

Reactions involving Fluoride Ion. Part 23.¹ Thermolytic Defluorination of Perfluoroalkenes in the Synthesis of Fluorinated Dienes and Cyclobutenes

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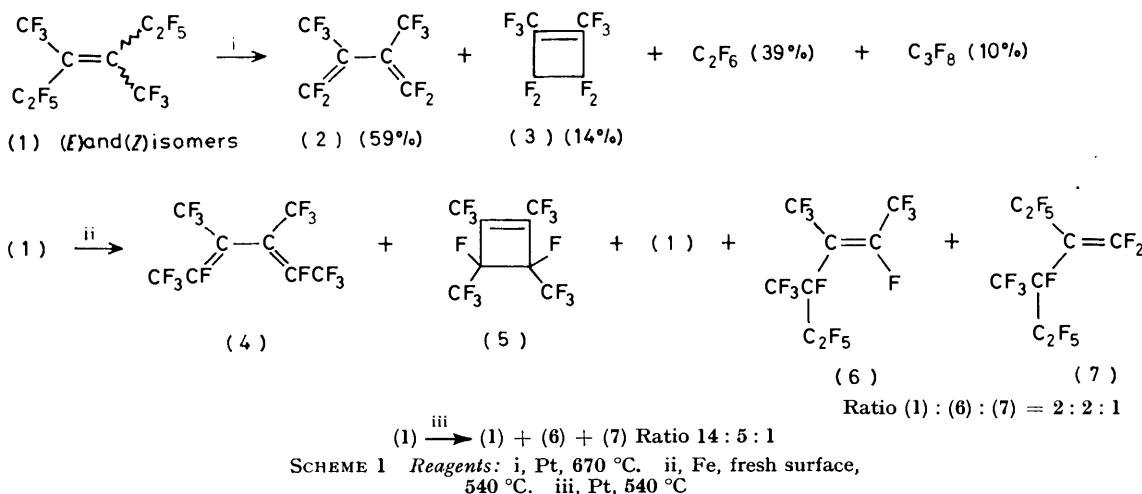
Passage of perfluoro-3,4-dimethylhex-3-ene over iron or platinum at elevated temperatures leads to defluorination and fragmentation, giving fluorinated dienes, *e.g.* perfluoro-2,3-dimethylbutadiene (over Pt) and perfluoro-3,4-dimethylhexa-2,4-diene (over Fe), together with other products. Similar reactions occur with other fluorinated alkenes and the variation between fragmentation and defluorination is rationalised on the basis of the metal used, *etc.* The fluoride induced reaction between perfluoropropene and perfluorobut-2-ene gives perfluoro-2,3-dimethylpent-2-ene.

PERFLUOROALKYLAROMATIC compounds and dimers, or oligomers, of perfluorinated alkenes are now synthetically accessible by various fluoride-ion induced reactions.²⁻⁵ In this paper we describe further development of some of these compounds in synthesis by the introduction of unsaturated sites *via* thermal elimination processes. There are many reports in the literature of thermally induced elimination reactions involving fluorocarbon compounds,⁶⁻⁸ the most widely explored specific process being the metal-induced defluorination of cyclic fluorocarbons to give aromatic compounds.⁹ A more limited range of synthetically useful thermal fragmentations involving the elimination of, *e.g.*, difluoromethylene or tetrafluoroethylene units from a molecule have been reported.¹⁰⁻¹² So far, however, these processes have not seemed valuable for the synthesis of fluorinated dienes.

The alkene derivative (1) may be obtained by a fluoride-ion induced oligomerisation of tetrafluoroethylene^{3,4} or a similar dimerisation of perfluorobut-2-ene.¹³ We have now established that a smooth fragmentation occurs when (1) is passed, in a stream of nitrogen, through a platinum-lined tube at 530–700 °C, giving the diene (2),¹⁴ together with lesser amounts of the cyclobutene derivative (3) (Scheme 1).

