

Synthesis of ammonium-alkylaniline dihalides using the Green catalyst Maghnite-H⁺ and characterization

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ABSTRACT/RESUME

Abstract: The overall objective of this study is to synthesize ammonium salts by adding dihalogenated compounds such as dibromides and dichlorides to aniline using the green catalyst "Maghnite-H⁺", a new non-toxic catalyst.

The important part of this work consisted of carrying out the formation of these ammonium salts under suitable conditions without solvent, at room temperature, for different durations and using several catalyst contents.

The effect of time and amount of catalyst on the yield of the addition reactions was studied. All the synthesized products were characterized by IR spectroscopy, ¹H-NMR and ¹³C-NMR.

I. Introduction

Amines and their derivatives constitute more than two thirds of the comprehensive medicinal chemistry database [1-2], they are crucial precursors in the preparation of a wide variety of pharmacologically relevant therapeutic agents, natural products and agrochemicals [3-8].

In aromatic amines, N-alkylated [9] have useful biological activities and have many applications [10], on the other hand, secondary ones play a key role as antioxidants in petrochemicals and polymers [11-21].

In fact, there is growing interest in the development of simple and efficient methodologies for the synthesis of these amined compounds, used in pharmaceutical industries [22-28].

A new method was used to synthesize an ammonium-alkylaniline dihalide from the addition of dihalogenated compounds to aniline, activated by a solid, efficient and environment-friendly catalyst called Maghnite-H⁺. The reaction was carried out without solvent at room temperature and for different periods of time, also using several catalyst contents. Then, the operating conditions were chosen to obtain a maximum yield of bis-ammonium salts.

II. Materials and methods

II.1. Materials

Aniline used as monomer in this work provided by Polabo (Paris, France). Dihalogenated compounds such as 1,2-dichloropropane, 1,2-dibromopropane, 1,6-dichlorohexane, 1,6-dibromo-hexane were supplied by Polabo (Paris, France), were used as reagents. The chloroform was supplied by Polabo (Paris, France), was used as the solvent which is recovered after each experiment, distilled at a temperature of 62 °C and then reused another time.

II.2. Preparation of Maghnite-H⁺

Maghnite is a natural Algerian clay obtained from the region of Maghnia that is located in the northwest of Algeria [29]. This catalyst was developed in Polymer Chemistry Laboratory «LCP» [30-34], it has shown remarkable catalytic capabilities in polymerization reactions of various vinyl and heterocyclic monomers.

The new catalyst Maghnite-H⁺ was prepared according to the process reported in our previous study. 60 g of Raw-Maghnite was crushed for 20 minutes using a prolabo ceramic balls grinder. It

was then dried for 2 hours at 105°C. The Maghnite was placed in an Erlenmeyer flask together with 240 ml of distilled water. The Maghnite/water mixture was stirred using a magnetic stirrer and after 30 minutes, the suspension was combined with 200 ml of 0.23 M sulfuric acid solution, until neutralization was achieved over 2 days at room temperature, the mineral was then washed with distilled water to become sulfate free and then dried for 24 hours at 105°C. At the end, the Maghnite was ground and sieved (fine sieve 0.08 µm) and stored away from air and moisture.

II.3. Procedure for the synthesis of ammonium salts

The present study provide process for preparing ammonium salts, which comprises a mixture of catalyst and monomer (2 g of Maghnite-H⁺, 2.74 ml (3 x 10⁻² mol) of aniline in a two-necked flask, after the stirring at room temperature for 20 to 30 minutes, 10⁻² mol of dihalogenated compound were added, the set was left stirred for 2 hours. The crude reaction was washed with chloroform, the Maghnite was recovered by simple filtration on filter paper and was then dried on a rotary evaporator.

Dihalogenated compound:
 • 1,2-dichloropropane, a white product obtained with a yield of 80%
 • 1,2-dibromopropane, the product obtained was white with a yield of 68%.

