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NITRATION OF TOLUENE
USING SOLID ACID CATALYSTS

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Gary Lee Succaw

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NITRATION OF TOLUENE USING SOLID ACID CATALYSTS

by

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ABSTRACT

NITRATION OF TOLUENE USING SOLID ACID CATALYSTS

By

Gary Lee Succaw

Nitration of aromatics long has been performed with either fuming nitric acid or a mixture of sulfuric acid and nitric acid. However, one not only has a problem with disposing of the spent acid from this method of nitration, but also one has to deal with the environmentally undesirable phenylnitromethane. The goal of this research was to modify some existing methods of nitration and to develop some new nitration methods that selectively produce the desired nitrotoluenes, with greater regioselectivity and without laborious workup or recovery of spent catalyst. Toward this end three methods were chosen for study, namely, copper nitrate and acetic anhydride, fuming nitric acid, and n-butyl nitrate. Each of these reagents were used in conjunction with pillared clays and K10-montmorillonite. n-Butyl nitrate was not an effective reagent for nitrating toluene with either K10 or alumina-pillared clays nor was fuming nitric acid with K10. However, copper nitrate / K10 and acetic anhydride was effective and with greater regioselectivity. One can increase the selectivity of this reaction using another solid acid or by using another anhydride.

"'Not by might nor by power, but by My Spirit,' says the LORD Almighty."
Zechariah 4:6, NIV.

I would like to dedicate this work to my wife, Pam, whose patience and encouragement were indispensable in finishing this project.

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I would like to thank Professor T. J. Pinnavaia for his guidance and help in putting this work together and Dr. Kaviratna Padmananda, my research partner on this project, whose assistance and debating skills were a great help in organizing and directing this project.

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LIST OF ABBREVIATIONS

AA–Acetic anhydride
APAM–Aluminum pillared Arizona montmorillonite.
APB–Aluminum pillared Beidelite
APWM–Aluminium pillared Wyoming montmorillonite.
DNT-Dinitrotoluenes.
K10–K10-montmorillonite, an acid washed montmorillonite.
mNT-Meta nitrotoluene.
MNT-Mononitrotoluenes.
ONT-Ortho nitrotoluene
PNT-Para nitrotoluene
TFAA–Trifluoroacetic anhydride.
TFAN–Trifluoroacetic acetyl nitrate.

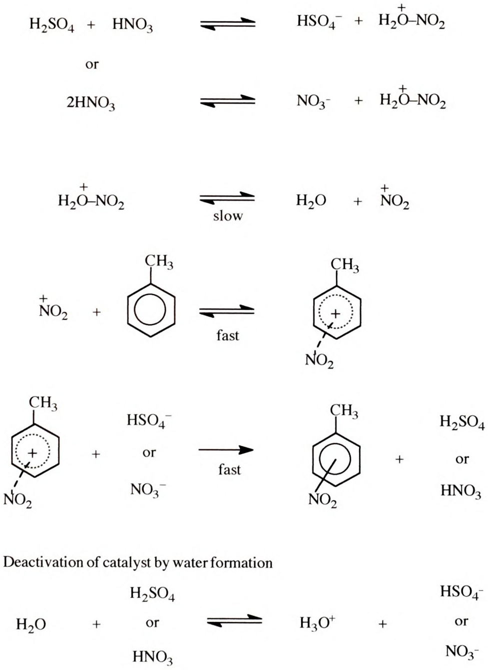
I. Introduction

A. Brief History of Nitration.

Nitration of aromatics long has been an important reaction in organic chemistry. The first reported synthesis was by Mitscherlich[1,2] (although Faraday may have performed it even earlier[3]) using fuming nitric acid and benzene to produce the almond scented nitrobenzene. Mansfield proposed the use of sulfuric acid as a dessicant to avoid the dilution of the nitric acid[1] and ever since this has been the most commonly used method of nitration, especially of toluene. The most likely mechanism for this reaction is shown in Scheme 1.[4,5]

The chemists utilizing HNO_3/H_2SO_4 as a nitrating agent for toluene have encountered some serious drawbacks. Neutralizing the spent sulfuric acid is an expensive and a time-consuming process but less so than to try to reclaim it. Also, this method produces an environmentally undesirable by-product at elevated temperature, namely, phenylnitromethane, which dissolves in water more appreciably than the mononitrotoluenes. Both phenylnitromethane and the nitrotoluenes absorb through the skin, but the added water solubility makes phenylnitromethane even more menacing than the mononitrotoluenes. Although, one could resort to multistep reactions and work-ups[6] to eliminate the phenylnitromethane, one still has to dispose of the spent acid.

The earliest nonacid method for aromatic nitration was employed by Menke.[7,8,9] He worked with various metal nitrates in conjunction with acetic anhydride as a dehydrating agent, as well as providing a reaction

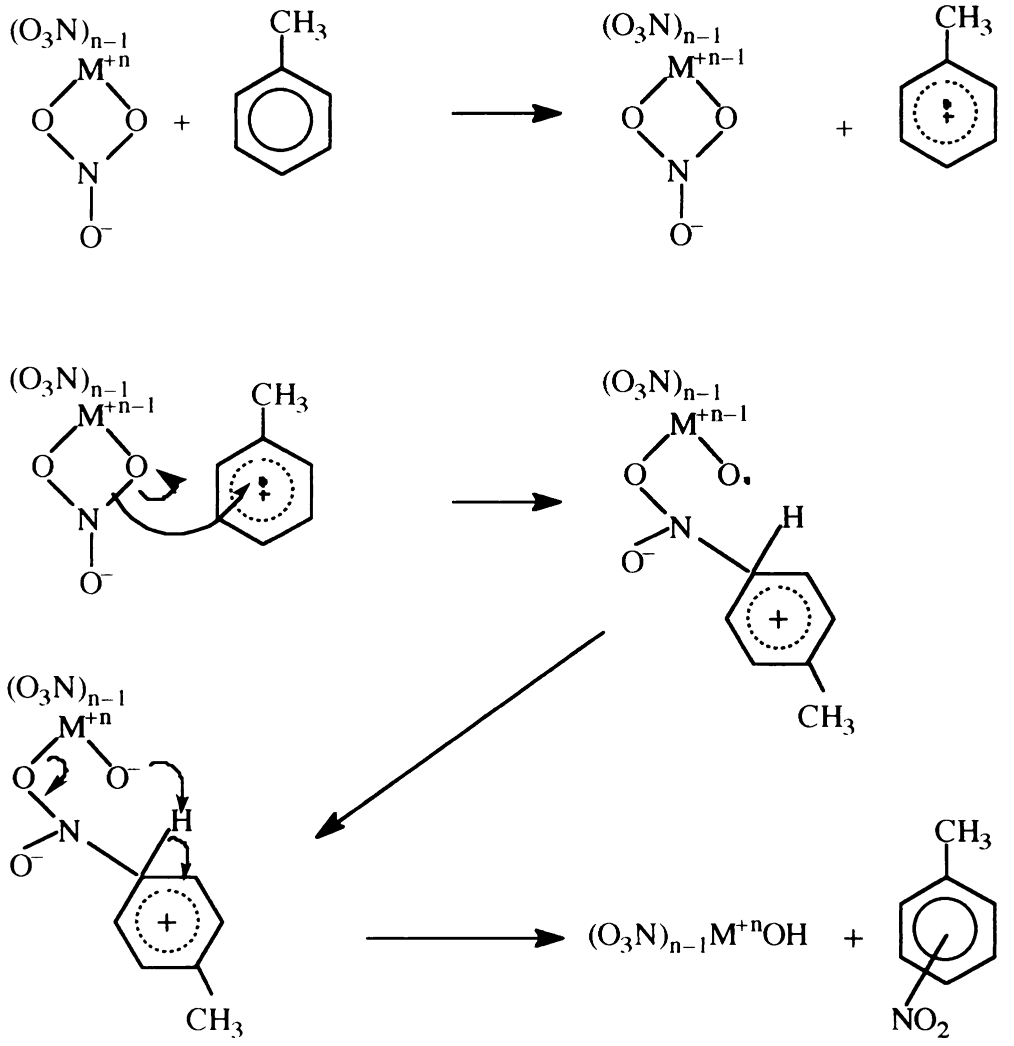


Scheme 1. Traditional mechanism for the nitration of toluene.

