

Reactions of Tetrafluoroethene Oligomers. Part 3.¹ Some Reactions of Tetrafluoroethene Hexamer with Nitrogenous Bases

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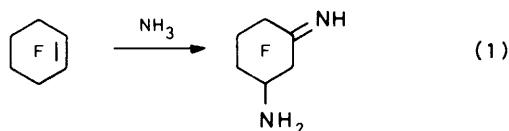
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Tetrafluoroethene (TFE) hexamer (1) [$R_f(R_f')C=CF_2$, $R_f = CF_3(C_2F_5)_2C-$, $R_f' = CF_3(C_2F_5)CF-$] reacted with ammonia to give R_fCH_2CN (11) and with primary amines RNH_2 ($R = Et, NH_2, Ph, CH_2CH_2OH$) to give the corresponding ketenimine $R_f(R_f')C=C=NR$ (14)–(17). With 1,2-diaminoethane the dihydroimidazole $C_2F_5(CF_3)C=C(R_f)C=NCH_2CH_2NH$ (20) was formed. With secondary amines (dimethylamine and piperidine) enamines of the type $R_f(R_f')C=CFNMe_2$ (18) and $R_f(R_f')C=CFN[CH_2]_4CH_2$ (21) were obtained. These latter products, on being heated, afforded respectively the ketenimines $R_f(R_f')C=C=NMe$ (19), and $R_f(R_f')C=C=N[CH_2]_3CH=CH_2$ (12), $R_f(R_f')C=C=N[CH_2]_5F$ (23).

In previous papers in this series we have described some chemistry of tetrafluoroethene pentamer¹ and some pyrolytic reactions of tetrafluoroethene oligomers and their fluorinated derivatives.² Epoxidations of these oligomers³ and reactions of some of the epoxides⁴ have also been studied.

Except for a brief mention in the patent literature and in some of our earlier papers, there are no reports of the chemistry of the hexamer (1). Some reactions of this hindered olefin with nitrogenous bases are now reported.

The reactions of highly fluorinated alkenes with amines are well known processes,⁵ though complicated. The products obtained depend both on the nature of the olefin and on the degree of substitution of the amine. Reactions of ammonia and primary amines with simple olefins, such as tetrafluoroethene or chlorotrifluoroethene, gives addition followed by elimination to afford nitriles or imidyl fluorides, whilst with higher olefins, e.g. hexafluoropropene, saturated nitriles of the type R_fCHFCN , are obtained. With molar proportions of secondary amines, the simple adduct, e.g. $HCF_2CF_2NMe_2$, is observed, but with excess of amine the dehydrofluorinated product, e.g. $CF_2=CFNMe_2$, often results and in some cases may react further. Cyclic fluoro-olefins⁶ react by addition elimination to give iminoamines by multisubstitution, e.g. reaction (1).



There have been two reports of the reactions of tetrafluoroethene oligomers with amines; the first⁷ was directed to the production of surface-active agents and was mainly confined to the pentamer, which yielded compounds of the type $[CF_3(C_2F_5)_2]C(CF_3)=C(CF_3)NR_2$. A more recent paper⁸ was concerned with the reactions of the tetramer oligomer with amines. A variety of products was found since fluoride ion-induced rearrangements occurred and the compounds produced depended critically on the relative reactivities of the particular amine with all of the olefin isomers with the same carbon skeleton. In general it was found that $C_2F_5-(CF_3)C=C(CF_3)C_2F_5$ reacted more slowly with bulky amines than did $C_2F_5CF(CF_3)C(C_2F_5)=CF_2$.

