POLYMER CHEMISTRY. PART 1. MODEL COMPOUNDS RELATED TO HEXAFLUOROPROPENE-VINYLIDENE FLUORIDE ELASTOMER*

G.C. APSEY, R.D. CHAMBERS*, M.J. SALISBURY

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE (U.K.)

and G. MOGGI

Montefluos CRS, V.S. Pietro 50, 20021 Bollate (MI) (Italy)

SUMMARY

Model compounds related to the important elastomer derived from $CH_2=CF_2/CF_2=CFCF_3$ are synthesised from telomers $(CF_3)_2CF(CH_2CF_2)_nI$, by coupling and by fluorodeiodination reactions. These models, in reactions with bases, give information relating to mechanisms of cross-linking of the polymer and indications of factors that limit its working life. Novel use of SbF₅ for dehydrofluorination in synthesis of fluorinated mono-enes and di-enes is described.

INTRODUCTION

Co-polymers formed from hexafluoropropene and vinylidene fluoride are extremely important as high-performance elastomers and are used in an increasing range of aggressive environments [1] but cross-linking procedures vary for the processing of the elastomer and, this has a significant effect on the stability of the final product. One such procedure involves base-induced cross-linking with bisphenol AF [2] and Schmiegel [3] has investigated this system and made proposals, based on n.m.r. evidence, for the mechanism of interaction of bases with the crude polymer. Here we describe the synthesis of model compounds related to this system, partly based on earlier studies that were initiated in this

Dedicated to Emeritus Professor W.K.R. Musgrave on the occasion of his 70th birthday.

laboratory [4], and the aim of this approach is to define more precisely the processes that are likely to occur with the polymer.

Ferguson [5] has deduced from n.m.r. studies, that the structural arrangements (1), (1a) and (2), (2a) are present in the polymer, although principally (1) and (2). The ratio of (1):(1a) and (2):(2a) is constant but the ratio of (1):(2) obviously varies with monomer ratios. Therefore, we have targeted model compounds that incorporate structures (1) and (2).

 $\begin{array}{cccc} (CH_2 CF_2 CH_2 CF_2)_{0.95} & (CH_2 CF_2 CF_2 CH_2)_{0.05} \\ (1) & (1a) \\ \\ [CH_2 CF_2 CF_2 CF_2 CF(CF_3)]_{0.93} & [CH_2 CF_2 CF(CF_3) CF_2]_{0.07} \\ (2) & (2a) \end{array}$

RESULTS AND DISCUSSION

An approach developed earlier [4] involves reactions of iodoperfluoroalkanes with 1,1-difluoroethylene, giving telomers e.g. (3,4). Useful model compounds e.g. (5,6) have now been prepared by coupling of the corresponding telomer iodides, using mercury under ultra-violet irradiation [6] or reaction with zinc in acetic anhydride [7]; models (7) were obtained simply by replacement of iodine by fluorine using antimony pentafluoride [8]. A more complex model (10) was obtained by a series of additions, as shown in the sequence (8)-(9)-(10).

$$\begin{array}{rcl} R_{F}I &+& CH_{2}CF_{2} & \underbrace{(1)}_{} & R_{F}(CH_{2}CF_{2})_{n}I \\ R_{F} &=& CF(CF_{3})_{2} & (3a, n = 1 \\ & 3b, n = 2 \\ & 3c, n = 3) \\ R_{F} &=& CF_{2}CF_{3} & (4a, n = 1 \\ & 4b, n = 2) \\ i, 180\text{-}200^{\circ}, \text{ Autoclave}, 24\text{-}36 \text{ h.} \end{array}$$

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$$R_{F}(CH_{2}CF_{2})_{n}I \xrightarrow{i \text{ or }} [R_{F}(CH_{2}CF_{2})_{n}]_{2}$$

$$R_{F} = CF(CF_{3})_{2} \quad (5a, n = 1)$$

$$R_{F} = CF_{2}CF_{3} \quad (6a, n = 1)$$

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 $R_F = CF(CF_3)_2$, i, 200°, 48 h; ii, $CH_2=CF_2$, 185°, 24 h; iii, SbF_5 , $CF_2C1CFC1_2$, 0°C

We have also attempted to prepare some compounds that would usefully serve as models for unsaturated sites that might be produced by base-induced elimination of hydrogen fluoride from sites (1) and (2) in the polymer. However, reaction of (5a) with tri-n-butylamine led to a remarkable transformation to the cyclic compound (12); little reaction occurred until 100° C and then almost quantitative conversion to (12) was observed. The di-ene (11) is, undoubtedly, an intermediate, but this is smoothly converted (see later) to (12). A likely mechanism for this process is contained in Scheme 1, involving addition of fluoride ion to (11) and then cyclisation of the resulting anion. This cyclisation is very surprising in that the ring closure step brings together some bulky substituents into eclipsing situations. However this is, apparently, rapidly relieved by elimination of fluoride ion to give (12).

A further interesting complication arose in a reaction of tri-n-butylamine with (13), giving a product (14) which formally involves reduction of 'tertiary' fluorine. In a separate reaction, however, it was demonstrated that the alkene derivative (15) (see later) also gave (14) and it is reasonable to conclude therefore that (15) is an intermediate in the formation of (14) from (13). Hydrogenation of an alkene with tri-n-butylamine is unusual and a 1-electron transfer process seems likely since the process is reminiscent of other reactions of halides that involve electron transfer. A likely mechanism is outlined in Scheme 2.



Scheme 2

Fluoride ion will function as a strong base [10] and heating (13) and (16) with caesium fluoride, in sulpholane at 150° , gave good yields of the corresponding alkenes (15) and (17). It is significant, however, that

this system was unable to promote elimination of hydrogen fluoride from a site involving difluoromethylene.

We have been frustrated in, for example, the synthesis of the di-ene (11) by the occurrence of further reactions of (11) in the presence of nucleophiles and, consequently, we turned to the use of Lewis Acid to promote elimination of hydrogen fluoride. This approach was remarkably effective, giving essentially a quantitative conversion of (5a) to the di-ene (11). Subsequent treatment of (11) with fluoride ion gave conversion to the cyclic derivative (12), thus confirming our earlier mechanism for the formation of (12) using tri-n-butylamine shown in Scheme 1. Use of antimony pentafluoride for the synthesis of unsaturated fluorocarbons is quite effective, providing that the product itself remains inert to strong electrophiles e.g. (18) was converted quantitatively to (19). However, many of the products that we have investigated are not inert to antimony pentafluoride but, instead, led to remarkably stable carbocations or some unusual further reactions and this topic will be discussed separately [12].

The n.m.r. spectra of these model compounds are extremely useful for identification and assignment of structural features in the polymer, e.g. (1) and (2), and these n.m.r. analyses will be discussed separately [11].