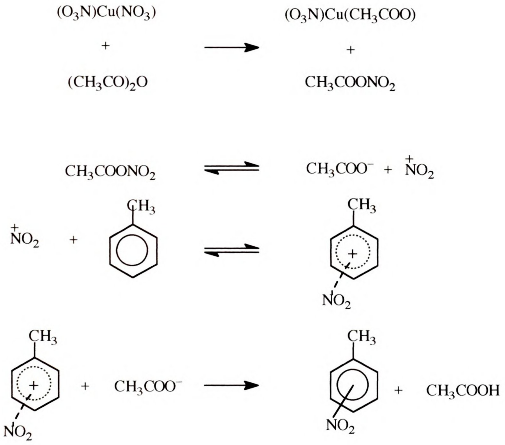
intermediate, by formation of acetyl nitrate. The best metal nitrates were those of the transition metals which had a lower oxidation state energetically availible, such as Cu^{+2} and Fe^{+3}. The mechanism of this reaction is not so clear; but, a possible mechanism is shown in Scheme 2.[10] Evidence that electron transfer may occur between Cu^{+2} or Fe^{+3} and aromatic rings comes from Pinnavaia[11] who showed that exchanged clays can produce a radical cation from an aromatic hydrocarbon. However, if the reaction occurs by formation of acetyl nitrate, then there would be no need for a radical cation intermediate, and a second mechanism could operate as shown in Scheme 3. The relative merit of these two schemes will be examined later.

B. Clays as General Catalysts.

The use of clays, especially the smectites as solid acid catalysts goes back to the early twentieth century when they were used in the petroleum cracking industry. Their unit cell structure, as shown in Figure 1, is that of a 2:1 tetrahedral to octahedral layer with the exchangeable cations located in-between the layers. In the octahedral part of the layer, there are three octahedral positions that are completely occupied only in certain clays. Fluorohectorite (FH) is an example of a trioctahedral clay in which all of the octahedral positions in the unit cell are occupied by Mg^{2+} with occasional substitution by Li^{+}. Wyoming montmorillonite (WM) and beidelite (B) are examples of dioctahedral clays in which the octahedral positions are occupied by Al^{3+}; however, in WM the octahedral positions are occasionally substituted with Mg^{2+} and in beidelite[12] the tetrahedral Si^{4+} are occasionally substituted with Al^{3+}. These substitutions allow for the presence of exchangeable interlayer or gallery cations (M^{n+}) which can be replaced with protons and/or oligomeric polycations.



Scheme 2. Alternate one electron transfer step: M^{+n} can be Cu^{+2}, Fe^{+3}, Ti^{+4}, or any other transition metal that can be reversibly reduced and oxidized.



Scheme 3. Possible mechanism for the nitration of toluene using cupric nitrate and acetic anhydride.

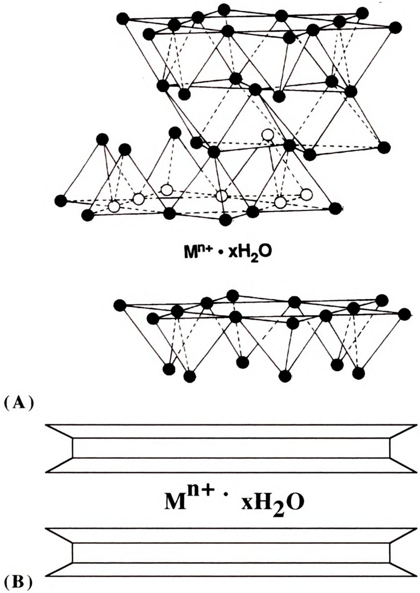


Figure 1. Generalized 2:1 structures of smectite clays. (A) is the 3-dimensional structure, (B) is an abbreviated representation. A typical unit cell formula for montmorillonite is $M^{n+}{}_{0.7/n}\,[Al_{3.3}Mg_{0.7}]Si_8O_{20}(OH)_4$ with Al and Mg in the octahedral layer and Si in the tetrahedral layer. In fluorohectorite, F^- replaces OH^- in the layer, and the unit cell formula is $M^{n+}{}_{1.5/n}\,[Mg_{4.5}Li_{1.5}]Si_8O_{20}F_4$.

With the discovery of nanopourous zeolites in the 1960's,[13] clays were replaced as petroleum cracking catalysts. Zeolites are aluminum silicates whose structures are characterized by the presence of interconnected cavities which can be linked in one direction to form fibrous crystals or in two or three directions to give lamellar or 3D structures, respectively[14]. Zeolites typically exhibit regularly ordered micropores (pore size less than 20 angstroms), except in the case of MCM-41 developed by Mobil[16] which has an entirely mesoporous structure (pore size less than 500Å but greater than 20Å). This microporous structure does not allow very easy access for larger molecules, although this results in a large surface area by N_2 absorption, as in mordenite. The advantage of the zeolites over the clays was their high acidity and thermal stability which resulted in higher conversion. However, the selectivity of the zeolites could not be tailored easily by systematically altering their structure, which rendered them of only specific use. Mordenite, a zeolite of interest in the present work, consists of elongated cavities linked by 24-membered rings consisting of 12 oxygen atoms, each oxygen bridges two silicon, or aluminum atoms. The pore openings can accommodate molecules with kinetic diameters less than 6.5Å.

As of the late1970's[13] a new type of catalyst was introduced--aluminum pillared clays. These are made by cation exchange of the smectite clays with the Keggin-like "Al_{13}^{+7}" oligomer (Figure 2) and then by calcining the exchanged clay to obtain the "Al_2O_3" pillared derivative (Figure 3). After the discovery of Al-pillaring, many other pillaring agents were developed, including chromia, imogolite, and zirconia, etc. Previous work[16] with Al-pillared clays found that the best catalysts for isopropylation of biphenyl had two requirements: higher Bronsted acidity,

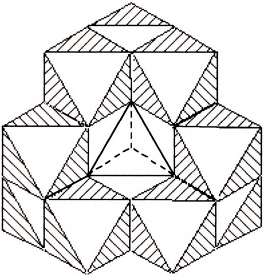


Figure 2. The "Al_{13}^{+7}" oligomer ($Al_{13}O_4(OH)_{24}(H_2O)_{12}^{+7}$). Vertices represent the positions of O, OH, and H_2O. The central tetrahedral aluminium is surrounded by twelve octahedral aluminums.

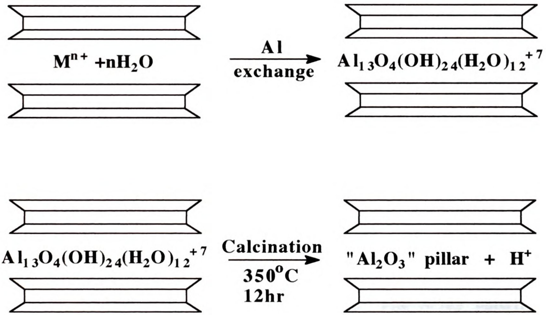


Figure 3. Process for preparing of alumina-pillared clay. Processes are similar for other pillared clays.

and greater access to these acid sites. Of these, accessibility is most important. In some unpublished results (see Table 1.), the alkylation of benzene with 2-chlorobutane has been accomplished using various Al-pillared clays as well as K10-montmorillonite, an acid washed montmorillonite, which demonstrates the potential of these clays for catalyzing many well-known organic reactions.

Pillared clays have a less regular pore structure than zeolites with both micropores and mesopores being present and surface areas smaller than that of zeolites. Surface areas of selected materials are summarized in Table II.[15] It is this mesoporosity that gives the pillared clays their advantage over zeolites. The size, as well as the number, of mesopores in a pillared clay can be modified by use of surfactants.[17] Pillar size can only be changed by changing the polycation anion, such as a chromia pillared clay[18] (~19Å, if properly prepared) or an imogolite pillared clay[19] (~19Å). The exact structure of the chromia pillaring clay is not known, but that for imogolite pillared clay is shown in Figure 4. The X-ray patterns for calcined chromia-pillared Wyoming montmorillonite, alumina-pillared Wyoming montmorillonite, and alumina-pillared fluorohectorite are shown in Figure 5. Chromia pillared clays are stable indefinitely at room temperature, as are the alumina pillared clays, but the imogolite pillared clays collapse over a period of a couple of weeks.

Enhanced Bronsted acidity of pillared clays may be achieved by the proper choice of clay or by acid modification. For example, beidelite has the largest Bronsted acidity of the natural clays, the sites of which are more accessible since they are located in the tetrahedral part of the layer instead of in the octahedral sheet, as in Wyoming Montmorillonite. K10 montmorillonite not only has greater acidity due to modification by H_2SO_4,

Table I. Alkylation of benzene with 2-chlorobutane using various catalysts.*

Catalyst	Amount of catalyst (in g)	%yield
APAM350	1.0	50
K10	1.0	69.1
APFH350	1.0	8.2
EPZ10**	20.0	77

* Reaction was carried out at 80°C for 5 to 6 hours in excess benzene with 4.4g (5ml) of 2-chlorobutane. The catalyst was filtered off, washed with hexane, and dried in the open air overnight (except for EPZ10).

