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POLYFLUOROCYCLOALKENES—VI[1]

THE REACTION OF DECAFLUOROCYCLOHEXENE WITH ETHYLENE GLYCOL IN THE PRESENCE OF BASE

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Abstract—Decafluorocyclohexene and potassium hydroxide in ethylene glycol gave octafluorocyclohex-2-enespiro-2'-dioxolan (II), a 5,6,7,7,8,8,9,10-octafluoro-(1,2,3,4,7,8,9,10-octahydro-1,4-dioxanaphthalene) (III) and 5,6,6,7,7,8,8,9-octafluoro-(1,2,3,4,6,7,8,9-octahydro-1,4-dioxanaphthalene) (IV), by what appears to be an addition-elimination pathway. A fourth isomeric ether, 5,5,6,6,7,7,8,8-octafluoro(1,2,3,4,5,6,7,8-octahydro-1,4-dioxanaphthalene) V, was prepared by potassium fluoride catalysed isomerization of III and IV.

THE reaction of cyclic perfluoro-olefins with alcohols in the presence of potassium hydroxide has been rationalized in terms of the addition of alkoxide ion to the electron deficient double bond followed by a β-elimination of fluoride ion to give both 1- and 3-alkoxy perfluoro-olefins.[2,3] The present work reveals the operation of similar processes when ethylene glycol and potassium hydroxide react with decafluorocyclohexene. A parallel investigation had been undertaken earlier by Henne and Latif using 1,2-dichlorohexafluorocyclopentene.[4] However, the products were not fully characterized and the structures proposed were subsequently disputed by Parker[5] by analogy with the products obtained in the reaction of the same olefin with methanol and potassium hydroxide, but the structures he suggested were not experimentally confirmed.[5] However, the present work clearly supports Parker's postulated structures.

Decafluorocyclohexene (1 mole I) reacted with potassium hydroxide (2 moles) in a large excess of ethylene glycol to give three components (II, III and IV) which were separated by preparative gas chromatography, and a sticky involatile liquid, probably a telomer.

The three volatile components (II, III and IV) each had the same, appropriate elemental analysis and mol. wt. and were characterized by IR and NMR spectroscopy and oxidation, as octafluorocyclohex-2-enespiro-2'-dioxolan (II), *cis* (?)-5,6,7,7,8,8,9,-10-octafluoro-(1,2,3,4,7,8,9,10-octahydro-1,4-dioxanaphthalene) (III) and 5,6,6,7,7,8,-8,9-octafluoro-(1,2,3,4,6,7,8,9-octahydro-1,4-dioxanaphthalene) (IV).

The most volatile product (II) was readily converted by potassium permanganate in acetone into 2-carboxy-2(1,1,2,2,3,3-hexafluoro-3-carboxy-propyl)-dioxolan (VI) which was characterized as its dianilinium and bis-S-benzylthiuronium-salts. Further,

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[1] Part V, A. B. Clayton, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 7370 (1965).

[2] A. B. Clayton, J. Roylance, D. R. Sayers, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 7358 (1965).

[3] S. F. Campbell and R. Stephens, *J. Chem. Soc.* 7367 (1965).

[4] A. L. Henne and K. A. Latif, *J. Indian Chem. Soc.* **30**, 809 (1965).

[5] C. O. Parker, *J. Amer. Chem. Soc.* **81**, 2183 (1959).

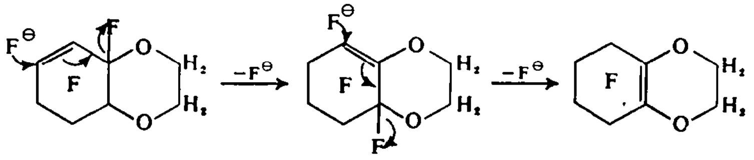
component II was converted by conc. sulphuric acid into the extremely hygroscopic hydrate of octafluorocyclohex-1-ene-3-one (VII), obtained in the same way from the known 3-methoxy-nonafluoro-cyclohexene;[1] this hydrated ketone (VII) was oxidized to hexafluoroglutaric acid (VIII).