• 1,6-dichlorohexane, the product was viscous, light yellow with a yield of 80%.

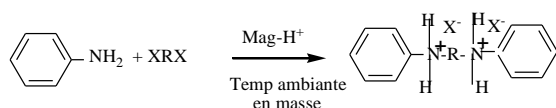
• 1,6-dibromohexane, the product obtained was light yellow with a yield of 72%.

II.4. Characterization

The molecular structure of products synthesized from the addition of aniline with dihalogenated compounds was characterized by FT-IR spectroscopy (Perkin Elmer System), ¹H nuclear magnetic resonance (NMR) and ¹³C nuclear magnetic resonance (NMR), measurements made on a 300 MHz Bruker NMR spectrometer.

III. Results and discussion

III.1. Addition reaction of dihalogen compounds on aniline



R = CH₂CH(CH₃), X = Br, the product (1)

R = CH₂CH(CH₃), X = Cl, the product (2)

R = (CH₂)₆, X = Br, the product (3)

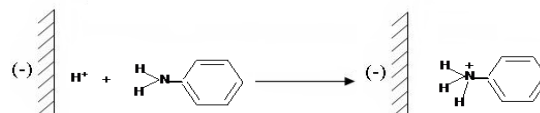
R = (CH₂)₆, X = Cl, the product (4)

Mechanism of reaction

We suggest the mechanism of the Synthesis of ammonium salts by addition reaction of aniline with dihalogenated compounds induced by Maghnite-H⁺.

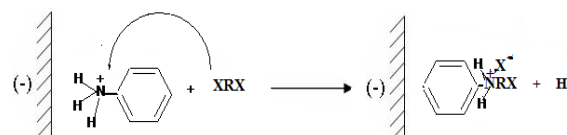
1° Priming:

In the first step, the protons carried by Maghnite-H⁺ sheets induced this reaction, we will have the protonation of aniline.



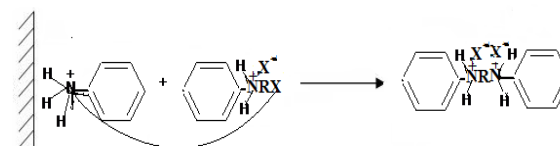
2° Propagation:

In the second step, the ammonium ions formed take place in the vicinity of the counter anion carried by the Magnetic sheets, then there will be a nucleophilic attack of positively charged nitrogen of aniline by the halogen of the dihalogenated compound with departure of the H⁺ proton and fixation of the RX radical.



3° Terminaison:

In the last step, we have a nucleophilic attack of positively charged nitrogen of the second ammonium molecule (formed by protonation of another aniline molecule) by the halogen of the ammonium salt obtained in the second step, we will have formation of the ammonium -alkylaniline dihalide molecule.



III.2. Spectroscopic characterization

Characterization of the product (2) ¹H NMR

In comparison with the ¹H NMR spectrum of the monomer with that of the product (2), we note the appearance of the peak associated with the proton H₂N⁺ (δ = 7.7 ppm) and the absence of the peak associated with the protons of the amine units (N-H) of aniline (δ = 6.22 ppm)

The spectrum of the product (2) (figure. 1) shows a signal at δ = 0.9 ppm of the methyl protons (3H, -CH₃) and another at 1.3 ppm corresponding to the proton carried by a carbon (-CH(CH₃)-N⁺), the peak

at 3.1 ppm is attributed to the two nitrogen protons ($2H, -CH(CH_3)-N^+H_2-$).

The protons of carbon ($2H, N^+CH_2$) are observed at 2.4 ppm, we also note a peak at 4.2 ppm corresponds to the methylen proton ($2H, -CH_2-N^+H_2-$) and another proton peak around 7.7 ppm due to the resonance of phenyl group protons ($5H, -N^+H_2C_6H_5$).

