Chapter 5

Preparation and Characterization of Organo Bromine Compounds and Selective Dehalogenation of Halo Phenols

5.1. Introduction

Bromine undergoes electrophilic substitution reactions with aromatic substrates such as aromatic hydrocarbons, phenols, anilines etc. The reaction may proceed with or without a catalyst depending on the electronic nature and type of substituent already present on the aromatic ring. Activated systems usually, are brominated without a catalyst. However, as the degree of bromine substitution increases, the steric effects play a predominant role on reaction rates. Organic compounds of bromine usually resemble their chlorine analogues but have higher densities and lower vapor pressures. The bromocompounds are more reactive towards alkali metals. On the other hand they possess less fire hazards, one bromine atom per molecule approximately reduces flammability about as much as that of two chlorine atoms. Although a great many bromine compounds are available in the literature, those considered here are mainly the ones that have some commercial applications.

Halogenated organic compounds are vital and valuable class of entities. These find many applications in various aspects of synthetic organic chemistry and often used as rudimentary materials for the synthesis of various value added products.[1,2] Of all the halogenated organic compounds, organobromines are of particular interest due to their optimum reactivity towards many reagents and high shelf life imparted by their reasonable stability.

5.1.1. Aromatic substitution reactions. Organobromine compounds are conventionally produced by the direct bromination of corresponding organic substrates with elemental bromine in the presence or absence of a catalyst.[3,4] However, the direct use of liquid

bromine causes serious handling difficulties and other environmental problems due to its high corrosiveness and volatility, especially when it is required to be used at large scale. Besides, the aromatic brominations with elemental bromine accompanies by the formation of equal quantity of hydrobromic acid (Eq 5.1), which needs to be reconverted to active bromine or to be neutralized before being discharged in the waste. Neither the modern outlook of atom efficient synthesis nor the economics of bromination allows this extra expenditure. Recently, a patent on the preparation of a new reagent combination optimistically hoping to offer an alternative to liquid bromine with high atom efficiency from alkaline bromine slurry, an intermediate in one of the bromine recovery processes, has been filed for the bromination reactions.[5]

$$ArH + Br_2 \longrightarrow ArBr + HBr \qquad (5.1)$$

A number of new reagents and methods for bromination reactions without the direct use of elemental bromine have been recently reported. Vona *et al.*[6] have used pyridiniumbromide-perbromide in acetic acid for the bromination of 2-naphthol, phenol, aniline and styrene. The reaction gives low yields and needs acetic acid as solvent, while the preparation of brominating reagent itself involves the corrosive bromine.[7] Oxybrominations using hydrobromic acid as a brominating reagent, H_2O_2 as oxidant[8-18] has been believed to be a possible alternative to elemental bromine, but many attempts have met partial success since hydrobromic acid is not too kind to the environment. The reported methods[9-14] of direct oxybromination of aromatic systems involve the use of expensive transition metal based catalysts and use of peroxides as oxidizing agents. Most of these reagents employ transition metal catalysts, which are costly and cumbersome to prepare. The leaching of toxic heavy metals discharged into the waste streams is potentially dangerous to the environment. In this list, our own procedure dispenses the use of metal catalyst and can be used for chlorination reactions as well.[18] In contrast to the hazardous elemental bromine in combination with or without heavy metal catalysts/peroxides, the other reagents reported for bromination of aromatic substrates include, Br_2-NaY zeolite,[19] Br2-Na-Y zeolite in presence of propylene oxide,[20] HBr-DMSO,[21] P_2O_5 – Bu_4NBr.[22] Most of these reactions have limitations of needing costly zeolite as catalysts, some require anhydrous reaction conditions, and hence requires much

care while performing the experiments, on the other hand none looks commercially viable. The other promising reagent is BrO_3^--H_2SO_4,[23-26] wherein the aromatic ring having electron deactivating substituents are brominated. Hence these systems have the limitations of electron withdrawing substituents in the aromatic ring. Fujisaki *et al.*[27] have brominated many amides and imides using $NaBrO_3$-HBr in sulfuric acid/acetic acid medium. These methods are again limited to only imides and amides, as they could not achieve the bromination of other substrates. The use of concentrated sulfuric acid and/ or acetic acid is environmentally hazardous. Das and Roy[28] used a *N*-bromosuccinimide-catalyst system for successive decarboxylation and selective bromination of terminal olefins. The preparation of the reagent *N*-bromosuccinimide is again involves the use of hazardous liquid bromine and the process will become uneconomical. Duan *et al* [29] have reported the bromination of aromatic ring carrying deactivated substituents with *N*-bromosuccinimide. Ramachandraiah *et al*[30] have reported the bromination of bisphenol-A in a two-phase solvent system comprising of a chlorinated solvent and water in 1:5 volumes while maintaining the temperature between 10-40 °C.

It is thus proposed here to use the non-hazardous solid brominating reagent combination,[5] BR(S) for substitution reactions as discussed in Chapter 3 of the present thesis for the bromination of some selected organic substrates such as phenols, amines, amides (acetanilide), imides (succinimide), ethers, and hydrocarbons as working paradigms.

5.1.2. Olefinic addition reactions of bromine. The most common chemical transformation of a carbon-carbon double bond is the addition reaction. A large number of reagents, both inorganic and organic, have been found to add to this functional group, and in this section we discussed these reactions. Bromine adds readily to unsaturated compounds, with the exception of those in which the unsaturated carbon are heavily substituted with aromatic or carbonyl groups. The reaction is normally carried out at low temperatures to avoid the substitution of hydrogen by bromine or elimination of hydrobromic acid from the product. The addition reaction is speeded up by visible and ultra-violet light, but the reaction is frequently carried out in the dark to minimize side reactions. Catalysts are rarely necessary for the addition reactions. Mercuric acetate is some times employed to catalize brominations carried out for analytical purposes. Bromination of unsaturated

compounds is normally carried out in an inert solvents such as chloroform, carbon tetrachloride, methylene chloride, carbon disulphide, o-dichlorobenzene of glacial acetic acid. Ether, dioxane, ethyl acetate and benzene have been employed at low temperatures. Some compounds can be brominated in solution or suspension in water, preferably in the presence of dispersing agent in the latter case. The reactions of bromine with olefins were relatively found to involve stereospecific, trans addition.[31] The bromine addition across olefin reactions were usually carried out using liquid bromine.[32] Though the olefinic addition of bromine with the elemental bromine has been investigated from the synthetic and mechanistic point of view, little about the addition of bromine by means of other reagents. Organo perbromides are considered as mild brominating agents. Avramoff *et al*[33] used tetramethyl ammonium tribromide for the preparation of dibromocyclohexane from cyclohexene. Here the preparation of the tetramethyl ammonium tribromide reagent involves the use of elemental bromine. In recent years Ryu *et al* [34] have prepared dibromo compounds from olefins in three-phase system using bromine and boron tribromide in highly fluorinated solvents. These systems are highly complicated and fluorocarbons environmentally hazardous. As explained in the introduction all these methods are complicated and the use of elemental bromine remains as hazardous.

It is thus proposed here to use the non-hazardous solid brominating reagent combination,[5] BR(A) for addition reactions as discussed in Chapter 3 of the present thesis for the bromination of some selected olefins such as cyclic and non-cyclic side chain aromatic substrates as working examples.

5.1.3. Olefinic addition reactions of hypobromous acid. The transformation of olefins into the corresponding halohydrins is quite commonly practiced in organic synthesis.[35] In particularly for the reaction of olefins with N-bromosuccinimide (NBS) is well known and being used since many years.[36] Bromohydrins are versatile intermediates in synthetic organic chemistry and have been used in many organic transformations as conversion of bromohydrins to ketones,[37] epoxides,[38] neighboring group transformation,[39] cyclization[40] and ∝-bromoacid[41] reactions. Other than N-bromosuccinimide (NBS), Masuda et al[42] have employed $NaBrO_3$-$NaHSO_3$ reagent combinations for the preparation of bromohydrins. LeTourneau *et al*[43] used N-bromoacetamide-perchloric acid for the preparation of bromohydrins from indazole derivatives. Andersson *et al*.[44] used H_2O_2-

KBr, catalyzed by NH_4VO_3. Another way of obtaining halohydrins is by the addition of elemental halogens[45-47] in presence of catalysts and metal bromides[48] from their corresponding epoxides. The reported procedures involves the use of either heavy metal catalysts of use of peroxides or per acids. Hence it is necessary to search for the easy, simple, and environmentally benign methods. As explained in the first section of the chapter for the preparation bromo compounds through aromatic substitution reactions, the efficacy of the reagent was extended for the preparation of bromohydrins using the eco-friendly brominating reagent developed in this institute.

The objective of the present work is to use the non-hazardous solid brominating reagent combination,[5] BR(S) as discussed in Chapter 3 of the present thesis for addition reactions across olefinic compounds as working examples.

5.1.4. Selective dehalogenation of halophenols. After preparation of variety of organobromine compounds in their pure isolated form, the idea was to initiate the selective debromination of poly-bromocompounds. In recent years, the halogens on aromatic rings have been used as potential protecting or blocking groups in synthetic organic chemistry.[49,50] Aromatic halides are readily reduced by metal-catalyzed transfer hydrogenolysis.[51] The process of reductive elimination of halogens from aromatic rings is relatively a quite difficult task. There are reports of the use of Pd(II) salts, to give the corresponding dehalogenated compounds.[52] Generally, debrominations have been carried out in hydrobromic acid in the presence of a suitable bromine scavenger such as aniline or phenol or sodium sulfite.[50,53] Dehalogenation by direct hydrogenolysis has been accompanied by the reduction of double bonds in the case of unsaturated halides and the formation of amines in case of nitro halides. Dehalogenation of aromatic halides has been reported over palladium deposited on carbon[54] in the presence of a proton donor substrates like limonene and *p*-menthene at 50-100 °C, but the nitrile group of *o/p* chlorobenzonitrile was also reduced. Cortese *et al*.[51] have achieved the dehalogenation of aromatic halides without affecting a nitrile group by employing triethylammonium formate/triarylphosphine catalyzed by palladium or palladium acetate at 50-100 °C. Nucleophilic reagents such as $LiEt_3BH$[55,56] and $2LiAlH(OCH_3)_3$-CuI[57] have been used in dehalogenation reactions. Tyrlik *et al*.[58] have employed a $TiCl_3$ /3THF-Mg system for

easy reduction and dehydrohalogenation of organic halides under a nitrogen/argon atmosphere obtaining moderately low yields.

In recent years there has been a trend to explore various solid acid catalysts for traditional processes involving mineral acids. Also in the recently the dehalonitration of poly-halo phenolic compounds[59] in diethyl ether at ambient conditions was reported. In this account we explored our preliminary findings for the selective dehalogenation of halophenols to utilizing Hβ-Zeolite[60] as a heterogeneous catalyst and also in a bisulfate ($KHSO_4$)-sulfite[61] (Na_2SO_3) medium. In both cases the catalyst acts as a source of proton to initiate the electrophilic dehalogenation reactions.

5.2. Experimental Section

5.2.1. Materials and methods. The brominating reagents BR(S) and BR(A) were prepared by the procedures as outlined in Chapter 3 of the present thesis utilizing the industrial aqueous alkaline bromine mixture (pH, 8-10) containing 25-35% bromine dissolved in sodium hydroxide were collected from M/s Agrocel Industries Limited, Dhordo, Greater Rann of Kutch, Bhuj, Gujarat, India and used as such in all aromatic substitution and olefinic addition reactions, respectively. Analytical grade organic substrates and hydrochloric acid used in all bromination reactions were purchased from S.D.Fine Chem. Ltd., India and used without further purification. Deionized water and laboratory grade dichloromethane/CCl_4, CH_3OH, 1,4-dioxane were used as solvents in all bromination reactions.

5.2.2. Instrumentation. ^{1}H-NMR spectra were recorded on Bruker-200 MHz FT-NMR DPX-200 in $CDCl_3$ with Tetramethylsilane (TMS) as an internal standard. Microanalyses were performed on Perkin-Elmer-4100 elemental analyzer and FT-IR spectra were recorded on Perkin Elmer GX-2000 spectrometer. Gas Chromatograms were recorded on Shimadzu GC-14B using SE-30 column. The purity of bromocompounds was verified by recording thermograms on Differential Scanning Calorimeter (DSC) Mettler Toledo Star^e Model DSC822^e. Melting points were recorded on Veego-instrument purchased from S.Kantilal & Co. Mumbai. Progress of the reactions was monitored by TLC using Aluchrosep Silica Gel 60/UV_{254} plates of S.D.Fine Chem. Ltd., India. Philips X'pert MPD system difractiometer was used to study the catalytic activity of the H-β-zeolite

catalyst. Compounds were purified by column chromatography over silica gel 100-200 mesh/neutral alumina from S.D.Fine-Chem. Ltd., India or neutral alumina using hexane-ethyl acetate as eluent.

5.2.3. Preparation of solid brominating reagents. BR(S) for substitution reactions. The reagent consisting of bromide and bromate salts in 2:1 mole ratio for aromatic substitution BR(S) reactions was prepared by the procedures developed in this laboratory (as explained in **Chapter 3** of the present Thesis) using the industrial alkaline-bromine intermediates of bromine recovery plants based on cold process. The alkaline-bromine slurry contained 29% (w/v) of dissolved bromine at pH 9.5. The analysis data revealed that the BR(S) contains 40.05% (w/w) bromine as available for substitution reactions.

BR(A) for addition reactions. The reagent consisting of bromide and bromate salts in 5:1 mole ratio for olefinic addition BR(A) reactions was prepared by the procedures developed in this laboratory (as explained in **Chapter 3** of the present Thesis) using the industrial alkaline-bromine intermediates of bromine recovery plants based on cold process. The alkaline-bromine slurry contained 29% (w/v) of dissolved bromine at pH 9.5. The analysis data revealed that the BR(A) contains 54.85% (w/w) bromine as available for addition reactions.

5.2.4. Synthesis and characterization. (a) Aromatic bromo compounds with BR(S). In general, a known quantity of the given organic substrate was taken in a single neck 100-250 ml round bottom flask containing dichloromethane/methanol in 1:5 (w/v) substrate to solvent ratio. To it, an aqueous solution containing the calculated quantity of brominating reagent of BR(S) was added under stirring at 25-40 °C. Then the required quantity of aqueous hydrochloric acid solution was added drop wise to the flask under stirring at room temperature over a period of 30-60 min. After complete addition of the acid solution, the stirring was continued for another 40 to 60 min and the product was extracted with 3 x 25 ml of dichloromethane/diethyl ether. The combined organic extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and concentrating under reduced pressure to get 66-99% of the desired product. The product was purified wherever required by column chromatography on silica gel using 2% ethyl acetate and hexane.

(i) Bromophenols. 4-Bromophenol (**1**). An aqueous solution (35 ml) containing 1.0 g (10.638 mmole) of phenol and 2.125 g BR(S) was taken in a single neck 100 ml round bottom flask. To it, about 10 ml of aqueous 1.326 N hydrochloric acid (11.0 mmole) solution was added drop wise under stirring at room temperature over a period of 30 min. After complete addition of the acid, the stirring was continued for another 30 min and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and concentrating to get 1.684 g (9.700 mmole) (91% yield) of bromophenol. The product was analyzed by gas chromatography and comparing with standard samples. The ratio of *p/o* bromophenol was estimated to be 82:18.

2,4,6-Tribromophenol (**2**). The aqueous solution, 50 ml containing 1.0 g (10.638 mmole) of phenol and 6.375 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, 30 ml of 1.326 N hydrochloric acid (11.0 mmole) solution was added drop wise under stirring at room temperature over a period of 30 min. After complete addition of the acid, the stirring was continued for another 30 min and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 5% ethyl acetate in hexane as eluent) column to get 3.260 g (9.850 mmole, 93%) tribromo phenol. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS): (δ) 7.7 (2H, s); 5.89 (1H, broad s) [Fig 5.1(A)]. IR: ν_{max} (KBr): 3407, 3070, 2358, 1552, 1454, 1379, 1317, 1263, 1228, 1158, 856, 736, 667, 552 cm^{-1} [Fig 5.14(A)]. CHN: Found C, 22.04%; H, 0.84%; Calcd. C, 21.75%; H, 0.90%. Melting point: Observed 91-93° C; Reported 92-94° C. Purity: 97% by DSC [Fig 5.23(A)].

