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REACTIONS INVOLVING FLUORIDE ION. PART 21 [1]. NUCLEOPHILIC
SUBSTITUTION REACTIONS OF PERFLUOROCYCLOBUTENE OLIGOMERS

RICHARD D. CHAMBERS, GRAHAM TAYLOR

Department of Chemistry, University Science Laboratories,
South Road, Durham, DH1 3LE (Gt. Britain)

and RICHARD L. POWELL

I.C.I. Ltd., Mond Division, P.O. Box No. 8, The Heath, Runcorn,
Cheshire, WA7 4QD (Gt. Britain)

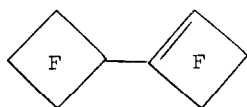
SUMMARY

Reaction of perfluorocyclobutene oligomers, (1) - (4), with some simple nucleophiles gives products arising from S_N2' displacement [N.B. this term is used here to describe the overall process of addition of a nucleophile to an alkene and elimination of an allylic fluorine and is not meant to imply that the reaction is concerted] or vinylic substitution of fluorine, or a mixture of both processes. The reactivity of the dimers, (1) and (2), is much greater than that of acyclic analogues and this can be attributed to the ring strain present in these compounds.

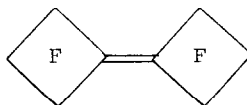
RESULTS AND DISCUSSION

A range of compounds, (1) - (4), can be obtained by fluoride ion [2,3] or pyridine [3-5] induced oligomerisation of perfluorocyclobutene. Whilst there exists a considerable literature on the reactions of compounds which, like (1) and (3), contain vinylic fluorine [6], the chemistry of compounds of the type $(R_f)_2C=C(R_f)_2$ [R_f = perfluoroalkyl or is part of a perfluorocycloalkyl group], e.g. (2) and (4), is much less developed,

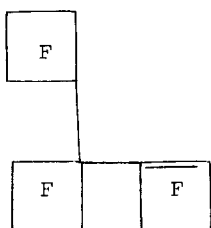
although several alkenes of this type have been prepared [2,7-11]. We have recently reported some fascinating reactions of one example, perfluoro-3,4-dimethylhex-3-ene (5), with nucleophiles [12]. In this paper we describe reactions of compounds (1) - (4) with some simple nucleophiles.



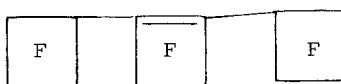
(1)



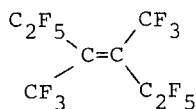
(2)



(3)



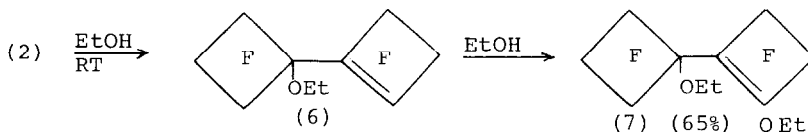
(4)

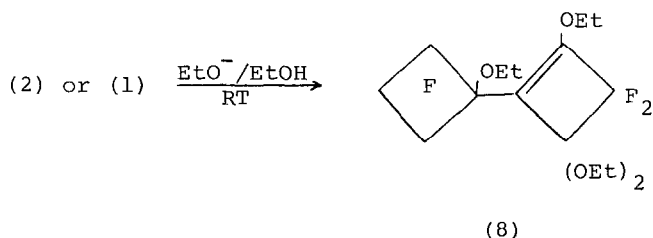


(5)

The presence of F in a ring means that all unmarked positions are attached to fluorine.

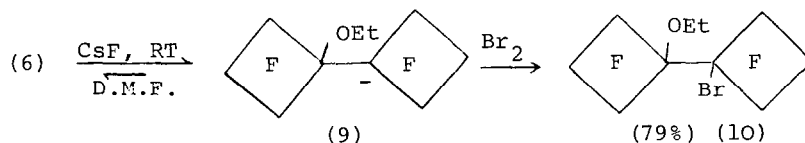
Formally dimer (2) is related to compound (5). However, the very great ring strain present in (2) leads to a much enhanced reactivity towards nucleophiles. Thus, in contrast to compound (5), dimer (2) reacts rapidly with neutral alcohols and, with ethanol, gives initially the monoethoxy derivative (6) which reacts further to give the diethoxy compound (7). With ethoxide ion, tetrasubstitution occurs to give compound (8).



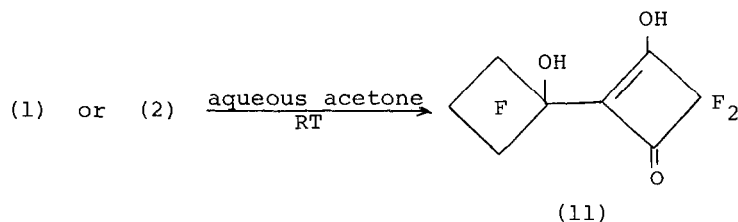


The initial step in all nucleophilic reactions of (2) is S_N2' displacement of fluorine, e.g. (2) \rightarrow (6), further reaction then occurs by vinylic substitution, e.g. (6) \rightarrow (7). Depending on the nucleophile and reaction conditions, the disubstituted product can then undergo further reaction with overall substitution of two allylic fluorines.

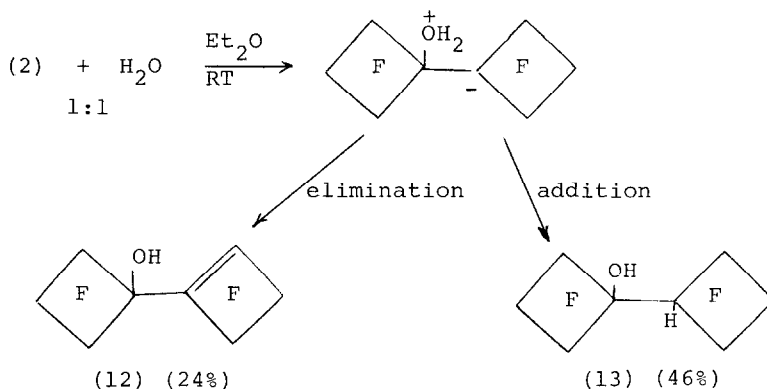
Interestingly, compound (6) dissolves in D.M.F. in the presence of fluoride ion to give a solution believed to contain anion (9); quenching of this solution with bromine yields compound (10).



