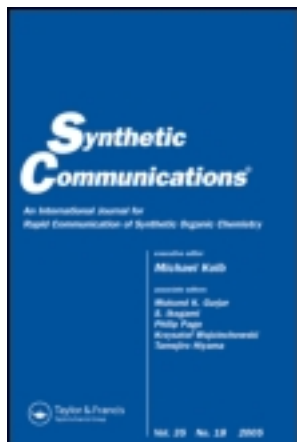


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### NATURAL BENTONITE CLAY/DILUTE HNO<sub>3</sub> (40%)—A MILD, EFFICIENT, AND REUSABLE CATALYST/REAGENT SYSTEM FOR SELECTIVE MONO NITRATION AND BENZYLIC OXIDATIONS

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**NATURAL BENTONITE CLAY/DILUTE  
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**ABSTRACT**

Selective mono nitration of Aromatic hydrocarbons and benzylic oxidations can be achieved in high yield using reusable catalyst/reagent system consisting of bentonite clay and dilute HNO<sub>3</sub> under relatively mild experimental conditions. The dual behavior of the catalyst reagent system is utilized for the regioselective synthesis of a variety of industrially important compounds.

*Key Words:* Nitration; Benzylic oxidation; Bentonite clay; Dilute HNO<sub>3</sub>

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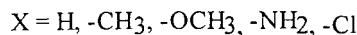
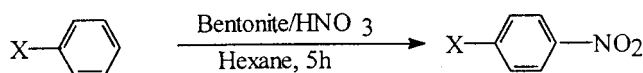


Among the industrially important synthetic processes nitration and oxidations are given high importance due to its wide variety of applications in the synthesis of pharmaceuticals and fine chemicals. The first half of this communication describes our recent achievements in selective mononitration using natural bentonite clay/dilute  $\text{HNO}_3$  system and the second half describes the performance of the above catalyst reagent system for benzylic oxidations.

Even though aromatic nitration is a well reviewed reaction,<sup>[1a-c]</sup> it still remains as an important area of research among the chemists practicing organic synthesis. In the laboratory aromatic compounds have usually been nitrated by a mixture of conc.  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ .<sup>[1c]</sup> Most of the industries are still using this methodology for preparing aromatic nitro compounds. However, this process creates severe environmental pollution caused by the gas evolution from oxidative degradation and disposal of used acids and waste water. In the conventional process of nitration using mixed acid, the role of  $\text{H}_2\text{SO}_4$  is in the generation of the nitronium ions ( $\text{NO}_2^+$ ). Here  $\text{H}_2\text{SO}_4$  is actually acting as a catalyst for the formation of nitronium ions.<sup>[1c]</sup> The acidity of the medium is a significant factor in this reaction.

In the industrial process, a large excess of  $\text{H}_2\text{SO}_4$  is required for compensating the retarding effect caused by the water molecule formed as byproduct, which dilutes the acid. The disposal of the spent acids is also a serious problem. In addition to that the reactions under high acidic conditions inevitably brings plant corrosion and occupational hazards for the people doing these jobs.

In recent years so many alternative methods are reported in literature using different catalyst/reagent systems.<sup>[2a-o]</sup> More recently, Choudary et al.<sup>[3]</sup> have reported a selective mononitration process for aromatic molecules using  $\text{HNO}_3$  over Zeolite beta-I catalyst. This process also has some disadvantages. The most important one being the difficulty in the synthesis of Zeolite beta catalyst, which is an energy consuming process involving, hydrothermal treatment of the starting materials under alkaline conditions and it is also dependant on experimental conditions. In the present method, we carried out the nitration reaction over a natural clay mineral using dilute  $\text{HNO}_3$  (Sch. 1).



*Scheme 1.*

BENTONITE CLAY/DILUTE HNO<sub>3</sub>


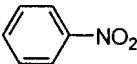
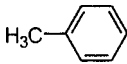

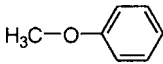
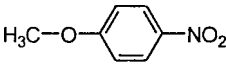
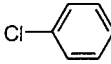
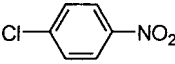
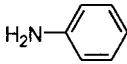

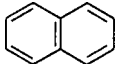
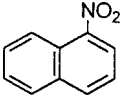
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All the reactions were carried out in hexane medium. The experimental procedure was very simple. In the first step the substrate molecule was uniformly adsorbed on the clay surface by stirring the substrate with the clay catalyst. To this hexane was added as solvent and the R. B. Flask was fitted with a Dean-Stark water separator. Then 40% HNO<sub>3</sub> solution was added to this in one lot and refluxed. The water formed as by product was separated in the Dean-Stark apparatus and removed at regular intervals. After the complete removal of water, the reaction was stopped and filtered for the removal of the catalyst and the products were separated by fractional distillation. The generality of the reaction was proved by performing the reaction with different aromatic substrates. All the substrates have shown a significantly high para selectivity towards nitration. In the case of benzene the conversion and para selectivity is ca. 100%. Toluene gave a mixture of products in which 81% of para isomer and 10% of dinitro derivative. The nitration of anisole and chlorobenzene yielded ca. 90% *para*-nitro derivative. The nitration of anisole yielded minor quantity of another compound and our attempts for its identification was unsuccessful.

