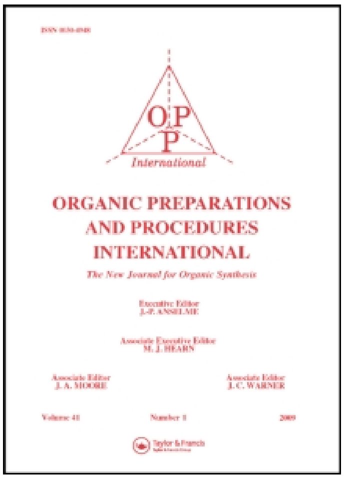

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Cuauhtemoc Pérez[a]; Salud Pérez-Gutiérrez[a]; Sergio A. Gómez[b]; Gustavo A. Fuentes[b]; Miguel A. Zavala[a]
[a] Department of Biological Systems, Universidad A. Metropolitana-Xochimilco, México, DF, MÉXICO [b] Department of Process Engineering, Universidad A. Metropolitana-Iztapalapa, México, DF, MÉXICO

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NITRATION OF PHENOL, CRESOL, AND ANISOLE USING CERIC AMMONIUM NITRATE SUPPORTED ON A CLAY AND ON A PILLARED CLAY

Cuauhtemoc Pérez*[†], Salud Pérez-Gutiérrez[†], Sergio A. Gómez[††],
Gustavo A. Fuentes[††] and Miguel A. Zavala[†]

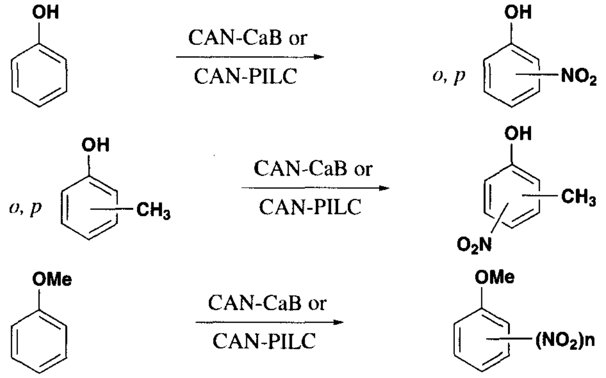
[†]Department of Biological Systems, Universidad A. Metropolitana-Xochimilco
A.P. 23-181, 04960 México D. F., MÉXICO
[††]Department of Process Engineering, Universidad A. Metropolitana-Iztapalapa
A.P. 55-534, 09340 México, D. F., MÉXICO
E-mail: cperezg@correo.xoc.uam.mx; gfuentes@xanum.uam.mx
Tel: (52) 55 54 83 72 63

The nitration of organic compounds is widely used as a step in the synthesis of pharmaceutical products and other fine chemicals. A large variety of nitrating agents are available, ranging from HNO_3 to metallic nitrates-H_2SO_4 and HCl,[1] as well as nitronium salts,[2-4] or acetyl nitrate.[5,6] However, in spite of the different studies performed and of the improvements made to the nitration process, there are still significant problems associated with poor regioselectivity, low yield, and environmental pollution, in addition to the risks involved in handling some of the reagents. Even in the case of some industrial processes, nitration produces a significant fraction of isomers that have no direct use. They have to be reprocessed or disposed of,[7] hence the overall economic balance is affected.

One interesting alternative to the use of liquid nitrating agents involves the development of solid reagents prepared from suitable solid supports[7] such as HNO_3 supported on graphite[8] or on zeolite β,[6] $Fe(NO_3)_3$ supported on a bentonite,[9,10] HNO_3 supported on silica,[11] and benzyl nitrate on zeolite.[12] The yield with solid reagents is, in general, better than when classical nitrating reagents are used, and environmental problems and handling risks are reduced. However, use of a solid reagent introduces new parameters that affect reaction activity and selectivity, so careful fine-tuning of the nitration process is required.

