

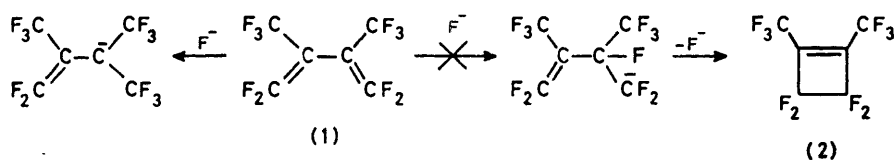
Reactions involving Fluoride Ion. Part 22.¹ Dimerisation of Perfluoro-2,3-dimethylbutadiene and Related Reactions

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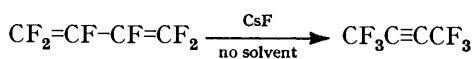
Reaction of perfluoro-2,3-dimethylbutadiene (1) with caesium fluoride gives two dimers, the ratios being very temperature-dependent. The structures of the dimers and mechanism of formation are proposed. A corresponding reaction but in the presence of bromine provides a good route to perfluoro-2,3-dimethylbut-2-ene. Further fluorination of the dimers of (1) occurs over cobalt trifluoride and the product may be rationalised on the basis of an intermediate radical cation.

THE formation of oligomers from perfluoro-olefins by presence of caesium fluoride and tetraglyme, giving two fluoride-ion catalysis is well known.²⁻⁶ These processes dimers, (3) and (4), as the main products.

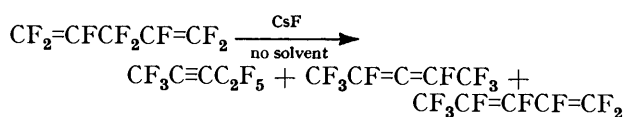


are generally explained in terms of stabilities and reactivities of the perfluoro-carbanions and -olefins involved and it is well established that the orders of reactivity for these species are as follows:^{7,8} (i) $R_F\bar{C}F_2 > (R_F)_2\bar{C}F > (R_F)_3\bar{C}$ (R_F = perfluoroalkyl); (ii) $CF_2=C(R_F)_2 > CF_2=CFR_F > CF_2=CF_2$; (iii) $CF_2=C(R_F)_2 > CFR_F=C(R_F)_2 > C(R_F)_2=C(R_F)_2$; indeed we have recently demonstrated reactivity order (iii) for a series of isomeric olefins.⁸

So far, only oligomerisation reactions of olefins containing one double bond have been reported. In principle, oligomers could be formed from simple perfluorodienes, providing that they do not undergo preferential isomerisation *e.g.* hexafluorobuta-1,3-diene is readily isomerised by fluoride ion to hexafluorobut-2-yne.⁹ Similarly, perfluoropenta-1,4-diene is isomerised to give internal isomers.⁹ In contrast, however,

