Reactions Involving Fluoride Ion. Part 38.[1,2] New Fluorinated Dienes by Defluorination

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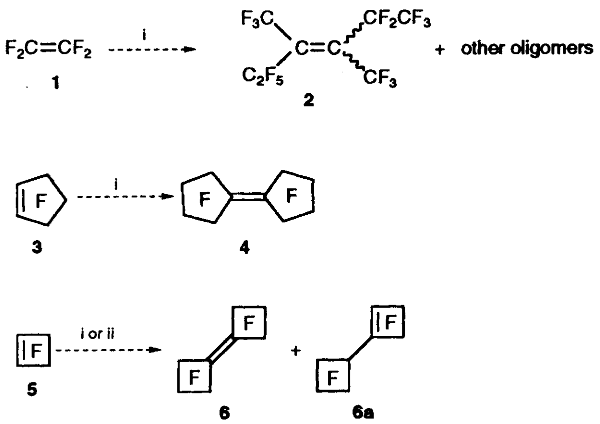
The oligomers **2**, **4** and **6**, **6a**, derived from tetrafluoroethene, octafluorocyclopentene, and hexafluorocyclobutene respectively, are converted into their corresponding dienes **7–9** by defluorination, using sodium amalgam. An alternative route using tetrakis(dimethylamino)ethene (TDAE) is also described and forms a fluoride salt of TDAE. The diene **7** shows a remarkably low extinction coefficient for UV absorption.

There is now a considerable literature[3,4] dealing with the formation of oligomers of various readily available fluorinated alkenes and cycloalkenes, initiated by fluoride ion. For example, systems **1**, **3** and **5**, may be converted into **2**,[5] **4**[6] and **6**, **6a**,[7] respectively (Scheme 1), and some of the unusual chemistry of these fluorinated alkenes has been described in earlier parts of this series. It is now clear that a further interesting development of this methodology arises, in that these useful and direct oligomerisation processes may be utilised for the synthesis of new fluorinated dienes, providing that methods are devised for selective defluorination of oligomers such as **2**, **4** and **6**, **6a**.



Scheme 1 *Reagents:* i, CsF, solvent; ii, pyridine, no solvent

Various methods of defluorination of organofluorine compounds have been described previously: Tatlow and co-workers have utilised the passage of fluorinated cyclohexanes and cyclohexenes *etc.* over hot metals, metal oxides and fluorides,[8] as well as electrochemical defluorination of perfluorocyclohexadienes, to give hexafluorobenzene.[9] Defluorinations over carbon have been reported[10] and, recently, controlled reduction of saturated fluorocarbons using sodium–benzophenone has been described.[11]

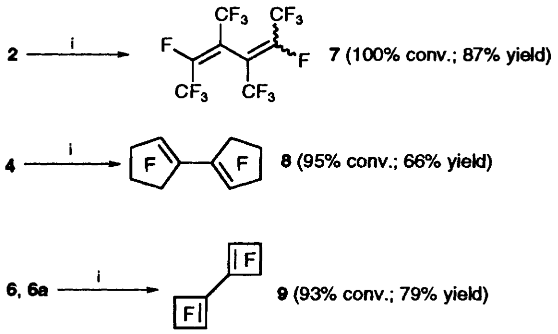
First, we considered electrochemical conversion of **2** into the diene **7** and cyclic voltammetry showed quasi-reversible reduction; the reduction potential of **2** as well as **4**, **6** and **6a** are shown in Table 1. These reduction potentials are all low, and this is consistent with the fact that **2**, **4** and **6** are all of the general structure $(R_F)_2C{=}C(R_F)_2$ (where R_F = perfluoro-alkyl or -cycloalkyl) and, clearly, these electron-withdrawing groups lower orbital energies, with the consonant effect on reduction potentials. Nevertheless, it is clear that perfluoroalkyl is significantly less effective than cyano (*cf.* tetracyanoethene +0.24 V).[12] The lower value of the cyclopentylidene system **4** than **2** is consistent with introduction of angle strain and the similar values of **6**, with greater angle strain, and **6a** reflect the fact that these isomers are obtained in approximately equal amounts at equilibrium in the presence of fluoride ion.[7] Internal isomers *e.g.* **6**, are normally more stable. Subsequently, we carried out a preparative-scale electrolysis of **2** and obtained evidence of formation of the diene **7**.

