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PROTODECARBOXYLATION OF BENZOIC ACID (SUBSTITUTED) BY USING TRANSITION METALS COMPOUND- COPPER CARBONATE ($CuCO_3$)

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ABSTRACT

In the case of benzoic acid derivatives particularly, monoprotodecarboxylation is a chemical reaction in which a single carboxyl group from a molecule is removed. A new molecule which is called a carbanion, which has one less carbon atom and a positive charge, is created as a result of this reaction. For the effective removal of a single carboxyl group from benzoic acid derivatives, copper (Cu) catalysts in monoprotodecarboxylation processes have gained popularity. Protodecarboxylation for a variety of benzoic acids (substituted) catalyzed by $CuCO_3$ and Acetic acid in DMSO is explained. The monoprotodecarboxylation is a process which can also done by this methodology for heteroaromatic carboxylic acid and aromatic carboxylic acid. Due to their capacity to form stable complexes with the substrate and promote the transport of electrons, copper catalysts have been discovered to be extremely effective in promoting this reaction. In comparison to conventional techniques that are use strong bases, it has been demonstrated that the use of copper catalysts in monoprotodecarboxylation processes results in the faster reaction rates, higher yields, suitable temperature and more selective product production. The potential of copper catalysts as an effective and affordable substitute for the monoprotodecarboxylation of benzoic acid derivatives is highlighted by this.

Keyword: Protodecarboxylation, benzoic acids (substituted), Copper carbonate, Dimethyl sulfoxide (DMSO)

1. INTRODUCTION

As a chemist student, Fundamental aim is building complexometric molecular from simple and rapidly available building blocks. Use of carboxylic acid as building blocks in organic chemistry synthesis extended due to development of numerous catalytic transformations **[1-8]**. In synthetic organic chemistry reaction of decarboxylation is very important transformations for the removal of carboxylate group which are not part of the target molecules but required as directing groups in other transformations **[9-10]**. Consequently, considerable effort has been directed to the study of the protodecarboxylation of aromatic carboxylic acid, which usually require the use of transitions metals such as Ag, Hg and Pd **[11-12]**.

The Silver, Mercury and Palladium metal-based catalyst which is only used for decarboxylation of ortho-substituted aromatic acid but these all-catalyst is cannot be decarboxylate simple benzoic acid. To perform the decarboxylation reaction in the presence of Ag, Hg and Pd catalyst require high temperature and these catalysts are verry costly **[13-15]**.

Copper base catalyst used for decarboxylation of ortho-substituted aromatic acid as well as used for decarboxylation simple benzoic acid. Decarboxylation of ortho-substituted aromatic acid by using copper catalyst required less temperature and time as compare to decarboxylation of simple benzoic acid. In this method the yield obtained is high when we use ortho substituted aromatic acid as compare to simple benzoic acid. This method also used for protodecarboxylation of various heteroaromatic carboxylic acid **[16]**.

The nature of the ortho substituent is extremely important, with only electron – withdrawing or alkoxy group leading to protodecarboxylation. Extending this method to heteroaromatic carboxylic acid, hetero could play the same role as the ortho substituent in previous studies and activating alpha position **[17-19]**. We would like to report a new Cu – promoted protodecarboxylation protocol that affords excellent yields when applied to a wide range of substitute benzoic acid.

We observed that electron withdrawing group attached to benzoic acid where more reactive than electron donating group attached with benzoic acid and interestingly ortho substituted generally show higher reactivity than meta and para substituted benzoic acid **[20]**.

Applications for this reaction in organic synthesis includes the synthesis of various pharmaceutical products, such as antiinflammatory medications and anticonvulsants, can be done by mono-proto decarboxylation, analyzing organic compounds Mono-proto decarboxylation can be utilized as a diagnostic tool because the reaction's products are simple to recognize using a variety of analytical techniques.

2. MATERIALS AND METHODS:

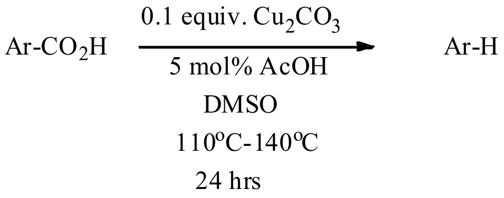
Materials:

Benzoic acid, Salicylic acid, Anthranilic acid, Acetic acid, Copper carbonate, Dimethyl sulfoxide (DMSO) Purchased from PRAYOPSHA CHEM ENTERPRISE. Sodium bicarbonate, Diethyl ether, Sodium chloride purchased from local suppliers.

