

## Sheet silicate catalysed demethylation and Fischer–Hepp rearrangement of *N*-methyl-*N*-nitrosoaniline

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### Abstract

*N*-methyl-*N*-nitrosoaniline (**I**) undergoes Fischer–Hepp rearrangement in clay microenvironment. Three different types of clays, K10-montmorillonite, KSF and bentonite clays (we found that the first two are active for this reaction) as well as cation-exchanged K10-montmorillonites are employed. In addition to the rearranged product, *N*-methyl-4-nitrosoaniline (**II**), the solid state reaction also yields the denitrosation product, *N*-methylaniline, and the denitrosated as well as demethylated product, aniline. When the reaction is studied in various solvents with K10-montmorillonite clay, the rearranged product **II** is predominant in polar protic solvents. This may be due to the fact that there is a possibility of the formation of the corresponding alkyl nitrite in polar solvents which will favour nitrosation. When nitrite traps such as hydrazine, sulphamic acid or sodium nitrite are added in the clay-catalyzed reaction (both in the solid state and in the solvent), the rearrangement is completely stopped. Based on our experimental observations, an intermolecular rearrangement is proposed.

**Keywords:** Montmorillonite clay; Cation-exchanged clays; KSF clay; Bentonite clay; Catalysis; Denitrosation; Demethylation

### 1. Introduction

Fischer–Hepp rearrangement of *N*-methyl-*N*-nitrosoaniline (**I**) to *N*-methyl-4-nitrosoaniline (**II**) has been studied with clays and cation-exchanged clays. In addition to the rearranged product the reaction in the solid state also yields denitrosation product, *N*-methylaniline and denitrosated and demethylated product aniline. In the clay catalysed reaction in a solvent, **II**, is the predominant product.

Clays, cation-exchanged clays and clay-sup-

ported reagents are efficient solid state catalysts in a number of Brønsted acid site assisted reactions [1–6]. Though previous studies [7–9] with conventional acid catalysts (HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>) have been undertaken to understand the mechanism of Fischer–Hepp rearrangement, on the basis of several experiments including labelling experiments, no clear cut distinction could be made whether the mechanism involves inter or intramolecular rearrangement [7].

Herein we discuss the product distribution in the Fischer–Hepp rearrangement of *N*-methyl-*N*-nitrosoaniline (**I**) carried out natural and cation-exchanged clays in solid state and in the presence of solvents and also the mechanism.

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## 2. Experimental

I was prepared by literature method [10] and purified by reduced pressure distillation.

Cation-exchanged montmorillonite clays were prepared [5,11] by stirring 1 g of montmorillonite (Aldrich) with 25 ml of 1 M aqueous solution of the appropriate salt (nitrate or chloride) for three days. The solution was filtered, washed repeatedly with distilled water and dried at 60°C. Bentonite and KSF were used without any treatment as received from Aldrich.

All the solvents used in the study were purified by standard procedures [10].

Reaction in solid state was performed by intimately mixing the clay (0.5 g; natural or cation-exchanged) with I (0.5 ml) and heating in a water bath for 24 h. The residue was extracted with chloroform and the product was analysed by hplc after removing chloroform. For the reaction in a solvent, the catalyst (0.5 g) was mixed with 0.5 ml of I and taken with 25 ml of the solvent in a 50 ml round bottomed flask with a condenser. The mixture was heated in a water bath for 24 h, filtered and the residue was analysed after the removal of the solvent.

In each case the reaction mixture was analysed in a Shimadzu LC-8A modular hplc system (reverse phase column (ODS), UV-detector at 258 nm) using 70% methanol as the mobile phase. The percentage conversion and the rela-

tive amounts of the different products are given in Tables 1 and 2. Products were identified by comparing them with authentic samples. For confirmation NMR spectra (Perkin-Elmer 90 MHz) and IR spectra (Perkin-Elmer model 577) of the starting material and the different products were recorded.