Component III was oxidized in exactly the same way as II to give 2,3-difluoro-2-carboxy-3(1,1,2,2-tetrafluoro-2-carboxy-ethyl)-1,4-dioxan (IX) which was characterized as its dianilinium and bis-S-benzylthiuronium salts. Attempted dealkylation of component III with conc. sulphuric acid gave a very high boiling liquid which appeared to be a hydrated form of hexafluorocyclohex-1-ene-3,4-dione (X). It was very easily oxidized by potassium permanganate in acetone to tetrafluorosuccinic acid (XI) in agreement with a —CF_2—CF_2—ring "backbone".

The oxidation of component IV was markedly less facile than that of its isomers. However, potassium permanganate in acetone eventually gave 2-(2-hydroxyethoxy) heptafluoroadipic acid (XIII) which was characterized as its dianilinium salt; it did not give a water-insoluble S-benzylthiuronium salt.

The structural relationship of components III and IV was clearly confirmed by their potassium fluoride catalysed isomerization to the same olefin (V). The latter was characterized by elemental analysis, mass spectrometry, IR and fluorine-19 NMR spectroscopy, and by its difficult oxidation to octafluoroadipic acid (XII), as 5,5,6,6,7,-7,8,8-octafluoro (1,2,3,4,5,6,7,8-octahydro-1,4-dioxanaphthalene) (V). It was clearly established by gas chromatography that the latter ether was not formed in the reaction of ethylene glycol and decafluorocyclohexene.

The isomerizations of olefins III and IV to olefin V is another example of a well known process in which a double bond migrates round a ring system, by successive additions and eliminations of fluoride ion, until the number of vinylic fluorine atoms is as small as possible;[6] i.e., until the thermodynamically most stable olefin is obtained as depicted by:



III IV V

A reaction pathway producing the above ethers, depicted in Fig. 2, is based on an addition-elimination sequence of the type applicable to simple alcohols.[2] For the sake of simplicity, four of the reaction intermediates are assumed to be carbanions (1,3 3a and 3b). The latter, however, might abstract a proton from the solvent and then eliminate hydrogen fluoride. Indeed, it is quite likely that the elimination step involves both the carbanions and the alcohol addition products. None of the addition products were isolated from the reaction mixture, however.

The first nucleophilic attack at the double bond of decafluorocyclohexene (I), as in the reaction with simple alcohols,[2] should effectively produce an anion (1) which can eliminate fluoride ion from C-1 or C-3, the former should be favoured,[2] to give the intermediate olefins 2 and 2′, respectively. The latter olefins can react either intra- or inter-molecularly to produce the anions 3,3a and 3b or telomeric species, respectively.

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[6] W. J. Feast and R. Stephens, *J. Chem. Soc.* 3502 (1965).

The anion 2′ would give exclusively 3 but the anion 2 could give either 3a or 3b. The latter might be expected to form preferentially since the vinylic carbon should be the more electropositive. However, the isolation of II as the major product clearly indicates a preference for 3a. Three factors are thought to result in this preference, *viz.*: (i) an electron density at C-1 approaching that at C-2; thus 1-methoxy nonafluorocyclohexene was converted to 1-methyl nonafluorocyclohexene in a substantial yield with methyl-lithium in diethyl ether;[7] (ii) there will be a less negative entropy of activation for the formation of the five- than the six-membered ring; (iii) "Courtauld" molecular models show more steric compression in 3b than in 3a.