An interesting result was obtained in the case of aniline. Laszlo et al. have reported the nitration of aniline with "claycop" in presence of Ac<sub>2</sub>O.<sup>[2k]</sup> Here the product obtained was 2-nitroacetanilide in very high yield. This method also have some serious limitations. Mainly on the use of large amounts of Ac<sub>2</sub>O, which is environmentally unacceptable, and the deprotection of anilides needs hydrolysis which increases the cost of production. While adopting our synthetic methodology we got 35% of *para*-nitro aniline along with a black tarry material which could not be identified. Results are summarized in Table 1.

Benzylic methylene compounds are converted into corresponding carbonyl compounds by a variety of reagents. The most prominent being chromium based reagents,<sup>[4a-f]</sup> KMnO<sub>4</sub>,<sup>[4g]</sup> DDQ,<sup>[4h]</sup> various polymer-anchored reagents,<sup>[4i-m]</sup> and silica,<sup>[4n-o]</sup> clays,<sup>[4p-q]</sup> and zeolite<sup>[4r]</sup> based oxidants. Some photochemical methods are also reported.<sup>[5a-b]</sup> The major drawbacks of chromium and manganese based catalysts are that their use in a large scale leads to the generation of large volumes of toxic wastes. The work-up of the final reaction mixture also liberates a large amount of acid and chromium waste. The combination of toxic metal, acid and organic residues represents a difficult form of waste which must be treated before disposal and this makes synthetic methodology environmentally unacceptable.<sup>[6]</sup> A recent communication from Clark et al.<sup>[7]</sup> showed the use of a membrane reactor in the presence of a phase transfer catalyst for the oxidation of benzyl alcohol to benzaldehyde which could be able to minimize environmental effects.

**Table 1.** Selective Mononitration of Aromatic Molecules Using Bentonite Clay/dil. HNO<sub>3</sub> (40%) System

Entry	Substrate	Product	Time (h)	Yield (%)
1		 (1)	5	99
2		 (2)	5	81
3		 (3)	5	90
4		 (4)	5	91
5		 (5)	5	35
6		 (6)	3	91

In the present method experimental procedure was same as described in the case of nitration. The substrates studied were ethyl benzene, isobutyl benzene, benzyl alcohol and diphenylmethane. In this case also, the oxidation reactions were carried out in a reaction vessel set up consisting of an R. B. Flask and Dean-Stark water separator. The substrate to be oxidized was uniformly mixed with the clay catalyst and was transferred to the flask along with the required amount of dil. HNO<sub>3</sub>

BENTONITE CLAY/DILUTE HNO<sub>3</sub>

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(40%) solution. It was then refluxed in hexane medium. Oxidation of ethylbenzene yielded 89% acetophenone and diphenylmethane yielded benzophenone (81%) in relatively low reaction time. Benzylalcohol underwent controlled oxidation to yield benzaldehyde in 90.5% yield. The only anomaly observed was in the case of isobutylbenzene which yielded the corresponding ketone, but the yield was less than 50%. The results are given in Table 2.

We wish to add an alternative synthesis for benzophenone (Entry 5 in Table 2) using the same bentonite clay without adding HNO<sub>3</sub>. Here benzene was mixed with excess CCl<sub>4</sub> in the presence of catalytic amount of bentonite clay (2g) as catalyst. This was then loaded in a Parr 50 mL pressure reactor and the reaction was carried out at 180°C under 200 psi pressure for 3 h. The dichloro compound obtained, on hydrolysis yielded benzophenone in greater than 90% yield. Here the yield was calculated based on the conversion of the used benzene (Sch. 3)

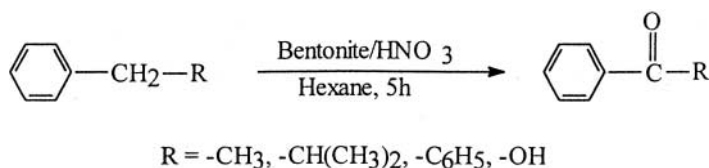
**Table 2.** Benzylic Oxidations of Aromatic Molecules Using Bentonite Clay/dil. HNO<sub>3</sub> System

