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Heterogeneous catalytic recovery using $NaBH_4$-Pd/C and homogeneous using PMHS-TBAF for nitrile compounds such as: N-ferrosylmethylamino (ortho, meta, para)-benzonitrile

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ABSTRACT

The reduction of certain organic functions requires the search for safe and clean experimental methods, with simple equipment and at the lowest cost and obtaining better yields to facilitate and contribute to the creation of new compounds effective and having applications in many medical and industrial fields, so there is always a subject of interest and research in depth before the chemists.

Among the reduction methods, there is what is called hybride reduction in very dry organic media that require difficult conditions.

In addition, there are many products, which makes separation more difficult. As well as reduction by catalytic hydrogenation will require a reactor resistant to high pressure and high heat where this method is considered as a little use, because it is very expensive and only reduires double bonds and aromatic compounds. we therefore suggested in this study a way restore or reduction some organic fonctions(the function nitrile)using neonatal hydrogen from $NaBH_4$ *through superticial reactions in aqueous medium under simple conditions and we will also tackle a comparative study of this method of reduction by* $NaBH_4$ *in presence of a heterogeneous catalyst (Pd/C10%) with the reduction by PMHS in organic medium in the presence of homogeneous catalyst TBAF..*

Keywords: *Reduction, Nitrile compounds,*$NaBH_4$*, Pd/C, PMHS,TBAF..*

1. Introduction

reductionactions are considered a good source for the manufacture of a large number of organic chemical compounds. Reduction reactions are defined in organic chemistry as the addition of at least one hydrogen atom or the removal of a halogen or oxygen atom [1], which is the opposite of an oxidation reaction. Reduction reactions occur in many different ways, including reduction with complex hydrides. The most widespread and widely used is sodium borohydride (NaBH4), which is known for its high selectivity, as in the presence of diiodine (I2) it is possible to restore esters, amides, and amino acids [2] and also in the presence of zirconium tetrachloride (ZrCl4) to restore the nitro-aliphatic and aromatic functions[3.]

Another reference that is no less important than the first reference is lithium aluminum hydride (LiAlH4) to restore the carboxylic function, halogen derivatives, and esters in the presence of ether (2OEt) [4]. This type of metal hydride is highly effective as it restores most of the organic functions, but it is not selective. Also, there is Dihydrogen-catalyzed hydrogenation recovery method: This method is often used to restore double and triple bonds, but it is sometimes considered dangerous.

Among the hydrides discovered recently (in 1946), polyethylhydrosloxane, which was initially used as a simple reagent in some organic preparations, and recently it has become used in reduction reactions with a wide range of catalysts. PMHS has been shown to be effective in reducing many organic functions with high efficiency.

In 1957, WackerchemieBurghausen developed the first process using silanes as a hydride source to avoid the use of aluminum hydrides**[5]**. PMHS has certain advantages because it is cheap, stable and can be considered a by-product of the silicone industry**[6]**. In 1973, Lipowitz and Bowman published the catalytic reduction of nitrobenzene to anilineby Pd/C and PMHS in ethanol at 40−60°**[7].**

Several studies have been done on the reduction of nitro aromatic groups to amines, at room temperature, this reduction can be achieved with high yield and short reaction times (30 min) using a combination of palladium (II) acetate, aqueous potassium fluoride and polymethylhydrosiloxane. When they replaced PMHS/KF with triethylsilane, they were able to reduce the aliphatic nitro groups to their corresponding hydroxylamines**[8].**

In 1997, Kobayashi et al. found that tetrabutylammoniumfluorid (TBAF) could effectively promote the PMHS reduction of aldehydes and ketones to alcohols **[9].**Analogous fluoride-catalysed reduction of ketones by PMHS was also reported by Lawrence et al**[10-12].**

Drid et al obtained amino alcohols by reduction of α-amino acids such as Glycine, Valine, Methyonine, isoleucine, tyrosine and vinyl by PHMS in the presence of TBAF with yields ranging from 54% to 85%. They also reduced the amide function in some aromatic compounds, converting them into amines with a yield of about 75%. Finally, with the nitro compounds that required reduction at a temperature above 50 ° C, they obtained average results for the nitroaniline compounds in both meta- and para- positions with yields ranging from 40% - 50%**[13].**

In the light of all the previous studies and on the basis of studies by Sekhri in 1998 which concerns the reduction by PMHS in the presence of the tetra-butylammonium fluoride catalyst (TBAF) of several chemical functions**[14].**

During any organic manufacturing process, the economic and security aspects are taken into account by using the simplest, easiest to prepare, safest and least expensive methods.