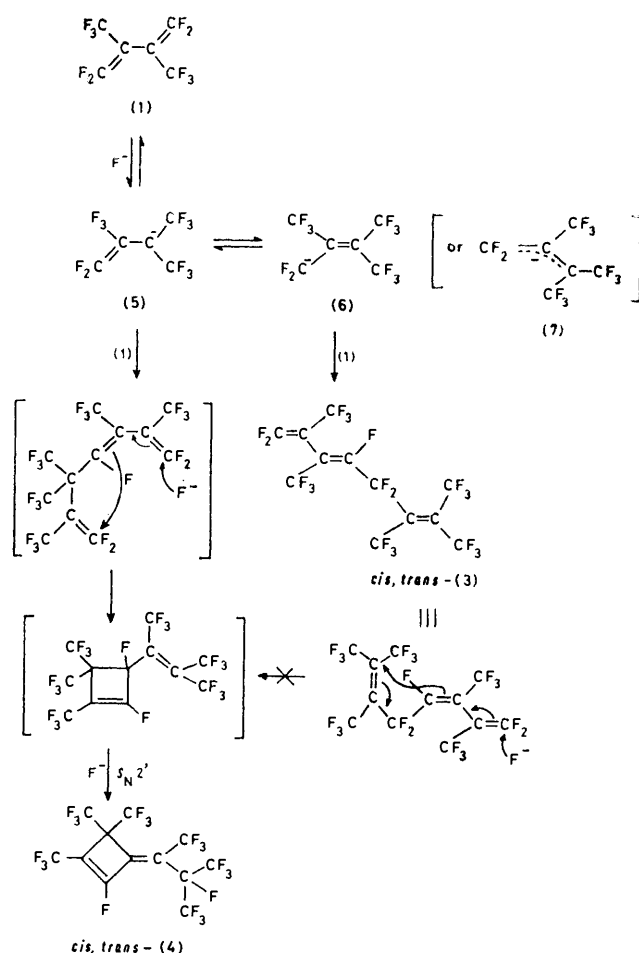


fluoride-ion-induced isomerisation of perfluoro-2,3-dimethylbutadiene (1) is a very unfavourable process. The cyclobutene derivative (2) is the only isomer that could



be produced, from (1), by fluoride-ion-induced isomerisation and its formation would involve fluoride ion attack on the least reactive side of the double bond in (1).

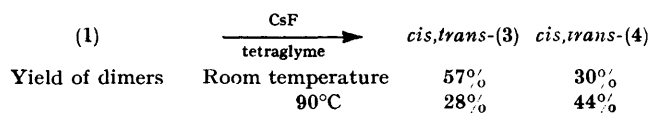
We have recently reported an accessible route to perfluoro-2,3-dimethylbutadiene (1),¹⁰ and now describe its fluoride-ion-induced dimerisation and some related reactions. This dimerisation occurs very readily in the



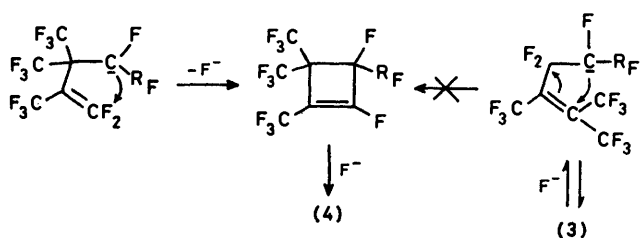
SCHEME Fluoride-ion-induced dimerisation of perfluoro-2,3-dimethylbutadiene

The ratio of dimers (3) and (4) is temperature-dependent. Interestingly, though, these isomers are not interconverted by caesium fluoride and tetraglyme at room temperature or at 90 °C.

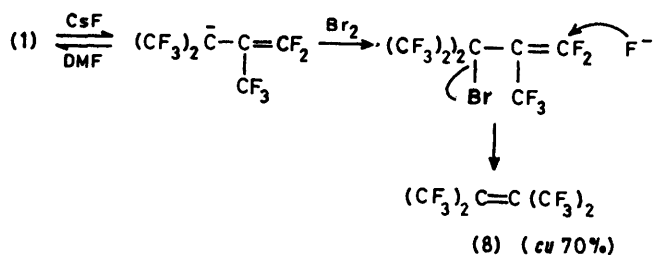
A mechanism accounting for these observations is given in the Scheme. The intermediate anion could be



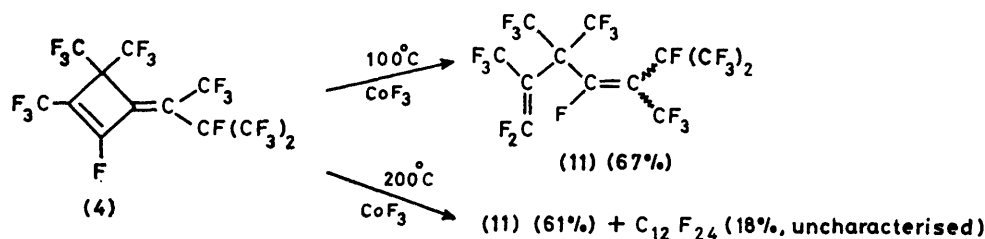
represented as the equilibrating carbanions (5) and (6), or the resonance-stabilised system (7). Whichever model is used, however, it is clear that more electron density is likely to be localised on the 'tertiary' carbanion centre represented by (5), than on the centre



represented in (6). Nevertheless, attack through (5) will be more inhibited, by steric effects, than through (6) and this seems to be the dominating influence on the reaction carried out at room temperature. At elevated