Reactions of Model Compounds with Bases and Nucleophiles

The saturated model compounds e.g. (5, n = 1 and 2), (7, n = 2) showed no evidence of elimination of hydrogen fluoride when heated to high temperatures in the presence of typical mixtures that are used for

cross-linking crude hexafluoropropene/1,1-difluoroethylene co-polymers. Typical mixtures involve addition of carbon black, Ca(OH)₂, MgO, Ph₃P+CH₂PhCl, and p-(HOC₆H₄)₂C(CF₃)₂(Bisphenol AF) [3]. Quite clearly, there is a marked difference between the activity of the polymer and that of the model compounds and this could be attributed to (a) a contact problem in the case of models, or (b) enhanced reactivity of solid-solid interaction which occurs in the polymer system or (c) intrinsic instability of the polymer towards elimination of hydrogen fluoride, which is not characteristic of lower molecular weight systems of similar structure. The most significant is probably (a) because treatment of model (7, n = 3) with D.B.U. in D.M.A.C., <u>i.e.</u> a homogeneous system, at room temperature, led to rapid dehydrofluorination in a manner similar to that which has previously been observed with the polymer [3].

$$(7, n = 3) \xrightarrow{i} (CF_3)_2 C=CHCF_2 CH_2 CF_2 CH_2 CF_3$$

$$(20)$$

i, D.B.U., D.M.A.C., room temp.

It has been argued [3] that in reaction of base with polymer sites (1) and (2), preferential elimination of hydrogen fluoride occurs from positions involving the "tertiary" fluorine. We have reached the same conlusions by observing the relative reduction in intensity in the signal arising from "tertiary" fluorine in the n.m.r. spectrum of a solution of the polymer, after treating with D.B.U. in D.M.A.C. as solvent; this is also confirmed by reaction of model compounds with bases in solution. Reaction of (7, n = 3) with D.B.U. gave (20) exclusively. Other examples of reactions of models with bases, that led exclusively to eliminations of hydrogen fluoride from sites involving "tertiary" fluorine, have been discussed earlier in this paper.

Having established the type of unsaturated site most readily produced in the polymer during curing, we have explored the further reaction of model compounds that involve the site $-C(CF_3)=CH$ - which is contained in (2c), with both phenoxide and methoxide. These reactions are illustrated in Scheme 3.

Reactions of phenol with models (19), (15), and (20) demonstrate that addition occurs extremely readily with systems containing sites $-C(CF_3)=CH$ - giving products of addition e.g. (21) and (22), but it is important to note the formation of both (23) and (24) since this

demonstrates that attack at the double bond can occur with allylic displacement of fluoride. A new unsaturated site is formed which reacts further with phenol, to give (23), (24) and this observation has great significance for the elastomer cross-linked with bis-phenol.

Scheme 3

n

Compound (25) is a more appropriate model for sites of unsaturation (2c) generated in the main polymer structure (2) and reactions of (25) illustrate further the allylic displacement process described above. Product (26) was obtained, arising from allylic displacement of fluoride ion, and this obviously occurs more readily with (25) than with (15) or (20) because the process involves loss of fluoride ion in the former case, from a difluoromethylene site and it is well known that a carbon-fluorine bond is weaker in a difluoromethylene group than in trifluoromethyl [13]. Indeed, it is worth stressing that no addition product was obtained from (25) and, undoubtedly, an analogous process, <u>i.e.</u> forming and <u>retaining</u> unsaturated sites, will predominate with the polymer. Therefore the cross-linking step with bis-phenol will always regenerate another vinylic fluorine site and the latter will obviously be a major source of chemical instability.

Schmiegel [3] recognised the production of sites in the polymer with fluorine attached at vinylic positions but found it necessary to suggest equilibration with fluoride ion, in order to produce these sites <u>i.e.</u> $-CF_2C(CF_3)=CH- \xrightarrow{F_{-}} -CF=C(CF_3)CHF-$. This equilibrium is, however, unlikely because attachment of perfluoralkyl is thermodynamically preferred over fluorine at double-bonds [14] and the allylic displacement process that we have described adequately demonstates how these vinylic sites attached to fluorine may be produced.

Conclusions relating to Bis-phenol cured elastomer

Some definite conclusions can now be drawn from these model compound studies, that relate to bis-phenol cured elastomer;

- 1. Unsaturated sites are initially generated predominately through elimination of the 'tertiary' fluorine. $-CF_2-CF(CF_3)-CH_2 \longrightarrow -CF_2-C(CF_3)=CH-$.
- 2. Phenol attack involves formation of new unsaturated sites, which will be highly vulnerable to further nucleophilic attack during the working life of the elastomer.

 $-CF_2 - C(CF_3) = CH - \xrightarrow{ArOH} - CF = C(CF_3)CH(OAr) - .$

Consequently, use of bis-phenol cured elastomer in circumstances like automobile radiator hoses etc., where amines are usually present, could be life-limiting.

EXPERIMENTAL

1. Telomers with 1,1-Difluoroethene [4]

i) A mixture of perfluoro-2-iodopropane (90.4 g, 0.305 mole) and 1,1-difluoroethene (24.0 g, 0.37 mole), contained in a sealed nickel tube (150 ml capacity), was rocked at 185° for 36 h under autogenous pressure. On opening the tube after cooling no gaseous products were recovered and a purple liquid (114 g) was poured from the tube. Analytical gas chromatography (column 0, 120° C) showed the presence of 4 components. Fractional distillation of the mixture using a packed insulated column vielded perfluoro-2-iodopropane (5 g, 0.017 mole), b.pt. 38°C; 2H,2H-nonafluoro-1-iodo-3-methylbutane (3a) (73 g, 67%), b.pt. 105° C, $\delta_{\rm H}$ (60 MHz, CCl₄) 2.8 (2H, t, 2-H), $\delta_{\rm F}$ (56.4 MHz; CCl₄) -76.4 (6F, d, 3,4-CF₃), -49.6 (2F, m, 1-F), -184.5 (1F, sept, 3-F), m/z 360 (M⁺ 8%) and 233 (M-127, 31%; 2H,2H,4H,4H-undecafluoro-1-iodo-5-methyl-hexane, $(CF_3)_2 CF(CH_2 CF_2)_2 I$ (3b) (26 g, 20%); b.pt. 157°C; δ_H (60 MHz; CCl₄) 2.8 to 3.2 (4H, m, 2-H, 4-H); $\delta_{\rm F}$ (56.4 MHz; CCl₄) -76.0 (6F, d, 5,6-CF₃), -49.2 (2F, m, 1-F), -93.6 (2F, m, 3-F), -185.0 (1F, sept, 5-F); m/z 424 (M⁺, 1%) and 297 (M-127, 15%).

