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POLYFLUOROCYCLOALKENES

PART XIII [1]. REACTIONS OF PERFLUOROCYCLOALKENES WITH 1-ETHOXY-1-(2-HYDROXYETHOXY) ETHANE IN THE PRESENCE OF BASE

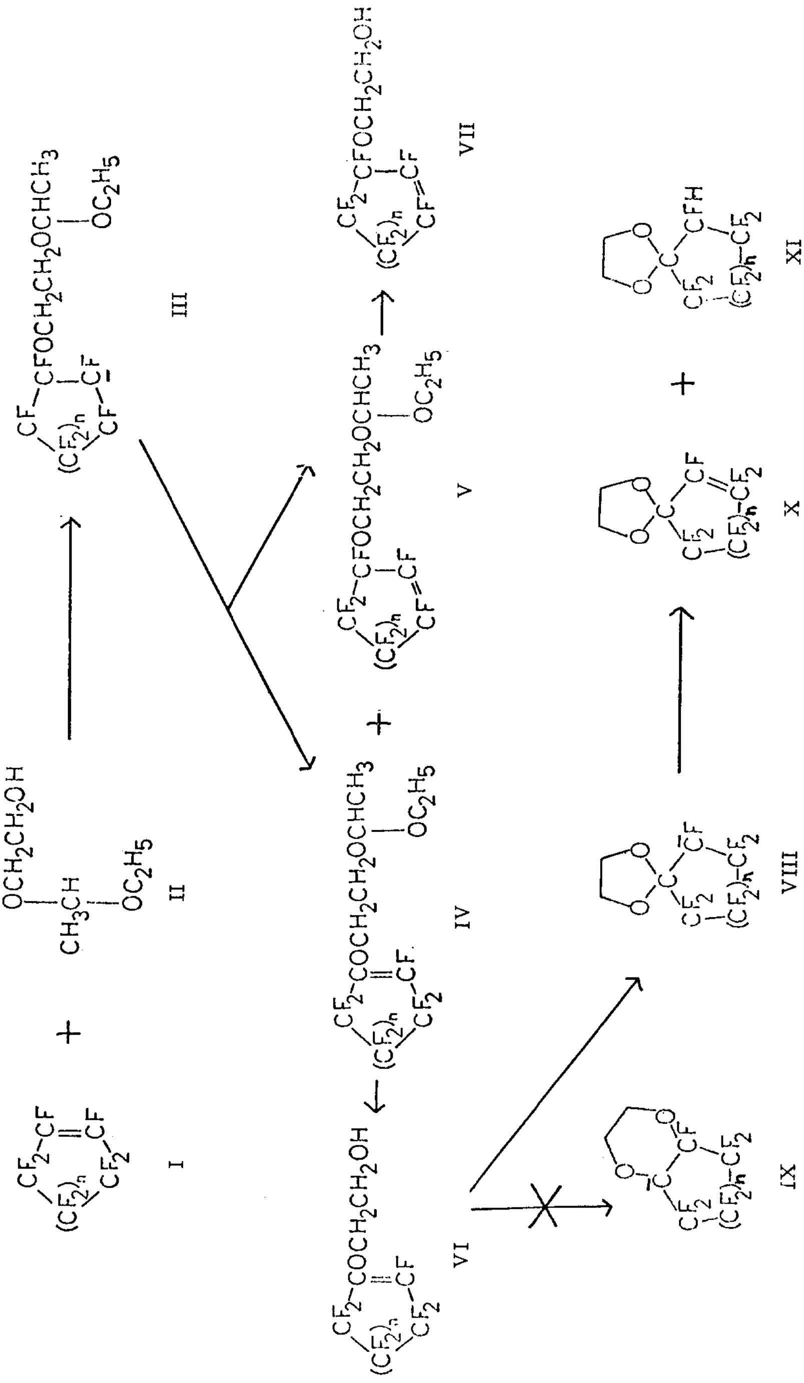
R. G. PLEVEY and R. E. TALBOT

Chemistry Department, The University of Birmingham, P.O. Box 363,
Birmingham B15 2TT (Great Britain).

