Formation and Trapping of Benzyne

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Abstract

Over the decades, several scientists have given a best representation for the structure of benzene. In this present study, Formation of benzyne and trapping achieving with by using furan and tetraphenylcyclopentadienone. The melting point of the crystalline compound was determined and the compound was analysed by InfraRed (IR) , GasChromatography-Mass Spectroscopy(GC-MS) , NMR (1H). IR confirmed that peak, might be due to carbonyl group present in the compound. According FTIR spectrum, strong and broad peaks were predicting may be due to atmospheric carbon dioxide and clearly showing aromatic C-C at 1688.6 cm⁻¹ and 1597.1 cm⁻¹. GC-MS spectra proving, all the compounds molecular weight is almost nearer to reference spectra. NMR spectra can explaining the structure of the compound by showing chemical shift of functional groups and correlating with the reference. Finally, concluded formation and trapping of benzyne producing adducts such as 1,4-dihydropyridoxalene-1,4-enolide and 1, 2, 3, 4-tetraphenylnapthalene compounds identifying in dark brown colour and crystalline in nature. The obtained solid products results are compared with that of the literature showing there is no mean deviation in their melting points.

Keywords: Benzyne; Trapping; Furan; Chromatography

Introduction

Over the decades, several scientists have given a best representation for the structure of benzene, that is indeed hexagonal with each C-C bond length being identical (140pm) and intermediate distance was explained by electron (p-orbital from each neighbouring C overlap) which extends around the ring giving added stability and decreased reactivity [1].

The compound C6H4, which is referred as ‘Benzyne’, is formally derived from benzene by removal of a pair of adjacent hydrogen atoms and the formation of a triple bond.

Chemistry of arynes

In chemistry, an aryne is an uncharged reactive intermediate derived from an benzene by removal of two ortho substituents leaving two orbitals with two electrons distributed between them. Benzyne is a general class of reactive intermediates known as 2 arynes.

Arynes can undergo three types of mechanisms:

• Nucleophilic aromatic substitution

• Cyclo addition reactions

Nucleophilic aromatic substitution: Nucleophilic aromatic substitution is an addition-elimination reaction that requires at least one substituent which is strongly electron-withdrawing by resonance to stabilise the anionic addition intermediate.

Some reactions explained by elevating a benzyne intermediate: In the below reaction chlorobenzene, having an isotopic labelled carbon atom gives substitution product (aniline-labelled carbon jumbled between two isotopes) and the reaction proceeds through a symmetrical intermediate benzyne, in which two anilines were equivalent [2,3]

Cycloaddition reactions: Cycloaddition reactions are those in which two or more unsaturated molecules combine with the formation of a cyclic adduct.

In the below example aryne intermediates are generated and then undergoes further reaction.

For many synthetic applications of arynes it is necessary to generate the reactive intermediate under mild conditions. These behave as intermediates in many organic syntheses.

Applications of arynes:

Synthesis of an Aporphine alkaloid

Synthesis of Ellipticene, an anti-cancer alkaloid

Synthesis of a Lysergic Acid N,N-Diethylamide precursor etc.

Benzyne

Benzyne is the parent molecule of arylene (yne = triple bond) compounds, derivative of benzene, produced by abstraction of two hydrogen atoms especially one produced by abstraction from neighbouring atoms to form a formal triple bond. Benzyne is a reactive intermediate in some reactions involving benzene compounds. More specifically, it is often found as a result of an elimination reaction with substituted aromatic compounds like halogenated or acylated benzene rings. The lifetime of benzyne (gas phase) is 20 nanoseconds (2 x 10⁻⁸ seconds), Benzyne is very reactive and rapidly dimerise.

Elimination of the substituent, often by nucleophilic attack, results in a carbocation. This electronic arrangement, due to its instability,
causes spontaneous (or base-assisted in the case of hydrogen) elimination of adjacent substituents resulting in a benzene ring with a triple bond.

In the above mechanism benzyne can be derived from halobenzene but this reaction needs a strong base such as NaNH₂, BuLi. This reagent undergoes elimination reaction to form benzyne intermediate which traps nucleophilic species.

Another possible mechanism is the abstraction of a group such as hydrogen resulting in a carbanion which causes the elimination of an adjacent group. Both mechanisms result in the formation of a benzyne intermediate.

In the above reaction diazotization of 2–aminobenzoic acid was carried out by using nitrous acid resulting a diazonium salt, which is not isolated, but allowed to undergo loss of CO₂ and N₂ to generate benzyne [4-6].

**Benzyne formation and the stepwise decomposition of benzenediazonium-2-carboxylate and trapping**

Common usage of the benzyne product involves a Diels–Alder Cyclo addition reaction. Reacting a diene with benzyne taking the place of normal alkene resulting in a bicyclic compound, one ring being

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**Figure 1:** Structure of benzene.

