Reactions of Tetrafluoroethylene Oligomers. Part 2.[1] Some Reactions of 4,4,5,5,5-Pentafluoro-3-pentafluoroethyl-3-trifluoromethylpentanoic Acid (Pentamer Acid) and Related Compounds

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The acid $R_fCH_2CO_2H$ (1) [$R_f = CF_3(C_2F_5)_2C$] derived from the tetrafluoroethylene pentamer (2) by base hydrolysis has been converted by Kolbe electrolysis into the dimer $R_fCH_2CH_2R_f$ (3). The salt $R_fCH_2CO_2Ag$ (4) with bromine afforded R_fCH_2Br (5) which was unreactive to nucleophiles under a variety of conditions. R_fCH_2COCl (6) with sodium azide under Curtius reaction conditions gave ($R_fCH_2NH)_2CO$ (7), whereas reaction of (6) with trimethylsilyl azide or sodium azide–18-crown-6 gave R_fCH_2NCO (8). R_fCH_2NCO and cyclohexylamine gave $R_fCH_2NHCONHC_6H_{11}$ (9). Neither urea, (7) or (9), could be hydrolysed. R_fCH_2COCl (6) reacted with ammonia to give $R_fCH_2CONH_2$ (10) and with cyclohexylamine to yield $R_fCH_2CONHC_6H_{11}$ (11). The amide (10) under Hofmann degradation conditions gave the urea (7). The acid (1) reacted with sodium azide in 25% oleum to yield $R_fCH_2NH_3{}^+$ $HSO_4{}^-$ (12) which, on reaction with dilute base, gave $R_fCH_2NH_2$ (13). Reaction of $R_fCH_2NH_3$ (13) or $R_fCH_2NH_3{}^+$ $HSO_4{}^-$ (12) with sodium nitrite afforded R_fCHN_2 (14) as a stable liquid.

In previous papers we have described some pyrolytic reactions of tetrafluoroethylene (TFE) oligomers and their derivatives,[1] and the formation of a stable α-lactone by epoxidation of the ketene derived from TFE hexamer.[2] In the present paper we report some reactions of the acid (1) derived from the pentamer (2) by alkaline hydrolysis as previously described in the patent literature.[3] Although some reactions of the acid (1) are known[4] they are mainly concerned with the preparation of surfactants. We were interested in the effects of the bulky electron-withdrawing group on the properties of the acid and its derivatives.

The silver salt (4) reacted with bromine to give the bromide (5) (Scheme). This latter compound was found to be totally unreactive under any nucleophilic displacement conditions we tried, even using the most forcing conditions of mercury(II) oxide and fuming sulphuric acid which are used to hydrolyse 1-bromo-2,2-difluoroethane to difluoroethanol,[5] or water in formic acid at 95 °C which is effective in the hydrolysis of 1-bromo-2,2-dimethylpropane (neopentyl bromide).[6] There would appear to be two effects operating in our case, firstly a steric effect, as observed in the S_N2-type reaction for neopentyl bromide[6] and secondly an electronic effect of the perfluoroalkyl group preventing the formation of the carbocation in an S_N1-type reaction, in sharp contrast to neopentyl bromide which is relatively readily hydrolysed under S_N1 conditions.[6]