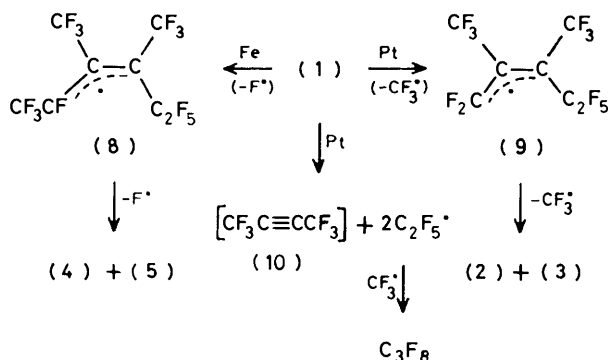
An interesting process occurred when (1) was passed over a hot iron surface. The product mixture obtained depended critically on the state of the surface, temperature, and contact time. However, when fresh iron filings were used at 540 °C, a *ca.* 50% conversion into the diene (4) and the cyclobutene (5) was obtained, but, more significantly, the C₈F₁₈ recovered in this reaction consisted of (1), together with the isomers (6) and (7) in the ratio *ca.* 2 : 2 : 1 (Scheme 1). Some isomerization of (1) also occurred over platinum at 540 °C, *i.e.* a temperature at which fragmentation was not significant. The production of (6) and (7) enabled us to compare, directly, the relative reactivities of the isomeric perfluorinated alkenes (1), (6), and (7) towards nucleophiles.¹⁵ Using an 'aged' iron surface, *i.e.* one which had been used for other defluorinations, formation of the compounds (4) and (5) was the main process.

Some isomerization of (1) to isomer (6) was observed over caesium fluoride, but, more interesting, significant amounts of the products of defluorination, (4) and (5), were obtained. We¹⁶ and others^{17,18} have noted previously that caesium fluoride may effect defluorination and the formation of (4) and (5) is a convincing example of the process. It is not obvious why caesium



fluoride should be effective in promoting defluorination, but a possible explanation could be the formation of caesium polyfluorides.

A simple mechanism may be advanced to account for both the fragmentation and defluorination processes, which involves initial formation of the intermediate allylic radicals (8) and (9). Preferential loss of a fluorine atom over iron giving the radical (8) is understandable, as well as the fact that higher temperatures are required for the fragmentation over platinum to give the radical (9), by the loss of a trifluoromethyl radical. Indeed, if compound (1) is passed over iron or nickel at these higher temperatures, then fragmentation as well as defluorination occurs. No doubt the stabilising influence of the perfluoroalkyl groups attached directly to the allylic system in the radicals (8) and (9) assists in their formation, as well as the relief of some steric strain which must also accompany this process. The small amount of perfluoropropane, formed over platinum, may be explained by some fragmentation involving the loss of pentafluoroethyl radicals and then recombination of pentafluoroethyl with trifluoromethyl radicals (see Scheme 2), although no hexafluorobut-2-yne was observed in the product.

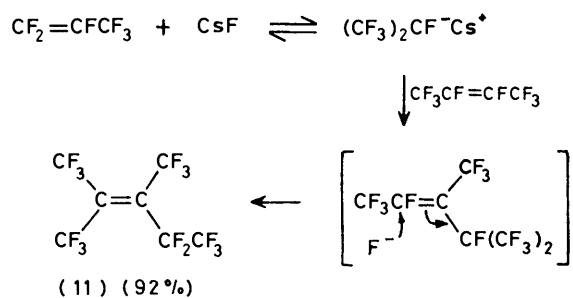


SCHEME 2

The mechanism of the isomerization of hexene (1) into (6) and (7), which accompanies defluorination and fragmentation, is of interest. A trivial S_N2' mechanism involving adventitious traces of fluoride in the tubes, could account for the isomerization, since vapour-phase isomerizations of other perfluoroalkenes over caesium fluoride have been observed.¹⁹ Nevertheless, this seems unlikely because the isomer (7), with a terminal difluoromethylene group, is obtained over platinum or iron, but not over caesium fluoride itself. It seems more likely, therefore, that the isomerizations over metals involve intramolecular 1,3-shifts of fluorine.