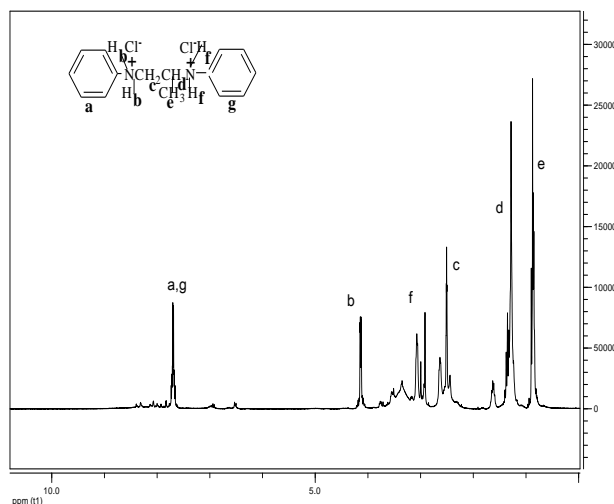


Figure 1. 1H NMR Spectrum of the product (2)

Characterization of product (2) ^{13}C NMR

A study was devoted to the analysis of the polymer(2) by ^{13}C NMR spectroscopy. This spectrum (figure 2) shows the presence of a peak at 28 ppm characteristic of the carbon resonance of the group ($-CH_3$) and another at 40 ppm attributed to the carbon linked to the methyl (N^+-CHCH_3).

The chemical shift at 30 ppm corresponds to carbon (N^+-CH_2), the phenyl group carbon ($C_6H_5-N^+H_2-CH$) resonates at 129 ppm, on the other hand that of the other phenyl appears at 132 ppm.

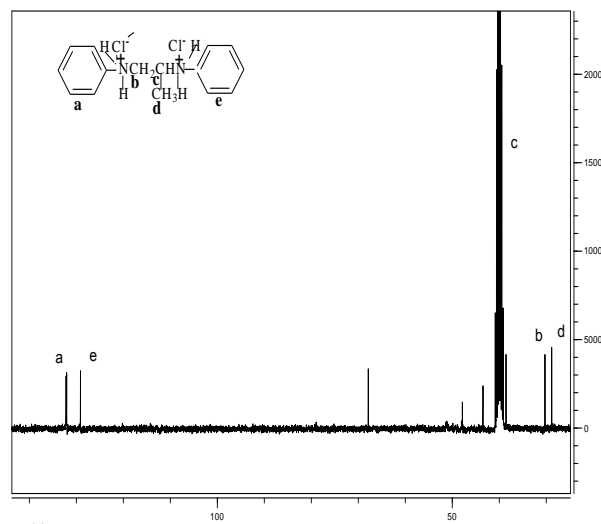


Figure 2. ^{13}C NMR Spectrum of the product (2)

Characterization of the product (2) by IR

Concerning the spectrum of the pure monomer "Aniline", the characteristic of the primary N-H group is the presence of the two broad bands located between 3250 and 3500 cm^{-1} . The IR spectrum of the product (2) (Figure. 3) does not contain the two wide bands at 3426 and 3351 cm^{-1} due to the elongation vibration of the N-H bond of the aniline and on the other hand the appearance of a strong band between 3200 and 3600 cm^{-1} due to the elongation vibration of the N^+-H and of another band between 1580 and 1680 cm^{-1} indicating the deformation vibration of the secondary ammonium group N^+-H . We note the presence of two peaks at 3000 and 2800 cm^{-1} due to the elongation vibration of the C-H of the aryl groups and of the CH_2 group respectively, of an intense peak between 1480 and 1320 cm^{-1} due to the elongation vibration of the C = C benzene bond. We also observe an intense peak between 1250 and 1300 cm^{-1} which characterizes the vibration of the C-N and another at 1000 cm^{-1} due to the vibration of deformation of the C-H of the benzene nucleus.

