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SHORT COMMUNICATION

Oxidative Cleavage of Partially or Perfluorinated Olefins by Ruthenium Tetroxide

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Regents for the oxidation of olefins in solution often proceed through pentacyclic intermediates and give addition or cleavage products. One of these reagents, ruthenium tetroxide gives cleavage products in high yield from various alkenes [1] and olefinic polymers [2]. Potasium Permanganate, the most widely used oxidant for fluoro olefins, is used for the fission of double bonds and production of fluorinated ketones and acids $[3,4_a]$. Inorganic peroxide afford fluorocarbon epoxides [4b,5,6]. Ozonolysis, which works well with (perfluoroalkyl) ethylenic compounds [7] gives with tetrafluoroethylene [8,9] or with <u>cis</u> and <u>trans</u> difluoroethylene [10] fluorinated epoxides ozonides, and acyl fluorides as the major products. Perfluorinated polyolefins generate carbonyl difluoride among other products [11]. Other weak oxidizing reagents have a low selectivity, for example with hexafluoropropene [12].

Since electron-donor substituents clearly accelerate the reaction with ozone or moderately with several oxoreagents [1], one can predict that the oxidation of fluoro-olefins that bear a highly electron withdrawing group F, CP_3 or R_p will be difficult.

The aim of this paper is to examine the yields and specificity of cleavage in the oxidation of partially or perfluoro-olefins with ruthenium tetroxide. Two (perfluoroalkyl) ethylenes, (perfluoro-octyl) ethylene 1 and (diperfluoro-hexyl) ethylene 2 and perfluoropropene 3 (from PCUK Lyon, France) were oxidized with a small amount of ruthenium tetroxide, which is continually regenerated during the reaction using a co-oxidant. 1 gives perfluoro-nonanoic acid and carbon dioxide, 2 gives perfluoro-heptanoic, and 3 gives perfluoroacetic acid and carbonyl difluoride. The reaction products were analyzed using ¹⁹F puclear magnetic resonance spectroscopy.

Example : 500 mg of 1 and 10 mg of ruthenium dioxide in 50 ml of freon-113 were placed under nitrogen in a threeneck round bottom flask equipped with a magnetic stirring bar and with a gas trap for collecting volatile products. Peracetic acid (or periodic acid or sodium hypochlorite) was then slowly added over about one hour. During the oxidation the color of the solution alternated between black (RuO_2) and yellow (RuO_4); at the end of the reaction, the mixture was yellow due to the remaining ruthenium tetroxide. The excess oxoreagent was destroyed by addition of methanol. The solution was filtered and evaporated under reduced pressure and the resulting perfluoro-carboxylic acid was then sublimed to give 480 mg, 92%. For 1 the yield can also be easily determined from the quantity of carbon dioxide that is evolved.

The ¹⁹F chemical shifts for 1 and 2 in carbon tetrachloride in ppm with reference to CFCl₃ at 56,44 MHz (JEOL C 60 HL) were : $CF_3^{-}(81.8)$, $CF_3^{-}CF_2^{-}(126.8)$, $-CF_2^{-}(122.1)$ and 124), $-CF_2^{-}CH=(114.8)$. The corresponding perfluoro-carbocyclic acids in ethanol gave : $CF_3^{-}(81.6)$, $CF_2^{-}CF_2^{-}(126.6)$, $-CF_2^{-}(122.1)$ and 123), $-CR_2^{-}COOH$ (118.8) in good agreement with the signals of authentic perfluoro-beptanoic acid and with the literature values [13]. The absence of a signal at 114.8 ppm in the spectra of the perfluorocarboxyclic acids is a clear indication of total oxidation of the starting materials. The ratio of the integration of the signals of inner $-CF_2^{-}$, relative to CF_3 or $-CF_2^{-}$ -COOH gives the expected value and therefore indicates that no cleavage occurred in the perfluoripated chain. ¹⁹F nmr using standardized solutions was used to determine the yield of the trifluoroacetic acid, the reaction product form 3.

Although no reactions rates were determined, no large differences in total reaction times were observed using 1-octene [2] and the olefins 1,2,3. This is consistent with previous work : (i) the reaction rates of ozone with E-2 butene and with perfluoropropene are also of the same order of magnitude [14], (ii) activation energy values, in kcal mol⁻¹, for the addition of trichloromethyl radicals to olefins vary pon-monotonously versus the number of fluorine atoms ; ethylene 2.2, 1,1-difluoroethylene 5.2,

tetrafluoroetnylene 3.7 [15] (iii) there is a variation in the same sense for π bond dissociation energies, obtained from thermochemical data in kcal mol⁻¹ in the series, ethylene (59.0), 1-1 diffuoroetnulene (62.8) and tetrafluoroetnylene (52.5) [16]. It seems that for these reactions, there is a greater similarity in the chemical reactivities of non-fluoro-olefins and perfluoro-olefins than one might have predicted.

In conclusion, rurnenium terroxide has been shown to be a powerful yet clean and selective oxoreagent for the high yield cleavage of fluoroolefins.

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