**Ref. Envirocats.

Table II. BET surface areas for selected materials.[16]

Material	S_{BET} (m^2/g)	%micropores
K10	233	0
APWM	334	87
APFH	214	75
APB	186	79
M8(48)*	725	81

*Mordenite zeolite with a Si/Al molar ratio of 48.

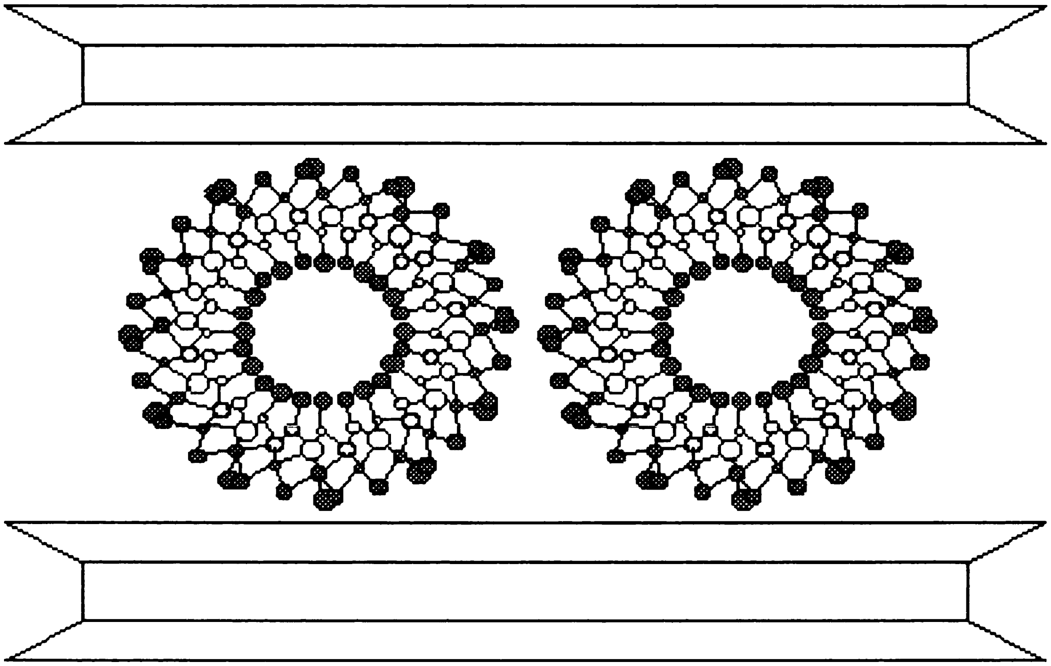


Figure 4. The structure of imogolite pillared smectite clays.

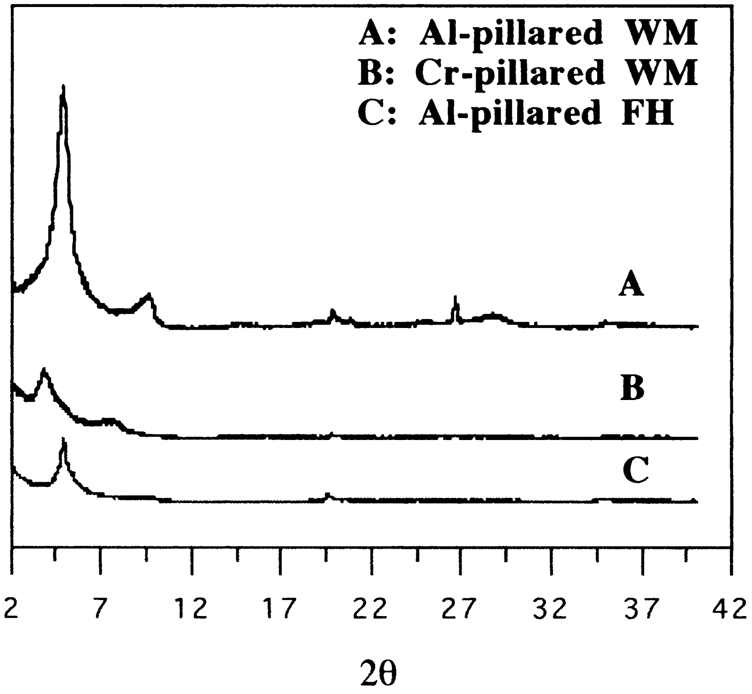


Figure 5. X-Ray patterns for selected pillared clays. Basal-spacings for each of the clays are A=18.1Å; B=22.9Å; C=18.0Å

but also, has an almost completely nonporous structure, which makes K10 one of the most active catalysts for the isopropylation of biphenyl,[15] but not necessarily the most selective. Nevertheless, the use of these catalysts in place of sulfuric acid in the nitration of toluene has just begun.

C. Solid Acids as Nitration catalysts.

Up to the present time the use of zeolites in the nitration of toluene has been limited to catalyzing the reaction with benzoyl nitrate,[20]although Laszlo reports using them in conjunction with $Cu(NO_3)_2$[25]. Benzoyl nitrate as a nitrating agent has serious drawbacks; it is not particularly stable and is difficult to work with. Nevertheless, Butters and his coworkers[20] obtained a yield of 94% with large pore mordenite (proton-aluminum exchanged) after 43.5 hours reaction time with a para-selectivity of 64%. They used a 1:1 mole ratio of nitrating agent to toluene (1.5g catalyst, 2.5mmol toluene, and 2.5mmol benzoyl nitrate).[20] They also reported the use of silica, alumina, and K10-montmorillonite with benzoyl nitrate, but these solid acids were not as effective as mordenite; however, they did not report the yields obtained with these solid acids.

In another study, K10-montmorillonite was found to be a very selective catalyst toward nitration with 100% HNO_3[21] (see Table III). However, owing to the exceedingly low HNO_3/toluene ratio (1:70) and high catalyst content, 70g/mole toluene, the reaction stoichometry is not practical for an industrial application. Also, an unexpected and undesirable coupling of the aromatic rings was observed.

Another investigation[21] employed an elaborate three phase system, namely, a liquid "Teflon" top layer, a HNO_3 and substrate layer, and a desiccant). The advantages of this method are not entirely clear, except that HNO_3 would not be diluted by water due to the absorption by desiccant

Table III. Nitration of Toluene with HNO_3 and K10 as a catalyst[21]*.

System	T(°C)	Selectivity MNT**	%Para	Selectivity DNT***	Selectivity MDPM†
Tol. + HNO_3	60	47	41	0	0
Tol. + HNO_3 + K10	25	95	50	0	0
Tol. + HNO_3 + K10	60	64	52	0	32
Tol. + HNO_3 + K10	110	52	46	3	42

*The conditions were as follows: 21 mmoles HNO_3, 90g K10, 1.45 mole toluene, and 3.5 hr reaction time.

**MNT–Mononitrotoluenes.

***DNT–Dinitrotoluenes.

†MDPM–Methyldiphenylmethanes.

and the nitrogen oxides would be absorbed by the liquid teflon. This system shows a higher para-selectivity than the conventional H_2SO_4-HNO_3 system. At 90% conversion, the systems H_2SO_4-HNO_3 and HNO_3-$CaSO_4$ gave o:m:p distributions of 58:4:38, and 45:2:53, respectively. $CuSO_4$ might be a better desiccant because it facilitated a greater conversion of para MNT to 2,4-DNT, but nothing was reported on its use in nitrating toluene.

D. Proposed methods of nitration.

The following methods have been investigated in the present study as to their effectiveness in the nitration of toluene:

1.) **n-Butyl nitrate and K10 or Al-pillared clays.** The use of n-butyl nitrate as a nitrating agent has been reported in the literature[23] with Nafion-H as a catalyst at 80°C. We propose the use of K10 in place of Nafion-H under the same conditions, because it is a less expensive reagent than Nafion-H. Also, because of their microporous nature, the alumina-pillared clays might prove to be more selective toward para nitrotoluene than Nafion-H.

2.) **Fuming nitric acid and K10 montmorillonite.** Because nitric acid is the most inexpensive reagent for the nitration of toluene, it would be beneficial if the reaction could be carried out without undesirable by-products as well as easy recovery of the nitric acid. This method has been modified from the literature[21] in that nitric acid has been used in excess instead of toluene.

3.) **Copper Nitrate / Acetic Anhydride / K10 ("Claycop").** This method used K10 as a activating agent for $Cu(NO_3)_2$, and provided an effective means of nitrating toluene at 25°C with an easy work up.[22] The

effect of the amount of K10, as well as the effect of replacing K10 with various pillared clays has been investigated in the present work. The rationale for this replacement is that the pillared clays are microporous materials, whereas K10 which is classified as nonporous, that is, no micropores. In addition the effect of different anhydrides has been explored.