Table 1 Reduction potentials of some perfluorinated alkenes and dienes

Alkene	Reduction potential (V)*	Diene	Reduction potential (V)*
2	−1.62 ± 0.05	**7**	−2.35 ± 0.10
4	−1.06 ± 0.03	**8**	−2.03 ± 0.01
6	−1.10 ± 0.03	**9**	−2.25 ± 0.01
6a	−1.23 ± 0.03	**9**	−2.25 ± 0.01

* Cyclic voltammograms were carried out in acetonitrile using tetrabutylammonium tetrafluoroborate as the electrolyte, and reduction potentials were measured against a standard calomel electrode.

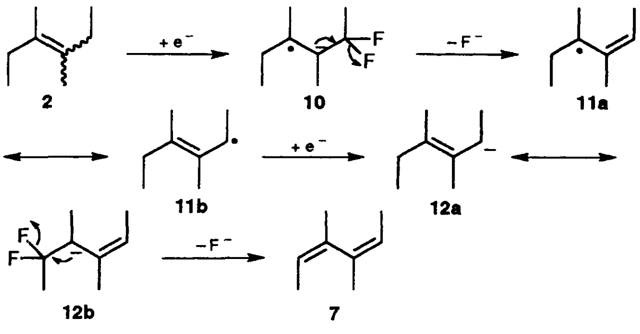
However, such preparative electrochemical procedures are difficult to scale up and we therefore attempted to mimic the process by using sodium amalgam. Remarkably, this procedure worked much more effectively than we could have expected and **2** gave complete conversion into the diene **7**, as the *sole* product, in 87% yield. Correspondingly, we also demonstrated that the cyclic derivatives **4** and **6**, **6a** gave the dienes **8** and **9** (Scheme 2).



Scheme 2 *Reagents and conditions:* i, Na, Hg (0.5% w/w), water cooling

The dienes **8** and **9** were occasionally obtained in low conversions (*ca.* 63%) and, at first, this posed problems of separation from the starting materials, but this isolation problem was solved very effectively by selective crystallisation. Thus, when the preparations of dienes **8** and **9** were carried out to comparatively low conversions, we then found that cooling these mixtures to *ca.* 0 °C led to crystallisation of each of **8** and **9** from the corresponding starting materials.

The mechanism of the defluorination process is most likely that indicated in Scheme 3, with initial single-electron transfer, giving a radical anion **10**, followed by loss of fluoride ion; further reduction of the allyl radical **11a, b** would lead to the anion **12a, b**, from which further loss of fluoride ion could occur, giving **7**.



All unmarked bonds are to fluorine

Scheme 3 Mechanism of defluorination

Sodium amalgam will react further with the dienes **7**–**9** if fresh sodium amalgam is added to the dienes; indeed this reaction can be quite vigorous and, for comparison, it should be borne in mind that biphenyl–sodium has been used for the efficient decomposition of highly fluorinated compounds to sodium fluoride, in a procedure for semi-micro determination of fluorine content.[13] Therefore, the surprisingly successful conversions of **2**, **4** and **6**, **6a** into dienes must reflect the highly selective reduction of these mono-enes over their corresponding dienes, up to the point of depletion of the amalgam. Furthermore, the basis of this selectivity is clear from Table 1, where in each case there is *ca.* 1 V difference in reduction potential between the alkenes **2**, **4** and **6**, **6a** and their corresponding dienes **7**–**9**, and this presents a very interesting illustration of the difference between the effect of a fluorine atom, F–C=C, and a perfluoroalkyl group, R_F–C=C, at a double bond. The presence of a perfluoroalkyl group lowers orbital energies by a significant amount. However, when a fluorine atom substituent is present, inductive electron withdrawal is offset by mutual repulsions between electron pairs. Therefore, only a small net effect accrues. In highly fluorinated systems, the overall effect of replacing a fluorine atom substituent by a hydrogen atom is small.[14] Therefore, the alkene and cycloalkene derivatives **2**, **4** and **6** each have only perfluoroalkyl or perfluorocycloalkyl groups at the double bond, whereas in the dienes, each has sites with a fluorine atom directly attached to the double bond. It is clearly a consequence of the vinylic fluorine sites that the reduction potentials of the dienes are higher.