**Figure 2:** Formation of benzyne from Chlorobenzene.

**Figure 3:** Formation of benzyne from Fluorobenzene.

**Figure 4:** Formation of benzyne from halosubstituted benzene.

**Figure 5:** Structure of Benzyne.

**Figure 6:** Formation of benzyne from Bromobenzene.

**Figure 7:** Formation of benzyne intermediate.

**Figure 8:** Decomposition of benzyne.

**Figure 9:** Formation of benzyne.
benzene, the other being the product of the Diels-Alder reaction.

Diazotisation of anthranilic acid is a common method to produce benzyne and substituted benzenes after the loss of nitrogen and carbon dioxide from the neutral diazonium salt. Benzenediazonium-2-carboxylate may be generated in situ from anthranilic acid by diazotisation in an aprotic medium, or by the removal of the elements of hydrogen chloride from 2-carboxybenzenediazoniumchloride. Benzenediazonium-2-carboxylate is a violently explosive benzyne precursor [7-9].

Benzyne formation is favoured in halogenated solvents and occurs by the concentrated loss of nitrogen and carbon dioxide.

Experimental
Materials
Anthranilic acid (2-(H₂N)C₆H₄CO₂H), 1,2-dimethoxyethane (CH₃OCH₂CH₂OCH₃), Tetraphenylcyclopentadienone and Sodium hydroxide are obtained from Sigma- Aldrich, United Kingdom.; Isoamyl nitrite, Furan (C₅H₄O) and Petroleum ether samples obtained from Fluka, United kingdom.

Methods
Two methods were carried out to derive the benzyne. The methods are as follows:
1. Formation of benzyne and trapping with furan.

2. Formation of benzyne and trapping with tetraphenylcyclopentadienone.

**Formation of benzyne and trapping with furan:** 10 ml of Furan (Mol.Wt 68.07) and 10 ml of 1, 2-dimethoxyethane (Mol. Wt 90.12) were taken in a 100 ml round bottomed flask, some bumping stones were added. The round bottomed flask was fitted to a reflux condenser and the solution was heated under steam. Meanwhile, two solutions were prepared in 25ml Erlenmeyer flasks first one containing 4ml of iso-amyl nitrite made up to 10ml with 1,2-dimethoxyethane and second solution containing 2.74 gm anthranilic acid with 1,2-dimethoxyethane. 2ml of each solution was added by using separate Pasteur pipettes through the condenser to the round bottom flask under steam with 8-10 min intervals. The solution turned to a dark orange colour after the solutions were fully added. Then the mixture
mixture was washed with 15 ml of distilled water for 2 times. Then the organic solution was dried over magnesium sulphate (drying agent), the drying agent was removed by suction. Finally the solution was decolourised with active charcoal powder. Then the colourless solution was put into rotatory-evaporator to obtain crystalline slurry by applying room temperature and pressure. Crystalline slurry obtained was repurified by sublimation using ice cold petroleum ether [10].

Table 2: Interpretation of GC-MS results Of 1,4-dihydro-1,4-epoxynaphthalene.

<table>
<thead>
<tr>
<th>Fragment</th>
<th>mass-to-charge ratio(m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{10}H_{8} (M+)</td>
<td>144</td>
</tr>
<tr>
<td>C_{10}H_{8}</td>
<td>128</td>
</tr>
<tr>
<td>C_{8}H_{6}O</td>
<td>118</td>
</tr>
<tr>
<td>C_{9}H_{7}</td>
<td>115</td>
</tr>
<tr>
<td>C_{7}H_{5}</td>
<td>89</td>
</tr>
</tbody>
</table>

Figure 14: GC-MS Spectra of 1,2,3,4-Tetraphenylnaphthalene.

Formation of benzene and trapping with tetracyclopentadienone:
Both Tetraphenylcyclopentadienone (0.3 M), 1, 2-dimethoxyethane (DME) were placed in 100ml round bottom flask fitted with an efficient reflux condenser and the solution was heated further under steam. On the other hand, two solutions were prepared in 25ml Erlenmeyer flasks first one containing iso-amyl nitrite (4 ml) made up to 10ml with 1,2-dimethoxyethane and second solution containing 2.74 gm of anthranilic acid with 1,2-dimethoxyethane. 2 ml of each solution were added by using separate Pasteur pipettes through the condenser to the round bottom flask under steam with 8-10 min intervals. The solution turned in to a dark orange colour after the solutions were fully added. Then the mixture was refluxed for 30 min, on cooling the mixture to room temperature a dark brown mixture was precipitated out.