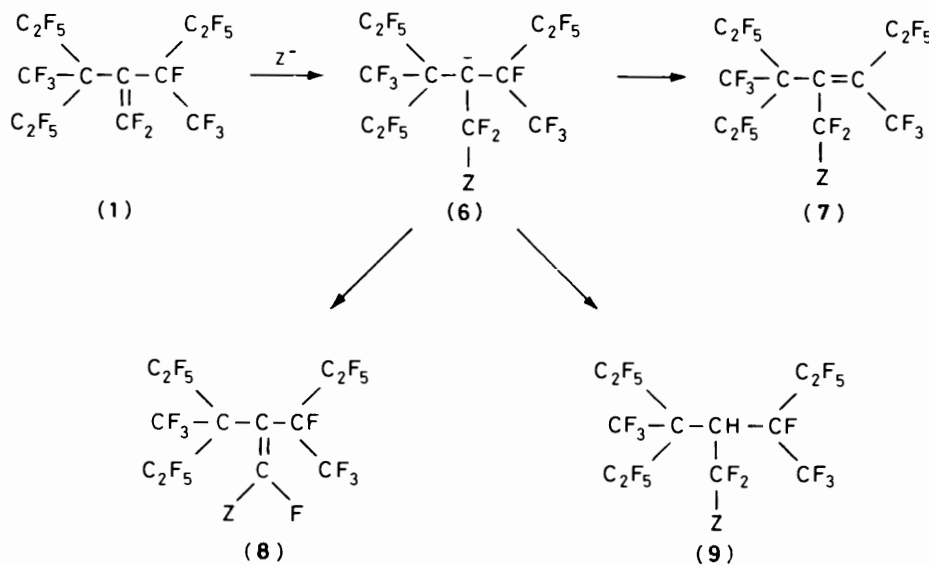
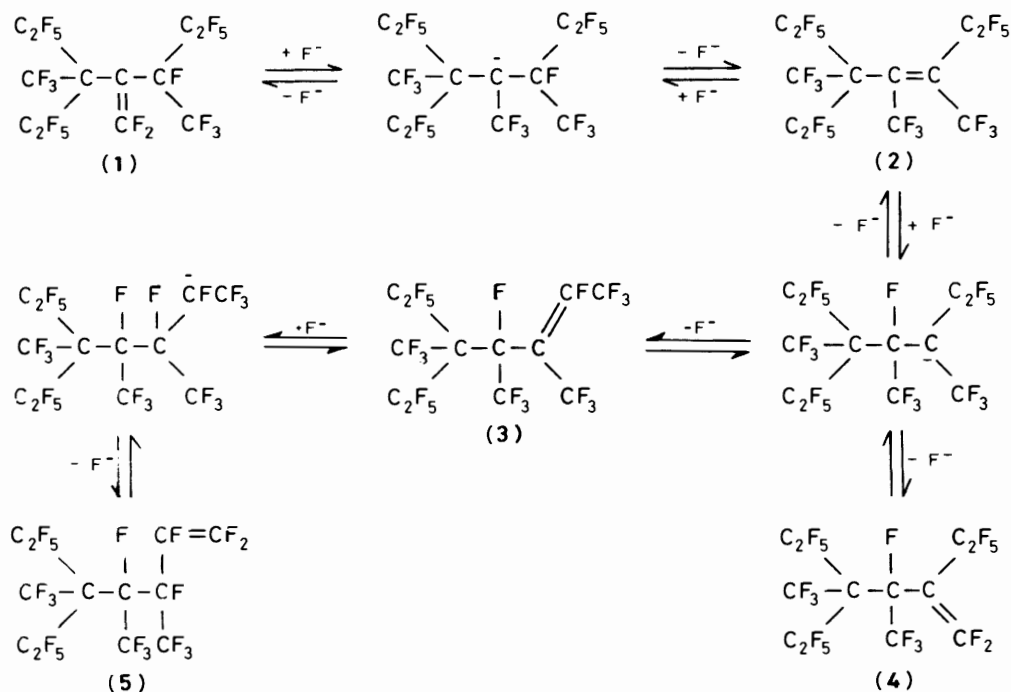
A similar situation but in reverse could apply in our case; an equilibrium (Scheme 1) is clearly possible. However, we would

expect the starting material (1) and the isomers (4) and (5) to be much more reactive than (2) and (3), in accord with the results discussed above,⁸ the CF_2 group reacting preferentially.

It was thus of interest to see if we could obtain products arising from any of the possible isomers of compound (1), i.e. (1)–(5), in the same way as reported for the tetramer. Further, compound (1) provides an opportunity to investigate the relative rates of elimination of tertiary fluorine in the so called 'outwards' elimination mode and secondary fluorine elimination in an 'inwards' elimination mode, i.e. the elimination of original vinylic fluorines. Reaction of compound (1) with nucleophiles affords a carbanion (6) (Scheme 2) which has a choice of elimination to give compound (7) 'outwards' or (8) 'inwards'; the carbanion may also undergo protonation to give the saturated product (9). To identify which of these possible reactions occurs we have studied the reactions of compound (1) with a number of primary and secondary amines and bifunctional compounds (ethylenediamine and 2-aminoethanol).

