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Electrochemical Epoxidation of Electron-Poor Olefins Using Silver Bipyridine Based Redox Mediators

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Abstract: Electrogenerated and regenerated silver(III)oxo bis(2,2′-bipyridine) and similar complexes can act as redox catalysts for the indirect electrochemical epoxidation of electron-deficient olefins in aqueous acetonitrile. Thus, isobutyl methacrylate is electrolyzed to form the epoxide with 87% material yield and 21% current yield.

The epoxidation of alkenes is one of the most important technical oxidations. Thus, the formation of ethylene oxide from ethylene is performed worldwide with a capacity of about 8 million tons per year applying heterogeneous catalysis with a silver based catalyst[1]. However, propylene oxide already has to be produced differently because of lacking selectivity. This is also true for other higher epoxides. Therefore, in these cases, either the chlorohydrine process or the oxirane process using hydroperoxides has to be applied, both producing couple products or being dependent on chlorine production. An electrochemical process in homogeneous solution would solve this problem because no couple products are formed, and the anode behaves as a clean, reagent-free oxidant. However, this reaction does not proceed directly at the anode but needs an electrogenerated oxygen transfer mediator. Such a process has first been established by *van der Eijk*[2]. In this case, silver acetate (120 mM) was used as a mediator in a mixed solvent system of either aqueous trifluoro acetic acid or aqueous acetic acid and pyridine. The active species formed at the anode is supposed to be the silver(III)oxo bis(pyridine) complex formed via disproportionation of the silver (II) tetrakis(pyridine) complex in the presence of water. Such a disproportionation has already been described in the case of the water oxidation by silver(II) in acidic solution[3]. Thus, simple short-chain alkenes could be transformed to the epoxides in high yields. However, the application of high concentrations of silver salts (120mM) together with high concentrations of pyridine (1.2M) and trifluoro acetic acid or acetic acid is a severe limitation.

We found that high concentrations of the catalyst and of the cosolvent pyridine can be avoided by performing an indirect electrochemical epoxidation procedure using silver(I) bis(2,2′-bipyridine) and similar complexes as mediators in aqueous acetonitrile (CH₃CN(0.1 M LiClO₄) / H₂O = 19:1) instead of the trifluoro acetic acid / pyridine solvent system. The electrolysis is carried out in a divided cell (see Fig. 1) equipped with a platinum or graphite foil (Sigraflex®) anode (12.5 cm²), a silver or platinum wire cathode, and an anion exchange membrane (Nepton A 103 PZL 183, Serva; or Neosepta® AM1, Tokuyama Soda).
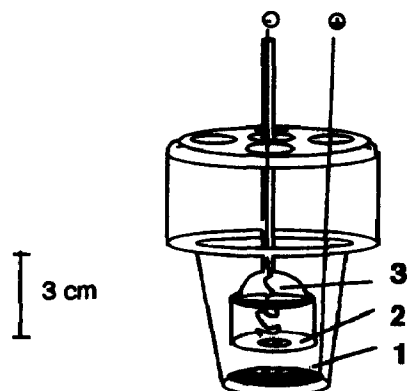
Figure 1: Divided electrolysis cell for the silver bipyridine mediated epoxidation of alkenes [1: anode (platinum or Sigraflex® graphite foil); 2: anion exchange membrane (held in place by a quickfit); 3: platinum or silver wire cathode]

The optimization using 1-hexene as starting material according to Scheme 1 gave the following results:

1. The silver bipyridine complex can be formed in situ starting from silver(I) acetate and 2,2'-bipyridine. A silver(I) to bipyridine ratio of 1:2 is totally sufficient. Higher concentrations of the ligand result in lower current yields. A silver concentration between 2 and 5 mM should be used.

2. A higher ratio of starting material to silver(I) leads to higher material yields, and up to an certain value also to better current yields. A silver(I) to hexene ratio between 1:20 and 1:80 gives best results.

3. The presence of small amounts of water is necessary. Thus, an acetonitrile to water ratio of 19:1 is used.

4. An efficient separation of the anode and cathode compartments is necessary, and most easily obtained by using an anion exchange membrane.

5. Sigraflex® graphite foil as anode material results in much higher current yields than the use of platinum. At platinum anodes, electrode passivation is observed, too.

6. The current density should be small.
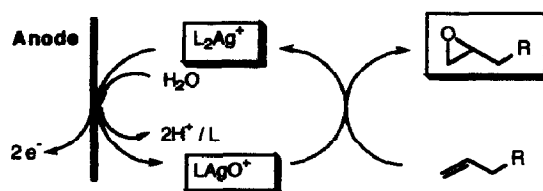
Scheme 1: Schematic representation of the indirect electrochemical epoxidation of alkenes (L = 2,2'-bipyridine or similar ligands)

Under these optimized conditions the reaction represented in equation 1 was performed using AgOAc (10 mM), 2,2'-bipyridine (20mM), 1-hexene (0.8M) in 20ml acetonitrile (0.1 M $LiClO_4$)/water (19:1) at a current density

of 2.3 mA/cm². As catholyte, a 5:2 mixture of acetonitrile (0.1 M LiClO₄) and 0.5 M aqueous sulfuric acid was used. 1-Hexene oxide was obtained with a current yield of 30%. A current yield of 33% is reached with a Ag(I) to substrate ratio of 1:20. Because of the high volatility of 1-hexene, the material yield could not be determined. However, the epoxide was formed as the only product.

