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Fluoro-alkene forming eliminations using antimony pentafluoride

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Abstract

Reactions involving perfluoro-2-iodopropane and 1,1-difluoroethene, give telomers (**1**) and these telomer iodides are coupled to give $[(CF_3)_2CF(CH_2CF_2)_n\text{-}]_2$ (**2**). Fluorodeiodination gives a series of compounds $(CF_3)_2CF(CH_2CF_2)_nF$ (**3**). Lewis acid-induced eliminations from these systems is very effective using SbF_5 and cyclisations can also be induced by this methodology. A series of conjugated polymers is obtained by exposure of films of PVC, PVDF, and polytrifluoroethene to SbF_5 vapour.

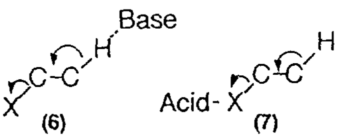
Keywords: Fluoro-alkene; Pentafluoride; Polyfluoroethene

1. Introduction

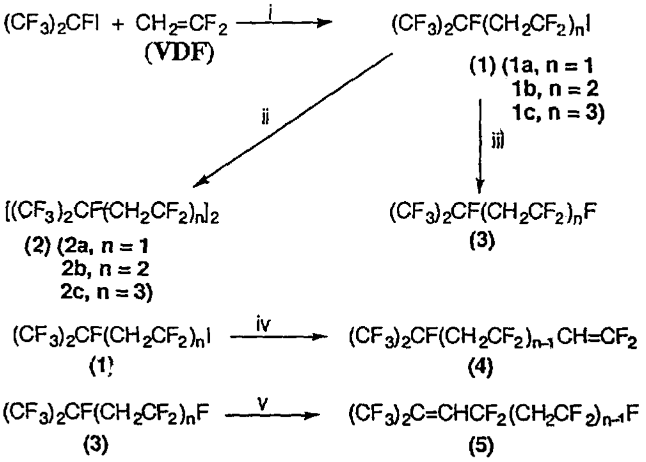
In a previous paper [1], we described syntheses of model compounds (Scheme 1) that relate to the structure of an important elastomeric system that is derived from the copolymer of hexafluoropropene and 1,1-difluoroethene [2], and we also reported syntheses, and attempted syntheses, of derived alkenes and di-enes, using bases to induce eliminations of hydrogen fluoride.

2. Results and discussion

In alkene-forming elimination reactions it is, perhaps, more common to think in terms of base-induced processes (**6**) and such procedures are satisfactory when the resultant alkene is not susceptible to nucleophilic attack. The use of base for eliminations from fluorinated systems, can often be successful e.g. for the formation of (**4**) from (**1**) but, in other cases, complications arise from nucleophilic attack on the resultant fluorinated alkene, giving undesirable by-products. Fluorinated alkenes are relatively resistant to electrophilic attack [3] and therefore we considered using antimony pentafluoride as a reagent for promoting elimination from the systems (**2**) and (**3**) via the acid-induced process (**7**).



This approach can, indeed, be very effective in a number of cases and Scheme 2 contains examples of formation of both fluorinated-alkenes e.g. (**9**), (**11**) and di-enes, e.g. (**12**), produced in this way. Formation of the di-ene (**12**) is particularly significant because we were quite unable to isolate this compound in a base-induced process [1]; instead, the cyclic product (**17**) was formed and we have demonstrated that the isolated di-ene (**12**) does indeed undergo the transformation to (**17**) extremely rapidly in the presence of fluoride ion. However, we found that further reactions occur with some of the fluorinated alkenes that are formed first in the presence of antimony pentafluoride, e.g. rapid conversion occurs of (**13**) and (**15**) to isomers (**9**) and (**16**) respectively. These results also indicate that the products obtained using anti-



i, 180°C, 24 h; ii, Hg/hν; iii, SbF_5, 0°C, $CF_2ClCFCl_2$; iv, Bu_3N; v, CsF, 120°C, sulpholan

Scheme 1. Syntheses of model compounds.