There appears to be no inhibition to the formation of radicals in this series since the Kolbe electrolysis of compound (1) under conditions we have previously reported[7] for polyfluoroacids afforded the dimer (3) in good yield.
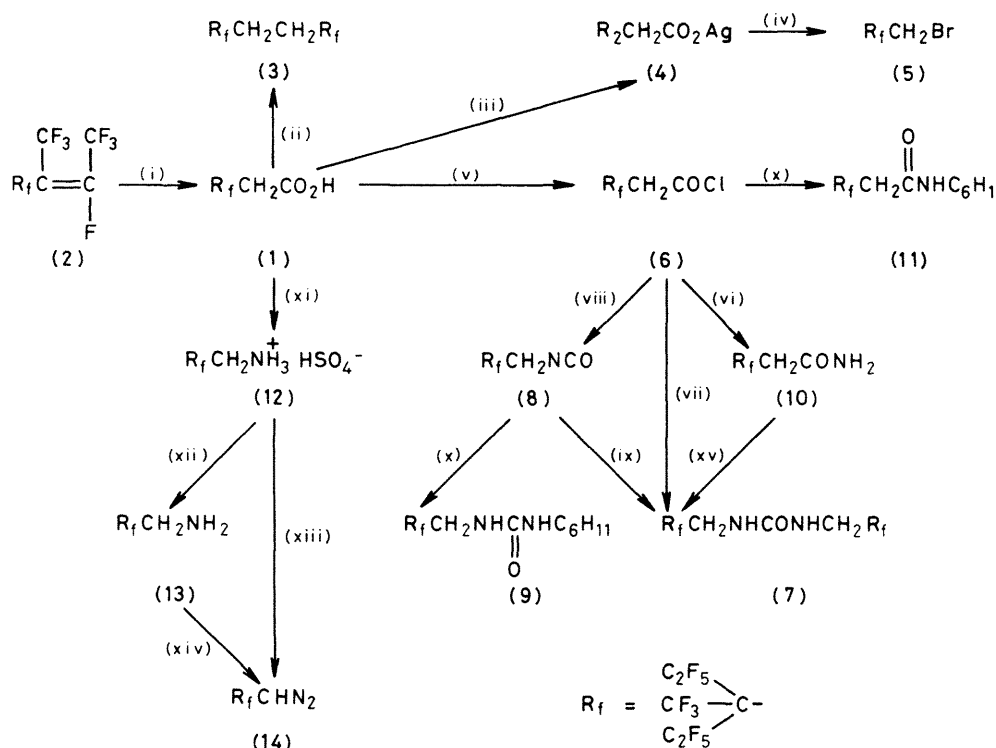
As part of another programme we required an amine containing a bulky fluorocarbon group and compound (8) seemed to be an ideal precursor. We first studied the Curtius reaction from the acid halide (6) and sodium azide, a method which has been used to prepare 4H-decafluorobicyclo[2.2.1]-heptylamine.[8] The acid halide (6) was obtained in good yield from the acid (1) and thionyl chloride without added base such as pyridine which has been found to lead, by loss of hydrogen chloride, to the known ketene.[9] The relatively unstable halide (6) was treated with sodium azide in water to give the urea (7). Heating the urea (7) for 48 h with 50% aqueous potassium hydroxide gave only unchanged starting

material; similar results were obtained when formic acid–sodium nitrite or acetic acid–concentrated sulphuric acid were used. Clearly, the first-formed azide is decomposing to the isocyanate (8) which is rapidly hydrolysing via the carbamic acid to the desired amine (13) which reacts with unhydrolysed isocyanate to give the urea (7).

To confirm this view the isocyanate (8) was prepared under anhydrous conditions. Treatment of the acid halide (6) with trimethylsilyl azide under nitrogen under a variety of conditions afforded mixtures of starting material (6) and the desired isocyanate (8). An alternative method[10] in which sodium azide was added to the neat acid halide (6) containing a small amount of 18-crown-6 polyether gave the pure isocyanate (8) in good yield.

The controlled hydrolysis of fluorocarbon isocyanates to the corresponding amines or ureas has been described by several groups. Careful hydrolysis of 4H-decafluorobicyclo[2.2.1]heptyl isocyanate with moist diethyl ether yields the corresponding amine,[8] but normal hydrolysis gives a urea.[8] However, the hydrolysis of perfluoro-t-butyl isocyanate with water in diglyme gives perfluoro-t-butylamine with no urea formation,[11] whilst the hydrolysis of trifluoromethyl isocyanate at low temperature with hydrogen chloride forms unstable trifluoromethylamine.[12] We have tried to hydrolyse the isocyanate (8) under all of these conditions and in each case the urea (7) resulted.

