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Heterocyclic Polyfluoro-compounds. Part 34 [1]. Two-way Photochemical Addition of Hexafluoroacetone to 1,2-Dichlorofluoroethylene, and the Preparation of an Oxete

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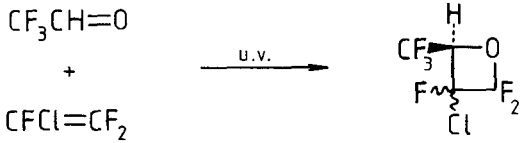
The well-known Paterno-Büchi reaction, which involves oxetan formation by the photochemical addition of a carbonyl compound to a carbon-carbon double bond [2], was extended to the fluorocarbon field by Harris and Coffman [3], who described the photochemical addition of fluoroaldehydes, fluoroketones, and fluoroacyl fluorides to terminal perfluoroolefins and chlorotrifluoroethylene, e.g.,



Subsequently, Bissel and Fields reported that low yields of oxetans were obtained from acetaldehyde and the olefins, $CF_2=CF_2$, $CF_2=CFCl$, and $CF_2=CCl_2$ [4]. The reaction of hexafluoroacetone with hexafluoropropene involves the triplet state of the ketone [5].

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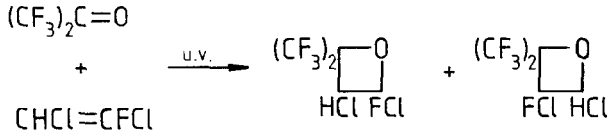
We have described the photochemical addition of chlorofluoroacetones [1] and perfluoroaldehydes [1] to 1,2-difluoroethylene, where little stereoselectivity is observed, so far as addition to the olefin is concerned. We here describe the addition of hexafluoroacetone to 1,2-dichlorofluoroethylene, with a view to investigating its regioselectivity.

Ultraviolet irradiation of hexafluoroacetone and a 1:1 mixture of (Z)- and (E)-1,2-dichlorofluoroethylene in the gaseous phase in Pyrex slowly led to the formation of oxetans (1) and (2), in the ratio 55:45:



(1) (2)

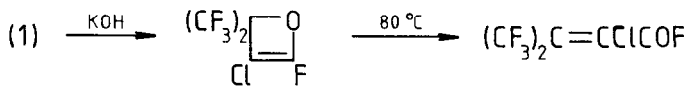
The individual oxetans (1) and (2) could be readily separated by g.l.c., although the individual cis/trans pairs could not. The additions to terminal perfluoroolefins [3], and of acetaldehyde to fluoro-olefins [4], appear to be completely regiospecific, an observation rationalised in terms of the formation of the most stable intermediate diradical, e.g., (3) from trifluoroacetaldehyde and chlorotrifluoroethylene.

(3) (4)

With 1,2-dichlorofluoroethylene, the CFCl radical site should be somewhat more stable than the CHCl site, since in general, an α-fluorine stabilises better than hydrogen [6]. Here, this is not a satisfactory explanation, since the diradical (4), expected to be more stable, gives rise to

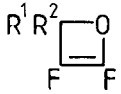
the minor product. Additions of hexafluoroacetone to fluoroethylene and 1,1-difluoroethylene are only moderately regioselective, although the expected product is favoured [7]; clearly this area calls for further study.

Oxetes are rare and synthesised only with difficulty. We therefore investigated very briefly the use of oxetans (1) and (2) as a source. Treatment of a mixture of these oxetans with powdered potassium hydroxide at room temperature led to the smooth and completely selective dehydrochlorination of the oxetan (1) to give the oxete (5), whose structure was confirmed by its ready ring opening to an acid fluoride rather than a chloride:



(5)

This interesting result can be accounted for, if the dehydrochlorination follows an E1cb mechanism. Removal of a proton from (2) would give a carbanionic site next to the ring oxygen in a rigid structure where lone-pair repulsion would be maximised [8]. A number of 2,3-difluoro-oxetes (6), obtained by dehalogenation or dehydrohalogenation of the appropiate oxetan, have been described in the patent literature [9].



(6) $R^1 = R^2 = CF_3$ or CF_2Cl;

$R^1 = CF_3$, $R^2 = CF_2Cl$

EXPERIMENTAL

Physical techniques were similar to those previously employed [1]. A 1:1 mixture of (Z)- and (E)-1,2-dichloro-fluoroethylene was prepared by the route [10]:

Photochemical Addition of Hexafluoroacetone to 1,2-Dichlorofluoroethylene.