II. Experimental

A. Materials.

The following chemicals were used without further purification: n-butyl nitrate (Pfaltz & Bauer), toluene, nitric acid, n-hexane, acetic anhydride, TFAA, propionic anhydride, and cupric nitrate 2.5 hydrate. K10-montmorillonite (Aldrich) and used without further preparation, except when used for the nitration of toluene with n-butyl nitrate, when it was heated to 125°C under vacuum. This heat treatment was done to avoid the leveling effect of any surface-bound water that might reduce the catalyst's effectiveness. G. C. analysis indicated that n-butyl nitrate contained a small quantity of n-butyl alcohol and other impurities amounting to about 10%.

Na^+–Wyoming montmorillonite was obtained from the Source Clay Minerals Repository at the University of Missouri, Columbia, MO. The clay was washed with 1.0 M sodium chloride to insure a complete sodium exchange and then washed free of chloride. The pillaring solution was made by adding slowly, while stirring vigorously, 2.4L of 0.4M NaOH (0.96 moles) to 1L of 0.4M $AlCl_3$ (0.4 moles). After the addition had been completed, the cloudy solution was stirred either overnight or until the solution becomes clear. The resulting solution was calculated to be 0.118M with respect to Al^{+3} cation. A portion of the $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{+7}$ ("Al_{13}^{+7}") pillaring solution corresponding to 12 mmoles Al^{+3} per 1 gram of WM clay or 15 mmoles Al^{+3}/1meq of any clay was stirred vigorously at 70°C while the proper amount of clay suspension was added at a rate of

approximately 150 mL per minute. This suspension was stirred at 70°C for another 2.5 hr or until well flocculated, and then the solid was washed free of chloride with 4 or 5 washings of equivalent volumes of deionized water. The washed suspension was poured out on a glass plate to air dry (1 or 2 days). The catalyst was then calcined by heating at 5°C per min to 350°C and then left at 350°C for 12hr. The pillared clay product was confirmed by XRD (18.5Å Basal spacing) and surface area (S_{BET} 334 m^2/g).

Chromia[18] pillared clay, imogolite[19] pillared clays and MCM-41 were obtained from co-workers[24] in the lab and used without further modification.

Copper nitrate supported on clay was made by the procedure of Corneleus et al.[22]. A 20 g quantity of cupric nitrate was dissolved in acetone in either a round bottom or a pear-shaped flask, and 30g of K10 (or Al-pillared clay) was added. The acetone was then evaporated in a rotary evaporator and the claycop was crushed to a powder and placed in a dessicator.

B. n-Butyl nitrate nitration of toluene[23].

Toluene and clay catalyst were placed into a 50-mL, three-necked, round bottom flask equipped with a distillation column, 25-mL addition funnel, and a magnetic stirrer. n-Butyl nitrate was poured into the addition funnel, and the reaction vessel was heated to the desired temperature. The n-butyl nitrate was added slowly and the reaction was allowed to continue until the desired time had elapsed. The clay catalyst was then gravity filtered off while hot and washed with hexane. Nitrobenzene was used as the internal standard (usually 1g) for analysis by GC.

C. Fuming (90%) Nitric acid nitration of toluene[21].

This reaction was carried out in a hood. The desired quantities of toluene and K10 (for amounts see Table V) were placed in a 250-mL, three-necked, round bottom flask equipped with a distillation column, 25-mL addition funnel, and magnetic stirrer (for higher amounts of K10 a mechanical stirrer was used). The fuming nitric acid was poured carefully into the addition funnel. A flow of N_2 was bubbled through the system and a water trap was employed to prevent the excess nitrogen oxides from escaping. The reaction vessel was placed in a water bath at room temperature. The acid was added slowly to the reaction flask and the reaction was continued for the desired time (see Table V). Na_2CO_3 solution (5 or 10%) was used to neutralize the excess HNO_3 in the reaction mixture and most of the water was removed by separatory funnel. The remaining water was removed with anhydrous $MgSO_4$, which was filtered off. Nitrobenzene (2g) was added and the mixture was then analyzed by GC.

D. Copper Nitrate / Acetic Anhydride nitration of toluene[22,25].

One milliliter of toluene and 50 mL of n-hexane were poured into a 250-mL, three-necked, round bottom flask equipped with a distillation column, 25-mL addition funnel, and magnetic stirrer. A quantity (5g) of 65% clay, 35% $Cu(NO_3)_2$ (1:1 mole ratio of $Cu(NO_3)_2$ to toluene) was then added to the solution. The reaction vessel was sealed, placed in a water bath at room temperature, and stirred vigorously. The acetic anhydride (or trifluoroacetic anhydride) was added slowly from an

addition funnel to the slurry and the reaction was allowed to continue for 3hr. The clay-copper nitrate solid was filtered off, and the product was washed with water, and dried with $MgSO_4$. The hexane was removed by rotoevaporation and 0.5 g of nitrobenzene was then added to the filtrate as an internal standard for GC analysis. In order to keep the mole ratios the same, experiments that used other anhydrides, solid acids, or percentages of clay followed the same procedure except that the amounts differed.

E. Gas chromatographic analysis of nitration.

The mononitrated toluene products were analyzed by GC with FID detection using nitrobenzene as the internal standard. The column that was employed was a Supelco SPB-1, nonpolar, capillary column with an internal diameter of 0.75 mm and a length of 60 m. The peak areas of the mononitrotoluenes were divided by the peak area of the nitrobenzene, multiplied by 0.857 (the carbon number of nitrobenzene, 6, divided by the carbon number of nitrotoluene, 7), and then multiplied by the molar amount of the nitrobenzene to obtain the moles of the mononitrotoluene. The rationale for this comes from the work with isopropylation of biphenyl[15] in which the response factor of different hydrocarbons is simply the carbon number of the internal standard divided by the carbon number of the desired hydrocarbon. Because the nitrobenzene and the MNT only differ by one carbon, this method of calculation is valid.

This calculation could not be used for the dinitrotoluenes because of the second nitro group. Therefore, known solutions of differing molar ratios of nitrobenzene and dinitrotoluenes were analyzed and the relative peak areas (y) were plotted vs. the molar ratio (x) of the NB/DNT. The

slope of this equation is the response factor, but the entire equation was used to calculate the molar amount of the desired DNT.

A sample gas chromatogram is shown in Figure 6, and the results of the GC analysis are summarized in Table IV.

Table IV. Retention times and equations for nitrotoluenes.

Compound	Retention Time(min) *	Equation**
Nitrobenzene (NB)	13.48	Internal Standard
o-Nitrotoluene (ONT)	16.30	$\frac{\text{area ONT}}{\text{area NB}}(0.8571429)(\text{moles of NB})$
m-Nitrotoluene (mNT***)	17.68	$\frac{\text{area mNT}}{\text{area NB}}(0.8571429)(\text{moles of NB})$
p-Nitrotoluene (PNT)	18.29	$\frac{\text{area PNT}}{\text{area NB}}(0.8571429)(\text{moles of NB})$
2,4-Dinitrotoluene	28.58	$\frac{\frac{3.998 \times 10^{-3}}{\text{area NB}}}{\text{area 2,4-DNT}} + 6.6955 \times 10^{-2}$
2,6-Dinitrotoluene	26.07	$\frac{\frac{3.599 \times 10^{-3}}{\text{area NB}}}{\text{area 2,6-DNT}} + 1.5378 \times 10^{-2}$

*GC conditions are a column flow rate of 32 mL/min, column head pressure of 10 psi, initial temperature of 60°C for one minute, and they increased at a rate of 4 degrees per minute to a final temperature of 225°C

**Each equation reads as"moles MNT (or DNT)=····".

***mNT was used instead of MNT to distinguish it from mononitrotoluene.

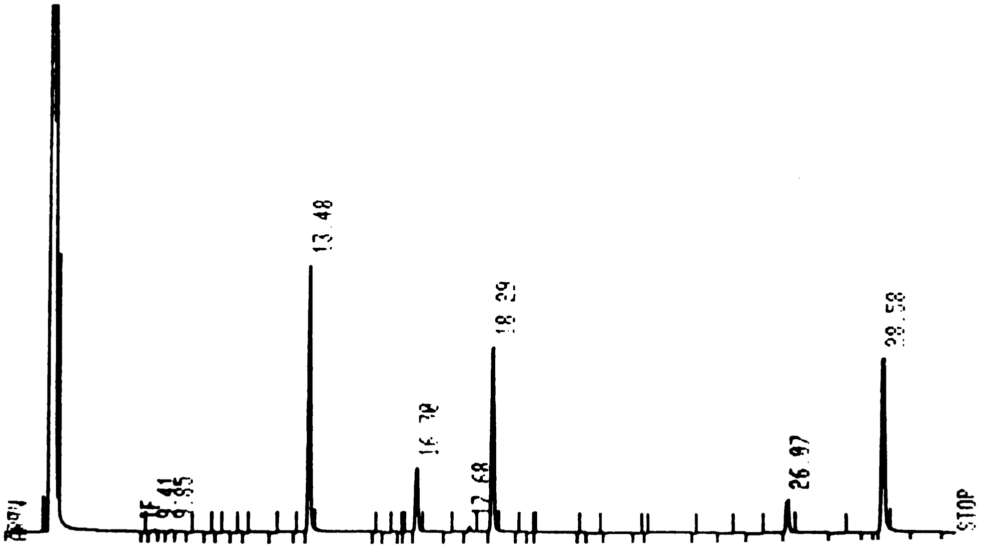


Figure 6. Sample gas chromatogram used to analyze the products of the nitration of toluene. Peak positions are nitrobenzene, 13.48 min; o-nitrotoluene, 16.30 min; m-nitrotoluene, 17.68 min; p-nitrotoluene, 18.29 min; 2,6-dinitrotoluene, 26.07 min; 2,4-dinitrotoluene, 28.58 min.

