# REDUCTIVE COUPLING OF FLUOROLEFINES

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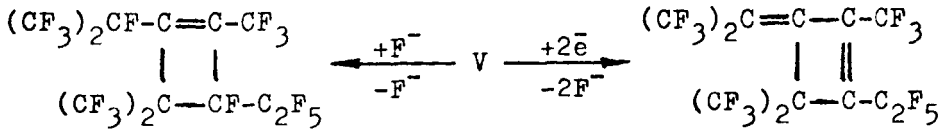
Perfluorolefines at cathodic reduction or with one-electron donor reagent ($C_{10}H_8Na$) in aprotic solvents undergo to the defluorination with formation of new double bonds. Such defluorination in the case of perfluoro-2-methylpentene-2 (I) is accompanied by the dimerization and cyclization producing cyclo-butene $C_{12}F_{22}$ (II) and diene $C_{12}F_{20}$ (III) in 40 to 70% yields. The proposed reaction scheme includes the next steps: (a) - the successive two-electron transfer on olefine with elimination of $F^-$ and formation of the anion (IV); (b) - the nucleophilic attack of the double bond by IV and the following cyclization giving olefine (V);

$$(CF_3)_2C{=}CF{-}C_2F_5\ (I) + 2e \xrightarrow{-F^-} (CF_3)_2C{=}CF{-}\bar{C}F{-}CF_3\ (IV) \quad (a)$$

$$I \xrightarrow{IV} \begin{matrix}(CF_3)_2C{=}CF{-}CF{-}CF_3\\ \quad\quad\quad\quad\ |\\ (CF_3)_2C{-}CF{-}C_2F_5\end{matrix} \xrightarrow{-F^-} \begin{matrix}(CF_3)_2C{=}C{-}CF{-}CF_3\\ \quad\quad\quad\ |\ \ |\\ (CF_3)_2C{-}CF{-}C_2F_5\end{matrix} \quad (b)$$

(V)

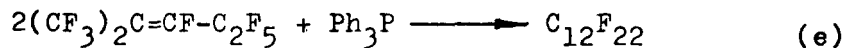
(c) - the isomerization of V into the more stable butene II and/or (d) - the furthur reduction and defluorination of V.



(II) (III)

The nucleophilic isomerization of V is a main process at electrolysis of I in the presence of fluoride ion at low current density (II:III = 10:1). The furthur defluorination becomes preferable pathway when electrolysis of I is carried out at high current density and with $Et_4NBF_4$ as a supporting electrolyte (II:III = 1:9).

I undergoes similar defluorination and coupling reactions with some three-valent phosphorus compounds.



(I) (VI) (e)

However, the structure of VI occurs to be different from II and so the coupling reaction *via* a nucleophilic addition (e) leads to another products as compared with the electron-transfer reactions.