Methods:

General procedure:

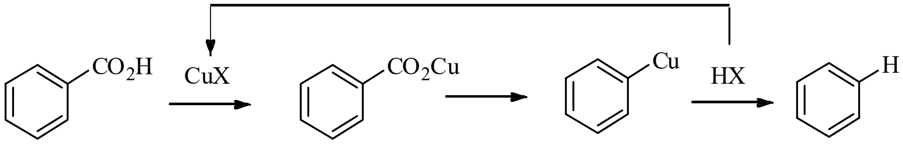
A mixture of benzoic acid (substituted) and $CuCO_3$/AcOH in dry DMSO was stirred for 16 - 20 hours at 100 -120 °C after the completion of reaction separate the aqueous layer and organic layer by using saturated sodium bicarbonate and diethyl ether. The two layers were separate and then organic layer washed with saturated sodium chloride solution. Diethyl ether evaporate by rota evaporator final product will be obtained.



$$\mathrm{Ar\text{-}CO_2H} \xrightarrow[\substack{\text{5 mol\% AcOH} \\ \text{DMSO} \\ 110^{o}\text{C-}140^{o}\text{C} \\ \text{24 hrs}}]{\text{0.1 equiv. } Cu_2CO_3} \mathrm{Ar\text{-}H}$$

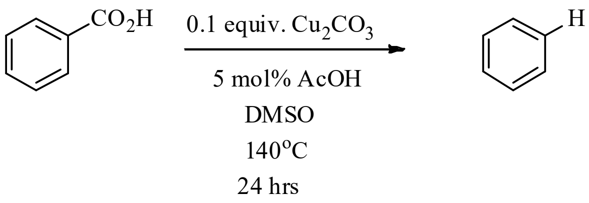
General mechanism:

The Cu-catalyzed protodecarboxylation of benzoic acid's suggested mechanism



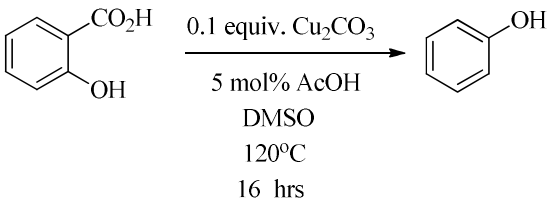
Benzoic acid:

The reaction was carried out following the general procedure with benzoic acid (100 mg/0.82 mmol), $CuCO_3$ (10.13 mg /0.082 mmol), AcOH (2.34 ml/0.041 mmol) in dry DMSO solvent.



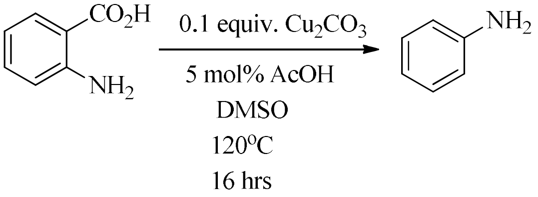
Salicylic acid:

The reaction was carried out following the general procedure with Salicylic acid (100 mg 0.72 mmol), $CuCO_3$ (8.95 mg/0.072 mmol), AcOH (2.08 ml/0.036 mmol) in dry DMSO solvent.



Anthranilic acid:

The reaction was carried out following the general procedure with anthranilic acid (100mg/0.72 mmol), $CuCO_3$ (8.94mg/0.072mmol), AcOH (2.08ml/0.036 mmol) in dry DMSO solvent.



3. RESULT AND DISCUSSION:

Result:

Sr. No.	Starting material	T/°C	Solvent	Catalyst	Time (in hrs.)	Product	Yield (%)	Boiling point
1.	Benzoic acid	120°C-140°C	DMSO	$CuCO_3$	24	Benzene	65	80.1°C
2.	Salicylic acid	100°C-120°C	DMSO	$CuCO_3$	16	Phenol	80	181.7°C
3.	Anthranilic acid	100°C-120°C	DMSO	$CuCO_3$	16	Aniline	80	184.1°C