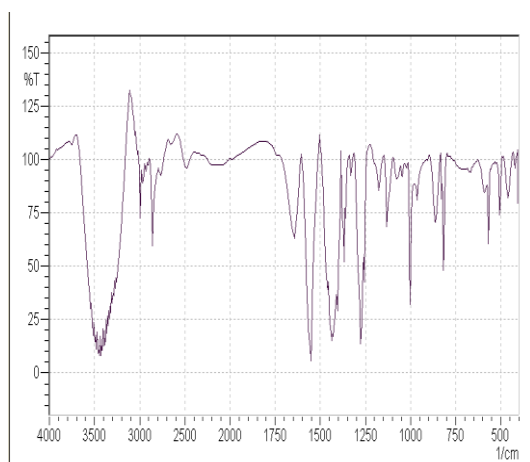


Figure 3. IR spectrum of the product (2)

Characterization of the product (3)

Characterization of product (3) by ^1H NMR

An investigation was devoted to the analysis of the product (3) by ^1H NMR spectroscopy (figure 4). This spectrum confirms the absence of the peak associated with the protons (N-H) of aniline ($\delta = 6.22$ ppm) with the appearance of the peak associated with the proton H_2N^+ ($\delta = 7.3$ ppm). The experimental spectrum reveals the existence of a signal at 1.7 ppm of the methylene protons ($2\text{H}, \text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2$), the protons chemical shift ($2\text{H}, \text{N}^+\text{CH}_2$) is observed at 6.7 ppm, there are also a peak at 3.8 ppm corresponding to the proton ($2\text{H}, \text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2$) and another peak at 6.9 ppm for the protons carried by nitrogen ($2\text{H}, \text{N}^+\text{H}_2$), another signal appears at 7, 3 ppm corresponding to the phenyl group protons ($5\text{H}, \text{C}_6\text{H}_5$).

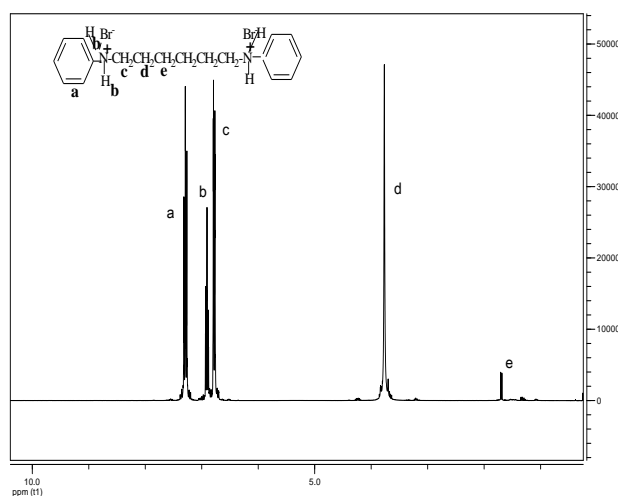


Figure 4. ^1H NMR Spectrum of the product (3)

Characterization of product (3) by ^{13}C NMR

^{13}C NMR spectroscopic data (figure 5) of the compound (3) shows the existence of a signal at 113 ppm attributed to carbon of the para position of phenyl, another at 120 ppm attributed to carbon displacement chemical of the meta position of

phenyl, on the other hand that of the ortho position appears at 115 ppm, we also note the presence of a signal at 130 ppm characteristic of the carbon resonance $\text{C}=\text{N}^+\text{CH}_2$ of the phenyl group. The chemical shifts of certain carbons at 45, 33 and 26 ppm are attributed respectively to the carbons (N^+CH_2 , $\text{N}^+\text{CH}_2\text{-CH}_2\text{CH}_2$, $\text{N}^+\text{CH}_2\text{-CH}_2\text{CH}_2$).