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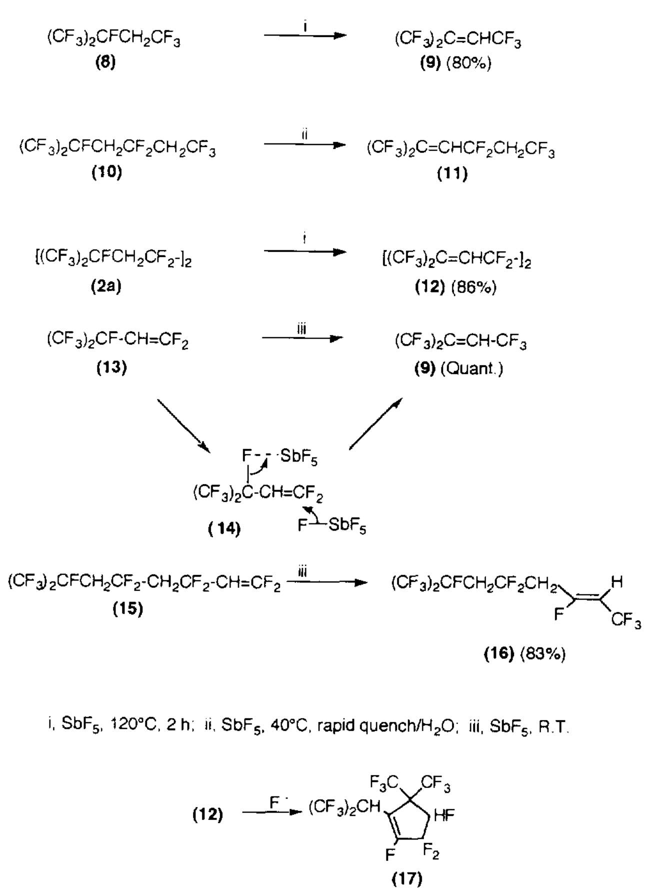
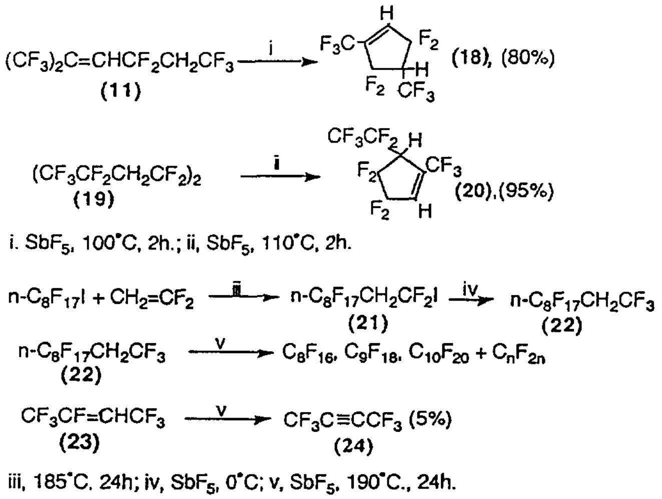


Scheme 2. Fluorinated-alkenes and -di-enes formed using antimony pentafluoride.

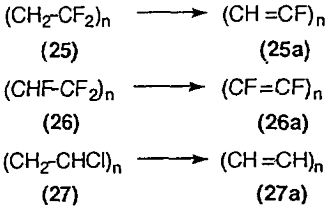
mony pentafluoride are under thermodynamic control because, generally, those isomers of alkenes most substituted by *perfluoroalkyl groups* rather than *fluorine atoms* at the double bond, are the most stable [4]. It is important to emphasise that electron withdrawal by perfluoroalkyl groups is greater than by fluorine atoms, because the latter can return electron–density by interaction of non-bonding electron–pairs with the double bond. Of course, electron withdrawal by perfluoroalkyl lowers orbital energies [5,6] and this stabilisation accounts for the fact that the isomers (**9**), (**11**), and (**12**) are obtained, where there are no fluorine atoms attached directly to the double bond. The mechanism of isomerisation of (**13**) and (**15**) probably involves concerted removal and transfer of fluoride ion, from one site to another as indicated (**14**). Indeed, Professor German and his co-workers, who have made considerable pioneering contributions to this field, have observed a variety of rearrangements of fluorinated alkenes, induced by antimony pentafluoride, and they have also stressed the probability of concerted processes, for their systems, similar to (**14**) [7].