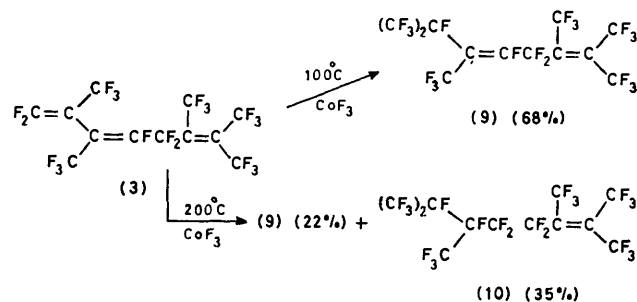
temperatures it is probable that electron-density distribution is the more important factor, therefore leading to a greater proportion of reaction through (5), giving (4).



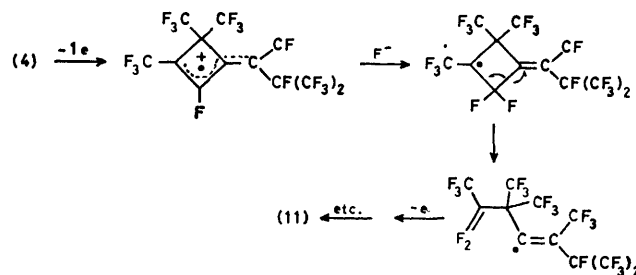
The fluoride-ion-induced cyclisation, leading to (4), involves an internal vinylic substitution of fluoride from a $\text{C}=\text{CF}_2$ group. It is not surprising that the analogous cyclisation of dimer (3) does not occur, as this would

require an internal nucleophilic attack on a much less reactive $\text{C}=\text{C}(\text{CF}_3)_2$ group.

Like other perfluorocarbon anions,^{11,12} the anions (5)



and (6) are trapped by bromine. In this case, however, no bromine-containing products were actually isolated because further reaction with fluoride ion readily occurs. This leads to the known perfluoro-2,3-dimethylbut-2-ene (8)¹³ as the main product and this reaction provides a viable route to (8).



Further confirmation of the structures assigned to dimers (3) and (4) was obtained from their fluorination over cobalt trifluoride at 100 and 200 °C, when some fragmentation occurred. Acyclic dimer (3) adds one molecular proportion of fluorine across the terminal double bond at 100 °C. At 200 °C a second molecular proportion of fluorine is added across the least substituted of the two remaining double bonds.

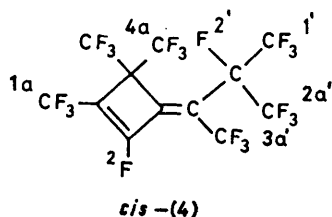
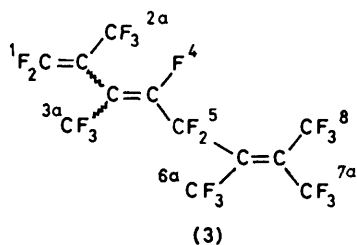
The cyclic dimer (4) also adds one molecular equivalent of fluorine, at 100 °C, giving the ring-opened diene (11). The formation of (11), at first sight surprising, is nevertheless quite readily explained on the basis of the radical

cation mechanism proposed for CoF_3 fluorinations.^{14,15} Although (11) has a terminal double bond it does not readily react further with CoF_3 at 200 °C. This may well be due to steric effects.

EXPERIMENTAL

^{19}F 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. 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. G.l.c. columns were packed with 30% silicone gum rubber SE-30 (column O), or 20% di-isodecyl phthalate (Column A) on Chromosorb P.

