Journal of Fluorine Chemistry, 15 (1980) 75–78

Received: July 24, 1979

SHORT COMMUNICATION

An Unusual Oxidation

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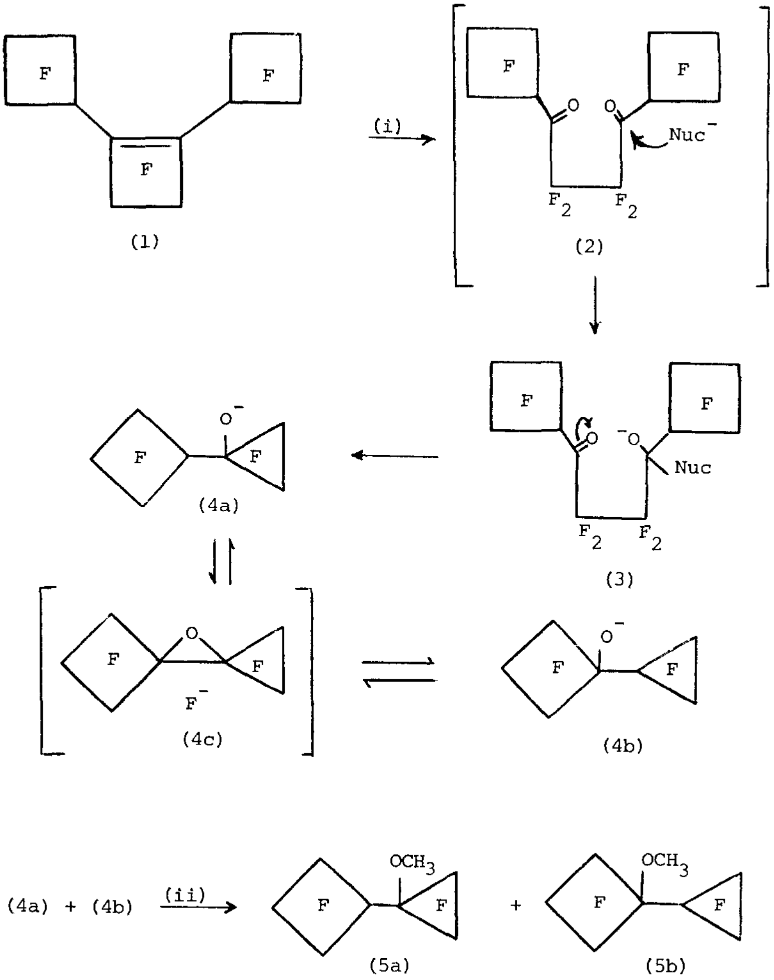
We have recently [1] found that a trimer obtained from reaction of F-cyclobutene with pyridine has structure (1), rather than the structure proposed in a very early investigation [2]. During development of the chemistry of (1) we have discovered a very unusual reaction that occurs on oxidation with potassium permanganate.

Reaction of (1) with potassium permanganate in acetone at room temperature, followed by work-up (addition of water, reaction with sulphur dioxide, ether extraction) gave a mixture of two isomers, $C_7F_{11}OH$. These could not be separated but reaction of the mixture with diazomethane in ether gave two isomeric methyl ethers (5a and 5b). These isomers were separated by preparative-scale g.l.c.; mass-spectrometry together with elemental analysis showed that each corresponds to the formula $C_8F_{11}OH_3$. Furthermore the ^{19}F n.m.r. spectrum of each isomer showed one 'tertiary' fluorine (182.7 and 185.6 p.p.m.) and five CF_2 groups (signals between 122 and 138 p.p.m.). The infrared spectra of the isomers showed no C=C stretch. Consequently, the two sites of unsaturation required by the molecular formulae of the isomers can only be accommodated by structures (5a) and (5b), although we cannot distinguish between these as yet.

A mechanism is shown in the Scheme, to account for this very unusual process. Perfluorinated alkenes of the type $(R_F)_2C{=}C(R_F)_2$ usually [3,4] give diols, rather than diketones on oxidation with potassium



(i) $KMnO_4$, acetone, room temp.