We investigated a range of other compounds but the success of this technique, so far, seems to be restricted. Saturated compounds, *e.g.* perfluoro-cyclohexane, -decalin or -methyldecalin reacted only with extensive degradation and unsaturated systems such as **13**, **14** and **15** reacted in a similar fashion (Scheme 4).

However, the dihydrofuran derivative **16** reacted smoothly to give the perfluorotetramethylfuran **17**. Thus, we conclude that, for this defluorination procedure to operate successfully, we require a structure of the general type $R_FCF_2C(R_F)=C(R_F)CF_2R_F$, so that fluorine can be eliminated from difluoromethylene in the primary step, to leave an allyl radical (Scheme 1). Further reaction leads to dienes. The feature that characterises the successful reaction is that, in these cases, the dienes have vinylic fluorines and such sites are absent in the precursor monoenes and this leads to a higher reduction potential of the dienes (see earlier). Thus, it is possible to isolate them. We have investigated reactions of **2** with amalgams derived from other metals, including potassium (lower yields), magnesium and aluminium (no reaction) as well as direct reaction of **2** with some metals, including zinc and aluminium foil (no reaction), while direct reaction with alkali metals presents too great a hazard.

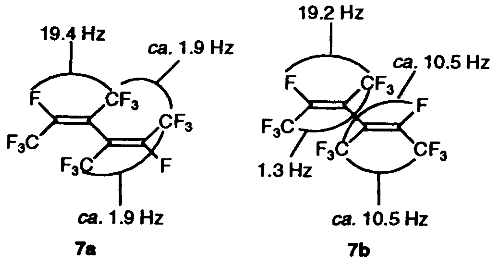
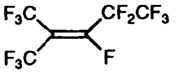


Fig. 1



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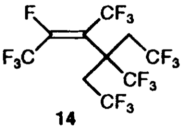

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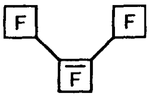

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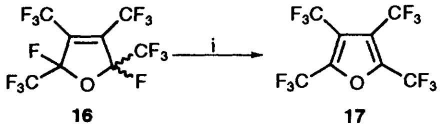
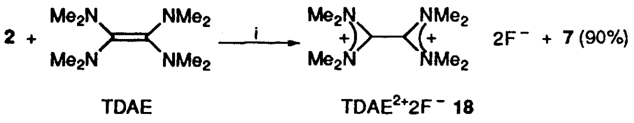


Scheme 4 *Reagents and conditions:* i, Na, Hg (0.5 w/w %), water cooling

Remarkably, tetrakis(dimethylamino)ethene (TDAE) has a reduction potential that has been variously described as being equivalent to Zn[15] or to alkali-metals[16] and this reagent has been successfully used for dechlorination.[17] We now find that TDAE is extremely useful for promoting the defluorinations described above; mixing **2** with TDAE either in a solvent or as neat liquids led to smooth defluorination, giving **7** in *ca.* 90% yield, together with a difluoride salt of TDAE.



Scheme 5 *Reagents and conditions:* i, CH_2Cl_2, 0 °C to room temp.

The other halide salts of TDAE have been reported previously but we are unaware of any report of a corresponding fluoride. This salt is itself of interest in that the fluoride **18** is soluble in some organic media, *e.g.* acetonitrile, and this has interesting consequences for carbanion formation, *etc.* with the dienes **8** and **9** and these reactions will be described later.[18]

The dienes **7**–**9** were characterised by elemental analysis and spectroscopy and the structures of **8** and **9** followed simply from the data (see Experimental section). Analysis of the ^{19}F NMR data for **7** indicates two isomers, **7a** and **7b**, in a ratio of 37:10, and identification of each of these isomers followed from analysis of J_{CF_3,CF_3} and $J_{CF_3,F}$ values, Fig. 1.

