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Synthesis of Tri –Bromoaniline: A Novel Green Approach

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Abstract:
Bromination is one of the most important organic reactions and involves the use of bromine water. Bromine water or bromine in glacial acetic acid is highly toxic. This reaction is present in most university syllabi, at undergraduate level. And therefore used extensively by the students. The aim of this study was to prepare tri-bromoaniline using a green reagent which develops sustainable chemistry. The harmful products formed in the conventional method of preparation, are not obtained in this reaction.
Bromination of aniline is carried out using a green brominating reagent tetra-butyl ammonium bromide (TBATB) in water. The atom economy and E factor was found to be 100% and 0 respectively indicating no generation of by-products, as also confirmed by TLC. Therefore, a greener reaction was introduced using TBATB in order to synthesize tri-bromoaniline which has varied applications.

Keywords: Green Chemistry, bromination, TBATB.

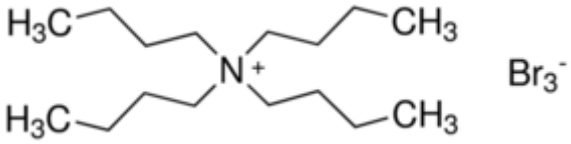
Introduction

Green chemistry is the design of chemical products and processes that reduce or eliminate the generation of hazardous substances. Green chemical methods have resulted in complete reduction of hazardous wastes at all reaction scale. The development of greener reactions thus helped in the production of safer reagents that can be used instead of conventional chemical methods and is an investment for the future.(1) Some of the principles of green chemistry are to design chemical products that are efficient but less toxic, to avoid the use of auxiliary substances (e.g.: solvents, separation agents, etc.) whenever possible, use of renewable and economical raw materials, substances chosen are to reduce chemical accidents and so on. Bromination, aldol condensation, etc. are some of the reactions in which green methodologies can be applied. (8)
Bromination of organic compounds is an important and popular industrial process due to multiple uses like: In water purification, agriculture, healthcare, photography etc. Brominated organic substances are important synthetic intermediates and potent antitumor, antifungal, antibacterial and antiviral compounds. Organic compounds are brominated by either addition or substitution reactions. Bromine water or in carbon tetrachloride are the common reagents used for bromination. .(7) Classical bromination of aromatic compounds, for example, utilizes only 50% of the halogen, with the other half forming hydrogen bromide

$ArH + Br_2 \rightarrow ArBr + HBr$

Bromine is widely used in pharmaceuticals but at the same time has many disadvantages.(2) The major issue is transportation and storage of large quantities of molecular bromine and HBr, which is a by-product, is extremely hazardous. Orange fumes of bromine from bottles, when opened, may lead to suffocation and its vapours are toxic if inhaled and irritates the eye as well. When in liquid form, it is corrosive to human tissues. Bromine is very dense (density=3.1 g/cm^3) and hence makes it difficult to measure and transfer.(4) Few bromine containing compounds are found to cause ozone depletion or bio accumulate in living organisms. As a result, many industrial bromine compounds are no longer manufactured and are being banned.(3)

Hence synthesis of a green reagent can aid bromination of organic substrates. One such green brominating reagent is terbutylammonium tribromide (TBATB).



It is a safer starting material and environmentally clean. TBATB is economical and are crystalline and thus easy and safe to work with. Tetrabutylammonium tribromide (TBATB) has attracted the attention of researchers because of its stability, easier method of preparation and its advantages over liquid bromine such as its use at higher temperature.(5)

Aldol condensation reaction between acetophenone derivatives and benzaldehyde is another example of green chemistry reaction, as it is a solvent free reaction, which is one of the principle of green chemistry. The reaction in which two molecules of an aldehyde or ketone combine to form a β-hydroxy aldehyde or β-hydroxy ketone, under the influence of a dilute base or acid is called aldol condensation. In the reaction between 3,4-dimethoxybenzaldehyde and 1-indanone, the reactants are in the solid state at room temperature, and only a single product is expected as the aldehyde bears no α hydrogen. Remarkably a high degree of conversion is achieved and produces only a small quantity of aqueous acidic waste. (6)

Materials and Methods:

All materials used were of commercial gradient and purified according to the established procedures. Reactions were monitored by TLC.

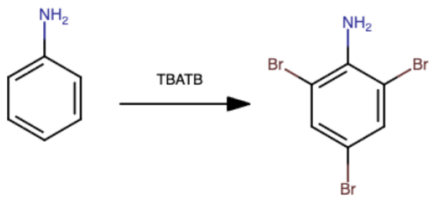
a. Preparation of TBATB

Molybdic acid monohydrate (0.087g) was taken in a beaker into which 30% hydrogen peroxide (5.28 cm^3) was added and the mixture was stirred for 30 mins at room temperature.

This mixture was filtered, collected and cooled in an ice-bath. To this tetra-butyl ammonium bromide (15g) and KBr (11.07g) dissolved in 0.3M H_2SO_4(155.1 cm^3) was added with continuous stirring to form a yellow precipitate. The mixture was kept in an ice-bath for almost 2 hrs and the orange yellow compound of TBATB was obtained by filtration under suction, was dried and recrystallised using 50% alcohol.

b. Synthesis of Tribromoaniline:

5 drops of aniline was taken in a beaker containing about 7 $cm^3$of water in it. To this crystals of TBATB (1.706g, 1:3 ratio) were added. The reaction mixture was stirred continuously for about 2 hours. It was then filtered using Whatman filter paper No.1 under suction and dried.

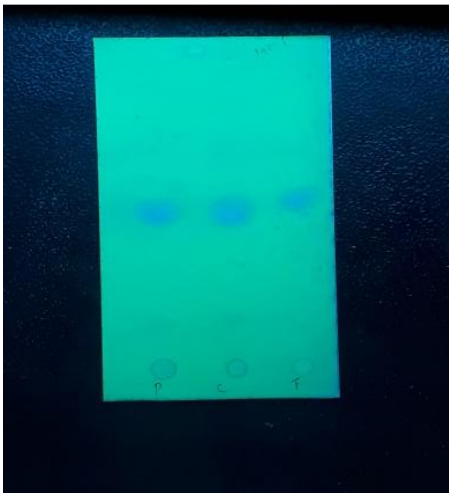


Results

Crystals of tribromo aniline were obtained which was confirmed by TLC and melting point using tribromo aniline prepared by conventional method (Bromine water). The solvent system used was hexane and 1-2 drops of ethyl acetate. Melting point – 117°C

Practical yield = 0.380g

% yield = $\frac{0.380 \times 100}{1.166}$ = 32.59 %



Conclusion

Development in health and environment sectors are milestones of the contemporary world, and therefore focusing on minimizing waste is important. Bromination of aniline using TBATB and water as solvent is an environment safe method which does not produce any harmful wastes. TBAT formed after the reaction can be recovered and reused. Though that is procedure is not attempted in the present work. According to the 12 principles of green chemistry higher atom economy and lower E factor makes the reaction greener. Contrary the conventional method is harmful not only for the environment but also for people handling it. Since bromination is very common reaction performed at an undergraduate level, this method can be used to perform bromination reaction. The only drawback could be the longer duration of reaction time.

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