2,4,4,6-tetrabromo-2,5-cyclohexadienone (**3**). The aqueous solution, 150 ml containing 5.0 g (53.19 mmole) of phenol and 42.50 g BR(S) was taken in a single neck 500 ml round bottom flask. To it, about 50 ml of aqueous 5.3 N hydrochloric acid (214.9 mmole) solution was added under stirring at room temperature over a period of 2 h. After complete addition of the acid, the stirring was continued for another 2 h to get the product

in solid form. The precipitated product was filtered, washed twice with deionized water and dried in vacuum for 6 h. The total crude yield of 2,4,4,6-tetrabromo-2,5-cyclohexadienone was 20.5 g (94% yield). Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.78 (2H, s) [Fig 5.1(B)]. IR: ν_{max} (KBr) 3051, 1680, 1582, 1454, 1310, 900, 702, 663, 634 cm^{-1} [Fig 5.14(B)]. CHN: Found C, 17.16%; H, 0.24%; Calcd. C, 17.56%; H, 0.49%. Melting point: Observed 123-125° C. Purity: 99% by DSC [Fig 5.23(B)].

4-Bromo-2-chloro phenol (**4**). The aqueous-methanolic solution 50 ml (1: 5 CH_3OH/H_2O) containing 2.0g (15.625 mmole) of 2-chlorophenol and 3.121 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 20 ml of aqueous 1.0 N hydrochloric acid (15.779 mmole) solution was added under stirring at room temperature over a period of 30 min. After complete addition of the acid, the stirring was continued for another 30 min, and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and concentrating to get 3.0057g (14.520 mmole, 93%). The product was analyzed by gas chromatography and comparing with standards, the ratio of 4-bromo, 6-bromo, 4,6-dibromo chlorophenols were found to be 69:16:15.

4,6-Dibromo-2-chlorophenol (**5**). The aqueous-methanolic solution 30 ml (1: 5 CH_3OH/H_2O) containing 1.0 g (7.8125 mmole) of 2-chlorophenol and 3.121 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 20 ml of aqueous 1.0 N hydrochloric acid (17.779 mmole) solution was added under stirring at room temperature over a period of 60 min. After complete addition of the acid, the stirring was continued for another 30 min, and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and the organic solvent was concentrated. The obtained crude product was purified by column chromatography on silica gel (100-200 mesh) using 5% ethyl acetate and hexane to get 2.0452 g (7.151m moles, 91%) of product. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.56 (1H, s); 7.46 (1H, s); 5.91 (1H, broad s) [Fig 5.1(C)]. IR: ν_{max} (KBr) 3501, 3081, 1707, 1580, 1477, 1399, 1324, 1277, 1184, 1084, 814, 765, 710, 626, 553 cm^{-1} [Fig 5.14(C)]. CHN : Found

C, 25.01%; H, 0.84%; Calcd. C, 25.17%; H, 1.04%. Melting point: Observed 74-84° C. Purity: 99.6% by DSC [Fig 5.23(C)].

2,6-Dibromo-4-chlorophenol (**6**). The aqueous-methanolic solution 60 ml (1:5 CH_3OH/H_2O) containing 2.840 g (22.187 mmole) of 4-chlorophenol and 8.864 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 50 ml of aqueous 1.106 N hydrochloric acid (44.812 mmole) solution was added under stirring at room temperature over a period of 60 min. After complete addition of the acid, the stirring was continued for another 30 min, and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and concentrating to get 6.24 g (21.818 mmole 98.5%) of product. Analysis data:^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.45 (2H, s); 5.86 (1H, broad s). IR: ν_{max} (KBr) 3410, 3078, 1555, 1458, 1385, 1319, 1265, 1216, 1158, 855, 740, 701 cm^{-1}. CHN : Found C, 25.07%; H, 0.87%; Calcd. C, 25.17%; H, 1.04%.

4-Bromo-2-methyl phenol (**7**). The aqueous-methanolic solution 30 ml (1: 5 CH_3OH/H_2O) containing 1.0 g (9.26 mmole) of 2-methylphenol and 1.85 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 10 ml of aqueous 1.152 N hydrochloric acid (9.33 mmole) solution was added under stirring at room temperature over a period of 60 min. After complete addition of the acid, the stirring was continued for another 30 min, and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and concentrating to get 1.684 g (9.010 mmole, 97%). The product was analyzed by gas chromatography and the ratio of 4-bromo, 6-bromo, and 4,6 dibromo –2-methylphenols were found to be 87: 7: 3.

4,6-Dibromo-2-methyl phenol (**8**). The aqueous-methanolic solution 30 ml (1: 5 CH_3OH/H_2O) containing 1.0 g (9.26 mmole) of 2-methylphenol and 3.70 g BR(S) was taken in a single neck 250ml round bottom flask. To it, about 20 ml of aqueous 1.152 N hydrochloric acid (18.667 mmole) solution was added under stirring at room temperature over a period of 60 min. After complete addition of the acid, the stirring was continued for another 30 min and the product was extracted thrice with 25 ml of diethyl ether. The

combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and concentrating to get 2.3987 g (7.151 mmoles, 97.5%) of product. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.431 (1H, s); 7.21 (1H, s); 5.54 (1H, broad s); 2.27 (3H, s) [Fig 5.2(A)]. IR: ν_{max} (KBr) 3499, 3404, 3079, 1588, 1565, 1465, 1396, 1316, 1222, 1136, 997, 855, 677, 555 cm^{-1} [Fig 5.14(D)]. CHN: Found C, 31.14%; H, 2.12%; Cacld. C, 31.57%; H, 2.25%. Melting point: Observed 55-60° C. Purity: 99% by DSC [Fig 5.24(A)].

2,6-Bromo-4-methyl phenol (**9**). The aqueous-methanolic solution 30 ml (1: 5 CH_3OH/H_2O) containing 1.0 g (9.26 mmole) of 4-methylphenol and 3.70 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 20 ml of aqueous 1.152 N hydrochloric acid (18.667 mmole) solution was added under stirring at room temperature over a period of 60 min. After complete addition of the acid, the stirring was continued for another 30 min and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and concentrating to get 2.4356 g (9.156 mmole 99% crude yield. Analysis data:^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.33 (2H, s); 5.84 (1H, broad s); 2.25 (3H, s). IR: ν_{max} (KBr) 3632, 3497, 2923, 1681, 1560, 1476, 1319, 1274, 1234, 1161, 852, 776, 737, 704, 559 cm^{-1} [Fig 5.14(E)]. CHN : Found C, 31.14%; H, 2.12%; Cacld. C, 31.57%; H, 2.25%. Melting point: Observed 49-51°C. Reported 49-50° C.

4-Bromo-2,6-dimethyl phenol (**10**). The aqueous-methanolic solution 30 ml (1: 5 CH_3OH/H_2O) containing 1.0 g (8.197 mmole) of 2,6dimethylphenol and 1.6373 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 10 ml of aqueous 1.02 N hydrochloric acid (8.277 mmole) solution was added under stirring at room temperature over a period of 60 min. After complete addition of the acid, the stirring was continued for another 60 min, and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and the organic solvent was concentrated. The obtained crude product was purified by column chromatography on silica gel (100-200 mesh) using 5% ethyl acetate/hexane to get

1.5928 g (7.9241 mmole, 97%). Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.25 (2H, s); 4.61 (1H, broad s); 2.21 (6H, s) [Fig 5.2(B)]. IR: ν_{max} (KBr) 3372, 2977, 2946, 2916, 1609, 1474, 1329, 1188, 1029, 939, 853, 716 cm^{-1} [Fig 5.14(F)]. CHN : Found C, 48.23%; H, 4.00%; Cacld. C, 47.76%; H, 4.47%. Melting point: Observed 76-81° C (Reported. 79-81° C). Purity: 98.5% by DSC [Fig 5.24(C)].

2-Bromo-4-Bu^t phenol (**11**). The an aqueous-methanolic solution 30 ml (1: 5 CH_3OH/H_2O) containing 1.0 g (7.246 mmole) of 4-Bu^t phenol and 1.4475 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 10 ml of aqueous 0.903 N hydrochloric acid (7.29 mmole) solution was added under stirring at room temperature over a period of 60 min. After the completion of the acid addition the contents were for 30 min, and the product was extracted thrice with diethyl ether 30 ml. After stripping out the solvent the 1.289 g (82% yield) of the crude product was obtained. By H^{1}NMR-it showed approximately 77:23 mono, dibromo-derivatives.

2,6 Dibromo-4-Bu^t phenol (**12**). The aqueous-methanolic solution (50 ml 1: 5 CH_3OH/H_2O) containing 1.0 g (7.246 mmole) of 4-Bu^t phenol and 2.895 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 20 ml of aqueous 0.9 N hydrochloric acid (14.583 mmole) solution was added under stirring at room temperature over a period of 60 min. After completion of the acid, stirring was continued 60 min and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and concentrating to obtain the light orange oil 1.9499 g (6.588 mmole, 95%). Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.42 (2H, s); 5.95 (1H,broad s) 1.24 (9H, s). IR: ν_{max} (KBr) 3634, 3506, 2963, 2908, 2869, 1725, 1558, 1478, 1393, 1364, 1321, 1243, 1205, 1162, 1044, 870, 821, 737, 710 cm^{-1}. CHN: Found C, 38.96%; H, 4.00%; Calcd. C, 38.96%; H, 3.89%.

4,6-Dibromo-2-nitrophenol (**13**). The aqueous-methanolic solution (50 ml 1: 5 CH_3OH/H_2O) containing 1.0 g (7.194 mmole) of 2- nitrophenol and 2.874 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 20 ml of aqueous 0.9 N hydrochloric acid (14.583 mmole) solution was added under stirring at room temperature over a period of 60 min. After complete addition of the acid, the stirring was continued

for another 60 min, and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and the organic solvent was concentrated. The product 2.1041 g (7.085 m mole, 98.5% yield) was obtained in the pure without any purification and satisfies the all analysis data. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 8.41 (1H, s); 8.24 (1H, s); 11.05 (1H, s). IR: ν_{max} (KBr) 3551, 3473, 3414, 3163, 3074, 1599, 1531, 1450, 1393, 1327, 1242, 1151, 1111, 885, 761, 736, 674, 607, 554 cm^{-1} [Fig 5.15(A)]. CHN: Found C, 24.85%; H, 0.76%; N, 4.54%; Calcd. C, 22.71%; H: 0.95%; N, 4.42%. Melting point: Observed 115-117° C (Reported 118° C). Purity: 95% by DSC [Fig 5.24(B)].

2,6-Dibromo-4-nitrophenol (**14**). The aqueous-methanolic solution (50 ml 1: 5 CH_3OH/H_2O) containing 1.0 g (7.194 mmole) of 2- nitrophenol and 2.874 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 20 ml of aqueous 0.9 N hydrochloric acid (14.583 mmole) solution was added under stirring at room temperature over a period of 60 min. After complete addition of the acid, the stirring was continued for another 60 min, and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and the organic solvent was concentrated. The crude product weighed as 2.050 g (6.902 mmole, 96%). Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.431 (1H, s); 7.21 (1H, s); 5.54 (1H, broad s); 2.27 (3H, s) [Fig 5.2(C)]. IR: ν_{max} (KBr) 3499, 3404, 3079, 1588, 1565, 1465, 1396, 1316, 1222, 1136, 997, 855, 677, 555 cm^{-1} [Fig 5.15(B)]. CHN: Found C, 31.14%; H, 2.12%; Calcd. C, 31.57%; H, 2.25%. Meltimg point: Observed 55-60° C. Purity: 96.4% by DSC.

1-Bromo-2-naphthol (**15**). The aqueous-methanolic solution (30 ml 1: 5 CH_3OH/H_2O) containing 1.0 g (6.944 mmole) of 2- naphthol and 1.3872 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 10 ml of aqueous 0.864 N hydrochloric acid (7.0 mmole) solution was added under stirring at room temperature over a period of 30 min. After complete addition of the acid, the stirring was continued for another 30 min, and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by

drying over anhydrous sodium sulfate and the organic solvent was concentrated. The product was purified by column chromatography on silica gel (100-200 mesh) using 5% ethyl acetate/hexane to get 1.3392 g (6.005 m mole,86% yield). Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 8.04 (1H, d); 7.79 (2H, d); 7.59 (1H, t); 7.42 (1H, t); 7.27 (1H, d); 5.21 (1H, broad s) [Fig 5.3(A)]. IR: ν_{max} (KBr) 3275, 3056, 1629, 1601, 1500, 1432, 1347, 1301, 1234, 984, 928, 810, 744, 517 cm^{-1} [Fig 5.15(C)]. CHN: Found C, 54.09%; H, 2.65%; Cacld. C, 53.80%; H, 3.13%. Melting point: Observed 78-82° C (Reported 78-81 ° C); Purity: 99.5% by DSC [Fig 5.25(A)].

1,6-Dibromo-2-naphthol (**16**). The aqueous-methanolic solution (50 ml 1: 5 CH_3OH/H_2O) containing 2.0 g (13.889 mmole) of 2- naphthol and 2.7743 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 20 ml of aqueous 0.9 N hydrochloric acid (14.580 mmole) solution was added under stirring at room temperature over a period of 60 min. After complete addition of the acid, the stirring was continued for another 30 min and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 5% ethyl acetate in hexane as eluent) column to get 2.7744 g (9.186 mmole, 66 %) of the product. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.93-7.86 (2H, d); 7.66-7.59 (2H, t); 7.29 (1H, d); 5.94 (1H, s) [Fig 5.3(B)]. IR: ν_{max} (KBr) 3484, 3444, 1617, 1586, 1559, 1495, 1461, 1402, 1381, 1335, 1202, 1183, 1129, 1068, 927, 871, 804 cm^{-1} [Fig 5.15(D)]. CHN: Found C, 37.80%; H, 2.02%; Calcd. C, 39.73%; H, 1.65%. Melting point: Observed 104-108° C (Reported 105-107° C). Purity: 96% by DSC .

Tetrabromobisphenol-A (**17**). 500 g (2.193 mol) of bisphenol-A (BPA), 1.5-liters dichloromethane (DCM), 1.7522 kgs of BR(S) in 3.1 liters water were taken in a 10 liters glass reactor. To this reaction mixture, 912 ml (8.86 mol) of 12 N hydrochloric acid was added drop wise over a period of 12 h under stirring at room temperature. After the complete addition of acid, stirring was continued for further 30 min. The pure colorless crystals of tetrabromobisphenol-A (TBBP-A) formed were separated out from the biphasic mixture. The 800 g (1.471 mol) of TBBPA 67% yield was obtained after drying

at 100 °C for 3 h, which melts at 180-184°C. The organic layer 850 ml was separated from the aqueous layer. The organic layer was recycled in the second batch by charging with 650 ml fresh DCM, BPA and BR(S) as mentioned above and following the above procedure. 1070 g (1.97 mole, 90%) of TBBPA as isolated product was obtained. From the separated (950 ml) organic layer from the aqueous layer gave another 380 g (31%) of impure product melting at 164-170°C, after distillation of 500 ml of dichloromethane. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.25 (4H, s); 5.79 (2H, s); 1.58 (6H, s) [Fig 5.3(C)]. IR: ν_{max} (KBr) 3514, 3479, 2987, 1554, 1472, 1396, 1363, 1321, 1273, 1239, 1160, 1129, 868, 778, 731, 707, 615 cm^{-1} [Fig 5.15(E)]. CHN: Found C: 32.80%; H, 2.25; Cacld. C, 33.08%; H, 2.20%. Melting point: Observed 178-180° C (Reported 179-182 °C). Purity: 99% by DSC [Fig 5.25(B)].

(ii) Amines. 2,4,6-Tribromoaniline (**18**). The aqueous-methanolic solution (50 ml 1: 5 CH_3OH/H_2O) containing 0.50 g (5.376 mmole) of aniline and 3.222 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 20 ml of aqueous 1.34 N hydrochloric acid (21.68 mmole) solution was added under stirring at room temperature over a period of 60 min. After the completion of the acid, stirring was continued further 60 min. The solid separated was filtered through a suitable device under vacuum, washed thoroughly first with 5% sodium bicarbonate and then with water and it in the oven at 90° C for one hour. The weight of the final product obtained was 1.725 g (5.227 mmole, 97 % yield). Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.5 (2H, s); 4.55 (2H, broad s) [Fig 5.4(A)]. IR: ν_{max} (KBr) 3414, 3290, 1615, 1562, 1541,1454, 1382, 1066, 859, 732, 706,547 cm^{-1} [Fig 5.16(A)].. CHN: Found C, 22.10%; H, 1.04%; N, 4.14%; Cacld. C, 21.81%; H, 1.21%; N, 4.24%. Melting point: Observed 120-123° C (Reported 120-122° C). Purity: 98% by DSC [Fig 5.25(C)].