We were surprised to discover some very unusual examples of what are, formally, 1,5-eliminations (Scheme 3)! When the fluorinated alkene (**11**) was heated with antimony pentafluoride at 100 °C, then 1H, 4H-2,4-bis(trifluoromethyl)tetrafluorocyclopentene (**18**) was obtained in good yield. Similarly, the hydrofluoroalkane (**19**) when heated with antimony pentafluoride gave almost quantitative conversion to 1H, 3H-2-trifluoromethyl-3-pentafluoroethyltetrafluorocyclopentene (**20**). At this stage, however, we are unable to propose a convincing mechanism for these eliminations; the process obviously involves elimination of hydrogen fluoride but it is also likely that further elimination of fluoride is involved, leading to carbocations, and the cyclisation steps probably involve such species. However, Professor German and co-workers have shown that fluorinated di-enes can be cyclised, using antimony pentafluoride, and proposed carbocations as intermediates [8,9]; they also made direct observation of the perfluoropentadienyl cation [10]. We synthesised compound (**22**), via (**21**), to explore the possibility that simple eliminations of hydrogen fluoride could occur from remote positions in a saturated hydrofluorocarbon but no reaction occurred between (**22**) and antimony pentafluoride at temperatures below 190 °C. At that temperature, however, breakdown occurred to give a series of fluorocarbons. We also considered the possibility of a Lewis acid induced elimination to convert the fluorinated alkene (**23**) to hexafluoro-butyne (**24**). However, (**24**) was obtained in only 5% yield and this suggests that the transition-states for these eliminations have significant carbocation character, rather than being concerted as in (**7**), because we would then anticipate much greater difficulty in removing fluoride from a vinylic position, since vinyl cations are energetically unfavourable species.

Reactions of (**11**) and (**19**) were carried out because we anticipated that it would be possible to produce more conjugated systems by this approach but, obviously, cyclisation intervened under these forcing conditions. However, when we allowed other systems, e.g. (**10**), (**11**), to stand at room temperature with antimony pentafluoride, rather than the rapid quenching procedure referred to in Scheme 2, then indeed further elimination occurred but, remarkably, the products in this case were long-lived observable carbocations



Scheme 3. Attempted eliminations using antimony pentafluoride.



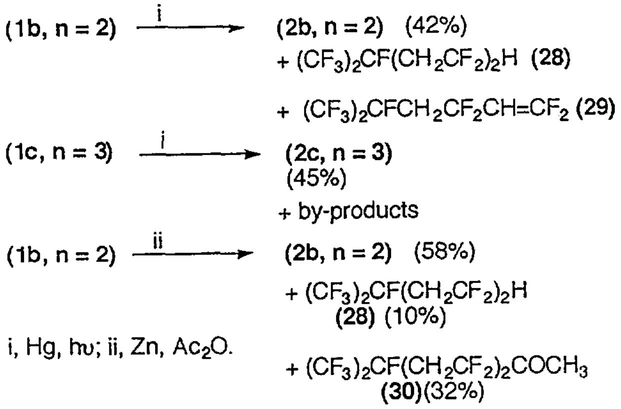
Scheme 4. Formation of polyconjugated systems.

[11,12] and further discussion of these interesting systems will be described [13].

There is much interest in conjugated polymers [14] and the effect of replacement of hydrogen by fluorine on the properties of polyacetylene has been speculated upon [15,16]. Polymerisation of difluoroacetylene has been claimed [17] and this is surprising, considering the inherent instability of difluoroacetylene [18]. The reactions of antimony pentafluoride described above suggested an alternative approach to polyacetylene derivatives by promoting eliminations from a saturated polymer with this reagent and, indeed, we have found that the process is remarkably effective. When a thin film of polyvinylidene fluoride (**25**) was simply exposed, under vacuum, to vapour of antimony pentafluoride, then the film rapidly darkened and went through black to a lustrous black appearance, all at room temperature (Scheme 4). Similarly, polytrifluoroethylene (**26**) went through the same sequence although this system required heating. In marked contrast, a film of PVC (**27**) went *instantly* black, through analogous but more rapid elimination of hydrogen chloride, when a tap was opened to allow vapour contact under vacuum between antimony pentafluoride and the PVC film, (**27**). It is clear that extensive elimination of hydrogen-fluoride or -chloride occurs in these systems, induced by antimony pentafluoride, but it is important to stress that the resulting highly conjugated films are not simply polyacetylene and derivatives (**25a**–**27a**), because the products of elimination must also contain a number of charged sites. This is evident from the fact that long-lived fluorinated carbocations are observed in analogous low molecular-weight model systems [12,13]. Consequently, the infrared spectrum of the product from PVC resembled closely that recorded for doped polyacetylene, rather than polyacetylene derivative (**27a**) [19].