$$\text{AgOAc / bipy / Anode} \quad \xrightarrow{\text{ACN (0.1M LiClO}_4\text{) / H}_2\text{O}}$$

(1)
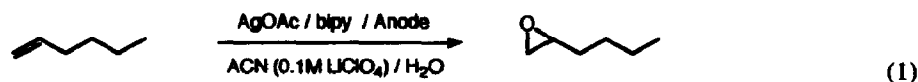
Under similar conditions (Ag(I)/substrate ratio = 1:20; current density 5 mA/cm²) isobutyl methacrylate was epoxidized (eq. 2) with 80% material yield and 24% current yield. With a mediator (1 mM AgOAc) to substrate ratio of even 1:400, the material yield was 87%, and the current yield 21%. In a blind experiment without any silver ions present, no epoxide was formed.

$$\xrightarrow[\text{ACN (0.1M LiClO}_4\text{) / H}_2\text{O}]{\text{AgOAc / bipy / Anode}}$$

87%

(2)
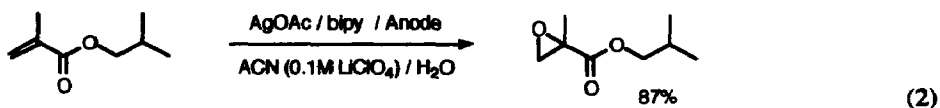
The current yield depends essentially on the current density; the lower the current density, the higher the current yield. This can be rationalized by the fact that the chemical follow-up reaction of the electrogenerated [Ag(II)(bipy)₂]²⁺ under regeneration of Ag(I) is rather slow. Therefore, higher concentrations of Ag(I) will allow for higher current densities and better current yields. Figure 2 shows the dependence of the current yield (cy) and the material yield (my) on the Ag(I) concentration for the epoxidation of isobutyl methacrylate.
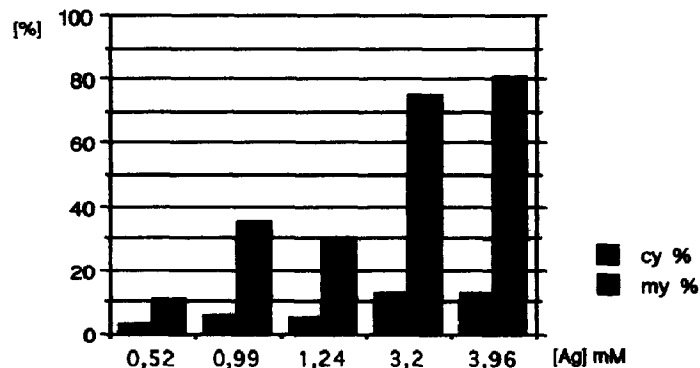

Figure 2: Dependence of the current yield (cy) and material yield (my) on the Ag(I) concentration for the epoxidation of isobutyl methacrylate at a current density of 5 mA/cm² after consumption of 10 F/mol.

Similarly, methyl-2-octenoate, dimethyl glutaconate, and isophorone could be epoxidized. Methyl (E)-2-octenoate was electrolyzed at 3 mA/cm² using a Ag(I) concentration of 2.65 mM with a Ag(I)/substrate ratio of 1:22.5. After consumption of 8 F/mol, the trans-epoxide[4] was obtained with 80% material yield (eq. 3) and 20% current yield.

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(3)
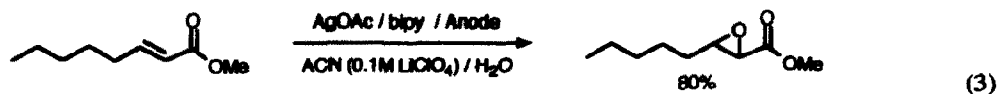
Under similar conditions, (E)-dimethyl glutaconate was oxidized to the *trans*-epoxide with 90% material yield and 20% current yield (eq. 4).

(4)
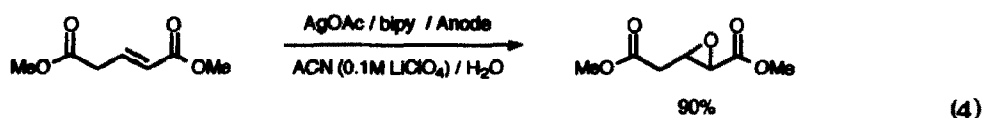
The epoxidation of isophorone was not totally selective. Besides the expected epoxide, the products of the allyl oxidation, 2,5,5-trimethylcyclohexen-1,4-dione and 2,5,5-trimethyl-4-hydroxy-cyclohexenone, were obtained as side products.

Methyl-2-octenoate was also oxidized using the chiral (1'S, 5'R,7'R)-2-hydroxy-9-(10,10-dimethyl-4-aza-3,3-dioxo-3-thiatricyclo[5.2.1.0$^{1.5}$]decan-4-yl)-1,10-phenanthroline silver(I) tetrafluoroborate complex as catalyst[5]. Using a 31 mM concentration of the complex and a Ag(I)/substrate ratio of 1:36, 4 F/mol of electricity were passed at 5 mA/cm^2. The *trans*-epoxide was obtained with 80% material yield and 20% current yield, but only in racemic form. This result may indicate that the oxygen transfer occurs in a stepwise fashion.

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