Synthesis of fluorinated ethers from fluoroolefins and polyatomic alcohols.

V.M Andriushin, V.V.Kirillov

Part II. Ether fluorination on the basis of fluoroolefins and polyatomic alcohols.

The regime of substitution of hydrogen atoms with fluorine by direct fluorination was preliminarily carried out using the formals of the general formula $Rf\text{-}OCH_2O\text{-}Rf$ (where Rf is the residue of telomeric alcohol) which are close analogues of the ethers described in Part I. Such formals are stable enough components and therefore were convenient model compounds. Instability ascribed to them is connected in fact with the presence of admixtures of diformals of $Rf\text{-}OCH_2OCH_2O\text{-}Rf$ structure which are thermally and chemically unstable indeed.

It is easy to produce the mentioned formals and the goal compounds may be produced in quantitative yield and with good quality if one takes a telomeric alcohol carefully purified and a big excess of acid to bind separating water.

The fluorination of formals was carried out in R-113 medium at a mole ratio of Formal/R-113= 1:10 at a temperature from -20^o to 20^{o}C and a fluorine concentration in a fluorine-nitrogen mixture of 16 to 99%. The interaction is absent under "soft" conditions (low temperature, diluted fluorine), an increase in temperature leads to the complete molecule destruction almost without any transition zone. The treatment of the formals with undiluted fluorine within the temperature range of -20^{o}C to -5^{o}C results in 6 products of substitution and 4 products of decomposition identified by GLC, IR- and NMR-spectroscopy methods. The fluorination starts at -20^{o}C and runs smoothly up to the formation of mono- and difluoro-derivatives, then a temperature increase to -15^{o}C - (-10^{o}C) is required. At a higher temperature, only destruction products were isolated.

Ethers of structure $(CF_3)_2\ CH\text{-}CF_2OCH_2(CF_2CF_2)_nH$ behave similarly.

The procedure worked out on model compounds was used in fluorination of goal compounds also. Ether based on ethylene glycol and trifluorochloroethane was of our greatest interest. As it had been expected, the results of its fluorination were more successful: substitution of hydrogen took place rather smoothly to complete fluorination of the fluorine central fragment. The destruction degree did not exceed 20-30%. Gradual increase in temperature from -20^{o}C to -5^{o}C resulted in the reaction mixture of the following approximate composition: 65-66% of monofluoroderivative, 15-16% of difluoro-, 12-13% of trifluoro- and 3-

4% of perfluoroderivatives of the diether (with regard to the central fragment). Attempts to increase the polyfluoroether share by toughening the reaction conditions or by increasing the contact time led only to increasing the destruction degree.

Isolation of separate components of the reaction mixture and their further fluorination is possible but it is not expedient technologically. Therefore, a procedure to produce perfluoroderivatives using the Swarts exchange reaction has been developed. The formal on the basis of telomeric alcohol (n=1) and diether on the basis of ethylene glycol and trifluoroethylene were studied.

First, the chlorination of the starting compounds was carried out to the most possibly complete degree, then the chlorine atoms were substituted with fluorine.

The chlorination was carried out in different ways. The easiest and the most effective route was the chlorination with elemental chlorine under irradiation. The chlorination runs according to the conventional scheme, the radical mechanism. The chlorination should be stopped at the content of tetrachloro-derivative of 34-35% to avoid the destruction process.

The analysis of literature data on the conditions of the Swarts reaction shows that the reaction conditions in our case should be harsh enough. Therefore, antimony pentafluoride has been chosen as a fluorinating agent. The reaction was carried out at a smooth temperature increase from 20^{o}C to 250^{o}C at vigorous stirring.

The intermediate and end diethers were isolated as individual compounds and characterized by the mentioned methods:

$Cl_2CF\text{-}CF_2\text{-}O\text{-}CF_2\text{-}CCl_2\text{-}O\text{-}CF_2\text{-}CFCl_2$ b.p.=112^{o}C,

$Cl_2CF\ \text{-}CF_2O\text{-}CCl_2\text{-}CCl_2\text{-}O\text{-}CF_2\text{-}CFCl_2$ b.p.= 122^{o}C,

$Cl_2CF\text{-}CF_2\text{-}O\text{-}CF_2\text{-}CF_2\text{-}O\text{-}CF_2\text{-}CF_2Cl$ b.p.=107^{o}C

The latter is of great practical interest as an intermediate product in synthesis of dibasic perfluorooxacaronic acids and their derivatives by means of substitution of the chlorine atoms for necessary functional groups.

Conclusion

The presented materials allow to conclude that the proposed synthesis scheme may be used (after additional process development) for production of fluorinated di-, tri- and tetraethers and derivatives on their basis.