In this work, we addressed the return of the aromatic function of nitriles to their corresponding amines in ferrocinyl compounds, first through heterogeneous catalytic recovery using sodium borohydride ($NaBH_4$) in the presence of palladium loaded on carbon (%Pd/C10), and secondly through homogeneous catalytic recovery using... With polymethylhydrosiloxane (PMHS) in the presence of the homogeneous catalyst represented by the quaternary ammonium salt TBAF in an organic medium (THF).

A comparative study was conducted between the two methods.

2.Experimental

2.1. Materials and instrumentation

- All chemicals were of reagent grade quality purchased from commercial sources and used as received. These included:polymethylhydrosiloxane (PMHS) 99% (Sigma-Aldrich), tetrabutylammonium fluoride (TBAF) 98% (Sigma-Aldrich), Tetrahydrofuran (THF) 99.9% (Sigma-Aldrich).
- N-(ferrocenylmethyl)benzonitrile;(2-$FcCH_2NHPhCN$, 3-$FcCH_2NHPhCN$ and 4-$FcCH_2NHPhCN$).
- ^{1}H-and^{13}C-NMR spectra were recorded on BRUKER 400MHz spectrometer (AVANCEIII 400) in $CDCl_3$. Chemical shift values are reported in ppm and coupling constants in Hz. ^{1}H-NMR spectra were referenced internally using residual protons in the deuterated solvent ($CDCl_3$: δ(S) = 7.24 ppm) and values reported relative to tetramethylsilane (δ = 0.00 ppm). ^{13}C-NMR spectra were similarly referenced internally to the solvent resonance ($CDCl_3$: δ(t) = 77.0) with values reported relative to tetramethylsilane (δ=0.0ppm).The infrared spectra were recorded using Perkin Elmer spectrum 100 FT-IR spectrometer and the data are reported as percentage transmittances at given wave numbers**[15].**

The general method used in this study for heterogeneous catalytic recovery is as follows:

We take 0.05 g of the Pd/C10% catalyst in 10 ml of distilled water, shaking, then we add the materials to be returned in an amount (kg, 1.63 mmol), and immediately after that we add 0.12 g of $NaBH_4$ in batches, after which we leave the reaction for 15 minutes [16, 17].

2.2. General synthesis of N-(ferrocenylmethyl)4,3, 2-aminomethylaniline

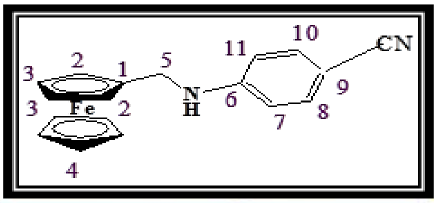
2.2.1. Synthesis of N-(ferrocenyl methyl) 4-aminomethylaniline(4-$FcCH_2NHPhCHNH_2$) (Fig 01)

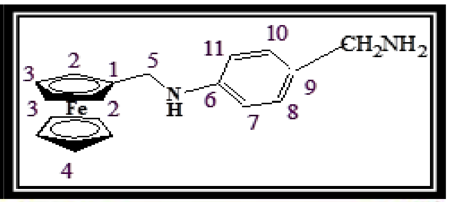
0.0047g of Pd/C was placed in a container, then we added 3ml of distilled water to it and shook. On the other hand, we dissolved 0.05g of (ferrosylmethylamino) 4-benzonitrile in 10ml of methanol, then we mixed the two mixtures, then added 0.022 g of $NaBH_4$ with the arlene covered to avoid the release of hydrogen gas. We left the reaction for 15 minutes and followed the course of the reaction with CCM (siliceous gel - ethyl acetate - dichloromethane 2/1), where we discovered the presence of a new compound with a path difference Rf = 0.5 1 is different from marching bands The reactant Rf=0.64.