Preparative scale gas liquid chromatography (column 0, 200^oC) carried out using the distillation residue yielded 2,2,4,4,6,6-hexa-hydroterdecafluoro-1-iodo-7-methyloctane; (CF₃)₂CF(CH₂CF₂)₃I (3c) (1 g, 0.6%); $\delta_{\rm H}$ (60 MHz; CCl₄) 2.8 to 3.2 (6H, m, 2-H, 4-H, 6-H); $\delta_{\rm F}$ (56.4 MHz; CCl₄) -76.2 (6F, d, 7,8-CF₃), -49.0 (2F, m, 1-F, -90.3 to -92.0 (4F, M, 3,5-F), -185.0 (1F, sept, 7-F); m/z 488.

ii) A stainless steel autoclave of capacity 150 ml was charged with 2H,2H-nonafluoro-1- iodo-3-methylbutane (3a) (49 g, 0.14 mol) and hexafluoropropene (35 g, 0.23 mol). The autoclave was rocked for 48 h at 200° and, on cooling a liquid (64 g) was recovered. Analysis of this liquid by glc (column 0, $100^{\circ}-220^{\circ}$) showed three major components. Fractional distillation of the mixture yielded (3a) (11 g), b.pt. $105^{\circ}C$; 5H,5H-pentadecafluoro-2-iodo-6-methylheptane (8) (nc) (49 g, 71%); b.pt. $70-71^{\circ}$ (27 mmHg); Analysis: Found: C, 18.5; H, 0.4%. C_8H_2F_{15}I requires C, 18.8; H, 0.4%; $\delta_{\rm H}$ (60 MHz) 2.8 (dt, J 17 and 17 Hz, 5-H); $\delta_{\rm F}$ (56.4 MHz) -75 (3F, dt, J 9 and 9 Hz, 1-CF₃) -80 (6F, d, J 6 Hz, 6,7-CF₃) -110 (4F, m, 3,4-F) -146 (1F, m, J 13 Hz, 2-F) -188 (1F, m, 6-F); m/z 510 (M⁺) and

7H,7H-perfluoro-2-iodo-4,8-dimethylnonane (nc) (29) (6 g, 7%); b.pt. 109-110°C (28 mmHg); Found: m/z 659.9787. $C_{11}H_2F_{21}I$ requires M⁺ 659.8865; δ_H (250 MHz; CDCl₃) 2.9 (m, 7-H); δ_F (235 MHz; CDCl₃) -70.2 (3F, dd, J 108 and 100 Hz, 1-F) -72.7 (3F, m, J 8Hz, 4-CF₃) -77.1 (3F, d, J 6 Hz, 8,9-CF₃) -100.6 to -114.1 (4F, m, 3,5-F) -110.6 (2F, m, 6-F) -145.4 (1F, m, 2-F) -181.6 (1F, dm, J 80 and 26 Hz, 4-F) -185.5 (1F, m, 8-F); m/z 660 (M⁺).

iii) A stainless steel autoclave of 125 ml capacity was charged with 1,1-difluoroethene (15.5 g, 0.24 mol) and (7) (99.4 g, 0.19 mol). The autoclave was rocked at 185°C for 24 h and, on opening, a liquid (112.7 g) was recovered. Analysis by glc showed the presence of two major components which were separated by fractional distillation. The fractions isolated were 2H,2H,6H,6H,6H,heptadecafluoro-1-iodo-3,7-dimethyloctane (nc) (9a) (83.0 g, 74%); b.pt. 91-92°C (13 mmHg); Analysis: Found: C, 20.5; H, 0.7; F, 56.9%. $C_{10}H_4F_{17}I$ requires C, 20.9; H, 0.7; F, 56.3%; $\delta_{\rm H}$ (60 Hz) 3.3 (m, 2,6-H), $\delta_{\rm F}$ (56.4 MHz) -39 (2F, m, 1-F) -78 (3F, dt, J 9 and 9 Hz, 3-CF₃) -80 (6F, dt, J 7 and 7 Hz, 7,8-CF₃) -113 (2F, n, 5-F) -121 (2F, m, 4-F) -186 and -188 (2F, m, 3,7-F); m/z 447 (M⁺-I) and 2.2.4.4.8.8hexahydrononadecafluoro-1-iodo-5,9-dimethyldecane (nc) (9b) (24.1 g, 21%); b.pt. 125^oC (15 mmHg); Analysis: Found: C, 22.5; H, 1.0; F, 56.9%. $C_{12}H_6F_{19}I$ requires C, 22.6; H, 0.9; F, 56.6%; $\delta_{\rm H}$ (60 MHz) 3.2 (m, 2,4,8-H); $\delta_{\rm F}$ (56.4 MHz) -40 (2F, m, 1-F) -78 (3F, dt, J 9 and 9 Hz, 5-CF₃) -79 (6F, dt, J 7 and 7 Hz, 9,10-CF₃) -91 (2F, m, 3-F) -112 (2F, m, 7-F) -121 (2F, m, 6-F) -186 and -188 (2F, m, 5,9-F); m/z 638 (M⁺).

2. Coupling Reactions

i) $(CF_3)_2 CFCH_2 CF_2 I$ (3a)

A mixture containing $(CF_3)_2$ CFCH₂CF₂I (3a) (40 g, 0.086 mole), acetic anhydride (25 ml) and zinc metal (25 g) was stirred mechanically in a 3-necked glass vessel at 50° C for 4 h. Volatile products were transferred under high vacuum and then stirred with aqueous HCl (100 ml, 0.05 M) for 1 h followed by washing with water (2 x 50 ml). The fluorocarbon layer was removed and dried (MgSO₄), filtered, and then stored over molecular sieve (type 4Å). Analysis by glc-ms showed the product to be (> 95% 3H, 3H, 6H, 6H-octadecafluoro-2,7-dimethyloctane, $[(CF_3)_2 CFCH_2 CF_2]_2$ (5a) (15.0 g, 75%); m/z 466 which was confirmed by comparison of the infra-red spectrum with that of an authentic sample [15].

ii) $CF_3CF_2CH_2CF_2I$ (4)

A glass ampoule containing $CF_3CF_2CH_2CF_2I$ (4a) (5 g, 16 mmmol) and mercury (10 ml) was irradiated using a 1 KW ultra-violet lamp at $60^{\circ}C$ for 5 d. Volatile material transferred from the tube under vacuum was shown by glc-ms (column 0, $120^{\circ}C$) to be one component (> 95% purity), identified as 3,3,6,6-tetrahydrotetradecafluorooctane, $[CF_3CF_2CH_2CF_2]_2$ (6a); δ_H 3.0 (m, 3,6-H); δ_F -87.1 (6 F, s, 2,7-CF₃), -114.5 (4 F, br, 4,5-F), -117.8 (4 F, m, 2,7-F), m/z 366. Further identification was provided by comparison of infrared spectra with that given in the literature [15].

