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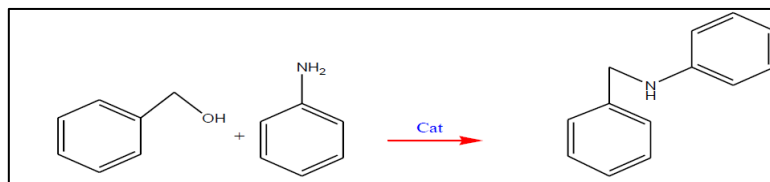
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## N-Alkylation aniline by Cu-Chromite catalyzer self-transmitting Hydrogen

**Pouresmaeily Seyed Mohammad, H. Shirkavand Behzad, Shahidzadeh Mansour and Ebrahimi Sobhan**

### Abstract

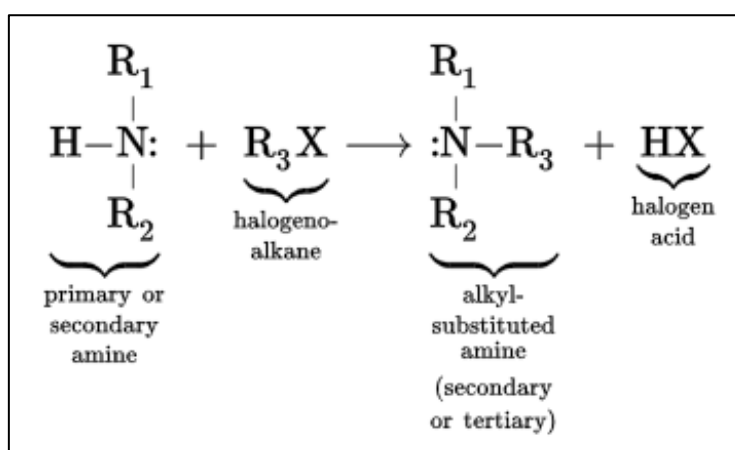
In last years, leading the N-Alkylation Amines reaction by Alcohols in presence of Cu catalyzer to act in low pressure and temperature conditions. Among the used catalyzers can point Cu-Acetate (Cu(OAC)<sub>2</sub>) and Cu-Oxide (CuO) also Aniline with Benzyl alcohol reaction.



**Keywords:** N-Alkylation Amines, Cu-Chromite catalyzer, alcohols

### 1. Introduction

Amine alkylation (amino-de-halogenation) is a type of organic reaction between an alkyl halide and ammonia or an amine. The reaction is called nucleophilic aliphatic substitution (of the halide), and the reaction product is a higher substituted amine. The method is widely used in the laboratory, but is less important industrially, where alkyl halides are not preferred alkylating agents.



#### 1.1 N-Alkylation aniline

First, mix 30 ml of Ortho Xylene as solvent, 15 mmole Benzyl Alcohol with 20 mmol Aniline and 5mole Cu-Chromite nano catalyzer then 35 mmole Potassium Carbonate in 50 ml volumetric flask and temperature of 110oc for 8 hrs. Solution separating process was that after reaction time, solution filtered and washed by Ethyl Acetate and observed two phases of Organic and Aqueous solutions in separatory funnel. The Organic phase included synthesized compound. Then dried the Organic phase by Sodium sulphate finally specification tests performed.

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## 1.2. N-Alkylation aniline reaction

In the reaction of Aniline and Benzyl Amine by self-transmitting Hydrogen, the production is N-Phenyl Benzyl Amine then perform physical (melting point determination) and chemical (PH and Heisenberg) tests on production after purification by Ethyl Acetate and no-water Sodium sulphate extractions. After pilot N-Phenyl Benzyl Amine synthesis, performed H-NMR and IR spectroscopy test that confirmed the intended product. The mechanism of this reaction is so

complex and there isn't any acceptable mechanism for that but the proposed mechanism (showed in figure 1) is that catalyzer provide the intermediate product for Nucleophilic Amine groups reaction by separating the alcoholic Hydrogen. Finally by acting the Nucleophilic Amine reaction with provided intermediate, Imine synthesize. In the reduction step that is the most complex step, Imine reduce by catalyzer that absorbed the alcoholic Hydrogen and Amine produce.

