RESEARCH ARTICLE

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Process Analysis and Selection for The 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 isoproterenol 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.

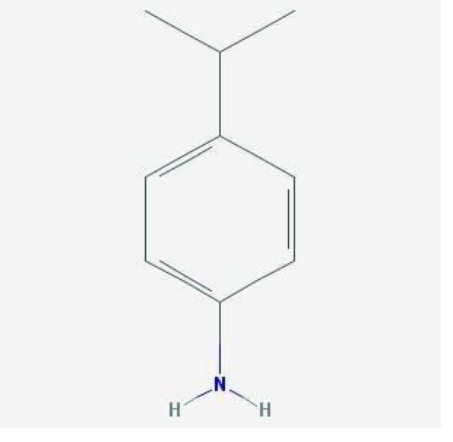
Keywords: P-cumidine, Intermediate, Agrochemical, Isoproterenol, Cumene, Nitration, Hydrogenation.

1. 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 Isoproterenol 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 nitro cumene (major p-nitro cumene) and then hydrogenation of nitro cumene 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 –



Formula: C9H13N
Generic Name: 4-Isopropylaniline
1-Amino-4-isopropylbenzene
4-Aminocumene
4-Aminoisopropylbenzene p-Isopropyl aniline
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/m3
8	Vapour Pressure	10 Pa
9	Solubility	Soluble in Organic Solvents like Alcohol

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 dependent on the kinetics and mixing efficiency. This nitration reaction gives the mixture of 68% p-nitro cumene (major), 24-28% o-nitro cumene, 1-2% m-nitro cumene and 1- 2%dinitrocumenes.

Hydrogenation of nitrocumenes –

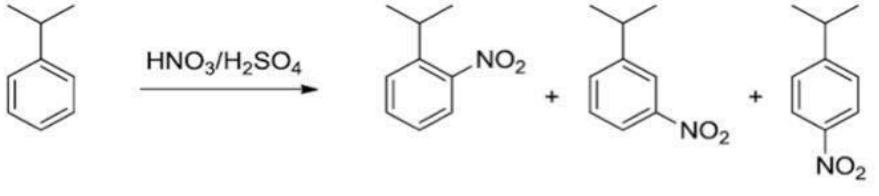


Figure. Nitration Reaction

In this process step hydrogen is introduced and nitro cumenes are made to react with it to form cuisines. 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.

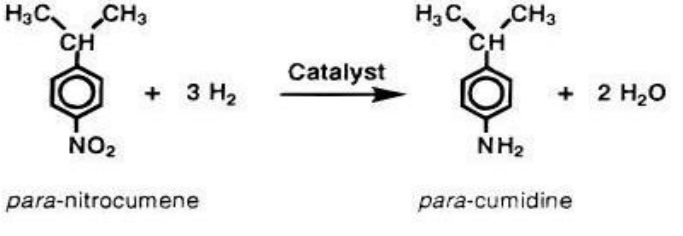


Figure: Hydrogenation Reaction

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.

Following are some modifications required for safe and industrially economic production

- One can separate cumidines after hydrogenation or nitro cumenes before hydrogenation. But separation of cumidine is preferred and not separation of nitro cumenes. Because in mixture of nitro cumenes some amount of dinitro cumene may present which is explosive. So, separation of p-cumidine i.e. after hydrogenation is preferred.
- The conversion of cumene can be done up to 99%. But if conversion is stopped and limits upto 90% then probability of formation of dinitro cumenes decreases. As dinitro cumenes are explosive and harmful, reaction conversion kept up to 90% in industries. And unreacted cumene is recycled back to nitration reactor.

Alkylation of aniline with α-methyl styrene

Man Mohan Sharma and Sandeep Chitnis have explained the alkylation of aniline with α-methyl styrene using acid-treated clay catalyst, Engelhard F-24. In this reaction a mixture of 4-(a,a-dimethylbenzyl)aniline, i.e., monocumylaniline (MCAs), and 2,4-bis- (a,a-di-methylbenzyl)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 behavior appears to be the steric hindrance to the bulky cumyl group at the ortho position of NH2 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 microporous 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.

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.

Conclusions

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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Conflict of interest: NIL