3. Fluorination of the Telomer Iodides (3) (CF₃)₂CF(CH₂CF₂)_nI

A mixture of the telomer iodides $(CF_3)_2 CF(CH_2 CF_2)_n I$ (36 g) of approximate molar composition n=1, 40%, n=2, 30%; and n=3 10%, dissolved in CF₂ClCFCl₂ (100 ml), was stirred mechanically in a 3-necked glass vessel. The temperature in the flask was maintained at $0{}^{\rm O}{\rm C}$ using an ice bath while a solution of antimony pentafluoride (40 g, 0.19 mole) in $CF_2ClCFCl_2$ (50 ml) was added over a period of 0.5 h. The contents of the flask which became viscous and intensely coloured due to the deposition of iodine, were stirred for a further 0.5 h after the addition was complete. After this time further $CF_2ClCFCl_2$ (50 ml) was added and the resulting mixture filtered to remove solid material. The solid residue was washed with CFCl₂CF₂Cl (30 ml) and the washings added to the initial filtrate. The resulting solution was then washed with water (250 ml) and neutralised by addition of solid NaHCO3 until effervescence ceased. The fluorocarbon layer was separated and $CFCl_2CF_2Cl$ removed by distillation to leave a pale vellow liquid (16 g) which, on distillation gave three fractions; (i) b.pt. 50-55°C, (ii) b.pt. 80-85°C and (iii) 120-130°C. Analysis by glc (column 0, 70-110 $^{\circ}$ C) showed that the separation was not complete. Therefore the major component of each fraction was isolated using preparative scale gas chromatography (30% column 0, 100° C). The first component was identified as $(CF_3)_2 CFCH_2 CF_3$ (7a); m/z 252 and by comparison of the infrared spectrum that of an authentic sample [15]. The second

component was 2H,2H,4H,4H-dodecafluoro-5-methylhexane (nc) (CF₃)₂CFCH₂CF₂CH₂CF₃ (7b), (Found: C, 26.8; H, 1.1; F, 71.7; C₇H₄F₁₂ requires C, 26.58; H, 1.23; F, 72.15%); $\delta_{\rm H}$ 3.0 to 3.2 (br m, 2,4-H); $\delta_{\rm F}$ -63.0 (3F, t, J 14 Hz, 1-CF₃) -77.9 (6F, dt, J t and 7 Hz, 5,6-CF₃) -90.8 (2F, br m, 3-F) -185.8 (1F, br m, 5-F); m/z 297 (M⁺ -19). The third component was 2,2,4,4,6,6-hexahydrotetradecafluoro-7-methyloctane (nc) (CF₃)₂CFCH₂CF₂CH₂CF₂CH₂CF₃ (7c); Analysis: Found: C, 28.7; H, 1.5; F, 69.4%. C₉H₆F₁₄ requires C, 28.4; H, 1.6; F, 70.0%; $\delta_{\rm H}$ -3.0 to -3.2 (br m, 2,4,6-H); $\delta_{\rm F}$ -64,3 (3F, t, J 13 Hz), 1-CF₃ -79.3 (6F, d, J 8 Hz, 7,8-CF₃) -91.1 (2F, br.m, 5-F) -92.7 (2 F, br m, 3-F) -187.3 (1F, br m, 7-F); m/z 361 (M⁺ -19).

When the residue from the distillation was analysed using glc-ms (column 0, 180° C), two major components were resolved which were isolated using preparative scale glc (column 0, 200° C) and identified as the n=4 and n=5 telomers (CF₃)₂CF(CH₂CF₂)_nF 2,2,4,4,6,6,8,8-octahydrohexadeca-fluoro-9-methyldecane (nc) (7d); Analysis: Found: C, 29.6; H, 1.7; F, 69.0%. C₁₁H₈F₁₆ requires C, 29.73; H, 1.82; F, 68.46%; $\delta_{\rm H}$ (60 MHz) 2.6 (m, 2,4,6,8-H); $\delta_{\rm F}$ (56.4 MHz) 63.8 (3F, m, J 9 Hz, 1-F) 78.7 (6F, dt, J 6 and 6 Hz, 9-CF₃) 92.5 (6F, m, 3,5,6-F) 186.7 (1F, m, 9-F); m/z 435 (M*-F); and 2,2,4,4,6,6,8,8,10,10-decahydrooctadecafluoro-11-methyldodecane (nc) (7e); Analysis: Found: C, 30.9; H, 1.9; F, 66.8%. C₁₃H₁₀F₁₈ requires C, 30.71; H, 1.9; F, 67.31%; $\delta_{\rm H}$ (60 MHz) 2.5-3.4 (m, 2,4,6,8,10-H); $\delta_{\rm F}$ (56.4 MHz) 64.2 (3F, m, J 9 MHz, 1-F) 79.2 (6F, dt, J 6 and 6 Hz, 11-CF₃) 93.0 (8F, m, 3,5,7,9-F) 187.4 (1F, m, 11-F); m/z 489 (M*-19).

4. Treatment of (9a) with Tri-n-butylamine

Tri-n-butylamine (6.9 g, 37.1 mmol) and the iodide (9a) (21.2 g, 36.9 mmol) were stirred vigorously until the mixture became solid due to the formation of the amine hydroiodide. Volatile material was transferred under vacuum and subsequent distillation of this material yielded the alkene 2,6,6-trihydroheptadecafluoro-3,7-dimethyloct-1-ene (nc) (30) (14.1 g, 86%); b.pt. 71-72° (44 mmHg); Analysis: Found: C, 26.9; H, 0.7; F, 72.7%. C₁₀F₁₇H₃ requires C, 26.91; H, 0.68; F, 72.42%; $\delta_{\rm H}$ (60 MHz) 2.6 (2H, dt, J 17 and 17 Hz, 6-H) 4.3 (1H, dd, J 20 and 20 Hz, 2-H); $\delta_{\rm F}$ (56.4 MHz) -76 (2F, m, 1-F) -80 (3F, m, 3-CF₃) -80 (6F, dt, J 7 and 7 Hz, 7,8-CF₃) -113 (2F, m, 5-F) -124 (2F, m, 4-F) -188 (2F, m, 3,7-F); m/z 427 (M⁺-F); $\nu_{\rm max}$ (C=C) 1750 cm⁻¹.

5. Preparation of $Z-(CF_3)_2$ CFCH₂ CF₂ CF₂ C(CF₃)=CHCF₃ (25)

A two-necked 50 ml round-bottomed flask was fitted with a condenser and dropping funnel. Under an atmosphere of dry nitrogen the alkene (30) (14.8 g, 33.2 mmol) was dropped into antimony pentafluoride (7.2 g, 33.2 mmol). Stirring of the mixture was continued for 2 h at room temperature. After this time water (15 ml) was added carefully to the sytem; two layers were observed and the lower fluorocarbon layer was washed with further quantities of water, dried (MgSO₄), and distilled to give 2,2,6,6trihydrohepta-decafluoro-3,7-dimethyloct-2-ene (nc) (25) (12.3 g, 83%); b.pt. 73^OC (47 mmHg); Analysis: Found: C, 26.9; H, 0.8; F, 71.7%. C₁₀F₁₇H₃ requires C, 26.9; H, 0.7; F, 72.4%; $\delta_{\rm H}$ (250 MHz; CDCl₃) 2.7 (2H, dt, J 17 and 17 Hz, 6-H) 6.3 (1H, q, J 8 Hz, 2-H); $\delta_{\rm F}$ (235 MHz; CDCl₃) -60.7 (3F, m, 3-CF₃) -61.6 (3F, qd, J 11 and 8 Hz, 1-F) -79.5 (6F, dt, J 7 and 7 Hz, 7,8-CF₃) -111.3 (2F, m, 4 or 5-F) -112.4 (2F, m, 4 or 5-F) -188.0 (1F, m, 7-F); m/z 427 (M*-F).