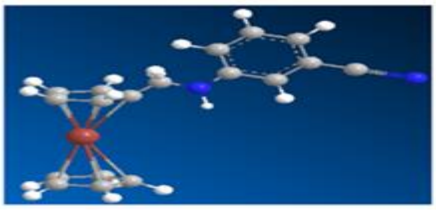
Then we filtered the solution to get rid of the catalyst, then evaporated the methanol, then carried out a liquid-liquid extraction using dichloromethane at PH = 8.5 to get rid of the remainder, while evaporating the organic phase after drying it with $MgSO_4$. Then we raised the pH of the medium to 13.5 to extract the expected product with CH_2Cl_2, then dried the organic phase, then Evaporating it, we obtain a substance Solid, brownto blackcolour.

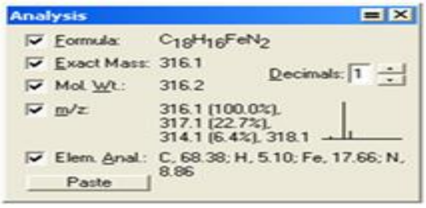
After optimization of the operating conditions, all reactions are carried out at 60 °C in THF solvent and the reducing system TBAF/PMHS.

Dans un tricol, on a mis (0,2 g - 0,63 mmol) du composé N-(ferrocénylméthylamino)4-benzonitrile, qui est de couleur marron, et on y a ajouté 30 ml de THF, la couleur est donc devenue jaune. Ensuite, nous avons ajouté (0,00795 g - 0,0252 mmol.) de TBAF resté de la même couleur après quelques minutes d'agitation. Nous avons ajouté (0,423 g - 1,89 mmol) de PMHS, où nous avons constaté la formation de solides après une période d'agitation. Pendant environ 6 heures, on a ajouté au mélange 50 ml de NaOH, goutte à goutte, et on a laissé agiter le mélange pendant une nuit entière. Puis on a filtré la solution et on a obtenu un échec,Then we evaporated the solvent, after which we extracted the liquid-liquid with CH_2Cl_2 once at pH = 9 in order to get rid of the remainder, then dried the organic phase with: $MgSO_4$, evaporated again, then changed the acidity of the medium to 11.. pH = and extracting four times CH_2Cl_2.(400ml). After drying and evaporation, a brown to black-coloured solid product was obtained which is pure according to TLC analysis and yield R= 87.48%, m= 0.175g. IR: (KBr¸ cm^{-1}): 3492.2(F¸ ∂_{NH}), 2920(m¸ ∂_{CH}), 1627.8(F¸ $\partial_{N\text{-}H}$), 1521.7 (F¸ $\partial_{C=C}$), 1350.1 (m¸ $\partial_{C\text{-}N}$), 1110.9(m¸ $\partial_{C\text{-}C}$), 736.8.8($\partial_{\text{Aromatic Substituid}}$), 489.9($\partial_{Fc\text{-}CP}$).RMN ^1H (400MHz, $CDCl_3$) ; δ =1.61(2H, NH_2) ; 3.99(t, 2H, CH_2); 4,21 [11 H: (d, 2H, C_5); (s, 2H, C_2ou C_3); (s, 7H, (5H) C_4 and 2H, C_3ou C_2)]; 4.42(s, 1H, NH); 6.60(d, 1H, C_{11}); 6.63(dd, 1H, C_9) ; 7.40(d, 1H, C_8) ; 7(t, 1H, C_{10}). .RMN ^{13}C (400MHz, $CDCl_3$ δ = 42,67(1C, C_5) ; 68.25 (2C, C_3ou C_2) ; 68,31(2C, C_2 ou C_3) ; 68.63(5C, C_4) ; 84,97(1C, C_1) ; 98.74(1C, CN) ;112.14 (1C, C_{11}) ; 114,46(1C, C_9) ; 120.57(1C, C_8) ; 133.83 (1C, C_7-NH_2) ; 133,87(1C, C_{10}) ; 150,92(1C, C_6).