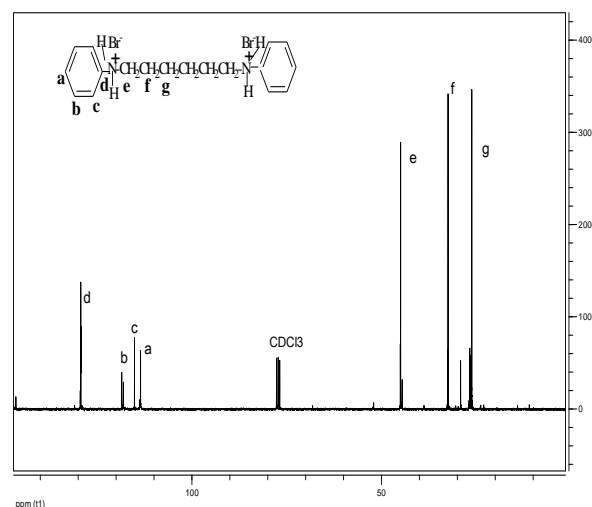


Figure 5. ^{13}C NMR Spectrum of the product (3)

Characterization of product (3) by IR

The comparison between the IR spectrum of the product (3) with that of pure aniline shows the disappearance of two bands located between 3250 and 3500 cm^{-1} due to the symmetrical and asymmetrical elongation vibration of the N-H bond of aniline and the appearance of a band at 1499.76 cm^{-1} indicating the deformation vibration of the secondary ammonium group $\text{R}_3\text{N}^+\text{-H}$.

The spectrum (Figure 6) shows the appearance of a strong band at 3221.40 cm^{-1} due to the elongation vibration of the $\text{R}_3\text{N}^+\text{-H}$ bond. We observe two neighboring bands at 2819, 53 and 2746.00 cm^{-1} attributed to the elongation vibration of the C-H bond of methylene, a strong peak at 2934.49 cm^{-1} due to the stretching vibration of the C-H bond of aryl groups, two intense peaks at 1266.12 and 1127.37 cm^{-1} characterizing the elongation vibration of the C-N bond, an intense peak 1371.45 due to the valence vibration of the $\text{C}=\text{C}$ bond of benzene, a strong peak at 839.58 cm^{-1} due to the deformation vibration of the C-H of aryl and another peak at 612.06 cm^{-1} which corresponds to the deformation frequency of the $\text{C}=\text{C}$ bond of the benzene nucleus.

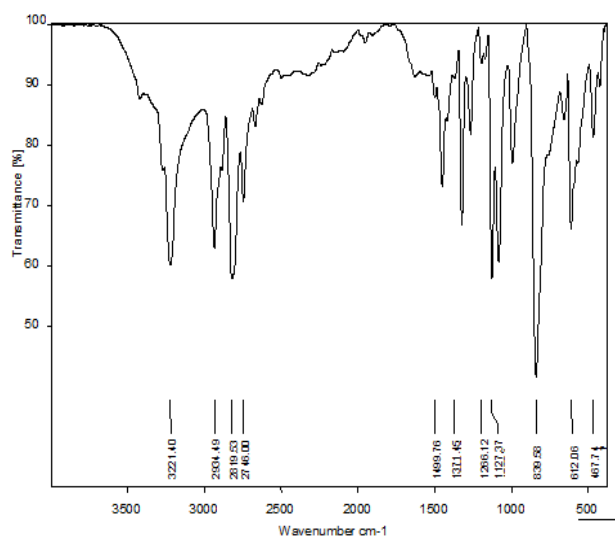


Figure 6. IR Spectrum of the product (3)

* Characterization of product (4)

IR (KBr); ν (cm^{-1}) = (3300 cm^{-1} a band due to the elongation vibration of $\text{N}^+\text{-H}$, 2804,12 cm^{-1} strong peak due to the valence vibration of the C-H of the aryl groups, 1516.37 cm^{-1} a strong peak assigned to the deformation vibration of $\text{N}^+\text{-H}$ of secondary ammonium, 1499, 59 cm^{-1} an intense peak due to the valence vibration of the C=C bond of benzene, 1057.38 and 1024.64 cm^{-1} two intense peaks characterizing the elongation vibration of the C-N bond, 737.73 cm^{-1} strong peak due to the deformation vibration of C-H aryl. 616.92 cm^{-1} a strong peak attributed to the deformation frequency of the C=C bond of the benzene nucleus. We notice the disappearance of the two bands located between 3250 and 3500 cm^{-1} due to the symmetrical and asymmetrical elongation vibration of the N-H bond of aniline.

