

Electrochemical Method for the Preparation of Dibromomethyl, Bis(bromomethyl), and Bis(dibromomethyl) Arenes

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Abstract: Electrochemical bromination of alkyl aromatic compounds by two-phase electrolysis yields the corresponding α,α -dibrominated products. The reaction has been carried out in a single-compartment electrochemical cell using aqueous sodium bromide (40–50%), containing a catalytic amount of HBr as electrolyte, and chloroform, containing an alkyl aromatic compound, as the organic phase with a Pt plate as anode at 10–15°C. Two-phase electrolysis results in high yields (70–90%) of dibromomethyl, bis(bromomethyl), and bis(dibromomethyl) arenes, depending upon the charge passed.

Keywords: Alkyl aromatic compound, dibromomethyl arene, electrochemical bromination, two-phase electrolysis

The conventional benzylic bromination process for producing benzyl or benzal bromide consists of contacting gaseous bromine with a reaction mixture having an organic liquid phase with an (un)substituted aromatic ring-containing compound bearing one or more benzylic carbon atoms. The temperature of the liquid phase is maintained at 100–170°C with light irradiation to effect benzylic bromination of the benzylic methyl group.^[1–8] Alternatively, N-bromosuccinimide can be used along with azobisisobutyronitrile (AIBN) or benzoyl peroxide as a catalyst at high

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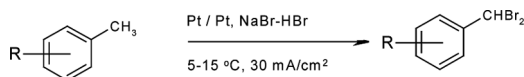
temperatures.^[9–11] However, these methods have the drawbacks of prolonged heating, light irradiation, and the use of bromine as vapor (a serious safety problem).

Herein, we report a simple method for the preparation of dibromomethyl, bis(bromomethyl), and bis(dibromomethyl) arenes from methylarenes by two-phase electrolysis at 10–15°C in a single-compartment cell as shown in Scheme 1. We have previously described the electrochemical method of side-chain bromination and nuclear bromination using an NaBr–HBr system.^[12,13]

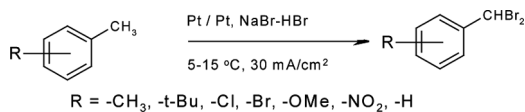
A number of alkyl aromatic and substituted alkyl aromatic compounds were conveniently subjected to side-chain bromination by two-phase electrolysis using a 40–50% NaBr solution as an electrolyte, containing a catalytic amount of HBr (5%) in the aqueous phase, along with an organic phase of chloroform, containing an alkyl aromatic compound. The product distributions from the reactions are listed in Table 1.

This process allows the preparation of dibromomethyl, bis(bromomethyl), and bis(dibromomethyl) arenes, depending upon the total charge passed, in reasonable purities. These can be used for further transformations and as building blocks in material chemistry. To avoid the formation of α,α,α -tribromomethyl arenes, the electrolysis temperature was reduced to 5°C from 15°C after passing 75% of the charge (mentioned in Table 1) to control the reactive species Br_2O .

When the reaction was not controlled at the final stage, a mixture of α,α,α -tribromomethyl and nuclear brominated arenes was formed along with α,α -dibromomethyl arene. Initial attempts to obtain pure bis(dibromomethyl) arene were not successful when the reaction was conducted at 15°C throughout the experiment and resulted in the formation of α,α,α -tribromomethyl arene in 30–40%. The reaction proceeded under mild conditions in the presence of a less hazardous brominating agent than Br_2 (N-bromosuccinimide and pyridinium tribromide) and at a lower temperature than the conventional methods. Although dibromine monoxide is exceptionally reactive in the side-chain bromination of nonactivated (entry 1) and deactivated alkyl aromatic arenes (entries 2 and 3), activated compound 3,5-dimethyl phenol (entry 9) gives nuclear brominated compound as a sole product.



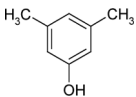
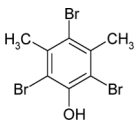
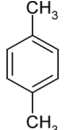
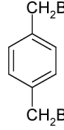
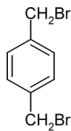
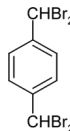
Scheme 1. Electrochemical dibromination of arenes.