☑ Formula: $C_{18}H_{16}FeN_2$
☑ Exact Mass: 316.1
☑ Mol. Wt.: 316.2
☑ m/z: 316.1 (100.0%), 317.1 (22.7%), 314.1 (6.4%), 318.1
☑ Elem. Anal.: C, 68.38; H, 5.10; Fe, 17.66; N, 8.86

Fig 01: Reduction reaction of 4- $FcCH_2NHPhCN$ by (TBAF-PMHS) and Optimized geometrical structure of4- $FcCH_2NHPhCH_2NH_2$

2.2.2 Synthesis of N-(ferrocenyl methyl) 3-aminomethylaniline(3-$FcCH_2NHPhCH_2$ NH_2)

A tricol flask was filled with (0.2g, 0.57mmol) of the compound N-(ferrosylmethylamino) 3-benzonitrile and 30ml of THF, (0.00719g, 0.0228mmol) of TBAF and (0.386g, 0.0017mmol) of PMHS which showed a variety of colorations during addition and agitation. After stirring for 6 hours, 50ml of 3N NaOH was added dropwise to the mixture. The mixture was then filtered and the solvent evaporated, after which the mixture was extracted once with CH_2Cl_2 at pH=9, the organic phase was dried with $MgSO_4$ and the solvent evaporated to obtain a dark gray solid with a yield of R =82.14.6%, m = 0.164. IR: (KBr¸ cm^{-1}): 3484.3(F¸ ∂_{NH}), 2910(m¸ ∂_{CH}), 1654.8(F¸ $\partial_{N\text{-}H}$), 1583.4 (F¸ $\partial_{C=C}$), 1344.2 (m¸ $\partial_{C\text{-}N}$), 1132.1(m¸ $\partial_{C\text{-}C}$), 774..2($\partial_{\text{Aromatic Substituid}}$), 492.4($\partial_{Fc\text{-}CP}$).RMN ^1H (400MHz, $CDCl_3$) ; δ =1.81(2H, NH_2) ; 3.94(t, 2H, CH_2); 4,23 [11 H: (d, 2H, C_5); (s, 2H, C_2ou C_3); (s, (s, 1H, NH); 6.67(d, 1H, C_{11}); 6.69(dd, 1H, C_9) ; 7.24(d, 1H, C_8) ; 7. 33(t, 1H, C_{10}). .RMN ^{13}C (400MHz, $CDCl_3$ δ = 42,26(1C, C_5) ; 67.68 (2C, C_3ou C_2) 68.35(2C, C_2 ou C_3) ; 68.72(5C, C_4) ; 85.19(1C, C_1) 95.54(1C, CN) ;110.64 (1C, C_{11}) ; 116.57(1C, C_9) ; 118.14(1C, C_8) ; 132.79 (1C, C_7-NH_2) ; 134,43(1C, C_{10}) ; 150 (1C, C_6).

2.2.3.Synthesis of N-(ferrocenyl methyl) 2-aminomethylaniline(2-$FcCH_2NHPhCH_2$ NH_2)

In a tricol flask, N-(ferrosylmethylamino) 2-benzonitrile compound (0.2g, 0.57mmol) was placed (0.2g, 0.57mmol) and 30ml, then (0.386g, 0.0017mmol) of TBAF was added, the color was changed to black after a few minutes of stirring, then (0.386g, 0.0017mmol) of PMHS was added, of which we noticed the formation of a large quantity of solids and an increase in temperature, which forced us to increase the volume of solvent and with a quick stirring we were able to destroy the solids formed, the color turned yellowish green. After 6 hours of stirring, we added 50ml of 3N NaOH drop by drop and left the mixture under stirring for a complete night.After filtration of the mixture and evaporation of the solvent, it was extracted with CH_2Cl_2 once at pH 9. Then the organic phase was dried with $MgSO_4$ and evaporated once more.The acidity of the medium was changed to pH 11 and extracted 4 times with CH_2Cl_2 (400 ml).