1. Characterization of benzene:

➢ IR spectrum of benzene

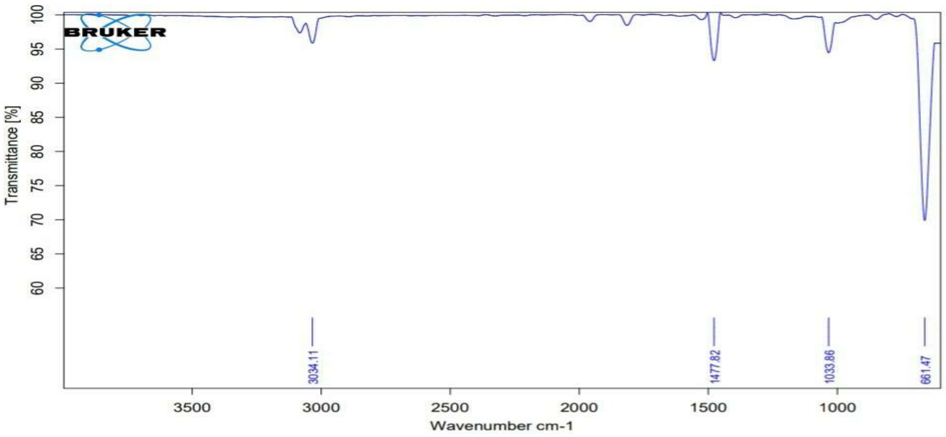


Figure 1.1

IR: The stretching vibration of the aromatic C-H bonds is seen at 3034.11 cm^{-1}. Two peaks of the C=C double bond vibrations are seen in the 1600-1650 cm-1 region. The C-H bonds' bending vibrations are seen at1477.82cm^{-1}. These IR spectral characteristics can be utilized to identify benzene and separate it from other chemicals that are similar to it **(Figure 1.1)**.

- ➢ **^{1}H-NMR of benzene**

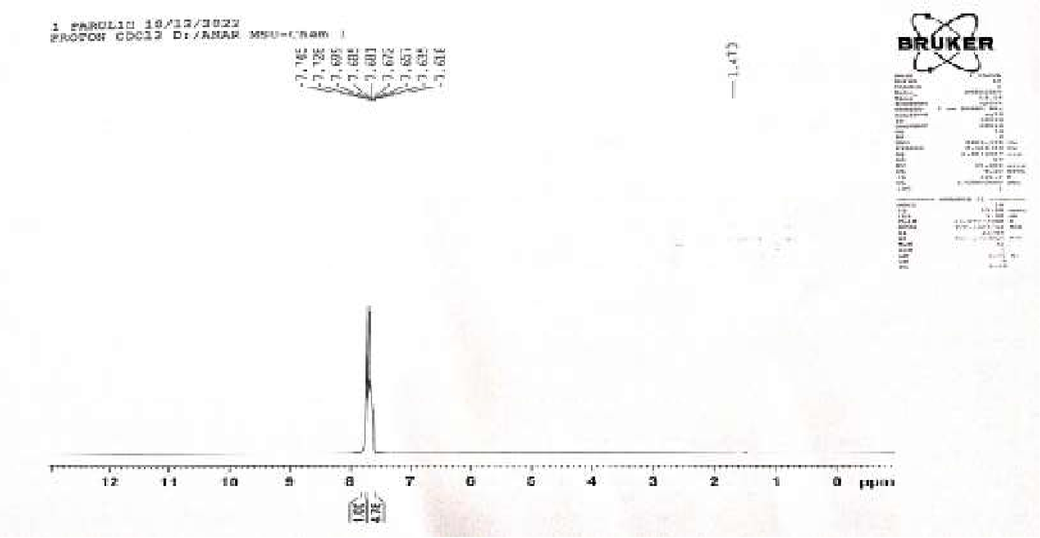


Figure 1.2

^{1}H NMR : 1H NMR (500 MHz, CDCl3) δ 7.62 (m, 6H)

The existence of six analogous aromatic protons (ring hydrogen atoms) results in a single, broad peak in the 1H NMR spectra of benzene that is centered at about 7.62 ppm. The 1H NMR signal is amplified as a result of magnetic interactions between these protons **(Figure 1.2)**.

