

# Electrochemical dimerization of benzyl chloride on a powder cathode of silver, graphite or silver-graphite mixture

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Keywords: cavity cell, benzyl halides, solvent-free

# INTRODUCTION

The main challenge in organic synthesis is the formation of new C-C bonds in order to construct more complex carbon skeletons in a defined arrangement. In contemporary electrochemical publications, such C-C couplings are still a minor subject<sup>1</sup>. Herein we reported an application of a new electrochemical cell which uses graphite powder, silver powder or mix graphite/silver powder in the cathode cavity combined with an aqueous anolyte<sup>2-4</sup> to promote the dimerization of benzyl chloride in good yield.

# **RESULTS AND DISCUSSION**

Voltammetries of benzyl chloride (1) were carried out, using the electrochemical cavity cell with very slow scan rates<sup>2-5</sup> in powder cathode of silver, graphite or graphite-silver mixture with different mass ratios for producing toluene (2) and bibenzyl (3) (Figure 1), and are summarized in Table 1.

PhCH<sub>2</sub>CI 
$$\xrightarrow{\text{ne}^2}$$
 PhCH<sub>3</sub> + PhCH<sub>2</sub>CH<sub>2</sub>Ph
1 2 3

Figure 1. Electrochemical dimerization of benzyl chloride.

The observed peak potentials ( $E_{peak}$  vs. Ag/AgCl, saturated KCl) show that increasing the amount of graphite in the silver/graphite mixture promotes a slightly peak shift towards negative values, however still remains higher (less negative) than  $E_{peak}$  value observed for reduction reaction performed at pure graphite, showing a significant electrocatalytic activity of the silver.

The better yields of the dimer **3** were observed in entries 3 and 4. During these voltammetries, it was observed a chromatographic yield of 18 to 11% of toluene. In summary, the presence of 75% and 50%

of graphite in the powder cathode mixture improves significantly the yield of **3**.

Table 1. Electrochemical dimerization of benzyl halides

<sup>a</sup> Entry	%Ag	<sup>b</sup> E <sub>peak</sub>	<sup>c</sup> 2	<sup>c</sup> 3
1	100	-0.65 / -0.82	48	13
2	75	-0.73	29	71
3	50	-0.82	18	82
4	25	-0.95	11	89
5	0	-1.36	23	70

 $^{\rm a}$  Voltammograms recorded at electrode containing 150 mg of mixture x% silver/ 100-x% graphite powders (noted x% Ag + 100-x% G) in different proportions (with x = 25%, 50% and 75%), impregnated with 0.52 mmol of PhCH<sub>2</sub>Cl at 0.1 mV s $^{\rm -1}$  using anolyte 0.1 mol L $^{\rm -1}$  KCl.  $^{\rm b}$  (vs. Ag/AgCl sat. KCl);  $^{\rm d}$  Chemical yield determined by H $^{\rm 1}$ NMR.

# CONCLUSION

We demonstrated here the potential use of the powder cathode of silver, graphite or graphite-silver mixture on the reductive homo-coupling of benzyl halides, in a cavity cell. The procedure eliminates organic solvents, supporting electrolytes and sacrificial anodes, traditionally used in electrosynthetic methods. This procedure can be highlighted by low environmental impact.

#### **ACKNOWLEDGEMENTS**

The authors wish to thank CNPq and CAPES by financial support.

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Souza, R. F. M.; Areias, M. C. C.; Bieber, L. W.; Navarro, M. RSC Advances: an international journal to further the chemical science, 2013, 3, 6526.