

## Electrochemical homo-coupling of benzyl halides on a powder cathode in a cavity cell

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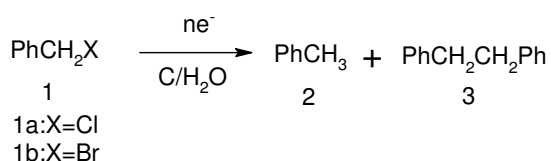
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## INTRODUCTION

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 in the cathode cavity combined with an aqueous anolyte<sup>2-4</sup> to promote the dimerization of benzyl halides in good yield.

## RESULTS AND DISCUSSION

Explorative voltammetry of benzyl chloride (**1a**) and bromide (**1b**) using the same electrolytic cell with very slow scan rates<sup>2-4</sup> in cathode of graphite indicated reduction potentials of the -1.40 and -1.32 V (vs. Ag/AgCl, saturated KCl) for producing toluene (**2**) and bibenzyl (**3**). On this silver-doped electrode material the peak potential was displaced to -0.88 for **1a** and -1.07 V to **1b**. Proper choice of controlled potential, catalyst and leaving group allows highly selective dimerization (Figure 1).



**Figure 1.** Electrochemical dimerization of benzyl halides

For both halides with method A, the yield of **3** increased continuously from more negative to less negative potentials, reaching 81% in the case of **1b** (entry 4). Consequently, **2** was favored by more cathodic potentials and was the main product in all experiments with **1a** (entries 1-3). The effect of silver catalysis (method B) in controlled potential electrolyses also was observed. No clear difference in the reaction rate and conversion of **1a** and **b** was observed. Also the product distribution became very similar with maximum yields of dimer **3** of 64 and 80%, respectively, at -1.0 V (entries 9 and 13).

**Table 1.** Electrochemical dimerization of benzyl halides

<sup>a</sup> Entry	PhCH <sub>2</sub> -X	<sup>b</sup> Method	<sup>c</sup> E / V	<sup>d</sup> 2	<sup>d</sup> 3
1	1a	A	-1,0	46	27
2	1a	A	-1,2	59	10
3	1a	A	-1,4	91	8
4	1b	A	-0,8	1	81
5	1b	A	-1,0	24	73
6	1b	A	-1,2	48	49
7	1b	A	-1,4	46	39
8	1a	B	-0,8	13	59
9	1a	B	-1,0	28	64
10	1a	B	-1,2	64	24
11	1a	B	-1,4	55	35
12	1b	B	-0,8	11	79
13	1b	B	-1,0	14	80
14	1b	B	-1,2	25	69
15	1b	B	-1,4	30	60

<sup>a</sup> General reaction conditions described in the references 2; <sup>b</sup> Method A= graphite, Method B= graphite silver-doped; <sup>c</sup> (vs. Ag/AgCl sat. KCl); <sup>d</sup> Chemical yield determined by <sup>1</sup>H NMR

## CONCLUSION

In summary, we demonstrated the synthetic efficiency of cavity cell in reductive homo-coupling of benzyl halides. The procedure eliminates organic solvents, supporting electrolytes and sacrificial anodes of traditional electrosynthetic methods and is characterized by experimental simplicity and low environmental impact.

## ACKNOWLEDGEMENTS

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