2,6-Dibromo-4-methylaniline (**19**). The solution of 50 ml biphasic mixture (1:5 $CH2Cl_2$-H_2O) containing 1.0 g (9.26 mmole) 4-methyl aniline and 3.884 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 40 ml of aqueous 0.91 N hydrochloric acid (29.4538 mmole) solution was added under stirring at room temperature over a period of 60 min. After the completion of the acid, stirring was continued further 60 min. The product was extracted thrice with 25 ml of

dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, with 5% sodium bicarbonate, water and then brine followed by drying over anhydrous sodium sulfate and the organic solvent was concentrated. The product was purified by column chromatography on neutral alumina (active) using 5% ethyl acetate and hexane to get 2.069 g (7.778 mmole, 84% yield) of the product. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.2 (2H, s); 4.38 (2H, broad s); 2.07 (3H, s) [Fig 5.4(B)]. IR: ν_{max} (KBr) 3422, 3306, 2914, 1618, 1581, 1477, 1285, 1212, 1058, 853, 733, 706, 637, 557 cm^{-1} [Fig 5.16(B)]. CHN: Found C, 32.19%; H, 2.18%; N, 5.18%; Cacld. C, 31.69%, H, 2.64%; N, 5.28%. Melting point: Observer 73-76° C (Reported 74-76° C). Purity: 97.8% by DSC [Fig 5.26(A)].

4-Bromo N, N-dimethylaniline (**20**). The solution of 30 ml biphasic mixture (1:5 $CH2Cl_2$-H_2O) containing 1.0 g (9.714 mmole) N,N dimethyl aniline and 1.8325 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 20 ml of aqueous 1.14 N hydrochloric acid (18.528 mmole) solution was added under stirring at room temperature over a period of 60 min. After complete addition of the acid, the stirring was continued for another 60 min and the product was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, 5% sodium bicarbonate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on neutral alumina (active, 5% ethyl acetate in hexane as eluent) column to get 1.417 g (7.537 mmole, 85% yield) of the pure product. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.31 (2H, d); 6.6 (2H, d); 2.91 (6H, s) [Fig 5.4(C)]. IR: ν_{max} (KBr) 3550, 3474, 3415, 2880, 2805, 1592, 1501, 1445, 1354, 1223, 1190, 1165, 1062, 944, 805, 750, 579, 505 cm^{-1} [Fig 5.16(C)]. CHN: Found C, 47.22%; H, 4.33%; N, 6.74%; Cacld. C, 48.00%; H: 5.00%; N, 7.00%. Melting point: Observed 53-55° C (Reported 54-55° C). Purity: 90% by DSC .

4,6-Dibromo-2-nitroaniline (**21**). The solution of 50 ml biphasic mixture (1:5 $CH2Cl_2$-H_2O) containing 1.0 g (7.246 mmole) 2-nitroaniline and 2.895 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 30 ml of aqueous 0.903 N hydrochloric acid (21.953 mmol) solution was added under stirring at room temperature over a period of 60 min. After the completion of the acid, stirring was continued further

60 min. The reaction mixture was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, with 5% sodium bicarbonate, water and then brine followed by drying over anhydrous sodium sulfate and the organic solvent was concentrated. The product 2.1110 g (7.132 mmole, 98.5% yield) was obtained in the pure form without any purification. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 8.29 (1H, s); 7.81 (1H, s); 6.64 (2H, broad s) [Fig 5.5(A)]. IR: ν_{max} (KBr) 3465, 3352, 1623, 1542, 1495, 1444, 1344, 1317, 1254, 1118, 1095, 873, 760, 689 cm^{-1} [Fig 5.16(D)]. CHN: Found C, 24.85%; H, 0.76%; N, 4.54%; Cacld. C, 22.71%; H, 0.95%; N, 4.42%; Melting point: Observed. 115-117° C (Reported 118° C); Purity 98% by DSC [Fig 5.26(B)].

2,6-Dibromo-4-nitroaniline (**22**). The solution of 50 ml biphasic mixture (1:5 $CH2Cl_2$-H_2O) containing 1.0 g (7.246 mmole) 4-nitro aniline and 2.895 g BR(S) was taken in a single neck 250 ml round bottom flask. To it, about 30 ml of aqueous 0.903 N hydrochloric acid (21.953 mmol) solution was added under stirring at room temperature over a period of 60 min. After the completion of the acid, stirring was continued further 60 min. The reaction mixture was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, with 5% sodium bicarbonate, water and then brine followed by drying over anhydrous sodium sulfate and the organic solvent was concentrated. The crude product weighed as 2.1162 g (7.149 mmole, 98.7 % yield). Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 8.34 (2H, s); 6.64 (2H, broad s). IR: ν_{max} (KBr) 3480, 3372, 1604, 1501, 1472, 1319, 1299, 1269, 1126, 899, 731, 693 cm^{-1}[Fig 5.16(E)]. CHN: Found C, 24.70%; H, 1.21%; N, 9.10%; Cacld.. C, 24.32%; H, 1.35%; N, 9.45%. Melting point: Observed 205-207° C (Reported 206-208° C). Purity: 97% by DSC [Fig 5.26(C)].

(iii) Ethers, amides/imides and hydrocarbons. 4-Bromoanisole (**23**). 1.0 g (9.26 mmole) of anisole, 5 ml dichloromethane, and 1.85 g BR(S) dissolved in 30 ml water were taken in a 250 ml round bottom flask. To it, about 10 ml of aqueous 1.2 N hydrochloric acid (9.722 mmole) solution was added under stirring at room temperature over a period of 45 min. After the completion of the acid, stirring was continued further 30 min. The reaction mixture was extracted thrice with 25 ml of dichloromethane. The

combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and the organic solvent was concentrated. The product 1.6791 g (8.979 mmole, 97 % yield) was obtained in the pure form without any purification. Analysis data: ^{1}H-NMR-($CDCl_3$) (δ) 7.38-7.33 (2H, d); 6.90-6.74 (2H, d); 3.83 (3H, s) [Fig 5.5(B)]. IR: ν_{max} (Nujal Mull) 3071, 3005, 2959, 2937, 2837, 2538, 2279, 2036, 1871, 1580, 1487, 1380, 1288, 1247, 1179, 1032, 871, 822, 750, 680, 621, 600, 507 cm^{-1} [Fig 5.17(A)]. CHN: Found C, 44.29%; H, 3.17%; Cacld. C, 44.92%; H, 3.74.

2,5-Dibromo-1,4-dimethoxy benzene (**24**). 1.0 g (7.246 mmole) of 1,4-dimethoxy benzene 10 ml dichloromethane, and 2.895 g BR(S) dissolved in 50 ml water were taken in a 250 ml round bottom flask. To it, about 20 ml of aqueous 0.9 N hydrochloric acid (14.583 mmole) solution was added under stirring at room temperature over a period of 60 min. After complete addition of the acid, the stirring was continued for another 60 min and the product was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (6-120 mesh, 5% ethyl acetate in hexane as eluent) column to get 2.0660 g (6.98 m mole, 96.4% yield). Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.10 (2H, s); 3.85 (6H, s). IR: ν_{max} (KBr) 3494, 3099, 2969, 2944, 1699, 1667, 1494, 1436, 1358, 1275, 1212, 1185, 1065, 1021, 859, 759 cm^{-1}. [Fig 5.17(B)]. CHN: Found C, 33.16%; H, 2.00%; Cacld. C,32.43%, H, 2.70%. Melting point: Observed 140-143° C (Reported 147° C).

4-Bromocetanilide (**25**). The an aqueous-methanolic solution 30 ml (1: 5 CH_3OH/H_2O) containing 1.0 g (7.407 mmole) of acetanilide and 1.480 g BR(S) was taken in a single neck 250 ml round bottom flask, to it, about 20 ml of aqueous 0.923 N hydrochloric acid (17.964 mmole) solution was added under stirring at room temperature over a period of 30 min. After complete addition of the acid, the stirring was continued for another 30 min; the white amorphous solid of 4-bromoacetanilide was separated out. The solid was filtered through a G-4 sintered crucible under vacuum, the residue was washed with, water till free from acid, finally with hot water and dried it in the oven at 100 °C about one hour. The weight of the product was 1.4742 g (6.889 mmole, 93%

yield). Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 8.3 (1H, broad s); 7.44 (4H, m); 2.04 (3H, s). IR: ν_{max} (KBr) 3557, 3477, 3294, 3259, 3185, 3113, 1671, 1604, 1535, 1487, 1392, 1369, 1312, 1257, 1170, 1005, 822, 743, 690, 504 cm^{-1} [Fig 5.17(C)]. CHN: Found C, 44.89%, H, 3.73%; N, 6.5%; Cacld. C, 44.85%; H, 3.36%; N, 6.54%. Melting point: 166-168° C (Reported 167-169° C); Purity: 97.7% by DSC [Fig 5.27(A)].

N-Bromosuccinimide (NBS) (**26**). 5.0 g (50.505 mmole) succinimide and 10.088 g of BR(S) were taken in 250 ml round bottom flask to it 100 ml of water was added, stirred for some time (5-10 min.) till the dissolving both the solids at room temperature. Then 50 ml of 2.0 N sulfuric acid was added slowly under stirring during a period of 3.0 hours. After completion of the acid, stirring was continued further 1.0 hour. The white solid crystals of N-bromosuccinimide (NBS) separated out. The flask was allowed to cool in the refrigerator over night for complete crystallization of NBS. The solid was filtered through 250ml G-4 sintered crucible under vacuum. The product was washed with 3x50 ml of cold water and dried it in the oven at 100 °C about three hour. The weight of the product NBS was 8.22 g (46.179 m mole, 91.5% yield). When the above experiment was repeated using hydrochloric acid in place of sulfuric acid; 77% of the NBS was obtained after isolation. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 2.97(4H, s) [Fig 5.5(C)]. IR: ν_{max} (KBr) 3184, 3057, 2934, 2649, 2541, 1696, 1417, 1309, 1199, 919, 638, 581, 425 cm^{-1} [Fig 5.17(D)]. CHN: Found C, 28.05%; H, 2.47; N, 7.78%; Cacld. C, 29.63%; H, 1.98%; N, 8.64%. Melting point: Observed 180-183 ° C (Reported 180-183° C); Purity: 97% by DSC [Fig 5.27(B)].

4-Nitrobenzyl bromide (**27**). A biphasic mixture 50 ml (1:5 $CH2Cl_2$-H_2O) containing 1.0 g (7.3 mmole) of 4-nitrotoluine and 2.916 g BR(S) was taken in a 250 ml round bottom flask. To it, about 20 ml of aqueous .0.912 N hydrochloric acid (7.684 mmole) solution was added under stirring at room temperature over a period of 60 min. After the completion of the acid, stirring was continued further 60 min. After the completion of the acid, stirring was continued further 60 min. The reaction mixture was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and the organic solvent was concentrated. The crude product was separated by

column chromatography on silica gel (100-200 mesh) using 2% ethyl acetate and hexane to get 1.2323 g (5.705 mmole, 84% yield) of 4-nitrobenzyl bromide [0.195 g (1.423 m mole) starting material was recovered]. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) δ 8.23-8.19 (2H, d); 7.58-7.54 (2H, d); 4.52 (2H, s) [Fig 5.6(A)]. IR: ν_{max} (KBr) 1610, 1539, 1348, 1225, 1105, 858, 799, 695, 598cm^{-1} [Fig 5.18(A)]. CHN: Found C, 36.15%; H, 2.75%, N, 5.64%. Found C, 38.88%; H, 2.77%; N, 6.48. Melting point: Observed 97-99° C (Reported 98-100° C). Purity: 99.6% by DSC [Fig 5.27(C)].

1-Bromonaphthalene (**28**). A biphasic mixture 25 ml (1:5 $CH2Cl_2$-H_2O) containing 1.0 g (7.81 mmole) of naphthalene and 1.561 g BR(S) was taken in a 250 ml round bottom flask. To it, about 10 ml of aqueous 0.984 N hydrochloric acid (7.9 mmole) solution was added under stirring at room temperature over a period of 120 min. After the completion of the acid, stirring was continued further 60 min. After complete addition of the acid, the stirring was continued for another 60 min and the product was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 5% ethyl acetate in hexane as eluent) column to get 0.5822 g (1.738 mmol, 36% yield) of 1-bromonaphthalene. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 8.21 (1H, d); 7.71-7.68 (3H, d); 7.54-7.39 (2H, p) 7.23-7.16 (1H, t) [Fig 5.6(B)]. IR: ν_{max} (Neat) 3054, 1591, 1561, 1501, 1378, 1253, 1199, 1161, 1135, 1021, 955, 790, 764, 650 cm^{-1} [Fig 5.18(B)]. CHN: Found C,55.01%; H, 3.33%; Cacld. C, 57.97%; H: 3.38%.

Benzyl bromide (**29**). A biphasic mixture 40 ml (1:5 $CH2Cl_2$-H_2O) containing 1.0 g (10.869 mmole) of toluene and 2.1712 g BR(S) was taken in a 250 ml round bottom flask. To it, about 10 ml of aqueous 1.35 N hydrochloric acid (10.977 mmole) solution was added under stirring at room temperature over a period of 60 min. After the completion of the acid, stirring was continued further 60 min. After the completion of the acid, stirring was continued further 60 min. The reaction mixture was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and the organic solvent was concentrated. The crude product was separated by

column chromatography on silica gel (100-200 mesh) using 2% ethyl acetate and hexane to get 1.4233 g (8.323 mmole, 38.5% yield) of benzyl bromide along with 1.6 % benzaldehyde. Analysis data: ^{1}H-NMR-($CDCl_3$-TMS) (δ) 7.37 (5H, m); 4.5 (2H, s) [Fig 5.6(C)]. IR: ν_{max} (Neat) 3064, 3031, 2967, 1493, 1453, 1226, 1202, 1069, 804, 757, 695604cm^{-1} [Fig 5.17(E)]. CHN: Found C, 45. 10%; H, 3.61%; Cacld.C, 49.12%; H, 4.09%.

*(iv) Bromobenzene. (***30***) Trial 1.* 29.1 g of BR(S) was dissolved in 75 ml water taken in 500 ml three neck round bottom flask fitted with an water condenser. To it, 5 equivalents (57 ml, 0.73 mol) of benzene per atom of bromine and 0.1 g of sodium lauryl sulfate were added and then the flask was slowly heated to 70°C under stirring. A solution of 16.4 ml (50%) sulfuric acid (0.15 mol) was added to the hot reaction mixture over a period for 10 hours. The mixture was stirred for another 30 h at 70°C and then cooled to room temperature. The organic and aqueous layers were separated. The aqueous layer was extracted at least three times with minimum quantity of ether. The extracts were combined with the organic layer, washed successively with water and brine and dried over anhydrous sodium sulfate. Solvent was stripped at reduced pressure to get crude product which was purified by vacuum distillation to give 20 g or 87.5% of clear and colorless liquid bromo benzene having boiling point 154-156°C.

Trial 2. 116.4 g of BR(S) was dissolved in 300 ml water taken in 1000 ml three neck round bottom flask fitted with an water condenser. To it, 5 equivalents (228 ml, 2.92 mol) of benzene per atom of bromine and 0.4 g of sodium lauryl sulfate were added and then the flask was slowly heated to 70°C under stirring. A solution of 65.6 ml (50%) sulfuric acid (0.60 mol) was added to the hot reaction mixture over 10 hours. The mixture was stirred for another 30 h at 70°C and then cooled to room temperature. The organic and aqueous layers were separated. The aqueous layer was extracted at least three times with minimum quantity of ether. The extracts were combined with the organic layer, washed successively with water and brine and dried over anhydrous sodium sulfate. Solvent was stripped at reduced pressure to get crude product which was purified by vacuum distillation to give 82 g or 89.7% of clear and colorless liquid bromo benzene having boiling point 154-156°C.

Trial 3. 29.10 g of BR(S) was dissolved in 75 ml water taken in 500 ml three neck round bottom flask fitted with water condenser. To it, 5 equivalents (57 ml, 0.73 mol) of benzene per atom of bromine and 0.1 g of sodium lauryl sulfate were added and then the flask was slowly heated to 70°C under stirring. A solution of 15.5 ml (35%) hydrochloric acid (0.15 mol) was added to the hot reaction mixture over 10 hours. The mixture was stirred for another 30 h at 70°C and then cooled to room temperature. The organic and aqueous layers were separated. The aqueous layer was extracted at least three times with minimum quantity of ether. The extracts were combined with the organic layer, washed successively with water and brine and dried over anhydrous sodium sulfate. Solvent was stripped at reduced pressure to get crude product which was purified by vacuum distillation to give 18.6 g or 81.3% of clear and colorless liquid bromo benzene having boiling point 154-156°C.