## 3. Results and discussion

We have employed K10-montmorillonite, KSF and bentonite clays and found that the first two are active for the reaction. Before arriving at the mechanism, the following experimental observations have to be noted: (i) The conventional Fischer–Hepp rearrangement of I in the presence of HCl gives II as the major product along with *N*-methylaniline (footnote in Table 1); (ii) the reaction with clay as the catalyst in a solvent yields almost quantitatively the rearranged product II (Table 2) and (iii) in the solid state the products are II, *N*-methylaniline and aniline, almost in equal proportion (Table 1). For the first time a denitrosated and demethylated product in the rearrangement has been isolated. It shall be observed that in all the cases only the *para*-rearranged product is obtained. The various products formed from I under different conditions are shown in Scheme 1.

Table 1  
Product distribution in solid state reaction of I<sup>a,b</sup>

Nature of clay	% conversion	II	Products distribution		
			<i>N</i> -methyl aniline	aniline	mixture of 2- and 4-nitrosoaniline
K10-mont	100	38	30	28	04
K10-mont–H <sup>+</sup>	100	32	30	36	02
K10-mont–Fe <sup>3+</sup>	100	45	28	25	02
K10-mont–Al <sup>3+</sup>	100	40	26	32	02
K10-mont–Cr <sup>3+</sup>	100	25	28	47	00
K10-mont–Cu <sup>2+</sup>	100	43	30	22	05
K10-mont–Co <sup>2+</sup>	100	22	30	43	05
K10-mont–Mn <sup>2+</sup>	100	35	30	22	13
KSF	64	38	15	11	00

<sup>a</sup> The products analysed by hplc; error limit  $\pm 3\%$ .

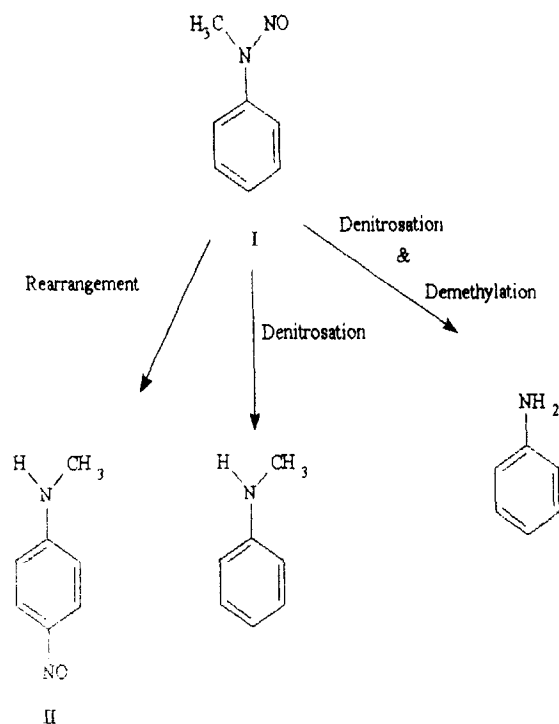
<sup>b</sup> Rearrangement in the conventional reaction with HCl as the catalyst after heating for 24 h resulted in 89% conversion yielding 69% of II and 20% of *N*-methylaniline.

Table 2  
Product distribution in different solvents in K10-mont.<sup>a</sup>

Solvents	% conversion	II	Aniline
Methanol	100	95	05
Ethanol	100	97	03
Propan-2-ol	100	95	05
Isobutanol	100	90	10
Dichloro-methane	100	100	00
Benzene	68	68	00

<sup>a</sup> The products analysed by hplc; error limit  $\pm 3\%$ .

When nitrite traps such as hydrazine, sulphamic acid or sodium nitrite are added in the clay catalysed reaction (both in the solid state and in the solvent), the rearrangement has been completely arrested. This is in contrast to the rate enhancement of the rearrangement on the introduction of such nitrite traps in the conventional Fischer–Hepp rearrangement of 3-methoxy-*N*-methyl-4-nitrosoaniline and considered to be in favour of intramolecular rearrangement [8]. Further in the clay catalysed reaction in solvents when aniline is added, *ortho*- and



Scheme 1.

*para*-nitrosoanilines are formed. These experimental observations with clay point out that the rearrangement is likely to be intermolecular in the present study.