We have been interested for some time in the utilization of clays in chemistry, in particular that of montmorillonite, the main component of bentonites.[10] The lamina comprising this material consists of an octahedral AlO_x layer sandwiched between tetrahedral SiO_y layers. Charge compensating cations such as Na^+, Ca^{+2} and K^+ are located in octahedral holes in the interlaminar space. In the intermediate charge density range for silicoaluminates, where montmorillonite is located, it is possible to separate the lamina by absorption of water or other polar compounds. Consequently, montmorillonite swells and it readily accepts "guest" structures in its interlaminar space. The process is usually reversible, provided no permanent bonds are created between the new interlaminar species and the lamina. This characteristic of montmorillonite has been exploited in different fields, including the preparation of solid nitration reagents such as Clayfen,[14] $Fe(NO_3)_3$ supported on K-10 bentonite, or Claycop ($Cu(NO_3)_2$ supported also on K-10).[15,16] The structure of the clay can also be altered irreversibly by exchanging the charge compensating cations with large oligomeric inorganic cations such as $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$. These oxyhydroxides dehydroxylate upon heating and form nanometer-sized proto-oxide structures that remain in the interlaminar space. The resulting materials, generically known as pillared clays (PILC), have thermally stable permanent microporosity. A new microenvironment for reaction is hence made available because both polar and non-polar compounds of practical interest can diffuse inside the newly created interlaminar space and interact with active sites on the surface of the solid. PILC are suitable catalysts or supports for catalysts,[17] and they have applications as adsorbents.[18,19] It is then expected that the activity of solid reagents prepared from PILC may differ from that of reagents prepared using untreated montmorillonite because of the different local environment for reaction.

This article presents results of the nitration of oxygen-bearing aromatic hydrocarbons, particularly of phenol, *o*- and *p*-cresol, and anisole because of the industrial importance of the products. Ceric ammonium nitrate (CAN) supported on a Ca-bentonite (CAN-CaB) or on a pillared bentonite (CAN-PILC) were used as nitrating agent.



Nitration of Phenol, Cresols and Anisole Using CAN-clay Adducts

Scheme 1

Both CAN-CaB and CAN-PILC had excellent nitrating activities in some of the solvents used, with no indication of oxidation reactions. We checked this last possibility because CAN has been used to oxidize aliphatic alcohols.[20-22] A report states that CAN supported on a K-bentonite (K-10) has little or no activity as a nitrating agent in tetrahydrofuran.[6] Another report shows that CAN supported on K-10 is active in the nitration of coumarin.[23] Our results allow explanation of that apparent contradiction; we show in this work that solvent effects are important during nitration with solid reagents, altering significantly both activity and regioselectivity.

To determine the scope of the reactivity of our nitrating materials, we attempted to nitrate toluene, a moderately activated molecule. Tests were performed with the CAN-PILC adduct in hexane, $CHCl_3$ or water as solvents, and no activity was observed. Neat CAN in methanol or THF also failed to nitrate or oxidize phenol. *Tables 1-3* summarize the results of the nitration of phenol with CAN-CaB or CAN-PILC using solvents with different polarities. The only products formed were *o*- and *p*-nitrophenol. Complete regioselectivities of either isomer could be attained depending on the solvent-adduct combination. In the case of CAN-PILC, complete reversal in selectivity occurred when high polarity solvents such as dimethyl sulfoxide or water were used. Although the literature reports yields of nearly 100% to *o*-nitrophenol when metallic nitrates are used as nitrating agents in solution,[15] in most cases a mixture of *ortho*- and *para*-isomers is obtained. Nitration of phenols generally lacks positional selectivity and a statistical distribution (67% *ortho*- and 33% *para*-nitration) is frequently observed.[7] Our results show that either *o*- or *p*-nitrophenol can be produced essentially pure or at least in significant excess by using CAN-CaB or CAN-PILC. *o*-Nitrophenol can be produced with 100% regioselectivity only when CAN-PILC is used. *p*-Regioselectivity, on the other hand, is possible with both adducts, but the solvent plays a key role. An interesting case because of its ecological implications is that of CAN-PILC in water, a system that gives only *p*-nitrophenol, a chemical frequently used in the