III. Results and Discussion

A. n-Butyl nitrate nitration of toluene.

Using n-butyl nitrate as a nitrating agent and Nafion-H as a catalyst, Olah[23] reported a yield of 96% of mononitrotoluenes with a o:m:p distribution of 50:3:47 over a reaction period of 6 hr at 80°C and a mole ratio of 0.365 moles of n-butyl nitrate per mole of toluene. In an effort to repeat this result, Nafion-H was purchased from Aldrich and was used in the present work at a 2:1 mole ratio of n-butyl nitrate / toluene, but the conversion of toluene was only 4%, even in the presence of a greater amount of n-butyl nitrate than used by Olah. The results indicate that commercially available Nafion-H is not as reactive as Olah's material. Further work with Nafion-H is needed to determine the reproducibility of Nafion-H as a catalyst for nitration with n-butyl nitrate.

Also, in the present work H_2SO_4, K10 and alumina pillared clays were used in place of Nafion-H. The results are summarized in Table V. the best reactions (using H_2SO_4 as catalyst), after work-up with 5% Na_2CO_3 and anhydrous $MgSO_4$, gave a 33% yield with a distribution of mononitrotoluenes of o:m:p = 53:4:42. The results of nitration of toluene with H_2SO_4 as catalyst provide a reference for comparison with Nafion-H and the clays. At reaction conditions and n-butyl nitrate / toluene ratios comparable to those used by Olah (0.37-2.0), K10 as a catalyst afforded yields in the range 4.9-9.3% and o:m:p product distributions of 44:3:53.

Table V. Nitration of toluene with n-butyl nitrate.

Reaction	catalyst	Mole ratio* N/Tol	Amount of catalyst (g)	Time (hr)	Temp (°C)	Yield %**	Distribution (o:m:p)
4.5ml n-Butyl nitrate and 2mL toluene	Nafion-H	2	1	4.33	100-110	4.0	50:3:46
4ml n-Butyl nitrate and 10mL toluene	H_2SO_4	0.365	1	20	100-110	33	53:4:42
same	K10	0.365	1	6	80	4.9	45:3:52
same	K10	0.365	1	20	100-110	5.6	44:3:53
same	K10	0.365	2	48	100-110	8.2	44:3:53
same	K10	0.365	2	132	100-110	9.2	44:3:53
4.5ml n-Butyl nitrate and 2mL toluene	K10	2	2	20	100	9.3	45:3:53
4.5ml n-Butyl nitrate and 2mL toluene	Al-pillared Wyo. Mont.	2	2	72	100-110	2.6	48:3:48
4.5ml n-Butyl nitrate and 2mL toluene	Al-pillared F. Hectorite	2	2	72	100-110	5.9	37:2:60

*Mole ratio of n-butyl nitrate to toluene.

**Based on limiting reagent.

Alumina-pillared clays afforded smaller yields than K10 (2.6-5.9%), but the product distribution showed a greater regioselectivity toward the para isomer (60% with aluminium pillared F-hectorite). Also, the yield of meta isomer was a minimum with aluminium pillared F-hectorite. The low yields would indicate that the acidity of neither K10 nor the alumina-pillared clays is sufficiently strong to facilitate this reaction in a reasonable time under these conditions (not a very reasonable possibility considering that both materials are very strong acids) or that the accessibility of the acid sites for n-butyl nitrate is not very good (equally unreasonable, since K10 has the larger sized mesopores). It is more likely that the n-butyl nitrate is not an especially effective reagent for this type of reaction.

B. Fuming (90%) Nitric acid nitration of toluene[21].

As reported earlier, the method of nitrating toluene proposed by Gubelmann who used a 1:70 mole ratio of HNO_3 to toluene and 0.58g of K10 per mL of toluene is not practical for commercial nitration. Therefore, the same method of nitrating toluene was performed in the present work except that the molar ratios of nitric acid / toluene were much larger (0.56-2.23). Nitration without catalyst afforded yields of 32-37% with a mononitrotoluene product distribution (o:m:p) of 57:5:38 at a mole ratio of 1.12 moles of nitric acid per mole of toluene, and over a reaction time of 3 hr at 25°C. As summarized by the results in Table VI, the nitration of toluene under the same conditions in the presence 20g of K10 as catalyst gave no noticeable change in yield (36%) nor in product distribution (56:5:39). Decreasing the mole ratio of HNO_3 / toluene to 0.56 afforded the same yield (35%), and the distribution of products changed only sightly (53:5:42). It would appear from these results that

Table VI. Nitration of toluene with 90% HNO_3 and K10 as catalyst.

Reaction	Mole ratio*	Amount of K10 (g)	Reaction time (hr)	Temp (°C)	Yield. %**	Distribution (o:m:p)
50mL toluene and 25mL 90% HNO3	1.12	0	2	25	32	57:5:38
same	1.12	0	3	25	37	57:5:38
25mL toluene and 25mL 90% HNO_3	2.23	0	3	25	81	58:4:38
50mL toluene and 25mL 90% HNO3	1.12	20	3	25	36	56:5:39
100mL toluene and 25mL 90% HNO3	0.56	50	3	25	35	53:5:42

*Mole ratio of HNO_3 to toluene.

**Based on limiting reagent.

K10 is not an effective catalyst for nitration of toluene with HNO_3 at practical HNO_3 / toluene ratios.

C. Copper Nitrate / Acetic Anhydride nitration of toluene.

Laszlo and coworkers have reported 75-97% yields of MNT with product distributions (o:m:p) of (44:3:53).[21,24] In the present study the method employed by Laszlo, et al was repeated to determine whether their results could be duplicated. As shown by the results in Table VII, a similar conversion was achieved, but the MNT product distribution differed significantly (49:3:48). Laszlo et al varied the amounts of acetic anhydride (6-9.5mL) in the reaction, as well as the amount of $Cu(NO_3)_2$ they impregnated on the catalyst (20-26g of $Cu(NO_3)_2$ per 30g of K10) with no reason given as to why.

In the present study an aluminum-pillared Wyoming Montmorillonite (APWM) was used as a catalyst instead of K10 in the nitration of toluene with $Cu(NO_3)_2$ and $(CH_3CO)_2O$. The results, as seen from Table VII, were almost identical to those obtained with K10, namely, 88% yield of mononitrotoluenes with a (o:m:p) MNT product distribution of 49:3:48. The lack of any change in regioselectivity prompted the use of other catalysts. The conversions of toluene ranged from 11% with mordenite (58:3:39) to 74% with imogolite pillared beidelite (Figure 4) (45:2:53). The only differences between the catalysts in Table VII were a result of changing the pillar size (chromium pillared and imogolite pillared WM vs. APWM) or changing the catalyst (mordenite and MCM-41 (<40Å) vs. APWM). The probable cause of these differences will now be examined.

Table VII. Nitration of toluene with $Cu(NO_3)_2$ at 25°C.

Support	Amt of catalyst *	Toluene (mL)	Acetic Anhydr. (mL)	Solvent	Mole ratio** Cu /Tol	time (hr)	% Yield of MNT***	Distribution MNT (o:m:p)
100% $Cu(NO_3)_2$†	1.77	1 (9.4×10^{-3} mol)	9.5 (0.10 mol)	50mL n-hexane	1	3	42	60:3:37
K10	5	1	9.5	50mL n-hexane	1	3	87	49:3:48
Al-pillared Wyoming mont.	5	1	9.5	50mL n-hexane	1	3	88	49:3:48
Al-pillared F-Hectorite	5	1	9.5	50mL n-hexane	1	2.7	51	51:2:46
Imogolite pillared Wyoming Mont.	2.9	0.58	5.5 (0.058 mol)	50mL n-hexane	1	3	72	45:2:52
Imogolite pillared Beidelite	5	1	9.5	50mL n-hexane	1	3	74	45:2:53
Chromia-pillared Wyoming Mont.	1.9	0.38	9.5	50mL n-hexane	1	3	72	46:2:51
MCM-41 (<40Å)	2.3	0.47	9.5	50mL n-hexane	1	3	71	56:3:41
Mordenite	5	1	9.5	50mL n-hexane	1	3	11	58:3:39

*The compositions of all catalysts, except for 100% $Cu(NO_3)_2$, are 35% $Cu(NO_3)_2$ and 65% clay support.

