

STUDY AND SELECTION OF THE PROCESS FOR PRODUCTION OF P-CUMIDINE

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Abstract: P-cumidine is very important intermediate for many chemical and agrochemical industries. The product, Para cumidine is versatile chemical intermediate that has applications in dyes, pharmaceuticals, and herbicides. The major use of para cumidine as an intermediate in the manufacturing of isoproturon which is a selective herbicide belonging to the family of substituted ureas and acts principally after root absorption, either pre-emergence or post-emergence. There are many different processes from which p-cumidine can be manufactured. But industrially used process is nitration of cumene followed by hydrogenation. The processes for manufacturing of p-cumidine are alkylation of aniline, nitration of cumene followed by hydrogenation, nitration of cumene followed by reduction using caustic lye and sulphur. But industrially used process is nitration of cumene followed by hydrogenation.

Keywords: P-cumidine, intermediate, agrochemical, isoproturon, cumene, nitration, hydrogenation.

I. Introduction

The product, p-cumidine is versatile chemical intermediate that has applications in dyes, pharmaceuticals, and herbicides. The major use of para cumidine as an intermediate in the manufacturing of Isoproturon which is a selective herbicide belonging to the family of substituted ureas and acts principally after root absorption. There are different processes by which p-cumidine can be manufactured that are alkylation of aniline, nitration of cumene followed by hydrogenation, nitration of cumene followed by reduction using caustic lye and sulphur. Industrially used process is nitration of cumene followed by hydrogenation. In alkylation of aniline, the conversion of aniline is low i.e.70% and selectivity for p-cumidine is low. So this process is not commercial and economical. Nitration of cumene followed by hydrogenation of process is best among all above the processes. For nitration process mixed acids are used i.e. nitric acid and sulphuric acid which are easily available at low cost. So this is economical and commercially used process. The raw material to be used is cumene. This process is mainly divided into two parts i.e. nitration of cumene which gives isomers of nitrocumene (major p-nitrocumene) and then hydrogenation of nitrocumene which yields the mixture of ortho, meta and para-cumidine. To get para cumidine the mixture is to be separate out by different techniques and can be separated by distillation.

About p-cumidine –

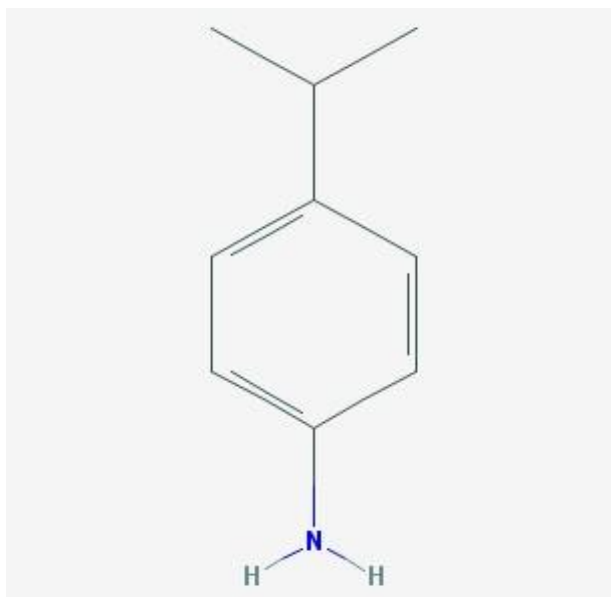


Figure: Structure of p-cumidine

Formula: C₉H₁₃N

Generic Name: 4-Isopropylaniline

1-Amino-4-isopropylbenzene

4-Aminocumene

4-Aminoisopropylbenzene

p-Isopropylaniline

4-propan-2-ylaniline

CAS No.: 99-88-7

CAS Name: 4-(1-Methylethyl)benzenamine

Properties of p-Cumidine

Table: Physical and Chemical Properties

| Sr. No. | Properties | Value |
|---------|------------------------------------|--|
| 1 | Molecular Weight | 135.21 |
| 2 | Physical State at Room Temperature | Liquid |
| 3 | Colour | Dark Red |
| 4 | Odour | Aromatic Odour |
| 5 | Boiling Point/Range | 226-227 °C |
| 6 | Flash Point | 92 °C |
| 7 | Density | 980 kg/m ³ |
| 8 | Vapour Pressure | 10 Pa |
| 9 | Solubility | Soluble in Organic Solvents like Alcohol |

1. Nitration of Cumene followed by Hydrogenation

The selected process for production of para-cumidine is nitration of cumene followed by hydrogenation. And separation of isomers of cumidine after hydrogenation is done by vacuum distillation for that a tall fractionator is used.

Raw materials – Cumene, mixed acid i.e. mixture of nitric acid and sulfuric acid, hydrogen, raney nickel as catalyst, methanol as solvent for hydrogenation.

- Nitration of cumene –

In this process reaction between cumene and nitric acid is carried out. Actually mixed acid i.e. mixture of nitric acid and sulfuric acid is prepared separately and after that it treated with cumene. This reaction is highly exothermic and is conducted in batch or continuous reactors. Typically the nitrating agent is a mixture of 56–60% (w/w) H₂SO₄, 27–32% (w/w) HNO₃, and 8–17% (w/w) H₂O. The reaction mixture forms two phases and the rate of reaction is accordingly dependant on the kinetics and mixing efficiency. This nitration reaction gives the mixture of 68% p-nitrocumene (major), 24-28% o-nitrocumene, 1-2% m-nitrocumene and 1-2% dinitrocumenes.