The mixture of (Z)- and (E)-1,2-dichlorofluoroethylene (4.78 g, 41.6 mmol) and hexafluoroacetone (6.25 g, 37.6 mmol), sealed in vacuo in a Pyrex ampoule (ca. 300 cm^3) and irradiated for 28 days with u.v. light from a Hanovia UVS 500 lamp at a distance of 25 cm, gave a product which was fractionated by trap-to-trap distillation in vacuo. A mixture (by i.r. spectroscopy/g.l.c., 3.5 m trixylyl phosphate on Celite at 24 °C) of recovered hexafluoroacetone (2.18 g., 13.1 mmol, 35%), (Z)- (0.13 g, 1.1 mmol) and (E)-1,2-dichlorofluoroethylene (0.12 g, 1.1 mmol) condensed at -130 °C, and a liquid mixture (8.60 g) condensed at -25 and -45 °C. The latter fraction was distilled, using a column (15 cm by 1 cm i.d.) packed with nickel Dixon rings, to give (Z)- and (E)-1,2-dichlorofluoroethylene [1.72 g, 14.9 mmol; ratio of (Z)- to (E)-isomers = 1.00:0.96], b.p. 35-37 °C at 762 mmHg, and a pot residue which was separated by g.l.c. (3.5 m trixylyl phosphate on Celite at 30 °C) to give inseparable 1:1 mixtures of trans- and cis-2,2-bis(trifluoromethyl)-3,4-dichloro-4-fluoro-oxetan (3.76 g, 13.4 mmol, 55% yield based upon hexafluoroacetone consumed) (Found: C, 21.6; H, 0.5; F, 47.7. Calc. for $C_5HCl_2F_7O$: C, 21.3; H, 0.4; F, 47.3%), b.p. (Siwoloboff) 97.5 °C at 761 mmHg, and trans- and cis-2,2-bis(trifluoromethyl)-3,4-dichloro-3-fluoro-oxetan (3.13 g, 11.1 mmol, 45%) (Found: C, 21.7; H, 0.6; F, 47.6. Calc. for $C_5HCl_2F_7O$: C, 21.3; H, 0.4; F, 47.3%), b.p. (Siwoloboff) 102 °C at 761 mmHg, which were identified by i.r. and n.m.r. spectroscopy, and mass spectrometry.

The individual oxetans were identified largely on the basis of their individual n.m.r. parameters. For the 4-fluoro-oxetans, the trans-isomer showed δ_F (positive values to low field of external CF_3CO_2H) 0.2 [CF_3, $J(CF_3, CF_3)$ 9 Hz], 4.4 [CF_3, $J(CF_3,F)$ 7 Hz], and 21.8 p.p.m. [CF, $^3J(H,F)$ 7.5 Hz], and δ_H (internal $SiMe_4$) 5.24 p.p.m., and the cis-isomer showed δ_F -0.1 [CF_3, $J(CF_3,CF_3)$ 9 Hz],

5.4 (CF_3), and 40.2 p.p.m. [CF, ^3J(H,F) 9 Hz]. For the 3-fluoro-oxetans, the trans-isomer showed δ_F 3.5 [CF_3, $J(CF_3,CF_3)$ 10.5 and $J(CF_3,F)$ 3.5 Hz], 5.3 [CF_3, $J(CF_3,F)$ 21 Hz], and -42.0 p.p.m. [CF, ^3J(H,F) 7 Hz], and δ_H 6.30 p.p.m., and the cis-isomer showed δ_F 4.5 ($2CF_3$, complex), and -28.8 p.p.m. [CF, $J(CF_3,F)$ ~20 and J(H,F) 11.5 Hz], and δ_H 6.38 p.p.m. The 4-fluoro-oxetans were readily distinguished from the 3-fluoro-compounds by the low-field shift of the fluorines in the former and the protons in the latter adjacent to the ring oxygen. The assignment was further supported by the presence of a large coupling (~20 Hz) of one trifluoromethyl group nuclei to the adjacent ring fluorine in the 3-fluoro-oxetans. A similar cis four-bond coupling has been observed in the 3,4-difluoro-oxetans obtained from the addition of chlorofluoroketones to 1,2-difluoroethylene [1]. The individual cis- and trans-isomers were identified on the basis of the magnitudes of the vicinal H,F coupling constants where $\left|^3J_{cis}\right| > \left|^3J_{trans}\right|$ [11].

Dehydrochlorination of the Mixture of 2,2-Bis(trifluoromethyl)-3,4-dichloro-3- and 4-fluoro-oxetans.

An equimolar mixture of the above four oxetans (13.84 g, 49.3 mmol) was added dropwise to finely powdered potassium hydroxide (5.60 g, 100.0 mmol) at room temperature with stirring during 50 min. Stirring was continued for a further 4.5 h and volatile product was collected in a trap cooled to -196 °C. Fractionation of the product by trap-to-trap distillation in vacuo gave a trace of trifluoromethane, 3-chloro-2-fluoro-4,4-bis(trifluoromethyl)-2-oxete (nc) (1.54 g, 6.3 mmol) (Found: C, 24.5; F, 54.3%; M, 245. C_5ClF_7O requires C, 24.6; F, 54.3%; M, 244.5), $\nu_{max.}$ 1770 cm^{-1} (C=C str.) and δ_F 1.2 (CF_3, ^5J = 2.0 Hz) and 3.3 p.p.m. (CF), which condensed at -130 °C. There remained in the flask a residue which was removed in vacuo, dried (molecular sieve), and shown by g.l.c. (3.5 m trixylyl phosphate on Celite at 25 °C) and i.r. and n.m.r. spectroscopy to comprise the above oxete (1.13 g, 4.6 mmol;

total yield 100% based upon 4-fluoro-oxetan consumed) and the recovered 4-fluoro-oxetan (3.85 g, 13.7 mmol, 56%) and the 3-fluoro-oxetan (6.92 g, 24.7 mmol; 100%).

A sample of the 3-chloro-2-fluoro-4,4-bis(trifluoromethyl)-2-oxete, when heated to 80 °C for 120 min, gave 2-chloro-4,4,4-trifluoro-3-trifluoromethylbut-2-enoyl fluoride (nc) (86% conversion) (Found: C, 24.6; F, 54.2%; M, 244.5. C_5ClF_7O requires C, 24.6; F, 54.5%; M, 244.5), identified by i.r., with $\nu_{max.}$ 1872 vs (C=O str.) and 1660 s cm^{-1} (C=C str.) and n.m.r. spectroscopy, with δ_F 15.5 ($2CF_3$, complex) and 58.3 p.p.m. (COF). The oxete isomerised to the extent of 29% during 5 days at room temperature.

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