These observations reflect the greater nucleophilicity of the amine in which a CH_2 groups is interposed between the fluorocarbon group and the amino function, since in all the cases above the CH_2 group is absent. This is a further demonstration of the rapid fall-off in the inductive effect in fluorine-substituted alkyl groups with chain length (*cf.* the fall-off in acid strength in the series $CF_3[CH_2]_nCO_2H$, $n = 0, 1, etc.$[13]). Recent results of the reactions of new isocyanates of the type $CF_3(C_2F_5)_2CNCO$ suggest that such compounds may be less reactive to certain reagents than $CF_3(C_2F_5)_2CCH_2NCO$ (8). The reactivity of the isocyanate (8) towards amines was demonstrated using cyclohexylamine to give the urea (9) which also could not be hydrolysed. A measure of the effect of the fluorocarbon group on the reactivity of its derivatives can be observed from the result that so far we have been unable to *N*-nitrosate either of the nitrogen atoms in com-

$R_fCH_2CH_2R_f$ (3)

$R_2CH_2CO_2Ag \xrightarrow{(iv)} R_fCH_2Br$ (4) (5)

$CF_3 \ CF_3$
$R_fC{=}C$
$\ \ \ \ \ F$
(2) $\xrightarrow{(i)}$ $R_fCH_2CO_2H$ (1) $\xrightarrow{(ii)}$ (3); $\xrightarrow{(iii)}$ (4); $\xrightarrow{(v)}$ R_fCH_2COCl (6) $\xrightarrow{(x)}$ $R_fCH_2\overset{O}{\overset{\|}{C}}NHC_6H_1$ (11)

$R_fCH_2\overset{+}{N}H_3 \ HSO_4^-$ (12)

R_fCH_2NCO (8)

$R_fCH_2CONH_2$ (10)

$R_fCH_2NH_2$ (13)

$R_fCH_2NHCNHC_6H_{11}$
$\ \ \ \ \ \ \ \ \ \ \ \ \|$
$\ \ \ \ \ \ \ \ \ \ \ \ O$
(9)

$R_fCH_2NHCONHCH_2R_f$ (7)

R_fCHN_2 (14)

$R_f = \overset{C_2F_5}{\underset{C_2F_5}{CF_3{-}C{-}}}$

Scheme. *Reagents:* (i) KOH; (ii) electrolysis; (iii) AgNO₃; (iv) Br₂; (v) SOCl₂; (vi) NH₃; (vii) NaN₃–H₂O; (viii) NaN₃, 18-crown-6; (ix) H₂O–diethyl ether; (x) C₆H₁₁NH₂; (xi) NaN₃–oleum; (xii) aq. NaHCO₃; (xiii) NaNO₂–H₂O; (xiv) NaNO₂–HCl; (xv) Br₂–NaOH

pound (9) using conditions when such reactions in some of our other work usually occur rapidly.[14]

The Hofmann degradation of fluoroamides leads to iso-cyanates only under special conditions.[15] We investigated this reaction with the amide (10), readily obtained from the acid halide (6) and aqueous ammonia. Under Barr–Haszeldine conditions [15] the only isolable product, apart from unchanged starting material, was the urea (7).

Having thus failed to obtain the desired amine by con-ventional methods, a variation of the Schmidt reaction [16] was attempted which used sodium azide in 20% oleum. This somewhat hazardous procedure was applied to the acid (1) which was dissolved in 25% oleum at 70—80 °C and very small portions of sodium azide added. After work-up, the reaction afforded, in good yield, a crystalline solid, the di-hydrogen sulphate (12) of the desired amine (13). The free amine (13), which was subsequently shown to be relatively unstable, particularly under basic conditions,[17] was obtained from its sulphate (12) by careful treatment with dilute aqueous sodium hydrogen carbonate.

There are relatively few reports of polyfluorodiazoalkanes [18] and apart from CF₃CHN₂ their chemistry has been little studied. Diazotisation of the amine (13) offered a route to a potentially interesting diazoalkane in which the effect of a bulky electronegative substituent on the properties of the diazo group could be studied. Reaction of the salt (12) with aqueous sodium nitrite also gave the expected diazoalkane (14) in good yield. The chemistry of this species is now being investigated.

