# Oxidative monobromination of electron-rich arenes by conc. H$_2$SO$_4$ / alkali metal bromides

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The reaction of electron-rich arenes with alkali metal bromides such as sodium and potassium bromides in the presence of conc. H$_2$SO$_4$ to give *p*-bromoarenes is reported. The reaction is possible in the absence of any specialised oxidising agents and the yields are high.

**Keywords:** monobromination, arenes, sodium bromide, potassium bromide, conc. H$_2$SO$_4$

Halogenation of organic compounds and the chemistry of organic halides are of interest as major chemical fields due to the theoretical and practical value of halogenation reactions and their products. Their industrial application is wide.[1] Electrophilic substitution of aromatic hydrocarbons by bromine is a well-known organic reaction.[2] Classical nuclear bromination of aromatic compounds involves the use of bromine in the presence of a catalyst like FeCl$_3$, FeBr$_3$, iodine, thallium(III) acetate or light in a suitable solvent. These conditions often yield undesired co-products. [3]

Siddiq *et al.*[4] have shown that a mixture of HgO/Br$_2$ in the presence of conc.H$_2$SO$_4$ in CCl$_4$ at reflux gives the monobrominated arenes. Prestwich *et al.*[5] have explored the tetrabromination of *p*-toluic acid by dibromoisocyanuric acid dissolved in conc. H$_2$SO$_4$. Mattern[6] has described the periodination of benzene with HIO$_4$/KI in conc. H$_2$SO$_4$ at 100°C after 10h. Minisci *et al.*[7] have investigated the chlorination of alkyl benzenes with *N*-chlorodicyclohexylamine in 98% H$_2$SO$_4$. Recently, the reagents such as NBS in DMF,[8] bromine adsorbed on Al$_2$O$_3$,[9] bromine and thallium(III) acetate,[10] quaternary ammonium polyhalides,[11-17] KBr / NH$_4$VO$_3$ in a two-phase (H$_2$O/CHCl$_3$) system,[18] HF/SbF$_5$ with sodium or potassium bromide,[19] CuBr$_2$[20] and dodecyltrimethylammonium bromide (DTAB)/HNO$_3$,[21] have been used for the selective monobromination of aromatic rings. Most of these reagents are complex with potential environmental problems due to the generation of hazardous waste and the polybromides obtained from quaternaryammonium bromides and Br$_2$ are generally found to be unstable under normal conditions. However, each example has its own specific set of conditions and hence, the reagents have their own advantages and limitations.

Recent work from this laboratory[22-25] has described reduction of different functional groups by metals such as aluminium or zinc in the presence of ammonium salts under neutral conditions. As the metals are non-reactive in the absence of ammonium salts, the ammonium salts are expected to participate in these reactions. In order to explore the possibility of utilising the alkyl groups attached to the symmetric tetraalkylammonium halides (R$_4$NY, Y= Br, I) the reaction of R$_4$NY with arenes in presence of an acid was undertaken. Surprisingly, instead of alkyl group being transferred in a Friedel–Crafts manner *p*-haloarenes were obtained in high yields.[26]

As the reaction developed by us involves the use of complex tetraalkylammonium bromides for the bromination of arenes, an attempt has been made in our laboratory to synthesise *p*-bromoarenes from simple alkali metal bromides in the presence of conc. H$_2$SO$_4$.

Initially, we carried out the reaction of aromatic hydrocarbons with sodium bromide in the presence of conc. H$_2$SO$_4$ and it

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was found that bromination of arenes is also possible with this reagent. When, sodium bromide was replaced by potassium bromide the reaction still occurred. In this paper, we report a simple and extremely efficient method of *p*-bromination of substituted arenes by very simple reagents, sodium bromides and potassium bromides in the presence of conc.H$_2$SO$_4$ (Scheme 1).

In order to understand the mechanism of this reaction, a set of three Lewis acids and three Brönsted acids were chosen for the study (Table 1). The effect of the nature of these acids on the course of the reaction of chlorobenzene with sodium bromide has been studied in detail.