Reaction of the olefin (1) with dry gaseous ammonia in ether afforded an oil. ¹⁹F N.m.r. spectroscopy showed the loss of a large part of the molecule, but gave a pattern of peaks characteristic of the $CF_3(C_2F_5)_2C$ group. ¹H N.m.r. spectroscopy showed a single resonance and the i.r. spectrum indicated the presence of a $C\equiv N$ group. These data suggested that the product was 2*H*,2*H*-tridecafluoro-3-ethyl-3-methylpentanenitrile (11), which was confirmed by an alternative synthesis by dehydration of 2*H*,2*H*-tridecafluoro-3-ethyl-3-methylpentanamide.^{1,9} In a repetition of the original reaction but using a Dricold condenser to contain any very volatile material, a product was isolated which showed i.r. bands at 3 300 and 3 450 cm^{-1} and 1 690 cm^{-1} , indicative of NH and C=N stretch bonds. The ¹⁹F n.m.r. spectrum showed three sets of peaks consistent with a CF_3 and a C_2F_5 group. These data are consistent with the product being 1,1,1,3,3,4,4,4-octafluoro-2-iminobutane (12). We were, however, unable to isolate the material pure for further characterisation. The formation of products (11) and (12) can be rationalised as shown in Scheme 3. It seemed that loss of HF between CF_2 and NH_2 was rapid compared with loss of β -fluorine, as has been observed previously.⁵ Since there was no evidence for ketenimine formation, although this could rearrange to a nitrile, the intermediate cyanoolefin (10), presumably first formed, is very reactive. This was confirmed using a deficiency of ammonia, when only some of the same products, together with unchanged starting material, were isolated.

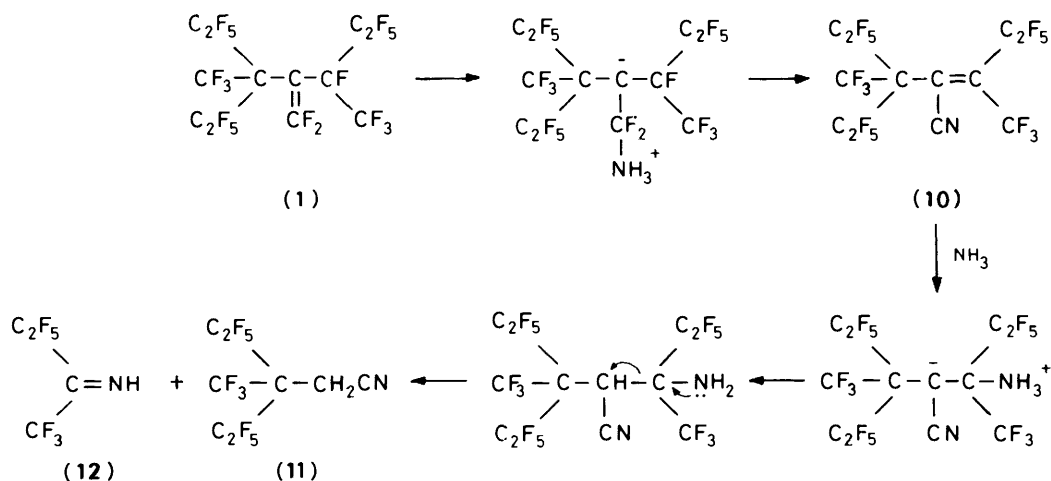
The olefin (1) was next treated with dry ethylamine in ether at



0 °C; an oily product was obtained from a very rapid reaction. In this case ^{19}F n.m.r. spectroscopy indicated that most of the fluorocarbon skeleton had remained intact; only the vinylic fluorine signal was missing. The ^1H spectrum showed the presence of an $\text{N}-\text{C}_2\text{H}_5$ group. The i.r. spectrum proved surprising in that a very strong band at 2080 cm^{-1} was observed. Bands in this region of the spectrum are usually assigned to functions of the type $>\text{C}=\text{C}=\text{Y}$ ($\text{Y}=\text{O}, \text{N}, \text{S}$). Thus the indication was that we had a ketenimine of the type $\text{R}_f(\text{R}_f')\text{C}=\text{C}=\text{NET}$. Together with the elemental analysis, this confirmed the structure of the product as *N*-{perfluoro-[3-ethyl-3-methyl-2(1-methylpropyl)pent-1-enylidene]}ethylamine (14) (Scheme 4). In the same way, aniline and hydrazine were found

to give the corresponding ketenimines (15) and (16), both of which showed the characteristic i.r. band at *ca.* 2080 cm^{-1} . We obtained no evidence under a variety of temperature and solvent conditions for products arising by elimination of the tertiary fluorine atom, the presence of which is shown very clearly by ^{19}F n.m.r. spectroscopy. All of the crude reaction products were carefully investigated and we were unable to detect any compounds derived from fluoride ion-catalysed rearrangement of the hexamer (1).