After drying and evaporation of the solvent, a solid product with a brown color was obtained. The yield R was 55.19%, m= 0.110g. IR: (KBr¸ cm^{-1}): 3492.2(F¸ ∂_{NH}), 2930.8(m¸ ∂_{CH}), 1654.2(F¸ $\partial_{N\text{-}H}$), 1530.4 (F¸ $\partial_{C=C}$), 13441 (m¸ $\partial_{C\text{-}N}$), 1117.5(m¸ $\partial_{C\text{-}C}$), 780.2($\partial_{\text{Aromatic Substituid}}$), 495.7($\partial_{Fc\text{-}CP}$).RMN ^1H (400MHz, $CDCl_3$) ; δ =1.74(2H, NH_2) ; 3.74(t, 2H, CH_2); 4.38 [11 H: (d, 2H, C_5); (s, 2H, C_2ou C_3); (s, 7H, (5H) C_4 and 2H, C_3ou C_2)]; 4.66(s, 1H, NH); 6.84(d, 1H, C_{11}); 6. 93(dd, 1H, C_9)

; 7.12(d, 1H, C_8) ; 7.42(t, 1H, C_{10}). .RMN ^{13}C (400MHz, $CDCl_3$ δ = 43.81(1C, C_5) ; 68.88 (2C, C_3ou C_2) ; 69.02(2C, C_2ou C_3) ; 69.74(5C, C_4) ; 84,57(1C, C_1) 88.96(1C, CN) ;116.22 (1C, C_{11}) ; 117.52(1C, C_9) ; 125.73(1C, C_8) ; 127.71 (1C, C_7-NH_2) ; 128.03(1C, C_{10}) ; 146.10(1C, C_6).

3.Results and discussion :

3.1. Reduction of N-(ferrocenylmethylamino) 4-benzonitrile ($FcCH_2NHPhCN$) (fig02) (fig 03)

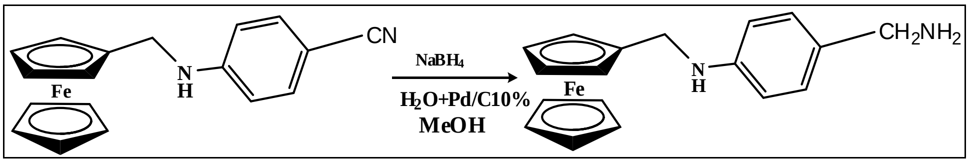


Fig 02: Reduction reaction of 4- $FcCH_2NHPhCN$ by ($NaBH_4$;Pd/C)

We followed the course of the reaction with a CCM, where we discovered the presence of a new compound with a path difference Rf = 0.51 that differs from the path difference of the reactant Rf = 0.64, so we extracted liquid-liquid using dichloro 13.5 PH = and obtained a solid substance with a light brown color. We determined the melting point and found it to be 124^0C, which is different from the reactant,132^0C and this confirms the progress of the reaction.

The result was analyzed with infrared spectroscopy, and we found the disappearance of the CN band at (2208 cm^{-1}), the appearance of the amine band at (3332 cm-1), and the appearance of the CH_2 band at (2900 cm^{-1}),

A nuclear magnetic resonance spectrophotometric analysis was performed, the ^{13}C NMR spectrum showed that the compound contains 18 carbon atoms (Fig 01) as shown in the above structural formula and the ^1H NMR spectrum showed that the compound contains20 (Fig 01) hydrogens.

The same thing happened when we used the reflux reaction using the reactive formula PMHA - TBAF. We obtained the same product with a better yield that reached 87.48%,

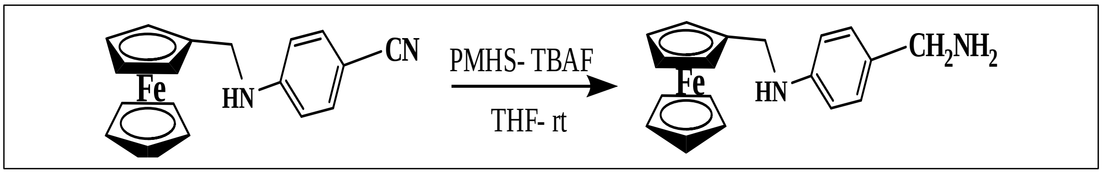


Fig 03 : Reduction reaction of 4- $FcCH_2NHPhNO_2$ by (TBAF-PMHS)