Table 1. Phenol Nitration in Low Polarity Solvents

Solvent	ε	Adduct	Phenol Conversion	Nitrophenol Yield[a]		
				ortho	*para*	$\frac{p}{p+o}$
Hexane	1.890	CAN-CaB	45.8	0.0	45.8	1.00
		CAN-PILC	----	----	----	----
CCl_4	2.238	CAN-CaB	32.2	17.4	14.2	0.45
		CAN-PILC	72.0	50.8	36.3	0.42
Benzene	2.284	CAN-CaB	56.5	17.2	39.8	0.70
		CAN-PILC	47.6	0.0	47.6	1.00
Ethyl ether	4.335	CAN-CaB	59.9	34.9	25.0	0.42
		CAN-PILC	21.6	21.6	0.0	0.00
$CHCl_3$	4.806	CAN-CaB	49.7	31.6	18.3	0.64
		CAN-PILC	66.6	0.0	66.6	1.00
AcOEt	6.02	CAN-CaB	67.1	0.0	67.1	1.00
		CAN-PILC	21.6	21.6	0.0	0.00

a) *meta*-Nitrophenol was not formed.

manufacture of fine chemicals.[7] It is plausible to ascribe the high regioselectivities observed in this study to preferred interactions between surface groups and molecules of the reagent. Such interactions are absent when homogeneous nitrations are employed.

Table 2. Phenol Nitration in Medium Polarity Solvents

Solvent	ε	Adduct	Phenol Conversion	Nitrophenol Yield[a]		
				ortho	*para*	$\frac{p}{p+o}$
Acetone	20.7	CAN-CaB	19.9	8.2	11.7	0.59
		CAN-PILC	21.32	14.12	7.2	0.34
MeOH	33.62	CAN-CaB	0.0	----	----	----
		CAN-PILC	73.9	35.6	38.3	0.51
DMF	36.7	CAN-CaB	30.0	10.8	19.2	0.64
		CAN-PILC	17.2	17.2	0.0	0.00
CH_3CN	38.8	CAN-CaB	91.1	0.8	90.3	0.99
		CAN-PILC	94.5	63.65	30.9	0.32

a- *meta*-Nitrophenol was not formed.

Besides the effect of the clay, both activity and regioselectivity were highly dependent upon the solvent used. It is known that the solubility of the substrate, in this case of phenol, depends upon the solvent used. In addition, each solvent swells the untreated clay to different extents and its molecules alter the coordination structure of Ce^{4+}.

Table 3. Phenol Nitration in High Polarity Solvents

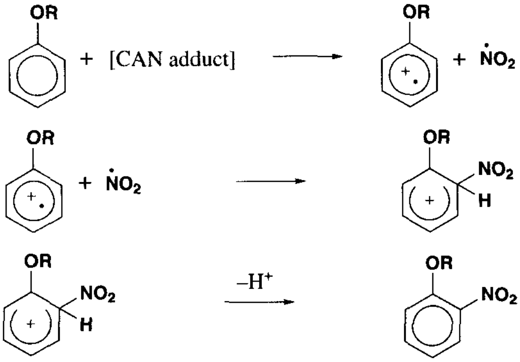
Solvent	ε	Adduct	Phenol Conversion	Nitrophenol Yield[a]		
				ortho	*para*	$\frac{p}{p+o}$
DMSO	46.7	CAN-CaB	0.0	----	----	----
		CAN-PILC	28.8	28.8	0.0	0.00
H_2O	86.37	CAN-CaB	0.0	----	----	----
		CAN-PILC	30.7	0.0	30.7	1.00

a- *meta*-Nitrophenol was not formed.