In the Mean time NaOH (0.1 M) solution was prepared and added to dark brown mixture. And the mixture was transferred to 100ml separating funnel, organic layer was separated by extracting the product with petroleum ether (15 ml). Then the mixture was washed with 15 ml of distilled water for 2 times. The organic solution was dried over magnesium sulphate (drying agent), the drying agent was removed by suction. Finally the solution was decolourized with active charcoal powder. Then the colourless solution was put into rotatory-evaporator to obtain crystalline slurry by applying room temperature and pressure. Crystalline slurry obtained was repurified by sublimation using ice cold petroleum ether [10].

Treatment of 1, 4-dihydronaphthalene-1, 4-endoxide with acid: This step is optional for the method development.1,4-dihydronaphthalene-1,4-endoxide (432 gm) was placed in 25ml Erlenmeyer flask and dissolved in ethanol (10 ml), concentrated HCl (5 ml) was added to the mixture and placed at room temperature for one hour. After one hour the mixture was poured into 100ml separating funnel, by adding diethyl ether (20 ml). Extraction of the organic part was carried out by shaking the separating funnel. Then the organic part was refluxed for 30min, on cooling this mixture to room temperature a dark brown mixture was precipitated out.

In the mean time NaOH (0.1 M) solution was prepared and added to dark brown mixture. The mixture was then transferred to 100ml separating funnel, organic layer was separated by extracting the product with 15ml petroleum ether. This procedure was repeated for three times to get efficient organic solution. The organic mixture was washed with 15ml of distilled water for 6 times. Then the organic solution was dried over magnesium sulphate (drying agent) and it was removed by suction. Finally the solution was decolourized with active charcoal powder, the solution was taken into rotatory-evaporator to obtain colourless crystalline slurry by applying room temperature and pressure. Crystalline slurry obtained was repurified by sublimation using ice cold petroleum ether [10].
Infrared spectroscopy: Infrared spectroscopy is used in the determination of functional groups in organic materials, determination of the molecular composition of surfaces, Identification of chromatographic effluents, Determination of molecular conformation (structural isomers) and stereochemistry

And determination of molecular orientation. FT-IR spectra were recorded on a PerkinElmer Paragon 1000 FT-IR and Processing software, Copyright © 2005 PerkinElmer Instruments LLC. It is used for the identification and structural analysis of organic compounds in that absorption of electromagnetic radiation occurs due to changes in the vibrational energy of the molecules, It influences on molecular vibrations and rotational transitions. Substance was crushed in a mortar to make a fine powder and mixed further with nujol to make a slurry. It was rubbed on glass disc and placed in a chamber for analysis.

Nuclear Magnetic Resonance Spectrometry (NMR)

NMR is a technique using for identification and structural analysis of organic compounds and chemical properties of the molecules in which they are contained. The principle behind NMR is that many nuclei have spin and all nuclei are electrically charged. If an external magnetic field is applied, an energy transfer is possible between the base energy to a higher energy level. The energy transfer occurs at the same frequency. The signal that matches this transfer is measured and processed in order to yield an NMR spectrum for the nucleus concerned. 3 mg of substance was taken in a vial and dissolved it in CDCl3 using sonicator. 1% of Tetra Methyl Silane (TMS) was added and made the volume up to 5 cm in a nmr tube. All NMR spectra were recorded at 400 MHz (1H) on a Jeol Eclipse+ 400 NMR spectrometer using Jeol Delta version 4.3.6 control software, Jeol, USA, Inc. Chemical shifts are reported in ppm, downfield from chloroform-d(CDCl3) as an internal reference.

Results and Discussion

The obtained solid products from the above three procedures were analysed to know whether the desired compound was formed or not by various analytical techniques. And these results are compared with that of the literature reference.

Melting point

1,4-dihydronaphthalene-1,4-endoxide and 1,2,3,4-tetraphenyl naphthalene producing the reproducing yield values i.e. 32.4 % and 71.0 % respectively.

IR spectra of the products

Infrared spectroscopy is a reliable means of identifying different functional groups present on the product by their characteristic vibration frequency and comparing it with the groups present in the starting material.

1,4-dihydronaphthalene-1,4-endoxide: The FT-IR spectrum obtained for the compound showed the peak at 2923.8 cm⁻¹ which was due to Nujol. This was further confirmed from the peaks 1462.8 cm⁻¹ and 1377.1 cm⁻¹. The peak 1729.7 cm⁻¹ might be due to carbonyl group present in the compound.

There are other peaks obtained which may be due to the presence of impurities or solvent.

Gc-Ms spectra of the products

The gas chromatography-mass spectrometry is a combination of two techniques, where gas chromatography separates different organic compounds and chemical properties of the molecules in which they are contained.
components in the sample and mass spectra provides the structural details by fragmentation of the sample.