Experimental

General details are given in Part 1.[1]

1,1,1,2,2,7,7,8,8,8-Decafluoro-3,6-bis(pentafluoroethyl)-3,6-

bis(trifluoromethyl)octane (3).—The acid (1) (10 g) in aceto-nitrile (60 cm³) and 10% aqueous sodium hydroxide (5 cm³) was electrolysed with platinum electrodes (2 × 2½ cm) at an average current of 0.4 A for 3.5 h, during which time the current rapidly fell to 0.15 A. The reaction mixture was poured into water (200 cm³) and the lower layer was separated to give 1,1,1,2,2,7,7,8,8,8-*decafluoro-3,6-bis(pentafluoro-ethyl)-3,6-bis(trifluoromethyl)octane* (3) (6.9 g), b.p. 161.5—162.5 °C (Found: C, 24.9; H, 0.5; F, 74.5. C₁₄H₄F₂₆ requires C, 25.2; H, 0.6; F, 74.2%); ¹H- and ¹⁹F-n.m.r. spectra were consistent with the proposed structure.

Silver 4,4,5,5,5-Pentafluoro-3-pentafluoroethyl-3-trifluoro-methylpentanoate (4).—A solution of the sodium salt of the acid (1) (39 g) in hot water (50 cm³) was treated with a solution of silver nitrate (25 g) in water (50 cm³). The reaction mixture was filtered to remove precipitated silver oxide and the filtrate was extracted with diethyl ether (6 × 25 cm³). The combined extracts were mixed with water (30 cm³) and the solvent was distilled off to leave white crystals which were filtered off and dried *in vacuo* (silica gel) to give *silver 4,4,5,5,5-pentafluoro-3-pentafluoroethyl-3-trifluoromethylpentanoate* (4) (37.3 g), m.p. 285—290 °C (sealed tube) (Found: C, 19.6; H, 0.6; F, 51.1. C₈H₂AgF₁₃O₂ requires C, 19.8; H, 0.4; F, 50.9%).

4-Bromo-1,1,1,2,2-pentafluoro-3-pentafluoroethyl-3-trifluoromethylbutane (5).—Bromine (12 g) was added drop-wise to the stirred dry silver salt (4) (10 g). The mixture was heated at 75 °C for 3 h, cooled, and was washed in turn with 10% aqueous sodium metabisulphite (disodium pyrosulphite) (25 cm³) and water (25 cm³). The organic layer (5.9 g) was transferred from the inorganic residue *in vacuo* and then distilled to give *4-bromo-1,1,2,2,2-pentafluoro-3-pentafluoro-ethyl-3-trifluoromethylbutane* (5) (5.75 g), b.p. 122—123 °C (Found: C, 20.1; H, 0.5; Br, 19.5; F, 60.0. C₇H₂BrF₁₃ requires

C, 20.3; H, 0.5; Br, 19.4; F, 59.8%); m/z 414 and 412 (C_7H_2-$^{81}BrF_{13}$) and ($C_7H_2{}^{79}BrF_{13}$) in the expected isotopic ratio.

4,4,5,5,5-Pentafluoro-3-pentafluoroethyl-3-trifluoromethyl-pentanoyl Chloride (6).—Freshly distilled thionyl chloride chloride (50 g) was slowly added during 0.7 h to the acid (1) (78 g) at 60 °C. The mixture was heated under reflux for 1.5 h and then fractionally distilled through a vacuum-jacketed column (15 cm) packed with glass helices to give a fraction (b.p. 124—125 °C), redistillation of which gave 4,4,5,5,5-*pentafluoro-3-pentafluoroethyl-3-trifluoromethylpentanoyl chloride* (6) (58 g), b.p. 124—125 °C (Found: C, 24.4; H, 0.5; Cl, 8.9; F, 62.6. $C_8H_2ClF_{13}O$ requires C, 24.4; H, 0.5; Cl, 8.9; F, 62.6%); $\nu_{max.}$ 1 810 cm^{-1} (CO).

Curtius Reaction of the Acid Chloride (6).—The acid chloride (6) (5 g) was added to a stirred solution of sodium azide (5 g) in water (20 cm^3) at 48 °C. The mixture was heated under reflux for 4 h, cooled, and filtered to give a white solid (3.7 g). Recrystallisation from propanone afforded N,N'-*bis-*(3,3,-4,4,4-*pentafluoro-2-pentafluoroethyl-2-trifluoromethylbutyl)-urea* (7) (3.4 g), m.p. 244—248 °C (Found: C, 24.7; H, 1.0; F, 68.0; N, 4.3. $C_{15}H_6F_{26}N_2O$ requires C, 24.9; H, 0.8; F, 68.2; N, 3.9%); $\nu_{max.}$ 3 350 (ν NH), 1 640 (CO), and 1 575 cm^{-1} (δ NH).