**Mole ratio of $Cu(NO_3)_2$ to toluene, excluding clay where appropriate.

***Percent yield of MNT's based on toluene as limiting reagent.

†The $Cu(NO_3)_2$ was subjected to the same acetone treatment used to prepare the clay supported reagent.

1. *Pore effect on nitration.*

A study of the effect of the K10 content of the supported copper nitrate catalyst was carried out. The results are listed in Table VIII and plotted in Figure 7. The graph shows that above 40% K10 no significant difference in the yield of nitrated products nor in regioselectivity was observed for the K10 supported reagent. Similar results were obtained with APWM supported copper nitrate. The increase in yield can be attributed to the acidity of K10 up to 65wt% K10 (87% yield) above which the clay seems to act as a physical barrier to the reactants. The increase in selectivity towards the para isomer most likely is caused by physical restriction of the reagents within the mesopores (randomly distributed in K10) as well as by the steric hinderance of the methyl group on toluene toward ortho attack.

A possible explanation for the observed regioselectivity in the K10 supported copper nitrate would be that the mesopores allow the reagents access to the copper nitrate but are small enough to restrict attack on toluene to the para position provided that one does not have immediate access to another mesopore as in MCM-41. The micropores within the pillared clay derivatives are accessible for this nitration method only with a larger pillar size and then a mesopore is necessary to provide access to a micropore.[15]

Evidence for this explanation comes from the results of changing the clay pillar size and from the use of zeolites. The larger pillars give rise to higher para selectivity (the o:m:p MNT product distributions with imogolite pillared beidelite or imogolite pillared WM is 45:2:53 versus 49:3:48 with K10) due to the fact that the micropores are larger in the imogolite pillared clays, which can incorporate the reactants more easily

Table VIII. Nitration of toluene with $Cu(NO_3)_2$ at 25°C. Effect of loading of $Cu(NO_3)_2$ on K10-Montmorillonite.

%Clay in K10-$Cu(NO_3)_2$	Amt of catalyst (g)	Toluene (ml)	Acetic Anhydr. (ml)	Solvent	Mole ratio* Cu/Tol	time (hr)	Conv. %**	Distribution (o:m:p)
***0	1.77	1	9.5	50mL n-hexane	1	3	42	60:3:37
5	1.86	1	9.5	50mL n-hexane	1	3	32	59:3:38
10	1.96	1	9.5	50mL n-hexane	1	3	37	57:3:40
20	2.20	1	9.5	50mL n-hexane	1	3	60	53:3:44
40	2.94	1	9.5	50mL n-hexane	1	3	80	50:3:47
65	5.00	1	9.5	50mL n-hexane	1	3	87	49:3:48
90	17.63	1	9.5	50mL n-hexane	1	3	81	50:3:47

*Mole ratio of $Cu(NO_3)_2$ to toluene, excluding clay where appropriate.

**Percent yield of MNT's.

***Addition of just 5 drops of H_2SO_4 to the $Cu(NO_3)_2$ increases the yield to 80% with an o:m:p MNT product distribution of 59:3:38.

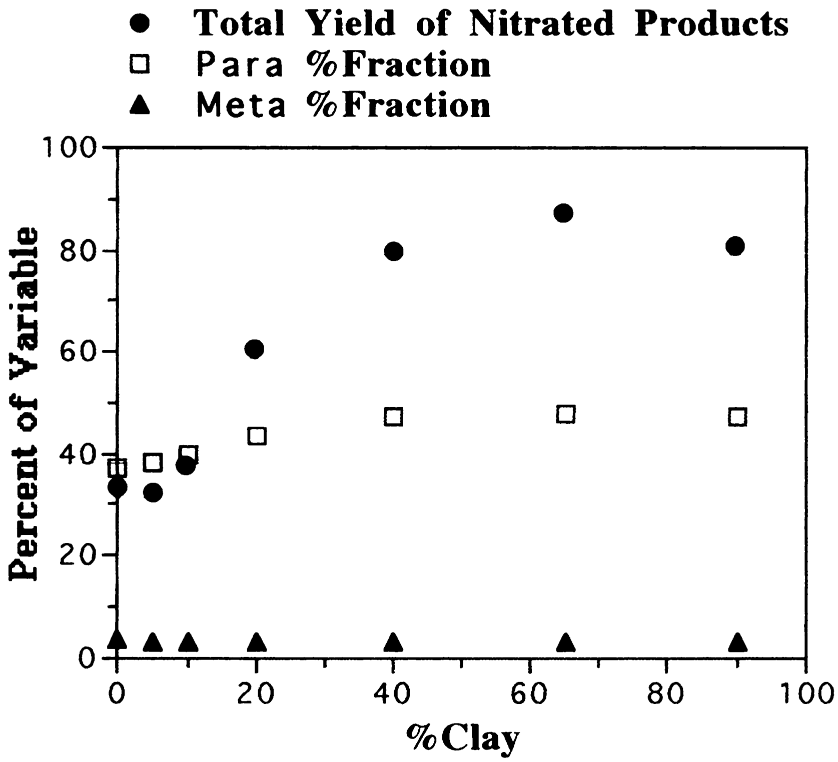


Figure 7. Effect of clay content in K10 supported $Cu(NO_3)_2$ (Claycop) on yield and selectivity in the nitration of toluene. Reaction Conditions: 3hr reaction time, 25°C, 50ml hexane, 1.00ml (9.40×10^{-3}mol) of toluene, 9.50ml (0.100mol) of acetic anhydride, the amount of catalyst used was varied in order to maintain a 1 to 1 mole ratio of $Cu(NO_3)_2$ to toluene.

than their alumina-pillared derivatives. This results in greater access to the acid sites in imogolite pillared WM. Zeolites have the opposite effect. In mordenite we have an entirely microporous structure which means not only lower access to the acid sites, but also, most of the copper nitrate has been restricted to the pores where the toluene cannot access it. Thus the nitration of toluene is restricted to the surface of the catalyst. Zeolites have higher affinity for water than clays. The adsorbed water can react with the anhydride to form carboxylic acid and lower the reactivity of the nitrating agent. This results in a lower yield (11%) than obtained in the absence of the zeolite (42%). Also, a MNT distribution resembling the uncatalyzed nitration (58:3:39). The MNT yield (71%) is increased significantly in the presence of MCM-41. The MCM-41 structure is more ordered than the pillared clay structure, which results in a less diffusion controlled reaction that favors the ortho isomer (56:3:42), as in the uncatalyzed nitration.

2. *Acidity effect on nitration.*

It has been stated already without proof that the acidity of the clays is what causes the increase in yield relative to anhydrous copper nitrate. An experiment was performed to test this hypothesis in which a few drops of H_2SO_4 replaced the clay as catalyst (Table VIII). As expected, the yield was doubled (80%) relative to the uncatalyzed nitration (42%), as was the case with the clay; however, the MNT product distribution (59:3:38) remained very close to that obtained for the uncatalyzed nitration (60:3:37), which gives further evidence for the proposed effect of the pores on selectivity.

3. *Anhydride effect on nitration.*

In Scheme 3 it is proposed that acetyl nitrate is the actual nitrating agent formed by reaction of acetic anhydride and copper nitrate. The clay could function as the base in place of the acetate ion, as well as protonating the acetyl nitrate. Laszlo et al[22,26] stated that acetic anhydride might perform this function as well as that of a dehydrating agent, although they did not offer any evidence to support this intermediate. Experiments were performed to see which of these functions acetic anhydride actually was performing. In the first experiment in which acetic anhydride was omitted altogether, no reaction resulted. Even the addition of H_2SO_4 did not faciltate the reaction (about one percent yield). Therefore, a molar amount of $MgSO_4$ equal to that of acetic anhydride was added to the reaction in case water was interfering with the catalyzing effect of H_2SO_4. The results were similar (no reaction), suggestive that the mechanism proposed in Scheme 2 is not happening to any appreciable extent, with this catalyst. In another experiment, not shown in Table VII, $Cu(NO_3)_2{\cdot}2.5H_2O$ (without acetone treatment to remove water) and acetic anhydride were employed in the nitration of toluene. The results were similar (42% conversion, o:m:p MNT product distribution of 60:3:38) to those of the acetone treated copper nitrate (42% yield, 60:3:37). These results strongly suggest that acetyl nitrate is the actual nitrating agent and the dehydrating effect of acetic anhydride is of little importance.