It is known that ^5J(*cis*-CF_3, CF_3) values are greater than 10 Hz and ^5J(*trans*-CF_3, CF_3) values are typically less than 2 Hz; also, ^4J(*trans*-CF_3, F) values are less than for ^4J(*cis*-CF_3, F).[19] Interestingly, the *Z,Z*-isomer **7a** displays a pseudo-septet, generated by the $(A_3)_2(X_3)_2$ system, with a *J* value of 1.9 Hz, indicative of a *trans-trans* diene (Fig. 1).

Table 2 UV data for conjugated perfluorodienes

Diene	$\pi \longrightarrow \pi^*$ Transition	
	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}
7	234	272
8	278	10 900
9	277	18 800

The UV data for **7**–**9** are of interest (see Table 2), showing a very low value of the extinction coefficient for **7**, and this reflects the fact that steric interactions between trifluoromethyl groups force the double bonds out of conjugation.

This effect has been most dramatically demonstrated previously by the fact that polyhexafluorobut-2-yne, $[C(CF_3)=C(CF_3)]_n$, an often overlooked but easily accessible polyacetylene,[20] is an off-white solid. The extinction coefficients increase substantially from **7** to **9** and this, no doubt, stems from the fact that decreasing bond angles reduces the extent of interaction between cycloalkyl groups.

Experimental

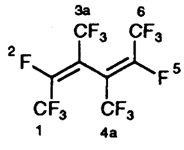
^{1}H NMR spectra were recorded on a Bruker AC250 spectrometer operating at 250.13 MHz or a Varian VXR400S spectrometer operating at 399.95 MHz. ^{19}F NMR spectra were recorded on the Bruker AC250 spectrometer operating at 235.34 MHz or on the Varian VXR400S spectrometer operating at 376.29 MHz. All spectra were recorded with tetramethylsilane and fluorotrichloromethane as internal references. *J* Values are given in Hz. GLC Mass spectra were recorded on a VG 7070E spectrometer linked to a Hewlett Packard 5790A gas chromatograph fitted with a 25 m cross-linked methyl silicone capillary column. All mass spectra were generated by electron impact.

CAUTION: *The unsaturated fluorocarbons described in this paper should be assumed to be toxic.*

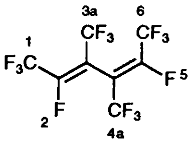
Sodium Amalgam Reductions: General Procedure.—Sodium amalgam was prepared using a Schlenk tube by the addition of small milligram lumps of sodium to mercury under an atmosphere of dry, oxygen-free, nitrogen until the amalgam concentration reached *ca.* 0.5% (w/w). After the amalgam had cooled, the fluorocarbon was carefully added to it and allowed to lie on its surface. A rubber 'Suba-seal' type stopper was used to seal the top of the vessel as a safety precaution (in order to act as a release point in the event of an explosion).

After disconnection from the nitrogen supply, the reaction mixture was vigorously shaken whilst the vessel was kept under a flow of cold water to prevent it from overheating. During the reaction, the consistency of the amalgam became very viscous making agitation difficult. The reaction was judged to have finished when a dark grey solid (sodium fluoride and mercury dust) was produced and free-flowing elemental mercury reformed in the bottom of the Schlenk tube. Volatile organic components were removed by transfer *in vacuo* to a cold trap.