In spite of these observations, it is not yet clear how or whether reactivity and solvent properties can be precisely correlated. It was decided to use the dielectric constant (ε) of the solvent[25] to help organize the results, but it must be acknowledged that there was only a rough correlation with conversion. For low values of ε (1.8-6), phenol conversion with CAN-CaB was clustered in the 30-60% range (*Table 1*). In solvents with intermediate values of ε (20-38), the reactivity was in general low (*see Table 2*). We observed an exception in the case of acetonitrile. Use of solvents with large ε such as DMSO or H_2O, resulted in total loss of reactivity with CAN-CaB, as is shown in *Table 3*, an effect in part to be attributed to excessive swelling of the lamina.

That favors their complete separation and the loss of the microenvironment where nitration occurs. It is remarkable that by supporting CAN on the clay it was possible to nitrate phenol even in non-polar solvents. This was probably caused by a variation in the symmetry of the complex, from symmetric bidentate to asymmetric[26]. Such a change would result in a lower oxidation state of the central atom, hence turning it into a more reactive species. CAN-PILC had a different nitration activity pattern, compared to CAN-CaB, while still producing only *o*- and *p*-nitrophenols. In general, there was an increase in the degree of conversion when solvents with low and intermediate ε were used (*Tables 1 and 2*). Perhaps most importantly, the use of the CAN-PILC adducts in high polarity solvents gave excellent selectivities, as shown in *Table 3*. This was unexpected because $(NH_4)_2Ce(NO_3)_6$, neat or as an adduct with calcium bentonite, was totally inactive under the same conditions. It was also remarkable that a change in solvent, from dimethyl sulfoxide to water, changed the selectivity from 100% *o*- to 100% *p*-nitrophenol.

As was previously mentioned, the presence of a microporous environment plays an essential role in conferring activity to the CAN-clay system. As CAN is not active while neat, it is likely that only the CAN fraction located inside the interlaminar space is active for the reaction. Differences in reactivity between the adduct formed with the clay and the one formed with the pillared clay are caused by variations in the microenvironment during reaction. Changes in the microenvironment are particularly strong in the case of the calcium bentonite, which can expand freely in polar solvents, ultimately becoming totally delaminated and losing its microporosity. The interlaminar space of the pillared clay has a polarity dictated both by silanols on the surface of the tetrahedral SiO_y layers, also present on the regular clay, and by hydroxy groups on the pillars, consisting in this case of $Ga_xAl_yO_z$ structures.[13] The presence of a permanent microporous structure with confined spacing probably played a role as well. Although these factors are difficult to isolate, it is evident that the presence of a solid during nitration does play a significant role during nitration of phenol. This fact is consistent with other reports in the literature.[6] The nitration of phenol seems to follow the classical cation-radical mechanism,[27] shown in *Scheme 2*.



Cation-radical Mechanism During Phenol Nitration

Scheme 2

The evidence for such mechanism includes the presence of Ce^{3+} and the absence of *m*-nitrophenol after the reaction.[28,29] In the case of cresols and anisole, there is insufficient evidence to reach a conclusion about the mechanism.

The CAN-CaB adduct was active in the nitration of *p*-cresol only in hexane or chloroform as the solvents. In both cases, there was a 100% selectivity towards 2-nitro-4-methylhydroxybenzene (*Table 4*). When *o*-cresol was the substrate, there was activity only in methanol, giving 4-nitro-2-methylhydroxybenzene with 100% selectivity. The nitrating activity of the CAN-PILC adduct toward *o*- (or *p*-) cresol was significant in all the solvents tested. *Table 5* shows results in chloroform, methanol, and H_2O. Nitration of *p*-cresol in chloroform yielded only the mononitro compound (2-nitro-4-methylhydroxybenzene), whereas in methanol a nearly 1:1 ratio of dinitrated products (2,6- and 2,5-dinitro-4-methylhydroxybenzene) was obtained. With H_2O as the solvent, nitration of *p*-cresol resulted in 100% selectivity towards 2,6-dinitro-4-methylhydroxybenzene. When *o*-cresol was nitrated in chloroform using CAN-PILC the main product was the 4,6-dinitro-2-methylhydroxybenzene isomer and there were only traces of the mononitrate. Use of methanol as the solvent yielded 100% of the same dinitro compound. In water, the product mixture consisted of 15% of the mononitrate (4-nitro-2-methylhydroxybenzene) and 85% of the 4,6-dinitro compound.