- ➢ **Mass Spectrum of benzene**

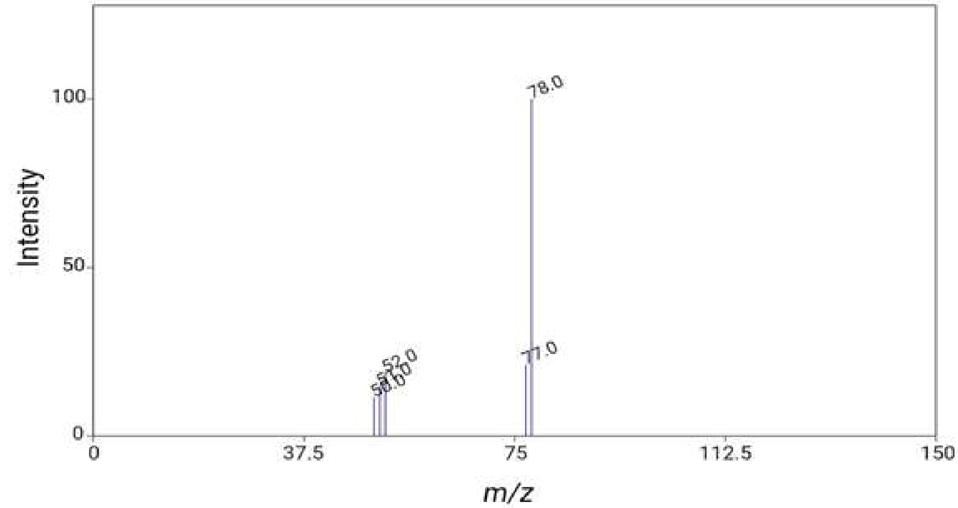


Figure 1.3

Mass: The mass spectrum MS (ESI): m/z 78 shows molecular weight of benzene **(Figure 1.3)**.

2. Characterization of phenol

- IR Spectrum of phenol

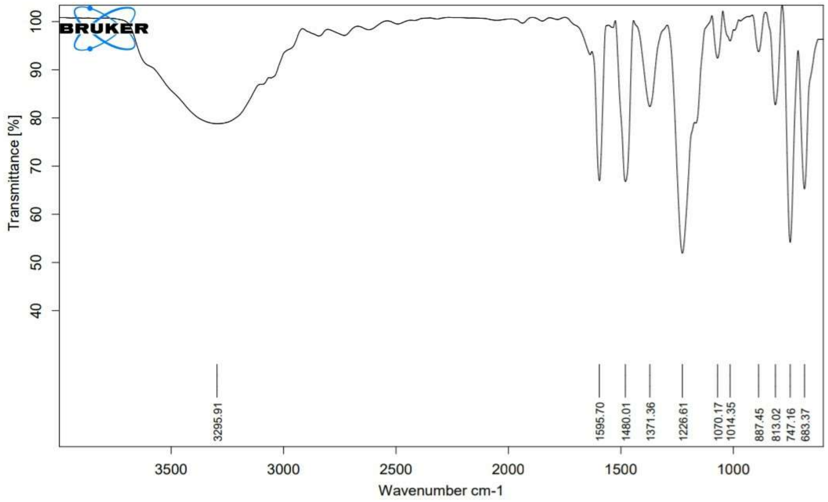


Figure 2.1

IR: The stretching vibration of the hydroxyl (-OH) group is seen at 3295.91 cm^{-1} as a broad, prominent peak in the IR spectra of phenol. This peak shows that phenol contains the hydroxyl functional group. The aromatic ring's C-H stretching vibrations are seen as a broad, powerful peak in the 3000–2800 cm^{-1} range. Two peaks of the C=C double bond vibrations are seen in the 1595.7 cm^{-1} and 1480.01 cm^{-1}. The C-H bonds' bending vibrations are seen at 1371.36 and 1226.61 cm^{-1} **(Figure 2.1)**.

