ELECTROLYTIC REDUCTIVE COUPLING. ADDITION OF PERFLUOROALKYLIODIDES TO ALCENES

Patrick CALAS and Auguste COMMEYRAS

Laboratoire de Chimie Organique, USTL, Montpellier Cédex France

Addition of perfluoroalkyliodides (R_FI) to alcenes has been and is extensively studied using radical initiators and UV light irradiation.

In this work, the addition of R_FI ($R_F = CF_3(CF_2)_n$ n = 4,6,8) to allylic and propargylic alcohol, and to diallyl ether is performed using and electrochemical initiation.

Electrolysis is realised in two kinds of cell :

- mercury cathode, DMF, $LiClO_4$ electrolyte.
- fiber carbon cathode, water Kcl electrolyte.

We obtain addition compounds and/or products resulting from the electrochemical increase of pH in the catholyte.

When using an aqueous electrolyte, the organic phase is dispersed in water. This heterogeneous electrolysis appears as a very quick, high yield route, expected compounds being obtained in a pure phase.

The mechanism observed when working with allylic alcohol is :

Fiber carbon cathode : $R_FI + e^- \longrightarrow R^{\cdot}_F + I^-$

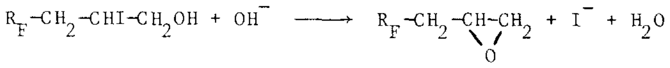
$$\begin{tikzcd} R^{\cdot}_F + CH_2{=}CH{-}CH_2OH \arrow[r] & R_F{-}CH_2{-}\dot{C}H{-}CH_2OH \\ & + \\ R^{\cdot}_F + R_F{-}CH_2{-}CHI{-}CH_2OH \arrow[uu] & R_FI \arrow[l] \end{tikzcd}$$

carbon anode : $I^- - e^- \longrightarrow 1/2\ I_2$.

The formation of the iodhydrine appears as resulting from a radical catalytic process initiated by the electrochemical reduction of R_FI.

When the organic phase ($R_FI + CH_2 = CH{-}CH_2OH$) is completely converted to iodhydrine, the electrolysis of the water phase produces an increase of pH in the catholyte.

Consequently, the iodhydrine is converted to the epoxide :



$$R_F{-}CH_2{-}CHI{-}CH_2OH + OH^- \longrightarrow R_F{-}CH_2{-}\underset{O}{CH{-}CH_2} + I^- + H_2O$$

Similar reactions have been performed :