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PRELIMINARY NOTE

Relative Reactivities of Isomeric Perfluoroalkenes

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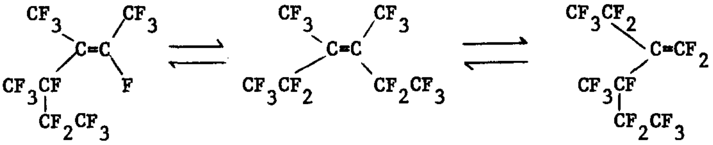
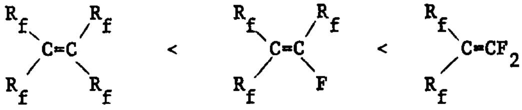
We have already reported on some reactions of perfluoro-3,4-dimethyl-3-hexene (1) with O-nucleophiles and the products are derived from attack on both (1) and its isomer (2), which are apparently in equilibrium in solution and in the presence of fluoride ion [1].



(2) (E and Z isomers)

(1) (E and Z isomers)

(3)



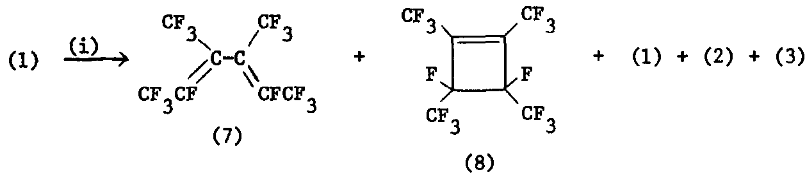
(6) < (5) < (4)

R_f = perfluoroalkyl

There is ample evidence in the literature to illustrate that perfluorinated alkenes containing a terminal difluoromethylene group (4) are more reactive towards nucleophiles than those with an internal double bond

[3]. Also, there is evidence to indicate that systems with a vinylic fluorine atom (5) are more reactive than systems with four perfluoroalkyl groups attached to the double bond (6) [1,3,4]. We are now able to demonstrate the relative reactivities of a series of isomers corresponding to (4), (5), and (6).

We have previously reported [5] that defluorination occurs when (1) is passed over iron, in a stream of nitrogen, at elevated temperatures.



(i) short contact, unactivated Fe surface, 540°

However, under conditions of short contact time and using a fresh i.e. unactivated iron surface, the product contained (7) and (8) ca. 50% together with C_8F_{16} which was, in fact, a mixture containing the starting material (1) and the isomers (2) and (3), (ratio 2:2:1). Isomerization also occurs to a limited extent over platinum at the same temperature. A mixture containing (1) - (3) was obtained by distillation but the isomers could only be partly resolved by preparative scale g.l.c. However, the structures of (2) and (3) followed simply from the ^{19}F n.m.r. spectra of samples containing different proportions of (2) and (3).

$$(1) + (2) + (3) \xrightarrow[\text{R.T.}]{\text{MeOH}} \text{products} + (1) + (2) \xrightarrow[\text{Reflux}]{\text{MeOH}} \text{products} + (1)$$

Reaction of the mixture of isomers (1) - (3) with neutral methanol at room temperature gave products from isomer (3) only. The remaining mixture of (1) and (2) was heated under reflux with methanol and then only isomer (2) reacted under these conditions. Isomer (1), however, was recovered unchanged from this sequence. Therefore, these observations quite clearly demonstrate the reactivity order for an isomeric system (4) > (5) > (6) which, with neutral methanol, is sufficiently different to allow complete selectivity of reaction.

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3 H.H. Evans, R. Fields, R.N. Haszeldine, and M. Illingworth, J. Chem. Soc. Perkin I (1973) 649.

4 K.N. Makarov, L.L. Gervits, Yu. A. Cheburkov and I.L. Knunyants, J. Fluorine Chem., 10 (1977) 323.

5 R.D. Chambers, A.A. Lindley, H.C. Fielding, J.S. Moilliet and G. Whittaker, J. Chem. Soc. Chem. Comm. (1978) 475.