These films are extremely difficult to characterise but the elimination procedure offers a potentially simple methodology for generating polyconjugated films or surfaces and it is clear that their electrical properties could be useful, especially because the approach presents the opportunity for preparing conducting surfaces sandwiching an insulator.

Returning to the subject of synthesis of starting materials, we used coupling reactions to form (**2b**) and (**2c**), from (**1b**) and (**1c**), respectively (Scheme 5). When mercury and ultraviolet light was used as the coupling process [1,20]. (**2b**) was accompanied by the by-products (**28**) and (**29**) and these mercury-induced reactions are critically dependent on providing a large and mobile mercury surface (see experimental section), otherwise the by-products predominate. Because of these uncertainties, we also explored the use of zinc with a solvent [21] for the coupling process and, in this case, the by-product (**28**) that arises from reduction of the iodide (**1b**), was also accompanied by the ketone (**30**), which must arise from reaction of an intermediate organo–zinc compound with acetic anhydride. This sheds some light on the mechanism of the coupling process for formation of (**2**) from telomer iodides (**1**) and suggests an SET process at the surface of the zinc. However, when dioxane was used as solvent for coupling of the iodide (**1b**), then only the product of reduction (**28**) was obtained, indicating the formation of an organozinc compound and this observation is consistent with the fact that dioxane is known to stabilise perfluorinated organo–zinc compounds [22].



Scheme 5. Coupling of fluorocarbon iodides (**1b**) and (**1c**).

3. Experimental

Gas liquid chromatography was carried out using a Hewlett Packard 5890A gas liquid chromatograph equipped with a 25 m cross-linked methyl silicone capillary column. Preparative scale g.l.c. was performed using a Varian Aerograph Model 920 (catharometer detector) gas liquid chromatograph with packed columns (3 m 10% SE 30). Elemental analyses for carbon, hydrogen, and nitrogen were obtained using a Perkin–Elmer 240 Elemental Analyser or a Carlo Erba Strumentazione 1106 Elemental Analyser. ^1H, ^{19}F, and ^{13}C n.m.r. spectra were recorded using a Bruker AC 250, a Varian Gemini VXR200, or a Varian VXR400S spectrometer, with TMS and fluorotrichloromethane as internal references, J values being given in Hz. Infrared spectra were recorded on a Perkin–Elmer 457 or 577 Grating spectrometer using KBr discs (for solid samples) or thin films between two KBr plates (for liquid samples). Gaseous samples were condensed into a cylindrical cell fitted with KBr plates. Mass spectra of solid samples were recorded on a VG 7070E spectrometer. GLC mass spectra were recorded on the VG 7070E spectrometer linked to the Hewlett Packard 5790A gas chromatograph fitted with a 25 m cross-linked methyl silicone capillary column. Fractional distillation of product mixtures was carried out using a Fischer Spahltrohr MMS255 small concentric tube apparatus.

3.1. Thermal telomerisation of vinylidene fluoride and perfluoro-2-iodopropane

A mixture containing perfluoro-2-iodopropane (61 g, 0.206 mol) and vinylidene fluoride (27 g, 0.432 mol) was condensed into a stainless steel autoclave (150 ml), degassed and rocked under autogenous pressure for 24 h at 180 °C. The autoclave was vented and no VDF was recovered. The residual liquid mixture obtained was separated by distillation (reduced pressure) giving: $(CF_3)_2CFI$ (0.8 g), $(CF_3)_2CF(CH_2CF_2)I$ (**1a**) (22.6 g, 30%), $(CF_3)_2CF(CH_2CF_2)_2I$ (**1b**) (38.4 g, 44%) bp 92 °C/60 mmHg, and $(CF_3)_2CF(CH_2CF_2)_3I$ (**1c**) (17 g, 17%) bp 61–65 °C/1 mmHg, identified by comparison of spectra with those of authentic samples [1,23]; $(CF_3)_2CF(CH_2CF_2)_4I$ (4.5 g, 4%) b.p. 92–96 °C/1 mmHg, [m/s, 425, $(M^+ - I)$], δ_F -39 [Int. 2, m, CF_2I], -78.0 [Int. 6, D (J=6) of T (J=6), CF_3], -186.4 [Int. 1, m, CF]; $(CF_3)_2CF(CH_2CF_2)_5I$, [m/z, 469, $(M^+ - I$, -HF)], (trace), δ_F -39.0 [Int. 2, m, CF_2I], -78.0 [Int. 6, D (J=6) of T (J=6), CF_3], -91.2 [Int. 8, m, CF_2], -186 [Int. 1, m, CF]. Pure samples of these compounds were isolated by preparative-scale glc. for purposes of identification.