During a general study of the reactions of fluorinated alkenes with alkali-metal fluorides, we have been able to synthesise perfluoro-2,3-dimethylpent-2-ene (11) in high yield, by reaction of hexafluoropropene with perfluorobut-2-ene, in the presence of caesium fluoride (Scheme 3).

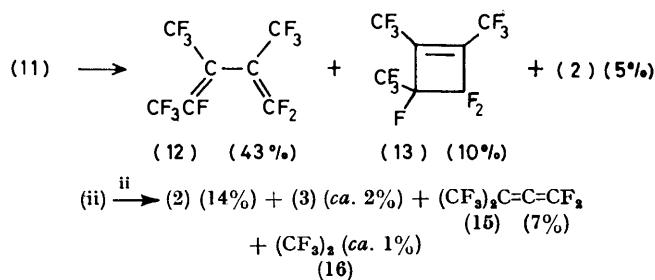
Pyrolysis of (11) over iron required higher temperatures than for (1) to effect the reaction and, over iron



SCHEME 3

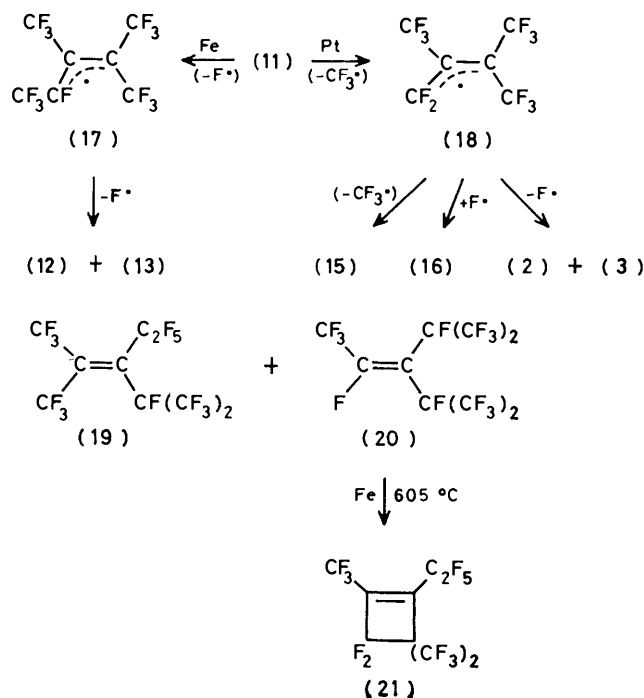
at 675 °C, a mixture of the diene (12) and the corresponding cyclobutene (13) was observed. Over platinum, however, only low yields of the products (2), (3), (15), and (16) were recovered (Scheme 4).

Again, the products can be explained by intermediate



SCHEME 4 Reagents: i, Fe, 675 °C. ii, Pt, 715 °C

allylic radicals, in this case (17) and (18) (Scheme 5). However, whereas the radical (9) may lose a trifluoromethyl radical, in a simple way, the comparable process for the radical (18) involves the much more difficult loss of



SCHEME 5

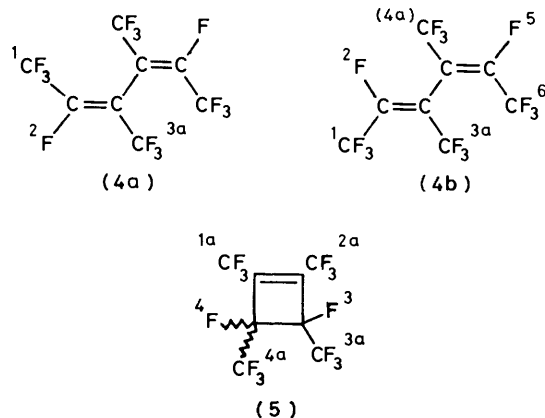
a fluorine atom to give (2) or (3) which, in this case, are only obtained in low yield. Obviously, other fragmentation processes compete in this case and account for the greater range of products and low yields. Defluorination of a mixture of the perfluoropropene trimers⁵ (19) and (20) (ratio 3 : 1) at 605 °C gave the cyclobutene derivative (21) as the main product.