Entry	Substrate	Product	Time (h)	Yield (%)
1			5	89
2			5	81
3			5	41
4			3.5	90.5
5			3	92

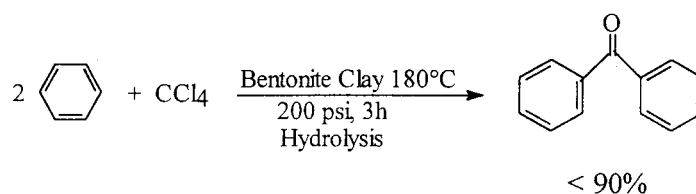


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Scheme 2.



Scheme 3.

The same reaction was reported in literature<sup>[8]</sup> using  $\text{AlCl}_3$  as catalyst. Its main disadvantages were that one molecule of  $\text{AlCl}_3$  liberated 3 molecules of  $\text{HCl}$  and also during hydrolysis unreacted  $\text{AlCl}_3$  liberates a large volume of  $\text{HCl}$  vapors. The present method totally avoids these problems.

## PART II

In continuation of the nitration process we tried the nitration of ethyl benzene with bentonite/ $\text{HNO}_3$  system. The reported procedures for the nitration of alkyl benzenes include Laszlo's "calycop"/ $\text{Ac}_2\text{O}$ <sup>[2k]</sup> system and Olah's Nafion-H/ $\text{Hg}(\text{NO}_3)_2$  system.<sup>[2o]</sup> These authors successfully isolated the different nitroalkyl benzenes. But in our experiments we did not get any nitrated product. The major product obtained was acetophenone in 89% yield. Based on these observations we tried the same reagent/catalyst system for benzylic oxidation reactions (Sch. 2).

Recycling studies were also done with used clay. The performance of the catalyst was unaltered upto 5 cycles of operation. The used  $\text{HNO}_3$  was also recycled by adjusting the concentration by adding the sufficient amount of fresh acid.

In conclusion we have developed an efficient catalyst/reagent system based on a natural clay/ $\text{HNO}_3$  system for the regioselective nitration and

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benzylic oxidations. The studies regarding the origin of the dual behavior of this catalyst/reagent system is under progress.

**EXPERIMENTAL****General**

All products were systematically characterized by <sup>1</sup>H NMR, IR spectral and GC/MS analysis. Melting points were determined in an Aldrich Mel-temp instrument and are uncorrected. IR spectra were recorded in a Nicolet-Magna 560 FT-IR spectrometer. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance DPX 300 MHz spectrometer. GC/MS analysis were done on an HP 5890 Series-II instrument. X-Ray analysis of the clay catalyst was done with a Philips 1710 instrument using Cu K- $\alpha$  radiation. B. E. T. surface area of the catalyst was measured in a Micromeritics Gemini III 2375 surface area analyzer. The reagents used were purchased from M/s Aldrich Chemicals and used as such. The solvents used were purchased from commercial sources and were doubly distilled and dried before use. The yields reported are based on the isolated products.

**Preparation of the Clay Catalyst**

The clay samples were collected from Ashapura mines of Gujarat state India. The preparation of the catalyst involves separation of the fines by sedimentation technique, followed by calcination of the clay samples at 450°C for removing the organic impurities usually humic acid. Characterisation of the clay samples were done by chemical assay and X-ray analysis [SiO<sub>2</sub> 56.19%, Al<sub>2</sub>O<sub>3</sub> 15.56% Fe<sub>2</sub>O<sub>3</sub> 7.59%, TiO<sub>2</sub> 0.79%, CaO 5.68%, MgO 4.98%, L.O.I. 14.21%, H<sub>0</sub> (mmol) 0.043, B.E.T. surface area 98.30 m<sup>2</sup>/g].

**General Procedure for Nitration**

The following procedure for the preparation of nitrobenzene (**I**) is representative. A dry 100 mL two-necked round bottom flask is fitted with a Dean-Stark apparatus and was charged with benzene (7.8 g, 0.1 mol) and bentonite clay (5 g). To this 50 mL of dry hexane was added and the setup was fitted with a water cooled reflux condenser. Twenty milliliters of dilute HNO<sub>3</sub> (40%) was added to this in one lot and refluxed for 5 h. At this time the water level in the Dean-Stark apparatus remained constant and this indicated





the completion of the reaction. After filtering the clay catalyst, the product and solvent were separated by vacuum distillation. Yield 13.4 g, (99%).