6. Treatment of saturated model compounds with base

i) <u>Tri-n-butylamine</u>

A mixture of (5a) (5 g, 0.011 mol) and NBu₃ (3.5 g, 0.024 mol) was heated at 110⁰ under reflux for 5 h, with stirring, in a 50 ml flask. Product material was transferred from the flask under vacuum and then washed with water (10 ml), to leave a pale yellow liquid (3.5 g). Analysis by glc showed this liquid to be essentially one component (> 95%); a small sample was isolated using preparative scale glc (column A, 130°C) and identified as 1-(2H-hexafluoro-2-propyl)-3-hydrodecafluoro-2,2-dimethylcyclopentene (nc) (12) (3.5 g, 74%), Analysis: Found: C, 28.0; H, 0.5; F, 71.6%; C10H2F16 requires C, 28.16; H, 0.47; F, 71.37%; ν_{max} 1695 cm⁻¹ (C=C); δ_{H} (neat, capill) -3.9 (1H, sept, J 7.2 Hz, 2-H), -5.5 (1H, ddd, J 4.2, 12.3 and 48.0 Hz, 3-H); $\delta_{\rm F}$ -630 (3F, m, 2-CF₃), -64.6 (3F, m, 2-CF₃), -68.6 (6F, d, m, 2-C(CF₃)₂), -1116 (1F, sept, J 16 Hz, 5-F), -112.0 (2F, AB, J 265 Hz, 4-F), -212.0 (1F, d, J 48.0 Hz, 3-F), δ_C -47.4 (1C, sept, J 33 Hz, 1-CH), -59.5 (1C, sept, J 36 Hz, 2-C), -86.6 (1C, ddd, J 13, 34 and 223 Hz, 3-C), -106.6 (1C, s, 1-C), -117.5 (1C, t, J 260 Hz, 4-C), -121.9 to -122.9 (1C, q, J 285 Hz, 2-(CF₃)₂ and 3-(CF₃)₂), -159.2 (1C, dt, J 27 and 309 Hz, 5-C); m/z 426 (M⁺, 5%) and 275 (M⁺ -151, 17%).

The reaction was repeated as described above except at the lower temperature of 100° C for 1 h. The product obtained consisted of three components (gas chromatography; column A, 100° C) which were isolated using preparative scale glc (column A, 130° C) and identified as (5a), (12) and 3H,6H,6H-heptadecafluoro-7-methyloct-2-ene (nc), (CF₃)₂C=CHCF₂CF₂CH₂CF(CF₃)₂ (31), Analysis: Found: C, 27.15; H, 0.40%; C₁₀H₃F₁₇ requires C, 26.60; H, 0.44%; ν_{max} 1655 cm⁻¹ (C=C); δ_{H} 6.8 (1H, t, J 14 Hz, 3-H), 2.9 (2H, t, J 17.3 Hz, 6-H); δ_{F} -61.0 (3F, br, 2-CF₃ (z)), -68.0 (3F, q, J 8 Hz, 2-CF₃ (E)), -79.0 (6F, dt, J 6.8 and 6.8 Hz, 7 and 8-CF₃), -111.3 (2F, t, J 14 Hz, 4-F), -113.3 (2F, br, 5-F), -185.6 (1F, br, 7-F); m/z 427 (M⁺ -18).

ii) <u>Reduction of (7b) by Tri-n-butylamine</u>

A mixture of (7b) (1.5 g, 4.7 mmol) and tri-n-butylamine (2.0 g, 14 mmol), sealed in a small glass ampoule, was heated to 130° C for 12 h. On opening the tube a colourless liquid was distilled under vacuum and was shown by glc (10% DIDP, 95° C) to consist of one major component, together with a small amount of the starting material (7b). A sample of the product was isolated using preparative scale glc (10% DIDP, 120° C) and identified as 2,3,3,5,5-pentahydroundecafluoro-2-methylhexane (nc) (14); Analysis: Found: C, 28.1; H, 1.6; F, 69.6%. C₇H₅F₁₁ requires C, 28.19; H, 1.68; F, 70.13%; $\delta_{\rm H}$ 3.0 (1H, sept, J 8 Hz, 2-H) 1.9 to 2.5 (4H, m, 3,5-H); $\delta_{\rm F}$ -62.5 (3F, tt, J 9 and 9 Hz, 6-F) -69.2 (6F, m, 2-CF₃) -98.5 (2F, m, 4-F); $\nu_{\rm max}$ (C=C) absent; m/z 298 (M⁺).

iii) <u>Fluoride Ion Induced Dehydrofluorination Reactions on Model</u> <u>Compounds</u>

A mixture containing sulpholane (4 ml) caesium fluoride (1.8 g, 11.8 mmol) and $(CF_3)_2 CF(CH_2 CF_2)_2 CH_2 CF_3$ (16) (4.2 g, 11.0 mmol) was sealed in a Carius tube under vacuum, and rocked at $150^{\circ}C$ for 6 h. On opening the tube, volatiles were transferred under vacuum and analysis by glc showed two components, one of which was the starting material (16). Separation was effected by fractional distillation to give (16) (0.5 g) and

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3,5,5,7,7-pentahydroterdecafluoro-2-methyloct-2-ene (nc) (17) (2.8 g, 70%); b.pt. 55-56°C (15 mmHg); Analysis: Found: C, 30.2; H, 1.3; F, 68.9%. C₉H₅F₁₃ requires C, 30.0; H, 1.4; F, 68.6%; $\delta_{\rm H}$ (60 MHz) 2.6 (4H, m, 5,7-H) 6.4 (1H, t, J 13 Hz, 3-H); $\delta_{\rm F}$ (56.4 MHz) -61 (3F, m, 2-CF₃(Z)) -65 (3F, m, J 9 Hz, 8-F) -69 (3F, q, J 7 Hz, 2-CF₃(E)) -93 (2F, m, 4-F) -94 (2F, m, 6-F); $\delta_{\rm C}$ (63 MHz) 40.9 (m, J 30 Hz, 7-CH₂) 43.7 (m, J 26 Hz, 5-CH₂) 116.2 (t, J 246 Hz, 4-CF₂) 117.3 (t, J = 239, 6-CF₂) 120.3 (q, J 275 Hz, 8-CF₃) 123.2 (q, J 278 Hz, 1- or 2-CF₃) 123.3 (q, J 277 Hz, 1- or 2-CF₃) 126.0 (m, 2-C(CF₃)₂) 137.7 (t, J 32 Hz, 3-CH); $\nu_{\rm max}$ (C=C) 1690 cm⁻¹; m/z 341 (M⁺-F).