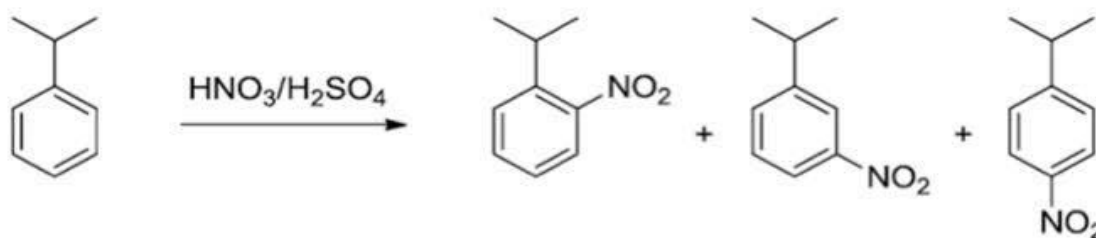


Figure: Nitration Reaction

- Hydrogenation of nitrocumenes –

In this process step hydrogen is introduced and nitrocumenes are made to react with it to form cumidines. Hydrogenation is carried out in presence of a catalyst and the is raney nickel. Hydrogen addition is started at specified temperature. Methanol is used as a solvent for hydrogenation. The reaction is conducted under controlled conditions. The temperature is maintained at 333K. This hydrogenation reaction yields mixture of isomers of cumidine i.e. p-cumidine(major), o-cumidine, m-cumidine. Out of which p-cumidine is main product. After complete reaction, catalyst filtered and mixture of isomers transferred for distillation. Separation is done by vacuum distillation for that tall fractionator column is needed.

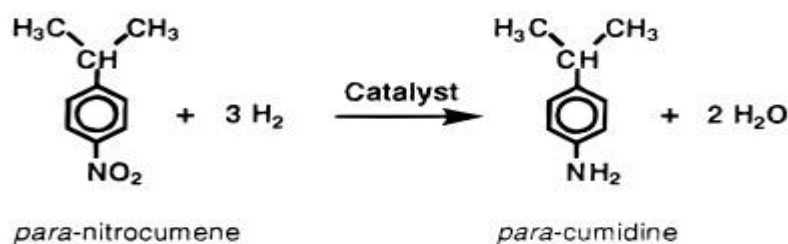


Figure: Hydrogenation Reaction

- Following are some modifications required for safe and industrially economic production –
- i. One can separate cumidines after hydrogenation or nitrocumenes before hydrogenation. But separation of cumidine is preferred and not separation of nitrocumenes. Because in mixture of nitrocumenes some amount of dinitrocumene may present which is explosive. So separation of *p*-cumidine i.e. after hydrogenation is preferred.
- ii. The conversion of cumene can be done upto 99%. But if conversion is stopped and limits upto 90% then probability of formation of dinitrocumenes decreases. As dinitrocumenes are explosive and harmful, reaction conversion kept upto 90% in industries. And unreacted cumene is recycled back to nitration reactor.

2. Alkylation of aniline with α -methylstyrene

Man Mohan Sharma and Sandeep Chitnis have explained the alkylation of aniline with α -methylstyrene using acid-treated clay catalyst, Engelhard F-24. In this reaction a mixture of 4-(α , α -dimethylbenzyl)aniline, i.e., monocumylaniline (MCAs), and 2,4-bis-(α , α -dimethylbenzyl)aniline, i.e., dicumylaniline (DCA) are formed. The reaction was studied in the temperature range of 423-463 K, since no significant conversion of aniline was obtained at temperatures below 423 K. They observed that the rate of conversion of aniline to MCA was quite high, but the rate of subsequent reaction of conversion of MCA to DCA was significantly low. Therefore, nearly up to 70% conversion of aniline, MCA was obtained exclusively in the reaction mixture. DCA was formed in significant amount only beyond 70% conversion of aniline. The reason for this behaviour appears to be the steric hindrance to the bulky cumyl group at the ortho position of NH_2 group of aniline. In the reaction between aniline and AMS where aniline : AMS mole ratio was 1 : 4 temperature 453 K and 5% loading of Engelhard F-24 catalyst, 58% selectivity of DCA was obtained after 21600 s of reaction. The conversion of aniline was 100%. The reaction was unsuccessful with the macroporous ion-exchange resin catalyst, Amberlyst-15 but Engelhard F-24 proved to be an effective catalyst for the alkylation/dealkylation reactions. They also suggested that suitable strategy could be developed for the separation of close boiling aromatic amines OT/PT, MT/PT and OC/PC through selective alkylation with AMS followed by dealkylation of the alkylated product(s). Engelhard F-24 proved to be an effective catalyst for the alkylation/dealkylation reactions.

3. Nitration of cumene followed by Reduction using Caustic lye and Sulphur

Cumene is nitrated with a mixture of nitric acid and sulphuric acid to produce nitrocumenes. Nitrocumenes are reacted with sulphur and caustic soda (NaOH) to give cumidine. The separation of Ortho-cumidine and Para-cumidine is done by distillation.

II. Conclusion

In alkylation of aniline, the conversion of aniline is low i.e. 70% and selectivity for *p*-cumidine is low. Nitration of cumene followed by hydrogenation of process is best among all above the processes as it has high selectivity for *p*-cumidine i.e. 70% and conversion of cumene is 99%. For nitration process mixed acids are used i.e. Nitric acid and sulphuric acid which are easily available at low cost. So this is economical and commercially used process.

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