Dimerisation of Perfluoro-2,3-dimethylbutadiene (1).—(a) *At room temperature.* A mixture containing (1) (7.1 g, 27.1 mmol), caesium fluoride (2.5 g, 16.5 mmol), and tetraglyme (20 ml) was stirred for 18 h, when a one-phase system remained and most of the caesium fluoride had dissolved. The fluorocarbon products (6.7 g) were recovered by transferring under vacuum to a cold trap. Analysis by g.l.c. (column O, 50 °C) and m.s.-g.l.c. showed that the product contained (1) (2%), (4) (32%, 30% yield), (3) (60%, 57% yield), and an unidentified less-volatile component (6%). Separation of samples by preparative-scale g.l.c. column O, 60 °C gave *cis,trans*-perfluoro-3-(1,2-dimethylpropylidene)-1,4,4-trimethylcyclobutene (4) (unresolved by g.l.c.) (Found: F, 72.9%; M^+ , 524. $\text{C}_{12}\text{F}_{20}$ requires F, 72.5%; M , 524), b.p. 137 °C; λ_{max} (cyclohexane) 232 nm (ϵ 17 700); ν_{max} 1 640 cm^{-1} and 1 730 cm^{-1} (C=C str.); δ_{F} (ratio *cis* : *trans* = 2.2 : 1), *cis* 56.8 (3a'-CF₃, m), 62.7 (1a-CF₃, m), 68.1 [4a-(CF₃)₂, br d, $J_{4a,2'}$ 38 Hz], 74.6 (2a'-CF₃ and 1'-CF₃, br d, $J_{1',2'} = J_{2a',2'} = 8$ Hz), 77.1 (2-F, m), and 174.5 (2'-F, septet of m); *trans*, 56.8, 58.6 (2-F, 3a'-CF₃, m's), 62.7 (1a-CF₃, m), 68.1 [4a-(CF₃)₂, br d], 75.4 (1'-CF₃ and 2a'-CF₃, m), and 167.7 (2'-F, d, $J_{2,2'}$ 136 Hz): and *cis*- and *trans*-perfluoro-2,3,6,7-tetramethylocta-1,3,6-triene (3) (unresolved by g.l.c.) (Found: F, 72.3%; M^+ , 524), b.p. 148 °C; ν_{max} 1 720 and 1 730 cm^{-1} (C=C str.); δ_{F} (isomer ratio = 2 : 1, unassigned) 58.2, 60.5 (6a- and 7a- or 7a- and 8-CF₃, m's), 62.0, 62.8 (3a-CF₃, m), 64.9 (1-CF₂, 2a-CF₃, m), 67.8 (6a- or 8-CF₃, m), 88.2, 90.0 (4-F, br), and 103.1 (5-CF₂, br).



(b) *At 90 °C.* A mixture of (1) (2.1 g, 8 mmol), caesium fluoride (1 g, 6.6 mmol), and tetraglyme (5 ml) was stirred at 90 °C for 15 h in a sealed ampoule. The product (1.6 g), recovered as above, contained, by g.l.c., (4) (58%, 44% yield) and (3) (37%, 28% yield).

Reactions of Dimers with Caesium Fluoride.—(a) *At room temperature.* A mixture of (3) and (4) [ratio (3) : (4) = 95 : 5] (0.25 g, 0.5 mmol), caesium fluoride (0.2 g, 1.3 mmol), and tetraglyme (2 ml) was stirred for 31 days. The product, recovered as before, contained (3) (90%) and (4) (10%).

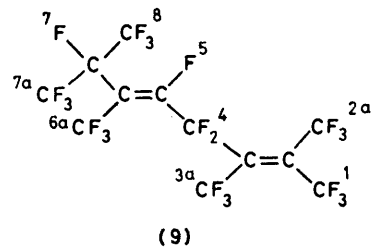
(b) *At 80 °C.* A similar mixture at 80 °C for 68 h gave a product containing mainly (3) (*ca.* 90%).

(c) *At room temperature.* A similar mixture, but containing (3) (5%) and (4) (95%) was stirred at room temperature giving a product containing (4) (98%).

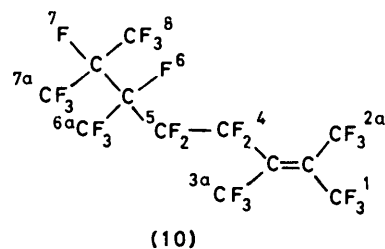
The products from examples (a)–(c) contain a slightly greater proportion of (4) than the starting materials. This is not because (3) is isomerised to (4), but because (3) forms a more stable anion in solution. Thus, on transferring under vacuum, (3) is less readily recovered.

