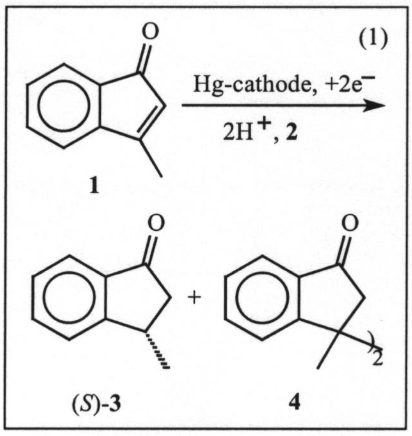
Enantioselective Electroreduction of 3-Methylinden-1-one in the Presence of Chiral Catalysts

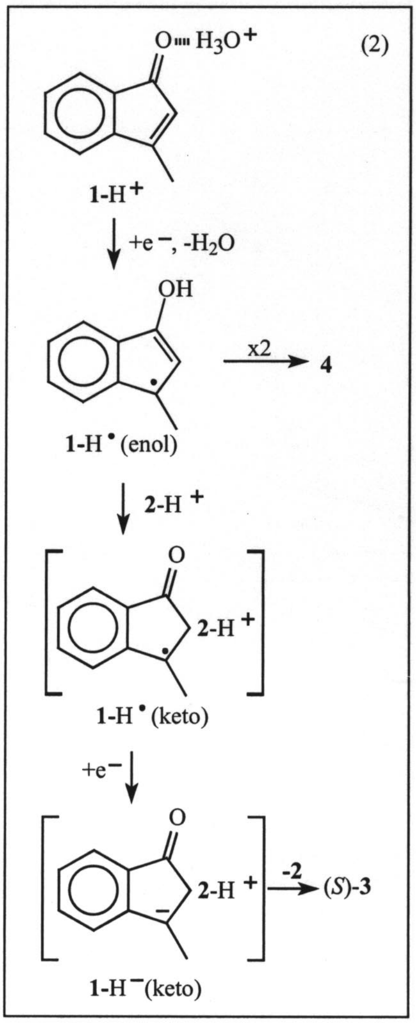
Tim Küpper and Hans J. Schäfer
Institute of Organic Chemistry, Uniersity of Münster, Correns-Str. 40, D-48149 Münster, FRG

Enantioselective chemical conversion has just been honored by the Nobel prize of 2001 in Chemistry. Whilst indirect electrolysis already leads to high enantioselectivities, the progress is less advanced in direct electrolysis.

For several reasons 3-methylinden-1-one (**1**) is a suitable substrate to study the direct cathodic enantioselective reduction.[1] Cathodic reduction of **1** in citrate buffered methanol/water in the presence of strychnine (**2**) yields 71 % of the hydrogenation product: (*S*)-3-methylindan-1-one (**3**) with 35% *ee* (enantiomeric excess) together with the hydrodimer **4** as side product (eq. 1). Based on cyclovoltammetric measurements and preparative scale electrolysis, we developed a mechanistic scheme (eq. 2) for this enantioselective reduction. According to this scheme protonated **1** is reduced in a one electron reduction to an intermediate enol radical **1-H**$^+$(enol), which is tautomerized by protonated strychnine (**2**-H$^+$) to the more easily reducible keto radical **1**-H· (keto) to the indanonyl anion 1-H$^-$(keto), that is enantioselectively protonated to enantioenriched (*S*)-**3**. The fast tautomerization suppresses the radical dimerization of the enol radical to **4** and favors the formation of **3**.

The mecahnistic scheme enabled us not only to explain the experimental results but also to design non racemic catalysts with a much simpler structure than strychnine (**2**) as for example (*L*)-N-Methylprolinoctadecylester, which led to 66 % (*S*)-**3** with 26% *ee*.





---

[1] For results on a related compound see: R.N. Gourley, P.G. Millar, J. Grimshaw, Chem. Commun. **1967**, 1278; M.F.Nielsen, H.J.Schäfer, E.U.Würthwein, T. Löhl, B. Batanero, R. Fröhlich, Chem. Eur. J. *2* (**1997**), 2011.