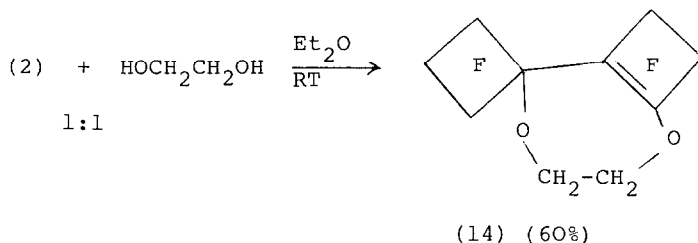
The reaction with excess water parallels that with ethoxide ion and yields the hydroxy ketone (11).



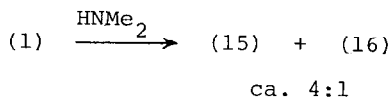
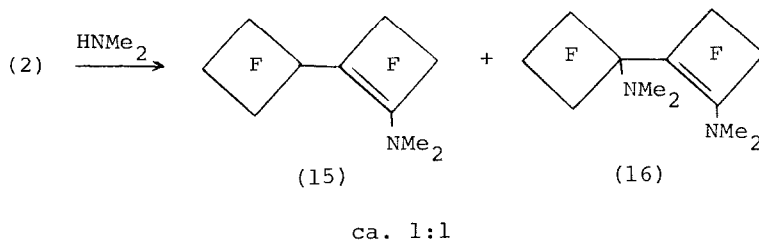
Under the same conditions compound (5) is unreactive. With an equivalent of water dimer (2) not only undergoes the expected S_N2' displacement to give the alcohol (12), but also straight-forward addition to give (13). With aqueous acetone both compounds (12) and (13) are hydrolysed further to (11).



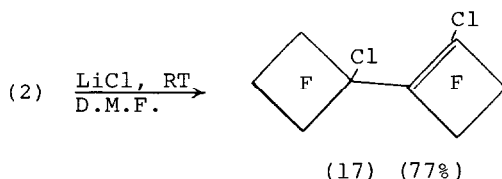
Reaction of (2) with ethylene glycol gave a cyclic product (14) corresponding to the diethoxy compound (7). A similar product was obtained with compound (5) but only in the presence of a base [12].



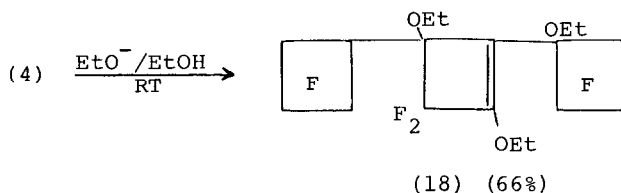
Dimer (2) reacts vigorously and very exothermically with dimethylamine to yield a mixture of a mono- and a di-substituted compound, (15) and (16) respectively. The same two products are obtained with dimer (1) and it seems probable that fluoride ion, formed during the reaction, causes some isomerisation of the dimers.



With lithium chloride reaction occurs to give the dichloro compound (17). Once again this can be contrasted with the failure of alkene (5) to react at all under the same conditions [12].

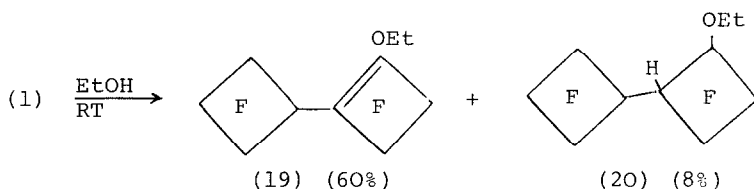


Trimer (4) is another example of an alkene of the type $(R_F)_2C=C(R_F)_2$ and, since the ring strain is much less than that present in dimer (2), its reactivity might be expected to parallel that of compound (5). This is, indeed, the case, i.e. (4) is unaffected by neutral ethanol but reacts rapidly with ethoxide ion [4] to give the triethoxy derivative (18), by a mixture of S_N2' displacement and vinylic substitution of fluorine.



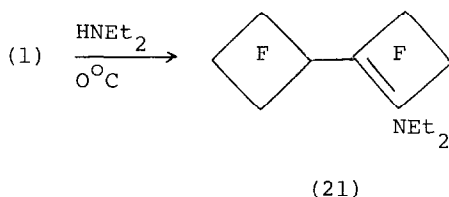
Trimer (4) is unaffected by aqueous acetone but reacts in the presence of sodium carbonate to give a heat sensitive oil which has not yet been characterised. Similarly, vigorous reactions occur with diethylamine and sodium borohydride but in both cases complex mixtures are obtained and these have yet to be investigated. The highly novel reaction with fluoride ion is described elsewhere [13].

Dimer (1) is a member of the well known class of compounds containing vinylic fluorine and, depending on the nature of the nucleophile, undergoes either mono- or tetra-substitution. Like its isomer (2) it reacts rapidly with neutral ethanol to yield mainly the monoether (19) together with an addition product (20) and other, unidentified species.

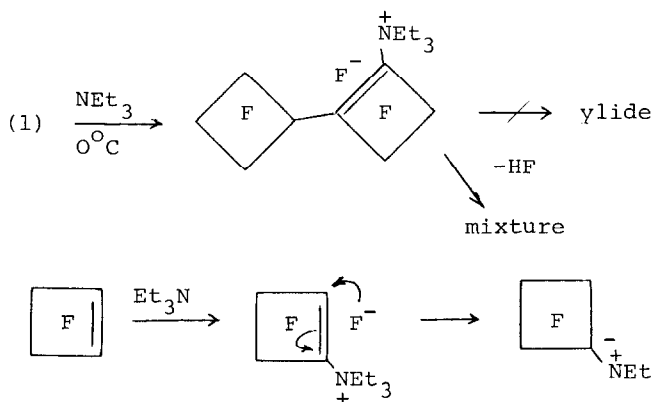


With ethoxide ion, tetrasubstitution occurs to give (8) whilst with water compound (11) is formed.