Trial 4. 29.10 g of BR(S) was dissolved in 75 ml water taken in 500 ml three neck round bottom flask fitted with water condenser. To it, 2 equivalents (22.8 ml, 0.292 mol) of benzene per atom of bromine and 0.1 g of sodium lauryl sulfate were added and then the flask was slowly heated to 70°C under stirring. A solution of 16.4 ml (50%) sulfuric acid (0.15 mol) was added to the hot reaction mixture over 8 hours. The mixture was stirred for another 25 h at 80°C and then cooled to room temperature. The organic and aqueous layers were separated. The aqueous layer was extracted at least three times with minimum quantity of ether. The extracts were combined with the organic layer, washed successively with water and brine and dried over anhydrous sodium sulfate. Solvent was stripped at reduced pressure to get crude product which was purified by vacuum distillation to give 11.9 g or 52.3% of clear and colorless liquid bromo benzene having boiling point 154-156°C. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.46 (2H, d); 7.19 (3H, d). IR: ν_{max} (Neat) 3065, 1577, 1474, 1442, 1068, 1019, 999, 735, 682, 673 cm^{-1}. CHN: Found C, 45.66%; H, 3.22%; Cacld. C, 45.86%, H, 3.18%. Boiling point: Observed 154-156°C (Reported 156°C).

(b). Dibromo compounds with BR(A). In general, the substrate (10 mmol) was taken in a single neck 100-250 ml round bottom flask containing 5-15 ml of dichloromethane and aqueous 25-75 ml solution containing 2.92 g of BR(A). To it about 4-5 ml of 50%

aqueous sulfuric acid solution was added to the flask at room temperature over a period of 30-60 min under stirring. After complete addition of the acid, the stirring was continued for another 40 to 60 min and the product was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate and concentrating under reduced pressure to get 68-95% of the desired brominated product.

1,2-Dibromocyclohexane (**31**). 1.0 g of cyclohexene (12.195 mmol), 10 ml dichloromethane and 3.5574 g of BR(A) dissolved in 50 ml water were taken in a single neck 250 ml round bottom flask. To it, 2.7 ml of aqueous 50% sulfuric acid was added to the flask at room temperature over a period of 20 min under stirring. After complete addition of the acid, the stirring was continued for another 10 min and the product was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 2% ethyl acetate in hexane as eluent) column to get 55% (1.6232 g, 6.707 mmole) of 1,2-dibromo cyclohexane and 26% (0.5676 g 3.171 mmole) of 2-bromocyclohexanol. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 1.48-1.54 (2H, m) 1.72-1.85 (4H, m) 2.41-2.45 (2H, q); 4.45 (2H, d) [Fig 5.7(A)]. IR: ν_{max} (Neat) 2940, 2861, 1446, 1434, 1359, 1338, 1256, 1178, 1088, 998, 972, 903, 861, 811,687,663 cm^{-1}.[Fig 5.19(A)]. CHN: Found C, 31.13%; H, 4.28%; Cacld. C, 29.80%; H, 4.13%.

The same compound **31** was prepared, by the above procedure using carbon tetrachloride instead of dichloromethane. The total isolated brominated product was 79% containing 38% (1.1205 g (4.630 m mole) of 1,2-dibromo cyclohexane and 41% (0.8902 g 4.9730m mole) of 2-bromocyclohexanol.

1,2-Dibromocyclooctane (**32**). 1.0 g cyclooctene (9.091 mmole), 10 ml of dichloromethane and 2.6519 g of BR(A) dissolved in 30 ml water were taken in a single neck 250 ml round bottom flask. To it about 2.0 ml of aqueous 50% sulfuric acid solution was added at room temperature over a period of 30 min under stirring. After complete addition of the acid, the stirring was continued for another 15 min and the product was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed

successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 2% ethyl acetate in hexane as eluent) column to get 57 % (0.694 g, 2.570 mmole) 1,2-dibromocyclooctane and 28% (0.260 g, 1.256 mmole) 2-bromocyclooctanol were obtained. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 1.52-1.85 (8H, m) 2.04-2.14 (2H, pen); 2.35-2.47(2H, q); 4.57-4.59(2H, d) [Fig 5.7(B)]. IR: ν_{max} (Neat) 3020, 2929, 2855, 1463, 1445, 1342, 1295, 1262, 1226, 1189, 1155, 1074, 1013, 899, 859, 822, 760, 739, 695 cm^{-1} [Fig 5.19(B)]. CHN: Found C, 32.68%; H, 4.71%; Cacld. C, 35.56%, H, 5.18%.

Styrene dibromide or (1,2-dibromo)-ethyl benzene (**33**). 1.0g styrene (9.615 mmole), 10 ml of dichloromethane and 2.805 g of BR(A) dissolved in 40 ml water were taken in a single neck 250 ml round bottom flask. To it about 2.2 ml of aqueous 50% sulfuric acid solution was added at room temperature over a period of 30-60 min under stirring. After complete addition of the acid, the stirring was continued for another 60 min and the product was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 2% ethyl acetate in hexane as eluent) column to get 65% (1.650 g, 6.250 mmole) white solid styrenedibromide and 25% (0.5526 g, 2.750 mmole) styrenebromohydrin. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 4.01-4.13 (2H, d); 5.10-5.18 (1H, t); 7.25-7.39 (5H, m) [Fig 5.7(C)]. IR: ν_{max} (Neat) 3028, 2916, 2857, 1909, 1609, 1515, 1430, 1233, 1200, 1156, 1135, 911, 819, 718, 591cm^{-1} [Fig 5.19(C)]. CHN: Found C, 36.55%; H, 2.52%; Cacld. C, 36.40%; H, 3.03.

1,2-Dibromo-1-(4-methyl phenyl) ethane (**34**). 1.0 g 4-methyl styrene (8.475 mmole), 10 ml of dichloromethane and 2.4683 g of BR(A) dissolved in 30 ml water were taken in a single neck 250 ml round bottom flask. To it about 1.9 ml of aqueous 50% sulfuric acid solution was added at room temperature over a period of 30 min under stirring. After complete addition of the acid, the stirring was continued for another 30 min and the product was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-

200 mesh, 2% ethyl acetate in hexane as eluent) column to get 73% (1.7182 g, 6.180 mmole) 1,2-Dibromo-1- (4-methyl phenyl) ethane and 21.5% (0.39 g, 1.814 mmole) corresponding bromohydrin. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 2.36(3H, s); 4.01-4.07 (2H, d); 5.10-5.18 (1H, t); 7.21-7.28 (4H, m) [Fig 5.8(A)]. IR: ν_{max} (Neat) 3436, 3028, 2979, 2917, 2857, 1909, 1610, 1513, 1431, 1377, 1233, 1200, 1156, 1135, 1111, 910, 819, 718, 663, 591cm^{-1} [Fig 5.19(D)]. CHN: Found C, 38.67%; H, 3.45%; Cacld. C, 38.85%; H, 3.60%.

1,2-Dibromohexane (**35**). 1.0 g of 1-hexene (11.904 mmole), 10 ml of dichloromethane and 3.4727 g of BR (A) dissolved in 40 ml water were taken in a single neck 250 ml round bottom flask. To it about 2.6 ml of aqueous 50% sulfuric acid solution was added at room temperature over a period of 30 min under stirring. After complete addition of the acid, the stirring was continued for another 15 min and the product was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 2% ethyl acetate in hexane as eluent) column to get 63% (1.8276 g, 7.486 mmole) 1,2-dibromo hexane and 5.1% (0.1085 g, 0.600 mmole) 1-bromo-2-hexanol. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 0.90-0.97 (3H, t); 1.38-1.56 (4H, m); 1.74-2.19 (2H, d of p) 3.58-3.88 (H, d of t); 4.15-4.25 (1H, p) [Fig 5.8(B)]. IR: ν_{max} (Neat) 2958, 2932, 2864, 1462, 1433, 1379, 1220, 1178, 1149,928, 733, 645 cm^{-1} [Fig 5.20(A)]. CHN: Found C, 26.97%; H, 4.42%; Cacld. C, 29.63%; H, 4.53%.

1,2-Dibromooctane (**36**). 1.0 g of 1-octene (8.928 mmole), 10 ml of dichloromethane and 2.60 g of BR (A) dissolved in 30 ml water were taken in a single neck 250 ml round bottom flask. To it about 1.95 ml of aqueous 50% sulfuric acid solution was added at room temperature over a period of 30 min under stirring. After complete addition of the acid, the stirring was continued for another 15 min and the product was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 2% ethyl acetate in hexane as eluent) column to get 83% (2.015 g, 7.408 mmole) 1,2-dibromo octane and 8.2

% (0.152 g, 0.727 mmole) 1-bromo-2-octanol. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 0.89 (3H, t); 1.30-1.54 (8H, m); 1.73- 2.12 (2H, d of p); 3.57-3.86 (2H, d of t); 4.17-4.21 (1H, p) [Fig 5.8(C)]. IR: ν_{max} (Neat) 2956, 2928, 2857, 1462, 1434, 1378, 1263, 1226, 1146, 989, 885, 725, 646 cm^{-1} [Fig 5.20(B)]. CHN: Found C, 35.85%; H, 5.85%; Cacld. C, 35.29%; H, 5.89%.

α, β-Dibromostyrene (**37**). 1.0 g of phenyl acetylene (9.804 mmole), 10 ml of dichloromethane and 2.88 g of BR (A) dissolved in 30 ml water were taken in a single neck 250 ml round bottom flask. To it about 2.2 ml of aqueous 50%sulfuric acid solution was added at room temperature over a period of 30 min under stirring. After complete addition of the acid, the stirring was continued for another 15 min and the product was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 2% ethyl acetate in hexane as eluent) column to get 76% (1.550 g, 5.916 mmole) α, β - dibromostyrene and 8.0% (0.152 g, 0.727 mmole) β-bromo-α-hydrxy styrene. The starting material recovered was 0.203 g (2.0 m mole). Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 6.74 (1H, s); 7.46-7.63 (3H, d t); 8.05-8.09 (2H, d) [Fig 5.9(A)]. IR: ν_{max} (Neat) 3079, 3033, 1586, 1483, 1267, 1225, 1211, 1161, 1074, 919, 888, 868, 787, 761, 737, 693 cm^{-1} [Fig 5.19(E)]. CHN: Found C, 35.39%; H, 2.09%; Cacld. C, 36.64%; H, 6.29%.

α, β-Dibromochalcone (**38**). 1.0 g of chalcone (4.807 mmole), 10 ml of dichloromethane and 1.4024 g of BR (A) dissolved in 30 ml water were taken in a single neck 250 ml round bottom flask. To it about 1.05 ml of aqueous 50% sulfuric acid solution was added at room temperature over a period of 30 min under stirring. After complete addition of the acid, the stirring was continued for another 30 min and the product was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on neutral alumina (active, 2% ethyl acetate in hexane as eluent) column to get 78% (1.3724 g, 3.37 mmole) white solid α, β-Dibromochalcone and 15% (0.220 g 0.721 mmole) corresponding bromohydrin. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ)5.70 (1H, d); 5.95 (1H, d); 7.40-

7.74 (8H, m); 8.19-8.21 (2H, d) [Fig 5.9(B)]. IR: ν_{max} (KBr) 3060, 3026, 1679, 1594, 1449, 1381, 1328, 1272, 1229, 1148, 981, 776, 722, 697, 683,579 561 cm^{-1} [Fig 5.19(F)]. CHN: Found C, 50.52%; H, 3.13%; Cacld. C, 48.9%; H, 3.25%. Melting point: Observed 155-158 °C.

2,3-Dibromo-1-propanol (**39**). 1.0 g of allylalcohol (7.817 mmole), 10 ml of dichloromethane and 5.03 g of BR(A) dissolved in 60 ml water were taken in a single neck 250 ml round bottom flask. To it about 3.8 ml of 50% aqueous sulfuric acid solution was added at room temperature over a period of 30 min under stirring. After complete addition of the acid, the stirring was continued for another 30 min and the product was extracted thrice with 25 ml of dichloromethane. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 2% ethyl acetate in hexane as eluent) column to get 20% (0.755 g, 3.463 mmole) 2,3–dibromo-1-propanol. Analysis data: ^{1}H-NMR ($CDCl_3$-TMS) (δ) 2.21 (1H, br s); 3.79-3.82 (2H, d); 4.01-4.03 (2H, d); 4.28-4.32 (1H, m) [Fig 5.9(C)]. IR: ν_{max} (Neat) 3391, 2931, 1453, 1431, 1376, 1258, 1224, 1045, 964, 903 cm^{-1} [Fig 5.20(C)]. CHN: Found C, 47.80%; H,4.48%; Cacld. C, 48.055; H, 4.75%.

(c). Bromohydrins with BR(S). In general the organic substrate (10-15 mmole) was dissolved in dioxane or CCl_4 (5-10 ml) and mixed with a 20 ml aqueous solution of 2.43 g BR(S) in a 100 ml round bottomed flask. To it, a solution of 50% H_2SO_4 (5-15 mmole) was added drop wise over a period of 30-60 min at room temperature. The mixture was stirred for further 15-30 min after the complete addition of the acid. The reaction mixture was then extracted thrice with 30 ml of diethyl ether. The combined organic layers was dried over anhydrous sodium sulfate, the solvent was evaporated under reduced pressure to leave behind the crude materials which were separated by column chromatography on silica gel (100-200 mesh) to give obtain the desired bromohydrin derivative.

2-Bromocyclohexanol (**40**). 1.0 g of cyclohexene (12.195 mmole), 10 ml of carbon tetrachloride and 2.436 g of BR (S) dissolved in 30 ml water were taken in a single neck 250 ml round bottom flask. To it about 1.34 ml of aqueous 50% sulfuric acid solution was added 65°C over a period of 30 min under stirring. After complete addition of the

acid, the stirring was continued for another 30 min and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 2% ethyl acetate in hexane as eluent) column to get 61% (1.3304g, 7.432 mmole) 2-bromocyclohexanol and 21 % (0.3192 g, 1.32 mmole) 1,2 dibromocyclohexane (w.r.t. active bromine atom taken) in the ratio 75:25 bromohydrin to dibromo derivatives.

The compound (**40**) was also prepared in 1,4-dioxane-water as solvent instead of carbon tetrachloride-water, at room temperature, the acid was added over a period of 15 min and stirred for further 30 min. After the purification by column chromatography 67% (1.4536 g, 8.12 mmole) 2-bromocyclohexanol and 18% (0.2651 g, 1.095 mmole) 1,2-dibromocyclohexane (w.r.t. brominating reagent) in the ratio 79:21 bromohydrin to dibromo derivatives were obtained. Analysis data: ^{1}H-NMR- ($CDCl_3$-TMS)- (δ) 1.22-1.42 (3H, m); 1.65-1.88 (3H, m); 2.09-2.16 (1H, m); 2.24-2.37 (1H, m); 2.57 (1H, s); 3.55-3.67 (1H, m); 3.84-3.96 (1H, m) [Fig 5.10(A)]. IR: ν_{max} (Neat) 3400, 2938, 2861, 1726, 1449, 1360, 1253, 1186, 1073, 956862, 690 cm^{-1} [Fig 5.21(A)]. CHN: Found C, 40.30%; H, 6.14%; Cacld. C, 40.06%; H, 6.19%.

1-Bromo-2-phenylethanol (**41**). 1.0 g of styrene (9.615 mmole), 10 ml of carbon tetrachloride and 1.9207 g of BR (S) dissolved in 30 ml water were taken in a single neck 250 ml round bottom flask. To it about 1.06 ml of aqueous 50% sulfuric acid solution was added at 65°C over a period of 30 min under stirring. After complete addition of the acid, the stirring was continued for another 30 min and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 2% ethyl acetate in hexane as eluent) column to get 63% (1.222 g, 6.080 mmole) 1-Bromo-2-phenylethanol and 18% (0.2284 g, 0.865 mmole) 1,2-dibromo ethylbenzene (w. r. t. active bromine atom taken) in the ratio 79:21 bromohydrin to dibromo derivatives.