Table 4. Nitration of *o*- and *p*-cresol using CAN-CaB

Solvent	Substrate	Conversion
Hexane	*o*-cresol	0.0
	p-cresol	97.7[a]
$CHCl_3$	*o*-cresol	0.0
	p-cresol	98.5[a]
MeOH	*o*-cresol	98.0[b]
	p-cresol	0.0

a) 2-nitro-4-methylhydroxybenzene. b) 4-nitro-2-methylhydroxybenzene. CAN-CaB was inactive in Ethyl ether, DMF, DMSO, or H_2O

Nitration of anisole using CAN-PILC resulted in polynitration in each of the three solvents tested (*Table 5*). This indicates the high nitrating activity of this adduct.

In conclusion, the formation of adducts between $(NH_4)_2Ce(NO_3)_6$ and clays activates the nitrating capacity of the reagent, while allowing for the control of selectivity during nitration of phenol. It is possible to direct yields and selectivities by changing the solvent and/or the structure of the CAN-clay adduct. Nitration with the $(NH_4)_2Ce(NO_3)_6$-pillared clay adduct can be directed to give only *ortho*- or *para*-nitrophenol, depending on the solvent used. The $(NH_4)_2Ce(NO_3)_6$ - clay adduct gave mainly the statistical *ortho/para* distribution, but the selectivity can be chosen in order to obtain only the *para*-isomer. The presence of *o*- and *p*-nitrophenols agrees with an ion-radical mechanism, although the effect of restricted geometries during reaction is not yet fully understood. The possibility of employing water instead of organic solvents, is attractive because pollution could be minimized. With water as the solvent, we attained 100% selectivity towards *para*-nitrophenol when the $(NH_4)_2Ce(NO_3)_6$-pillared clay adduct was used. This is the first report of such regioselectivity in water. Nitration of cresols and anisole were readily accomplished when the $(NH_4)_2Ce(NO_3)_6$-pillared clay adduct was used. In the case of *para*-cresol, the production of 2,6-dinitro-4-methylhydroxybenzene was favored by increasing the dielectric constant of the solvent. Water is also a good solvent for nitration of cresols and anisole. Moderately activated molecules such as toluene were not reactive with the CAN-clay adducts reported in this work.

Table 5. Nitration of *o*- and *p*-cresol and of anisole using CAN-PILC

Solvent	Substrate	Conversion	(2,5-; 2,6-; 4,6-dinitro)
$CHCl_3$	*o*-cresol	99.8[a]	(0; 0; 99.6)
	p-cresol	100[b]	----
	anisole	100[c]	----
MeOH	*o*-cresol	100[d]	(0; 0; 100)
	p-cresol	90.2[e]	(47.2; 43; 0)
	anisole	100[c]	----
H_2O	*o*-cresol	69.7[f]	(0; 0; 59.4)
	p-cresol	100[g]	(0; 100; 0)
	anisole	21.3[c]	----

a) 0.2% 4-nitro-2-methylhydroxybenzene and 99.3% of 4,6-dinitro-2-methylhydroxybenzene. b) 2-nitro-4-methylhydroxybenzene. c) Four polynitro compounds. d) 4,6-dinitro-2-methylhydroxybenzene. e) 43% of 2,6-dinitro-4-methylhydroxybenzene, and 47.2 of 2,5-dinitro-4-methylhydroxybenzene. f) 10.3% 4-nitro-2-methylhydroxybenzene and 59.4% of 4,6-dinitro-2-methylhydroxybenzene. g) 2,6-dinitro-4-methylhydroxybenzene

EXPERIMENTAL SECTION

The clay used was a calcium bentonite (BL3, Southern Clay Products, Inc.) with a cation exchange capacity of 80 meq/100g. The pillaring process was reported elsewhere.[13] The original clay and the pillared clay are referred to as CaB and PILC. N_2 physisorption at 75.7 K (Micromeritics 2001 E) and X-ray diffraction (Siemens D500, using Cu-Kα radiation (λ=1.5418 Å) with a Ni filter) were used to characterize the surface area, pore volume of the solids, and the expansion of the interlaminar distance of the pillared clay. The introduction of $GaAl_{12}$-polyoxocations $(GaO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+})$ by ion exchange in the interlamellar space of CaB increased permanently the surface area, pore volume, and the d(001) distance of the resulting material.[13] The XRD d(001) reflection increased from 1.26 nm for CaB to 1.94 nm in the case of the pillared clay.

