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A Novel Furan Synthesis

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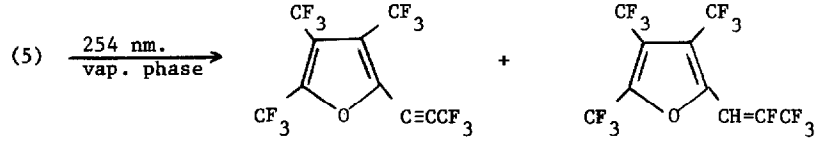
Summary. γ-ray induced addition of acetaldehyde to perfluoro-3,4-dimethyl-3-hexene gives a product which, in two novel steps, may be converted to a fluorinated furan.

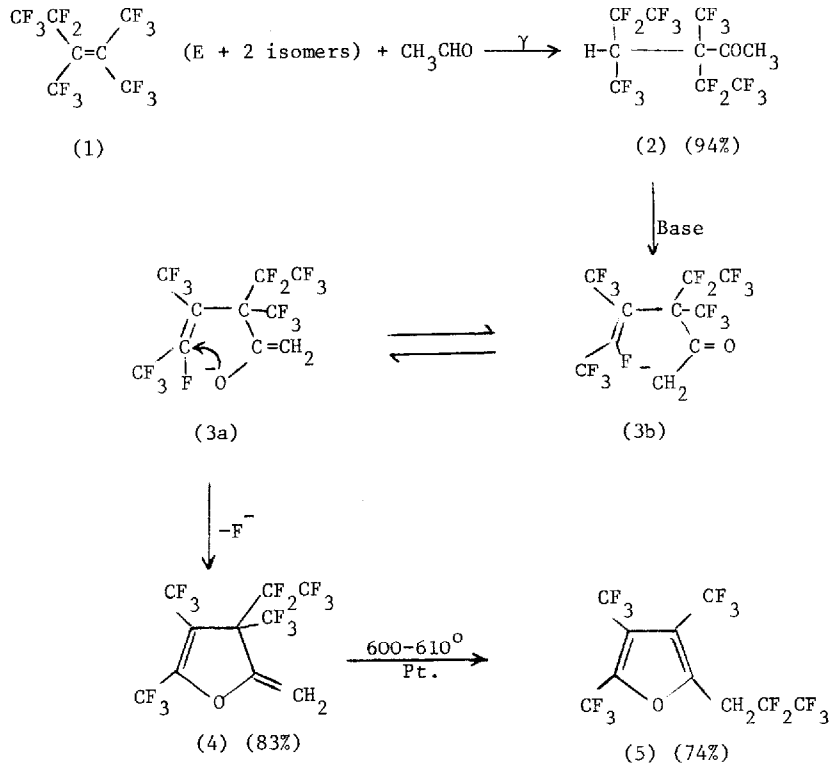
In pursuing the unusual chemistry of fluorinated olefins of the type $(R_F)_2C{=}C(R_F)_2$ [1] (where R_F is a perfluoroalkyl group) we find that free-radical addition of acetaldehyde to perfluoro-3,4-dimethyl-3-hexene (1) occurs in very high yield, by γ-ray initiation giving compound (2).

Reaction of (2) with tri-n-butylamine in tetraglyme induced a novel cyclisation, which is shown in the Reaction Scheme. This cyclisation step is interesting because it involves exclusive attack through oxygen (3a), rather than carbon (3b) in the enolate anion. Consequently, this step is a useful demonstration of the 'hardness' of a site $F\overset{\delta-}{-}C\overset{\delta+}{=}C$ towards nucleophilic attack.

Pyrolysis of the cyclic compound (4) led to an efficient 1,3-sigmatropic shift of pentafluoroethyl, giving the new fluorinated furan (5). The chemistry of (5) and its precursors (2) and (4) is under investigation. Surprisingly, photolysis of (5) did not give ring opening, which has been reported for other fluorinated furans,[2] but instead, loss of hydrogen fluoride, giving derivatives (6) and (7).



(6) (6%) (7) (54%)



Reaction Scheme

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REFERENCES

1. See R.D. Chambers, A.A. Lindley, P.D. Philpot, H.C. Fielding, J. Hutchinson, and G. Whittaker, J.C.S. Perkin I, 1979, 214, and references contained.

2. R.D. Chambers, A.A. Lindley, and H.C. Fielding, J. Fluorine Chem., 1978, 12, 337.

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