- **^{1}H-NMR of phenol**

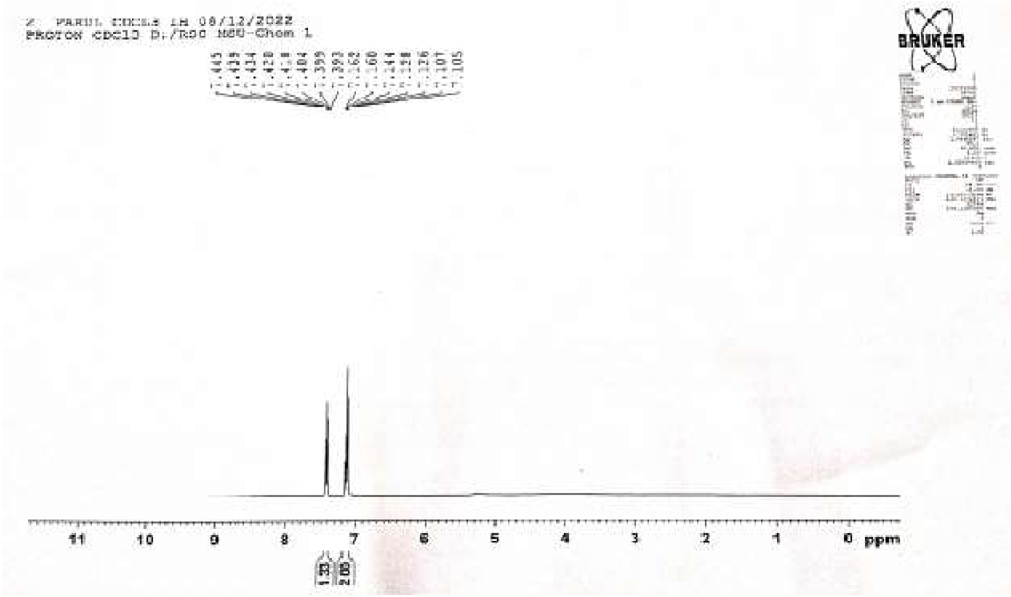


Figure 2.2

^{1}H NMR: 1H NMR (400 MHz, CDCl3) δ 7.14 (m, 2H), 7.43(m,2H), 5.3 (s,1H)

^{1}H NMR Spectroscopy: The signal for the aromatic hydrogen atoms in phenol's 1H NMR spectrum is seen as a singlet peak in the 7-8 ppm region. A singlet peak in the 5-6 ppm range is the signal for the hydroxyl proton. Depending on the strength of their connection, the hydrogen atoms in the ring emit a signal that appears as a number of peaks in the 7-8 ppm region **(Figure 2.2)**.

- **Mass spectrum of phenol**

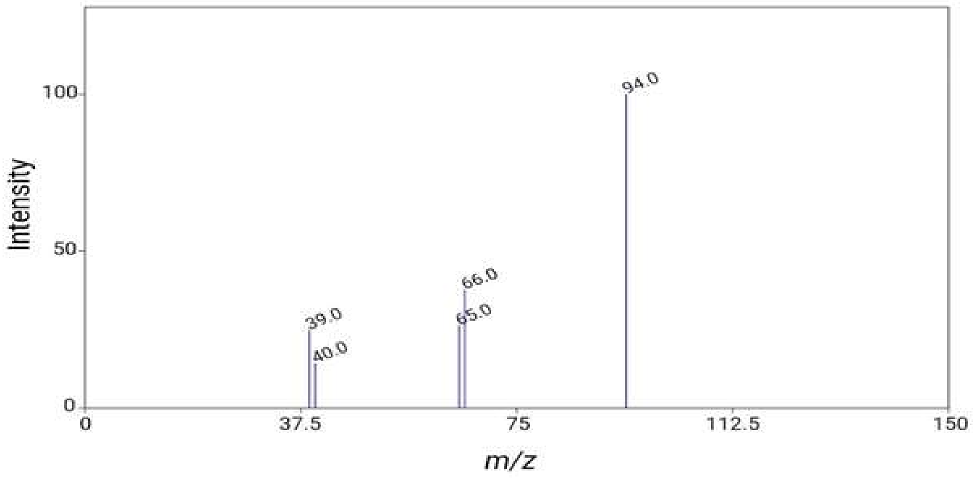


Figure 2.3

Mass: As the complete molecule, the molecular ion (M+) at m/z 94 generally exhibits a dominating peak in the mass spectrum of phenol. Other ions, such as fragment ions, which are produced as a result of the breaking of bonds within the molecule, are also produced in addition to the M+ ion. These fragment ions can reveal details about the molecular structure **(Figure 2.3)**.