SUMMARY

1-Ethoxy-1-(2-hydroxyethoxy) ethane and sodium hydride with octafluorocyclopentene, decafluorocyclohexene and dodecafluorocycloheptene produced acid-labile acetals which were hydrolysed to the corresponding 1-(2-hydroxyethoxy) perfluorocycloalkenes. Cyclisation of these compounds under basic conditions gave substituted dioxolans and not 1,4-dioxanes.

The multicomponent mixtures of partially fluorinated heterocycles resulting from the base-assisted reactions of decafluorocyclohexene and ethane-1,2-diol have been explained [2] as the products of subsequent reactions of postulated primary substitution products, 1- and 3-(2-hydroxyethoxy) nonafluorocyclohexenes, compounds VI (n = 2) and VII (n = 2). These have not so far been made, an attempt to prepare them using 2-acetoxyethanol being unsuccessful [1]. We report now the successful preparation of 1-(2-hydroxyethoxy) nonafluorocyclohexene VI (n = 2), and of the analogous compounds VI (n = 1, 3) from decafluorocyclohexene, octafluorocyclopentene and dodecafluorocycloheptene respectively.


I
II
III
IV
V
VI
VII
VIII
IX
X
XI

1-Ethoxy-1-(2-hydroxyethoxy) ethane II, formed from ethane-1,2-diol and ethyl vinyl ether at 200-225° [3], was chosen as a mono-substituted derivative of the diol which is stable under basic conditions. This acetal reacted with hexafluorobenzene and with the three perfluorocycloalkenes under basic conditions. The products, also acetals, were not isolated but were hydrolysed by the addition of acid to give 2-pentafluorophenoxyethanol and the 1-(2-hydroxyethoxy) cycloalkenes VI (n = 1, 2 and 3). These cycloalkenes were characterised by i. r. spectroscopy, all spectra containing absorptions characteristic of the group -CF = C(OR)-, [4] and ^{19}F n. m. r. spectroscopy, which showed signals attributable to one vinylic fluorine atom in each compound. Also the conversion of compound VI (n = 2) to 1-(2-chloroethoxy) nonafluorocyclohexene, prepared originally by the reaction of 2-chloroethanol with decafluorocyclohexene [7], confirmed the structure of this compound.

The cycloalkenes VI are formed by reactions of the oxy-anion from acetal II with the cycloalkenes I to give carbanions III which can revert to an alkene by loss of fluoride ion. "Inwards" elimination of fluoride ion from C-1 gives rise to the 1-alkoxy derivatives IV whereas "outwards" elimination from C-3 would lead to the isomeric 3-alkoxycycloalkenes V. None of the 3-alkoxy isomers were isolated except from the decafluorocyclohexene reaction in which a small quantity of VII (n = 2) was indicated tentatively by g. l. c., i. r. spectroscopy and by conversion of the reaction mixture with phosphorus pentachloride to the known 1- and 3-(2-chloroethoxy) nonafluorocyclohexenes [7]. These results are consistent with reported observations, since in reactions of simple alcohols with perfluorocycloalkenes the 1-alkoxy derivative is always the major product but the amounts of the isomeric 3-alkoxycycloalkene increase with increasing ring size to a maximum for decafluorocyclohexene [5] and then decrease with cycloheptene [6] and also decrease with increasing size of the alcohols [5]. This ignores the possibility that 3-alkoxycycloalkenes may be generated initially in substantial amounts but, still possessing a -CF = CF- double bond, may then react preferentially with more base.

The hydroxy ethers VI (n = 1, 2 and 3) were heated in a solution of potassium hydroxide in ethane-1,2-diol. Spiro-compounds X (n = 1, 2) were the sole isolated products from the reactions of compound VI (n = 1, 2), that from VI (n = 2) being identical with material made previously [1, 2]. However, from a similar reaction of compound VI (n = 3), the addition compound XI (n = 3) was isolated as well as the spiro-compound X (n = 3).

