of reaction time in dinitration of toluene with  $\text{HNO}_3/(\text{EtCO})_2\text{O}/\text{H}\beta$  system according to Scheme 2.<sup>a</sup>

Time (min)	Yields of products <sup>b</sup>				2,4-:2,6- ratio <sup>c</sup>	Mass balance (%) <sup>d</sup>
	3-NT	4-NT	2,4-DNT	2,6-DNT		
5	1.1	15	81	1.1	74	98.2
15	1.0	13	82	1.0	82	97.0
30	1.1	11	84	1.1	76	97.2
60	0.9	8.0	91	0.7	130	100.6
120	0.8	4.8	93	0.9	103	99.5
240	0.4	0.8	98	0.8	123	100.0

<sup>a</sup> Propanoic anhydride (16.90 g, 130 mmol) was added to a stirring mixture of nitric acid (7.65 g, 100%, 120 mmol) and  $\text{H}\beta$  (2.00 g) at 0 °C and the mixture was stirred for 5 min. Toluene (3.22 g, 35 mmol) was added dropwise and the mixture was allowed to warm to room temperature. The mixture was then stirred at 50 °C under a calcium chloride guard tube for the time indicated.

<sup>b</sup> By quantitative GC. Recorded to the nearest 1% (above 10%) or 0.1% (below 10%).

<sup>c</sup> Ratio calculated directly from GC data and not from the rounded figures in the Table.

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2	OEt	trace	trace	trace	96	1	97 <sup>d</sup>
3	Me	—	0.4	0.8	98	0.8	100 <sup>e</sup>
4	Et	7	trace	17	73	trace	97
5	Pr	5 (3) <sup>f</sup>	trace	31 (7) <sup>f</sup>	61 (89) <sup>f</sup>	trace	97 (99) <sup>f</sup>
6	F	7	trace	85	5	—	97
7	Cl	2	—	92	2	2	98
8	Br	2	—	92	2	2	98

<sup>a</sup> Propanoic anhydride (16.90 g, 130 mmol) was added to a stirring mixture of nitric acid (7.65 g, 100%, 120 mmol) and zeolite H $\beta$  (2.00 g) at 0 °C and the mixture was stirred for 5 min. Substituted benzene (35 mmol) was added dropwise and the mixture was allowed to warm to room temperature then stirred at 50 °C for 4 h under a calcium chloride guard tube. (The order of addition was found not to be important for halobenzenes, but it was important for the more reactive substrates.) The mixture was allowed to cool to room temperature and the catalyst was removed by filtration and washed with acetone (3  $\times$  10 mL). Water (30 mL) and DCM (30 mL) were added to the combined filtrate and washings and the layers were separated. The aqueous layer was extracted with DCM (20 mL) and the organic layers were combined. The combined organic extract was washed with aq. saturated NaHCO<sub>3</sub> solution (30 mL) and water (30 mL), dried (MgSO<sub>4</sub>) and evaporated under reduced pressure to give the crude product.

<sup>b</sup> By weight of products and their <sup>1</sup>H NMR spectra.

<sup>c</sup> The sum of the calculated percentage yields of nitro products based on weight of products and their <sup>1</sup>H NMR spectra.

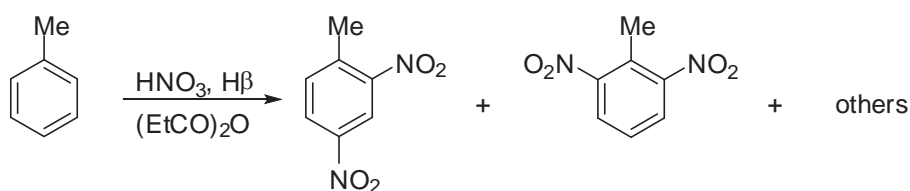
<sup>d</sup> Traces of other dinitro compounds, possibly arising from 3-nitro derivative were also seen.

<sup>e</sup> Yields of isomers calculated by use of quantitative GC.

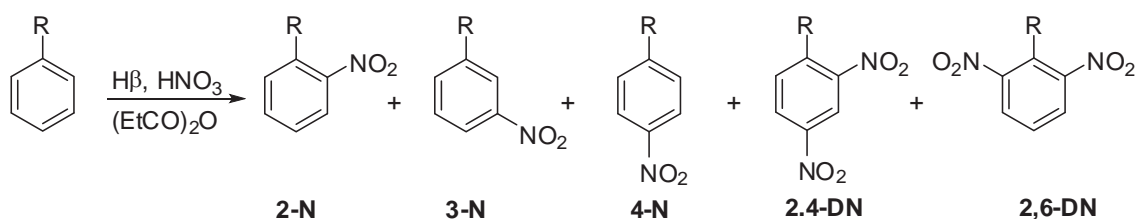
<sup>f</sup> When 4.00 g of H $\beta$  was used.



**Scheme 1.** Generation of propanoyl nitrate.



**Scheme 2.** Nitration of toluene over a HNO<sub>3</sub>/(EtCO)<sub>2</sub>O/Hβ system.



**Scheme 3.** Nitration of mono-substituted benzenes with a HNO<sub>3</sub>/(EtCO)<sub>2</sub>O/Hβ system.

**Supplementary Materials**

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