Table 1. Ratio of reactants and products of the electrochemical bromination of alkyl aromatic compounds by two-phase electrolysis

Entry	Reactant	Product ^a	Yield ^b (%)	Charge passed (F/mole)	Current efficiency (%)
1			72	20	20
2			72	17	24
3			70	25	16
4			70	17	24
5			80	20	20
6			50 ^c	33	12
7			85	19	21
8			51 ^d	16	25

(Continued)

Table 1. Continued

Entry	Reactant	Product ^a	Yield ^b (%)	Charge passed (F/mole)	Current efficiency (%)
9			90	6	81
10			90	12	30
11			76	24	15

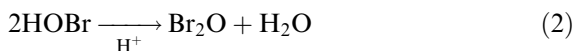
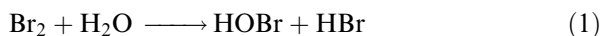
^aStructures were confirmed from their spectra (NMR, IR) data.

^bIsolated yield.

^cp-Nitro bromomethyl benzene (50%) is present along with 50% p-nitro dibromomethyl benzene.

^dIsolated as a solid after trituration with n-hexane.

However, if the phenolic group is protected as methyl ether, the product obtained is α -bromomethyl arene at the first stage. On further bromination, nuclear-brominated α -bromomethyl arene was obtained as a sole product instead of α,α -dibromomethyl arene (entry 5). Because of the high deactivating nature of the nitro group in the *p*-nitrotoluene, the current efficiency of product formation is comparatively less. Side-chain bromination of alkyl aromatic compound follows a radical mechanism, and the brominating species is dibromine monoxide (Br_2O), which is formed in aqueous phase as shown in Eqs. (1) and (2) and extracted by the organic phase, where the selective bromination occurs:



As the reactive Br_2O cleaves homolytically into Br^\cdot and $^\cdot\text{OBr}$, the more reactive $^\cdot\text{OBr}$ abstracts benzylic hydrogen to form HOBr.

Subsequently, the bromine radical attacks the benzyl radical, giving the products benzyl bromide and subsequently α,α -dibromomethyl arene.

In conclusion, the electrochemical method for the side-chain bromination of alkyl aromatic compounds to yield α,α -dibromomethyl arenes is a convenient and efficient procedure.

EXPERIMENTAL

Representative Procedure for Electrochemical Bromination

1,4-Bis(bromomethyl)benzene

A solution of 1,4-dimethyl benzene (entry 10) (1.06 g, 10 mmol) in 30 ml chloroform was taken in a beaker-type undivided cell. A 40% aqueous sodium bromide solution (50 ml) containing 5 ml of HBr (46% solution) was added to the solution. Platinum electrodes (each of 10 cm² area) were placed in the upper layer of the aqueous phase. The organic phase alone was stirred with a magnetic stirrer at a rate of 40 rpm in such a way that the organic layer did not touch the electrodes. The electrolysis was conducted galvanostatically at a current density of 30 mA/cm² until the quantity of charge indicated in Table 1 was passed at a temperature of 15°C. The electrolysis was monitored by high-performance liquid chromatography (HPLC) using a Shimpack ODS column (120 × 4.5 mm) as the stationary phase. The eluent consisted of methanol–water (70:30) at a flow rate of 1 ml/min. Samples were analyzed using an ultraviolet (UV) detector at a wavelength of 254 nm. After completion of electrolysis, the lower organic phase was separated, washed with 10% sodium thiosulphate solution followed by water (2 × 25 ml), and dried with anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The residue obtained was crystallized with ethanol to give 1,4-bis(bromomethyl)benzene (2.37 g, 90%); mp 145°C; ¹H NMR (400 MHz, CDCl₃): δ 4.5 (s, 4H), 7.4 (s, 4H).

1,4-Bis(dibromomethyl)benzene

1,4-Bis(bromomethyl)benzene (1.32 g, 5 mmol) in 35 ml of chloroform was electrolyzed in a similar manner. After passing 75% of the charge mentioned in Table 1, the temperature of the electrolyte was reduced to 5°C and the electrolysis was continued. The electrolysis was monitored by HPLC. After completion of electrolysis, the organic phase was separated and worked up as mentioned previously. The solvent volume was

reduced by one third under reduced pressure. After cooling the solution, 1,4-bis(dibromomethyl) benzene was separated out as a solid product and crystallized with chloroform (1.6 g, 76%); mp 169°C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.7 (s, 2H), 7.6 (s, 4H).

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