EXPERIMENTAL

¹⁹F N.m.r. spectra were measured at 40 °C, using a Varian A56/60D spectrometer, with trichlorofluoromethane as external reference. Upfield shifts are quoted as positive and all values are in p.p.m. Gas chromatography was carried out using columns packed with 30% silicone gum-rubber SE-30 on Chromosorb P (Column O) and 20% diisodecyl phthalate on Chromosorb P (Column A). Unless otherwise stated, percentage yields and conversions were determined by g.l.c. analysis (using a gas-density balance detector) of the crude product mixture. Distillations were carried out using Fischer-Spaltrohr MMS 200 and HMS 500 systems.

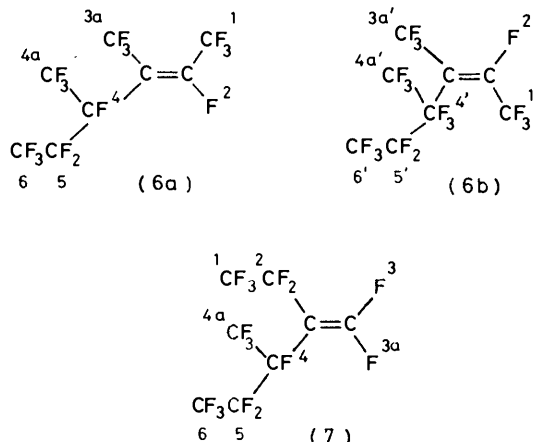
Pyrolysis Reactions: General Procedure.—All of the reactions herein involved passing the reactant, in a stream of nitrogen, over packing material contained in a hot silica tube. The products were collected in a trap cooled with liquid air or solid carbon dioxide. The tube was heated by a cylindrical furnace (*ca.* 30 in) and temperatures were measured using a thermocouple situated outside the silica tube. Nitrogen was bubbled through the reactant, which was warmed in the case of less volatile compounds, and a flow rate of *ca.* 50 ml min⁻¹ gave a contact time of *ca.* 25 s. Silica tubes packed with quartz wool, caesium fluoride, or coarse iron filings, and a silicon tube fitted with a platinum-foil liner and packed with platinum foil were employed. Iron filings were renewed regularly.

(a) *Perfluoro-3,4-dimethylhex-3-ene* (1). (i) Over iron



(with P. D. Philpot). Compound (1) (30 g) was passed over iron filings at 540 °C and gave a product mixture containing C₈F₁₄ isomers (*ca.* 50 wt. %) as well as C₈F₁₆ isomers (m.s.-g.l.c.). A combination of distillation and preparative-scale g.l.c. (Column O, 80 °C) gave only partial resolution of the C₈F₁₄ isomers, but ¹⁹F n.m.r. indicated a mixture of perfluoro-*trans,trans*- and -*cis,trans*-3,4-dimethylhexa-2,4-dienes, (4a) and (4b) respectively, and perfluoro-1,2,3,4-tetramethylcyclobutene (5), in the ratios 3 : 0.8 : 1 respectively. For (4a), δ_F 64.5 (3 F,

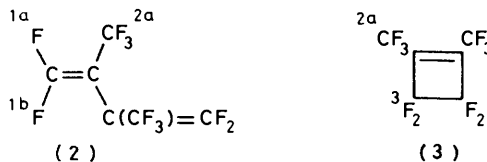
3a-F, J_{2,3a} 18 Hz), 73.5 (3 F, 1-F, J_{1,2} 4 Hz), and 106.4 (1 F, 2-F, J_{2,3a} 18 Hz); for (4b), 60.9 (3 F, 3a-F), 64.6 (3 F, 4a-F, J_{4a,5} 18 Hz), 72.4 (3 F, 1-F, J_{1,2} 6, J_{1,3a} 10 Hz), 73.3 (3 F, 6-F), 103.3 (1 F, 2-F), and 106.5 (1 F, 5-F); for (5), 67.2 (6 F, 1a-, 2a-F), 78.8 (6 F, 4a-, 3a-F, J_{3a,4a} 7 Hz), and 172.2 (2 F, 3-, 4-F). In a similar manner, partial separation of the C₈F₁₆ isomer mixture could be achieved giving (1), (6a), (6b), and (7) (ratio 2 : 2 : 1 by ¹⁹F n.m.r. spectroscopy),