Preparation of the Ce-containing Adducts.- The method used was adapted from the Clayfen procedure.[9] Ethyl ether (200 mL) and 10 g de $(NH_4)_2Ce(NO_3)_6$ (referred to as CAN) were mixed at 0°C in a 500 mL flask using magnetic strirring until complete dissolution. Then 10 g de CaB or PILC were added and stirring was continued for another 5 min. The solvent was evaporated under vacuum at 25°C using a rotatory evaporator. The resulting solids (CAN-CaB and CAN-PILC) were then crushed in a mortar and kept at 4°C in a refrigerator until further use.

Characterization of the Nitrating Adducts.- In the case of CAN-CaB samples, we only found significant changes in the structure of the clay after reaction in high polarity solvents; the XRD d(001) reflection was lost, suggesting that the clay was delaminated. The long-range layered structure of the pillared clay, given by the d(001) reflection, was masked after synthesis of the adduct as a result of the filling-up of the microporous volume by the cerium salt. After the reaction, the d(001) reflection of the original pillared clay was recovered after washing with water. This indicated that the permanent microporous structure generated by the pillaring process was maintained during adduct synthesis and through reaction. $Ce(NO_3)_3$ was identified in the spent adduct after reaction using X-ray diffraction. That compound was not present in the fresh adduct. This is evidence that Ce^{4+} was involved in a redox process during nitration.

Standard Nitration Procedure and Analysis.- The reaction was carried out using 603 mg (1.1 mmol) of CAN, the weight of the substrate equivalent to 1.06 mmol (99.64 mg of phenol; 114.5 mg *o*- or *p*-cresol; 111 mg of anisole), and 5 mL of solvent in a 25 mL Erlenmeyer flask. The mixture was stirred for 48 h at 25°C. The nitrating solid reagent was separated from the reaction mixture by suction filtration. The composition of the reaction mixture (filtrates) and the selectivity of each run were obtained using High Pressure Liquid Chromatography (HPLC) (Varian-5000 with Varichrome UV detector set at 280 nm). Samples were eluted with MeOH-H_2O (35:65 ratio) flowing at 0.6 mL/min through a 4 mm x 250 mm MCH-5 column.

A prep HPLC system was used to isolate each of the nitro compounds and to determine yields in the case of water, chloroform or acetonitrile as solvent. Half of the solvent was evaporated from the filtered mixture and the remaining solution was injected in a HPLC (Varian Pro Star 310) equipped with a prep column (22.5 mm x 250 mm Econosil C18 - 10 m). The liquid phase (MeOH-H_2O at a 35:65 ratio) was fed at 6 mL/min. The diode array detector (Pro Star) was set at 280 nm. The fractions were collected every minute using a Varian 740 fraction collector. All the compounds were identified by ^{1}H-NMR and ^{13}C-NMR. The preparative results are given in *Table 6*.

Table 6. Nitration of phenol with CAN-PILC or CAN- CaB using prep conditions

Substrate	Solvent	ε	Adduct	Phenol Conversion	Nitrophenol Yield[a]		
					ortho	*para*	$\frac{p}{p+o}$
phenol	$CHCl_3$	4.806	CAN-CaB	47.6	30.1	17.5	0.63
phenol	CH_3CN	38.8	CAN-CaB	89.3	1.2	88.1	0.98
phenol	H_2O	86.37	CAN-PILC	27.8	----	27.8	1.00

a) *meta*-Nitrophenol was not formed.

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