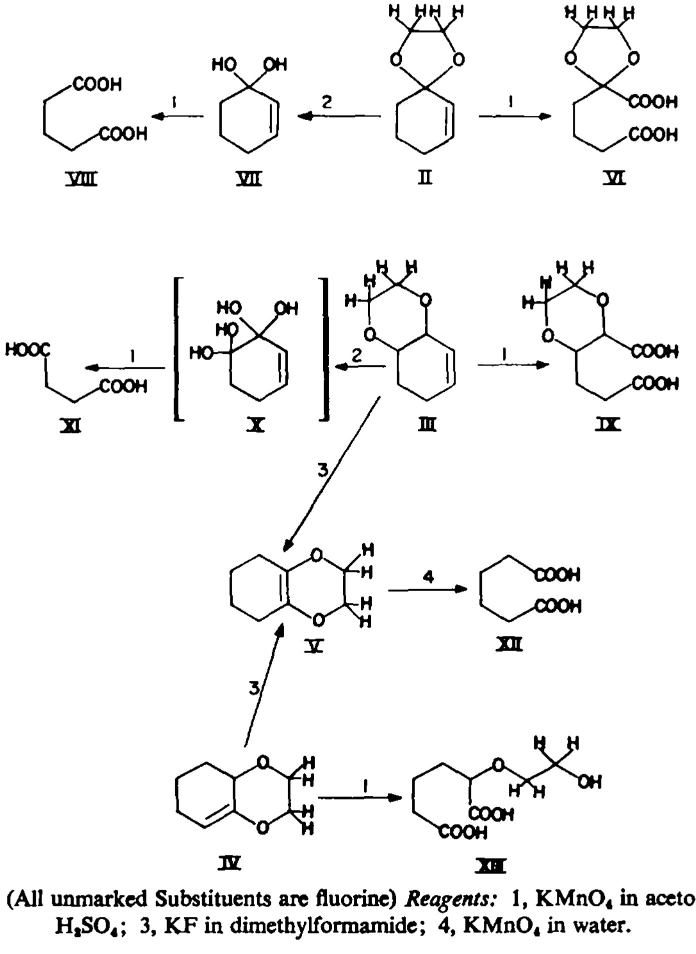

FIG. 1. (All unmarked Substituents are fluorine) *Reagents:* 1, $KMnO_4$ in acetone; 2, H_2SO_4; 3, KF in dimethylformamide; 4, $KMnO_4$ in water.

The absence of V does not exclude the presence of the anion (3b) since this would be expected to eliminate entirely in the direction giving IV; assuming the normal *trans* addition to the double bond occurs.

The intramolecular addition reaction of anion 2′ would be expected to give a *cis*-ring fusion in anion 3 if it is assumed that the bulky alkoxide side chain occupies the pseudo-equatorial position in the preferred conformation of olefin 2′ and the ionic

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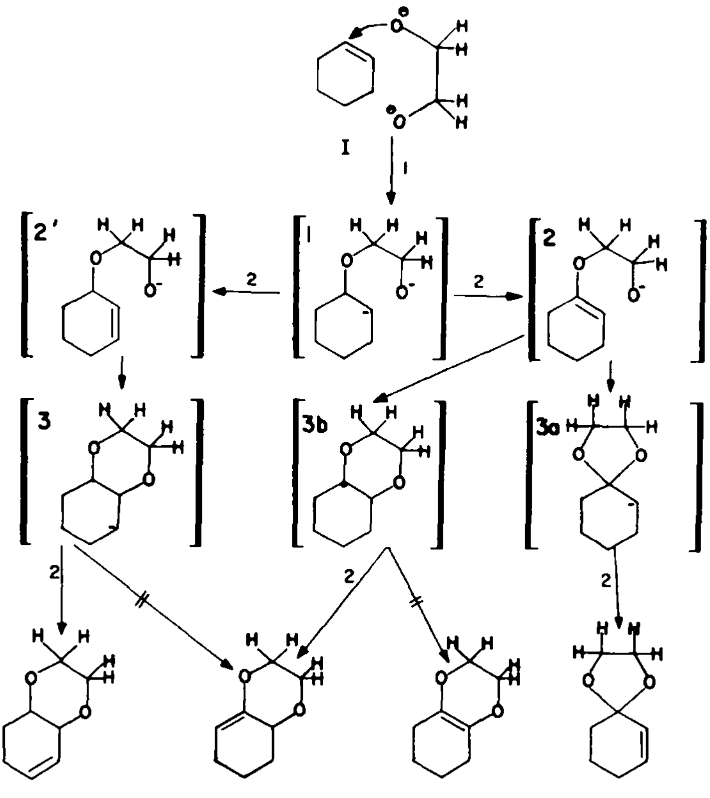
[7] A. B. Clayton, R. Stephens and J. C. Tatlow, unpublished work.

