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A NEW ROUTE TO PERFLUOROKETONES VIA THE ELECTROCHEMICAL OXIDATION OF SECOND HYDRYL-F-ALKANES AND F-CYCLOALKANES

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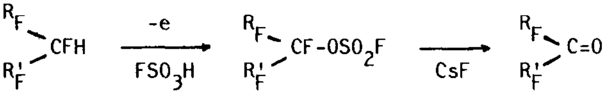
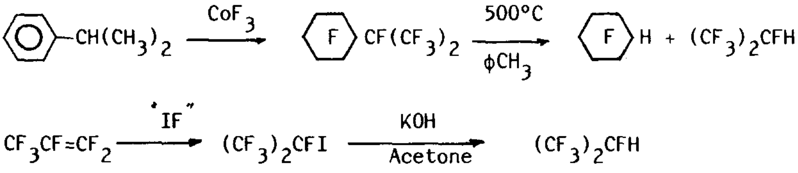
A new route to perfluoroketones and their derivatives was investigated via the electrochemical oxidation of secondary hydryl-F-alkanes and F-cycloalkanes according to the following reactions :



Starting fluorocarbon materials are prepared using fluorination of hydrocarbons with cobalt trifluoride and/or chemical modifications :



Anodic oxidation of secondary hydryl-F-alkanes $R_FR'_FCFH$ carried out in fluorosulfuric acid leads to the formation of the fluorosulfuric ester $R_FR'_FCFOSO_2F$ via the action of the peroxide $(FSO_3)_2$. A CIDNP phenomenon is observed on the ^{19}F NMR spectra at the signal of the fluorine atom α to the OSO_2F group of the perfluoroester. The application of Kaptein's rule shows that the mechanism involves the formation of a radical pair from the encounter of freely diffusing radicals $FSO_3^{\bullet}$ and $R_FR'_FCF^{\bullet}$ as :

$$2FSO_3^- \xrightleftharpoons{-2e} 2FSO_3^{\bullet}$$

$$FSO_3^{\bullet} + R_FR_F'CFH \longrightarrow FSO_3H + R_FR_F'CF^{\bullet}$$

$$FSO_3^{\bullet} + R_FR_F'CF^{\bullet} \longrightarrow \overline{FSO_3^{\bullet}\,{}^{\bullet}CFR_FR_F'}^{F} \longrightarrow FSO_2OCFR_FR_F'$$

The ester can be hydrolysed in basic aqueous medium to give ketone dihydrate or heated in the presence of anhydrous cesium fluoride to give pure perfluoroketone in good yield.

These results can clearly be extended to other unsymmetrical perfluoro-analogues (R_F R_F') and possibly perfluoropolyketones.