The above compound **41** was prepared using dioxane-water medium instead of carbon tetrachloride and at room temperature, the acid was added over a period of 15 min

and stirred for further 30 min. After the purification by column chromatography 79 % (1.5232 g, 7.578 mmole) 1-bromo-2-phenylethanol and 12% (0.1513 g, 0.573 mmole) 1,2-dibromo ethylbenzene (w .r .t. active bromine atom taken) in the ratio 87:13 bromohydrin to dibromo derivatives were obtained. Analysis data: ^{1}H-NMR($CDCl_3$-TMS)- (δ) 2.53 (1H, s); 3.53-3.61 (2H, m); 4.87-4.94 (1H, dd); 7.18-7.30 (5H, m) [Fig 5.10(B)]. IR: ν_{max} (Neat) 3403, 3063, 3031, 2962, 2893, 1956, 1887, 1813, 1680, 1493, 1452, 1420, 1256, 1217, 1198, 1118, 1061, 1028, 990, 917, 870, 813,762, 701, 666, 592 cm^{-1} [Fig 5.21(B)]. CHN: Found C, 47.80%; H, 4.48%; Cacld. C, 48.05%; H, 4.75%.

1-Bromo-2-(4-methyl phenyl) ethanol (**42**). 0.776 g of 4-methyl styrene (6.566 mmole), 10 ml of carbon tetrachloride and 1.6903 g of BR (S) dissolved in 20 ml water were taken in a single neck 100 ml round bottom flask. To it about 0.94 ml of aqueous 50% sulfuric acid solution was added at 65°C over a period of 30 min under stirring. After complete addition of the acid, the stirring was continued for another 30 min and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 2% ethyl acetate in hexane as eluent) column to get 71% (0.998 g, 4.641mmole) 1-bromo-2- (4-methyl phenyl) ethanol yield and 17% (0.2015 g, 0.735 mmole) 1,2-dibromo-1-(4-methyl phenyl)ethane (w. r. t active bromine atom taken) in the ratio 81:19 bromohydrin to dibromo derivatives.

The above compound **42** was also prepared in dioxane-water medium, in carbon tetrachloride and at room temperature, the acid was added over a period of 20 min and stirred for further 20 min. After the purification by column chromatography 82% (1.3721 g, 6.382 mmole) 1-bromo-2- (4-methyl phenyl) ethanol and 8% (0.0853 g, 0.307 mmole) 1,2-dibromo-1- (4-methyl phenyl)ethane (w. r. t. brominating reagent) in the ratio 91:09 bromohydrin to dibromo derivatives were obtained. Analysis data: ^{1}H-NMR- ($CDCl_3$-TMS)- (δ) 2.36 (3H, s); 3.54-3.61 (2H, m); 4.88-4.94 (1H, dd); 7.25-7.36 (5H, m) [Fig 5.10(C)]. IR: ν_{max} (Neat) 3400, 3024, 2960, 2922, 1613, 1514, 1421, 1379,1312, 1217, 1198, 1067, 1021, 993, 818, 765, 722, 643 cm^{-1} [Fig 5.21(C)]. CHN: Found C, 47.80%; H, 4.48%; Cacld. C, 48.05%; H, 4.75%.

β-Bromo-α-hydroxy styrene (**43**). 1.0 g of phenyl acetylene (9.803 mmole), 10 ml of carbon tetrachloride and 1.960 g of BR (S) dissolved in 20 ml water were taken in a single neck 100 ml round bottom flask. To it about 1.08 ml of aqueous 50% sulfuric acid solution was added at 65°C over a period of 15 min under stirring. After complete addition of the acid, the stirring was continued for another 15 min and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 2% ethyl acetate in hexane as eluent) column to get 42% (0.8175 g, 4.108 mmole) β-bromo-α-hydroxy styrene and 17% (0.4373 g, 1.67 mmole) α,β-dibromo styrene (w. r. t. active bromine atom taken) in the ratio 71:29 bromohydrin to dibromo derivatives.

The above compound **43** was prepared using 1,4 dioxane-water medium instead of carbon tetrachloride and at room temperature, the acid was added over a period of 10 min and stirred for further 15 min. After the purification by column chromatography 60 % (1.160 g, 5.829 mmole) β-bromo-α-hydroxy styrene and 12% (0.1541 g, 0.590 mmole) α,β-dibromo styrene (w. r. t. active bromine atom taken) in the ratio 83:17 bromohydrin to dibromo derivatives were obtained. Analysis data: ^{1}H-NMR - ($CDCl_3$-TMS)- (δ) 6.81 (1H, s); 7.38-7.53 (5H, m) [Fig 5.11(A)]. IR ν_{max} (Neat) 3378, 3062, 3017, 1967, 1905, 1813, 1697, 1594, 1580, 1491, 1448, 1320, 1270, 1192, 1162, 999, 981, 931, 802, 782, 722, 704, 684, 628, 566 cm^{-1} [Fig 5.21(D)]. CHN: Found C, 47.80%; H, 4.48%; Cacld. C, 48.05%; H, 4.75%.

1-Bromo-2-hexanol (**44**). 1.0 g of 1-hexene (11.904 mmole), 10 ml of carbon tetrachloride and 2.378 g of BR (S) dissolved in 30 ml water were taken in a single neck 100 ml round bottom flask. To it about 1.3 ml of aqueous 50% sulfuric acid solution was added at 65°C over a period of 30 min under stirring. After complete addition of the acid, the stirring was continued for another 30 min and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 2% ethyl acetate in hexane as eluent) column to get 17% (0.3616 g, 2.00 mmole) 1-bromo-2-hexanol and 48 % (0.697

g, 2.856 mmole) 1,2-dibromohexane (w. r. t. active bromine atom taken) in the ratio 26:74 bromohydrin to dibromo derivatives.

The above compound (**44**) was performed using dioxane as solvent medium instead of carbon tetrachloride and at room temperature, the acid was added over a period of 10 min and stirred for further 20 min. After the purification by column chromatography 50% (1.0654g, 5.886 mmole) bromohexanol (regioisomers, 1-bromo-2-hexanol and 2-bromohexanol in the ratio about 7:1) and 16% (0.2325 g, 0.952 mmole) 1,2-dibromohexane (w. r. t. active bromine atom taken) in the ratio 76:24 bromohydrin to dibromo derivatives were obtained. Analysis data: ^{1}H-NMR - ($CDCl_3$-TMS)- (δ) 0.875-0.91 (3H, t); 1.36-1.57 (6H, m); 2.16 (1H, br s); 3.34-3.53 (2H, m); 3.77 (1H, m) [Fig 5.11(B)]. IR: ν_{max} (Neat) 3393, 2958, 2932, 2862, 1463, 1423, 1379,1254, 1221, 1125, 1032, 903, 833, 789, 730, 663 cm^{-1} [Fig 5.21(E)]. CHN: Found C, 47.80%; H, 4.48%; Cacld. C, 48.05%; H, 4.75%. *2-Bromohexanol* (**44a**). ^{1}H-NMR($CDCl_3$/TMS)- (δ) 0.87-.91 (3H,t); 1.26-1.39(4H, m); 1.79-1.86 (2H,t); 2.14 (1H,d); 3.68-3.8 (2H, m); 4.10-4.16 (1H, m) [Fig 5.11(C)]. IR: ν_{max} (Neat) 3494, 2962, 2925, 2854, 1460, 1265, 740 cm^{-1} [Fig 5.22(F)]. CHN: Found C, 47.80%; H, 4.48%; Cacld. C, 48.05%; H, 4.75%.

1-Bromo-2-octanol (**45**). 1.0 g of 1-octene (8.911 mmole), 10 ml of carbon tetrachloride and 1.78 g of BR (S) dissolved in 30 ml water were taken in a single neck 100 ml round bottom flask. To it about 1.0 ml of aqueous 50% sulfuric acid solution was added to the flask at 65°C over a period of 20 min under stirring. After complete addition of the acid, the stirring was continued for another 25 min and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 2% ethyl acetate in hexane as eluent) column to get 20% (0.358 g, 1.713 mmole) 1-bromo-2-octanol and 55% (0.6605 g, 2.430 mmole) 1,2-dibromooctane (w. r. t. active bromine atom taken) in the ratio 27:73 bromohydrin to dibromo derivatives.

The above compound **45** was also prepared in dioxane-water medium instead of carbon tetrachloride-water, at room temperature, the acid was added over a period of 10 min and stirred for further 20 min. After the purification by column chromatography,

67% (1.2489 g, 5.975 mmole) of bromooctanols (regioisomers, 1-bromo-2-octanol and 2-bromooctanol in the ratio about 6:1) and 18% (0.223 g, 0.819 mmole) 1,2-dibromooctane (w. r. t. active bromine atom taken) in the ratio 76:24 bromohydrin to dibromo derivatives were obtained. Analysis data: ^{1}H-NMR- ($CDCl_3$-TMS)- (δ) 0.84-0.88 (3H, t); 1.28-1.53 (10H, m); 1.99 (1H, s); 3.33-3.56 (2H, m); 3.78-3.82 (1H, m) [Fig 5.12(A)]. IR: ν_{max} (Neat) 3393, 2928, 2857, 1463, 1423, 1378, 1223, 1127, 1036, 663 cm^{-1} [Fig 5.22(A)].CHN: Found C, 47.80%; H, 4.48%; Cacld. C, 48.05%; H, 4.75%. *2-Bromooctanol* **45a**: ^{1}H-NMR($CDCl_3$-TMS)- (δ) 0.86-0.89 (3H, t); 1.29-1.52 (9H, m); 1.82-1.86 (2H, m); 3.74-3.86 (2H, m); 4.12-4.18 1H, m) [Fig 5.12(B)]. IR: ν_{max} (Neat) 3373, 2956, 2928, 2858,1462, 1430, 1379, 1271, 1237, 1121, 1077, 1029, 725 cm^{-1} [Fig 5.22 (B)]. CHN: Found C, 47.75%; H, 4.58%; Cacld. C, 48.05%; H, 4.75%.

2,3-Dibromo-1-propanol (**46**). 1.0 g of allyl alcohol (17.241 mmole), 10 ml of dioxane and 3.444 g of BR (S) dissolved in 50 ml water were taken in a single neck 250 ml round bottom flask. To it about 1.9 ml of aqueous 50% sulfuric acid solution was added to the flask at room temperature over a period of 15 min under stirring. After complete addition of the acid, the stirring was continued for another 20 min and the product was extracted thrice with 25 ml of diethyl ether. The combined extracts were washed successively with 5% sodium thiosulfate, water and then brine followed by drying over anhydrous sodium sulfate, concentrating and separating on silica gel (100-200 mesh, 2%ethyl acetate in hexane as eluent) column to get 24% (0.4441 g, 2.037 mmole) of 2,3-dibromo-1-propanol. Analysis data: ^{1}H-NMR($CDCl_3$-TMS)- (δ) 2.21 (1H, br s); 3.79-3.82 (2H, d); 4.01-4.03 (2H, d); 4.28-4.32 (1H, m). IR: ν_{max} (Neat) 3391, 2931, 1453, 1431, 1376, 1258, 1224, 1045, 964, 903 cm^{-1}. CHN: Found C, 47.80%; H, 4.48%; Cacld. C, 48.05%; H, 4.75%.

(d). Dehalogenation of halophenols. Dehalogenation of 1-bromo-2-naphthol (**47**). A mixture of 1-bromo-2-naphthol 0.10 g (0.45 mmol) H β-Zeolite 0.05 g; (50% w/w, w. r. t. the substrate) and sodium sulfite 0.283 g; (2.24 m mol) were taken in 100 ml round buttoned flask in dry methanol (20 ml). The mixture was refluxed at 90°C while the progress of the reaction was monitored by tlc. After 48 h the reaction mixture was cooled and filtered through suitable device, the catalyst Hβ-Zeolite was washed several times

with methanol and diethyl ether to completely recover the product. The organic extracts were collected and concentrated, and the product was purified by column chromatography over silica gel (60-120 mesh) using 10% ethyl acetate in hexane to obtain pure 2-naphthol in 87% yield (0.0565 g; 0.392 mmole) which showed satisfactory spectral data.

The above compound 47 was performed using $KHSO_4$ 0.183 g (1.345 mmole) as a catalyst in place of H β-Zeolite, and sodium sulfite 0.17 g (1.345 m mole). After 24 h the reaction was cooled and the product was extracted thrice with 20 ml diethyl ether, concentrated the organic solvent. After separation by column chromatography 92% yield 0.0594 g (0.412m mole) 2-naphthol was obtained. Analysis data: ^{1}H-NMR($CDCl_3$/TMS)-(δ) 8.04-8.00 (1H, d); 7.79-7.71 (2H, t); 7.59-7.52 (1H, t); 7.38-7.34 (1H, d); 7.28-7.24 (1H, d) [Fig 5.13(A)]. IR: ν_{max} (KBr) 3251, 3051, 1630, 1600, 1582, 1511, 1465, 1406, 1276, 1242, 1215, 1171, 958, 904, 878, 845, 813, 741 cm^{-1}. CHN: Found C, 82.1%; H, 5.67%; Cacld. C, 83.30%; H, 5.5%; Melting point: Observed 123-124°C; (Reported 122-123 °C).

Deiodination of 1-iodo-2-naphthol (**48**). A mixture of 1-iodo-2-naphthol 0.27 g; (1.0 mmole), Hβ-Zeolite 0.135 g (50% w/w, w. r. t. the substrate) and sodium sulfite 0.63 g; (5.0 m mole) were taken in 100 ml round buttoned flask in dry methanol (20 ml). The mixture was refluxed at 90°C while the progress of the reaction was monitored by tlc. After 48 h the reaction mixture was cooled and filtered through suitable device, the catalyst Hβ-Zeolite was washed several times with methanol and diethyl ether to completely recover the product. The organic extracts were collected and concentrated, and the product was purified by column chromatography over silica gel (60-120 mesh) using 10% ethyl acetate in hexane to obtain pure 90% (0.13 g, 0.903 mmole) of 2-naphthol, which showed satisfactory spectral data.

The above compound **48** was also obtained by taking 0.25 g (0.926 mmole) 0f 1-iodo-2-naphthol, $KHSO_4$ 0.63 g (4.63 mmole) as a catalyst in place of Hβ-Zeolite, and sodium sulfite 0.70 g (5.55 mmole). After separation by column chromatography 98% yield 0.130 g (0.903 mmole) of 2-naphthol was obtained. Analysis data: ^{1}H-NMR($CDCl_3$/TMS)- (δ) 8.04-8.00 (1H, d); 7.79-7.71 (2H, t); 7.59-7.52 (1H, t); 7.38-7.34

(1H, d); 7.28-7.24 (1H, d) [Fig 5.13(A). IR: ν_{max} (KBr) 3251, 3051, 1630, 1600, 1582, 1511, 1465, 1406, 1276, 1242, 1215, 1171, 958, 904, 878, 845, 813, 741 cm^{-1}. CHN: Found C, 82.1%; H, 5.67%; Cacld. C, 83.30%; H, 5.5%; Melting point: Observed 123-124°C; (Reported 122-123 °C).

2,6-dibromo phenol (**49**). A mixture of 2,4,6-tribromophenol 0.10 g (0.30 mmole), Hβ-Zeolite 0.05 g (50% w/w, w. r. t. the substrate) and sodium sulfite 0.20 g; (5.0 m mole) were taken in 100 ml round buttoned flask in dry methanol (20 ml). The mixture was refluxed at 90°C while the reaction was monitored by gas chromatography, after 48 h the conversion of tribromo to dibromo phenol was found to be 57% .

The above compound **49** was also obtained by taking 0.2 g (0.604 mmole) 0f 2,4,6 tribromophenol, $KHSO_4$ 0.493 g (3.625 mmole) as a catalyst in place of Hβ-Zeolite, and sodium sulfite 0.4568 g (3.625 m mole). After 48 h the conversion of tribromo to dibromo phenol was 45% by gas chromatography.

2,6-Diiodophenol (**50**). A mixture of 2,4,6-triiodophenol 0.10 g; (0.21 mmole), Hβ-Zeolite 0.05 g; (50% w/w, w. r. t. the substrate) and sodium sulfite 0.133 g; (5.0 m mole) were taken in 100 ml round buttoned flask in dry methanol (20 ml). The mixture was refluxed at 90°C, the progress of the reaction was monitored by tlc. After 48h the reaction mixture was cooled and filtered through suitable device, the catalyst Hβ-Zeolite was washed several times with methanol and diethyl ether to completely recover the product. The organic extracts were collected and concentrated, and the product was purified by column chromatography over silica gel (100-200 mesh) using 2% ethyl acetate in hexane to obtain pure 67% (0.039 g, 0.113 m mole) of 2,6-diiodophenol based on the starting material (0.02 g, 0.042 mmole) recovered.