Other anhydrides were examined for their possible use as a substitute for acetic anhydride. The results are shown in Table IX. Propionic anhydride is not as reactive as acetic anhydride, which is shown by the lower MNT yield (38%), but the MNT distribution is about the same (49:2:49).

Table IX. Nitration of toluene with $Cu(NO_3)_2$ at 25°C(Anhydride effect).

Anhydride	Amt of Anhydr. (ml)	Tol. (ml)	Amt of catalyst 65% K10 & 35% $Cu(NO_3)_2$ (g)	Solvent	Mole ratio* Cu /Tol	time (hr)	% Yield **	%MNT ***	Dist. (o:m:p)	%Di ***	Dist. (2,6-:2,4-)
Acetic	9.5 (0.10 mol)	1	5	50mL n-hexane	1	3	87	100	49:3:48	0	0
Propionic	12.1 (0.094 mol)	1	5	50mL n-hexane	1	3	38	100	49:2:49	0	0
Trifluoro acetic	13.2 (0.094 mol)	1	1.77 g ($Cu(NO_3)_2$ only)	50mL n-hexane	1	3	97	89	45:1:54	11	25:75
Trifluoro acetic	13.2 (0.094 mol)	1	5	50mL n-hexane	1	3	75	65	31:2:67	35	25:75

*Mole ratio of $Cu(NO_3)_2$ to toluene, excluding clay where appropriate.

**Percent yield of nitrated products with toluene as limiting reagent.

***Percent fraction of MNT and DNT.

In an experiment performed by Masci[27a] trifluoroacetic anhydride (TFAA) was used to activate tetrabutylammonium nitrate toward nitration of various aromatics, but neither he nor anyone[27b] else experimented with TFAA and copper nitrate. TFAA gave surprising results, the first observed yield of dinitrotoluenes at room temperature. TFAA is rather reactive in its own right which accounts for the high yield without clay [96% yield of nitrated products with 89% MNT (45:1:54) and 11% DNT with a product distribution of 2,6-DNT: 2,4-DNT of 25:75]. The yield is reduced in the presence of clay, but the higher DNT yields obtained can be accounted for by the reactivity of trifluoroacetyl nitrate vs. that of acetyl nitrate. The TFAN doesn't need an acid catalyst to enhance its reactivity because the electron withdrawal of the fluorines atoms enhances the disassociation of nitronium and trifluoroacetate ions. Also, upon filtering, the TFAA seems to be able to complex the Cu sufficiently enough to leach it out of the clay into the hexane solvent, which results in a blue-green solution that turns yellow after washing with water.

Because $Cu(NO_3)_2$/TFAA was the first case in which clay inhibited the reaction, a detailed investigation with different percentages of K10 was carried out with TFAA as was done with acetic anhydride. The results are listed in Table X and plotted in Figures 8, 9, and 10. They indicate that the mononitration is not catalyzed by K10 and occurs homogeneously. However, the clay now catalyzes heterogeneously the formation of dinitrotoluenes to a more appreciable extent than does uncatalyzed copper nitrate and at a different optimum amount of K10 (40% instead of 65% for acetic anhydride). At first glance the results indicate that this reagent is more selective towards para; but the distributions of MNT with respect to the percentage of K10 seems to indicate that the ortho MNT steadily

Table X. Nitration of toluene with $Cu(NO_3)_2$ and TFAA at 25°C.

%K10 in catalyst	Amt.	TFAA (mL)	Tol. (mL)	Solvent	Mole ratio *Cu. /Tol	time (hr)	% Yield **	%MNT ***	Dist. (o:m:p)	%Di ***	Dist. (2,6- :2,4-)
0	1.763	13.2 (0.094 mol)	1 (9.4x 10^{-3} mol)	50mL n-hexane	1	3	97	89	45:1:54	11	25:75
10	1.959	13.2	1	50mL n-hexane	1	3	80	80	42:1:57	19	18:82
20	2.204	13.2	1	50mL n-hexane	1	3	81	63	33:2:65	37	15:85
40	2.938	13.2	1	50mL n-hexane	1	3	75	51	25:2:73	49	16:84
65	5	13.2	1	50mL n-hexane	1	3	75	65	31:2:67	35	16:84
90	17.63	13.2	1	50mL n-hexane	1	3	73	100	46:2:52	0	0:0

*Mole ratio of $Cu(NO_3)_2$ to toluene, excluding clay where appropriate.

**Percent yield of nitrated products with toluene as limiting reagent.

***Percent fraction of MNT and DNT.

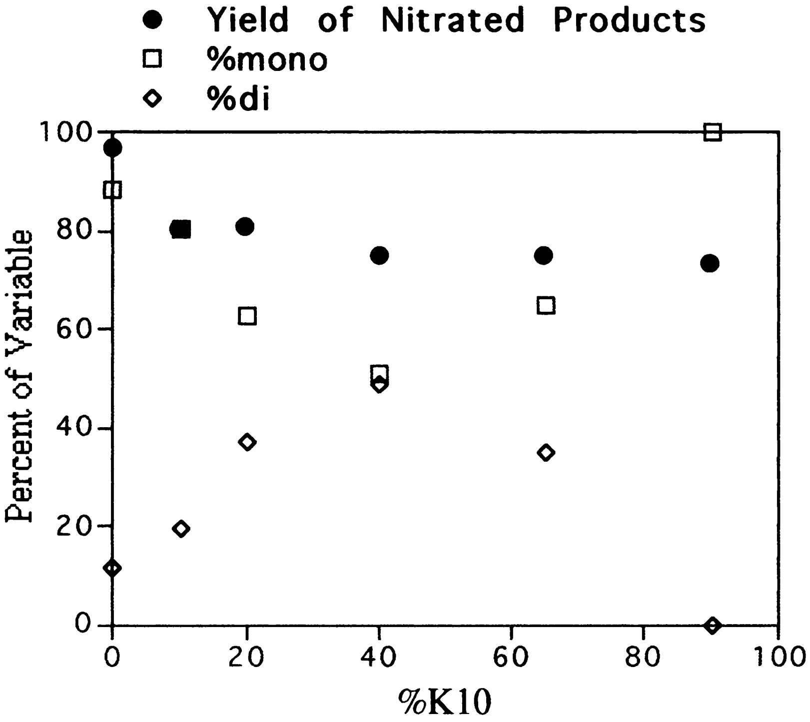


Figure 8. Distribution of mono and dinitrotoluene derivatives in the TFAA / $Cu(NO_3)_2$ nitration of toluene in hexane (1 mL toluene/50 mL hexane). Reaction temperature, 25°C; reaction time, 3 hr. Values represent the percent of the nitrotoluene derivative with respect to the total molar amount of all the nitrotoluene derivatives.

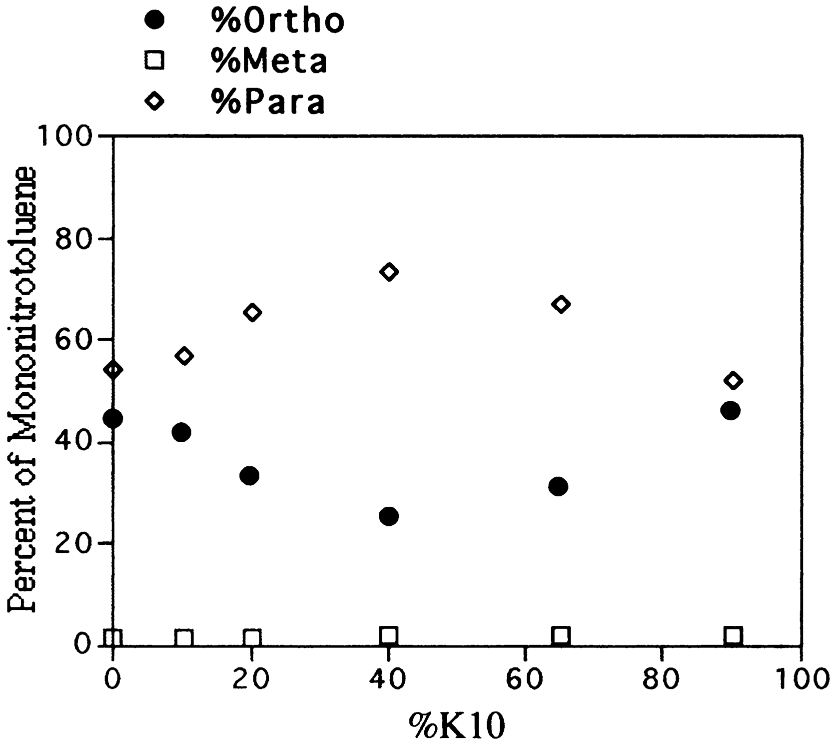


Figure 9. Distribution of mononitrotoluenes in the TFAA / $Cu(NO_3)_2$ nitration of toluene in hexane (1 mL toluene/50 mL hexane). Reaction temperature, 25°C; reaction time, 3 hr. Values represent the percent of mononitrotoluene with respect to the total molar amount of all mononitrotoluenes.