3.2. Fluorodeiodination of telomer iodides. Preparation of $(CF_3)_2CFCH_2CF_3$ (8)

Reactions were carried out as described previously and typically, a two necked round bottom flask was fitted with a dropping funnel, and a condenser. Antimony pentafluoride (4.3 g, 19 mmol) in 1,1,2-trichloro-1,2,2-trifluoroethane (R-113) (10 ml) was added drop-wise to a stirred solution of $(CF_3)_2CFCH_2CF_2I$ (3.7 g, 10.4 mmol) in R-113 (5 ml) over 20 minutes at -5 °C. The mixture was stirred for a further hour and then water was added cautiously to the mixture, which was allowed to warm to room temperature and then thoroughly washed with a saturated sodium carbonate solution. The fluorocarbon layer was separated, dried (molecular sieve), and distilled to give $(CF_3)_2CFCH_2CF_2F$ (1.7 g, 65%) bp 47–49 °C. The product was identified by comparison of its IR and NMR spectra with those of an authentic samples [1].

3.3. Coupling reactions of telomer iodides

3.3.1. Using hν and mercury

*3.3.1.1. Preparation of $[(CF_3)_2CFCH_2CF_2]_2$ (**2a**)*

Typically, a mixture of $(CF_3)_2CFCH_2CF_2I$ (5 g, 9 mmol) and Hg (54 g), contained in a Carius tube, was degassed and sealed. The tube was then placed on a horizontal roller so that the tube rotated whilst being irradiated for 2 days under a 1 Kw medium pressure mercury lamp; then the tube was cooled in liquid air, opened, and a mixture of gases (0.35 g) was recovered. This gaseous mixture was analysed by GLC/MS and the products identified as $(CF_3)_2CFCH{=}CF_2$, $(CF_3)_2CFCH_2CF_2H$, and $[(CF_3)_2CFCH_2CF_2]_2$, (5:5:85, respectively) by comparison of their spectra with those of authentic samples. The mixture remaining in the tube, containing mercury residues, was extracted with dichloromethane and separated. Solvent was removed by distillation at atmospheric pressure and then distillation under reduced pressure gave $[(CF_3)_2CF(CH_2CF_2)]_2$ (1.5 g, 82%), identified by comparison of IR and NMR spectra [1].

*3.3.1.2. Preparation of $[(CF_3)_2CF(CH_2CF_2)_2]_2$ (**2b**)*

A mixture of $(CF_3)_2CF(CH_2CF_2)_2]_2I$ (**1b**), (5.3 g, 12.5 mmol) and Hg (90 g), contained in a Carius tube, was irradiated, as described above and the products were isolated and identified as indicated. The gaseous mixture (0.3 g) recovered, contained $(CF_3)_2CFCH_2CF_2CH{=}CF_2$ (**29**), and $(CF_3)_2CFCH_2CF_2CH_2CF_2H$ (**28**) (45:55, respectively), and residual liquid gave $[(CF_3)_2CF(CH_2CF_2)_2]_2$ (**2b**), (1.55 g, 42%) on distillation, (product identified by comparison of IR and NMR spectra, with those of an authentic sample, prepared by a different method, see later).

*3.3.1.3. Preparation of $[(CF_3)_2CF(CH_2CF_2)_3]_2$, (**2c**, **n=3**)*

A mixture of $(CF_3)_2CF(CH_2CF_2)_3I$ (**1c**) (7 g, 14.3 mmol) and Hg (100 g) was sealed in a Carius tube, irradiated, and product isolated as described above giving: 3,3,5,5,7,7,10,10,12,12,14,14-dodecahydro-2,15-bis(trifluoromethyl)-perfluorohexadecane, (**2c**, **n=3**), (2.3 g, 45%), (Found: C, 30.1; H, 1.8; F, 68.7. $C_{18}H_{12}F_{26}$ requires: C, 29.9; H, 1.7; F, 68.4%); δ_F -76.9 (Int. 12, s, CF_3), -88.7, -89.6, -113.6 (each Int. 4, s, CF_2), -185.6 (Int. 2, s, CF).