addition step is *trans*. This being so, the subsequent elimination of fluoride ion should occur exclusively in the direction producing III [i.e., 5,6,7,7,8,8,9,10-octafluoro-*cis*-(1,2,3,4,7,8,9,10-octahydro-1,4-dioxanaphthalene)]. It then follows that the isolation of olefin IV strongly suggests the intermediacy of anion 3b.

The involatile sticky residue, which amounted to 25% of the reaction product, was not identified; its IR spectrum displayed several absorption bands between 1750 and 1650 cm^{-1} which might be attributed to systems of the type $F—\overset{|}{C}=\overset{|}{C}—F$, $F—\overset{|}{C}=\overset{|}{C}—O—$ and $—O—\overset{|}{C}=\overset{|}{C}—O—$. It may be a telomer produced by intermolecular reactions of species such as 2 or 2′ with decafluorocyclohexene (I) or any of the isolated reaction products (II, III or IV). Indeed reactions of this type probably influence the proportions of the latter compounds isolated, since the reactivities of their double bonds will differ considerably.



III IV V II

Fig. 2. (All unmarked substituents are fluorine) *Reagents:* 1, Ethylene glycol-KOH; 2, loss of F$^-$.

EXPERIMENTAL

Techniques. Analytical gas chromatography was carried out using a glass column (1·83 m × 4 mm diam) packed with silicone gum (S.E. 301)-kieselgular (1:7). In preparative scale work a Cu column

[8] L. F. Thomas, unpublished work.

(4·9 m × 75 mm diam) containing the same packing was used. The F-19 NMR spectrum was measured[8] on a Mullard S.L. 44 Mk. 1 instrument at 30·107 mc/s and the figures quoted are F chemical shifts and are in ppm from trifluoroacetic acid as external reference. The Proton NMR spectrum was measured on a Varian instrument at 60 Mc/s and the figure quoted is a chemical shift in ppm from tetramethylsilane as external reference. Mass spectra were measured[9] on a Metropolitan Vickers M.S.2 instrument.

Reaction of ethylene glycol with decafluorocyclohexene (I)

This olefin (32·0 g) was added to a well-strired solution of KOH (13·7 g) in ethylene glycol (45 ml). When the addition was complete the mixture was heated under reflux for 16 hr, then shaken with water (200 ml) and separated. The liquid product (31·3 g) was distilled to give the following fractions: (i) b.r. 50–70° (1·4 g); (ii) b.r. 50–80°/10 mm (21·8 g); (iii) a residue (7·0 g). Fraction (i) was shown to consist largely of decafluorocyclohexene by IR spectroscopy and analytical GPC. Fraction (iii) was a highly viscous, involatile, yellow liquid which, when kept, became increasingly dark and sticky and eventually swelled with the evolution of HF. Fraction (ii), a colourless liquid, was shown by analytical GPC (132°, N_2 flow-rate 4·9 l./hr) to contain a small amount of decafluorocyclohexene and three major components which were separated on a preparative scale (118°; N_2, flow-rate 56 l./hr) to give: (i) *octafluoro-cyclohex-2-enespiro-2′-dioxolan* (II; 6·9 g), b.p. 164°, retention time 1 hr, 27 min. (Found: C, 33·9; H, 1·4. $C_8H_4F_8O_2$ requires: C, 33·8; H, 1·4%), ν_{max} 1760 cm^{-1} (—CF=CF—, mass spectrometry gave a top mass peak at 284 ($C_8H_4F_8O_2$), the proton NMR spectrum consisted of a singlet at 4·1; (ii) a 5,6,7,7,8,8,9,10-*octafluoro*-(1,2,3,4,7,8,9,10-*octahydro*-1,4-*dioxanaphthalene*) (III; 4·9 g), b.p. 184°, retention time 2 hr 16 min. (Found: C, 33·7; H, 1·4%), ν_{max} 1756 cm^{-1}. (—CF=CF—), mass spectrometry gave a top mass peak of 284 ($C_8H_4F_8O_2$); (iii) 5,6,6,7,7,8,8,9-*octafluoro*-(1,2,3,4,6,7,8,9-*octahydro*-1,4-*dioxanaphthalene*) (IV; 3·0 g), b.p. 195°, retention time 3 hr 12 min. (Found: C, 34·0; H, 1·4%), ν_{max} 1733 cm^{-1} (—CF=C—O-system), mass spectrometry gave a top mass peak of 284 ($C_8H_4F_8O_2$).

