Perfluorinated Derivatives of Furan *via* Novel Cyclisation Reactions of Perfluoro-olefins

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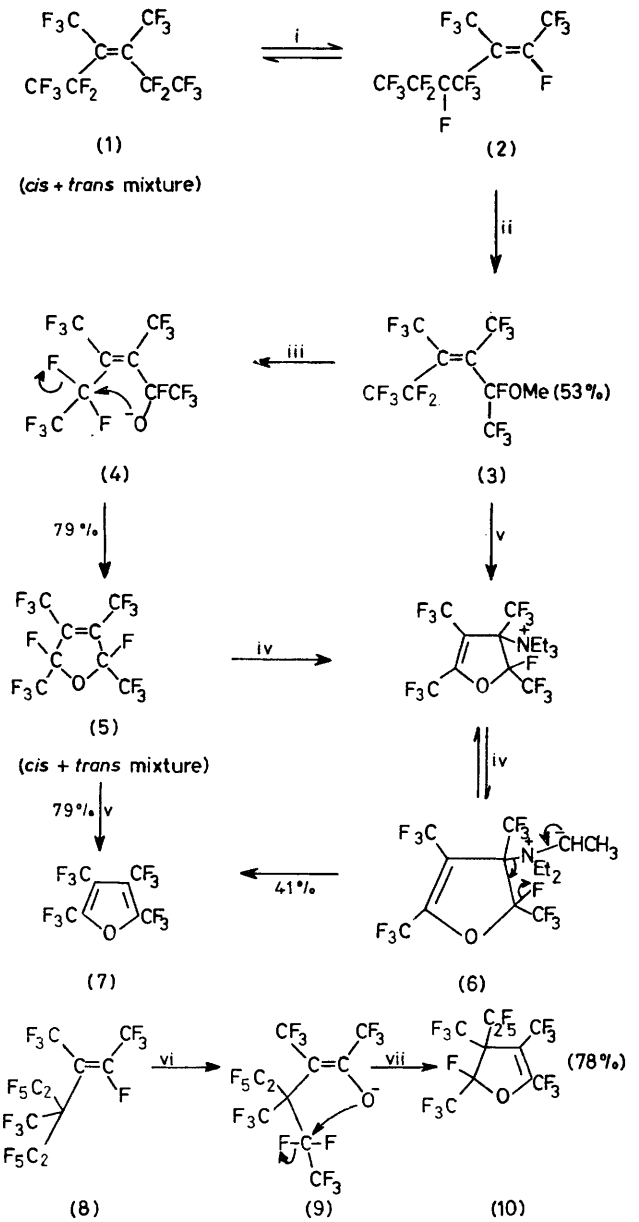
Summary Perfluorotetramethylfuran (**7**) is obtained in a cyclisation reaction of the perfluoro-olefin (**1**) using triethylamine and methanol, the process involving a novel defluorination; a cyclisation is described which

clearly involves the rare displacement of fluoride ion from a saturated position in a perfluoroalkyl group.

In the course of investigating the chemistry of the interesting internal olefin (**1**),[1,2] we have found that caesium fluoride induces isomerisation to (**2**), so that subsequent reaction with methanol gave a monomethyl ether (**3**) which is derived from (**2**), and not from (**1**). Reaction of (**3**) with pyridine led to ether cleavage and a novel cyclisation followed, giving (**5**). This cyclisation, of (**4**) to (**5**), is represented as an intramolecular nucleophilic displacement from a difluoromethylene group, because of a direct analogy with an example presented later. Reaction of the ether (**3**) with triethylamine gave the cyclic product (**5**) but, also obtained, was the interesting new system, perfluorotetramethylfuran (**7**). Fluoride-ion induced defluorination is known[3] but this defluorination of (**5**) to (**7**) was not effected by caesium fluoride, nor was (**7**) detected in the reaction of (**3**) with pyridine. Therefore a process involving formation and disproportionation of the ylide (**6**) is suggested. Conversion of (**5**) into (**7**) was, however, achieved more efficiently by defluorination of (**5**) over iron at 580 °C. A related cyclisation has also been observed in the reaction of the olefin (**8**)[1] with aqueous base. The enolate anion, which may be isolated as the keto-form after subsequent reaction with acid,[4] cyclises to (**10**) on heating and the important point to note is that conversion of (**9**) into (**10**) can only occur *via* an intramolecular nucleophilic displacement from a difluoromethylene group. There is little precedent for this reaction in organo-fluorine chemistry,[5] since it is well known that perfluoroalkyl groups are inert to direct nucleophilic attack, although S_N2' processes occur readily. Clearly, no S_N2' scheme can be written for the conversion of (**9**) into (**10**), although in the conversion of (4) into (5), described earlier, it is possible that (4) is in equilibrium with an isomer which could cyclise *via* an intramolecular type of S_N2' process.

Structures of the new cyclic compounds follow simply from elemental analysis and spectral data. For example, only two resonances were observed in the ^{19}F n.m.r. spectrum of (**7**): ^{19}F, δ 60 and 65 p.p.m. rel. to ext. CFCl$_3$, each consistent with CF$_3$·C=, while the spectrum of (**5**) shows two sets of signals (*ca.* 65 : 35), indicating geometric isomers: ^{19}F δ, 63 (relative intensity 3), 85 (3), and 122 (1); and 62 (3), 83 (3), and 112 (1) p.p.m. The spectrum of (**10**) showed five non-equivalent CF$_3$ groups, one CF$_2$, and one >C–F at ^{19}F δ 117 p.p.m.; *cf.* data for (**5**). It is possible that compound (**10**) is a mixture of geometric isomers but these are neither resolved by g.l.c. nor identifiable separately in the ^{19}F n.m.r. spectrum.



Reagents: i, CsF; ii, MeOH; iii, pyridine; iv, Et$_3$N; v, Fe, 580 °C; vi, H$_2$O + Et$_3$N; vii, 80—100 °C.

Added in proof. Since the manuscript was submitted, two preliminary reports[6] have described alternative syntheses of perfluorotetramethylfuran (7).

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