**1,4-dihyronaphthalene-1,4-endoxide**

The full scan default mode with selected ions at m/z 89, 115, 118, 128 and 144, was shown in above graph. As it can be seen in the figure, sample was well separated in a run time of 7-7.5 min, and the spectra showing last peak at 144 (m/z).

From the spectra, if we observe the molecular peak at 144 m/z (last peak) and comparing it with the molecular weight of the desired product, and also verifying it with reference library search ensured that this spectra of the compound is almost nearer to reference spectra. Hence I conclude that the product is reliable with the desired product.

**1,2,3,4-Tetraphenynaphthalene:** The full scan default mode with selected ions at m/z 77, 156, 355 and 432, was shown in above graph. As it can be seen in the figure, sample was well separated in a run time of 25.5-26.5 min, and the spectra showing most abundant peak at 432 (m/z) following 26 min retention time. But between 20-26min of retention time so many other benzene compounds were eluted which may be due to the reaction mixture or handling procedures.

The fragmentation of 1,2,3,4-tetraphenynaphthalene, it showed:

<table>
<thead>
<tr>
<th>δ (ppm)</th>
<th>Multiplicity</th>
<th>Coupling constant J in (hertz)</th>
<th>Integrals</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.26</td>
<td>Doublet of doublet</td>
<td>5.03, 3.3</td>
<td>2H</td>
</tr>
<tr>
<td>7.0234</td>
<td>Doublet of doublet</td>
<td>1.10, 0.92</td>
<td>2H</td>
</tr>
<tr>
<td>6.97</td>
<td>Doublet of doublet</td>
<td>5.13, 2.93</td>
<td>2H</td>
</tr>
<tr>
<td>5.7094</td>
<td>Doublet of doublet</td>
<td>-</td>
<td>2H</td>
</tr>
</tbody>
</table>

Table 4: Interpretation of NMR results of the 1,4-dihyronaphthalene-1,4-endoxide.
loss of phenyl rings from the attached naphthalene ring, simultaneously spectra showing peaks at m/z 355,156,77 respectively.

From the spectra, if we observe the molecular peak at 432 m/z, comparing it with the molecular weight of the desired product, and also verifying it with reference library search ensured that this spectra of the compound is almost nearer to reference spectra. Hence I conclude that the product is reliable with the desired product.

**Nuclear magnetic resonance –proton spectroscopy:** The 'H NMR spectra was obtained by using CHCl₃ as solvent and spectra can explain the structure of the compound by showing chemical shift of functional groups.

From the above structure of 1,4-dihydro-1,4-epoxynaphthalene contains symmetrical structure and showing four different types of doublet protons which are indicated as Ha, Hb, Hc, Hc, Hb, Hc, Hc, Hb, Ha, Hb, Hc, Hc, Hb, Ha, and having equal integration ratio, The spectra of 1,4-dihydro-1,4-epoxynaphthalene showing that all the four protons are attached to the epoxide naphthalene base and located in same environment and strongly deshielded by the π orbitals of the ring and absorbed in the low field, ranging from 5.7094ppm-7.2695ppm. While, the protons Ha, Hb, Hc, Hd showing the multiplication at 6.9439-6.9874, 7.2260-7.2695, 5.7094, 7.0103-7.0332 respectively. And all these doublets are having one neighbouring protons. Ha, Hb, Hc, Hd are respective of neighbouring protons Hb, Hc, Hd, Ha and showed a signal that split into a doublet. Each proton on the structure had two neighbouring protons which indicates one proton is non-equivalent and the other is equivalent and gives a signal that is split into a doublet of doublet.

All the peaks in Ha, Hb, Hc, Hd mostly similar and remaining peaks were found between 1.219ppm-5.2038ppm which may be due to the impurities or the small changes in the local shielding environment of the CHCl₃ induced by the solute via intermolecular interactions.

**Conclusion**

Formation and trapping of benzene has been successfully done by using two different trapping agents which are Furan and tetr phenyl cyclopentadienone with significant results.

In the first experiment, benzene was trapped by furan and the adduct obtained was 1,4-dihyodonaphthalene-1,4-endoxide. The yield obtained in the first experiment was low when compare to the second experiment. The compound synthesised was crystalline in nature and yellow orange in colour. The compound was confirmed by its melting point, Infrared, GC-MS and NMR Spectra compared with that of the literature values.

Similarly the benzene was also trapped by using 1, 2, 3, 4-tetraphenylynaphthalene. Here, the adduct obtained was 1, 2, 3, 4-tetraphenylnaphthalene. The compound was dark brown in colour and crystalline in nature. It was also confirmed by comparing the obtained melting point values with the literature values.

**References**