From Table 1, it is clear that, the reaction of chlorobenzene and sodium bromide is not possible in the absence of an acid (entry 6). It is also found from this table that, the reaction is facilitated by Brönsted acids only. Lewis acids on the other hand are found to be either non-reactive or to give a complex mixture of products (TLC). The presence of conc.H$_2$SO$_4$ was observed to have a profound effect upon the course of the reaction between sodium bromide and chlorobenzene. Two and three moles of acid were used to study the effect of the acid on the course of the reaction per mole of sodium bromide and it was found that two moles bring about the conversion and there was no significant change in the yield or the time of the reaction by increasing the amount of the acid used.

In a typical experiment, 10 mmole of sodium bromide and 20 mmole of conc. H$_2$SO$_4$ were treated with 10 mmole of arene. The contents were heated at 60°C with constant stirring, until the initial dark orange colour substantially faded (– 2 h).



X= CH$_3$, C$_2$H$_5$, Cl, OCH$_3$, OH, NH$_2$

M= Na, K
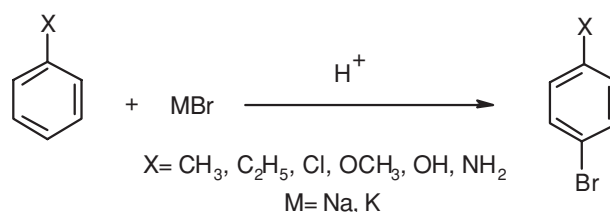
**Scheme 1**

**Table 1** Reaction of sodium bromide with chlorobenzene in the presence of different acids at 60°C

| Entry | Acid | Time h | Product | Yield % |
|---|---|---|---|---|
| 1 | AlCl$_3$ | 2 | a | – |
| 2 | ZnCl$_2$ | 2 | a | – |
| 3 | FeCl$_3$ | 2 | b | – |
| 4 | conc.H$_2$SO$_4$ | 2 | *p*-bromochlorobenzene | 90 |
| 5 | 35%HCl | 2 | b | – |
| 6 | 67%HNO$_3$ | 2 | b | – |
| 7 | No catalyst | 24 | a | – |

aThere was no reaction.
bA complex mixture of products was obtained (TLC) which was not characterised.

The reaction mixture was extracted with ether and the ethereal extract was washed with saturated sodium bicarbonate solution, water and the solvent was removed to get the crude product. Silica gel chromatography of the crude material using pentane as a solvent gave the *p*-bromoarene (90%).
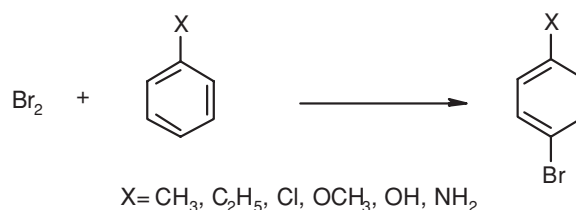
In order to standardise this reaction, the reaction of chlorobenzene and sodium bromide was carried out at different reaction temperatures (25°, 40°, 60°, 80°, 100°, 120°C) in the presence of acid and it was found that, the reaction went to completion within 2 h at 60°C to give *p*-bromochlorobenzene in 90% yield. It was also found that at lower temperatures (≤ 60°C) the reaction was either incomplete or the product is a mixture of *o*- and *p*-bromochlorobenzenes; for example, at 25°C, the reaction went about 40% conversion and the *o/p* ratio of the product was 23:77 by GC analysis. There was no significant change in the yield or the time of the reaction by increasing the reaction temperature above 60°C. This observation is attributed to the fact that, at lower temperatures the kinetic control predominates and at higher temperatures thermodynamic control of the product formation predominates to give *p*-brominated arenes.[27]

To explore the possibility of using sodium and potassium bromides for bromination of arenes, different substituted aromatic hydrocarbons were chosen and the reaction was carried out under similar reaction conditions. The reaction went to completion smoothly giving the expected products, *p*-bromoarenes in excellent yields (Table 2).

