The catalytic influence of clays on Bamberger rearrangement: unexpected formation of *p*-nitrosodiphenyl amine from N-phenylhydroxylamine

Kannan P. Naicker[a,b], Kasi Pitchumani[a] and Rajender S. Varma[b,*]

[a] *School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India*
[b] *Department of Chemistry and Texas Research Institute for Environmental Studies (TRIES), Sam Houston State University, Huntsville, TX 77341-2117, USA*
E-mail: chm_rsv@shsu.edu

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The microenvironment of montmorillonite K 10 clay and its various cation-exchanged forms, promote the formation of an unexpected product, *p*-nitrosodiphenyl amine, from N-phenylhydroxylamine rather than the typical Bamberger products, aminophenols. A plausible mechanism for the unusual formation of *p*-nitrosodiphenyl amine is proposed.

Keywords: montmorillonite K 10 clay, cation-exchanged clays, catalysis, unexpected product, *p*-nitrosodiphenyl amine, Bamberger rearrangement

1. Introduction

More than hundred years ago, Bamberger, in a series of contributions [1–5], described the rearrangement of N-phenylhydroxylamine to aminophenol that bears his name. Among several rearrangements of N-substituted arylamines that were discovered and explored around the turn of the century, Bamberger rearrangement appears to have received the least attention.

Cation-exchanged montmorillonites, clay-supported reagents and pillared clays [6–11] find extensive applications in organic synthesis under milder reaction conditions. These clay materials, unlike other conventional catalysts, enjoy considerable advantages such as ease of handling, regeneration, low cost and facile modulation of acidity by suitable exchange of cations. Our interest in synthetic utility of clays and modified clay materials [11] prompted us to study the Bamberger rearrangement in the interlayers of montmorillonite K 10 clay and its various cation-exchanged forms.

2. Experimental

2.1. Reagents and catalysts

Montmorillonite K 10 clay (Aldrich) was used as received. Cation-exchanged montmorillonite clay materials were prepared by standard procedure [11,12]. In brief, sodium-exchanged clay (1 g) was admixed with 25 ml of 1 M solution of the corresponding salt (nitrate or chloride) and stirred at room temperature for 3 days. The solution was filtered, washed repeatedly with distilled water and dried overnight in an oven at 100–110 °C. N-phenylhydroxylamine was prepared by literature method [13].

2.2. Reaction procedure and work-up

To 0.2 g of N-phenylhydroxylamine in 2 ml of distilled water, 0.2 g of clay material was added and the reaction mixture was stirred for 15–30 min. After completion of the reaction, monitored by TLC (1 : 9 v/v EtOAc : hexane), the reaction mixture was extracted (3×20 ml) with CCl_4. The solvent was removed under reduced pressure and the residue was analyzed by HPLC. For solid state reaction (neat solvent free condition), 0.2 g of the substrate was intimately mixed with 0.2 g of natural or cation-exchanged clay materials, the remaining protocol being the same as above for the solution phase experiment.

2.3. Analysis of the reaction mixture

The data pertaining to the percentage conversion of the product were obtained by analysing the reaction mixture using a Shimadzu LC-8A modular HPLC system (reverse phase column (ODS), UV-detector at 258 nm) with 70% aqueous methanol as the mobile phase.

3. Results and discussion

To our surprise, N-phenylhydroxylamine, in the interlamellar spaces between the aluminosilicate layers of

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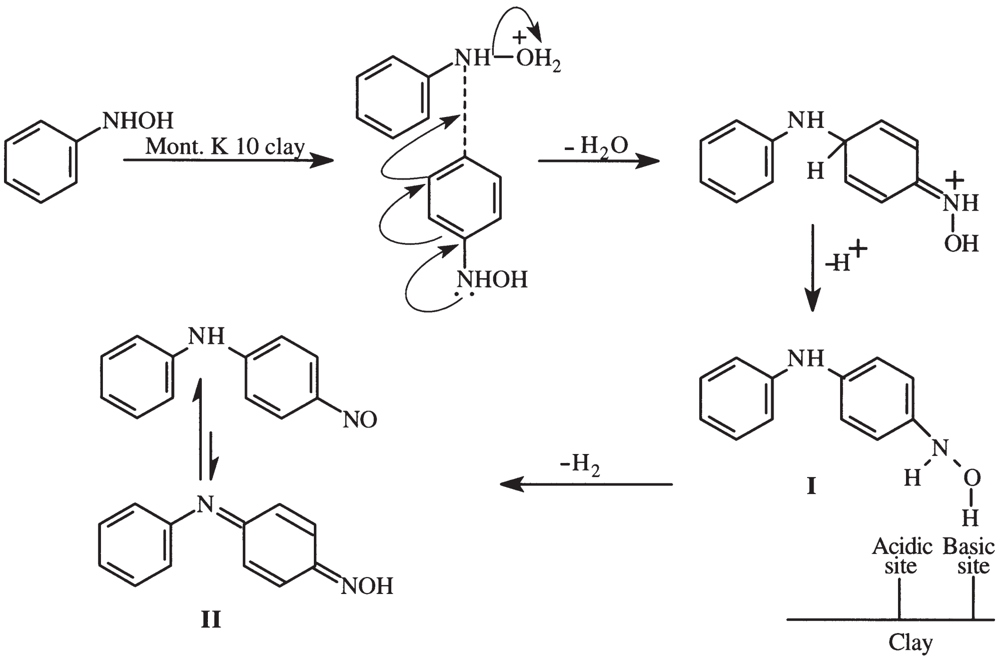
[*] To whom correspondence should be addressed.