sufficient to enable assignment of the n.m.r. spectra. For (6a) and (6b) (ratio 4 : 1), δ_F 60.0 (3 F, 3a-, 3a'-F), 66.0 (J_{1',4'} 48 Hz), 67.4 (3 F, 1-, 1'-F, J_{1,3a} 15 Hz), 75.6 (3 F, 4a-, 4a'-F), 82.7 (3 F, 6-, 6'-F, J_{4,6} 16 Hz), 87.8 (J_{2',3a'} 20 Hz) 90.0 (1 F, 2-, 2'-F), 119.7 (2 F, 5-, 5'-F), and 183.1 (1 F, 4-, 4'-F); for (7), 62.3 (1 F, 3a-F), 68.1 (1 F, 3-F), 75.6 (3 F, 4a-F), 83.0 (3 F, 6-F), 88.3 (3 F, 1-F), 109.1 (2 F, 2-F), 119.7 (2 F, 5-F), and 183.0 (1 F, 4-F).

(ii) Over caesium fluoride. Passage of compound (1) over caesium fluoride at 540 °C gave a product mixture slightly different to that described above, containing the C₈F₁₆ isomers (1) and (6) (*ca.* 60 wt. %) and the C₈F₁₄ isomers (4) and (5) (30%), but the isomer (7) was not detected.

(iii) Over platinum. Passage of compound (1) (100 g) over platinum at 670 °C gave, after fractionation on a vacuum line, a volatile fraction (13.5 g), consisting of mainly perfluoroethane (39% yield) and a liquid mixture (55.5 g), which consisted of perfluoropropane (10%), compound (3) (16%), and compound (2) (70%) [yields based on the amount of compound (1) used are: perfluoropropane (12%), (3) (14%), and (2) (59%)]. The liquid mixture was fractionally distilled giving perfluoropropane (-39 °C); compound (3) (36 °C),¹⁴ and compound (2)

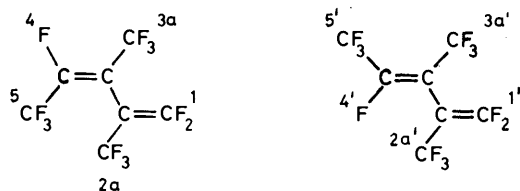


(49–51 °C)²⁰ (28.7 g). Perfluoro-ethane and -propane were identified by mass-spectrometry and by comparison of i.r. spectra. Compounds (2) and (3) were also identified by comparison of spectra^{14,20} with those of authentic samples. For (2), δ_F 63.8 (3 F, 2a-F), 71.4 (1 F, 1a-F, J_{1a,2a} 20 Hz), and 73.1 (1 F, 1b-F); for (3), 66.0 (3 F, 2a-F), 117.5 (2 F, 3-F).

Two other C_9F_{10} isomers and other $C_{10}F_{16}$ isomers (ca. 3%) were contained in the distillation residue, as indicated by m.s.-g.l.c., but these compounds were insufficient for separation and characterisation.

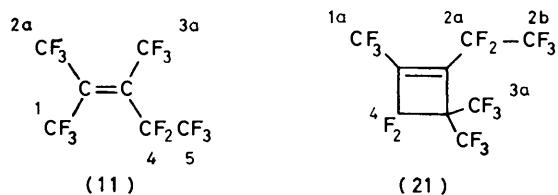
Passage of (1) (1.8 g) over platinum at 540 °C gave a mixture (1.8 g) containing (1) (70%), (6) (25%), and (7) (5%), identified by m.s.-g.l.c. and comparison of ^{19}F n.m.r. spectra.