The above compound **50** was also obtained in presence of $KHSO_4$ 0.1441 g (1.06 m mole) as catalyst in place of Hβ-Zeolite, and sodium sulfite 0.1601 g (1.27 mmole). After 48 h of reflux, the reaction mixture was cooled and the product was extracted thrice with 20 ml diethyl ether, concentrated the organic solvent. After column separation, 57% (0.034 g, 0.099 mmole) of 2,6-diiodophenol was obtained based on the starting material (0.0181 g, 0.0383 mmole) recovered. Analysis data: ^{1}H-NMR ($CDCl_3$/TMS)- (δ) 7.69-7.65 (2H, d); 6.43-6.35 (1H, t); 5.75 (1H, s) [Fig 5.13(B)]. IR: ν_{max} (KBr) 3462, 1552,

1432, 1313, 1265, 1233, 1167, 1124, 1030, 826, 752, 687 cm^{-1} [Fig 5.28(B)]. CHN: Found C, 21.07%; H, 1.19%; Cacld. C, 21.07%; H, 1.15%. Melting point: Observed. 67-68°C. Purity by DSC 98% [Fig 5.28(B)].

6-Bromo-2-naphthol (**51**). A mixture of 1, 6- dibromo-2-naphthol 0.10 g; (0.331 mmole), Hβ-Zeolite 0.05 g; (50% w/w, w. r. t. the substrate) and sodium sulfite 0.21 g; (5.0 mmole) were taken in 100 ml round buttoned flask in dry methanol (20 ml). The mixture was refluxed at 90°C, while the progress of the reaction was monitored by tlc. After 48 h the reaction mixture was cooled and and filtered through suitable device, the catalyst Hβ-Zeolite was washed several times with methanol and diethyl ether to completely recover the product. The organic extracts were collected and concentrated, and the product was purified by column chromatography over silica gel (100-200 mesh) using 10% ethyl acetate in hexane to obtain 29% (0.0216 g, 0.1 mmole) of 6-bromo-2-naphthol and 11% (0.0153 g, 0.034 mmole) of 6,6′-dibromo-1,1′-bi-2-naphthol based on the starting material (0.036 g, 0.119 mmole) recovered.

The above compound **51** was obtained using $KHSO_4$ 0.271 g (2.0 mmole) as a catalyst in place of Hβ-Zeolite, and sodium sulfite 0.250 g (1.98 mmole). After separation by column 55% yield (0.0321 g, 0.145 mmole) of 6-bromo-2-naphthol was obtained based on the recovery of starting material (0.021 g, 0.07 mmole starting material was recovered). Analysis data: ^{1}H-NMR ($CDCl_3$/TMS)- (δ) 7.91 (1H, s); 7.67-7.62 (2H, d); 7.51-7.49 (1H, d); 7.10 (12H, s); 5.28 (1H, s) [Fig 5.13(C)]. IR: ν_{max} (KBr) 3563, 3238, 1626, 1587, 1502, 1436, 1388, 1347, 1266, 1239, 1201, 1147, 1062, 958, 906, 857, 808 cm^{-1}. CHN: Found C, 53.26%; H, 2.93%; Cacld. C, 53.80%, H, 3.13%. Melting point: Observed 127-129°C (Reported 127-130 °C). Purity by DSC 93%[Fig 5.28(B)].

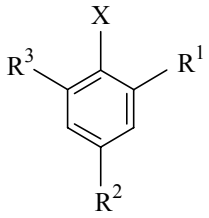
5.3. Discussion and conclusion

Part I: Organo bromine compounds

5.3.1. Aromatic substitutions with BR(S). The experimental data (reaction conditions, product yields, solvent systems used etc) related to bromination of aromatic substrates such as phenols, amines, and other organic substrates s such as ethers, amides, imides and

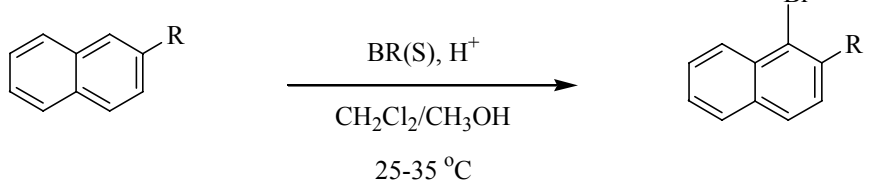
aromatic hydrocarbons are depicted in Tables 5.1-5.3. A general method of aromatic substitution reaction is assumed to occur as illustrated in Eq 5.2 and 5.3.

Typically, the bromination of phenols was carried out in homogeneous aqueous or aqueous-organic reaction conditions. In the case of unsubstituted phenols water was used as solvent to carry out these bromination reactions. Phenols and substituted phenols gave higher yields of bromo compounds. The high yields of phenols are due to spontaneous formation and reactivity of active species i.e. BrOH generated during the reaction of BR(S) with the mineral acid.



$$\xrightarrow[CH_2Cl_2/CH_3OH,\ 25 - 40\ ^{\circ}C]{BR(S),\ H^+} \text{Bromo derivative} \qquad (5.2)$$

where X= –OH, $–NH_2$, $–N(CH_3)_2$, $–OCH_3$, $–NHCOCH_3$, –H when R^1 = –H, –Cl, $–CH_3$, $–NO_2$; R^2 = –H, –Cl, $–CH_3$, $–OCH_3$, $–Bu^t$, $–NO_2$; R^3 = –H, $–CH_3$.



(5.3)

where R = –H, –OH.

Bromination of the selected anilines was carried out in a two-phase solvent system comprising of dichloromethane and water. To the solution of amine and the BR(S) corresponding to the desired degree of bromination, was added drop-wise an aqueous solution containing one equivalent more than the requisite quantity of hydrochloric acid over a period of 1-2 h under stirring at room temperature. As seen in Table 5.2, admirable yields up to 99% of bromo derivatives with aniline and substituted anilines were obtained.

Assiduous efforts have been made to make accurate assessment about the nature of the brominating species involved in Eqs 5.2 and 5.3. The reactions of BR(S) were independently investigated spectrophotometrically in the absence of organic substrates with a mineral acid in stoichiometric or less than stoichiometric quantities.[62] After the

addition of acid, the BR(S) instantly developed a sharp absorption band at 260 nm, a characteristic band for BrOH species[63] and a low intense broad band at 390 nm. The former band was progressively intensified over a period of about one hour (Figure 5.29) and reached to a steady state in a period of about 4 to 5 days. Hence, the reaction of BR(S) which was initiated in the present investigations by the addition of mineral acid undeniably generates BrOH (Eq 5.4), believed to be a very good brominating species in acidic solutions.[64,65] The consequential BrOH is supposed to be an electrophilic/cationic bromine Br^+ or its equivalent ($BrOH_2^+$–OH^- conjugate acid-base pair, Eq 5.5), rather it is truly a covalent molecule because of its frail acid-base property (pKa, 2×10^{-9}).[66-68] Rao *et al.*[64] have failed to prove $BrOH_2^+$ ion existence by adding an acid to a solution of BrOH

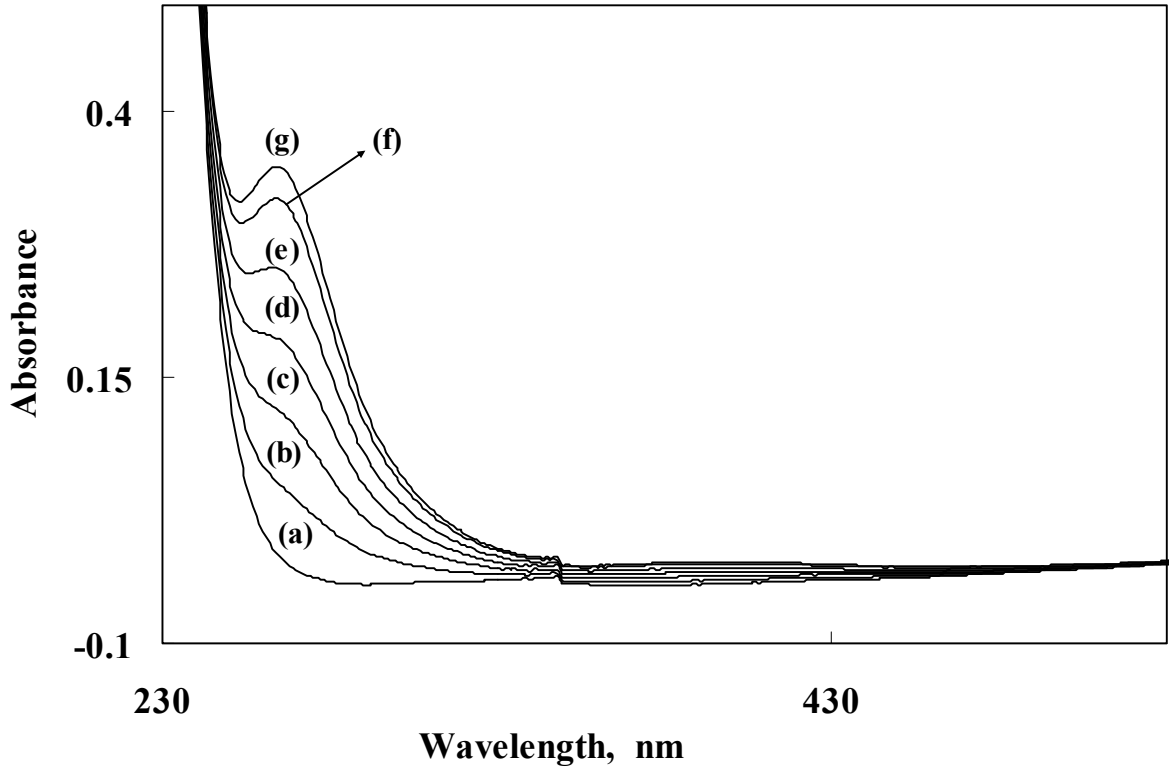


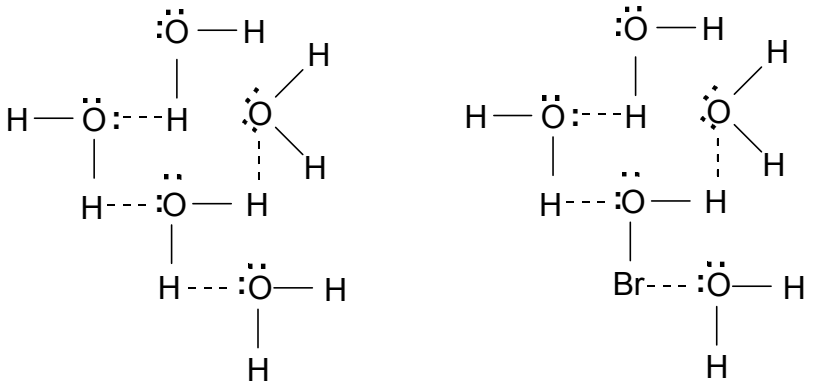
Figure 5.29. Absorption spectral changes of BR(S) (24 mM of utilizable bromine) in 8 mM H_2SO_4. (a) 0 min.; (b) 10 min.; (c) 20 min.; (d) 30 min.; (e) 40 min.; (f) 50 min.; (g) 55 min. at 25 °C.

through conductometry which could be due to its strong acidity. They have further examined its existence in the light of Lowry-Bronsted theory of acids and bases. The

$BrOH_2^+$ formation in the absence of external acid is accounted for the interaction of O-atom (EN, 3.5) of BrOH with H–atom (EN, 2.2 close to 2.7 of Br-atom) of H_2O giving relatively stronger H–bond in aq-BrOH solution than that in pure water (Figure 5.30). The hydrogen bonded BrOH ($BrOH_2^+$–OH^-) moves into the inter phase of two-phase solvent system, wherein the bromination reaction proceeds. In homogeneous phase (aqueous-methanolic solutions), the attacking entity is probably the hydrogen bonded BrOH ($BrOH_2^+$–OH^-).

$$2Br^- + BrO_3^- + 3H^+ \longrightarrow 3\ BrOH \qquad (5.4)$$

$$BrOH + H_2O \rightleftharpoons BrOH_2^+ + OH^- \qquad (5.5)$$



EN of O = 3.5 EN of Br = 2.7 EN of H = 2.2

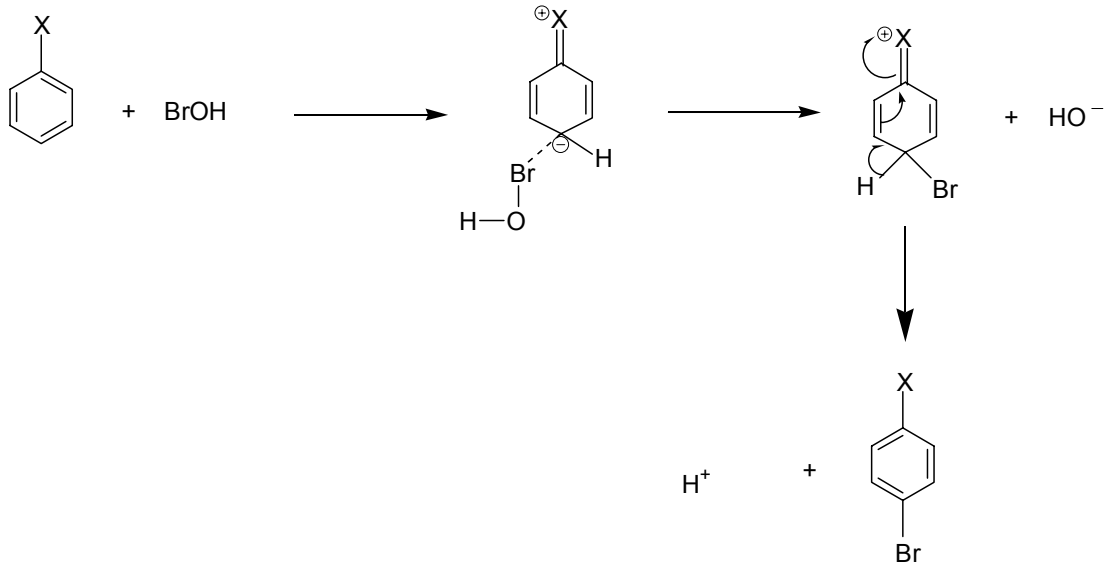
Figure 5.30. H–bonding in water and Aq-HOBr.

The feasible reaction mechanism of BrOH through electrophilic substitution on the aromatic ring with the present brominating reagent BR(S) is as shown in the **Scheme 5.1.**

Contrastingly, Kikuchi *et al.*[69] have proposed that the BrOH would decompose gradually in aqueous solution with the liberation of $Br^{\cdot}$ or the equivalent which moves into the organic phase for its involvement in the bromination reaction. This kind of alternative is obsolete, as our spectrophotometric studies did not suggest such a decomposition of BrOH species in dilute conditions in absence of excess acid. The preferential alkyl bromination in case of toluene instead of aromatic ring substitution suggests a Br-radical generation from BrOH in organic phase of two-phase solvent system. A similar strategy has been observed in the case of aryl alkyl hydrocarbons

bromination by brominating reagents such as molecular bromine, bromotrichloromethane and N-bromosuccinimide in chlorinated solvents.[70]

Scheme 5.1. General bromination of aromatic compounds by substitution mechanism.



where X = –OH, $–NH_2$, $–N(CH_3)_2$, $–OCH_3$, $–NHCOCH_3$, –H

Phenols. From the data in Table 5.1 it is evident that the time required in all subsequent brominations is relatively less as compared to that of mono bromination. This is obvious as the option of bromination sites for incoming HOBr group decreases with the increase in the degree (*di–, tri–* and *tetra– etc)* of bromination on aromatic ring. In practical, the para substitution is more preferred to the ortho because the intermediate bromonium complex ion formed during the substitution is more stable at *para* position. In the present study, a maximum of 82% *para* and 18% *ortho* selectivity was achieved in the mono bromination of phenol at room temperature without the use of any catalyst.