Scheme 1.

Table 1
Product distribution in the presence of natural and various cation-exchanged clays.[a]

Nature of clay	Reaction time (min)	Percentage of products	
		p-nitrosodiphenyl amine	unidentified products
K10-mont.	30	88	12
K10-mont.[b]	30	100	00
K10-mont.[c]	15	98	02
K10-mont.–Al^{3+}	15	79	21
K10-mont.–Fe^{3+}	15	100	00
K10-mont.–Cr^{3+}	15	99	01
K10-mont.–Co^{2+}	15	92	08
K10-mont.–Mn^{2+}	15	100	00
K10-mont.–Ni^{2+}	15	92	08
K10-mont.–Cu^{2+}	15	94	06
K10-mont.–Ti^{4+}	15	100	00
K10-mont.–Zr^{4+}	15	92	08

[a] Clay and substrate (1 : 1 w/w) are stirred in distilled water at room temperature; products are analyzed by HPLC; error limit ±3%. No reaction is observed in the absence of clay materials.

[b] Clay and substrate are admixed (1 : 1 w/w) in solid state (without water).

[c] A ten-fold excess of clay is employed.

clay materials, undergoes a novel reaction to afford p-nitrosodiphenyl amine as the sole product instead of the well known Bamberger rearrangement which utilizes conventional mineral acids. Interestingly, nitrosophenyl amines are a valuable class of compounds useful as gasoline and lubricant additives, antioxidants, stabilizers, rubber additives, insecticides, bactericides and pharmaceutical intermediates [14]. The exclusive and unique intermolecular *para* addition of the phenylhydroxylamine in this reaction (scheme 1) prompted us to investigate the effect of a variety of cation-exchanged montmorillonites (Al^{3+}, Fe^{3+}, Cr^{3+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Zr^{4+} and Ti^{4+}) wherein the acidity and the size factors are varied. We noticed that it is a general reaction and proceeds relatively faster with cation-exchanged materials when compared to unmodified montmorillonite K 10 clay (table 1). The catalytic role of clay materials is apparent since no marked improvement in reaction rate is noticeable by varying the amount of the catalysts. In the solid state, an exothermic reaction ensues expeditiously. In all the cases investigated, the recovered mass balance is ≈90%. The product yields under a variety of conditions are summarized in table 1.

The solitary reaction product is identified as p-nitrosodiphenyl amine based on the physical and spectral data. The FT-IR spectra show a very strong N=O stretching at 1481 cm^{-1} and a weak O–H stretching at 3400 cm^{-1} ascribable to minor tautomeric oxime form (**II**). The UVspectrum exhibits characteristic peaks at 321 (n–π^*), 401 and 732 nm (π–π^* transitions), that match with that of the known model compound, N-ethyl-p-nitrosoaniline (280, 401 and 732 nm, respectively) [15]. When the spectrum is recorded in 0.1 M H_2SO_4, a peak at 256 nm is observed in accordance with the literature report [15]. ^{1}H-NMR spectrum displays signals at δ 7.45–7.75 (6H, m) and δ 8.25–8.55 (4H, m), the latter exhibiting a symmetrical AB-type pattern. ^{13}C-NMR and MS m/z 198 (M^+) confirms the identity of the isolated compound as p-nitrosodiphenyl amine, m.p. 142–143 °C (lit. 144 °C) [16].

It is also pertinent to note that neither the p-aminophenol nor o-aminophenol (expected from Bamberger rearrangement) are isolated in any of these cases. The plausible mechanism appears to involve initial protonation of the NHOH group by the Brønsted acidic sites, followed by attack of a second molecule of N-phenylhydroxylamine resulting in the formation of a dimeric intermediate **I**. Simultaneous hydrogen removal (gas evolution, although not quantitated, could be visibly noticed during the reaction) from **I** by the adjacent acidic and basic sites of clay presumably results in the generation of the nitroso compound (scheme 1) and its formation itself explains why the reaction stops at the dimeric stage and does not propagate further.

The reluctance of O-protonated N-phenylhydroxylamine to loose H_2O in the constrained clay microenvironment may be responsible for the deviation from the Bamberger rearrangement that normally results in the formation of aminophenols. It is also likely that the paucity of protons in clay interlayer as compared to concentrated acids may be responsible for the intermolecular dehydration (scheme 1) at the expense of the competitive intramolecular path, a shift in mechanism that is reminiscent of alcohol dehydration [7b].

The accelerated dehydrogenation of **I**, in comparison to the starting material may be prompted in part by the following factors: (a) presence of the electron releasing amino group in the p-position facilitating an extension of conjugation with the nitroso group, and (b) hydrogen migration from the NH-moiety to the nitroso group to form an oxime (scheme 1, **II**). When the reaction is conducted on a relatively large scale (2 g, 18.34 mmol), we observe some gas evolution and also the liberation of heat in the solid state reaction. The absence of any *ortho*-attack in this reaction may be due to the layered clay structure and also, in part, due to the bulky transition state for an *ortho*-attack.

4. Conclusions

The formation of an unexpected product under slightly modified reaction conditions employing a solid acid, clay, when compared to a normal acid-catalyzed Bamberger rearrangement of N-phenylhydroxylamine, points out clearly the uniqueness of the clay microenvironment as an efficient “nanoscopic microreactor” for the catalysis of organic reactions and generation of novel products.

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