

A STUDY OF THE REGIOSELECTIVITY IN THE ZEOLITE-ASSISTED
NITRATION OF TOLUENE

Joel M. Barden, III

A Thesis Submitted to the
University of North Carolina at Wilmington in Partial Fulfillment
Of the Requirements for the Degree of
Master of Science

Department of Chemistry

University of North Carolina at Wilmington

2003

Approved by

Advisory Committee

Chair

Accepted By

Dean, Graduate School

TABLE OF CONTENTS

ABSTRACT.....	iii
ACKNOWLEDGEMENTS.....	iv
DEDICATION.....	v
LIST OF TABLES.....	vi
LIST OF FIGURES.....	vii
INTRODUCTION.....	1
Aromatic.....	1
Aliphatic.....	4
EXPERIMENTAL.....	14
RESULTS AND DISCUSSION.....	27
CONCLUSIONS.....	88
LITERATURE REFERENCES.....	90
APPENDIX.....	92

ABSTRACT

Nitration of toluene has been an important industrial process for many years. The conventional method is effective in nitrating toluene, but it produces an ortho:meta:para (o:m:p) ratio of approximately 57:4:39, respectively. There has been considerable effort studying the potential for various zeolites to influence regioselectivity towards the *para*-isomer, which is the most desirable isomer. By introducing zeolites into the process, the regioselectivity can be directed with the proper selection of the pore size of the zeolite used. The use of the zeolite catalysts improved the regioselectivity of the reaction and has produced the *para*-isomer as high as 80%.

It has been reported that the increase in regioselectivity is related to the silica/alumina ratio (SAR) of the zeolites used. This is somewhat unexpected based upon size selective reactions in other zeolite systems. Our investigations of the zeolite assisted reactions led to the conclusion that the increase in the regioselectivity of these reactions did not depend on the SAR, as previously reported, but is due to the pore size of the zeolite. The improved zeolite reaction produced an isomeric distribution of 18% ortho-, 0.52% meta-, and 82% para-monomonitrotoluene with more readily available zeolites.

While investigating the regioselective zeolite reaction, a side product was noted that had not previously been reported with respect to this reaction. This side product was considered a contaminant initially and its production was minimized during the reaction. The contaminant was identified as phenylnitromethane, PNM and it was determined that its production was significantly different from the nitrotoluene in that a radical reaction was responsible instead of an aromatic substitution. After identification, it was decided

to take advantage of this side reaction to produce the PNM, as the reported methods were difficult and/or time-consuming syntheses.

The zeolite method for producing the PNM was investigated and yielded 3.00g of phenylnitromethane (94% purity by GC).

ACKNOWLEDGEMENTS

I would like to thank Dr. John Tyrell for all of his help and support throughout this project. Without his patience and humor, these past months would have been a far less enjoyable journey.

To Heather McCreery, I give heartfelt thanks for all of the moral support and for being there to listen to the gripes and groans of a frustrated graduate student (whom I believe she once was).

My thanks to the rest of the faculty of the Chemistry Department for loaning materials, time, and experience to that same frustrated graduate student.

To Ned Hill who kept the computers, printers and various other gizmos and gadgets in the lab running when they should have been consigned to oblivion long ago, many thanks.

To Miss Shearon and Miss Libbie for all their help and for putting up with the seemingly unending stream of questions about when, where, and how to do just about everything.

Finally, I must thank Jennifer Jones for putting up with me through the good and the bad and for always telling it like it is.

DEDICATION

I would like to dedicate this thesis to my family for without their guidance and support this would not have been possible. And a special dedication of the knowledge represented in this work to my nephews, Chandler and Gannon, who represent the bright possibilities of the future.