We presume that the mechanism as detailed in Scheme 2 seems to operate in consistent with various experimental observations. Initially

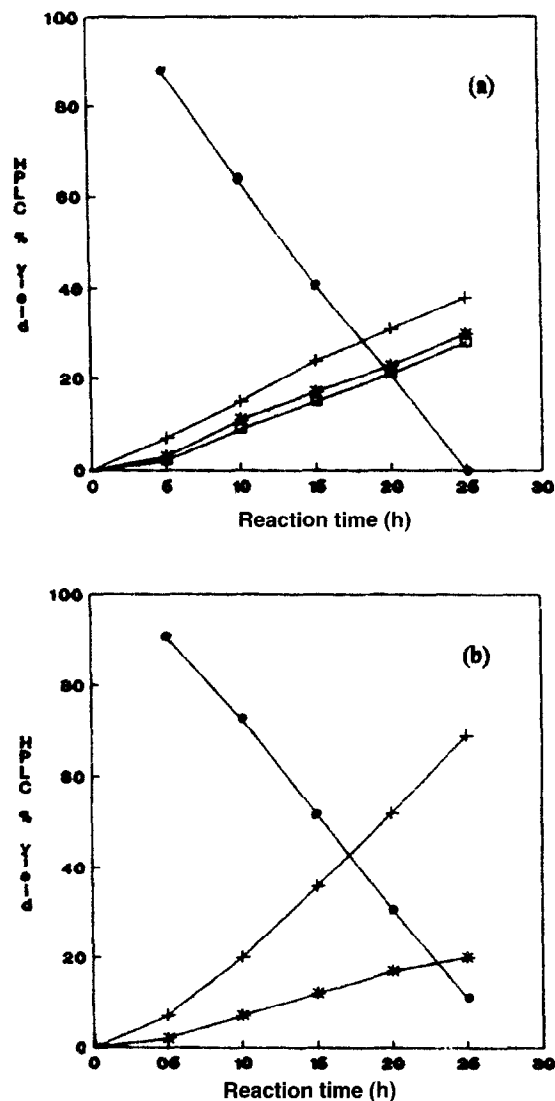
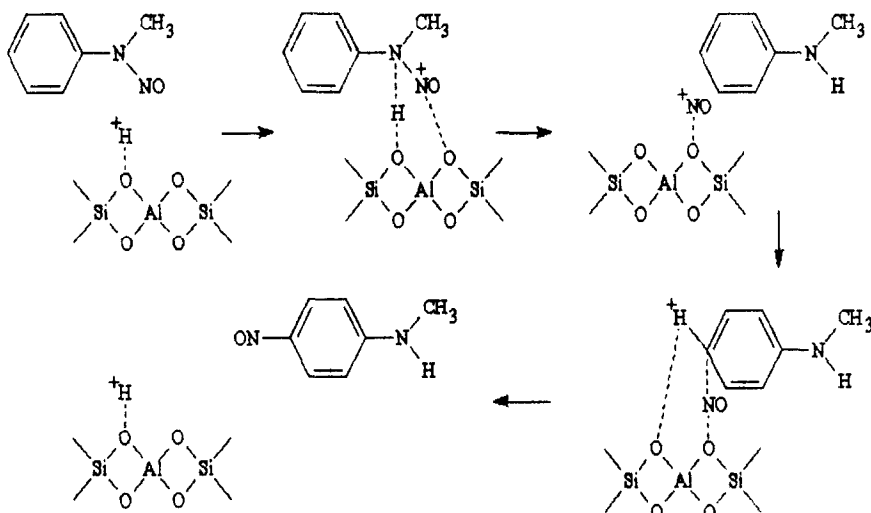


Fig. 1. The decrease in the [*N*-methyl-*N*-nitrosoaniline] and the increase in the yield of various products with time. (a) Reaction in clay: (●) *N*-methyl-*N*-nitrosoaniline, (+) *N*-methyl-4-nitrosoaniline, (\*) *N*-methylaniline, (□) aniline. (b) Reaction in HCl: (●) *N*-methyl-*N*-nitrosoaniline, (+) *N*-methyl-4-nitrosoaniline, (\*) *N*-methylaniline.