The bromination of substituted phenols was carried out in 20% aqueous methanol. 2-Chloro phenol when subjected to mono-bromination at room temperature gave three bromo derivatives. Among the three, 4-bromo-2-chlorophenol was the predominant product while the other (6-bromo-, and 4,6-dibromo-2-chlorophenols) were present in almost equal molar ratio. Chromatographic analysis revealed that the isomers, 6-bromo-, 4-bromo- and 4,6-dibromochlorophenols were in 69:16:15 mole ratio. When 2-chloro phenol was subjected to dibromination, it gave 91% of 4,6-dibromo-2-chlorophenol as

isolated yield under similar experimental condition. On the other hand, 4-chlorophenol gave a single product of 2,6-dibromo-4-chlorophenol (98.5%) when it was subjected to

Table 5.1. Bromination of phenols

Substrate	Degree of bromination	Solvent	Time (h)	Isolated Yield (%)	Bromo compound
Phenol	1	S_1	2	91	4-Bromo : 2-bromo (82:18)[b]
	3	S_1	2-3	93	Tribromo
	4	S_1		94	2,4,4,6-tetrabromo-2,5-cyclohexadienone
2-Chloro phenol	1	20% S_2	2-3	93[a]	4-Bromo:6-Bromo:4,6-Dibromo- (69:16:15)[b]
	2	20% S_2	2-3	91	4,6-Dibromo
4-Chloro phenol	2	20% S_2	2-3	98.5[a]	2,6-Dibromo
2-Methylphenol	1	20% S_2	2	97[a]	4-Bromo:6-Bromo:4,6-Dibromo (87.6:9.3:3.1)[b]
	2	20% S_2	2	97.5[a]	4,6-Dibromo-
4-Methylphenol	2	20% S_2	2	99[a]	2,6-Dibromo-
2,6-Dimethylphenol	1	20% S_2	2	97	4-Bromo-
4-Bu^t-phenol	1	20% S_2	2-3	82	2-Bromo:2,6-Dibromo (84:16)[a]
	2	20% S_2	2-3	95	2,6-Dibromo
2-Nitrophenol	2	20% S_2	2	98.5	4,6-Dibromo
4-Nitrophenol	2	20% S_2	2	96	2,6-Dibromo
2-Naphthol	1	20% S_2	2	86	1-Bromo
	2	20% S_2	2-3	66	1,6-Dibromo
Bisphenol-A	4	1:5S_3-S_1	4	92-94	Tetrabromo

[a]Crude yields, [b]GC analysis, S_1 = Water, S_2 = CH_3OH, S_3 = CH_2Cl_2

dibromonation under similar experimental conditions. In the case of *o*-cresol, mono-bromination gave three bromo (mono at 4 or 6 positions and di at 4 and 6 positions) derivatives with a overall conversion of 97%. Gas chromatographic analysis showed that the three derivatives (4-bromo-, 6-bromo-, and 4,6-dibromo-) were present in 87.5:9.5:3.0 mole ratio, respectively. However in the dibromination, the same substrate yielded a single product (4,6-dibromo-2-methyl phenol) as found by tlc accounting to 97.5% conversion. The mono bromination reaction of *p*-cresol failed to give any single identifiable product. However, it generously gave high yield (99%) of 2,6-dibromo-4-methyl phenol during the dibromination.

2,6-Dimethyl phenol in monobromination showed a 97% of 4-bromo-2, 6-dimethylphenol formation. Vibrantly, two methyl groups blocked the two ortho positions,

the only available position for the bromine substitution is para with respect to hydroxyl group. Therefore, it gave only one 4-bromo substituted product. In case of 4-tertiary butyl phenol, it gave both mono and dibromo derivatives in the ratio 77:23 amounting to 82% overall conversion during monobromination indicating the competitive nature among the two *ortho* positions. While, in the dibromination, 4-tertiary butyl phenol gave a single product (2,6-dibromo-4-tertiary butyl phenol) with 95% overall yield.

The nitrophenols, which had both electron releasing and electron withdrawing groups already on the aromatic ring, were considered for bromination reactions. Like other substituted phenols, the dibromination of 2-nitrophenol was carried out. The -OH group being an electron releasing group direct the incoming group to *para*- (C_4) and *ortho*- (C_6) positions which are further favored by $–NO_2$ group as it being an electron withdrawing group has *meta*- (C_4 and C_6) directing property. As a result, the bromine atom substitution at C_4 and C_6 positions is highly favored in 2-nitrophenol. However, the attempts of mono bromination of it did not give satisfactory results. Obviously, the dibromination of 2-nitrophenol gave 4,6-dibromo-2-nitrophenol in high yields (98.5%). Similarly, the dibromination of 4-nitrophenol produced 96% of isolated 2,6-dibromo-4-nitrophenol. In general it was found that the bromination of methyl and nitro substituted phenols under go fast brominations as compared to that of chlorophenols.

2-Naphthol gave a single product 1-bromo-2-naphthol in methanol in 2 h with an isolated yield of 86%. On dibromination, 2-naphthol gave 66% of 1,6-dibromo-2-naphthol in a period of 3 h, indicating that the second bromination is slow and difficult. Probably, the first substitution takes place at C_1 position while the second substitution occurs on C_6-carbon, which gives relatively stable bromocarbonium ion intermediates during the process. The tetra bromination reaction of bisphenol-A (BPA), appears to be slow in 20% aqueous methanol as it gives intermediate products more. The reaction when conducted in biphasic dichloromethane-water medium, went smoothly at room temperature and resulted in high yield of tetrabromobisphenol-A (TBBPA) in pure crystalline solid. The organic layer containing the partial brominated products of BPA, was recycled in subsequent batches after charging with fresh BPA and organic solvent to obtain maximum yield of the product.

The comparison of data given in Table 5.1 showed that paradoxically, the bromination of 2-chlorophenols shows less *para*- (64.2%) selective than that of unsubstituted phenol because of competitive formation of 4,6-dibromo derivative. On the other hand, the 4-chlorophenol yielded 2,6-dibromo derivative with 98.5% yield. However, 2-methylphenol gave nearly 21% more para- derivative than that of 2-chlorophenol, probably the more electron donating property of methyl than that of chloro. Both, 2-methyl and 4-methylphenols gave high yields of corresponding dibromo derivatives, while 2,6-dimethylphenol also gave maximum (97%) yield of 4-bromo derivative. 4-Bu^t-phenol gave 69% of 2-bromo derivative along with 13% of 2,6-dibromo derivative during the mono bromination and 95% of 2,6-dibromo derivative during di-bromination. Like 2-chloro-, 4-chloro-, 2-methyl- and 4-methylphenols, the corresponding nitrophenols also gave dibromo derivatives in brilliant yields. Conversely, the 2-naphthol gave moderate yields of 1,6-dibromo derivative during the dibromination and high (86%) yields of 1-bromo derivative in the mono-bromination indicating that the second bromination at C_6 position is a sluggish process.

Amines. The bromination reactions except with aniline were carried out in biphasic medium using dichloromethane and water. Usually amines have the tendency to form their corresponding acid salts when a mineral acid is added. The same phenomenon occurs even during the bromination reactions wherein a mineral acid is added to brominating reagent to liberate active brominating species BrOH. Hence, it is presumed that the acid salts of all amines are produced first and under go bromination in the latter part of acid addition. Hence it is necessary to add acid one equivalent more than the stoichiometric amount required. At the end of the reaction, the reaction mixture was washed thoroughly first with sodium bicarbonate and then with water to free from its salt. Bromination of aniline was carried out using three equivalents of brominating reagent in methanol. As the reaction progresses, the tribromoaniline separates out as light brown solid. The product was isolated in 96% yield. When 4-methyl aniline subjected to dibromination it gave, 84% of 2,6-dibromoderivative and N,N-dimethyl aniline gave 85% of 4-bromo- N,N-dimethyl aniline after isolation. In this case the formation of otho bromoderivative was absent. This could possibly be due to the steric repulsion of two methyl groups already present on nitrogen atom of aniline. The 2-nitro-, and 4-nitro

anilines gave very high yields more than 98% of dibromoderivatives. The data in Table 5.2 depicts admirable (95-99%) yields of bromo derivatives with aniline and nitro substituted anilines, while very good (84-85%) yields with methylated anilines.

Table 5.2. Bromination of aromatic amines

Substrate	Degree of bromination	Solvent	Reaction Time, h	Isolated Yield (%)	Bromo compound
Aniline	3	20% S_2	2	97	Tribromo
4-methylaniline	2	1:5 S_3-S_1	2	84	2,6-Dibromo-
N,N-dimethyl aniline	1	1:5 S_3-S_1	2	85	4-Bromo
2-Nitro aniline	2	1:5 S_3-S_1	2	98.5	4,6-Dibromo
4-Nitroaniline	2	1:5 S_3-S_1	2	98.7	2,6-Dibromo

S_1 = Water, S_2= CH_3OH, S_3 = CH_2Cl_2

Other organic compounds. Bromination of methyl ethers such as anisole, 3-methyl anisole, 1,4-dimethoxy benzene was carried out in biphasic dichloromethane-water medium under ambient reaction conditions. Anisole gave very clean monobrominated product in high (97%) yield with high *para*-selectivity. Probably, the higher electron releasing property of methoxy group in anisole on phenyl ring than that of hydroxyl group in phenol could be the reason for its enhanced para selectivity. Similarly, the dibromination of 1,4-dimethoxy benzene took longer reaction time as compared to that of anisole for which, the reason could be due to steric repulsions caused by two methoxy groups when two bromine atoms approach simultaneously the two ortho positions. The observed yield in the crude reaction mixture was 96.5%.

Table 5.3. Bromination of ethers, amide/imide and hydrocarbons with BR(S).

Substrate	Degree of bromination	Solvent	Reaction Time, h	Yield (%)	Bromo compound
Anisole	1	1:5 S_3-S_1	1.5	97	4-Bromo
2-Methoxynaphthalene	1	1:5 S_3-S_1	2	86.6	1-Bromo
1,4-Dimethoxybenzene	2	1:5 S_3-S_1	2	96.5[a]	2,5-Dibromo
Acetanilide	1	20% S_2	1	93	4-Bromo
Succinimide	1	S_1	4	91.4	N-Bromo
Benzene	1	C_6H_6-H_2O	>24 h	89.7	[b]Bromo-
Toluene	1	1:5 S_3-S_1	2	40.0	Benzylbromide(38.5), Benzaldehyde (1.5), 4-Bromotoluene (traces)
4-Nitrotoluene	2	1:5 S_3-S_1	2	84	4-nitrobenzylbromide
Naphthalene	1	1:5 S_3-S_1	2	36	1-Bromo

[a]Crude yields, [b]At reflex temperature, S_1 = Water, S_2= CH_3OH, S_3 = CH_2Cl_2

The monobromination of acetanilide in aqueous-methanol yielded 93% of isolated product after 2 h reaction. As bromination proceeded, the product 4-bromoacetanilide separated out as color less solid. When the reaction was carried out in dichloromethane-water medium, the product did not separate from the reaction mixture and the yield obtained was comparatively low to that found in methanol-water system. Succinimide was brominated in pure water wherein the product N-bromosuccinimide (NBS) separates out as the reaction proceeded leading to 91% isolated product. However, the reaction when conducted in methanol-water gave unsatisfactory yields due to limited solubility of BR(S) and high solubility of substrate and the resulting bromo compound in methanol.

The other aromatic hydrocarbons brominated with BR(S) were benzene, toluene, and nitrotoluene. Bromination of benzene was carried out at reflux temperature in water and five mole equivalent excess of benzene per atom of bromine substitution medium. The conversion of benzene to bromobenzene was insignificant at room temperature even after prolonged reaction. However at reflux conditions, the conversion proceeded slowly and yielded 87% product after 24 h reaction. Unlike benzene, toluene under went mono-bromonation at room temperature but the substitution took place on the alkyl group rather on the aromatic ring. The yield of benzyl bromide against the total 40% conversion was estimated to be 38.5%. Benzaldehyde was formed as the side product to the extent of 1.5%. The reported methods[71] on toluene bromination revealed that the reaction proceeds via free radical mechanism and it gives benzyl bromide if it is carried out with liquid bromine in chlorinated solvents. A similar mechanism is assumed in the present study as the product is same in both the case. Similarly, the attempts on the dibromination of 4-nitrolouene failed to give ring-substituted bromo derivative. Instead, bromination took place on alkyl group leading to 4-nitrobenzyl bromide as the main product. The isolated yield of this product was 84%. Naphthalene under went bromination and yielded 36% 1-bromonaphthalene as isolated product.

From the data in Table 5.3, it is concluded that the bromination reactions with the present solid brominating reagent BR(S) gave excellent yields like that of liquid bromine between 90–98% in case of ethers, moderate yield (84%) in case of 4-nitrotoulene and low yields between 35–39% in case of toluene and naphthalene. Anisole also gave similar yields when a solution of oxalic acid was used instead of hydrochloric acid.

5.3.2. Olefinic additions with BR(A). The bromination of olefins conventionally carried out in carbon tetrachloride medium at low temperature was well established in the literature. These bromination reactions were also conducted in the present study, with the brominating reagent BR(A), in carbon tetrachloride-water and dichloromethane-water medium at room temperature. Two products bromohydrins and dibromo derivative were found in both the solvent media with almost all substrates. Although, the total conversion was almost comparable in both the media, the dibromo:bromohydrin ratio was found to be less in carbon tetrachloride-water and better in the other solvent. The bromination reaction with cyclohexene was fast and showed 81% total conversion wherein the dibromo to bromohydrin ratio was found to 68:32. When the same reaction was carried out carbon tetrachloride, under similar conditions gave 79% of total products with dibromo and bromohydrins in 48:52 mole ratio. Surprisingly the yields in both cases (See entry 1 in Table 5.4) were almost same but, the ratio dibromo and bromohydrin varied considerably implying that the combination of BR(A)-dichloromethane-water system offers a better role for all addition reactions across C=C double bonds than that of BR(A)-carbon tetrachloride-water system. Cyclooctene gave 85% of total brominated product dibromocyclooctane and 2-bromocyclooctanol in 67:33 ratio. Cyclohexene yielded more 1,2-dibromo derivative than cyclooctene which may be due to high volatility of cyclohexene than the cyclooctene, and also due to increase in the ring size of cyclooctene, the intermediate formed during the reaction will be more stable than the corresponding lower members. The same properties were observed in styrene and 4-methyl styrenes. Styrene was subjected to the addition reaction of aqueous bromine in

Table 5.4. Bromination of olefins by addition reaction BR(A)

Substrate	Solvent	Reaction Time, min	Total Yield (%)	Bromo compound Dibro : Bromohydrin
Cyclohexene	1:5 S_3-S_1	30	81	68 : 32
	1:5 S_4-S_1	45	79	48 : 52
Cyclootene	1:5 S_3-S_1	45	85	67 : 33
Styrene	1:5 S_3-S_1	60-120	90	65 : 25
4-Methylstyrene	1:5 S_3-S_1	60	94.5	77 : 23
Phenyl acetylene	1:5 S_3-S_1	45	84[a]	90 : 10
Chalcone	1:5 S_3-S_1	60	93	84 : 16
1-Hexene	1:5 S_3-S_1	45	68.1	92.5 : 7.5
1-Octene	1:5 S_3-S_1	45	91.2	91 : 9
Allyl alcohol	1:5 S_3-S_1	60	20	100 : 00

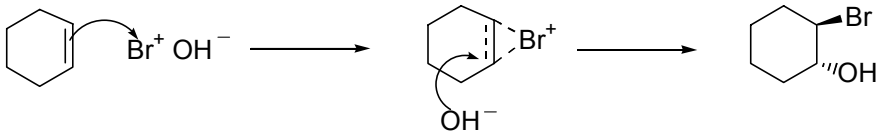
[a]Based on the recovery of starting material, S_1 = Water, S_3 = CH_2Cl_2, S_4 = CCl_4

dichloromethane, the addition of two bromine atoms across the double bond of vinyl group takes place. The addition of bromine to the olefinic double bond in the side chain of the aromatic ring will be preferred than the aromatic ring itself. Styrene gave 90% total yield containing styrenedibromide and styrene bromohydrin in 65:25 ratio. On the other hand 4-methyl styrene exhibited 94.5% as total yield of bromoinated product having dibromo and bromohydrin in 77:23 ratio. In the case of phenyl acetylene, the total converted product was 84%, while the dibromo to bromohydrin ratio was found as 90:10. The dibromo derivative formation is expected more because of high reactivity of acetylene group and the enhanced affinity of bromine towards addition across the triple bond.

The straight chain olefins have also exhibited similar properties like cyclohexene and cyclooctene. 1-Hexene in CH_2Cl_2-H_2O gave 68% converted product with high composition of dibromo and less bromohydrin (92.5:7.5). Similarly, 1-octene showed maximum 91.2% conversion with 91:9 dibromo to bromohydrin ratio. Finally, allyl alcohol gave only 20% dibromo derivative. Bromohydrin did not form.