3. Characterization of Aniline:

- **IR spectrum of aniline:**

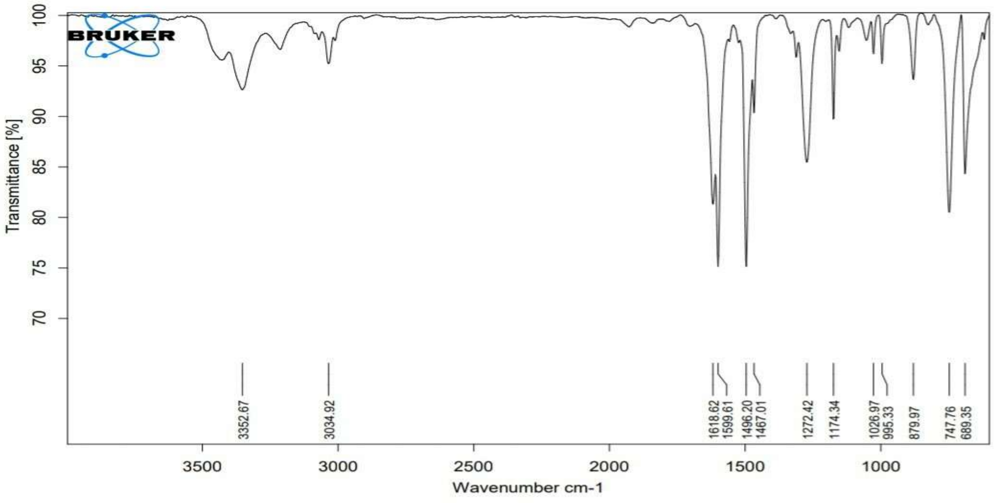


Figure 3.1

IR: Nitrile stretching is a strong, wide absorption band in the 2250–2100 cm^{-1} range that corresponds to the nitrile group's stretching vibration. A weak, wide absorption band in the 3300-3500 cm^{-1} range that corresponds to the main amine group's stretching vibration is known as amine stretching. Aromatic ring stretching: A succession of distinct, powerful bands that correspond to the aromatic ring stretching vibrations between 1600 and 1550 cm^{-1}.

- **^{1}H-NMR of aniline**

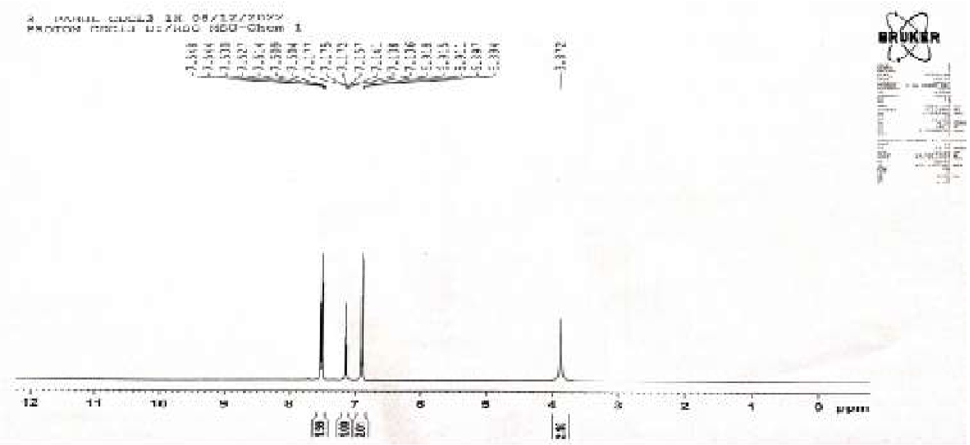


Figure 3.2

^{1}H NMR: 1H NMR (500 MHz, CDCl3) δ 7.31 (m,5H), 3.872 (d, J= 7.5 Hz, 1H).

The aromatic ring of aniline contains several protons, which normally manifest as a single signal in the 7-9 ppm range. A multiplet pattern results from the splitting of this signal by the protons nearby. Amine proton signals: The single proton that makes up the main amine group in aniline is detected 3.872bppm range.