From Table 2, it can be seen that, except anisole, bromination can occur in electron rich arenes with alkali metal bromides to give monobromoarenes in excellent yields. A competitive hydrolysis in anisole is noticed giving a mixture of *p*-bromoanisole and *p*-bromophenol (entries 5 and 6).

It is known that hot conc. $H_2SO_4$ oxidises sodium bromide or potassium bromide to give a mixture of bromine and hydrobromic acid.[28] The present reaction is also expected to proceed by the reaction of the bromine molecule which may form by the decomposition of respective metal bromides in the presence of conc. $H_2SO_4$ as shown in the Scheme 2.

In conclusion, we have demonstrated for the first time the direct generation of valuable synthons of bromoarenes from the readily available, less hazardous and inexpensive alkali-metal bromides and an inexpensive mild oxidising agent conc. $H_2SO_4$. The reaction may be considered as simple from practical point of view and has great potential for future applications. The obvious advantages of the proposed method

$$2KBr + H_2SO_4 \longrightarrow K_2SO_4 + 2HBr$$

$$2HBr + H_2SO_4 \longrightarrow 2H_2O + Br_2 + SO_2$$



X = CH₃, C₂H₅, Cl, OCH₃, OH, NH₂

**Scheme 2**

over previous methods are – simplicity, convenience, the high purity of the product and the less hazardous conditions.

## Experimental

All the standard *p*-bromoarenes were prepared by Sandmeyer reaction from respective anilines. A Nicolet 400D FT-IR spectrophotometer was used for IR spectral analysis and NMR spectra were recorded on a Jeol 90 FQ and Bruker AC 250 instruments and the chemical shift values (ppm) are reported relative to TMS in $CDCl_3$ as solvent. Boiling points are recorded using the open capillary method[29] and are corrected. Yields refer to the isolated yields of the products.

*General procedure for the bromination of arenes of p-bromochlorobenzene*: Sodium bromide (1.03 g, 10 mmol) and conc. $H_2SO_4$ (1.96 g, 20 mmol) were treated with chlorobenzene (1.125 g, 10 mmol) and the contents were heated with constant stirring in an oil bath maintained at 60°C. The reaction was monitored by TLC (pet. ether 40–60°C) and comparison with an authentic sample. After completion of the reaction (2 h), the reaction mixture was quenched with water (10 ml) and the organic layer was extracted with ether (3 × 10 ml). The combined ethereal extract was washed with saturated sodium bicarbonate solution and water and then dried over anhydrous sodium sulfate and the solvent removed. The silica gel chromatography of the crude material using pentane gave *p*-bromochlorobenzene as a colourless solid in 90% yield (1.72 g). *p*-Bromochlorobenzene was characterised by direct comparison with an authentic sample on TLC (pet. ether 40–60°C) and by IR and ¹H NMR spectral analysis and by melting point (Table 3).

Different substituted arenes were treated with alkali metal bromides in the presence of conc. $H_2SO_4$, and the respective *p*-bromoarenes were obtained. The yields based on 10 mmol of the starting arenes are presented in Table 2, and the physical and spectral data are given in Table 3.

**Table 2**  Reaction of different substituted arenes with alkali metal bromides in the presence of conc. $H_2SO_4$ at 60°C