In a further series of reactions we studied the reactions of compound (1) with bifunctional nucleophiles. Reaction of the olefin with 1,2-diaminoethane in ether afforded an oil. ^{19}F N.m.r. spectroscopy indicated that the fluoroalkyl groups had



Scheme 3.

remained intact, but in this case the tertiary fluorine and the vinylic fluorine atoms had disappeared. The ¹H n.m.r. spectrum showed the presence of a complex signal due to four protons and a single-proton resonance which disappeared on shaking the sample with D₂O. The i.r. spectrum showed a sharp NH stretch band at 3 510 cm⁻¹ and a strong band at 1 670 cm⁻¹, but no band at 2 080 cm⁻¹. The mass spectrum and elemental analysis indicated a compound with the molecular formula C₁₄H₅F₂₁N₂. We assigned the structure of the product as 2-[(*E*)-perfluoro-(5-ethyl-3,5-dimethylhept-2-en-4-yl)]-4,5-dihydroimidazole (20).

In a similar reaction of olefin (1) with 2-aminoethanol, again a high boiling oil was obtained. In this case the ¹⁹F n.m.r. spectrum showed only the loss of the vinylic fluorine atoms. The ¹H n.m.r. spectrum showed a complex four-proton band, and a single-proton resonance which disappeared on shaking the sample with D₂O. The i.r. spectrum showed a strong band at 3 350 cm⁻¹ and a sharp signal at 2 060 cm⁻¹, characteristic of the ketenimine structure (see above). These data were consistent with the structure *N*-{perfluoro-[3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-enylidene]}-2-hydroxyethylamine (17). Thus, no cyclisation had occurred, presumably due to the lower nucleophilicity of OH over NH₂ under these conditions.

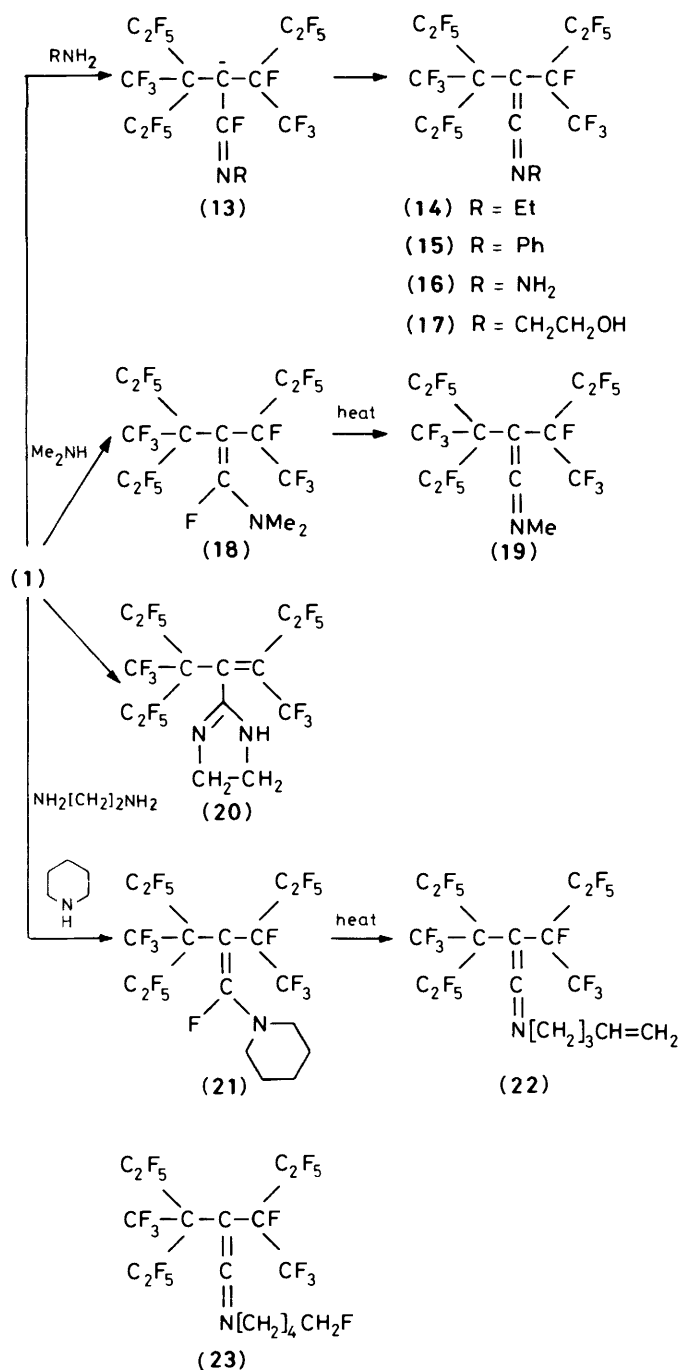
We next investigated the reactions of two secondary amines, dimethylamine and piperidine. The product from the reaction with dimethylamine showed, in its ¹⁹F n.m.r. spectrum, the presence of the original fluoroalkyl groups and a single olefinic fluorine atom. The ¹H spectrum indicated the dimethylamino function with a single sharp resonance. Thus, we concluded that the product was that expected from the classical addition-elimination reaction of fluoro-olefins, namely 1-dimethylaminoperfluoro-[3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-ene] (18). However, attempted distillation of compound (18) at atmospheric pressure led to decomposition to form a discrete new compound which showed the presence of the characteristic 2 060 cm⁻¹ ketenimine band in its i.r. spectrum. ¹⁹F N.m.r. spectroscopy showed the loss of the vinyl fluorine resonance apparent in compound (18). The structure of the product as *N*-{perfluoro-[3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-enylidene]}methylamine (19) was confirmed by an independent synthesis from olefin (1) and methylamine. Compound (19) was obtained from (18) in high yield by thermolysis at 130 °C in a sealed tube.

