Novel Method for the Bromination of Aromatic Polynitro Compounds

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Abstract

A simple method of bromination with a high yield is proposed for severely deactivated aromatic compounds, such as 1,3-dinitrobenzenes and polycyclic nitro compounds. The method proposed is based on the action of bromine in sulphuric acid in the presence of nitric acid. The reaction stoichiometry corresponds to the consumption of 0.5 mol of bromine and 0.5 mol of nitric acid per 1 mol of an aromatic substrate. The nature of the bromination agent is under discussion.

Key words: bromination, aromatic compounds, dinitrobenzenes, bromine, nitric acid

INTRODUCTION

Aromatic compounds containing bromine atom in the ring, are essential for organic synthesis. Bromine is introduced into the aromatic ring to impart either desired properties to the final product or a desired reactivity to intermediates. The first group is composed of combustion retardants, fuel additives, some pharmaceutical and agrochemical preparations, dyes produced on an industrial scale [1]. The compounds of the second group are much more diverse, since bromoarenes are able to enter into a large number of reactions involving the exchange of bromine. They include: nucleophilic aromatic substitution of halogen [2], substitution reactions with electron transfer [3], Ullmann reaction [4], cross-coupling reactions catalyzed by palladium compounds those were extensively developed within recent decades [5].

The main route for introducing the bromine into the aromatic ring consists in the substitution of hydrogen atom under the action of an electrophilic bromination agent. The electrophilic bromination proceeds readily in the presence of electron donating substituents in the ring those activate the aromatic system. Owing to the presence of electron accepting substituents those deactivate the system, it is required to develop special techniques.

The deactivation level of the arene depends on the total electron accepting effect of substituents on the aromatic system. Conventionally, the arenes could be divided into moderately deactivated and severely deactivated ones. The former contain one electron accepting substituent in the ring, whereas the latter contains two such substituents. The methods of bromination for moderately deactivated arenes are not always suitable for the bromination of severely deactivated arenes. Typical compounds of the first group include nitrobenzene that converts into 3-bromonitrobenzene in the course of monobromination, whereas the typical compound of the latter group is presented by 1,3-dinitrobenzene which is converted into 5-bromo-1,3-dinitrobenzene.

Unlike the activated compounds, the moderately deactivated aromatic compounds react with molecular bromine only in the presence of catalysts or co-reactants such as SbCl₅ in dichloroethane [6], Pb₃O₄ in trifluoroacetic acid [7], Ag₂SO₄ in sulphuric acid [8], etc.

The bromination of severely deactivated compounds with molecular bromine was scantily explored.
We have found a simple method for the bromination of severely deactivated compounds by means of bromine treatment in sulphuric acid in the presence of nitric acid [9, 10]. Heating 1,3-dinitrobenzene (1a) in concentrated H₂SO₄ with bromine and nitric acid (molar ratio 1 : 0.5 : 0.5) at 80 °C results in a high yield of 5-bromo-1,3-dinitrobenzene (2a). In a similar manner, the bromination of 1,3-dinitrobenzenes (1b–d) substituted in the 4-position, synthesized the corresponding 5-bromo derivatives (2b–d).

![Scheme 1](image)

In the absence of nitric acid, the same compounds are not changed. The introduction of one more electron accepting substituent (nitro or carboxy group) to the 5-position of 1,3-dinitrobenzene prevents the compound from bromination. At the concentration of H₂SO₄ less than 90 % the bromination activity of the system decreases, whereas in the case when the concentration of H₂SO₄ is less than 85 % the system loses its activity at all. This preparative method has found its application for obtaining 5-bromo-1,3-dinitrobenzene [11].

The mentioned method was extended to deactivated polycyclic nitro compounds. It was demonstrated that 2,4,7-trinitrofluorenone can be converted into 5-bromo derivative (3) [9], and 2,4,8-trinitro-6(5H)-phenanthridinone into 10-bromo-derivative (4) [12]. 2.5 Dinitro- and 2.7-dinitro-9,10-phenanthrenequinone are transformed into 7-bromo- and 4-bromo-substituted species, respectively. 1.5-Dinitroantraquinone under the action of excess bromine in concentrated H₂SO₄ in the presence of HNO₃ results in the formation of tetrabromo-substituted compound (5) [13] with a high yield. The structure of the compounds obtained was confirmed by means of XRD structural analysis (Scheme 1).