Oxidation of octafluoro-cyclohex-2-enespiro-2′-dioxolan (II)

This olefin (1·0 g) was oxidized[10] with $KMnO_4$ (2 g) in acetone (150 ml); an immediate exothermic reaction occurred. Aniline was added dropwise to an ethereal solution of the oxidation product to give a white precipitate of the *dianilinium salt* of 2-*carboxy*-2-(1,1,2,2,3,3-*hexafluoro*-3-*carboxy-propyl*)-*dioxolan* (VI; 1·54 g), m.p. 192–193° (from acetone–$CHCl_3$) (Found: C, 47·9; H, 4·0; Equiv., 499. $C_{20}H_{20}F_6N_2O_6$ requires: C, 48·2; H, 4·0%; Equiv., 498·4).

A portion of the dianilinium salt (0·2 g) in water (3 ml) was mixed with a warm, saturated solution of S-benzylisothiouronium chloride (0·5 g) in water. The precipitate so obtained was recrystallized twice from water to give the *bis*-(*S-benzylthiuronium*) *salt monohydrate* (0·19 g), m.p. 204–205°. (Found: C, 43·5; H, 4·0. $C_{24}H_{28}F_6N_4O_7S_2$ requires: C, 43·5; H, 4·3%.)

Oxidation of 5,6,7,7,8,8,9,10-*octafluoro*-(1,2,3,4,7,8,9,10-*octahydro*-1,4-*dioxanaphthalene*) (III)

This compound (1·5 g) was oxidized in the same way. Addition of aniline to an ethereal solution of the oxidation product gave the *dianilinium salt* of 2,3-*difluoro*-2-*carboxy*-3-(1,1,2,2-*tetrafluoro*-2-*carboxy-ethyl*)-1,4-*dioxan* (IX; 2·3 g), m.p. 170° (from acetone-$CHCl_3$). (Found: C, 48·1; H, 4·2%; Equiv., 496.)

A portion of the above dianilinium salt (0·2 g) in water (3 ml) and a saturated solution of S-benzyliso-thiuronium chloride (0·6 g) in water gave the bis (*S-benzylthiuronium*) *salt monohydrate* (0·3 g), m.p. 169°. (Found: C, 43·2; H, 4·4%.)

Oxidation of 5,6,6,7,7,8,8,9-*octafluoro*-(1,2,3,4,6,7,8,9-*octahydro*-1,4-*dioxanaphthalene*) (IV)

The olefin (2·5 g), $KMnO_4$ (4·5 g) and acetone (350 ml) were heated to the point of reflux and then shaken for ca. 20 min when reaction suddenly occurred and was then completed by shaking the mixture for ½ hr. The mixture was subjected to the usual isolation procedure and the dry ether extract treated with aniline to give *dianilinium* 2-(2-*hydroxyethoxy*)-*heptafluoroadipate* (3·4 g), m.p. 156° (from acetone–$CHCl_3$). (Found: C, 46·2; H, 4·2. $C_{20}H_{21}F_7N_2O_6$

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[9] J. R. Majer, unpublished work.