Reaction of olefin (1) with piperidine similarly afforded the addition-elimination product 1-piperidinoperfluoro-[3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-ene] (21). When compound

(21) was heated at 120 °C in a sealed tube, two products, (22) and (23), were obtained in roughly equal proportions. In both cases strong i.r. bands attributable to the ketenimine structure were observed. The structures of compounds (22) and (23) were clearly indicated by ¹⁹F and ¹H n.m.r. spectroscopy. The ¹⁹F spectra of both compounds showed that the fluoroalkyl groups were intact. In addition, the spectrum of compound (23) showed an additional complex resonance at ϕ_F 222.5 p.p.m. (-CH₂F), equivalent to one fluorine atom. The ¹H spectrum of compound (23) showed, in addition to a complex six-proton band at δ 1.40, a complex triplet, *J* 7 Hz, and a doublet of triplets at δ 4.2 (*J*_{HF} 47, *J*_{HF} 6 Hz). These latter clearly indicate a -CH₂CH₂F system and the total proton spectrum is consistent with a CH₂[CH₂]₃CH₂F system. The ¹H n.m.r. spectrum of compound (22) showed bands for three CH₂ groups and a complex three-proton pattern at δ 4.5–5.5, indicative of vinylic protons. These data suggest that the piperidine ring has opened to give -[CH₂]₃CH=CH₂ and -[CH₂]₄CH₂F groups in compounds (22) and (23) respectively. This result clearly parallels that found in the dimethylamine case, where loss of an alkyl group from nitrogen, and of fluorine from adjacent carbon, occurs. In the piperidine case the resultant alkyl fluoride structure remains within the product molecule. Some loss of HF occurs also. All these results are summarised in Scheme 4.

The results we have obtained show without doubt that the ready reaction of compounds of the type R_fR_f'C=CF₂ with nucleophiles, however bulky the groups R_f, gives results compatible with some of the recent observations by Chambers and co-workers¹⁰ concerning nucleophilic attack on fluoroalkenes. However, rearrangement of the olefin (1) to other isomers during the course of the reactions was not observed. This would support the view that compound (1) is sterically the most favourable of the hexamer isomers (1)–(4). A surprising result from this work is the ready formation of ketenimines, even when this necessitates the loss of fluoromethane, (18)–(19), or the ring opening of the piperidine (21) to form products (22) and (23).