| Entry | Substrate | Metal bromide | Product | Yield % |
|---|---|---|---|---|
| 1 | Chlorobenzene | NaBr | *p*-bromochlorobenzene | 90 |
| 2 | Chlorobenzene | KBr | *p*-bromochlorobenzene | 95 |
| 3 | Toluene | NaBr | *p*-bromotoluene | 89 |
| 4 | Toluene | KBr | *p*-bromotoluene | 92 |
| 5 | Anisole | NaBr | (i) *p*-bromoanisole | 68 |
|   |   |   | (ii) *p*-bromophenol | 17 |
| 6 | Anisole | KBr | (i) *p*-bromoanisole | 71 |
|   |   |   | (ii) *p*-bromophenol | 21 |
| 7 | Phenol | NaBr | *p*-bromophenol | 83 |
| 8 | Phenol | KBr | *p*-bromophenol | 87 |
| 9 | Aniline | NaBr | *p*-bromoaniline | 87 |
| 10 | Aniline | KBr | *p*-bromoaniline | 86 |
| 11 | *o*-cresol | NaBr | 4-bromo-2-methylphenol | 80 |
| 12 | *o*-cresol | KBr | 4-bromo-2-methylphenol | 76 |
| 13 | Naphthalene | NaBr | 1-bromonaphthalene | 74 |
| 14 | Naphthalene | KBr | 1-bromonaphthalene | 79 |
| 15 | 2-Naphthol | NaBr | 1-bromo-2-naphthol | 89 |
| 16 | 2-Naphthol | KBr | 1-bromo-2-naphthol | 86 |
| 17 | Ethylbenzene | NaBr | *p*-bromoethylbenzene | 81 |
| 18 | Ethylbenzene | KBr | *p*-bromoethylbenzene | 80 |

**Table 3**  Physical and spectroscopic data of *p*-bromoarenes

| Entry | Product | m.p/b.p Observed | °C Lit. | IR (C-Br) υ (cm⁻¹)[35] | ¹H NMR (CDCl₃) δ (ppm)[c] |
|---|---|---|---|---|---|
| 1 | *p*-bromochlorobenzene | 66[a] | 64.6[30] | 1020 | 7.15(*d*, 2H), 7.4(*d*, 2H). |
| 2 | *p*-bromotoluene | 184[b] | 183.6[31] | 1025 | 2.3(*s*, 3H), 7.2(*d*, 2H), 7.4 (*d*, 2H). |
| 3 | *p*-bromoanisole | 213[b] | 213[12] | 1040 | 3.7 (*s*, 3H), 6.7(*d*, 2H), 7.3 (*d*, 2H). |
| 4 | *p*-bromophenol | 64[a] | 63[17] | 1055 | 6.6 (*d*, 2H), 6.85 (*s*, 1H, broad), 7.25 (*d*, 2H). |
| 5 | *p*-bromoaniline | 66[a] | 66[13] | 1070 | 3.5 (*s*, 2H), 6.5 (*d*, 2H), 7.2 (*d*, 2H) |
| 6 | 4-bromo-2-methylphenol | 63[a] | 64[32] | 1065 | 2.1 (*s*, 3H), 4.9 (*s*, 1H), 7 (*m*, 3H). |
| 7 | 1-bromonaphthalene | 284[b] | 283–285[33] | 985 | 7.35 (*m*, 7H) |
| 8 | 1-bromo-2-naphthol | 80[a] | 79–81[34] | 1080 | 5.8 (*s*, 1H, broad), 7.45 (*m*, 6H). |
| 9 | *p*-bromoethylbenzene | 204[b] | 205[13] | 1070 | 1.2 (*t*, *J* = 7 Hz, –C$\underline{H}_3$), 2.5 (*q*, *J* = 7 Hz, –C$\underline{H}_2$-), 7.0 (*d*, 2H), 7.3 (*d*, 2H). |

[a]Melting point
[b]Boiling point at 760 torr.
[c]For all the products the coupling constant for aromatic protons is *J* = 8 Hz; the AA 'XX' system appeared as two doublets at 90MHz

