

Monobromination of Aromatic Rings Using Potassium Bromide - Sodium Nitrate Mixture in Sulphuric Acid

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(Received 27th February, 1992)

Summary: A simple and rapid method for the selective monobromination of aromatic rings involving the use of a mixture of potassium bromide and sodium nitrate in sulphuric acid (60% v/v) has been described.

Introduction

A number of methods [1] for nuclear monobromination of aromatic rings have been reported in view of the synthetic and commercial utility of bromoderivatives. Recently introduced reagents for selective monobromination of reactive aromatic rings include 2,4,4,6-tetrabromocyclohexa-2,5-dione [2,3], bromine thalium (III) acetate [4], NBS-DMF [5], NBS-silica gel [6,7], benzyltrimethylammoniumtribromide [8] or in the presence of zinc chloride [9], CuBr_2 [10], NO_2 -catalysed metal Bromides [11] (aluminium bromide, stannic bromide, titanium (IV) bromide) and alkali metal bromide in the presence of nitrogen containing oxidising agent [12]. Bromination with metal bromides has been scarcely studied due to the sus-

ceptibility of aromatic nucleus to undergo metallation [13], isomerization [14], polymerisation [15] and other side reactions in the presence of metal halides.

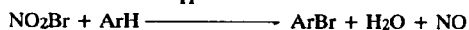
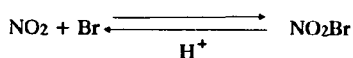
In the present investigation we report a simple and rapid method for the selective monobromination of aromatic rings involving the use of potassium bromide sodium nitrate mixture in sulphuric acid under aerobic conditions at ambient temperature.

Initial studies with benzene using a mixture of potassium bromide-sodium nitrate (1:1) in concentrated sulphuric acid (97% or 90%) at room

temperature resulted in the formation of a mixture of nitrobenzene and bromobenzene.

However, after some experimentation it was observed that by lowering the concentration of sodium nitrate and sulphuric acid in the reaction mixture, the formation of nitroderivative can be completely eliminated. A mixture of potassium bromide-sodium nitrate (molar ratio 1:0.2) in 60% sulphuric acid was found out to be an effective monobrominating agent for the non-activated and activated aromatic rings. The results obtained are summarised in the table. The identity of the products was established on the basis of their m.p., mixed m.p., b.p. and comparison of their spectral data with the authentic samples.

In the investigated system, the formation of nitryl bromide appears to be the brominating species formed through the following sequence of reactions. Formation of the same has been reported in an analogous system containing metal bromide in aqueous trifluoroacetic acid in the presence of nitrogen containing oxidizing agents [12].



All reactions proceeded smoothly and gave good yields (Table). Following are some of the distinguishing features of this method which establish its superiority over the reported methods for the monobromination of aromatic rings.

(i) It is specific and selective for the monobromination of non-activated and activated aromatic rings. Unlike the NO_2 -catalysed metal bromide in trifluoroacetic acid method [12] where the formation of isomers, dibromination and nitration have been reported. Regioselectivity in the bromination of toluene, xylene and anisole is attributable to the steric factor which has been reported [16] to dominate over electronic effect in such types of electrophilic substitution reactions. Another contributing factor in the regioselectivity of these reactions is the soft nature of the electrophilic species, the attack of which is determined by the frontier electron density [17].

Table : Bromination with potassium bromide - sodium nitrate mixture in sulphuric acid (60% v/v).

Products	Yield (%)	m.p. ($^{\circ}\text{C}$)	b.p. ($^{\circ}\text{C}/760$ mm. Hg)
1. Bromobenzene	84	-	155-156 (lit. [19] 156.2)
2. 1-Bromonaphthalene	80	-	280-281 (lit. [19] 281)
3. 9-Bromophenanthrene	45	64-65 (lit. [19] 65-66)	-
4. 9-Bromoanthracene	80	100-101 (lit. [19] 100)	-
5. 4-Bromotoluene	70	-	182-184 (lit. [19] 184)
6. 4-Bromom-xylene	60	-	205 (lit. [19] 205)
7. 4-Bromoanisole	75	-	216 (lit. [19] 215)
8. 2-Bromophenol	60	-	192-194 (lit. [19] 194)
9. 2-Bromop-cresol	65	54 (lit. [19] 56)	-
10. 4-Bromocatechol	60	86 (lit. [19] 87)	-
11. 4-Bromoresorcinol	50	100-102 (lit. [19] 100-102)	-
12. 2-Bromo-1,4-dimethoxybenzene	75	-	262 (lit. [19] 262-263)
13. 2-Bromop-xylene	70	-	199-200 (lit. [19] 198-199)
14. 1-Bromo-2,4,6-tri-methylbenzene	70	-	222-223 (lit. [19] 225)

(ii) Contrary to oxidation of anthracene to anthraquinone by NO_2^- -catalysed metal bromide method [12], the present method gave exclusively 9-bromoanthracene in high yield (80%).

(iii) Method can be used effectively and selectively for the monobromination of the substrates such as benzene, toluene, xylene and phenanthrene which cannot be brominated by NBS-DMF method [5].

(iv) The results with phenols are also noteworthy especially with catechol which has been reported to undergo oxidation with NBS-water [18], NBS-DMF [5] and metal bromide in the presence of nitrogen containing oxidizing agent in trifluoroacetic acid [12].

The method is not effective for amines and deactivated aromatic rings. The bromination of benzaldehyde and benzyl alcohol by this reagent

resulted in the formation of benzoic acid in almost quantitative yields. The general applicability and selectivity under mild conditions for the monobromination of non-activated and activated aromatic rings makes the method of synthetic value.

Experimental

General procedure for the monobromination of aromatic rings

To a mixture of sodium bromide (0.01 mole) sodium nitrate (0.002 mole) and the appropriate substrate (0.01 mole) was added sulphuric acid (60% v/v) (7 ml) gradually with continuous stirring over a period of 15-20 minutes. After stirring the reaction mixture at ambient temperature under aerobic conditions for 2.5 hours, the reaction mixture was poured into ice cold water (100-150 ml). The solid product was filtered out otherwise the solution was extracted with ether (3 x 10 ml). The combined ether extracts were washed with aqueous sodium sulphite solution and finally with water. The ether extract was dried over anhydrous magnesium sulphate. Evaporation of ether gave the bromo-derivatives which were further purified by crystallization or distillation. The results obtained are given in the Table.

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