$^1\text{H NMR}$ (300MHz, CHCl_3); δ (ppm) = 7,7 (5H, - $\text{N}^+\text{H}_2\text{C}_6\text{H}_5$), 4,1(2H, N^+H_2), 3,1 (2H, N^+CH_2), 2,4 (2H, $\text{N}^+\text{CH}_2\text{CH}_2$), 1,3(2H, $\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2$).

$^{13}\text{C NMR}$ (300MHz, CDCl_3); δ (ppm)=113 ppm (carbon of the para position of phenyl), 121 ppm (carbon of the meta position of phenyl), 115 ppm (carbon of the ortho position), 132 ppm ($\text{C}^+\text{N}^+\text{CH}_2$ of the phenyl group), 45 ppm (N^+CH_2), 34 ppm ($\text{N}^+\text{CH}_2\text{-CH}_2\text{CH}_2$) and 27 ppm ($\text{N}^+\text{CH}_2\text{-CH}_2\text{CH}_2$).

* Characterization of product (1)

IR (KBr); ν (cm^{-1}) = (3353.27 cm^{-1} a band due to elongation vibration of $\text{N}^+\text{-H}$, 2954, 69 cm^{-1} strong peak attributed to the elongation vibration C-H of the aryl groups, 1235.43 and 1285.57 cm^{-1} two intense peaks characterizing the elongation vibration of the C-N bond, 1145.51 cm^{-1} an intense peak due to the valence vibration of the C-C bond, 793.16 cm^{-1} strong peaks due to the C-H deformation vibration of the benzene nucleus. We note the absence of the two bands located between 3250 and 3500 cm^{-1} due to the valence vibration of N-H of aniline.

$^1\text{H NMR}$ (300MHz, CHCl_3); δ (ppm)=7,1(5H, - $\text{N}^+\text{H}_2\text{C}_6\text{H}_5$), 8,1(2H, N^+H_2), 4,7(2H, N^+CH_2), 1,6(1H, N^+CH), 1,3(3H, - CH_3), 7,3(2H, $\text{N}^+\text{C}^+\text{H}_2\text{CH}(\text{CH}_3)$), 6,7(5H, - $\text{CH}_2\text{CH}(\text{CH}_3)\text{N}^+\text{H}_2\text{C}_6\text{H}_5$)

The $^1\text{H NMR}$ spectrum of the product (1) shows the appearance of the peak associated to the proton H_2N^+ ($\delta = 7,7$ ppm) and the absence of the peak assigned to the protons of the amine units (NH) of aniline ($\delta = 6,22$ ppm)

$^{13}\text{C NMR}$ (300MHz, CDCl_3); δ (ppm)=77 ($\text{N}^+\text{-CHCH}_3$, $\text{N}^+\text{-CH}_2$), - CH_3), 130 ($\text{C}_6\text{H}_5\text{-N}^+\text{H}_2$),

III.3. Tests of solubility of products:

The products obtained were subjected to solubility tests (Table 1).

Table 1. Solubility of different products in various solvents (- not soluble, + soluble).