The progress of the reaction was always monitored by TLC, where it showed the appearance of a new compound of retention factor R_f= 0.79 different from the reagent of R_f= 0. 62.The product was analyzed by IR spectrophotometry,The results showed the disappearance of the sharp absorption of the nitrileCNfunction at 2206.4cm^{-1}, the appearance of the broad peak of the amineNH_2 group in the range (3097.5-3429.2cm^{-1}), and the appearance of the characteristic absorption of the methylene groupCH_2 at 2920 cm^{-1}. The melting points of reagent and product were determined to be 118°C and 127°C, respectively.

Based on the reduction reactions of the three (ferrocenylmethyl)aminomethylaniline compounds under the above experimental conditions and in the three positions; ortho, meta and para and as shown in (**table 01and table 02),** it was found that the position which gives a better reduction efficiency R= 87.48% is the para position, followed by the meta position with an efficiency equal to 82.14% and finally the orthoposition with a relatively low efficiency equal to 75.19%, This is linked to the simplicity of their molecular structure characterized by the presence of a "nitril" group (-CN) in the ortho, meta and para position of an electron-donating group, this can be explained in general bythe electronic benzonitril effect bat in these resultsthe steric hindrance caused by ferrocene and phenyl.

Table (01): results of reduction reactions by (TBAF- PMHS)

The efficiency of the reduction%	The resulting compounds	Reactive compounds
87.48	4- $FcCH_2NHPhCH_2NH_2$	4-$FcCH_2NHPhCN$
82.14	3- $FcCH_2NHPhCH_2NH_2$	3- $FcCH_2NHPhCN$
55.19	2- $FcCH_2NHPhCH_2NH_2$	2- $FcCH_2NHPhCN$

Table (02): results of reduction reactions by (NaBH4 - Pd/C10%,**)**

The efficiency of the	The resulting compounds	Reactive compounds
71.1	4- $FcCH_2NHPhCH_2NH_2$	4-$FcCH_2NHPhCN$
62.63	3- $FcCH_2NHPhCH_2NH_2$	3- $FcCH_2NHPhCN$
32.25	2- $FcCH_2NHPhCH_2NH_2$	2- $FcCH_2NHPhCN$

Based on reference[18].,the following mechanism for the reduction of the nitril group to the amine group can be proposed ; This process is called “Zipper” catalysis, in detail **(Fig 04)** and **(Fig 05)**.

