

## A simple and regioselective $\alpha$ -bromination of alkyl aromatic compounds by two-phase electrolysis

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**Abstract**—Electrochemical bromination of toluene and substituted toluenes by two-phase electrolysis yields the corresponding  $\alpha$ -brominated products. The reaction has been carried out in a single compartment cell with platinum electrodes at 0 °C in chloroform using an aqueous sodium bromide solution (60%) containing a catalytic amount of HBr. Two-phase electrolysis results in high yields (60–95%) of monobromo compounds with very high regioselectivity (>95%).  
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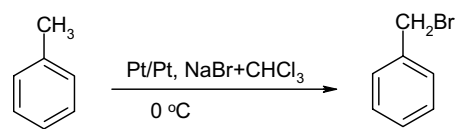
Substitution of C–H bonds in alkyl aromatic compounds by radical halogenation is one of the most important reactions for functionalisation of alkyl aromatics. Benzyl bromides and substituted benzyl bromides are primarily used as synthetic intermediates in the pharmaceutical and other fine chemical industries.

Radical bromination on benzylic positions has been achieved using bromine<sup>1–3</sup> and *N*-bromosuccinimide.<sup>4,5</sup> In addition, the bromine complex of the styrene vinylpyridine co-polymer<sup>6</sup> and bromotrichloroethane<sup>7,8</sup> and copper(II) bromide<sup>9</sup> have been reported to be effective for benzylic bromination. The majority of brominating agents require the presence of a peroxide or another radical initiator. Side-chain bromination using sodium bromate and bromotrimethylsilane has also been reported<sup>10</sup> but in only low yields. By using electrochemical technology, it is possible to carry out a desired reaction via a two-phase electrolytic reaction, resulting in high yields and selectivity.

Two-phase electrolysis has a distinct advantage over conventional homogeneous electrolysis in practical electro-organic synthesis.<sup>11</sup> In the homogeneous system, less selectivity is observed due to oxidation of the substrate on the surface of the electrode giving mixtures of nuclear (*ortho* and *para* isomers) and side-chain brominated

products. In a two-phase electrolysis system, the reactive species formed by the electrolytic oxidation of a halide ion in the aqueous phase can be taken continuously into the organic layer and then reacted with the substrate to give the products regioselectively. After the completion of the electrolysis, separation and concentration of the organic layer affords the product.

Electrochemical bromination has been investigated in different solvents<sup>12–19</sup> and most of the work deals with ring brominated products. Side-chain bromination has not been much explored. In continuation of our earlier work on electrochemical halogenation of aromatic compounds, we present a simple and regioselective electrochemical method for the  $\alpha$ -bromination of toluene and substituted toluenes to give the corresponding benzyl bromides in very good yields by two-phase electrolysis<sup>20</sup> at 0 °C in a single compartment cell as shown in Scheme 1. We observed smooth bromination at the  $\alpha$ -position of the side-chain without the formation of any poly-brominated product. A number of alkyl aromatics and substituted alkyl aromatic compounds were subjected to side-chain bromination by two-phase electrolysis using an aqueous 60% NaBr solution as the supporting



**Scheme 1.** Electrochemical bromination of toluene by two-phase electrolysis.

**Keywords:** Electrochemical bromination; Two-phase electrolysis;  $\alpha$ -Brominated products; Regioselectivity.

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**Table 1.** The ratio of reactants and products of the electrochemical bromination of toluene, substituted toluenes and substituted naphthalenes via two-phase electrolysis

Entry	Reactant	Product	Charge passed (F/mol)	Yield (%)	Current efficiency (%)
1			4.5	91	44
2			5.0	90	40
3			3.0	89	44
4			4.5	85	37
5			3.0	62	25
6			4.0	57 <sup>a</sup>	35
7			3.0	50	33
			6.0	48 <sup>b</sup>	32
			9.0	90	41
8			6.0	12 <sup>c</sup>	5
9			6.0	80	26

<sup>a</sup> Benzyl bromide 22% formed along with 10% recovered starting material.<sup>b</sup> 4-Methylbenzyl bromide 45% formed along with 2% recovered starting material.<sup>c</sup> 3-Bromo-4-methoxytoluene 39% and 2-bromo-4-methoxytoluene 37% were formed together with 12% recovered starting material.

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