Perfluoro-3,4-*dimethylhex*-3-*ene* **2**. The fluoroalkene **2** (20.0 g, 50.0 mmol) was reduced by vigorously shaking with sodium amalgam [Na 2.9 g, 126 mmol; Hg 500 g; 0.58% (w/w)]. The isolated volatile components (15.8 g) were found to be an inseparable mixture (37:10 by ^{19}F NMR spectroscopy) of the isomeric dienes (*Z*,*Z*)-*perfluoro*-3,4-*dimethylhexa*-2,4-*diene* **7a** and (*E*,*Z*)-*perfluoro*-3,4-*dimethylhexa*-2,4-*diene* **7b** (68%, 19% yields). For the mixture: b.p. 73–74 °C (Found: C, 26.3; F, 72.8. C_8F_{14} requires C, 26.5; F, 73.5%); ν_{max}/cm^{-1} 1680w (C=C), 1360s (C–F), 1290s–1190s (C–F); for **7a**: δ_F(376 MHz; CDCl$_3$) −60.46 (6 F, d, $J_{3a,2}$ 19.4 of pseudo-sept, $J_{3a,1+4a}$ 1.9, 3a-CF$_3$ and 4a-CF$_3$), −68.24 (6 F, d, $J_{1,2}$ 7.9 of pseudo-sept, $J_{1,3a+4a}$ 1.9, 1-CF$_3$ and 6-CF$_3$) and −100.94 (2 F, q, $J_{2,3a}$ 19.4 of q, $J_{2,1}$ 7.7, 2-CF and 5-CF); *m*/*z* 362 (M$^+$, 5%) and 343 (100); for **7b**: δ_F(376 MHz; CDCl$_3$) −56.56 (3 F, d, $J_{3a,2}$ 10.5 of q, $J_{3a,1}$ 10.5 of q, $J_{3a,4a}$ 2.3, 3a-CF$_3$), −60.27 (3 F, d, $J_{4a,5}$ 19.2 of q, $J_{4a,6}$ 2.6 of q, $J_{4a,3a}$ 1.3, 4a-CF$_3$), −67.94 (3 F, q, $J_{1,3a}$ 10.3 of d, $J_{1,2}$ 7.0, 1-CF$_3$), −68.80 (3 F, d, $J_{6,5}$ 7.1 of q, $J_{6,4a}$ 2.4 of q, $J_{6,3a}$ 1.2, 6-CF$_3$), −97.45 (1 F, q, $J_{2,3a}$ 10.6 of q, $J_{2,1}$ 7.0, 2-CF) and −102.22 (1 F, q, $J_{5,4a}$ 19.2 of q, $J_{5,6}$ 6.8, 5-CF); *m*/*z* 362 (M$^+$, 2%) and 343 (47).

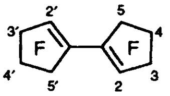


7a



7b

Perfluorobicyclopentylidene **4**.—The fluoroalkene **4** (6.0 g, 14.1 mmol) was reduced by vigorous shaking with sodium amalgam [Na 1.0 g, 43.5 mmol; Hg 180 g; 0.55% (w/w)]. The isolated volatile components were purified by crystallisation at 0 °C in a refrigerator to give *perfluoro*-1,1′-*bicyclopent*-1-*enyl* **8** (3.6 g, 66%), b.p. 130 °C (Found: C, 31.0; F, 68.5. $C_{10}F_{14}$ requires C, 31.1; F, 68.9%); ν_{max}/cm^{-1} 1680m (C=C) and 1550s–1180s (C-F); δ_F(235 MHz; CDCl$_3$) −107.52 (4 F, m, 5-CF$_2$ and 5′-CF$_2$), −107.81 (2 F, m, 2-CF and 2′-CF), −119.63 (4 F, m, 3-CF$_2$ and 3′-CF$_2$) and −130.34 (4 F, m, 4-CF$_2$ and 4′-CF$_2$); *m*/*z* 386 (M$^+$, 23%) and 367 (36).



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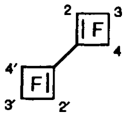
Perfluorobicyclobutylidene **6** *and Perfluoro*-1-*cyclobutylcyclobutene* **6a**.—A mixture (*ca.* 1:1) of the isomeric fluoroalkenes **6** and **6a** (6.0 g, 18.5 mmol of the mixture) was reduced by vigorously shaking with sodium amalgam [Na 1.1 g, 47.8 mmol; Hg 240 g; 0.46% (w/w)]. The isolated volatile components were purified by crystallisation at 0 °C in a refrigerator to give *perfluoro*-1,1′-*bicyclobut*-1-*enyl* **9** (4.2 g, 79%), b.p. 90–95 °C (Found: C, 33.9; F, 66.2. C_8F_{10} requires C, 33.6; F, 66.4%); ν_{max}/cm^{-1} 1680m (C=C), 1390s–1180s (C–F); δ_F(235 MHz; CDCl$_3$) −95.68 (2 F, m, 2-CF and 2′-CF), −115.68 (4 F, m, 4-CF$_2$ and 4′-CF$_2$) and −117.21 (4 F, m, 3-CF$_2$ and 3′-CF$_2$); *m*/*z* 286 (M$^+$, 17%) and 267 (32).