(b) *Perfluoro-2,3-dimethylpent-2-ene* (11). (i) Over iron. Passage of compound (11) (1.7 g) over iron at 675 °C gave a liquid product (0.85 g) containing compound (2) (5%) and the isomers of C_7F_{12} , (12) and (13) (95%, 53% yield). A mixture of the isomers (12) and (13) (ratio 4.3:1 by ^{19}F n.m.r. spectroscopy) was obtained by g.l.c. (Column O, 40 °C) but these could not be further separated; the mixture of perfluoro-*cis*- and -*trans*-2,3-dimethylpenta-1,3-diene (12) and 1,2,3-trimethylcyclobutene (13) gave (Found: F, 72.8%; M^+ , 312. C_7F_{12} requires F, 73.1%; M , 312);



for (12) δ_F 60.8, 62.5, 64.5 (6 F, 3a—3a', 2a-, 2a'-F, $J_{3a,4}$ 21 Hz), 70.8, 71.8, 73.1 (5 F, 1-, 1'-, 5-, 5'-F), 102.4, 105.0 (1 F, 4-, 4'-F, q , J 21 Hz of q , $J_{4,5}$ 6 Hz); for (13) δ_F 66.1 (6 F, 1a-, 2a-F), 78.1 (3 F, 3a-F), 115.3 (2 F, 4-F), and 173.8 (1 F, 3 F).

(ii) Over platinum. Passage of compound (11) (0.7 g) over platinum at 715 °C gave a liquid product (0.35 g) and gaseous material, which was not identified. Analysis of the liquid mixture by m.s.-g.l.c. identified compounds (2), (3), and (16)²¹ and the allene (15).²² The ^{19}F n.m.r. spectrum of the mixture was quite consistent with this composition and the i.r. spectrum showed an absorption at 2 045 cm^{-1} , giving further evidence for the presence of the allene (15).²²



(c) *Perfluoropropene trimers*. Passage of a mixture of the isomers (19) and (20) (ratio 3:1) (2.3 g) over iron at 605 °C gave a product (1.5 g) containing one main component (ca. 70%, 48% yield). This was separated by pre-

parative-scale g.l.c. giving *perfluoro-2-ethyl-1,3,3-trimethylcyclobutene* (21), b.p. 89 °C (Found: C, 25.9; F, 74.1%; M^+ , 412. C_9F_{16} requires C, 26.2; F, 73.8%; M , 412); ν_{max} (Raman) 1 708 cm^{-1} (C=C str); δ_F 65.7 (3 F, 1a-F, $J_{1a,2b}$ 5, $J_{1a,4}$ 2 Hz), 67.8 (6 F, 3a-F), 85.6 (3 F, 2b-F), 111.2 (2 F, 4-F), and 114.5 (2 F, 2a-F).

Preparation of Perfluoro-2,3-dimethylpent-2-ene (11).—A flask containing a stirred mixture of anhydrous caesium fluoride (7 g, 46.1 mmol) and tetraglyme (20 ml) under partial vacuum was attached to two variable-volume reservoirs, separately containing perfluoropropene (10.5 g, 70 mmol) and perfluorobut-2-ene (12 g, 60 mmol). Successive amounts from each bladder were introduced to the flask and the mixture was stirred for a total of 14 h, after which time both reservoirs had deflated. Volatile material (19.6 g) was removed from the flask by heating *in vacuo* and contained perfluorobut-2-ene (18 wt. %), compound (11) (70%, >90% yield, based on C_4F_8 consumed), and C_9F_{18} (12%) (m.s.). Distillation of the mixture gave *perfluoro-2,3-dimethylpent-2-ene* (11), b.p. 76 °C (Found: F, 75.8%; M^+ —19, 331. C_7F_{12} requires F, 76.0%; M 350), δ_F 60.1, 60.9, 61.4 (9 F, 1-, 2a-, 3a-F), 76.9 (3 F, 5-F), and 101.3 (2 F, 4-F).

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