The procedure was repeated using $(CF_3)_2 CFCH_2 CF_2 CH_2 CF_3$ (13) (4.2 g, 13.3 mmol), sulpholane (4 mls) and caesium fluoride (2.7 g, 17.8 mmol). Analysis by glc showed one major component which was subsequently identified as 3,5,5-trihydroundecafluoro-2-methylhex-2-ene (nc) (15) (3.1 g, 79%); Analysis: Found: C, 28.1; H, 0.9; F, 71.1%. $C_7H_3F_{11}$ requires C, 28.4; H, 1.0; F, 70.6%; δ_H (60 MHz) 2.7 (2H, m, 5-H) 6.5 (1H, t, J 13 Hz, 3-H); δ_F (56.4 MHz) -60 (3F, m, 2-CF₃(Z)) -63 (3F, m, J 9 Hz, 6-F) -67 (3F, q, J 8 Hz, 2-CF₃(E)) -92 (2F, m, 4-F); δ_C (62 MHz) 42.2 (m, J 30 Hz, 5-CH₂) 115.3 (t, J 245 Hz, 4-CF₂) 119.6 (q, J 274 Hz, 1- or 2-CF₃) 120.4 (q, J 274 Hz, 1- or 2-CF₃) 123.1 (q, J 277 Hz, 6-CF₃) 128.7 (sept, J 31 Hz, 2-C(CF₃)₂) 137.0 (t, J 32 Hz, 3-CH); ν_{max} (C=C) 1690 cm⁻¹; m/z 277 (M*-F).

7. <u>Preparation of the E- and Z-isomers of (CF₃)₂C=CH-CF=CHCF₃ (27, a and b)</u>

The dienes (27a) and (27b) were prepared from 2,4,4-trihydroundecafluoro-5-methylhex-1-ene which was synthesised by the following procedure.

A mixture of $(CF_3)_2CFCH_2CF_2CH_2CF_2I$ (3b) (15.2 g, 35.8 mmol) and tri-n-butylamine (7.0 g, 37.8 mmol) was stirred at room temperature for 3 h. After this time, volatile material was transferred under vacuum to a fresh vessel and distillation of the material afforded one product, 2,4,4trihydroundecafluoro-5-methylhex-1-ene (8.7 g, 82%) b.pt. 82-84°C; $\delta_{\rm H}$ (60 MHz) 2.9 (2H, m, 4-H) 4.8 (1H, m, 2-H); $\delta_{\rm F}$ (56.4 MHz) -78 (1F, m, J 23 Hz, 1-F(Z)) -80 (6F, dt, J 6 and 6 Hz, 5-CF₃) -82 (1F, m, 1-F(E)) -87 (2F, m, 3-F) -188 (1F, m, 5-F); m/z 296 (M⁺). The product was also identified by comparison of its infra-red spectrum with that of an authentic sample [15].

A mixture containing sulpholane (8 mls), caesium fluoride (3.8 g, 25.0 mmol), and the alkene (CF₃)₂CFCH₂CF₂CH=CF₂ (7.0 g, 23.6 mmol) was sealed in a glass ampoule, then rocked at 150°C for 4 h. On opening the tube, volatile material was transferred under vacuum. Analysis by glc showed two major components which were separated by fractional distillation and identified as Z-3,5-dihydrodecafluoro-2-methylhexa-2,4diene (nc) (27a) (4.2 g, 64%); b.pt. 109^oC; Found: m/z 275.9997. C₇H₂F₁₀ requires M⁺ 276.0001; δ_H (60 MHz) 6.7 (1H, d, J 24 Hz, 3-H) 5.6 (1H, dq, J 28 and 8 Hz, 5-H); $\delta_{\rm F}$ (56.4 MHz) -60 (3F, dq, J 30 and 8 Hz, 2-CF₃(Z)) -62 (3F, dd, J 18 and 8 Hz, 6-F) -68 (3F, q, J 8 Hz, 2-CF₃(E)) -102 (1F, m, 4-F); $\delta_{\rm C}$ (63 MHz) 109 (qd, J 38 and 10 Hz, 5-CH) 119 (q, J 272 Hz, 2-CF₃) 120 (q, J 274 Hz, 2-CF₃) 121 (d, J 144 Hz, 4-CF) 128 (m, 2-C(CF₃)₂) 129 (d, J 26 Hz, 3-CH); ν_{max} (C=C) 1680 cm⁻¹ (W) and 1650 cm⁻¹ (S); and E-3,5-dihydrodecafluoro-2-methylhexa-2,4-diene (nc) (27b) (2.2 g, 34%); b.pt. 86°C; Analysis: Found: C, 30.1; H, 0.9; F, 68.4%. C7H2F10 requires C, 30.4; H, 0.7; F, 68.8%; $\delta_{\rm H}$ (60 MHz) 5.8 (1H, qd, J 8 and 7 Hz, 5-H) 7.3 (1H, d, J 22 Hz, 3-H); $\delta_{\rm F}$ (56.4 MHz) -60 (3F, dd, J 11 and 8 Hz, 6-F) -62 (3F, dq, J 28 and 8 Hz, 2-CF₃(Z)) -68 (3F, q, J 8 Hz, 2-CF₃(E)) -98 (1F, m, 4-F); ν_{max} (C=C) 1680 cm⁻¹ (W) and 1640 cm⁻¹ (S); m/z 276 (M⁺).

8. <u>Reactions involving SbF5</u>

A mixture of (5a) (5 g, 10.7 mmol) and SbF₅ (3.3 g, 15 mmol) was stirred in a 50 ml glass flask under an atmosphere of dry N₂. The temperature of the flask was maintained at 120° C for 2 h after which time the product was transferred under vacuum onto dry NaF (10 g). The product remained in contact with NaF for 0.5 h and was then transferred under vacuum, washed with water (15 ml) and aq. NaHCO₃ solution (15 ml), and dried (MgSO₄) to yield a colourless liquid (3.9 g), identified as 3H,6H-hexadecafluoro-2,7-dimethyloct-2,6-diene,(nc) (CF₃)₂C=CHCF₂CF₂CH=C(CF₃)₂ (11) (3.9 g, 86%); Analysis: Found: C, 28.1; H, 0.1; F, 71.7%. C₁₀H₂F₁₆ requires C, 28.17; H, 0.47; F, 71.36%; ν_{max} 1680 cm⁻¹ (C=C); $\delta_{\rm H}$ 6.7 (2H, t, J 14 Hz, 3,6-H); $\delta_{\rm F}$ -60.8 (6F, m, 2,6-CF₃(z)), -68.2 (6F, q, J 8.8 Hz, 1,8-CF₃(E)), -111.0 (4F, t, J 15 Hz, 4,5-F); $\delta_{\rm C}$ 112.7 (tt, J 37 and 256 Hz, 4,5-C), 118.9 (q, J 277 Hz, 2,7-CF₃(z)), 120.1 (q, J 275 Hz, 1,8-CF₃(E)), 128.9 (t, J 26 Hz, 3,6-C), 132,5 (sept, J 34 Hz, 2,7-C); m/z 426 (M⁺).