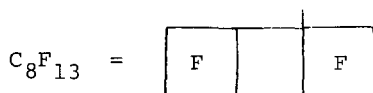
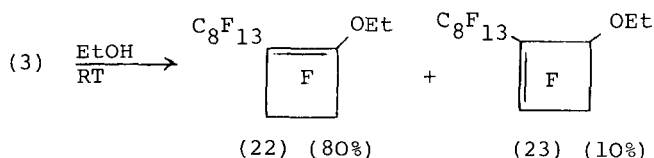
The reaction with dimethylamine has already been described, but with diethylamine (using different reaction conditions - see experimental) simple monosubstitution is the only process



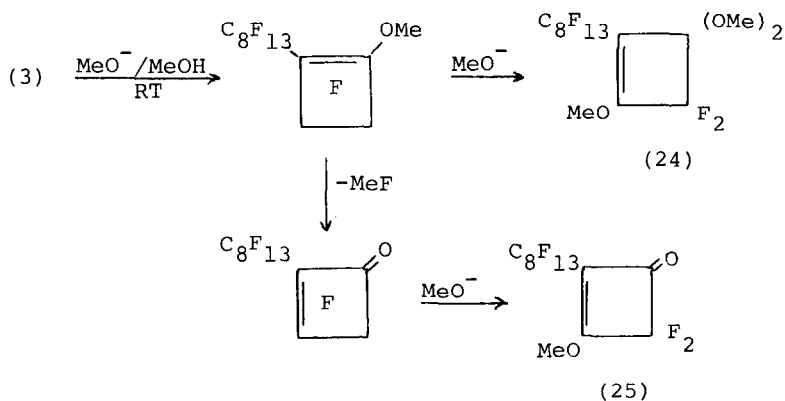
observed. With triethylamine, dimer (1) gave a complex mixture, resulting from loss of hydrogen fluoride and then further reaction of the initially formed adduct. This can be contrasted with the analogous reaction with perfluorocyclobutene where an ylide is formed [14].



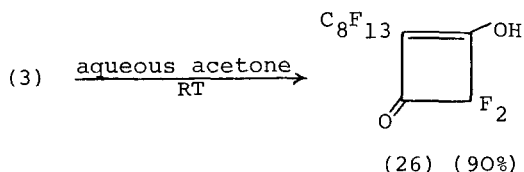
Trimer (3) also reacts with neutral ethanol, but less rapidly than the dimers, to give mono-ethers (22) and (23) by vinylic substitution and S_N2' displacement of fluorine respectively. With methoxide ion two products, (24) and (25),



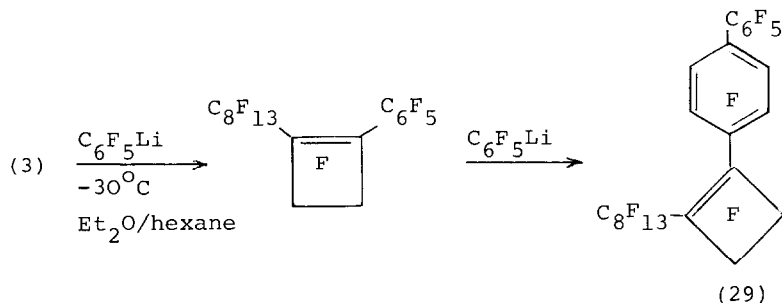
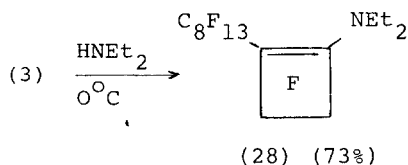
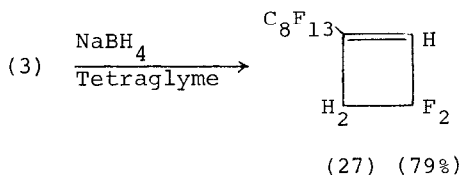
are obtained. Compound (24) is formed by a mixture of S_N2' displacement and vinylic substitution of fluorine, whilst production of (25) presumably involves loss of methyl fluoride from an intermediate product. As with the dimers, reaction with



water parallels that with alkoxide ion and gives a high yield of (26).

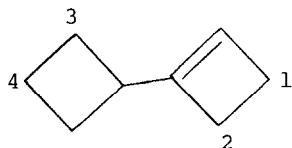


With sodium borohydride trisubstitution occurs to give compound (27), whilst with diethylamine, vinylic substitution gives (28). Vinylic substitution also occurs with pentafluorophenyl lithium but the product reacts with excess reagent to yield compound (29).



Structural Assignments

All the products described above gave satisfactory elemental analyses. Product identity usually followed simply from ^{19}F n.m.r. data. The numbering system for n.m.r. assignments of CF_2 groups in products derived from the dimers, (1) and (2), is given below:-



EXPERIMENTAL

^{19}F and ^1H n.m.r. spectra were recorded at 40°C using a Varian A56/60D spectrometer, with CFCl_3 or TMS as external reference. Upfield ^{19}F shifts are quoted as positive. G.l.c. was performed on a gas-density balance using two columns; 30% silicone gum (Col 'O') or 20% di-isodecylphthalate (Col 'A'). Molecular weights were determined on an AEI MS9 mass spectrometer.

Reactions of dimer (2)(a) With neutral ethanol

Dimer (2) (1.2 g, 3.7 mmol) was stirred with ethanol (5 ml) for two minutes. There was an exothermic reaction. The mixture was poured into water, the lower fluorocarbon layer removed, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid was shown by g.l.c. (Col 'O') to be essentially a single compound with traces of ethanol and other, unidentified species. The major component was separated by preparative scale g.l.c. and identified as 1-ethoxy-1-pentafluorocyclobutenyl-hexafluorocyclobutane (6) (nc) (1.0 g, 78%): b.p. 131°C ; Analysis: C, 34.6; H, 1.6; F, 59.4%; M^+ , 350. $\text{C}_{10}\text{F}_{11}\text{OH}_5$ requires: C, 34.29; H, 1.43; F, 59.71%; M, 350; λ_{max} 1711 cm^{-1} (C=C str); δ_{F} 98.9 (1F, triplet of triplets $J_1 = 16\text{ Hz}$, $J_2 = 18\text{ Hz}$; = CF-), 116.1 (2F, multiplet, 2-F), 121.1 (2F, multiplet, 1-F), 123.8 and 133.3 (4F, as AB, $J = 228\text{ Hz}$, 3-F) and 131.5 and 133.8 ppm (2F, as AB, $J = 223\text{ Hz}$, 4-F); δ_{H} 1.40 (CH_3 -, triplet $J = 7\text{ Hz}$) and 3.97 ($-\text{CH}_2$ -, quartet, $J = 7\text{ Hz}$).