LIST OF TABLES

Table	Page
1. Comparison of original U.S. patent study, conventional method, and current zeolite method product distribution by GC analysis (area %)	29
2. Comparison of the individual products of a typical zeolite nitration reaction with their boiling points.....	33
3. Variation of parameters for the production of PNM using the method reported by Baruah, et al.....	70
4. Characterization comparison of Kornblum product and JB-2-71 product using ¹ H-NMR, IR, and GC analyses	81

LIST OF FIGURES

Figure	Page
1. Isomeric distribution of a typical zeolite nitration reaction	16
2. Isomeric distribution of a typical chloroform pretreatment nitration reaction	18
3. Product distribution for a typical reaction to produce phenylnitromethane	20
4. Product distribution of high purity phenylnitromethane reaction.....	22
5. Product distribution of Kornblum reaction	24
6. GC chromatogram of 2,4-dichlorophenylnitromethane.....	25
7. GC chromatogram of a typical zeolite reaction, showing the major products. 1)benzaldehyde, 2) <i>ortho</i> -nitrotoluene, 3) phenylnitromethane, 4) <i>meta</i> -nitrotoluene, & 5) <i>para</i> -nitrotoluene	32
8. Comparison of isomeric distribution of 280 SAR and 1000 SAR reactions	37
9. Comparison of isomeric distribution of 280 SAR at 25° C, 65-70° C and 90-95° C	38
10. Comparison of isomeric distribution of 280 SAR: Effect of changing the zeolite:toluene ratio	39
11. Comparison of the isomeric distribution of 1000 SAR & 280 SAR: Effects of changing the zeolite:toluene ratio	41
12. Comparison of the isomeric distribution of 1000 SAR, 280 SAR & 80 SAR: Effects of changing the zeolite:toluene ratio.....	42
13. Comparison of PNM production with respect to the use of a nitrogen sweep	45
14. Percent of meta-isomer produced versus percent of PNM produced	46
15. Comparison of meta-isomer production vs. PNM production using 280 SAR	48
16. Comparison of meta-isomer production vs. PNM production using 80 SAR, 280 SAR, 1000 SAR.....	50

17.	Comparison of the isomeric distribution and PNM production after addition of sulfuric acid to zeolite reaction	51
18.	Comparison of product distribution using 305° C and 550° C temperatures for calcinating zeolites	53
19.	PNM production based on the addition of radical scavenger BHT	54
20.	Comparison of PNM production using a radical scavenger (BHT) with respect to temperature.....	56
21.	PNM production with respect to SAR (30, 80, 280 & 1000)	58
22.	PNM production as related to the purification of the nitric acid by addition of urea with air sparging at a reaction temperature of 90-95° C.....	60
23.	PNM production as related to temperature using purified nitric acid.....	61
24.	Comparison of the reproducibility of the best overall nitration reactions with respect to the isomeric distribution	63
25.	Isomeric distribution and PNM production with respect to the presence of zeolite.....	64
26.	Comparison of the isomeric distribution and PNM production with respect to improved reaction conditions (temperature, sparging, nitric acid purification, and pre-treatment)	67
27.	GC chromatogram of the Kornblum product.....	74
28.	GC chromatogram of JB-2-71 product	74
29.	GC chromatogram of Kornblum product and JB-2-71 product spiked	75
30.	¹ H-NMR spectrum of Kornblum product showing 2H at 5.41 ppm and 5H at 7.42 ppm.....	77
31.	¹ H-NMR spectrum of JB-2-71 product showing 2H at 5.41 ppm and 5H at 7.42 ppm.....	78
32.	IR spectrum of the Kornblum product.....	79
33.	IR spectrum of JB-2-71 product	79
34.	Composite IR spectrum of Kornblum product (A) and JB-2-71 product (B).....	80

35.	GC chromatogram of 2,4-dichlorophenylnitromethane.....	83
36.	¹ H-NMR spectrum of 2,4-dichlorophenylnitromethane showing the aliphatic protons at 5.50 ppm and the aromatic protons at 7.42 and 7.51 ppm.....	84
37.	IR spectrum of JB-2-101 product; 2,4-dichlorophenylnitromethane.....	85
38.	GC chromatogram of phenylnitroethane	87