

Classroom



In this section of *Resonance*, we invite readers to pose questions likely to be raised in a classroom situation. We may suggest strategies for dealing with them, or invite responses, or both. “Classroom” is equally a forum for raising broader issues and sharing personal experiences and viewpoints on matters related to teaching and learning science.

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A Safe Procedure for Bromination of Acetanilide

A non-hazardous procedure for bromination of acetanilide has been developed. The method uses potassium bromate, potassium bromide and an organic acid to generate bromine *in situ*.

Introduction

Electrophilic aromatic substitution is an important area of learning in introductory organic chemistry courses. Substituents already present on benzene nucleus determine the position and extent of substitution of the new incoming groups. These substituents are generally classified as strongly activating (e.g. $-\text{NH}_2$), moderately activating (e.g. $-\text{NHCOCH}_3$) and deactivating (e.g. $-\text{NO}_2$). Bromination of acetanilide provides a good example to study orientation of the incoming electrophile on a moderately activated aromatic nucleus. This reaction is a part of undergraduate organic synthesis experiments. The traditional experiment involves the use of $\text{Br}_2\text{-AcOH}$ and is described in several laboratory textbooks [1–3]. However, liquid bromine is extremely corrosive and is hazardous to handle. To avoid risks in using liquid bromine, methods to generate bromine *in situ* have been developed [4, 5]. In acidic medium, $\text{KBrO}_3\text{-KBr}$ is known to release bromine

Keywords

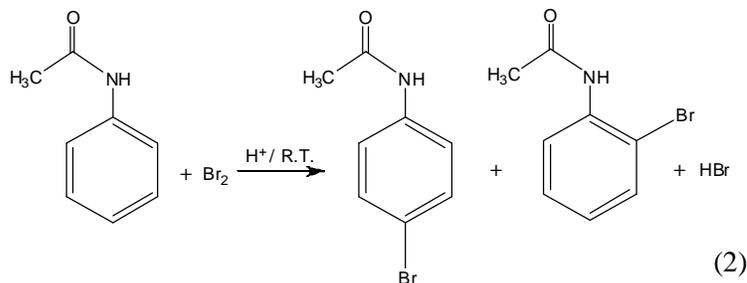
Acetanilide, safe bromination, non-hazardous brominating agent.



according to equation (1).



The liberated bromine reacts with the aromatic substrate as shown in equation (2).



Generally, concentrated HCl, CH_3COOH and HBr are the preferred acids used in the reaction (shown in (2)) to liberate bromine [3]. While concentrated HCl gives out corrosive fumes during handling, acetic acid too has a sharp pungent odour. To overcome these difficulties and to make bromination a safe procedure for students, we report here a method that uses potassium bromate, potassium bromide and solid, water-soluble organic acids (See *Table 1*) for bromination of acetanilide in excellent yields.

Experimental Procedure

A mixture of acetanilide, potassium bromate and potassium bromide (1:1:1 molar ratio) is placed in a conical flask fitted with a cork. The required volume of water (10 ml for 0.01 mol of acetanilide) is added and the mixture is gently stirred on a magnetic stirrer. An aqueous solution of organic acid mentioned in *Table 1* (0.01 mol in 10 ml of water) is added in small portions over a period of 15 minutes. The reaction mixture acquires a distinct yellow colour due to slight excess of bromine, indicating that no more bromine is required for the reaction. To ensure completion of bromination, the reaction mixture is stirred for another 15 minutes and the crude product is filtered. Thin-layer chromatography with solvent system toluene-ethyl acetate (4:1) revealed a major product with traces of impurities. Crystallization

The acetamido group ($-\text{NHCOCH}_3$) is ortho-, para-directing in nature. The para product predominates due to steric reasons.

Table 1. Bromination of acetanilide with $\text{KBrO}_3\text{-KBr}$ -organic acid

| Organic Acid | Yield of p-bromoacetanilide (%) |
|---------------|---------------------------------|
| Citric acid | 90 |
| Oxalic acid | 89 |
| Tartaric acid | 95 |

of the crude product from aqueous ethanol afforded a pure (single spot on TLC), white compound, melting point, 166–67 °C. The yields obtained with different organic acids are summarized in *Table 1*.

Conclusion

The present method of bromination avoids the use of hazardous liquid bromine. Instead, the required bromine is generated in situ and used up quickly. There will be very little pollution by bromine in the laboratory. The use of organic acids instead of mineral acids makes it safer and free from corrosive fumes. The yields of p-bromoacetanilide are excellent. In short, it is well suited for undergraduate laboratory experiments.

Suggested Reading

- [1] F G Mann and B C Saunders, *Practical Organic Chemistry*, Dorling Kindersley (India) Pvt.Ltd.2011
- [2] *Vogel's Textbook of Practical Organic Chemistry* revised by B S Furniss, A J Hannaford, P W G Smith and A R Tatchell, Longman Group UK, ELBS Edition, 1996.
- [3] A Ault, *Techniques and Experiments for Organic Chemistry*, University Science Books, Sausalito, California, 1998.
- [4] S Paul, P Nanda and R Gupta, Synthesis of α -bromoalkanones using urea-hydrogen peroxide complex and sodium bromide over silica gel-acetic acid, *Indian J.Chem.*, Vol.44B, pp.184–87, 2005.
- [5] G Joshi and S Adimurthy, Environment-friendly bromination of aromatic heterocycles using a bromide-bromate couple in an aqueous medium, *Ind. Eng. Chem.Res.*, Vol.50, pp.12271–75, 2011.