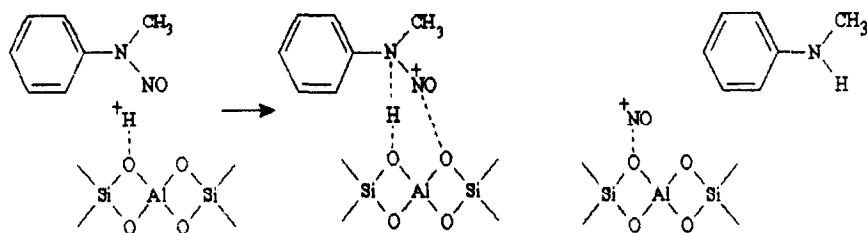
$\text{NO}^+$  is formed by the N–NO bond fission of I as a result of interaction between ring attached nitrogen and the acid site of the catalyst; this may be stabilised by the negatively charged oxygen atoms in the interlayer of clay. This is followed by the electrophilic attack of  $\text{NO}^+$  at the *para*-position of *N*-methylaniline to give II.

The formation of the *para*-rearranged product may be attributed to the facts that (i) the *para*-position is well exposed to the electrophilic attack of  $\text{NO}^+$  in the interlamellar space whereas the attack on the *ortho*-site may be hindered by clay layers on both sides and (ii) the steric effect for *ortho*-attack caused by methyl group.

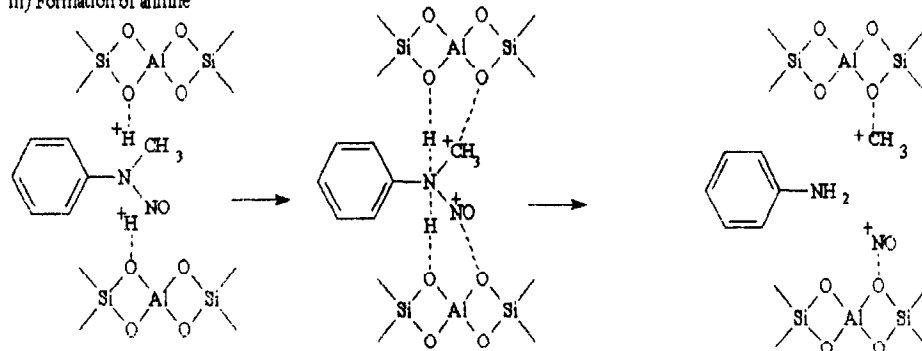
i) Formation of *N*-methyl-4-nitrosoaniline



ii) Formation of *N*-methylaniline



iii) Formation of aniline



Scheme 2.

The formation of aniline is visualised due to the interaction of two aluminosilicate layers with NO and CH<sub>3</sub> groups in I. A separate experiment has established that *N*-methylaniline undergoes demethylation in the presence of clays. As the various products formed increase fairly linearly with time, we conclude that the different products are formed by parallel reactions and not by consecutive reactions (Fig. 1a and b).

Scheme 2 is also supported by other experimental evidence. In the cation-exchanged clays such as K10-mont-Fe<sup>3+</sup> and K10-mont-Al<sup>3+</sup> the yield of II is slightly increased (Table 1) due to high Lewis acidity in these clays resulting in the strong interaction between the nitrogen atom of I and the Lewis acid site. The product distribution is also influenced with the quantity of the catalyst employed; with 2–3 fold excess of clay the major products are denitrosated product *N*-methylaniline and demethylated product aniline and not II. This supports the third step in Scheme 2.

When the reaction has been studied in various solvents with K10-montmorillonite, the rearranged product II is predominant (Table 2) in polar protic solvents. The high yield of II may be due to the fact that the loss of NO<sup>+</sup> ion in the solvent is less probable and the electrophilic attack of NO<sup>+</sup> takes place. In polar aprotic solvents such as DMSO, DMF, CCl<sub>4</sub> and diglyme the rearrangement is negligible. This may be explained by the fact that there is a possibility of the formation of corresponding alkyl nitrite in polar protic solvents and that will favour nitrosation. It is not clear why the reaction occurs to 100% conversion in dichloromethane and 68% conversion in benzene.

#### 4. Conclusion

This study establishes the efficiency and selectivity of natural as well as various cation-exchanged montmorillonite clays in Fischer–Hepp rearrangement of *N*-methyl-*N*-nitrosoaniline particularly in various solvents. In the solid state both denitrosation and demethylated products are formed. Various experiments point out the operation of intermolecular mechanism in the presence of clay catalysts.

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