A mixture of (6a) (6.8 g, 27 mmol) and SbF₅ (8.7 g, 40 mmol) was heated to 120° C for 3 h. Analysis of the product by glc (column A, 20° C) showed essentially a single component (> 95%) which was identified as 2H-nonafluoro-3-methylbut-2-ene, (CF₃)₂C=CHCF₃ (19) (5 g, 80%); $\delta_{\rm H}$ 6.7 (1H, q, J 8.0 Hzm 2-H); $\delta_{\rm F}$ -61.0 (3F, q, J 8.1 Hz, 3-CF₃(z)), -62.0 (3F, q, J 8.1 Hz, 4-CF₄(E)), -67.6 (3F, m, 1-CF₃); $\delta_{\rm C}$ 127.8 (sept, J 30 Hz, 3-C), 118.8, 118.0 and 117.0 (q, K 275 Hz, 1,3,4-CF₃), $\delta_{\rm C}$ for 3-C not observed.

9. Fluoride Ion Induced Cyclisation of the diene (11)

A mixture of (11) (0.4 g, 0.9 mmol), tetraglyme (0.5 ml) and caesium fluoride (0.2 g), sealed in an nmr tube, was heated to $100^{\circ}C$ for 2 h. When the ¹⁹F nmr spectrum was recorded the data indicated that conversion to the cyclopentene derivative (12) had occurred.

10. Examination of the Saturated Model Compounds

Response to curing agents, General Procedure - In each experiment a sample of the saturated model was sealed under vacuum in a small glass ampoule (equipped with a "Rotaflo" tap for use with vacuum-lines) with one or a combination of the curing agents. The mixture was then shaken and heated to the temperature indicated. Product was then transferred from the tube under vacuum and characterized. Solid residues remaining in the glass ampoule were extracted with CH_2Cl_2 and examined using ¹⁹F nmr spectroscopy.

i) <u>Response to MgO and Ca(OH)</u>₂

When a mixture of $(CF_3)_2 CFCH_2 CF_2 CH_2 CF_3$ (7b) (2 g, 0.063 mole) and MgO (2 g, 0.05 mole) was heated to $177^{O}C$ for 5 h a colourless liquid was obtained (1.9 g) which was examined using analytical gas chromatography (column A, $80^{O}C$) and found to be (> 95% purity) one component with a trace component. ¹⁹F nmr spectroscopy confirmed that the major component was (7b) and that the minor component contained the (CF₃)₂C=CH- group ($\delta_{\rm F}$ -61.0 and -68.4 ppm). When the experiment was repeated under identical conditions with Ca(OH)₂ a similar result was obtained. The residue did not contain fluorinated material.

Treatment of the models $[(CF_3)_2 CFCH_2 CF_2]_2$ (5a) and $[(CF_3)_2 CF(CH_2 CF_2)_2]_2$ (5b) under conditions identical to those described above also produced a similar result.

ii) <u>Response to Bisphenol AF</u>

When a mixture of $[(CF_3)_2 CFCH_2 CF_2]_2$ (2 g, 0.043 mole) and bisphenol AF (1 g, 0.03 mole) was heated to 200^OC for 3 hr a colourless liquid was obtained which was identified as pure (5a). When the residue was extracted with $CH_2 Cl_2$ and examined using ¹⁹F nmr spectroscopy only bisphenol AF was detected.

iii) <u>Response to Phosphonium Salts</u>

When a mixture of the model (5a) (1.5 g, 0.028 mole) and $Ph_4P^+Cl^-$ (1 g, 0.027 mole) was heated to $190^{\circ}C$ for 18 h a colourless liquid was obtained which was identified as pure (5a). The residue did not contain fluorinated material. When the experiment was repeated under identical conditions using $PhCH_2(Ph)_3P^+Cl^-$ there was also no reaction.

iv) Combinations of the Curing Agents

Table 1 summarizes the experimental conditions used. In each experiment which included the inorganic acid-acceptors, $Ca(OH)_2$ and MgO, a trace of unsaturation was detected using ¹⁹F nmr spectroscopy. In all other experiments no detectable chemical change occurred.

11. Dihydrofluorination of a Saturated Model Compound by D.B.U.

To a solution of the saturated model compound (6c) (0.5 g, 1.3 mmol) in dimethylacetamide (1.0 g), D.B.U. (0.2 g, 1.3 mmol) was added at room temperature. An immediate exothermic reaction was observed and analysis by ¹H and ¹⁹F nmr spectroscopy showed that elimination of hydrogen fluoride has occurred, exclusively at the 'tertiary' fluorine site, to yield the alkene 3,5,5,7,7-pentahydroterdecafluoro-2-methyloct-2-ene (17); $\delta_{\rm H}$ 6.4 (t, J 13 Hz, 3-H); $\delta_{\rm F}$ -61 (3F, m, 2-CF₃(Z)) -69 (3F, q J 7 Hz, 2-CF₃(E)).

12. Reactions of Unsaturated Model Compounds

i) A mixture of (19) (5.0 g, 21.5 mmol), PhOH (2.0 g, 21.5 mmol), K_2CO_3 (4.0 g, 28 mmol) and CH_3CN (10 ml), sealed in a glass tube was shaken at $20^{\circ}C$ for 12 h. The products were then added to water (150 ml), extracted with CH_2Cl_2 (10 ml), dried (MgSO₄), filtered and distilled to leave a colourless liquid (4.5 g) which was shown by glc (column A, $100^{\circ}C$) to consist of one component (> 95%) and identified as 2H,3H,2-phenoxynona-fluoro-3-methylbutane, (nc) (CF₃)₂CHCH(OPh)CF₃, (21) (85%), Analysis:

TABLE 1

Saturated	Curing Agents Conditions
Model	(1 g)
(5a)	bisphenol AF
	177 ⁰ C, 5 h Ca(OH) ₂ MgO
(5b)	bisphenol AF
	177 ⁰ C, 5 h Ca(OH) ₂ MgO
(5a)	bisphenol AF
	190 ⁰ C, 18 h PPh ₄ +Cl-
(5b)	bisphenol AF
	190 [°] C, 18 h PPh ₄ +Cl-
(5a)	bisphenol AF
	177 ⁰ C, 6 h PPh + Cl-
	MgO
	Ca(OH) ₂
(5a)	bisphenol AF
	177 ⁰ C, 2 h K ₂ CO ₃

Combinations of the Curing Agents

Found: C, 40.2; H, 1.85; F, 52.18%. $C_{11}H_7F_90$ requires C, 40.49; H, 2.15; F, 52.45%; δ_H 3.3 (1H, sept, J 8 Hz, 3-H), 4.9 (1H, q, J 7 Hz, 2-H), 7.0 (5H, m, ring-H); δ_F -62.4 and -67.6 (6F, m, 3 prochiral), -76.2 (3F, m, 1-F); m/z 326 (M*).