The urea (3.7 g) was heated under reflux with 50% aqueous potassium hydroxide for 48 h and was recovered unchanged.

3,3,4,4,4-Pentafluoro-2-pentafluoroethyl-2-trifluoromethyl-butyl Isocyanate (8) (with N. J. Goodchild).—Sodium azide (1.8 g) was added in small portions to the acid chloride (6) (6 g) containing the polyether 18-crown-6 (0.1 g) at 18 °C. A vigorous reaction occurred with evolution of nitrogen. When the addition was complete the mixture was stirred for 2 h at 18 °C and then at 50 °C for 16 h. Distillation *in vacuo* at 60 °C afforded a fraction which was then redistilled to yield 3,3,4,4,4-*pentafluoro-2-pentafluoroethyl-2-trifluoromethylbutyl isocyanate* (8) (4.2 g), b.p. 128—130 °C (Found: C, 25.7; H, 0.7; F, 66.2; N, 3.8. $C_8H_2F_{13}NO$ requires C, 25.6; H, 0.5; F, 65.9; N, 3.7%).

In similar experiments but using trimethylsilyl azide, the isocyanate (8) was obtained but was always contaminated with some unchanged acid chloride (6).

The isocyanate (8) (1 g) was stirred for 18 h with moist diethyl ether to yield the urea (7) (0.5 g).

Characterisation of the Isocyanate (8).—The isocyanate (8) (2.2 g) containing some unchanged acid chloride (6) was treated at 18 °C with cyclohexylamine (0.56 g) in diethyl ether (15 cm^3). The solution was stirred for 1 h and the precipitated solid (1.5 g) was filtered off. Recrystallisation from aqueous ethanol afforded N-*cyclohexyl*-N'-(3,3,4,4,4-*pentafluoro-2-pentafluoroethyl-2-trifluoromethylbutyl)urea* (9), m.p. 184—185 °C (Found: C, 35.2; H, 3.3; F, 51.6; N, 6.0. $C_{14}H_{15}F_{13}N_2O$ requires C, 35.5; H, 3.2; F, 52.1; N, 5.9%); ^{1}H- and ^{19}F-n.m.r. spectra were entirely consistent with the assigned structure; $\nu_{max.}$ 3 335 (ν NH), 1 630 (CO), and 1 570 cm^{-1} (δ NH). The filtrate and ethereal washings from the reaction were combined and the solvent was removed to give a white solid. Recrystallisation from tetrachloromethane afforded N-*cyclohexyl*-4,4,5,5,5-*pentafluoro-3-pentafluoro-ethyl-3-trifluoromethylpentanamide* (11) (0.25 g), m.p. 119—120 °C (Found: C, 35.7; H, 2.9; F, 54.2; N, 3.3. $C_{14}H_{14}F_{13}NO$ requires C, 36.6; H, 3.1; F, 53.8; N, 3.0%); $\nu_{max.}$ 3 500 (NH) and 1 660 cm^{-1} (CO).

The urea (8) was recovered unchanged after being heated at reflux with 50% potassium hydroxide solution for 18 h.

4,4,5,5,5-Pentafluoro)-2-pentafluoroethyl-2-trifluoromethyl-pentanamide (10).—The acid chloride (6) (9.4 g) was added dropwise to vigorously stirred aqueous ammonia (*d* 0.88) (40 cm^3). The mixture was stirred at 18 °C for 0.5 h and was then extracted with diethyl ether (3 × 20 cm^3). The combined extracts were washed with water and dried (MgSO$_4$). Evaporation of the diethyl ether gave, after recrystallisation from chloroform, 4,4,5,5,5-*pentafluoro-2-pentafluoroethyl-2-tri-fluoromethylpentanamide* (10) (5.5 g), m.p. 54—55 °C (Found: C, 26.0; H, 1.1; F, 65.5; N, 3.7. $C_8H_4F_{13}NO$ requires C, 25.5; H, 1.1; F, 65.5; N, 3.7%); $\nu_{max.}$ 3 460, 3 330 (CONH$_2$), 1 670, and 1 620 cm^{-1} (CO).