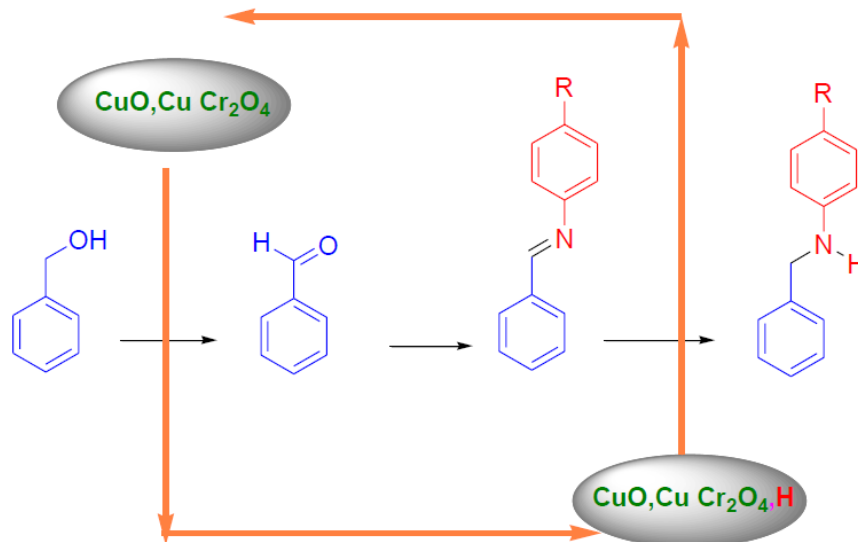


Fig 1: Proposed mechanism for self-transmitting hydrogen N-Alkylation

## 2. Chemical and Physical tests for specification of produced N-Phenyl Benzyl Amine

First performed PH test that confirmed Amine existence. Then for specifying the type of Amine, Heisenberg test performed. Also existence of HCl insoluble yellow oily layer confirmed second type of Amine. By ensure of second type Amine synthesis and given N-Phenyl benzyl Amine melting point (40oc), synthesized compound melting point specified that confirmed N-Phenyl benzyl Amine.

### 2.1. N-Phenyl benzyl Amine spectroscopy studying

As figure 2 show H-NMR spectrum of N-Phenyl benzyl Amine is match with standard sample (figure 3). By studying the N-Phenyl benzyl Amine structure, know that this compound has three protons that should appear in three areas. A proton is related to Ammine Hydrogen that connected to Benzene is about 4.1 ppm and other two protons are about 4.7 ppm. Ten protons relate to Phenyl cycles that about 6-8 ppm.

