Abstract No. 2526

Homo- and Heterocoupling of Aldehydes, Ketones, Acrylesters and Imines at a Graphite Cathode in Protic Electrolytes

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Protic electrolytes are often a necessity for larger scale electrochemical conversions. Homocoupling of aromatic aldehydes to pinacols is a reliable procedure in protic solvents, when mercury is used as cathode material.[1] Heterocoupling of ketones with methyl acrylates to γ-lactones can also be performed in protic medium when a mercury[2a] or lead cathode[2b] is applied. Imines couple to vicinal diamines in protic media at a mercury cathode.[3] The restriction of these synthetically important C,C-bond forming reactions to toxic cathode materials, that can produce even more toxic organometallics, is a severe drawback, that prohibits application of these methods to larger scale processes for environmental reasons.

To overcome this disadvantage we investigated the use of nontoxic graphite as cathode material, which also exhibits a sizable hydrogen overvoltage. In the reduction of benzaldehyde (**1**) we found that in water/dioxane 69 % benzpinacol (**2**) could be obtained in a potential controlled electrolysis in a divided cell (eq.1). This procedure could then be simplified to a current controlled electrolysis in an undivided cell affording a nearly quantitative yield of benzpinacol. These conditions permitted then the use of a capillary gap cell for larger scale conversions yielding 61% **2**. The scope of the reaction was then extended to substituted benzaldehydes (4-MeO: 76%; 4-Cl: 90 %). Aromatic ketones are reduced at more cathodic potentials than aldehydes, that makes their selective reduction in protic medium more difficult. After optimization of the reaction conditions acetophenone could be converted to 54 % 2,3-diphenyl-2,3-butandiol. Even for the aliphatic aldehydes: propanal and hexanal, that are reduced at very cathodic potentials, conditions could be found to dimerize them at a graphite cathode and in a protic electrolyte in 45 % yield.

The heterocoupling of different aliphatic aldehydes and ketones was probed with ethyl acrylate and other α,ß-unsaturated esters. After optimization of the reaction parameters the heterocoupling of ethyl acrylate (**3**) and 2-butanone (**4**) yielded 69 % of 5-ethyl-5-methyldihydrofuran-2-one (**5**) in an undivided cell at a graphite cathode and in ethanol/dioxane (eq. 2).

Also with N-benzylidene-N-benzylamine (**6**) the dimerization to the diamine **7** could be achieved at a graphite cathode, in an undivided cell and a protic electrolyte in fair yield (eq.3).

The scope of these reactions and details of their optimizations will be presented.

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