Product \ Solvent	Product (1)	Product (2)	Product (3)	Product (4)	Product (5)	Product (6)
H ₂ O	-	+	-	-	-	-
CH ₃ OH	+	-	-	-	-	-
EtOH	-	-	-	-	-	-
CH ₃ COOEt	-	-	-	-	-	-
CH ₃ COCH ₃	-	-	-	-	-	-
CHCl ₃	+	-	+	+	+	+
C ₆ H ₅ CH ₃	-	-	-	-	-	-
EtCOOH	-	-	-	-	-	-
CCl ₄	-	-	-	-	-	-
DMSO	-	+	-	+	+	+

III.3. Effect of Time on on the yield

In our case, we performed series of addition reaction experiments of dihalogenated compounds on aniline such as 1,6-dichlorohexane and 1,2-dibromopropane in the presence of of Maghnite-H⁺ by maintaining the quantities of reagents and by varying the time t (Table 2. and Figure 8.).

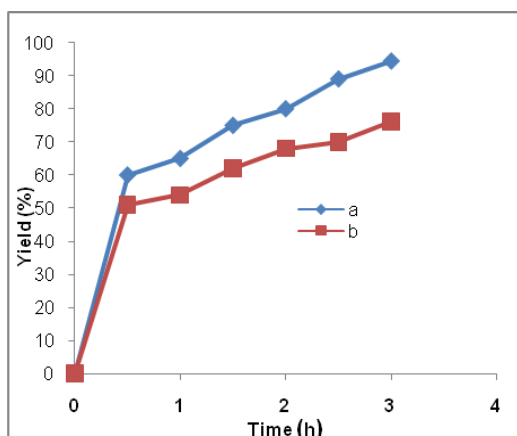


Figure 8 . Effect of time on the yield of the addition reaction of aniline with 1,6-dichlorohexane (a) and 1,2- dibromopropane (b)

We found that the yields of these reactions increase with time.

III.4.Effect of the amount of Maghnite-H⁺ on the yield of the reaction of aniline

In order to control the influence of the amount of catalyst on the yield of the bulk reaction of aniline.

we realized a series of experiments by maintaining the amounts of monomer and time and varying the amount of Maghnite-H⁺ (Table 3. and Figure 9.).

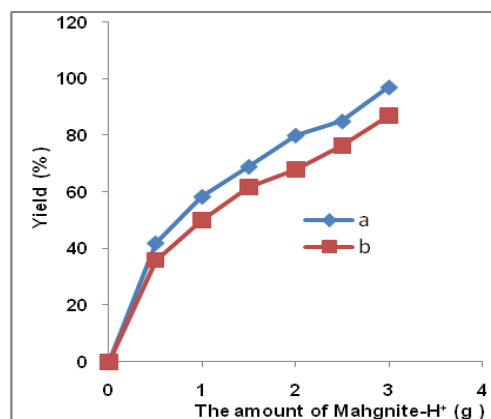


Figure 9. Influence of the amount of Maghnite-H⁺ on the yield of the addition reaction of aniline - with 1,6-dichlorohexane (a) and - with 1,2-dibromopropane (b)

The yields of the reactions carried out increase by raising the amount of catalyst

Table 3 . Effect of time on the yield of the addition reaction of aniline with 1,6-dichlorohexane (a) and 1,2-dibromopropane (b)

Time (hours)	0.5	1.0	1.5	2.0	2.5	3.0
yield (%) (a)	60	65	75	80	89	94.4
yield (%) (b)	51	54	62	68	70	76.2

Table 4. Influence of the amount of Maghnite-H⁺ on the yield of the addition reaction of aniline with 1,6-dichlorohexane (a) and 1,2-dibromopropane (b).

The amount of Maghnite-H ⁺ (g)	0.5	1.0	1.5	2.0	2.5	3.0
yield (%) (a)	42	58.4	69	80	85	97
yield (%) (b)	36	50	61.8	68	76.3	87

III. 5.Conclusion

This work shows that the addition reaction of aniline with different dihalides was induced by a proton exchange montmorillonite clay called Maghnite-H⁺ in high yield.without the use of a solvent.

The advantage of this method is that the acidic clay is inexpensive, stable and non-corrosive, These ammonium salts were produced by a very simple process, by simple filtration, the clay was separated

from the reaction mixture. All products have undergone spectroscopic characterizations.

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