Although the formation of ketenimines has been previously observed¹¹ or postulated⁸ in reactions of hindered olefins, or with bulky bases, *e.g.*, *t*-butylamine, it was expected that the elimination of the tertiary fluorine atom in compound (1) would be favoured, so that conjugated α,β unsaturated imidyl fluorides of the type RN=CFC(R_f)=CR_f'(R_f') would predominate. In fact in no case were products of this type obtained, indicating a considerable preference for elimination of the fluorine on the carbon having the double-bonded nitrogen. A possible



Scheme 4.

explanation of this observation follows from that used to explain the formation of hexamer (1). Loss of the tertiary fluorine would lead to an olefin with four bulky fluoroalkyl groups on the double bond, which would be unfavourable sterically. Further, the strength of the CF bond is greater than that of NF, which may well enhance the steric preference for ketenimine formation.

The ketenimines themselves are remarkably unreactive; only in the reaction using diaminoethane was any reactivity observed even when excess of amine was present. Preliminary studies of other reactions of the ketenimines confirm this view, in strong contrast to the analogous ketene¹² which is highly reactive. This lack of reactivity has been previously observed in other ketenimines.¹⁰

The high stability of the ketenimines is further exemplified by the very ready formation of compound (19) from (18) and of (22) and (23) from (21). Although the loss of alkyl fluorides to give heterocumulenes has previously been observed or postulated to give ketene,¹³ thioketenes,¹⁴ and ketenimines,⁸ the conditions of reaction have been mostly rather more vigorous than those we have found to be sufficient.

In this work we have clearly demonstrated further fascinating effects of bulky perfluoroalkyl groups on the reactivities of fluorinated alkenes with highly branched side-chains.

Experimental

Reactions of TFE Hexamer (1).—(a) *With ammonia.* Dry ammonia was bubbled through a solution of compound (1) (20 g) in dry ether (100 cm³) at 0 °C for 1 h. The resulting solution was filtered to remove the precipitate (3.6 g) of ammonium fluoride which had formed. The ether was evaporated off to leave a yellow liquid (12.2 g) which, on distillation, afforded 4,4,5,5,5-pentafluoro-3-(pentafluoroethyl)-3-(trifluoromethyl)pentanenitrile (11) (11.3 g), b.p. 146 °C, identical with an authentic sample prepared by dehydration of the corresponding amide¹ with phosphorus pentoxide (see below).

(b) *With ethylamine.* Dry ethylamine (10 cm³) and compound (1) (4.5 g) were stirred together in dry ether (25 cm³) at 0 °C; after 5 min a heavy precipitate was formed and ether (25 cm³) was added and the mixture was stirred for a further 1 h. The precipitated ethylammonium fluoride was filtered off and the ether and excess of ethylamine were evaporated off. Distillation of the residue afforded N-{perfluoro-[3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-enylidene]}ethylamine (14) (3.0 g), b.p. 170.5 °C (Found: C, 27.9; H, 0.9; F, 69.6; N, 2.3. C₁₄H₅F₂₂N requires C, 27.8; H, 0.9; F, 69.1; N, 2.3%); ν_{\max} 2 080 cm⁻¹ (C=C=N). ¹H and ¹⁹F n.m.r. were consistent with the proposed structure.

(c) *With aniline.* The olefin (1) (15 g), dry redistilled aniline (20 g), and dry trimethylamine (10 cm³) were heated and stirred under reflux in dry ether (100 cm³) for 17 h. The ether and trimethylamine were removed by rotary evaporation and ethanol (50 cm³) was added. The lower fluorocarbon (10.5 g) was removed and distilled *in vacuo* to yield N-{perfluoro-[3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-enylidene]}aniline (15) (3.4 g), b.p. 108–110 °C at 12 mmHg (Found: C, 32.8; H, 0.7; F, 64.0; N, 2.5. C₁₈H₅F₂₂N requires C, 33.1; H, 0.75; F, 64.0; N, 2.2 %); ν_{\max} 2 075 cm⁻¹ (C=C=N).

(d) *With hydrazine.* Hydrazine hydrate (20 g; 95%) was added during 20 min to a solution of the olefin (1) (36 g) in ether (70 cm³). The mixture was refluxed for 2 h, cooled, and washed successively with 2M sulphuric acid (50 cm³) and 2M aqueous sodium hydroxide. The ether layer was dried (MgSO₄) and distilled to yield an oil (28.3 g). Distillation *in vacuo* afforded N-{perfluoro-[3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-enylidene]}hydrazine (16) (23.3 g), b.p. 106–110 °C at 12 mmHg (Found: C, 24.4; H, 0.1; F, 71.1; N, 4.6. C₁₂H₂F₂₂N₂ requires C, 24.3; H, 0.3; F, 70.6; N, 4.7%); ν_{\max} 3 225, 3 330, 3 440 (N–H), 2 005 (C=C=N), and 1 625 cm⁻¹ (N–N). The ¹H and ¹⁹F n.m.r. spectra were fully consistent with the proposed structure.