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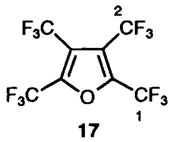
Perfluorotetramethyl-2,5-*dihydrofuran* **16**.—The furan derivative **16** (1.55 g, 4.56 mmol) was reduced by vigorous shaking with sodium amalgam [Na 0.30 g, 13.1 mmol; Hg 59.76 g; 0.50% (w/w)]. A clear, colourless liquid was isolated under reduced pressure and shown to contain one component by GLC. This was subsequently identified as perfluorotetramethylfuran **17** (1.05 g, 3.09 mmol, 75%), b.p. 101–103 °C (lit.,[21] 104–105 °C); ν_{max}/cm^{-1} 1420w (C=C), 1300s–1200s (C-F); δ_F(235 MHz; CDCl$_3$) −57.62 (6 F, m, CF$_3$) and −62.40 (6 F, m, CF$_3$); *m*/*z* 340 (M$^+$, 45%) and 321 (100).



17

*Reduction of Perfluoro-*3,4-*dimethylhex-*3-*ene* **2** *with TDAE and a Solvent.*—A solution of TDAE (5.00 g, 5.80 cm^3, 2.50 mmol) in CH_2Cl_2 (5 cm^3), was added dropwise, under nitrogen, to a mixture of **2** (11.00 g, 27.5 mmol) and CH_2Cl_2 (10 cm^3) at 0 °C, with the development of a deep red colour and a fine precipitate. Cooling was discontinued after 30 min and the mixture was stirred at room temperature for a further 30 min. A lower layer was then isolated by syringe and found to contain one component by GLC, identified as (*Z*,*Z*)- and (*E*,*Z*)-perfluoro-3,4-dimethylhexa-2,4-diene **7a**, **7b** (8.95 g, 90%) by comparison of the ^{19}F NMR spectrum with that of an authentic sample (see earlier).

The precipitate was then filtered off, under nitrogen, and washed with CH_2Cl_2 (3×5 cm^3) to afford a white solid which was identified as octamethyloxamidium difluoride **18** (4.50 g, 18.9 mmol, 68.6% based on **2**), δ_F[250 MHz; $(CD_3)_2SO$] -110.0 (2 F, s); δ_H[250 MHz; $(CD_3)_2SO$] 3.5 (1 H, s, CH_3) and 3.2 (1 H, s, CH_3); *m*/*z* 200 ($M^+ - 38$). This solid was extremely hygroscopic, causing further accurate analysis to be difficult.

*Reduction of Perfluoro-*3,4-*dimethylhex-*3-*ene* **2** *with TDAE.*—TDAE (5.00 g, 5.80 cm^3, 2.50 mmol) was added dropwise, under nitrogen, at 0 °C to the alkene **2** (11.00 g, 27.5 mmol). A dark red colour immediately developed, with the appearance of solid material. After *ca.* 15 min stirring stopped, owing to the formation of a red solid. This was allowed to stand at room temperature for 30 min, after which it was heated, *in vacuo*, at 80 °C for 30 min (in order to decompose it), whilst volatile material was collected in a cold finger. Volatiles were purified by distillation and found to contain one component by GLC, which was identified as (*Z*,*Z*)-and (*Z*,*E*)-perfluoro-3,4-dimethylhexa-2,4-diene **7a**, **7b** (9.20 g, 92%) by comparison of its ^{19}F NMR spectrum with that of an authentic sample (see earlier).

Acknowledgements

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