These products may be explained by intramolecular reactions involving the oxy-anions formed by deprotonation of compounds VI. Two modes of cyclisation leading to carbanions VIII and IX are feasable; subsequent loss of fluoride ion leads to the products. Clearly the mode via carbanion VIII greatly predominates. Protonation provides an alternative fate for the carbanions; thus the isolation of the appropriate saturated ether XI (n = 3) from one of the cyclisation reactions supports the proposed reactio scheme. A similar addition product was isolated, albeit in very small yield, from the reaction of sodium methoxide with decafluorocyclohexene [8]. No compounds, other than spiro compounds, were isolated from these reaction products suggesting that carbanions of type IX were not involved in these cyclisations. This emphasizes the easier formation of five-membered compared to six-membered rings and reinforces the belief that the substituted 1,4-dioxanes isolated from the reaction of ethane-1,2-diol with decafluorocyclohexene [2] arise entirely from the cyclisation of the 3-alkoxy isomer VII (n = 2).

EXPERIMENTAL

G.l.c. separations were performed using Pye Series 104 or 105 chromatographs with two columns (6 mm x 9.1 m), Unit A, silicone gum-Celite (1:7) or Unit B, Ucon oil (50-HB-2000)-chromosorb P (1:5). I.r spectra were measured with a Perkin-Elmer 257 grating spectrometer. ^{1}H (60 MHz) and ^{19}F (56.4 MHz) n.m.r. spectra were measured with Perkin-Elmer R10 or R12 spectrometers; samples were dissolved in tetrachloromethane or deuterotrichloromethane with tetramethyl silane or trichlorofluoromethane as internal standard.

Reactions of 1-ethoxy-1-(2-hydroxyethoxy) ethane II

II was prepared by heating a mixture of ethane-1,2-diol and methyl vinyl ether in a sealed Carius tube at 200-225° for 12-15 h [3].

(a) With hexafluorobenzene

Hexafluorobenzene (5.0 g), sodium hydride (1.1 g), II (5.0 g) and dry benzene (15 cm^3) were heated under reflux for 1 h. Excess hydrogen chloride in aqueous dioxan was added to the cooled mixture. After 15 h water (50 cm^3) was added and the mixture was extracted with ether (3 x 10 cm^3). Evaporation of the dried ($MgSO_4$) extract gave a liquid (6.05 g) which was distilled in vacuo to give 2-pentafluorophenoxyethanol (4.1 g) ^{19}F δ 158.0 (m) and 164.8 (m) (2:3), identical with an authentic sample [9].

(b) With octafluorocyclopentene

A mixture of II (10.0 g), sodium hydride (1.2 g) and dry benzene (20 cm^3) was kept at ambient temperature for 30 min. and then added to a mixture of octafluorocylopentene (10.6 g) and benzene (10 cm^3). After 45 min. hydrogen chloride in aqueous dioxan was added. 15 h later water (100 cm^3) was added and the mixture extracted with ether. Distillation of the residue (9.4 g) remaining after evaporation of ether from the dried ($MgSO_4$) extract gave a liquid (4.7 g) b.p. 80-120°/15 mm Hg and an involatile residue (4.1 g). An aliquot (2.0 g) of the former was separated by g.l.c. (Unit A: 150°, N_2, 6 lh^{-1}) to give (i) benzene (0.4 g), (ii) 1-(2-hydroxyethoxy) heptafluorocyclopentene (nc) (0.32 g) b.p. 187°. Analysis: Found: C, 33.0; H, 1.9; F, 52.0% $C_7H_5F_7O_2$ requires C, 33.1; H, 2.0; F, 52.4%. m/e 254 (M^+). ν (-OH), 3360 and ν (-CF = C (OR)-, C_5 ring), 1723 cm^{-1}. ^{1}H τ 5.6 (2H, m, $-OCH_2-$), 6.1 (2H, m, $-OCH_2-$) and 6.4 (1H, s, -OH), ^{19}F δ 116.2 (d), 117.0 (d), 130.6 (s) and 162.3 (s) (2:2:2:1), and (iii) a mixture (0.05 g) not investigated further.