### General Procedure for Oxidation

The following procedure for the oxidation of ethylbenzene to acetophenone (**7**) is representative. A dry 100 mL two-necked round bottom flask was fitted with a Dean-Stark water separator and it as charged with ethylbenzene (5.3 g, 0.05 mol) and bentonite clay (5 g). To this 50 mL of dry hexane was added and the setup was fitted with a water cooled reflux condenser. Twenty milliliters of dilute HNO<sub>3</sub> (40%) was added to this in one lot and refluxed for 5 h. At this time the water level in the Dean-Stark apparatus remained constant and T. L. C. analysis showed a well defined spot for a product. After filtering the clay catalyst, the solvent was removed in vacuum and the product was purified on a silica column (20 : 1 petroleum ether/ethyl acetate) to give acetophenone as a colorless liquid (5.3 g, 89%), IR (KBr; cm<sup>-1</sup>), 1700, 1600, 1580, 1450, <sup>1</sup>H NMR (300MHz; CDCl<sub>3</sub>) δ 2.6 (s, 3H, -CH<sub>3</sub>), 7.9 (s, 5H, -C<sub>6</sub>H<sub>5</sub>). GC/MS (OV 101) R<sub>t</sub> 3.96 min. MS(EI) (relative intensity): *m/z* 120 (M<sup>+</sup>)(25), 105 (100), 77 (83), 51 (30).

**Benzophenone (8):** Starting from 8.4 g (0.05 mol) diphenylmethane and 5 g of clay, purification on a silica column (10 : 1 petroleum ether/ethyl acetate) afforded a white solid which crystallized from petroleum ether/benzene mixture (10 : 1 v/v) as benzophenone. M.p. 49°C (7.37 g, 81%) IR (KBr; cm<sup>-1</sup>), 1660, 1600, 1580, <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>) δ 7.5–7.7 (m, 10H, 2 × -C<sub>6</sub>H<sub>5</sub>). GC/MS (OV 101) R<sub>t</sub> 8.53 min. MS (EI) (relative intensity): *m/z* 182 (M<sup>+</sup>) (54), 105 (100), 77 (54).

**2-Methylpropiophenone (9):** Starting from 6.7 g (0.5 mol) isobutylbenzene and 5 g of clay. Purification on a silica column (5 : 1 hexane/benzene) afforded 2-methylpropiophenone as a viscous liquid (3.03 g, 41%). IR (KBr; cm<sup>-1</sup>), 1656. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>) δ 7.3–7.8 (m, 5H, -C<sub>6</sub>H<sub>5</sub>) 1.9 (s, 1H, CH) 2.6 (m, 6H, 2 × CH<sub>3</sub>). GC/MS (OV 101) R<sub>t</sub> 5.28 min. MS (EI) (relative intensity): *m/z* 148 (M<sup>+</sup>) (28), 105 (100), 77 (90), 51 (89).

**Benzaldehyde (10):** Starting from 5.4 g benzylalcohol and 5 g clay. Yield 4.79 g (90.5%) IR (KBr; cm<sup>-1</sup>), 1659, 1667, 1557, 1449. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>) δ 7.4–8.0 (m, 5H, -C<sub>6</sub>H<sub>5</sub>) 10.0 (s, 1H, -CHO). GC/MS (OV 101) R<sub>t</sub> 3.38 min. MS (EI) (relative intensity): *m/z* 106 (M<sup>+</sup>) (90), 105 (92), 77 (100).

**Benzophenone (8) from benzene, CCl<sub>4</sub> and clay (Entry 5):** 7.8 g (0.1 mol) of benzene, 30 mL CCl<sub>4</sub> and 2 g of clay were loaded in a Parr 50 mL pressure reactor and the temperature was adjusted to 180°C at a stirring rate of 150 rpm for 3 h. At this condition a pressure of 200 psi was generated in the reaction vessel. After 3 h the reactor was switched off. After cooling the

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reaction mixture was transferred into a beaker and warmed with water on a boiling water bath for 30 min. The water was removed by filtration and the dried residue was dissolved in benzene and filtered for removing the clay catalyst. The filtrate after removing the charcoal was concentrated. It was then chromatographed on a silica column (10:1 petroleum ether/benzene) to yield benzophenone as a colorless solid m.p. 49°C (8.37 g, 92%).

**Regenerability of the Catalyst**

The catalyst filtered from the reaction mixture was thoroughly washed with acetone and dried at 110°C for 1 h in a hot air oven. This was then directly used for another fresh reaction. The process was repeated in five cycles and no considerable change was observed in the activity of the catalyst.

**ACKNOWLEDGMENTS**

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