(ii) CH_2N_2, Et_2O.

Reaction Scheme

permanganate but in this case relief of strain would obviously encourage formation of (2). The steps suggested (2) → (3) → (4), promoted by nucleophilic attack, are of course related to the well known benzyl-benzylic acid process; a similar process could be written involving hydrated species of the diketone (2) and we are uncertain about the stage at which ring closure occurs. We are only able to account for the formation of (4b) from (4a) via an intermediate epoxide (4c). The latter *would be so highly strained, however, that it would understandably be only* of a transient nature.

EXPERIMENTAL

The trimer (1) (3.5 g, 7.2 mmol) in dry acetone (20 ml) was added slowly to $KMnO_4$ (1.6 g, 10.1 mmol) in dry acetone (70 ml) with rapid stirring; the addition was accompanied by vigorous reaction. When the addition was complete, the mixture was allowed to stir for 2 h. at room temperature and then poured into water (100 ml). The mixture was then decolourised with sulphur dioxide and acetone was removed on a rotary evaporator. The residue was extracted with ether, the extracts washed with water, dried ($MgSO_4$) and the ether removed on a rotary evaporator to leave a colourless liquid (2.0 g) shown by g.l.c. & ^{19}F n.m.r. to be mainly a mixture of two compounds (4a) and (4b) in acetone. The mixture was treated with a slight excess of diazomethane in ether (brisk effervescence) and the ether removed on a rotary evaporator to leave a liquid (1.7 g) shown by g.l.c. to be a mixture of two major products with a small amount of acetone and two other unidentified components. The two major products were separated by preparative scale g.l.c. to give (5a) and (5b). These were identified as 1-methoxy-F-1-cyclobutylcyclopropane and 1-methoxy-F-1-cyclopropylcyclobutane, although we are unable, from the available data, to assign the individual isomers.

For (5a): b.p. 203°C; [Found: C, 29.3; H, 1.1; F, 64.0%; M^+, 324. $C_8F_{11}OH_3$ requires: C, 29.63; H, 0.93; F, 64.51%; M, 324] i.r. λ_{max} 7.17, 7.72, 7.94, 8.06, 8.24, 8.47, 8.58, 9.02, 4.17, 9.33, 9.46, 9.90, 10.55, 10.75 and 12.66 μm; δ ^{19}F 182.7 (1F, Broad singlet $>$CF) and signals between 124 and 138 p.p.m. (10F) which were not assigned δ ^{1}H 4.07 (singlet).

For (5b); a low melting solid, b.p. > 210°C; [Found: C, 29.6; H, 1.2; F, 64.2%; M^+, 324. $C_8F_{11}OH_3$ requires C, 29.63; H, 0.93; F, 64.51%; M, 324]; i.r. λ_{max} 7.14, 7.47, 7.72, 8.03, 8.20, 8.47, 8.60, 8.83, 9.03, 9.18, 9.35, 10.00, 10.59, 20.78, 11.49, 11.76 and 12.12 μm; δ ^{19}F, 185.6 (1F, pentet J = 16 Hz, $>$CF) and signals between 122 and 132 p.p.m. (10F) which were not assigned. δ ^{1}H 4.00 (singlet).

Similar reactions were carried out; in aqueous acetone; with a deficiency of permanganate; and with several hours refluxing after addition of the trimer to permanganate. In each case the product mixture was the same (by ^{19}F n.m.r.) as that obtained in the reaction described.

REFERENCES

1 R.D.Chambers, G. Taylor, and R.L. Powell, J.C.S. Chem. Comm. (1978) 433.

2 R.L. Pruett, C.T. Bahner and H.A. Smith, J. Amer. Chem. Soc., 74 (1952) 1638.

3 R.G. Plevey, I.J. Sallomi, D.F. Thomas and J.C. Tatlow, J.C.S. Perkin I (1976), 2270.

4 R.D. Chambers, A.A. Lindley, P.D. Philpot, H.C. Fielding, J. Hutchinson and G. Whittaker, J.C.S. Perkin I (1979) 214.