(c) With decafluorocyclohexene

In a similar manner to that described above decafluorocyclohexene (26.2 g) gave a liquid (8.6 g) b.p. 73-84°/15 mm Hg and an involatile residue (19.7 g). An aliquot (2.0 g) of the former was separated by g.l.c. (Unit A: 100°, N_2, 4 lh^{-1}) to give (i) 1-(2-hydroxyethoxy) nonafluorocyclohexene (nc) (1.05 g) b.p. 197-8°. Analysis: Found: C, 31.5; H, 1.6; F, 56.3%. $C_8H_5F_9O_2$ requires: C, 31.6; H, 1.6; F, 56.2%. m/e 304 (M^+), ν (-OH), 3360 and ν (-CF = C (OR)-, C_6 ring) 1702 cm^{-1}, ^1H τ 5.6 (3H, m, $-CH_2OH$) and 6.1 (2H, t, $-OCH_2$), ^{19}F δ 117.6 (m), 126.7 (m) and 151.7 (m) (4:4:1) and (ii) a mixture (0.93 g) of previous compound and another tentatively identified as 3-(2-hydroxyethoxy) nonafluorocyclohexene, ν (-CF = CF-, C_6 ring) 1741 cm^{-1}.

Reaction of an aliquot of this fraction (ii) with phosphorus pentachloride gave a mixture which was separated by g.l.c. to give 3- and 1-(2-chloroethoxy) nonafluorocyclohexenes identified by i.r. spectroscopy [7].

(d) With dodecafluorocycloheptene

In a similar manner to that described in the previous experiment dodecafluorocycloheptene (15.0 g) afforded a colourless liquid (14.9 g) which was distilled in vacuo and separated by g.l.c. (Unit A: 130°, N_2, 6 lh^{-1}) to give (i) ether (3.3 g), (ii) dodecafluorocycloheptene (1.5 g), (iii) 1-(2-hydroxyethoxy) undecafluorocycloheptene (nc) (3.1 g) b.p. 178° (decomp). Analysis: Found: C, 30.5; H, 1.4; F, 58.5%. $C_9H_5F_{11}O_2$ requires C, 30.5; H, 1.4; F, 58.7%. ν (-OH), 3360 and ν (-CF = C (OR)-, C_7 ring) 1680 cm^{-1}, ^1H τ 5.7 (2H, m, $-OCH_2-$), 6.1 (2H, t, $-OCH_2-$) and 7.9 (1H, s, -OH), ^{19}F δ 112.0 (m), 113.6 (m), 128.7 (m) and 139.8 (m) (2:2:6:1), and (iv) a mixture (0.3 g).

Reaction of 1-(2-hydroxyethoxy) nonafluorocyclohexene VI (n = 2) with phosphorus pentachloride

Compound VI (n = 2) (5.0 g), phosphorus pentachloride (10.0 g) and ether (100 cm^3) were mixed slowly, heated under reflux for 1 h and poured into water. The residue, obtained on evaporation of the dried ($MgSO_4$) ethereal extract, was distilled in vacuo to yield 1-(2-chloroethoxy) nonafluorocyclohexene (4.1 g) identified by i.r. spectroscopy [7].

The reactions of the 1-(2-hydroxyethoxy) perfluorocycloalkenes VI (n = 1, 2, 3)