In an analogous reaction dimer (2) (1.4 g, 4.3 mmol) was stirred with ethanol (5 ml) for 18 h. at room temperature. The mixture was poured into water, the lower layer removed, dried (P_2O_5) and transferred to a cold trap under vacuum. The resultant liquid (1.5 g) was shown by g.l.c. (Col 'O') to be a complex mixture. The three main components were identified by g.l.c.-m.s. as disubstituted compounds, $\text{C}_8\text{F}_{10}(\text{OEt})_2$. The major component was separated by preparative scale g.l.c. and identified as 1-(1'-ethoxyhexafluorocyclobutyl)-2-ethoxytetrafluorocyclobutene (7) (nc), (1.0 g, 65%): b.p. 192°C ; Analysis: C, 38.4;

H, 2.5; F, 50.3%; M^+ , 376. $C_{12}F_{10}O_2H_{10}$ requires: C, 38.30; H, 2.66; F, 50.53%; M , 376; λ_{\max} 1685 cm^{-1} (C=C str); δ_F 111.2 (2F, multiplet, 2-F), 116.1 (2F, triplet $J = 4$ Hz, 1-F), 123.9 and 133.3 (4F, as AB, $J = 224$ Hz, 3-F) and 131.7 and 133.8 (2F, as AB, $J = 223$ Hz, 4-F); δ_H 1.40 (CH_3^- , triplet, $J = 7$ Hz), 1.53 (CH_3^- , triplet $J = 7$ Hz), 3.83 ($-CH_2^-$, quartet, $J = 7$ Hz) and 4.53 ($-CH_2^-$, quartet, $J = 7$ Hz).

(b) With sodium ethoxide

Sodium metal (0.9 g, 39.1 mmol) was added to dry ethanol (20 ml) and when reaction was complete a mixture of dimers (1) and (2) (2.6 g, 8.0 mmol) was slowly added. There was a vigorous reaction with formation of a white precipitate. The mixture was left stirring overnight and the ethanol removed under reduced pressure. The residue was distilled in vacuo (up to 90°C, 0.1 mm Hg) to give a colourless liquid (2.3 g), shown by g.l.c. (Col 'O') to be a single compound identified as 1-(1'-ethoxyhexafluorocyclobutyl)-2,3,3-triethoxy-4,4-difluorocyclobutene (8) (nc) (67%): b.p. > 200°C; Analysis: C, 44.6;

112.7 (2F, singlet, 1-F), 122.8 and 133.1 (4F, as AB, $J = 219$ Hz, 3-F) and 130.5 and 133.3 (2F, as AB, $J = 219$ Hz, 4-F); δ_H 3.90, 3.96 and 4.42 (all $-CH_2^-$'s, quartets, $J = 7$ Hz, ratio 2:1:1) and signal centred at 1.5 due to overlapping CH_3^- resonances.

(c) Compound (6) with fluoride ion

A mixture of compound (6) (0.76 g, 2.17 mmol), caesium fluoride (1.43 g, 9.4 mmol) and DMF (5 ml) was stirred at room temperature for 30 minutes. A small sample of the resultant solution was removed and its ^{19}F n.m.r. spectrum recorded at various temperatures. These indicated the presence of the 1-(1'-ethoxyhexafluorocyclobutyl)-hexafluorocyclobutyl anion (9) in solution: δ_F 84.0 (very broad singlet, $-CF_2^-$'s adjacent to anionic centre [15] and signals between 119 and 138 ppm (uncertain integration). The residual solution was quenched with bromine (0.35 g, 2.19 mmol) and stirred at room temperature for 1 h. The volatiles were then transferred under vacuum to a cold

trap. The lower layer was removed, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (0.72 g) was shown by g.l.c. (Col 'O') to be a single compound identified as 1-ethoxy-1-(1'-bromohexafluorocyclobutyl)-hexafluorocyclobutane (10) (nc), (79%): b.p. $169^{\circ}C$; Analysis: C, 26.5; F, 51.5; Br, 17.1%. $C_{10}F_{12}OH_5Br$ requires: C, 26.73; F, 50.78; Br, 17.82%; no C=C str in I.R.; δ_F 109.7 and 119.3 (4F, as AB, J = 216, $-CF_2$'s adjacent to >CBr-), 125.7 (4F, broad complex signal, $-CF_2$'s adjacent to >C(OEt)-), 126.0 and 128.7 (2F, as AB, J = 221 Hz) and 131.2 (2F, singlet); δ_H 1.63 (CH_3 -, triplet (J = 7 Hz) of doublets (J = 1.5 Hz)) and 4.20 ($-CH_2$ -, quartet, J = 7 Hz).

(d) With excess water

A mixture of dimers (1) and (2) (3.0 g, 9.3 mmol) and aqueous acetone (20 ml) was stirred at room temperature for 24 h. The acetone was removed under reduced pressure and the residue molecular distilled (ca. $60^{\circ}C$, 0.1 mm Hg) to give a pale yellow, viscous liquid (1.9 g) identified as 1-hydroxy-2-(1'-hydroxy-hexafluorocyclobutyl)-4,4-difluorocyclobuten-3-one (11) (nc), (69%): Analysis: F, 51.1%; $C_8F_8O_3H_2$ requires: F, 51.01%; λ_{max} 1796 and 1641 cm^{-1} (broad) (C=C str. and C=O str.)

115.3 (2F, singlet, 1-F), 125.9 and 132.5 (4F, as AB, J = 222 Hz, 3-F) and 131.6 ppm (2F, doublet, J = 20 Hz, 4-F); δ_H sharp singlet at 8.25. Compound (11) decomposes on strong heating.