(e) *With 1,2-diaminoethane.* A solution of the olefin (1) (50 g) in dry ether (300 cm³) was added to a stirred suspension of 1,2-diaminoethane (50 cm³) in ether (200 cm³) at 0 °C. The mixture was stirred at 0 °C for 1 h and was then stirred for 2 h while the temperature rose to 18 °C. The precipitated solid (1,2-diaminoethane hydrofluoride) was filtered off and the ether was evaporated off to give a red oily residue (39.1 g). Distillation *in vacuo* afforded 2-[(E)-perfluoro-(5-ethyl-3,5-dimethylhept-3-en-4-yl)]-4,5-dihydroimidazole (20) (15.5 g), b.p. 112 °C (0.4 mmHg) (Found: C, 27.9; H, 0.8; F, 66.0; N, 5.0. C₁₄H₅F₂₁N₂

requires C, 28.0; H, 0.8; F, 66.5; N, 4.7%). I.r. and ^1H and ^{19}F n.m.r. spectra were in agreement with the proposed structure.

(f) *With 2-aminoethanol.* A solution of the olefin (1) (20 g) in dry ether (150 cm³) was added to a stirred suspension of 2-aminoethanol (20 g) in dry ether (50 cm³) at 0 °C during 15 min. The mixture was stirred at 0 °C for a further 30 min and then at 18 °C for 30 min. The resulting solution was washed successively with water (100 cm³) and 10% aqueous sodium chloride, (100 cm³), and was dried (MgSO₄). The ether was evaporated off to give a pale yellow liquid (18.2 g). Distillation *in vacuo* afforded N-{perfluoro-[3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-enylidene]}-2-hydroxyethylamine (17) (11.8 g), b.p. 100–105 °C (0.6 mmHg) (Found: C, 27.2; H, 0.8; F, 67.7; N, 2.3. C₁₄H₅F₂₂N requires C, 27.1; H, 0.8; F, 67.3; N, 2.3%). ^1H and ^{19}F n.m.r. spectra were consistent with the proposed structure.

(g) *With dimethylamine.* Dimethylamine (20 cm³) was added to a stirred solution of the olefin (1) (24 g) in dry ether (100 cm³) at 0 °C. After the mixture had been kept for 1 h at 0 °C, the ice-bath was removed and the mixture was stirred for a further 1.5 h. The mixture was washed with water (100 cm³) and dried (MgSO₄). Evaporation of the ether afforded a residue (20.0 g) which, on distillation *in vacuo*, afforded 1-dimethylamino-perfluoro[3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-ene] (18) (13.9 g), b.p. 144–146 °C (12 mmHg) (Found: C, 26.7; H, 0.8; F, 69.4; N, 2.5. C₁₄H₆F₂₃N requires C, 26.9; H, 0.9; F, 69.9; N, 2.3%). ^1H and ^{19}F n.m.r. spectroscopy suggested that the compound was a 50/50 mixture of the *E* and *Z* isomers.

(h) *With piperidine.* A solution of piperidine (30 cm³) in dry ether (50 cm³) was added during 15 min to a stirred solution of the olefin (1) (50 g) in ether (200 cm³) at 18 °C. The mixture was stirred for 2 h and the precipitated piperidine hydrofluoride was filtered off and washed with ether (2 × 50 cm³). The combined ether layers were washed with water (2 × 100 cm³), dried (MgSO₄), and evaporated to leave a solid residue (43.1 g) which, on recrystallisation from ethanol, afforded 1-piperidinoperfluoro[3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-ene] (21) (20.3 g), m.p. 51–52 °C (Found: C, 31.0; H, 1.5; F, 65.4; N, 2.1. C₁₇H₁₀F₂₃N requires C, 30.7; H, 1.5; F, 65.7; N, 2.1%). Evaporation of the mother liquors afforded a further crop (6.6 g) of compound (21). ^1H and ^{19}F n.m.r. spectroscopy indicated compound (21) to be a mixture of *E* and *Z* isomers.