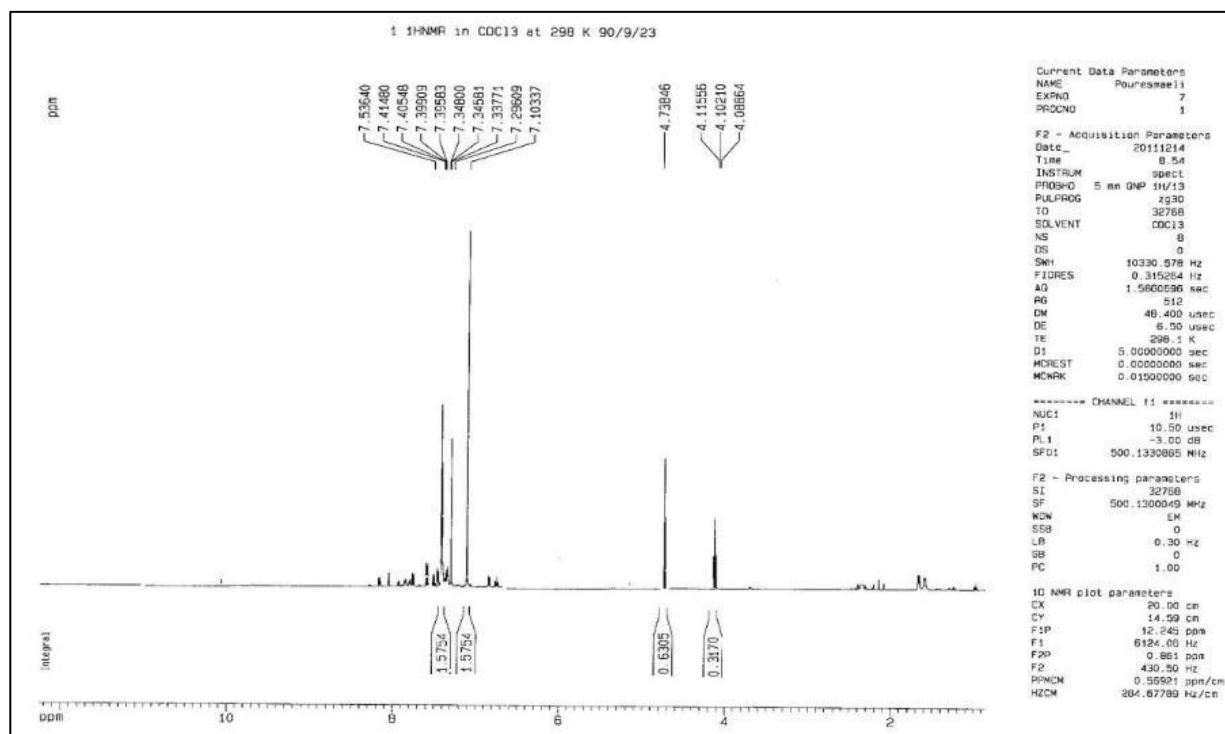


Fig 2: N-Phenyl Benzyl Amine H-NMR spectrum

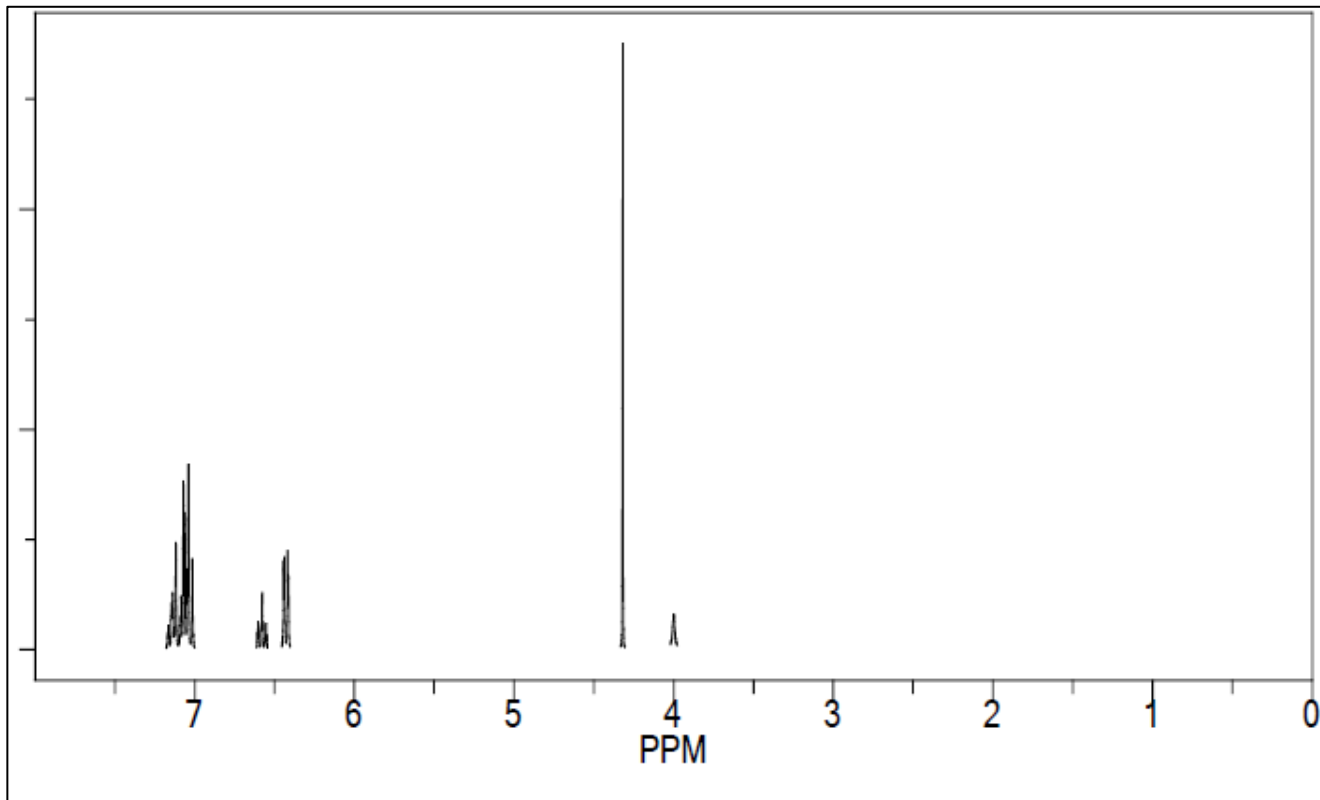


Fig 3: Standard H-NMR spectrum of N-Phenyl Benzyl Amine

Also used IR spectroscopy for specifying Functional groups. Synthesized and standard IR spectrum showed in figures 4, 5.

According to spectrums Amine groups has a peak of 3200-3600  $\text{cm}^{-1}$ . Because its second type so has one peak.