Hofmann Rearrangement of the Amide (10).—The amide (10) (3 g), suspended in water (2.5 cm^3), was added to a stirred solution of bromine (1.5 g) in aqueous sodium hydroxide [1.92 g in water (5 cm^3)] at 0 °C. The mixture was stirred at 0 °C for 1 h and was then heated at reflux for 1.5 h. The solution was cooled and extracted with diethyl ether (3 × 20 cm^3) and the combined extracts were evaporated to give an oily residue which slowly solidified. Recrystallisation from chloroform gave the urea (7) (1.2 g). Evaporation of the chloroform gave the unchanged pentanamide (10) (0.4 g).

3,3,4,4,4-Pentafluoro-2-pentafluoroethyl-2-trifluoromethyl-butylammoniumhydrogen Sulphate (12).—Sodium azide (12 g) was added with *extreme caution* in small portions (initially *ca.* 0.01 g) to a solution of the acid (1) (28.5 g) in oleum (25% SO$_3$) at 70—80 °C contained in a wide-necked vessel protected by a safety screen in a very efficient fume cupboard. The resulting solution was heated for 2 h at 80 °C after the addition was complete and was then cooled to 18 °C and cautiously poured onto crushed ice (1 kg). Filtration afforded a white solid (40.7 g). Recrystallisation from 20% sulphuric acid gave 3,3,4,4,4-*pentafluoro-2-pentafluoroethyl-2-trifluoromethyl-butylammoniumhydrogen sulphate* (12) (23.2 g), m.p. 201—205 °C (sealed tube) (Found: C, 18.5; H, 1.3; F, 55.1; N, 3.3. $C_7H_6F_{13}NO_4S$ requires C, 18.8; H, 1.35; F, 55.2; N, 3.1%).

The salt (38.7 g) was stirred with saturated aqueous sodium carbonate (500 cm^3) for 6 h and was then kept at 18 °C for 18 h. The lower layer was separated, dried (CaCl$_2$), and vacuum-transferred to give 3,3,4,4,4-*pentafluoro-2-pentafluoroethyl-2-trifluoromethylbutylamine* (13) (14.7 g), b.p. 68—69 °C (decomp.) (Found: C, 25.1; H, 1.1; F, 69.4; N, 4.5%; M^+, 349. $C_7H_4F_{13}N$ requires C, 24.1; H, 1.1; F, 70.7; N, 4.0%; *M*, 349); $\nu_{max.}$ 3 380, 3 460 (ν NH), and 1 630 cm^{-1} (δ NH); the ^{1}H n.m.r. spectrum showed signals at δ 1.55 (br s, NH$_2$) and 3.65 (brs, CH$_2$) in the integral ratio 1 : 1.

The amine (13) (0.4 g) and cyclohexyl isocyanate (0.15 g) were shaken together for 16 h at 18 °C. Recrystallisation of the solid residue from aqueous ethanol gave the urea (9) (0.2 g).

4-Diazo-1,1,1,2,2-pentafluoro-3-pentafluoroethyl-3-trifluoro-methylbutane (14).—Aqueous sodium nitrite [0.48 g in water (1.5 cm^3)] was added slowly to a solution of the amine (13) (2.1 g) in 3M hydrochloric acid (6 cm^3) at 0—2 °C. The mixture was stirred at this temperature for 1.5 h and then at 18 °C for 1.5 h. The lower, yellow green layer was separated and, after vacuum transfer, was distilled to give 4-*diazo*-1,1,2,2,2-*pentafluoro-3-pentafluoroethyl-3-trifluoromethylbutane* (14) (1.6 g), b.p. 113 °C (Found: C, 23.1; H, 0.4; F, 68.7; N, 8.1%; M^+, 360; $C_7HF_{13}N_2$ requires C, 23.4; H, 0.3; F, 68.6; N, 7.8%; *M*, 360); $\nu_{max.}$ 2 105 cm^{-1} (CN$_2$).

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