[10] J. Burdon and J. C. Tatlow, *J. Appl. Chem.* **8**, 293 (1958).

requires: C, 46·3; H, 4·1%.) A concentrated solution of this salt in water did not give a precipitate on treatment with a saturated solution of S-benzylisothiuronium chloride in water.

5,5,6,6,7,7,8,8-Octafluoro (1,2,3,4,5,6,7,8,-octahydro-1,4-dioxanaphthalene) (V)

(a) *From* 5,6,7,7,8,8,9,10-*octafluoro-(1,2,3,4,7,8,9,10-octahydro-1,4-dioxanaphthalene* (III). This olefin (1·5 g), anhydrous KF (1 g) and dry dimethylformamide (4·5 ml) were heated under reflux together for 72 hr. The dark-brown reaction product was distilled *in vacuo* (0·01 mm) and the clear distillate shaken with water and the organic layer dried (P_2O_5) and distilled *in vacuo* to give 5,5,6,6,7,7,-8,8-*octafluoro* (1,2,3,4,5,6,7,8-*octahydro*-1,4-*dioxanaphthalene*) (V) (1·2 g), b.p. 190°. (Found: C, 34·0; H, 1·7%), ν_{max} 1680 cm^{-1} (—O—C=C—O-system), mass spectrometry gave a top mass peak at 284 ($C_8H_4F_8O_2$), the F-19 NMR spectrum consisted of two bands of equal intensity at 40·3 and 57·3 (cf. decafluorocyclohexene with bands at 43 and 57). Analytical gas chromatography of a mixture of this olefin with the three previous isomers (117°; N_2, flow-rate 5·2 l/hr) revealed four peaks with retention times of 6 min 58 sec, 10 min 32 sec, 13 min 5 sec and 14 min 16 sec for the olefins II, III, V and IV, respectively.

(b) *From* 5,6,6,7,7,8,8,9-*octafluoro*-(1,2,3,4,6,7,8,9-*octahydro*-1,4-*dioxanaphthalene*) (IV). This olefin (1·5 g), anhydrous KF (1·0 g) and dry dimethylformamide (4 ml) were heated under reflux together for 72 hr. The above isolation procedure gave V (1·3 g) with a correct IR spectrum.

Oxidation of 5,5,6,6,7,7,8,8-*octafluoro* (1,2,3,4,5,6,7,8-*octahydro*-1,4-*dioxanaphthalene*) (V)

This olefin (1·0 g), $KMnO_4$ (2·8 g) and dil H_2SO_4 (ca. 1N; 25 ml) were stirred together under reflux for 48 hr and then extracted continuously with ether for 16 hr. The dried ($MgSO_4$) ether solution was evaporated and the residue shaken with dry ether (15 ml). Aniline was added dropwise to the filtered ether solution to give a precipitate of dianilinium octafluoroadipate (0·9 g), m.p. 211° (lit.[10] cites 210–211°), with a correct IR spectrum. A portion (0·4 g) of this salt was converted in the usual way, to bis-(S-benzylthiuronium) octafluoroadipate (0·4 g), m.p. 244° (lit.[10] cites 244°).

Octafluorocyclohex-1-ene-3-one

Compound II (4·3 g) and conc H_2SO_4 (15 ml) were heated under reflux until the two layers merged to give a black solution which was distilled to give the colourless slightly viscous VII (3·0 g), b.p. 83°/10 mm with a correct IR spectrum.[8] This liquid (0·3 g) was exposed to the atmosphere for ca. 2 days to give the crystalline octafluorocyclohex-1-ene-3-one trihydrate (0·4 g), m.p. 78–80° (lit.[8] cites 79–80°), with a correct IR spectrum.

The liquid (0·4 g) was oxidized, with $KMnO_4$ (0·7 g) in acetone (70 ml) to give XI (78%) which was characterized as its di-anilinium-and S-(benzylthiuronium)-salts.

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