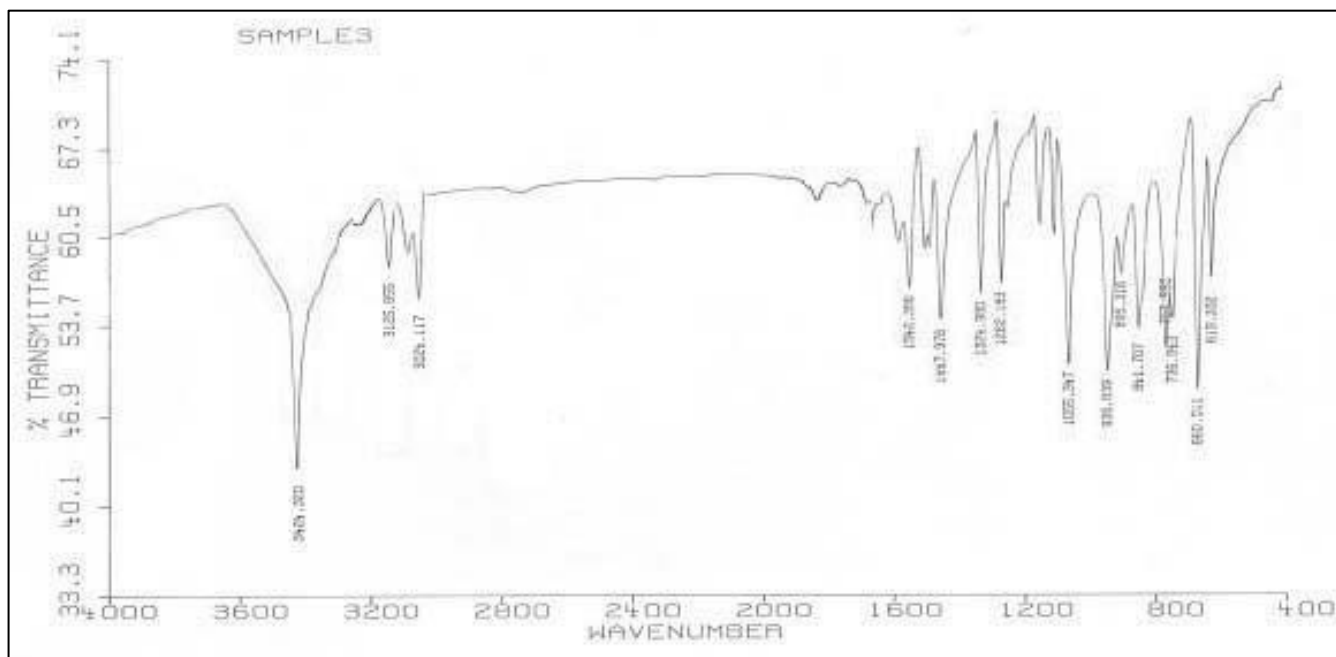


Fig 4: Synthesized N-Phenyl Benzyl Amine IR spectrum

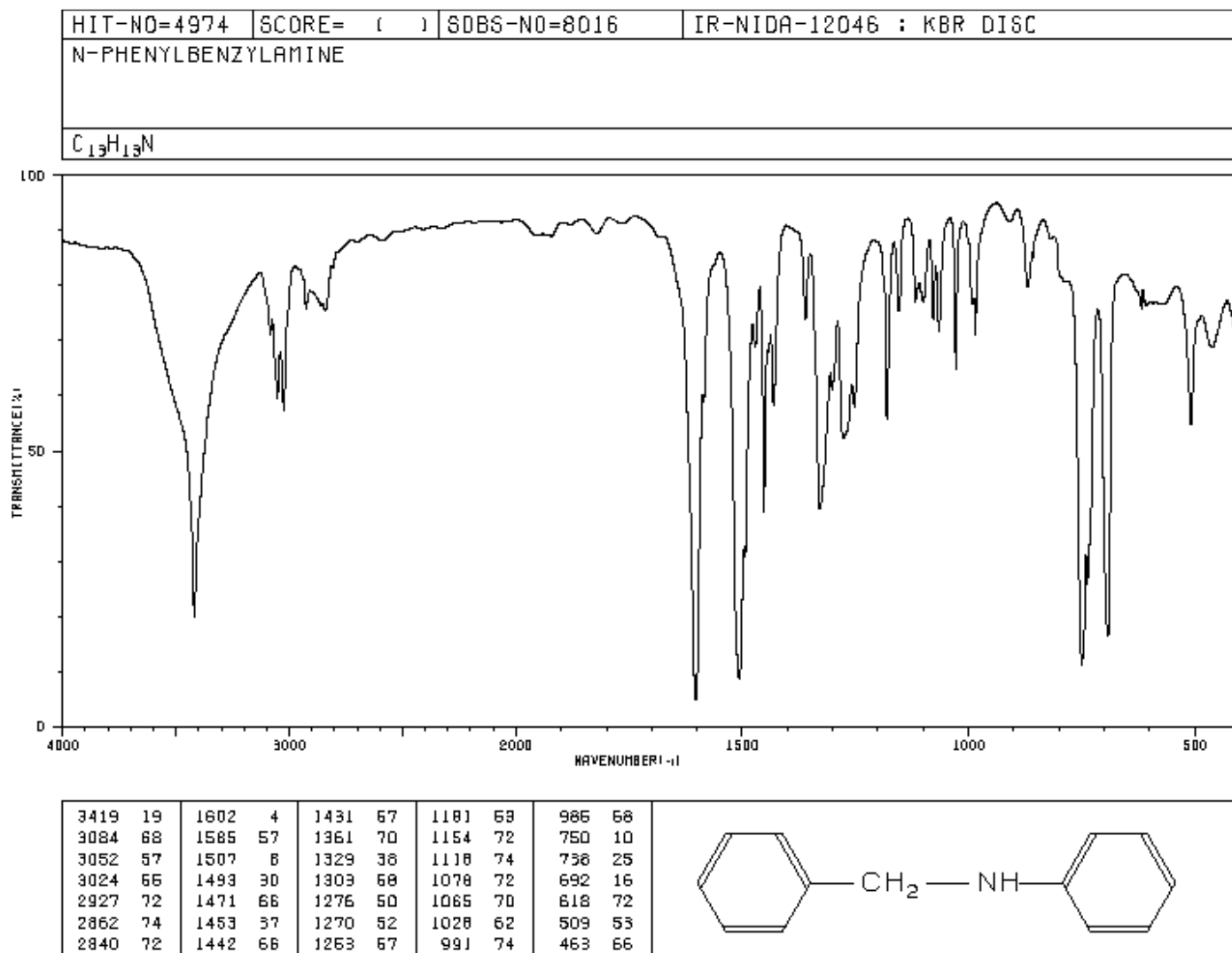


Fig 5: Standard N-Phenyl Benzyl Amine IR spectrum

### 3. Studying effect of nano Cu-Chromite catalyzer on N-Alkylation reaction

According to that reaction performed in different conditions by using the synthesized sample as control sample and thin layer chromatography technic the results are below:

As table 1 shows reaction is efficient in neutral Nitrogen gas atmosphere. This is because that Nitrogen prevents exiting of Benzyl alcohol and preventing oxidation of intermediate products by Oxygen. Rising heat cause efficiency reduction because of parallel reactions and bi-products.