3.3.2. Using zinc and acetic anhydride

*3.3.2.1. Preparation of $[(CF_3)_2CF(CH_2CF_2)_2]_2$ (**2b**, **n=2**)*

In a similar manner, using the apparatus described above, zinc (1.15 g, 22.9 mmol) was activated in acetic anhydride (10 ml). A solution of $(CF_2)_2CF(CH_2CF_2)_2I$ (**1b**) (7.5 g, 17.6 mmol) in acetic anhydride (5 ml) was added drop-wise to the zinc suspension, stirred overnight and the product isolated, as described above giving: $(CF_2)_2CF(CH_2CF_2)_2H$ (**28**), (0.5 g, 10%); $[(CF_3)_2CF(CH_2CF_2)_2]_2$ (**2b**, **n=2**), (3.1 g, 58%), b.p. 96–101 °C/1 mmHg, M^+ 594 δ_H -2.9 to -3.1 (br, m); δ_F -76.2 (Int. 12, br, CF_3), -94.5 (Int. 4, br, CF_2), -108.5 (Int. 4, br, CF_2) -184.6 (Int. 2, br, CF); and $(CF_2)_2CF(CH_2CF_2)_2COCH_3$ (**30**) (1.9 g, 32%), b.p. 118–123 °C/1 mmHg.

3.4. Synthesis of unsaturated fluorinated compounds using SbF_5. $(CF_3)_2C{=}CHCF_3$ (9)

An NMR tube was charged with antimony pentafluoride (2.8 g, 12.9 mmol) and $(CF_3)_2CFCH{=}CF_2$ (**13**) (0.5 g, 2.2

mmol). The tube was sealed and the contents agitated for a few minutes at room temperature. Changes in the composition of the mixture were followed by ^1H and ^{19}F nmr spectroscopy which indicated that rapid conversion of (**13**) to $(CF_3)_2C{=}CHCF_3$ (**9**) [1] occurred.

3.5. Elimination of hydrogen fluoride from $(CF_3)_2CFCH_2CF_3$ (8) and $(CF_3)_2CFCH_2CF_2CH_2CF_3$ (10)

General procedure. A mixture of the appropriate compound and antimony pentafluoride, contained in a Carius tube, was heated in an oil-bath. After allowing the tube to cool, products were transferred under vacuum onto sodium fluoride and then into a fresh flask, where the product was washed with water and aqueous sodium bicarbonate. The fluorocarbon layer was then separated and dried ($MgSO_4$).

A mixture of (**8**) (6.3 g, 27 mmol) and SbF_5 (8.7 g, 40 mmol) was heated at 120 °C for 3 h. Analysis of the product by glc showed a single component (> 95% purity) which was identified as 2H-nonafluoro-3-methylbut-2-ene, $(CF_3)_2C{=}CHCF_3$ (**9**) [1] (5 g, 80%); δ_H −6.7 (Int. 1, q, J 8.0 Hz, 2-H); δ_F −61.0 [Int. 3, q, J 8.1 Hz, 3-CF_3], −62.0 [Int. 3, q, J 8.1 Hz, 4-CF_3], −67.6 (Int. 3, m, 1 -CF_3); δ_C −127.8 (Int. 1, sept, J 30 Hz, 3-C), −118.8–118.0 and −117.0 (Int. 3, q, J 275 Hz, 1,3,4-CF_3).

A mixture of (**10**) (14.8 g, 0.05 mmol) and SbF_5 (15 g, 0.08 mol) was heated at 40 °C for 20 min. Analysis of the product by glc showed a single component (> 95% purity) which was identified as *2H,2H,4H-undecafluoro-5-methylhex-4-ene*, (**11**), $(CF_3)_2C{=}CHCF_2CH_2CF_3$ (11 g, 74%); (Found: C, 28.1; H, 0.9; F, 71.1. $C_7H_3F_{11}$ requires: C, 28.38; H, 1.01; F, 70.61%); $\nu_{max.}$ 1674 cm^{-1} (C=C); δ_H −2.8 (Int. 2, m, 2-H); −6.6 (Int. 1, t, J 13.5 Hz, 4-H); δ_F −61.0 [Int. 3, m, 1-CF_3], −64.0 [Int. 3, t, J 9.0 Hz, 6-CF_3), −167.0 [Int. 3, q, J 7.5 Hz, 5-CF_3], −92.0 [Int. 2, m, 4-F]; m/z 227 (M^+ -F).