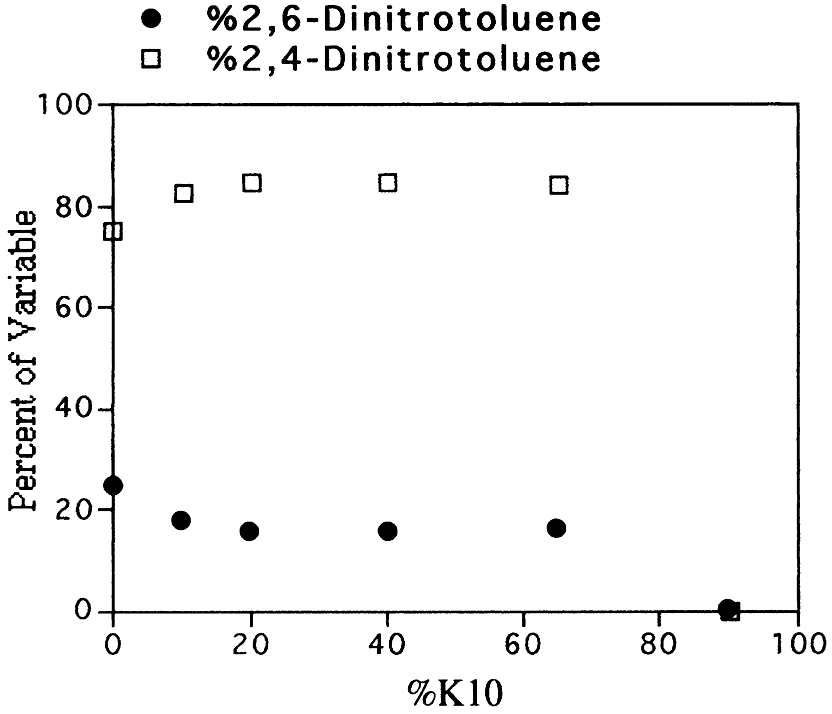


Figure 10. Distribution of dinitrotoluenes in the TFAA / $Cu(NO_3)_2$ nitration of toluene in hexane (1 mL toluene/50 mL hexane). Reaction temperature, 25°C; reaction time, 3 hr. Values represent the percent of dinitrotoluene with respect to the total molar amount of all dinitrotoluenes.

decreases as the amount of dinitrotoluenes increases. This implies that the dinitrotoluenes are primarily formed from the ortho MNT isomer. To verify this assumption, an experiment was conducted with the 40% K10 over a 15 min reaction time. A 92% yield (a result of adding the TFAA at once instead of slowly) and a MNT o:m:p distribution of 36:1:63 versus a 75% yield and a MNT isomer distribution of 25:2:73 for the 3 hour reaction with the 2,6:2,4- dinitrotoluene distribution remaining the same (15:85) with a substantially decreased DNT yield (30% vs. 49%) indicates that the assumption probably is correct.

4. *Solvent effect on nitration.*

It has been reported that the use of halogenated solvents also may increase the para selectivity for both the heterogeneous[22] reaction, using $Cu(NO_3)_2$/acetic anhydride as the nitrating agents, and the homogeneous[27] reaction, using tetrabutylammonium nitrate/TFAA as the nitrating agents. The effects of solvent were studied and the results are shown in Table XI. One can readily see from the table that at higher concentrations of toluene in CCl_4 (50 mL) there is a substantial difference in para selectivity between CCl_4 (45:2:53, 69% conversion) and hexane(49:3:48, 87% conversion). However, at a concentration of 1mL of toluene in 2000mL of solvent, which approximates infinite dilution, this difference disappeared and one finds that hexane gives a similar selectivity (27:2:71 in n-hexane vs. 25:2:73 in CCl_4), but almost doubles the yield (63% vs. 34). Laszlo, et al[22] and Bernardo[27] attribute the effect of the CCl_4 to solvent polarizability and the fact that substituted aromatic compounds tend to be polarized at the substituent position. Thus CCl_4 solvation which is more polarizable than hexane leads to easier solvation. This explanation is good for higher concentrations of CCl_4 but does not account for the observed

Table XI. Solvent and dilution effects in the nitration of toluene with $Cu(NO_3)_2$ at 25°C.

Catalyst (or nitrating agent)	Amt of catalyst (g)	Toluene (mL)	Acetic Anhydr. (mL)	Solvent	Mole ratio* Cu /Tol	time (hr)	Yield %**	Distribution (o:m:p)
$Cu(NO_3)_2$ "anhydrous"	5	1	6 (0.063 mol)	2L CCl_4	2.82	41	0	0
K10 & $Cu(NO_3)_2$	5	1	9.5 (0.10 mol)	50mL n-hexane	0.99	3	87	49:3:48
K10 & $Cu(NO_3)_2$	5	50	9.5	50 mL toluene		3	67†	49:2:49
K10 & $Cu(NO_3)_2$	5	1	6	2L CCl_4	0.99	41	34	25:2:73
K10 & $Cu(NO_3)_2$	5	1	6	2L n-hexane	0.99	28	63	27:2:71
K10 & $Cu(NO_3)_2$	5	1	9.5	50mL CCl_4	0.99	3	69	45:2:53
K10 & $Cu(NO_3)_2$	5	1	9.5	100mL CCl_4	0.99	3	69	42:2:56
K10 & $Cu(NO_3)_2$	5	1	9.5	200mL CCl_4	0.99	3	51	39:2:59
K10 & $Cu(NO_3)_2$	5	1	9.5	400mL CCl_4	0.99	3	50	34:2:64

*Mole ratio of $Cu(NO_3)_2$ to toluene, excluding clay where appropriate.

**Percent yield of MNT's based on toluene as limiting reagent.

†Percent conversion of nitrate groups.

effects under conditions of extreme dilution. A more complete explanation would be that at high dilution toluene is completely solvated no matter which solvent one uses and this leads to high steric hinderance in both solvents (hence high selectivity in both cases); however, hexane is not as tightly held by toluene as is CCl_4, therefore, the nitrating agent can more easily displace hexane (hence higher yield). Also, because the para position is more reactive, any added steric hinderance will affect the ortho position more so than the para.

Figure 11 summarizes the effectiveness of selected nitration methods. n-Butyl nitrate as a nitrating agent is not very reactive but this might be caused by not purifying the reagent before use. In order to increase the selectivity of nitric acid, K10 must be used in such large amounts that makes carrying out the reaction not very practical. By far $Cu(NO_3)_2$ and acetic anhydride or TFAA are the best systems for nitrating toluene at room temperature and the addition of K10 as a catalyst improves the selectivity significantly.

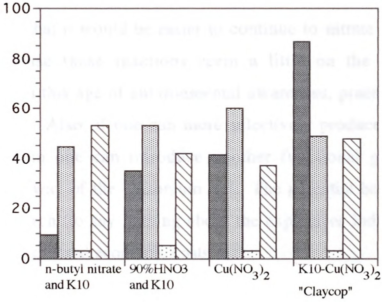


Figure 11. Selected examples of different methods for nitration of toluene. Each column represents percentage of overall yield (dark grey), and the distribution (%) of ortho (light grey), meta (sparse dots), and para (diagonal striped) mononitrated products. Reaction conditions for each are as follows: 4.50mL (3.86×10^{-2}mol) of n-butyl nitrate, 2.00mL (1.88×10^{-2}mol) of toluene, 2.00g K10, 100°C, 20hr; 25.0mL (5.25×10^{-1}mol) of 90%HNO_3, 100mL (9.40×10^{-1}mol) of toluene, 50g of K10, 25°C, 3hr; 1.77g (9.40×10^{-3}mol) of $Cu(NO_3)_2$, 1.00mL (9.40×10^{-3}mol) of toluene, 25°C, 3hr; 5.00g K10 Claycop (9.40×10^{-3}mol $Cu(NO_3)_2$), 1.00mL toluene (9.40×10^{-3}mol), 9.50mL (0.100mol) of acetic anhydride, 25°C, 3hr.

IV. Conclusions

After examining the results of this research one might come to the conclusion that it would be easier to continue to nitrate the old fashioned way, because these reactions seem a little on the impractical side. However, in this age of environmental awareness, practicality is of lesser importance. Also, if one can more selectively produce one isomer over another, then one can introduce another functional group at the nitro position by way of the diazonium salt. The potential benefits to medicine and to research (to say nothing about the explosives industry) may far out weigh the increased economic costs.

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