In the case of severely deactivated aromatic compounds under the conditions of competition between bromination and nitration, almost the only bromination occurs, whereas in the case of moderately deactivated compounds predominantly nitration is observed. So, 3,4-dichloronitrobenzene (6) under the action of bromine and nitric acid in concentrated sulphuric acid is converted primarily into 1,3-dinitro-4,5-dichlorobenzene (7) instead of 3-bromo-1-nitro-4,5-dichlorobenzene (8). In order to avoid the prevalence of nitration in the competition, it is worthwhile to use another oxidizer. 3-Bromo-1-nitro-4,5-dichlorobenzene (8) could be synthesized by means of the reaction between
compound 6 and bromine in concentrated sulphuric acid with a gradual adding of hydrogen peroxide [9]. The oxidizer in this case, to all appearance, is presented by peroxosulphuric acid under formation (Scheme 2).

The fact that with increasing the level of aromatic compound deactivation the nitration reaction is inhibited to a greater extent than the bromination reaction indicates the latter exhibits a lesser selectivity. This feature opens up the potentiality of combining the nitration and bromination reactions in one preparative stage.

4-Chloronitrobenzene (9) in the course of treatment with bromine and nitric acid in concentrated sulphuric acid is converted directly into 5-bromo-1,3-dinitro-4-chlorobenzene (10) as the result of former selective nitration and further bromination to occur. This was just the fact that became the basis of the method for preparing 6-bromo-2,4-dinitroaniline (11) as a diazo component for obtaining disperse dyes from 4-chloronitrobenzene (9) via a two-staged process [14].

Instead of the traditional way of the three-stage obtaining via 4-chloro-1,3-dinitrobenzene (12) and 2,4-dinitroaniline (13), we performed joint nitration-bromination and subsequent ammonolysis of bromodinitrochlorobenzene (Scheme 3).

Nitric acid, acting as an oxidizer is reduced to give dinitrogen tetroxide N₂O₄ which disproportionates in sulphuric acid to form nitric acid and nitrosonium hydrosulphate (nitrosylsulphuric acid). The total equation corresponds to the consumption of 0.5 M HNO₃ per 1 mol of aromatic substrate with a complete utilizing of 0.5 mol of bromine.

The role of an oxidizer consists in the generation of a highly active bromination agent from the molecular bromine. It is well known that nitric acid in sulphuric acid at the concentration of the latter greater than 90% exists in the form of nitronium cation [15]. The electron transfer from bromine to nitronium cation represents a key stage of the process:

\[ 2\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{N}_2\text{O}_4 + 2\text{H}_2\text{O} \]
\[ \text{Br}_2 + 2\text{NO}_2^-\text{HSO}_4^- \rightarrow \text{N}_2\text{O}_4 + 2\text{Br}^-\text{HSO}_4^- \]
\[ \text{N}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{HNO}_3 + \text{NO}^+\text{HSO}_4^- \]

The comparative analysis of different oxidizers demonstrated that the oxidizer efficiency in the bromination reaction is not directly connected with the value of the redox potential. Much more powerful oxidizers such as dichromates, bromates, chlorates (\( E_0 = 1.36–1.45 \text{ V} \)), are inefficient, whereas weaker oxidizers such as nitric acid, iodate, mercuric oxide (\( E_0 = 0.80–1.08 \text{ V} \)) result in the bromination reaction to occur.

To all appearance, the electron transfer from bromine to an oxidizer occurs via intermediate which decomposes to generate an electrophilic brominating agent stabilized in the medium of sulphuric acid. The efficiency of the oxidizer depends on the energy barrier of the intermediate formation. Structure of the intermediate could be specifically inherent in various oxidizers, but proper bromination agent generated from an intermediate in the sulphuric acid, is, to all appearance, generally the same for all the oxidizers. The bromine cation resulting from the electron transfer to the oxidizer in the course of the intermediate decomposition could be stabilized in the medium with a low nucleophilici-
ty at the expense of binding with HSO$_4^-$ counterion and the further association with non-ionized molecules of sulphuric acid in a complex such as Br$^+$HSO$_4^-$ nH$_2$SO$_4$. This associate is similar to the complex of nitronium ion in the sulphuric acid NO$_2^+$HSO$_4^-$ 2H$_2$SO$_4$ [17]. The ion pair of the complex could be considered a boundary structure of sulphohypobromite wherein the bond between the bromine atom and the oxygen atom of an outgoing group is strongly polarized:

Br$^+$OSO$_2$OH$^-$ ↔ Br$^-$OSO$_2$OH

**CONCLUSION**

Thus, for the bromination of highly deacivated aromatic compounds one can efficiently use the action of bromine and nitric acid or another suitable oxidizing agent in the concentrated sulphuric acid.

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