5.3.3. Bromohydrins with BR(S). The applications of BR(S) was extended beyond its substitution reactions to synthesize many useful intermediate bromohydrins. The reactive intermediate BrOH of BR(S) adds across the C=C double bonds of cyclic, aromatic side chain and simple olefins which will give rise the corresponding bromohydrin derivatives. The reaction of BrOH of BR(S) was initially examined with cyclohexene (**Scheme 5.2.**)

Scheme 5.2. Addition of BrOH across the symmetrical olefins

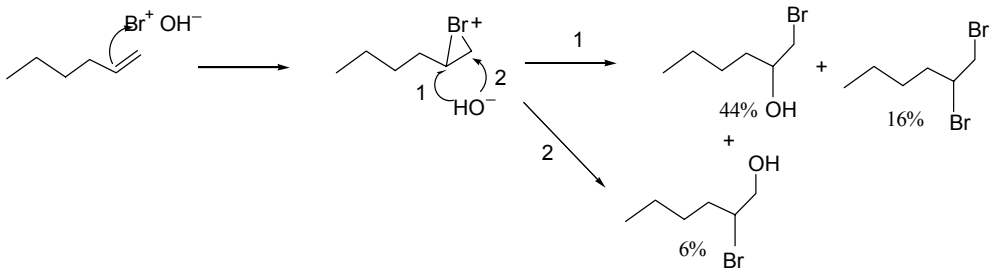


in biphasic carbon tetrachloride-water medium at 65-70°C.The reaction was completed in 1 h with 82% conversion having two products 2-bromocyclohexanol (75%) and 1,2-dibromocyclohexane (25%). When the reaction was carried out in dioxane-water medium at room temperature, it took 45 min to complete and gave 85% converted product containing 79% bromohydrin and 21% dibromo derivative. Similarly, the substrates,

styrene and 4-methyl styrene were reacted with BR(S) in carbon tetrachloride-water medium showed 81% bromination of styrene while 88% total conversion of 4-methyl styrene with bromohydrin to dibromo derivatives in 79:21 and 81:19 ratio, respectively. The yields were remarkably increased further to 91% (87:13 bromohydrin to dibromo ratio) in the case of styrene and 90% (91:9 bromohydrin to dibromo ratio) with 4-methyl styrene when the reactions were conducted in dioxane-water medium. Similar observations were made when phenyl acetylene was reacted with BR(S) in both the solvent media. The total observed conversions are 59% with 71:29 bromohydrin to dibromo derivatives in biphasic medium and 72% with 83:17 bromohydrin to dibromo derivatives in dioxane-water medium. From the data in Table 5 entries 1 to 4, it is very clear that, in all cases of biphasic medium, the reaction time is high and the yields are low compared to the homogenous dioxane-water medium. Even the bromohydrin formation appears to be less favored in biphasic medium relatively to that in homogeneous dioxane-water medium. One of the reasons for the dibromo-derivative formation in biphasic medium could be due to high reaction (65-70°C) temperature at which the bromohydrin may favorably undergo dehydration and convert itself to dibromo derivative through mono-bromo olefin intermediate.

The simple olefins like 1-hexene, 1-octene and allyl alcohol were subjected to react with BR(S) in the present study. Formation of regioisomers were found with 1-hexene, 1-octene while dibromo derivative with allyl alcohol in homogeneous dioxane-water reaction medium. 1-Hexene afforded regioisomers, 1-bromo-2-hexanol and 2-bromo-1-hexanol approximately in 7:1 ratio (**Scheme 5.3**). The product 1-bromo-2-hexanol is

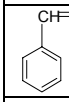
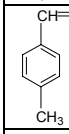
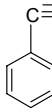
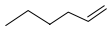
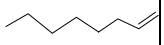
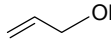
Scheme 5.3. Addition of BrOH across the unsymmetrical olefins



expected if the hydroxyl ion [BrOH = $Br^+ + OH^-$] adds on to the highly substituted carbon atom in the bromocarbonium ion intermediate following the Markovnikov's rule

(route 1, **Scheme 5.3**). The other isomer 2-bromo hexanol results when the addition of hydroxyl ion takes place on the least substituted olefinic carbon following the anti-Markovnikov's rule (route 2, **Scheme 5.3**). Route 1 seems to predominant over the route 2 as the former gives 38% more 1-bromo-2-hexanol. The substrate 1-hexene showed 66% overall yield while 44% 1-bromo-2-hexanol, 6% 2-bromo hexanol and 16% 1,2-dibromo hexane. The same reaction when conducted in biphasic carbon tetrachloride-water medium at 65-70°C, yielded 48% of 1,2-dibromohexane and 17 % 1-bromo-2-hexanol only. Here, the over all yield was 65% but the disadvantage is that the dibromo derivative formation was more than the required product bromohydrin.

Table 5.5. Preparation of bromohydrins from olefins with BR (S).

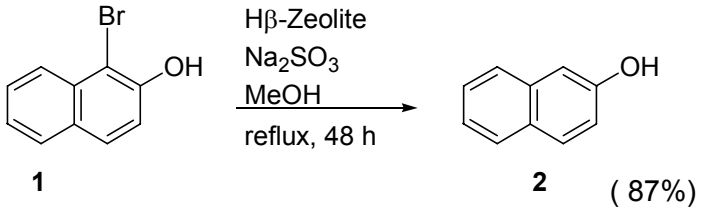
Substrate	Solvent	Temp (°C)	Reaction Time,(min)	Yield (%)	Bromohydrin/ Dibromo
	CCl_4	65	60	82	75 : 25
	Dioxane	r. t	45	85	79 : 21
	CCl_4	65	60	81	79 : 21
	Dioxane	r. t	45	91	87 : 13
	CCl_4	65	60	88	81 : 19
	Dioxane	r. t	40	90	91 : 9
	CCl_4	65	30	59	71 : 29
	Dioxane	r. t	25	72	83 : 17
	CCl_4	65	60	65	26 : 74
	Dioxane	r. t	30	66	76 : 24
	CCl_4	65	45	75	27 : 73
	Dioxane	r. t	30	85	79 : 21
	Dioxane	r. t	35	24	0 : 24

Like with 1-hexene, 1-octene also gave three products, 1-bromo-2-octanol (59%), 2-bromooctanol (10%) and 1,2-dibromooctane (18%) yield with BR(S) in homogeneous dioxane-water medium by the routes 1 and 2 as shown in **Scheme 5.3**. Similarly, in biphasic carbon tetrachloride-water medium at 65-70°C, 1-octene gave 20% of 1-bromo-2-octanol and 55% of 1,2-dibromooctane. There was no regioisomers observed.

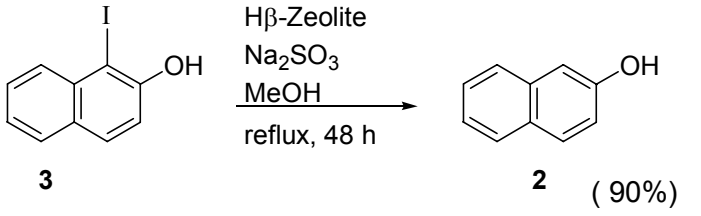
The simple chain olefins also showed high yields of dibromo derivative in biphasic medium and less in homogeneous medium. Allyl alcohol produced 24% of dibromo derivative only in dioxane-water at room temperature. From the data in Table 5.5 it is understood that as the length of the olefin increases the bromohydrin yields are improved better in homogeneous medium implying dioxane-water will be the better system for the preparation of bromohydrins using BR(S).

Part II. Selective dehalogenation of halophenols

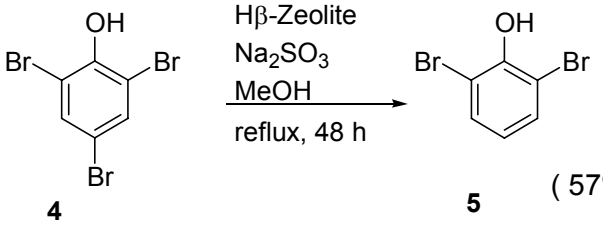
5.3.4. Dehalogenation using Hβ-Zeolite. Debromination of 1-bromo-2-naphthol, **1** was carried out with 50% (w/w) of Hβ-Zeolite as catalyst in presence of excess sodium sulfite (5 mol. equivalent) as bromine scavenger in dry methanol at reflux temperature, Eq 5.6. The course of reaction was followed by checking the formation of 2-naphthol, **2** by comparison of tlc with authentic sample. The reaction needed about 48 h for completion and debrominated product was isolated in 87% yield. The analogous deiodination of 1-iodo-2-naphthol, **3** under the identical conditions gave higher yields of 90%, in accordance with the expectations as iodo group being a better leaving group than bromo Eq 5.7. However, the dechlorination reaction of 1-chloro-2-naphthol was not found feasible in the reaction conditions as the material remained unchanged even after prolonged reaction.



1 **2** (87%) (5.6)

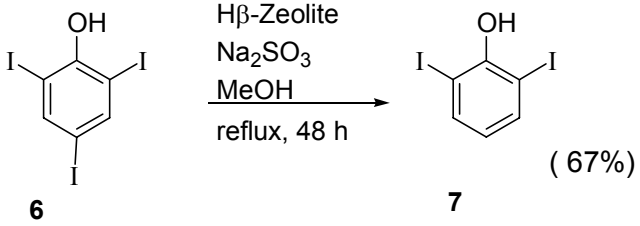


3 **2** (90%) (5.7)



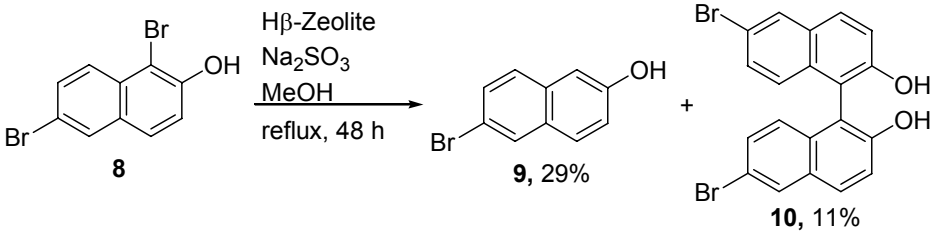
(5.8)

Another set of examples of 2,4,6-tribromophenol **4** and 2,4,6-triiodophenol **6** was subjected to similar reaction conditions to obtain 2,6-dibromophenol **5** and 2,6-diiodophenol **7** in moderate yields, Eq 5.8 and 5.9 respectively.

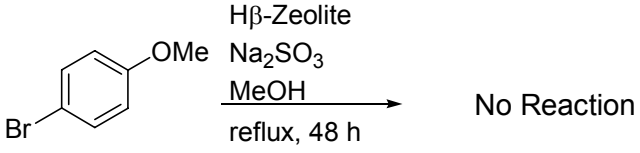


(5.9)

Compound 6-bromo-2-naphthol, **9** is an important industrial material and is prepared by selective debromination of 1,6-dibromo-2-naphthol **8**.[72] Although, selective debromination of bromine at 1 position and isolated 6-bromo-2-naphthol **9** was successfully achieved, the 2,2'-dihydroxy-6,6'-dibromo-1,1'-binaphthol **10**, probably formed by the oxidative coupling of **9**,[73] (Eq 5.10) was also observed in considerable amounts.



(5.10)



(5.11)

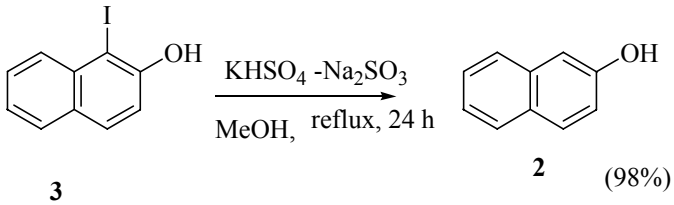
Reaction of debromination of 4-bromoanisole **11** under the identical conditions was not successful even after the long exposure to the zeolite in refluxing methanol, Eq 5.11.

This is probably indicative of the role of hydroxyl group to stabilize the intermediate benzonium ion.[53]

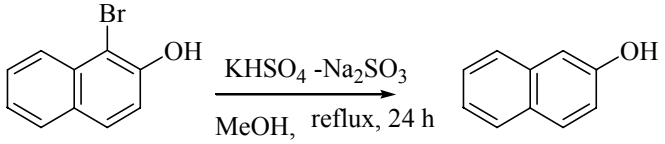
The catalyst recovered after the deiodination of **3** (Eq 5.7), was carefully washed with organic solvents, water and dried appropriately. The powder X-ray diffraction analysis (XRD) and FT-IR spectra of this material was found to be comparable with the fresh catalyst indicating the retention of physical properties of the material. The recovered zeolite was used in another set of reaction of deiodination of **3** to get comparable results to the first cycle. This clearly indicated the ability to recover and reuse the zeolite as catalyst for repetitive use in dehalogenation reaction.

5.3.5. Dehalogenations using sulfite-bisulfate medium. After the use of Hβ-Zeolite[60] as a heterogeneous catalyst for the selective dehalogenation the idea was extended for simple reagent methods such as $KHSO_4$-Na_2SO_3 [61] medium.

In the present case the reductive deiodination of 1-iodo-2-naphthol, **3** was chosen as a model reaction and carried out as shown in Eq 5.12 over a bed of $KHSO_4$ (5 mol equiv)-Na_2SO_3 (6 mol equiv) at reflux in dry methanol. The progress of the reaction was monitored by tlc analysis following the production of 2-naphthol, **2**.[60] The reaction was completed in 24 h and the product was isolated in 98% yield, showing the present system to be more efficient than the Hβ-zeolite-catalytic system,[60] wherein a 97% yield was achieved in a 48 h reaction. Under similar experimental conditions, 1-bromo-2-naphthol, **1** gave a 92% yield of **2**, Eq 5.13 while 1-chloro-2-naphthol was unchanged. The conversion of 1-iodo-2-naphthol was higher than its bromo analog.[58]

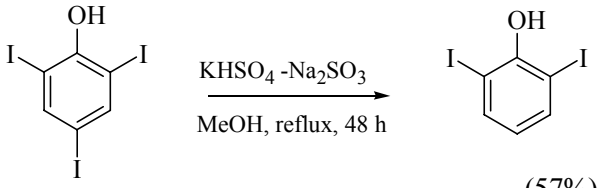


3 **2** (98%) (5.12)

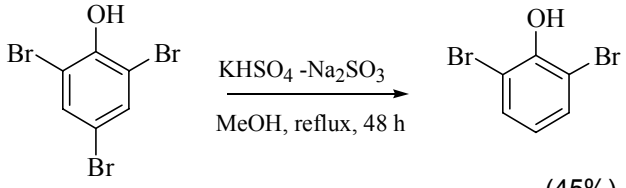


1 **2** (92%) (5.13)

The same strategy was extended to 2,4,6-triiodophenol and 2,4,6-tribromophenol to obtain the corresponding 2,6-dihalophenol in moderate yields after 48 h, Eqs 5.14, 5.15 respectively. The present investigations revealed that the halonaphthols are more easily dehalogenated than halophenols. Presumably this may be due to the intermediate (keto form) of halonapthol is more stable than that of phenols. Lin *et al.*[74] reported the debromination of *p*-bromophenol using $NaBH_4$ in the presence of a nickel catalyst and obtained less encouraging results.

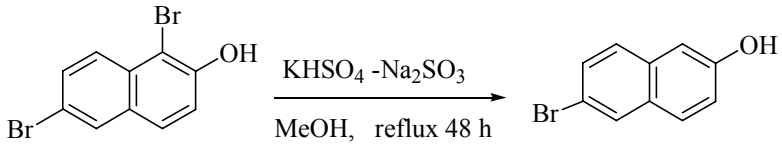


6 (5.14)



4 (5.15)

6-Bromo-2-naphthol, **9** is an important starting material in synthetic and industrial chemistry[75] and is conventionally obtained by selective debromination of 1,6-dibromo-2-naphthol, **7** using hydrobromic acid.[72,76] Vona *et al.*[6] reported the preparation of 6-bromo-2-naphthol in 45.5% yield by reacting 2-naphthol, pyridinium tribromide and excess tin in glacial acetic acid. In the present study, the preparation of 6-bromo-2-naphthol **9** was successfully achieved in 55% yield by selective debromination of 1,6-dibromo-2-naphthol, **8** using $KHSO_4$-Na_2SO_3, (Eq 5.16).



7 **8** (55%) (5.16)

Dehalogenation 2–CH_3, 2–NO_2 and 2–Cl derivatives of 4, 6-dibromophenol, the 4–I, 4–Br derivatives of phenol and anisole and the 1-I and 1-Br derivatives of 2-methoxy naphthalene was also tried but the trials failed to get the desired products even after prolonged reflux in methanol.