Reaction of (1) with Caesium Fluoride and Bromine.—Caesium fluoride (3 g, 19.7 mmol) was added gradually to a stirred mixture containing (1) (2 g, 7.6 mmol), bromine (9.4 mmol), and DMF (8 ml). After 3 days the recovered lower layer (1.8 g) contained, by g.l.c., mainly perfluoro-2,3-dimethylbut-2-ene (8) (90%, *ca.* 70% yield). Preparative-scale g.l.c. (Column O, 110 °C) gave (8) (1.1 g, 48% isolated yield) which was identified by its mass spectrum and by comparison of its ^{19}F n.m.r. spectrum with that reported in the literature.¹³

Fluorination of Dimers Using Cobalt Trifluoride.—(a) *At 100 °C.* A mixture of (3) and (4) (ratio 65 : 35) (3 g) was vaporized in a stream of dry N₂ into a stirred bed of CoF₃–CaF₂ heated at 100 °C.¹⁶ The product (2.3 g) was collected



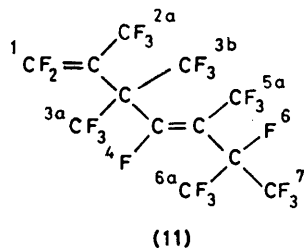
in a trap cooled in liquid nitrogen. Analysis by g.l.c. and g.l.c.-m.s. (Column A, 50 °C) showed three isomers of $\text{C}_{12}\text{F}_{22}$ (wt. % : 62, 33, and 5%). Samples of the two main isomers were separated by preparative-scale g.l.c. (Column O, 30 °C) giving perfluoro-2,3,6,7-tetramethylocta-2,5-diene (9) [68% yield based on (3)] (Found: F, 75.0%; M^+ — F, 543. $\text{C}_{12}\text{F}_{22}$ requires F, 74.4 %; M , 562); ν_{max} 1 705 cm^{-1} ,



(C=C str.); δ_{F} 60.7 (1-, and 2a-CF₃, br m), 64.7 (3a- and 6a-CF₃, br m), 72.1 (7a- and 8-CF₃, br m), 87.4 (5-F, br), 93.0 (4-CF₂, br), and 171.4 (7-F, br): and perfluoro-2,3,3,5,6-pentamethylhepta-1,4-diene (11) [67% yield based on (4)] (Found: F, 75.0%; M^+ , 562); ν_{max} 1 650 and 1 740 cm^{-1} (C=C str.); δ_{F} 60–66 (1-CF₂, and 2a-, 3a-, 3b-, and 5a-

CF₃, br), 76.0 (4-F, and 6a- and 7a-CF₃, br), and 180.0 (6-F, br).

(b) At 200 °C. Using the method described in (a) a mixture of (3) and (4) (ratio 63 : 37) (1.2 g) was fluorinated at 200 °C. The product (1 g) contained C₃F₈ (1% by weight), C₉F₁₈ (3%), C₉F₁₈ (9%), C₁₂F₂₂ (11) (29%), C₁₂F₂₂ (9) (19%), C₁₂F₂₄ (9%), and C₁₂F₂₄ (10) (30%). Yields of



C₁₂ products, from (3), are C₁₂F₂₂ (9) (22%) and C₁₂F₂₄ (10) (35%), and from (4), are C₁₂F₂₂ (11) (61%) and C₁₂F₂₄ (18%). Preparative-scale g.l.c. (Column O, 70 °C) gave *perfluoro-2,3,6,7-tetramethyloct-2-ene* (10) (Found: F, 75.7%; *M*⁺ - F, 581. C₁₂F₂₄ requires F, 76%; *M*, 600); ν_{\max} , 1700vw cm⁻¹ (C=C str.); δ_{F} 58.2 (3a-CF₃, br), 59.7 (1- and 2a-CF₃, br), 68.8 (6a-CF₃, octet, $J_{7a,6a'} = J_{8,6a} = 13.5$, $J_{6a,6}$ or $J_{6a,7}$ 13.5 Hz), 71.5, 72.5, (7a- and 8-CF₃, m's), 89.0 (4-CF₂, br), 106.8 (5-CF₂, br), and 166.2, 174.1 (6-F and 7-F, br).

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