Table 1: Different conditions of N-Alkylation Aniline results

| Reaction no. | Reaction temp. | Environment atmosphere | Efficiency (%) |
|--------------|----------------|------------------------|----------------|
| 1            | 110oc          | Air                    | 70             |
| 2            | 110oc          | Neutral Nitrogen gas   | 85             |
| 3            | 130oc          | Air                    | 65             |
| 4            | 130oc          | Neutral Nitrogen gas   | 65             |
| 5            | 145oc          | Air                    | 25             |
| 6            | 145oc          | Neutral Nitrogen gas   | 30             |

According to table 2, the effective factor of solvent performance is no-dehydrogenation property. As an example

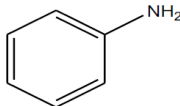
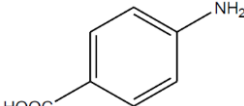
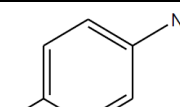
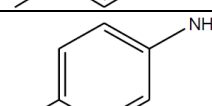
Aprotic solvents is more efficient relative to Protic solvents because of no dehydrogenation property. Protic solvents prevent production of Intermediates by providing Hydrogen. The amount of performance of Basic solvents depends on Nucleophilic property. Actually that Basic solvent has better performance that hasn't Nucleophilic property. If Basic solvent has Nucleophilic property, Nucleophile produces other excess productions among reaction performing.

Table 2: N-alkylation Aniline reaction in different solvents and Base

| Reaction no. | Solvent                | Base                            | Efficiency (%) |
|--------------|------------------------|---------------------------------|----------------|
| 1            | Ortho Xylene           | K <sub>2</sub> CO <sub>3</sub>  | 85             |
| 2            | Ortho Xylene           | Na <sub>2</sub> CO <sub>3</sub> | 80             |
| 3            | Ortho Xylene           | NaHCO <sub>3</sub>              | 65             |
| 4            | Ortho Xylene           | CH <sub>3</sub> COONa           | 50             |
| 5            | Ortho Xylene           | NaOtBu                          | 85             |
| 6            | Toluene                | K <sub>2</sub> CO <sub>3</sub>  | 75             |
| 7            | Tetra Hydro Furan      | K <sub>2</sub> CO <sub>3</sub>  | Negligible     |
| 8            | Di-Methyl Sulphoxide   | K <sub>2</sub> CO <sub>3</sub>  | Negligible     |
| 9            | Di-Methyl Formaldehyde | K <sub>2</sub> CO <sub>3</sub>  | Negligible     |

### 3.1. Studying effect of nano Cu-Chromite catalyzer in N-Alkylation of Aniline derivations.

**Table 3:** N-Alkylation reaction by Aniline derivations results

| Used derivations  | Reaction temp. | Environment atmosphere | Time  | Efficiency (%) |
|---|----------------|------------------------|-------|----------------|
|  | 110oc          | Neutral Nitrogen gas   | 8 hrs | 85             |
|  | 110oc          | Neutral Nitrogen gas   | 8 hrs | 60             |
|  | 110oc          | Neutral Nitrogen gas   | 8 hrs | 96             |
|  | 110oc          | Neutral Nitrogen gas   | 8 hrs | 85             |

It should be noted that produced Amines detection by mentioned physical and chemical methods for specification of N-Phenyl Benzyl Amine accepted. It has done chemical tests for specification of productions in this way, first performed PH test to ensure that synthesized material is Amine then studied type of Amine by Heisenberg test. After that determined the material melting point. All of this tests confirmed the intended Amine for any experiment. All of the steps include: preparing, recycling product and catalyzer, that done same as Aniline reaction.

#### 4. Conclusion

According to daily needs of producing different Amines use in military industries, pharmaceuticals, Health, trimming and chemical, finding new ways to producing them is logical. This new ways can be optimizing the common experiments for producing Amines, Using new primary materials in synthesis or using new catalyzers in producing Amines. Cu-chromite catalyzer used in N-Alkylation Amine reaction and due to results, this catalyzer is able to participate in this reaction. The results also shows that Cu-Chromite catalyzer can use as catalyzer in N-Alkylation Amine derivations with high efficiency. Cu-Chromite can introduce as a new catalyzer for N-Alkylation amines by alcohols and Hydrogen self-transmitting.

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