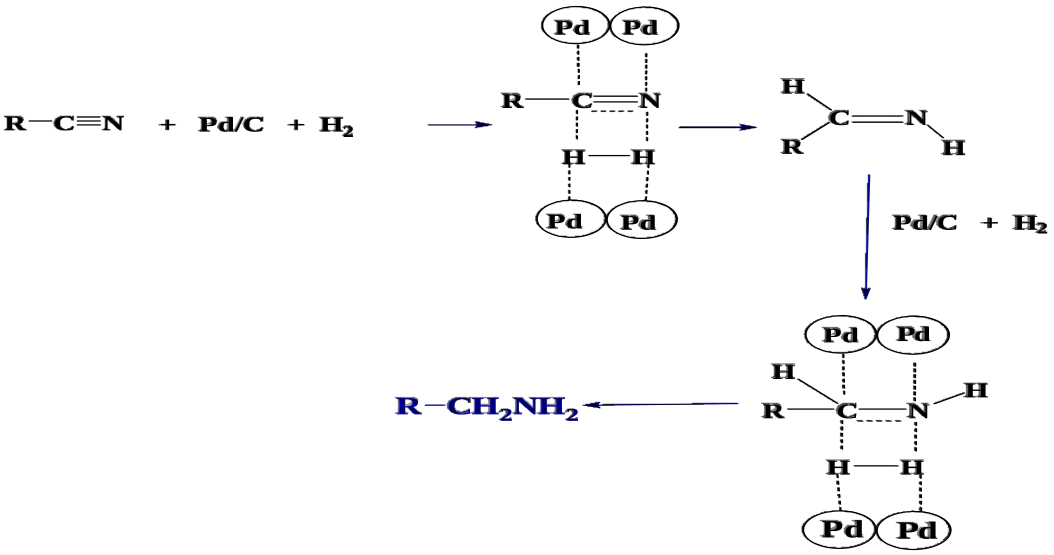


Fig 05 : Mechanism of reducing nitrile to primary amine with NaBH4 and Pd/C10%.

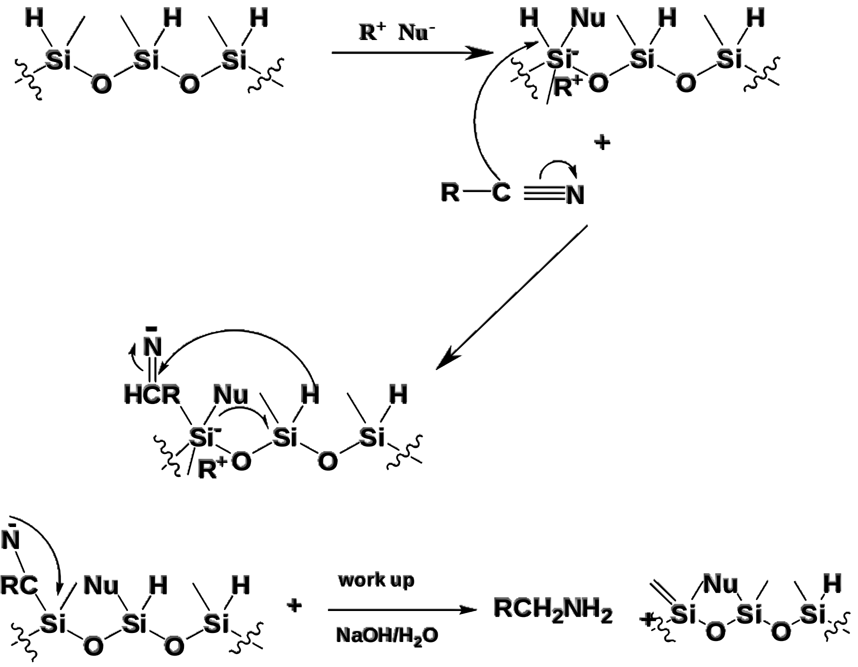


Fig 05 :Proposed mechanism of the nitro group reduction by TBAF-PMHS

4. conclusion

In this study, we returned the function of cyano (nitriles) by the heterogeneous catalytic recovery method using NaBH4 andPd/C10%, and the compounds we studied were N-ferrocenylmethylaminobenzonitriles in the ortho - meta - para positions in order to reduce them to primary amines.

The best results were in the case of reflux in the para mode, where the reaction yield for the product N-(ferrocenyl methyl) 4-methylamino aniline reached 71.1%, while for the product N-(ferrocenyl methyl) 3-methylaminoaniline it reached R=62.63%
As for the reaction yield in the ortho mode, it was weak as it was estimated at R = 32.25%This is probably due to vacuum obstruction. As for our second method of returning the cyano function in the previous ferrocenyl compounds, it gave very good results in all situations.
The reaction yield ranged from 55-87% using polymethylhydrosiloxane in the presence of the homogeneous catalyst tetrabutylammonium fluoride.

We conducted a comparative study between the homogeneous catalytic reaction method using PMHS in the presence of TBAF and the heterogeneous catalytic reaction method. The best results were in the case of homogeneous catalytic reaction, and this is due to the reaction kinetics, which is simple in this case. Unlike the heterogeneous catalytic reaction method, there is complex kinetics. Recycling with a high yield, and as we said previously, poisoning of the catalyst may occur, and this reduces the yield, but in general, the two methods are effective for recycling. By studying some experimental conditions in the future in the method of heterogeneous catalytic regeneration, this may lead to a good result, so that it can be applied in the industrial field.

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