Thermolysis of Compound (18).—The enamine (18) (3.9 g) was sealed under dry nitrogen in a Carius tube which was then heated at 130 °C for 20 h. The residue in the tube, after evaporation of any very volatile material, was distilled to give a mobile liquid (1.5 g). Separation of a portion (0.2 g) by semipreparative g.l.c. afforded N-{perfluoro-[3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-enylidene]}methylamine (19), identical with a sample previously prepared from olefin (1) and methylamine.

Thermolysis of Compound (21).—The enamine (21) (10 g) was heated under nitrogen in a Carius tube at 120 °C for 70 h to leave a brown oil which, on distillation *in vacuo*, afforded a mixture of two components (3.7 g). Separation (g.l.c.) of a sample (0.6 g) afforded (i) N-{perfluoro-[3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-enylidene]}pent-4-enylamine (22) (0.17 g) (Found: C, 31.5; H, 1.2; F, 64.7; N, 2.4. C₁₇H₉F₂₂N requires C, 31.6; H, 1.4; F, 64.8; N, 2.2%). ^1H and ^{19}F n.m.r. spectroscopy were in agreement with the proposed structure; and (ii), N-{perfluoro-[3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-enylidene]}-5-fluoropentylamine (23) (0.13 g) (Found: C, 30.8; H, 1.4; F, 65.2; N, 2.3. C₁₇H₁₀F₂₃N requires C, 30.7; H, 1.5; F, 65.7; N, 2.1%) with consistent ^1H and ^{19}F and i.r. spectra.

2H,2H-Tridecafluoro-3-ethyl-3-methylpentanenitrile (2).—2H,2H-Tridecafluoro-3-ethyl-3-methylpentanamide^{1,9} (6.5 g) and phosphoric oxide (15 g) were heated together for 10 min at 150 °C. The reaction product was distilled to yield 2H,2H-tridecafluoro-3-ethyl-3-methylpentanenitrile (11) (4.6 g), b.p. 146 °C (Found: C, 26.4; H, 0.5; F, 68.6; N, 3.6. C₈H₂F₁₃N requires C, 26.7; H, 0.56; F, 68.8; N, 3.9%); ν_{max} . 2265 cm⁻¹ (CN).

References

- Part 2, P. L. Coe, A. Sellars, J. C. Tatlow, H. C. Fielding, and G. Whittaker, *J. Chem. Soc., Perkin Trans. I*, 1983, 1957.
- P. L. Coe, S. F. Sellers, J. C. Tatlow, H. C. Fielding, and G. Whittaker, *J. Fluorine Chem.*, 1981, **18**, 417.
- P. L. Coe, A. Sellars, and J. C. Tatlow, *J. Fluorine Chem.*, 1983, **23**, 102.
- P. L. Coe, A. Sellars, J. C. Tatlow, H. C. Fielding, and G. Whittaker, *J. Fluorine Chem.*, in the press.
- R. D. Chambers and R. H. Mobbs, *Adv. Fluorine Chem.*, 1965, **4**, 64.
- P. Robson, J. Roylance, R. Stephens, J. C. Tatlow, and R. E. Worthington, *J. Chem. Soc., Suppl. 1*, 1964, 5748.
- H. C. Fielding, B. P. 1 148 486/1969 (*Chem. Abstr.*, 1969, **71**, 60675z).
- S. Bartlett, R. D. Chambers, A. A. Lindley, and H. C. Fielding, *J. Chem. Soc., Perkin Trans. I*, 1980, 1551.
- H. C. Fielding, private communication.
- M. R. Bryce, R. D. Chambers, and G. Taylor, *J. Chem. Soc., Perkin Trans. I*, 1984, 509.
- W. T. Flowers, R. N. Haszeldine, C. R. Owen, and A. Thomas, *J. Chem. Soc., Chem. Commun.*, 1979, 134.
- P. L. Coe, A. Sellars, J. C. Tatlow, H. C. Fielding, and G. Whittaker, unpublished results.
- I. L. Knunyants, Yu. A. Cheburkov, and M. D. Borgamova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1963, 1389.
- I. L. Knunyants, B. L. Dyatkin, S. R. Sterlin, L. G. Zhuravkova, R. N. Sterlin, and V. L. Isaev, U.S.S.R.P. 246508 (*Chem. Abstr.*, 1969, **71**, 101317e).

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