- **Mass Spectroscopy of Aniline**

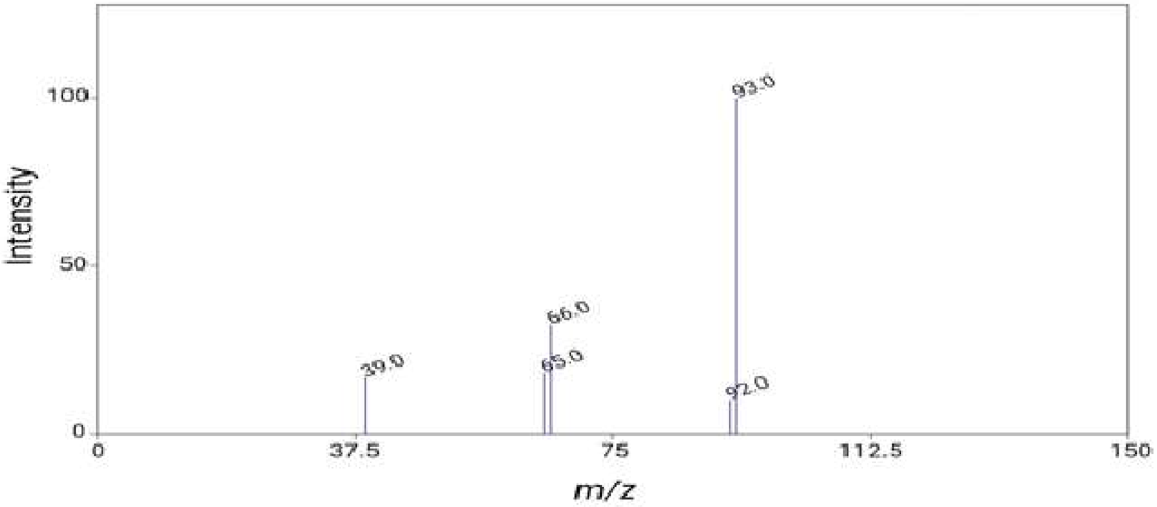


Figure 3.3

Mass spectroscopy: The molecular ion (M+) at m/z 93, which represents the whole molecule, often exhibits a dominating peak in the mass spectrum of aniline. As connections inside the molecule are broken, other ions, such as fragment ions, are produced in addition to the M+ ion. The structural characteristics of the molecule may be learned from these fragment ions.

DISCUSSION:

The removal of a single carboxyl group from benzoic acid while using a copper catalyst is referred to as mono-protodecarboxylation of benzoic acid. This reaction is an illustration of the cleavage of the C-C bond to generate a C-H bond.

The coordination of benzoic acid to the copper centre is the first step in the process of copper-catalyzed mono-protodecarboxylation of benzoic acid, which is followed by proton abstraction to create a carboxylate anion intermediate. The intermediate is then decarboxylated, releasing CO_2 and creating an intermediate species, which is later aromatized to create the end product.

The reaction may be seen and the intermediate species that are created during the reaction can be studied using spectroscopic methods including Nuclear Magnetic Resonance (NMR) and Infrared (IR) spectroscopy. While IR spectroscopy may be used to research changes in the vibrational frequencies of the molecule, NMR can be used to investigate changes in the chemical shift of the protons in the molecule. The mass of the finished product may be determined and its structure verified using mass spectrometry (MS).

When a carboxyl group is removed from a molecule, IR spectroscopy does not show that the C=O stretching frequency shifts from around 1700 cm^{-1} to about 1600 cm^{-1}.

In ^{1}H NMR spectroscopy, the changes in the chemical shifts of the protons in the molecule can be used to monitor the reaction and study the intermediate species formed during the reaction. For example, in the mono-protodecarboxylation of benzoic acid, the presence of the carboxyl proton at around 10-11 ppm can be observed in the ^{1}H NMR spectrum before the reaction. After the reaction, the disappearance of the carboxyl proton signal and the appearance of a new signal corresponding to the aromatic proton can be observed in the ^{1}H NMR spectrum.

Based on a sample's mass-to-charge ratio, mass spectrometry (MS) is a method used to determine the composition of the sample. The mass spectrum of benzene (C_6H_6) exhibits peaks for the molecular ion at m/z 78 as well as fragment ions at m/z 77, 52, 51 and 50.

The mass spectrum of phenol (C_6H_5OH). exhibits peaks for the molecular ion at m/z

94 as well as fragment ions at m/z 66, 65, 40 and 39.

The mass spectrum of Aniline ($C_6H_5NH_2$). exhibits peaks for the molecular ion at m/z 93 as well as fragment ions at m/z 92, 66, 65 and 39.

4. CONCLUSION:

In brief, our approach is to do decarboxylation of benzoic acid and ortho substituted benzoic acid to form a benzene and aromatic compound (substituted) by using Copper Carbonate as a catalyst, acetic acid as an additive in DMSO, at temperature 120ºC for 16 hrs this reaction was continuously monitored by using TLC plate and the result obtained is further studied by using IR spectra, ^{1}H NMR and Mass spectra. The improvement in this reaction is less time required, cheaper catalyst and sufficient yield.

5. Acknowledgments:

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