## References

1  M. Srebnik, R. Mechoulam and I. Yana, *J. Chem. Soc., Perkin Trans. 1.*, 1987, 1423.
2  R.O.C. Norman and R. Taylor, *Electrophilic Substitution in Benzenoid Compounds*, Elsevier, New York, 1965, 130.
3  J. March, *Advanced Organic Chemistry*, John Wiley & Sons, Inc., New York, 4th edn, 1992, 531.
4  M. Siddiq, S.A. Khan and M.A. Munawar, *J. Org. Chem.*, 1988, **53**, 1799.
5  G.D. Prestwich, G. Dorman, J.D. Olszewski, Y. Hong and D.G. Ahern, *J. Org. Chem.*, 1995, **60**, 2292.
6  D.L. Mattern, *J. Org. Chem.*, 1983, **48**, 4772.
7  F. Minisci, E. Vismara and F. Fontana, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1246.
8  A. McKillop, D. Bromley and E.C. Taylor, *J. Org. Chem.*, 1972, **37**, 88.
9  R.H. Mitchell, Y.H. Lai and R.V. Williams, *J. Org. Chem.*, 1979, **44**, 4733.
10  C.B. Ranu, C.D. Sarkar and R. Chakraborthy, *Syn. Commun.*, 1992, **22**, 1095.
11  L.F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, John Wiley and Sons, New York, 1967, 885, 1144.
12  S. Kajigaeshi, M. Moriwaki, T. Tanaka and S. Fujisaki, *J. Chem. Soc., Perkin Trans. 1*, 1990, 897.
13  J. Berthelot, C. Guette, P.L. Desbene, J.J. Basselier, P. Chaquin and D. Masure, *Can. J. Chem.* 1989, **67**, 2061.
14  S. Kajigaeshi, T. Kakinami, H. Yamasaki, S. Fujisaki and T. Okamoto, *Bull. Chem. Soc. Jpn*, 1988, **61**, 2681.
15  S. Gervat, E. Leonel, J.Y. Barraud and V. Ratovelomanana, *Tetrahedron Lett.*, 1993, **34**, 2115.
16  S. Kajigaeshi, T. Kakinami, K. Inoue, M. Kondo, H. Nakamura, M. Fujikawa and T. Okamoto, *Bull. Chem. Soc. Jpn*, 1988, **61**, 597.
17  S. Kajigaeshi, T. Kakinami, H. Nakamura, M. Fujikawa and T. Okamoto, *Bull. Chem. Soc. Jpn*, 1987, **60**, 4187.
18  F.D. Furia, V. Conte and S. Moro, *Tetrahedron Lett.*, 1994, **35**, 7429.
19  J. Sommer, J.C. Culmann and G. Cherry, *Tetrahedron Lett.*, 1990, **31**, 2007.
20  K. Holmberg, F. Currie and G. Westman, *Colloids and Surface A: Physicochem Eng Aspects.*, 2003, **215**, 51.
21  D. Mosnaim and D.C. Nonhebel, *Tetrahedron.*, 1969, **25**, 1591.
22  D. Nagaraja and M.A. Pasha, *Tetrahedron Lett.*, 1999, **40**, 7855.
23  K. Rama, E. Nagendra and M.A. Pasha, *Ind. J. Chem.*, 2000, **39B**, 563.
24  D. Nagaraja and M.A. Pasha, *Ind. J. Chem.*, 2002, **41B**, 1747.
25  D. Nagaraja and M.A. Pasha, *J. Saudi Chem. Soc.*, 2003, **7**, 99.
26  M.A. Pasha and Y.Y. Myint, *Ind. J. Chem.*, 2004, **43B**, 357.
27  P. Sykes, *A Guidebook to Mechanism in Organic Chemistry*, 6th edn, Pearson Education, India, 2004, 163.
28  P.L. Soni, *Text book of Inorganic Chemistry*, 5th edn. Delhi, 1970, 78.
29  I. Vogel, *A Text book of Practical Organic Chemistry,* 3rd edn, Longman Group Limited, London, 1975, 86.
30  J.N. Dorpat, *Ber.*, 1919, **52B**, 1028.
31  P. Kovacic and K.E. Davis, *J. Am. Chem. Soc.*, 1964, **86**, 427.
32  P. Klarmann, *J. Am. Chem. Soc.*, 1933, **55**, 4657.
33  P.S. Varma, D.N. Mozumdar and K.K. Rajah, *J. Ind. Chem. Soc.*, 1933, **10**, 595.
34  S.C. Bisarya and R. Rao, *Syn. Commun.*, 1993, **23**, 779.
35  W.W. Simons, *Sadtler Handbook of Infrared Spectra*, Sadtler Research Laboratories Inc, Philadelphia, U.S.A, 1978, 109.