3.6. Cyclisation reactions

3.6.1. Formation of (18)

A mixture of $(CF_3)_2C{=}CHCF_2CH_2CF_3$ (**11**), (2 g, 67 mmol) and SbF_5 (2 g, 100 mmol), contained in a round bottomed flask (50 ml), was stirred at 100 °C for 2 h. Volatile material (1.8 g) was then transferred from the flask under vacuum, washed with water (10 ml), and shown by analytical gas chromatography to consist of one major component (> 95% purity). A small sample was isolated by preparative scale gas chromatography and characterised as *1H-2,4-bis(trifluoromethyl)-4H-tetrafluorocyclopentene* (**18**) (1.8 g, 97%). (Found: C, 30.1; H, 0.4. $C_7H_2F_{10}$ requires C, 30.43; H, 0.72%); ν_{max} 1690 cm^{-1} (C=C); δ_H −3.2 (Int. 1, tq, J 4 and 8 Hz, 1-H); −6.4 (Int. 1, br, 4-H); δ_F −67.0 (Int. 3, br, 4-CF_3), −67.5 (Int. 3, br, 2-CF_3), −100.0 (Int. 2, AB, J 282 Hz) and −100.5 (Int. 2, AB, J 269 Hz) (3- and 5-CF_2); δ_C −57.1 (br m, 4-C), −122.1 (q, J 250 Hz) and −125.0 (q, J 279 Hz) (2 and 4-CF_3), −120.6 and −120.7 (Int. 2, t, J 257 Hz, 3- and 5-C), −137.4 (t, J 31 Hz, 1-C), −138 (br m, 2-C); m/z, 276 (M^+, 36%) and 257 (M^+ -F, 79%).

3.6.2. Formation of (20)

A mixture of $(CF_3CF_2CH_2CF_2)_2$ (**19**) (4 g, 11 mmol) and SbF_5 (5 g, 25 mmol), sealed in a Carius tube under vacuum, was stirred for 2 h at 110 °C. Volatile material was transferred under vacuum onto NaF (2.0 g) and then, after 30 min, to a fresh flask to yield a colourless liquid (3 g). This was shown by glc to consist of one component (> 95% purity) and characterised as *1H-2-trifluoromethyl-3H-3-pentafluoroethyltetrafluorocyclopentene* (**20**) (2.5 g, 70%), (Found: C, 29.5; H, 0.6; F, 69.5. $C_8H_2F_{12}$ requires C, 29.45; H, 0.61; F, 69.91%); δ_H −3.8 (Int. 1, t, J 20 Hz, 3-H), −6.6 (Int. 1, Br, 1-H); δ_F −69.0 (Int. 3, d, J 60 Hz, 2-CF_3), −85.0 (Int. 3, d, J 20 Hz, 3-$CF_2\mathit{CF_3}$), −115.0 (Int.2, AB, J 245 Hz, 4-F), −115.6 (Int.2, br, 3-$\mathit{CF_2}CF_3$); −117.0 (Int.2, AB, J 273 Hz, 5-F), δ_C −51.7 (m, 3-C), −114.0, −119.0, −122.0 (br m, 4,5-C and 3-$\mathit{CF_2}CF_3$), −119.5 (q, 3 272 Hz) and −120.6 (q, J 280 Hz) (-$\mathit{CF_3}$ and 3-$CF_2\mathit{CF_3}$), −134.4 (t, J 17 Hz, 1-C), −138.1 (q, J 39 Hz, 2-C); m/z 326 (M^+, 2%) and 207 (M^+ −119, 11%).