Similar reactions with the separate dimers both gave (11) as the only product.

(e) With an equivalent of water

Dimer (2) (1.70 g, 5.25 mmol) was dissolved in ether (10 ml) and water (94 μ l, 5.22 mmol) was added. The mixture was stirred for 2 h. at room temperature and then the ether removed by distillation to leave a colourless liquid (2.06 g) shown by g.l.c. (Col 'O') to consist of ether and two other components. These were separated by preparative scale g.l.c. to give 1-(1'-hydroxy-hexafluorocyclobutyl)-2,2,3,3,4,4-hexafluorocyclobutane (13) (nc) (0.59 g, 33%) and 1-hydroxy-1-pentafluorocyclobutenyl-hexafluorocyclobutane (12) (nc) (0.24 g, 14%). Yields by g.l.c. were 46 and 24% respectively.

For compound (13): b.p. 107°C; Analysis: C, 28.1; H, 0.7; F, 67.0%; M^+ , not observed, highest peak at $m/e = 322$, i.e. $M^+ - 20$ (HF). $C_8F_{12}OH_2$ requires: C, 28.07; H, 0.58; F, 66.67%; M, 342; I.R. shows no C=C str; δ_F signals between 110 and 140 ppm all unassigned; δ_H , 3.7 (broad singlet).

For compound (12): b.p. 111°C; Analysis: C, 29.6; H, 0.2; F, 64.7%; M^+ , 322. $C_8F_{11}OH$ requires: C, 29.81; H, 0.31; F, 64.91%; M, 322; λ_{max} 1721 cm^{-1} (C=C str); δ_F 99.9 (1F, triplet ($J = 15$ Hz) of triplets ($J = 18$ Hz), =CF-), 116.3 (2F, multiplet, 2-F), 121.5 (2F, multiplet, 1-F), 127.5 and 134.8 (4F, as AB, $J = 225$ Hz, 3-F) and 132.6 ppm (2F, doublet, $J = 12$ Hz, 4-F); δ_H 4.25 (broad resonance).

When stirred overnight in aqueous acetone, both compound (12) and (13) were hydrolysed to compound (11).

(f) With ethylene glycol

A solution of dimer (2) (1.89 g, 5.83 mmol) in ether (10 ml) was slowly added to a mixture of ethylene glycol (0.35 g, 5.65 mmol) and ether (20 ml) and the mixture stirred until an homogeneous solution was obtained. This was then allowed to stand at room temperature for 48 h and the ether removed on a rotary evaporator. Vacuum sublimation of the residue yielded a white solid (1.21 g) which was recrystallised from CCl_4 at 0°C to give large rhombohedral crystals identified as bicyclo-[5.2.-0]-2-spirohexafluorocyclobutyl-3,6-dioxa-8,8,9,9-tetrafluoronon-1,7-ene (14) (nc), (60%): m.p. 54-55°C; Analysis: C, 34.4; H, 1.1; F, 55.3%; M^+ 346. $C_{10}F_{10}O_2H_4$ requires: C, 34.68; H, 1.16; F, 54.91%; M, 346; λ_{max} 1688 cm^{-1} (C=C str); δ_F (in CCl_4) 109.3 (2F, broad singlet, 2-F), 121.4 (2F, singlet, 1-F), 124.9 and 132.4 (4F, as AB, $J = 221$ Hz, 3-F) and 131.2 and 133.3 ppm (2F, as AB $J = 224$ Hz, 4-F); δ_H 4.80 (doublet $J = 13$ Hz, unassigned) and 4.80 (doublet of doublets $J_1 = 25$ Hz and $J_2 = 3.5$ Hz, unassigned).

(g) With dimethylamine

Dimer (2) (1.4 g, 4.3 mmol) and dimethylamine (1.4 g, 31.1 mmol) were transferred under vacuum to a Carius tube. The tube

was sealed and allowed to warm; there was a vigorous, exothermic reaction. When the tube had cooled to room temperature, it was opened and the contents shaken with water. The lower layer was removed and molecular distilled (ca. 65°C, 0.1 mm Hg) to give a pale yellow liquid (1.4 g) shown by g.l.c.-m.s. (Col 'O') to be a mixture of a mono- and a di-substituted compound (46 and 54% respectively). These were separated by preparative scale g.l.c.

The monosubstituted compound (a liquid) was identified as 1-dimethylamino-2-heptafluorocyclobutyl-tetrafluorocyclobutene (15) (nc); Analysis: N, 4.1; F, 59.5%; M^+ 349. $C_{10}F_{11}NH_6$ requires: N, 4.01; F, 59.89%; M, 349; λ_{max} 1690 cm^{-1} (C=C str); δ_F 104.4 (2F, broad singlet, 2-F), 117.0 (2F, singlet, 1-F), 125.7 and 132.8 (4F, as AB J = 228 Hz, 3-F), 130.6 and 134.0 (2F, as AB J = 228 Hz, 4-F) and 154.9 ppm (1F, broad singlet, CF-); δ_H 3.31 (singlet).

The disubstituted compound (a solid) was identified as 1-dimethylamino-2-(1'-dimethylaminohexafluorocyclobutyl)-tetrafluorocyclobutene (16) (nc); Analysis: C, 38.2; H, 3.5; F, 51.3%; M^+ 374. $C_{12}F_{10}N_2H_{12}$ requires: C, 38.50; H, 3.21; F, 50.80%; M, 374; λ_{max} 1683 cm^{-1} (C=C str); δ_F 103.4 (2F, triplet (J = 18) of triplets (J = 24), 2-F), 115.8 (2F, singlet, 1-F), 111.1 and 124.9 (4F, as AB J = 222 Hz, 3-F) and 130.6 and 135.2 ppm (2F, as AB J = 226 Hz, 4-F); δ_H 2.72 and 3.13 (ratio 1:1 each a singlet).

