

Addition of Alcohol to Olefinic Bonds by Paired Electrosynthesis  
with Raney-Nickel Cathode

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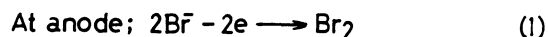
A one-pot addition reaction of an alcohol to an olefinic double bond was successfully performed by use of paired electrosynthesis with a Raney-nickel cathode.

Paired electrolysis provides sometimes convenient ways to produce useful compounds. Of great importance in the electrolyses of this category is the choice of the electrode material. Raney-nickel (R-Ni) would be one of the most interesting candidates. Park et al.<sup>1)</sup> proved the usefulness of such electrodes, although they used R-Ni for an independent cathodic reaction. We report here a one-pot addition reaction of an alcohol to a carbon-carbon double bond by paired electrosynthesis, taking advantage of the unique characteristics<sup>2)-4)</sup> of the R-Ni cathode.

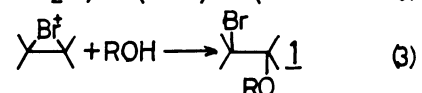
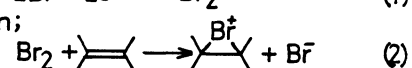
The electrolysis was carried out using a conventional cylinder-type cell without a separator using a constant current (100 mA). The cathode was R-Ni powder (1 g) dispersed onto a nickel plate (14 cm<sup>2</sup>) and the anode a graphite plate (10 cm<sup>2</sup>). R-Ni was prepared according to the reported procedure.<sup>4)</sup> The electrolyte consisted of an alcoholic (methanol, ethanol, n-propanol, or iso-propanol) solution (50 cm<sup>3</sup>) of a substrate (20 mmol/dm<sup>3</sup>) and tetraethylammonium bromide (20 mmol/dm<sup>3</sup>). The latter acts as a reactant as well as a supporting electrolyte.

The results of the present paired electrosynthesis are summarized in Table 1. The yields for methoxylated or ethoxylated products are satisfactory. The use of n-propanol or iso-propanol as a solvent resulted in relatively low yields due to the poor nucleophilicity. Cyclooctene has a lower solubility than the other substrates, and thus it tends to adsorb on the R-Ni cathode surface, forming cyclooctane. In methanol, 1-octene yielded mainly the 2-methoxy form. It is emphasized that among various cathodes investigated only R-Ni shows a marked ability for production of the desired alkoxy products.

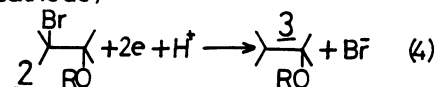
A plausible reaction mechanism of the present paired electrosynthesis is shown



In solution;



At R-Ni cathode;



Scheme 1. Plausible reaction mechanism.

in Scheme 1. At anode, bromide ion is oxidized to bromine. Then, bromine reacts with an olefin(1) to yield a bromoalkoxyl product(2) in solution.<sup>2)</sup> The cathodic reaction is the reductive dehalogenation yielding alkoxyalkane(3). This process proceeded smoothly on the R-Ni cathode. A Pd-C cathode showed slight activity for the dehalogenation. Other electrodes showed almost no activity as shown in Table 1. Repeated electrolyses by the addition of the olefins to the electrolysis solution provided almost

the same yield of alkoxy products. The ordinary catalytic dehalogenation of 1-bromo-2-methoxycyclohexane with R-Ni in the same solution showed only 11% yield. The addition of a large amount of a base (NaOMe) markedly improved the yield. Thus, we postulate that an electrogenerated base (probably alkoxide ion) plays an important role in the present electrolysis.

The overall reaction of the present electrolysis is the addition of the alcohol to the double bond and bromide ion acts as a mediator. The direct addition of alcohols to double bonds is difficult by ordinary chemical syntheses and the introduction was usually been done by stepwise reactions. The current efficiencies in this reaction were low (5-20%) due to the consumption of charge for the side reaction of the production of bromine and its reduction. However, the electrolysis with a divided cell has revealed that the individual cathodic and anodic reactions proceed smoothly and result in high current efficiencies (>80%). Therefore, the use of suitable electrolytic cells such as of flow-type cells with optimised electrolyte composition will improve the current efficiency.

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Table 1. Addition of alcohol to olefins by paired electrolysis

| Cathode<br>(area or weight)    | Substrate                      | Solvent | Yield a)/%      |
|--------------------------------|--------------------------------|---------|-----------------|
| R-Ni(1 g)                      | cyclohexene(4)                 | MeOH    | 83              |
|                                | 4                              | EtOH    | 72              |
|                                | 4                              | n-PrOH  | 30              |
|                                | 4                              | i-PrOH  | 32              |
|                                | cyclooctene(5)                 | MeOH    | 39              |
|                                |                                | EtOH    | 39              |
|                                | 1-octene                       | MeOH    | 57(1-,17;2-,40) |
|                                | trans-2-octene                 | MeOH    | 93(2-,52;3-,41) |
|                                | cis-2-octene                   | MeOH    | 77(2-,50;3-,27) |
|                                | Ni plate (14 cm <sup>2</sup> ) | 4       | MeOH            |
| Graphite (10 cm <sup>2</sup> ) | 4                              | MeOH    | 0               |
| Pb (4 cm <sup>2</sup> )        | 4                              | MeOH    | 0               |
| Pd-C (0.5 g)                   | 4                              | MeOH    | 30              |
| Pt-C (0.5 g)                   | 4                              | MeOH    | 3               |

a) For alkoxy products.

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