ii) A mixture of the alkene (17) (1.8 g, 5.0 mmol), phenol (0.5 g, 5.0 mmol), acetonitrile (2 mls) and potassium carbonate (0.6 g, 4.3 mmol) were stirred for 24 hours at ambient temperature. After this time the system was washed with water $(5 \times 5 \text{ ml})$, then dried $(MgSO_4)$. Analytical scale gas chromatography showed five major products. The component with the shortest retention time was isolated using preparative scale gas chromatography (30% SE30, column temp. 210°C) and identified as 2,3,5,5,7,7-hexahydro-3-phenoxyterdecafluoro-2-methyloctane (nc) (22); Found m/z 454.0572. $C_{15}H_{11}F_{13}0$ requires M⁺ 454.0602; δ_{H} (250 MHz; (CD₃)₂CO) 2.8 (4H, m, 5,7-H) 3.5 (1H, sept, J 8 Hz, 2-H) 4.9 (1H, dd, J 16 and 7 Hz, 3-H) 7.0-7.2 (5H, m, ring-H); $\delta_{\rm F}$ (235 MHz; $({\rm CD}_3)_2{\rm CO}$) -61.0 and -62.0 (6F, m, J 10z, 1- and 2-CF₃) -66.1 (3F, m, 8-F) -90.2 (2F, m, 6-F) -104.7 (2F, AB, J 264 Hz, 4-F). Separation of the other four components was not possible but they were identified as 3,5,5,7,7-pentahydro-3diphenoxyundecafluoro-2-methyloct-1-ene (24) (E and Z isomers); ν_{max} (C=C) 1695 cm⁻¹; m/z 415 (M⁺-OPh); and as 2,3,5,5,7,7-hexahydro-1,3diphenoxydodecafluoro-2-methyloctane (23) (two diastereoisomers); $\delta_{\rm H}$ (250 MHz; (CD₃)₂CO) 3.0-3.4 (5H, m, 3.5,7-H) 5.7 (1H, m, 3-H) 6.8-7.5 (10H, m, ring-H) $\delta_{\rm F}$ (235 MHz; (CD₃)₂CO) -56.2 (3F, m, 8-F) -61.7 (6F, dq, J 10 and 10 Hz, 1- and 2-CF₃) -94.2 (2F, m, 6-F) 104.6-107.1 (1F, m, 4-F); m/z 528 (M⁺).

iii) A mixture of the alkene (25) (1.9 g, 4.3 mmol) methanol (0.3 g, 9.3 mmol), acetonitrile (1 ml) and potassium carbonate (0.4 g, 2.9 mmol) was stirred vigorously at room temperature for 24 hours. The mixture was washed with water and analysis by gas glc (capillary column, 70° C to 170° C) showed two major products and no starting material. The products could not be separated, so were isolated together by preparative scale G.C. (30% SE30, column temp. 140° C) and identified as 2,6,6-trihydro-2-methoxyhexadecafluoro-3,7-dimethyloct-3-ene (nc) (26a) (E-isomer) and (26b) (Z-isomer); [Found: m/z 439.0370. C₁₁H₆F₁₆O requires 439.0179 (M⁺-F)]; $\delta_{\rm H}$ (250 MHz; CDCl₃) 3.0 (4H, m, 6-H) 3.5 (6H, s, 2-0CH₃) 4.6 (1H,

q, J 7 Hz, 2a-H) 4.9 (1H, q, J 7 Hz); $\delta_{\rm F}$ (235 MHz; CDCl₃) -55.6 (3F, m, J 6 Hz, 3a-CF₃) -58.2 (3F, dq, J 22 and 8 Hz, 3b-CF₃) -73.8 (3F, m, 1b-F) -74.9 (3F, m, 1a-F) -77.6 (12F, m, 7,8-CF₃) -92.1 (2F, AB, J 282 Hz, 5b-F) -96.4 and -98.4 (2F, m, 4-F) -96.8 (2F, m, 5a-F) -186.9 (2F, m, 7-F); $\nu_{\rm max}$ (C=C) 1678 cm⁻¹; m/z 439 (M⁺-F).

iv) The reaction was repeated using phenol (0.4 g, 4.3 mmol), (25) (2.0,4.5 mmol), K₂CO₃ (0.6 g, 4.5 mmol) and CH₃CN (1 ml). The mixture was stirred at room temperature for 4 hours and analysis by capillary G.C. $(90^{\circ}C \text{ to } 250^{\circ}C)$ showed two major components, together with a number of minor products. The major products could not be separated from each other, but they were isolated as a mixture using preparative scale G.C. (30% SE30, injector temp. 210° C, column temp. 210° C) and identified as 2,6,6-trihydro-2-phenoxyhexadecafluoro-3,7-dimethyloct-3-ene (nc) (26c) (E-isomer) and (26d) (Z-isomer); Found: m/z 520.0296. $C_{16}H_8F_{16}O$ requires 520.0320 (M⁺); $\delta_{\rm H}$ (250 MHz; CDCl₃) 2.9 (4H, m, 6-H) 5.5 (1H, q, J 6 Hz, 2d-H) 5.7 (1H, q, J 6 Hz, 2c-H) 7.0 (5H, m, ring-H for (26c)) 7.3 (5H, m, ring-H for (26d)); $\delta_{\rm F}$ (235 MHz; CDCl₃) -54.9 (3F, m, 3c-CF₃) -57.6 (3F, dq, J 21 and 7 Hz, 3d-CF₃) -73.8 (3F, m, 1d-F) -75.1 (3F, m, 1c-F) -77.8 (12F, m, 7,8-CF₃) -94.3 (2F, AB, J 287 Hz, 5d-F) -96.6 (1F, m, 4c-F) -96.8 $(1F, m, 4d-F) -97.4 (2F, m, 5c-F) -187.0 (2F, m, 7-F); \nu_{max}$ (C=C) 1678 cm⁻¹.

v) A mixture of E- and Z- dienes (27) (2.0 g, 7.2 mmol), methanol (0.3 g, 9.4 mmol), potassium carbonate (0.6 g, 4.3 mmol) and acetonitrile (1 ml) was stirred at room temperature for 24 hours. Capillary G.C. showed two major products and no starting material. The products could not be separated, so were isolated together using preparative scale G.C. (30% SE30, column temp. 140° C, injector temp. 150° C) and identified as 2,4,5-trihydro-4-methoxydecafluoro-5-methylhex-2-ene (nc) (28a) (E-isomer) and (28b) (Z-isomer); Analysis: Found: C, 31.5; H, 1.9; F, 61.1%. C₈H₆F₁₀O requires C, 31.2; H, 2.0; F, 61.7%; $\delta_{\rm H}$ (250 MHz; CDCl₃) 3.3 (2H, m, 5-H) 3.4 (3H, s, 4a) 3.5 (3H, s, 4b) 4.2 (1H, br.s, 4b) 4.6 (1H, dd, J 25 and 8 Hz, 4a) 5.5 (1H, dq, J 26 and 8 Hz, 2b) 5.8 (1H, m, 2a); $\delta_{\rm F}$ (235 MHz; CDCl₃) -56.1 (3F, m, 1a-F) -58.7 (3F, dd, J 17 and 8 Hz, 1b-F) -62.0 (3F, m, 5b- or 6b-CF₃) -65.3 (3F, m, 5b- or 6b-CF₃) -63.3 (3F, m, 5a- or 6a-CF₃) -64.6 (3F, m, 5a- or 6a-CF₃) -105.5 (1H, m, 3b) -106.9 (1H, m, 3a); ν_{max} (C=C) at 1715 and 1732 cm⁻¹; m/z 308 (M⁺).

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