(h) With lithium chloride

A mixture of lithium chloride (1.22 g, 28.80 mmol), dimer (2) (2.49 g, 7.69 mmol) and DMF (10 ml) was stirred at room temperature for 3 h. The volatiles were transferred under vacuum to a cold trap. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid was shown by g.l.c. (Col 'O') to be a single compound identified as 1-chloro-2-(1'-chlorohexafluorocyclobutyl)-tetrafluorocyclobutene (17) (nc) (77%): b.p. 129°C; Analysis: C, 26.7; F, 52.5; Cl, 20.5%; M^+ 356 (^{35}Cl). $C_8F_{10}Cl_2$ requires: C, 26.89; F, 53.22; Cl, 19.89%; M, 356; λ_{max} 1640 cm^{-1} (C=C str); δ_F 114.1 (2F, multiplet, 2-F), 120.7 (2F, multiplet, 1-F), 121.9 (4F, singlet, 3-F) and 129.6 ppm (2F, singlet, 4-F).

Reactions of trimer (4)(a) With neutral ethanol

Trimer (4) was stirred for several days with ethanol. The two layers did not homogenise and after two weeks g.l.c. (Col 'O') did not indicate the presence of any products in either layer.

(b) With sodium ethoxide

Sodium metal (0.65 g, 28.3 mmol) was added to ethanol (20 ml) and when reaction was complete, trimer (4) (2.6 g, 5.4 mmol) was added and the mixture stirred overnight at room temperature. The ethanol was removed under reduced pressure and the residue sublimed in vacuo (ca. 60°C, 0.1 mm Hg) to give a solid (2.0 g) which was recrystallised from methanol (low temperature) and identified as 1,3-diethoxy-2-(1'-ethoxyhexafluorocyclobutyl)-3-heptafluorocyclobutyl-4,4-difluorocyclobutene (18) (nc), (66%) m.p. 52-53°C; Analysis: C, 38.4; H, 2.7; F, 50.4%; M^+ 564. $C_{18}F_{15}O_3H_{15}$ requires: C, 38.30; H, 2.66; F, 50.53%; M, 564; $\lambda_{\max} 1681\text{ cm}^{-1}$ (C=C str); δ_F (CCl_4) 107.9 (2F, multiplet, $-CF_2-$ in unsaturated ring), 176.4 (1F, broad multiplet, $>CF-$) and signals between 122 and 136 ppm (12F, unassigned); δ_H (CCl_4) CH_3 -s centred at 1.6, $-CH_2$ -s at 4.2.

(c) With water

Stirring trimer (4) in aqueous acetone at room temperature did not lead to any detectable reaction. However, addition of the trimer (3.4 g) to a mixture of sodium carbonate (3.4 g), acetone (15 ml) and water (5 ml) resulted in an exothermic reaction. The mixture was left stirring overnight and then acidified (dil. HCl). The lower layer was removed and dissolved in ether (50 ml). The upper layer was ether extracted (2 x 50 ml) and the extracts combined with the lower layer. The solution was then washed with water, dried ($MgSO_4$) and the ether removed on a rotary evaporator to leave a yellow liquid (2.0 g). A ^{19}F n.m.r. spectrum indicated this to be a mixture. Various attempts to separate components were unsuccessful and the reaction was not pursued further.

(d) With diethylamine

Trimer (4) (3.3 g, 6.8 mmol) was slowly added to diethylamine (10 ml) with stirring and external cooling (ice-bath). A vigorous reaction occurred with precipitation of diethylamine-hydrofluoride. This was removed by filtration and the filtrate washed with water. Molecular distillation (0.1 mm Hg, up to 90°C) gave a pale yellow liquid (1.7 g). This was shown by ^{19}F n.m.r. and g.l.c. to be a complex mixture. Various attempts to separate components were unsuccessful and so the reaction was not pursued further.

(e) With sodium borohydride

To a suspension of sodium borohydride (1.0 g, 25.6 mmol) in tetraglyme (20 ml) at -18°C was added slowly trimer (4) (3.3 g, 6.8 mmol) with rapid stirring. When the addition was complete the mixture was stirred at room temperature for 1 h. and then carefully poured into water (100 ml) and ether extracted (3 x 50 ml). The ether extracts were bulked, washed with water, dried (MgSO_4) and the ether removed by distillation to leave a colourless liquid (3.1 g) shown by g.l.c. (Col 'O') to be a mixture of ether and ca. 20 other components.

In a similar reaction, after the addition was complete, the mixture was stirred for 1 h. on a steam bath and then flash distilled to give a small amount of a colourless liquid which was shown by g.l.c. (Col 'O') to be a highly complex mixture. In view of the low recovery and the complexity of the product, the reaction was not pursued.

Reactions of dimer (1)(a) With neutral ethanol

A mixture of dimer (1) (1.1 g, 3.4 mmol) and ethanol (5 ml) was stirred at room temperature for 18 h. The mixture was poured into water and the lower layer removed, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (1.0 g) was shown by g.l.c.-m.s. (Col 'O') to be a mixture of two monosubstituted compounds, an addition product and two disubstituted compounds. The major monosubstituted compound (0.61 g, 60%) was

separated by preparative scale g.l.c. and identified as 1-ethoxy-2-heptafluorocyclobutyl-tetrafluorocyclobutene (19) (nc). Also separated was the addition product (< 0.1 g, ca. 8% by g.l.c.) which was identified as 1-ethoxy-2-hydro-2-heptafluorocyclobutyl-pentafluorocyclobutane (20) (nc). Other components were not characterised.

For compound (19): b.p. 154°C; Analysis: C, 34.1; H, 1.0; F, 59.5%; M^+ , 350. $C_{10}F_{11}OH_5$ requires: C, 34.29; H, 1.43; F, 59.71%; M, 350; λ_{max} 1695 cm^{-1} (C=C str); δ_F 111.2 (2F, multiplet, 2-F), 116.3 (2F, multiplet, 1-F), 127.2 and 133.8 (4F, as AB J = 229 Hz, 3-F), 130.8 and 134.4 (2F, as AB J = 229 Hz, 4-F) and 179.4 ppm (1F, singlet, $>CF-$); δ_H 1.50 (CH_3- , triplet J = 7 Hz) and 4.48 ($-CH_2-$, quartet, J = 7 Hz).