(a) Cyclisation of 1-(2-hydroxyethoxy) heptafluorocyclopentene

The hydroxy compound VI (n = 1) (0.5 g), potassium hydroxide (0.11 g) and ethane -1,2-diol (3.0 cm^3) were heated at 100° for 15 h, poured into 4 M hydrochloric acid (20 cm^3) and extracted with ether (3 x 5 cm^3). Evaporation of the ether gave a residue which was separated by g.l.c. (Unit B: 120°, N_2,4 lh^{-1}) to give ether (0.19 g) and 6,7,8,8,9,9-hexafluoro-1,4-dioxaspiro (5,5) non-6-ene (nc) (0.18 g) b.p. 149°. Analysis: Found: C, 36.2; H, 1.9; F, 48.4%. $C_7H_4F_6O_2$ requires: C, 35.9; H, 1.7; F, 48.7%. m/e 234 (M^+), ν (-CF = CF-, C_5 ring) 1769 cm^{-1}, ^1H τ 5.8 (4H, s, $-OCH_2CH_2O-$), ^{19}F δ 113.2 (tt, J 12.0, 2.4 Hz), 124.0 (m, J 2.4 Hz), 142.4 (tt, J 12.0, 4.5 Hz) and 151.8 (tt, J 12.0, 4.5 Hz) (2:2:1:1).

(b) Cyclisation of 1-(2-hydroxyethoxy) nonafluorocyclohexene

In a similar manner to that described above the hydroxy compound VI (n = 2) (0.91 g) gave a residue which was separated by g.l.c. (Unit A: 120°, N_2, 7 lh^{-1}) to give ether (0.98 g) and 6,7,8,8,9,9,10,10-octafluoro-1,4-dioxaspiro (5,6) dec-6-ene (0.3 g) identified by comparison (i.r. and ^{19}F n.m.r. spectra) with an authentic sample [2,7].

(c) Cyclisation of 1-(2-hydroxyethoxy) undecafluorocycloheptene

In a similar manner to that described above the hydroxy ether VI (n = 3) (3.0 g) gave a residue which was separated by g.l.c. (Unit B: 150°, N_2, 4 lh^{-1}) to give (i) ether (0.6 g), (ii) 6,7,8,8,9,9,10,10,11,11-decafluoro-1,4-dioxaspiro (5,7) undec-6-ene (nc) (0.7 g) b.p. 190°. Analysis: Found: C, 32.6; H, 1.4; F, 56.7%. $C_9H_4F_{10}O_2$ requires: C, 32.3; H, 1.2; F, 56.8%. ν (-CF = CF-, C_7 ring) 1716 cm^{-1}, ^1H τ 5.8 (4H, s, $-OCH_2CH_2O-$), ^{19}F δ 114.7 (m), 126.5 (s), 1265 (m), 128.6 (m), 137.5 (t) and 150.3 (t) (2:2:2:2:1:1), and (iii) 6,6,7,7,8,8,9,9,10,10,11-undecafluoro-1,4-dioxaspiro (5,7) undecane (nc) (0.17 g) b.p. 198°. Analysis: Found: C, 30.5; H, 1.6; F, 59.0%. $C_9H_5F_{11}O_2$ requires:

C, 30.5; H, 1.6; F, 59.1%. ^{1}H τ 5.8 (4 H, s, $-OCH_2CH_2O-$) and 4.5-6.0 (1H, m, -CHF-), ^{19}F δ 223.1 (d, J ($^{1}H-^{19}F$) 48 Hz) and complex group of signals (1:10) and (iv) a mixture (0.4 g).

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REFERENCES

1 R. G. Plevey and D. J. Sparrow, Part XII, J. Chem. Soc. Perkin Trans. I, (1976) 573.

2 G. Camaggi and R. Stephens, Tetrahedron, 22 (1966) 1189.

3 M. F. Shostakovskii, N. A. Gershtein and Z. S. Volkova, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk., (1952) 671.

4 J. K. Brown and K. Morgan, Adv. Fluorine Chem. 4 (1965) 253.

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

6 J. A. Oliver, Ph.D. Thesis, University of Birmingham, 1965.

7 D. J. Sparrow, Ph.D. Thesis, University of Birmingham, 1970.

8 A. B. Clayton, R. Stephens and J. C. Tatlow, J. Chem. Soc. (C), (1969) 2329.

9 J. Burdon, V. A. Damodaran and J. C. Tatlow, J. Chem. Soc., (1964) 763.