Bromination of Some Aromatic Compounds by Bromine in Acetic Acid

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Summary: Bromination of some aromatic compounds is effected by means of bromine in acetic acid medium in the presence of a mixture of zinc dust and iodine as a catalyst. The compounds investigated here are classified according to their behaviour towards the brominating agent into' (a) compounds which undergo full bromination, (b) compounds which are partially brominated, and (c) compounds which are unchanged by the brominating agent.

Introduction

Brominations of some aromatic compounds by means of bromine in chlorosulphonic acid[1] and in tetrachloroethane medium[2] were reported by one of us. It was shown[1] that the former reagent can act as a brominating and oxidising agent for compounds which are susceptible to ring oxidation e.g. compounds containing –OH–OCH_3 and –NH_2 groups.

In this investigation, we report the bromination of some aromatic compounds by means of bromine in acetic acid medium in the presence of zinc dust-iodine mixture as a catalyst.

Experimental

2.1. *General method for bromination.*

In a round bottomed, three necked flask, fitted with a mechnical stirrer, a dropping funnel and a condenser, 20 g of the organic compound was placed together with a mixture of (0.1 g) zinc dust and (0.1 g) iodine. Glacial acetic acid (25 ml) was added. To the above mixture, (10 ml) bromine (excess) were added dropwise with stirring. The reaction mixture was heated on a steam-bath with continuous stirring for 5 h. The solution was then evaporated under reduced pressure till near dryness. The residue so obtained was treated with ice-cooled water, the solid obtained was filtered off, washed thoroughly with water, and finally recrystallised from the suitable solvent.

2.2. *Oxidation of pentabromophenol to bromanil.*

A mixture of (1.0 g) pentabromophenol and (10 ml) fuming nitric acid was heated on a steam-bath for 2 h. The reaction mixture was then cooled, poured on water. The product obtained was filtered off, washed thoroughly with water, and finally recrystallised from benzene-ethanol in yellow needles, m.p 298°C; Yield 60%. Mixed melting point experiment of this product with an authentic sample of bromanil[3] showed no depression.

2.3. *Hydrolysis of 2,4,6-tribromoacetanilide.*

A mixture of the tribromoanilide (1.0 g) and (25 ml) sulphuric acid (60%) was heated under reflux for one hr. The reaction mixture was then cooled and treated with sodium hydroxide solution (20%) dropwise with stirring, whereby, a colourless solid was separated out. The product obtained was filtered off, washed thoroughly with water and finally recrystallised from benzene in colourless crystals, m.p 121-2°C; Yield 65%. An authentic sample[4] of 2,4,6-tribromoaniline was prepared and shown by mixed melting point experiment to be identical with this product.

Results and Discussion

In this investigation, bromination of some aromatic compounds is carried out by means of bromine in the presence of acetic acid and a catalyst which consists of a mixture of zinc dust and iodine. The function of the catalyst is to act as a halogen carrier. Moreover, the presence of zinc dust in acetic acid medium may prevent oxidation of compounds containing groups which are sensitive to ring oxida-

Table 1. Compounds which undergo full bromination

Compound	Product of bromination	Yield (%)
Anisole	Pentabromophenol	40
Anisic acid	Pentabromophenol	45
Phenol	Pentabromophenol	70
p-Hydroxybenzoic acid	Pentabromophenol	60
o-Methyoxybenzoic acid	Pentabromophenol	45
Salicylic acid	Pentabromophenol	65
o-Xylene	1,2-Dimethyl-3,4,5,6-tetrabromobenzene	45
p-Xylene	1,4-Dimethyl-2,3,5,6-tetrabromobenzene	40
m-Xylene	1,3-Dimethyl-2,4,5,6-tetrabromobenzene	50

Table 2. Compounds which are partially brominated.

Compound	Product of bromination	Yield (%)
Aniline	2,4,6-Tribromoacetanilide	70
Anthranilic acid	2,4,6-Tribromoacetanilide	55
p-Aminobenzoic acid	2,4,6-Tribromoacetanilide	57
o-Bromoaniline	2,4,6-Tribromoacetanilide	60
p-Bromoaniline	2,4,6-Tribromoacetanilide	62
o-Chloroaniline	4,6-Dibromo-2-chloroacetanilide	65
Benzoic acid	m-Bromobenzoic acid	40
Toluene	2,4,6-Tribromotoluene	65

Table 3. Compounds unchanged by the brominating agent

Benzonitrile	o-Chlorobenzoic acid	o-Dinitrobenzene
p-Chlorobenzoic acid	p-Bromobenzoic acid	Nitrobenzene
p-Nitrobenzoic acid	o-Nitrobenzoic acid	p-Dinitrobenzene

tion. According to their behaviour towards this brominating agent, the compounds investigated here are classified into *three main classes:*

(a) Compounds which undergo full bromination (cf. Table 1). The constitution of pentabromophenol obtained from most of these compounds is based upon:

(i) It gives a violet colour with ferric chloride solution.

(ii) On treatment with fuming nitric acid, it undergoes oxidation to give bromanil[3].

(iii) An authentic sample[5] of pentabromophenol was prepared and shown by mixed m.p. experiment to be identical with the product obtained in each case.

Authentic samples of 1,2-dimethyl-3,4,5,6-tetrabromobenzene, 1,4-dimethyl-2,3,5,6-tetrabromobenzene and 1,3-dimethyl-2,4,5,6-tetrabromobenzene were prepared[6] and shown to be identical with the products of bromination of *o*-xylene, *p*-xylene and

m-xylene respectively. The formation of pentabromophenol from methoxy derivatives of acids may be explained on the basis of brominolysis of the carboxyl group and splitting of the ether linkage. The latter process, which takes place by the effect of hydrogen bromide evolving during the bromination, was also observed by previous investigators[2,7]

(b) Compounds which are partially brominated (cf. Table 2). The structure of 2,4,6-tribromoacetanilide is inferred from: (i) hydrolysis to 2,4,6-tribromoaniline (cf experimental part), and (ii) authentic sample of 2,4,6-tribromoacetanilide was prepared[8] and shown by mixed melting point experiments to be identical with the product in each case. Authentic samples of 4,6-dibromo-2-chloroacetanilide[9], m-bromobenzoic acid[10] and 2,4,6-tribromotoluene[11] were also prepared and shown to be identical with the products of bromination of o-chloroaniline, benzoic acid and toluene respectively. The formation of the tribromoanilides from anthranilic acid and p-aminobenzoic acid may be explained on the basis of brominolysis of the carboxyl group and acetylation of the amino group. Therefore, the reagent can act as a brominating as well as acylating agent for compounds containing amino groups.

(c) Compounds which are not affected with the brominating agent (cf. Table 3). Such compounds are recovered unchanged at the end of the reaction. The unreactivity of these compounds towards the brominating agent is not unexpected due to the deactivating properties of the groups present in such compounds.

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