For compound (20); Analysis: C, 32.4; H, 1.4%; M^+ , 370. $C_{10}F_{12}OH_6$ requires: C, 32.43; 1.62%; M, 370; I.R. shows no C=C str; δ_F 195.5 (1F, multiplet, $>CF-$) and signals between 113.6 and 138.5 ppm (11F, unassigned); δ_H 1.62 (CH_3 ; triplet (J = 7 Hz) of doublets (J = 1 Hz)), 4.28 ($-CH_2-$, quartet, J = 7 Hz) and 3.48 ($-CH<$, very broad).

In a similar reaction a mixture of dimer (1) and ethanol was stirred for 3 minutes. The reaction mixture was treated as above and the resultant liquid shown by g.l.c. to be a mixture of several components, the major one of which was identified as compound (19) by ^{19}F n.m.r. spectroscopy.

(b) With dimethylamine

The procedure was as for g. Thus dimer (1) (1.7 g, 5.2 mmol) and dimethylamine (0.9 g, 20.0 mmol) gave a mixture (1.5 g) of compound (15) (83%) and compound (16) (17%).

(c) With diethylamine

Dimer (1) (1.4 g, 4.3 mmol) was added slowly to diethylamine (5 ml) with stirring and external cooling (ice-bath). When the addition was complete, the mixture was shaken with water and the lower layer removed and molecular distilled (ca. 85°C, 0.1 mm Hg) to give a colourless liquid (1.2 g) which rapidly darkened. This was identified as 1-diethylamino-2-heptafluorocyclobutyltetrafluorocyclobutene (21) (nc), (74%); Analysis: F, 55.0%; M^+ 377.

$C_{12}F_{11}NH_{10}$ requires: F, 55.44%; M, 377; λ_{\max} 1676 cm^{-1} (C=C str); δ_F 104.2 (2F, multiplet, 2-F), 116.0 (2F, multiplet, 1-F), 125.9 and 132.0 (4F, as AB J = 226 Hz, 3-F), 130.1 and 133.6 (2F, as AB J = 228 Hz, 4-F) and 159.2 ppm (1F, singlet, $>CF-$); δ_H 1.42 (CH_3- , triplet, J = 7 Hz) and 3.55 ($-CH_2-$, quartet, J = 7 Hz).

(d) With trimethylamine

Dimer (1) (1.42 g, 4.38 mmol) was dissolved in ether (5 ml) and cooled at $-18^\circ C$ whilst a solution of triethylamine (1.05 g, 10.40 mmol) in ether (10 ml) was added slowly. The mixture was filtered under nitrogen to give a white solid (0.46 g), shown to be a quarternary ammonium salt (extremely soluble in water and resultant solution shows only a resonance corresponding to fluoride ion in its ^{19}F n.m.r. spectrum). The ether was removed from the filtrate on a rotary evaporator and the resultant oil shown by ^{19}F n.m.r. spectroscopy to be a complex mixture. Various attempts to separate components were unsuccessful and the reaction was not pursued.

Reactions of trimer (3)

(a) with neutral ethanol

Trimer (3) (2.0 g, 4.1 mmol) was stirred with ethanol (10 ml) for 8 h. at room temperature. The mixture was then poured into water and the lower layer removed, dried (P_2O_5) and transferred under vacuum to a cold trap. The resultant liquid (1.8 g) was shown by g.l.c.-m.s. (Col. 'O') to be a mixture of trimer (3), two monosubstituted products (ca. 90%) in the ratio 8:1 and traces of a disubstituted product. The monosubstituted products were separated by preparative scale g.l.c. and identified as 1-ethoxy-2-(1'-heptafluorocyclobutylhexafluorocyclobutyl)-tetrafluorocyclobutene (22) (nc) (major product), and 4-ethoxy-1-(1'-heptafluorocyclobutylhexafluorocyclobutyl)-tetrafluorocyclobutene (23) (nc).

For compound (22): b.p. $202^\circ C$; Analysis: C, 32.5; H, 0.7; F, 62.7%; M^+ , 512. $C_{14}F_{17}OH_5$ requires: C, 32.81; H, 0.98; F, 63.09%; M, 512; λ_{\max} 1678 cm^{-1} (C=C str); δ_F 174.2

(1F, singlet, >CF-) and signals between 108 and 133 ppm (16F unassigned); δ_{H} 1.60 ($\text{CH}_3\text{-}$, triplet, $J = 7$ Hz) and 4.58 ($\text{-CH}_2\text{-}$, quartet, $J = 7$ Hz).

For compound (23); Analysis: C, 32.7; H, 0.8%; M^+ , not observed, peak at $m/e = 483$, i.e. $\text{M}^+ - 29$. $\text{C}_{14}\text{F}_{17}\text{OH}_3$ requires: C, 32.81; H, 0.98%; M, 512; λ_{max} 1710 cm^{-1} (C=C str); δ_{F} 98.0 (1F, singlet; =CF-), 174-5 (1F, singlet; >CF-) and signals between 112 and 134 ppm (15F, unassigned); δ_{H} 1.53 ($\text{CH}_3\text{-}$, triplet, $J = 7$ Hz) and 4.22 ($\text{-CH}_2\text{-}$, quartet, $J = 7$ Hz).

(b) With sodium methoxide

Sodium metal (0.6 g, 26.1 mmol) was dissolved in methanol (20 ml) and when the resultant solution had cooled to room temperature, trimer (3) (4.2 g, 8.6 mmol) was added. There was an exothermic reaction. The mixture was stirred for 16 h. at room temperature and then the methanol was removed under reduced pressure. Volatile material in the residue was transferred under vacuum to a cold trap and the resultant liquid shown by g.l.c. (Col 'A') to consist of two components in the approximate ratio 3:1 (3.6 g). These were separated by preparative scale g.l.c. to give a liquid and a solid.