3.6.3. Attempted cyclisation reactions using (21, 22)

3.6.3.1. Synthesis of $C_8F_{17}CH_2CF_3$ (22)

A mixture of 1-iodoperfluorooctane (120 g, 0.2 mole) and 1,1-difluoroethene (9.9 g, 0.15 mole), contained in a sealed nickel tube (150 ml) was rocked under autogenous pressure at 185 °C for 36 h. On opening the tube solid products (122 g) were obtained by addition of CH_2Cl_2 (100 ml) and then solvent was removed by distillation. Further distillation of the residue (18 mm, Hg) afforded a fraction boiling at 75 °C, which was recovered 1-iodoperfluorooctane (23 g), and one at 110 °C which was identified as: *1-iodo-2,2-dihydrononadecafluorodecane*, $C_8F_{17}CH_2CF_2l$ (**21**) (66 g, 54%), (Found: C, 19.0; H, 0.2; F, 58.3; l, 20.2. $C_{10}H_2F_{19}l$ requires C, 19.60; H, 0.33; F, 59.18; l, 20.89%); δ_H −3.0 (Int. 2, tt, J 15 and 15 Hz, 2-H); δ_F −38.3 (Int. 2, m, 1-F), −80.5 (Int. 3, t, J 16 Hz, 10-F); 113.3 (Int. 2, br, 9-F), −123 (Int. 10, br, 4,5,6,7,8-F), −127.1 (Int. 2, br, 3-F); m/z 610 (M^+, 5%) and 483 (M^+ −127, 44%).

A solution of (**21**), (55 g, 85 mmol) in $CF_2ClCFCl_2$ (50 ml) was stirred, under an atmosphere of dry nitrogen, in a round bottomed three-necked flask (1 l), that was equipped with a reflux condenser. Then a solution of SbF_5 (25 g, 0.12 mole) in $CF_2ClCFCl_2$ (50 ml) was added with caution over a period of 1 h while the temperature in the flask was maintained at 0–5 °C using an ice-bath. After stirring for a further 30 min the products were added to water (300 ml) and then washed with aqueous $NaHCO_3$ (300 ml). The fluorocarbon layer was separated, filtered, and solvent was removed by evaporation to leave a pale yellow liquid (38 g) which was shown to consist of one component (> 95% purity) by glc. Distillation under high vacuum yield *2H,2H-eicosafluoro-*

decane, $C_8F_{17}CH_3CF_3$ (**22**) ((32 g, 75%) (Found: C, 23.4; H, 0.2; F, 75.3. $C_{10}H_2F_{20}$ requires C, 23.90; H, 0.40; F, 75.70%); δ_H −3.1 (Int.2, tq, J 15 and 15 Hz, 2-H); δ_F −62.0 (Int.3, t, J 17 Hz, 1-F), −78.5 (Int.3, t, J 20 Hz, 10-F), −113.0 (Int.2, br, 9-F), −123.0 (Int.10, br, 4,5,6,7,8-F), −128.5 (Int.2, br, 3-F); m/z 483 (M^+ −F, 17%).

3.6.3.2. Attempted cyclisation of (22)

A mixture of (**22**) (38 g, 76 mmol) and SbF_5 (32.8 g, 0.15 mol), contained in a sealed Carius tube, was stirred under autogenous pressure at 190 °C for 12 h, during which time the contents of the tube turned bright orange–red. Volatile material (20 g) was then transferred to a separate tube, using vacuum line techniques, and SiF_4 was identified as a component from a gas phase ir spectrum and this vapour-pressure component was vented cautiously from the tube. The remaining products were then washed with water (2 × 30 ml) and shown by glc to consist of three main components (ca. 80%) and less volatile material (ca. 20%). ^1H nmr examination of the products showed no resonances. A sample of each of the three main components was isolated (>95% purity) using preparative scale gas chromatography identified as C_nF_{2n} (n = 8–10) by nmr and ms data: n = 8, δ_F −82.5 (Int. 6, t, J 18 Hz), −113 to −127 (Int. 10, complex), [m/z 400]; n = 9, δ_F −83.0 (Int. 6, t, 18 Hz), −113 to −127 (Int. 12, complex), [m/z 450]; n = 10, δ_F −83 (Int. 6, t, J 18 Hz), −113 to −127 (Int. 14, complex), [m/z 500].

3.7. Isomerisation of $(CF_3)_2CFCH{=}CF_2$ (13)

A mixture of (**13**) (0.5 g, 2.1 mmol) and SbF_5 (0.6 g, 3 mmol) was sealed under vacuum in an nmr tube and shaken at 20 °C for 1 h. When the ^{19}F and ^1H nmr spectra were recorded $(CF_3)_2C{=}CHCF_3$ (**9**) was identified as the only product; δ_F −61.0 (Int.3), −62.0 (Int. 3) and −67.6 (Int. 3); δ_H −6.7 (1, Int. q, J 8.0 Hz).

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