The liquid (major product) was identified as 1,3,3-trimethoxy-2-(1'-heptafluorocyclobutylhexafluorocyclobutyl)-difluorocyclobutene (24) (nc): b.p. $> 210^\circ\text{C}$; Analysis: C, 34.7; H, 1.9; F, 54.2%; M^+ , 522. $\text{C}_{15}\text{F}_{15}\text{O}_3\text{H}_9$ requires: C, 34.48; H, 1.72; F, 54.60%; M, 522; λ_{max} 1679 cm^{-1} (C=C str); δ_{F} 172.6 (1F, singlet, >CF-) and signals between 111 and 133 ppm (14F, unassigned); δ_{H} 3.75 (=C-OCH_3 , singlet) and 4.30 ($\text{>C(OCH}_3)_2$, singlet).

The solid was recrystallised from CCl_4 and identified as 1-methoxy-2-(1'-heptafluorocyclobutylhexafluorocyclobutyl)-4,4-difluorocyclobuten-3-one (25) (nc) m.p. $53\text{--}54^\circ\text{C}$; Analysis: F, 59.7%; M^+ , 476. $\text{C}_{13}\text{H}_{15}\text{OH}_3$ requires: F, 59.87%; M, 476; λ_{max} 1815 cm^{-1} (C=C str) and 1641 cm^{-1} (C=O str); δ_{F} (in CCl_4) 178.6 (1F, pentet $J = 23$ Hz, >CF-) and signals between 111 and 133 ppm (14F, unassigned); δ_{H} (in CCl_4) 4.65.

A sample of compound (25) was left open to the atmosphere for 8 days to give the corresponding hydroxy derivative, (26), identified by comparison of its infrared spectrum with that of an authentic sample.

(c) With water

A mixture of trimer (3) (5.6 g, 11.5 mmol) and aqueous acetone (20 ml) was stirred for 24 h. at room temperature. The acetone was removed under reduced pressure and the residue sublimed in vacuo (90°C, 0.1 mm Hg) to give a white solid (4.8 g) identified as 1-hydroxy-2-(1'-heptafluorohexafluorocyclobutyl)-4,4-difluorocyclobuten-3-one (26) (nc) (90%): m.p. 181-183°C; Analysis: C, 31.1; F, 62.0%; M^+ , 462. $C_{12}F_{15}O_2H$ requires: C, 31.17; F, 61.69%; M, 462; λ_{max} 1804 cm^{-1} (C=C str) and 1640 cm^{-1} (C=O str); δ_F (H_2O) 178.2 (1F, pentet J = 22 Hz, >CF-) and signals between 115 and 137 ppm (14F, unassigned).

(d) With sodium borohydride

To a suspension of sodium borohydride (2.3 g, 53.7 mmol) in tetraglyme (20 ml) was added slowly trimer (3) (6.0 g, 12.3 mmol) with rapid stirring and external cooling. When the addition was complete the mixture was heated for 1 h. on a steam bath and then left stirring at room temperature overnight. The lower layer (3.1 g) was removed and the residue flash distilled to give a liquid (1.1 g) shown by g.l.c. to be identical with the lower layer. The two fractions were combined and identified as 1-(1'-heptafluorocyclobutyl)hexafluorocyclobutyl)-3,3-difluorocyclobutene (27) (nc) (79%): b.p. 164°C; Analysis: C, 33.3; H, 0.7; F, 65.6%; M^+ , 432. $C_{12}F_{15}H_3$ requires: C, 33.33; H, 0.69; F, 65.97%; M, 432; λ_{max} 1608 cm^{-1} (C=C str); δ_F , 109.6 (2F, singlet, $-\text{CF}_2-$ in unsaturated ring), 176.1 (1F, singlet >CF-) and signals between 118 and 133 ppm (12F, unassigned); δ_H 3.35 ($-\text{CH}_2-$, triplet J = 3 Hz) and 6.59 ($=\text{CH-}$, singlet).

(e) With diethylamine

Procedure was as for m. Thus, trimer (3) (3.4 g, 7.0 mmol) and diethylamine (5 ml) gave a pale yellow liquid product (2.8 g) identified as 1-diethylamino-2-(1'-heptafluorocyclobutyl)hexafluorocyclobutyl)-tetrafluorocyclobutene (28) (nc) (73%);

Analysis: F, 60.3%; M^+ , 539; $C_{16}F_{17}NH_{10}$ requires: F, 59.93%; M, 539; λ_{\max} 1662 cm^{-1} (C=C str); δ_F 172.9 (1F, singlet, $>CF-$) and signals between 103 and 133 p.p.m. (16F, unassigned); δ_H 1.36 (CH_3- , triplet $J = 7\text{ Hz}$) and 3.34 ($-CH_2-$, quartet $J = 7\text{ Hz}$).

(f) With pentafluorophenyl lithium

Pentafluorobromobenzene (5.3 g, 21.5 mmol) was dissolved in a mixture of ether (18 ml) and hexane (12 ml) and cooled, under nitrogen, to -30°C . n-Butyl lithium (13 ml of a 1.65M solution, 21.5 mmol) was added slowly, the temperature being maintained between -20 and -30°C . When the addition was complete trimer (3) (3.70 g, 7.61 mmol) was added slowly and the resultant mixture allowed to warm to room temperature and left stirring overnight. Water (50 ml) was added, the aqueous layer separated, ether extracted (2 x 20 ml) and the extracts combined with the organic layer. This was then washed with water, dried ($MgSO_4$) and the ether removed on a rotary evaporator. The residue was molecular distilled (0.1 mm, 80°C) to give a pale yellow liquid (1.17 g) and a white solid (2.41 g). The liquid was shown by g.l.c. (Col 'O') to be $> 90\%$ of a single compound, the solid being the same, pure compound. The solid was recrystallised from ether and identified as perfluoro-1-parabiphenyl-2-(1'-cyclobutylcyclobutyl)cyclobutene (29) (nc) (ca. 58%); m.p. $107-108^\circ\text{C}$; Analysis: C, 36.9; F, 62.8%; M^+ 782. $C_{24}F_{26}$ requires: C, 36.83; F, 63.17%; M, 782; δ_F (Et_2O) 136.4 (4F, disubstituted benzene ring), 138.1 (2F, ortho F, C_6F_5 ring), 150.5 (1F, para F, C_6F_5 ring), 161.8 (2F, meta F, C_6F_5 ring), 171.7 (1F, $>CF-$) and signals between 109 and 128 ppm (16F, unassigned).

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