# Fluoro-olefin Chemistry. Part 14.[1] Preparation and Photochemical Rearrangement of Some Acyclic Perfluoroalkyl and Polyfluoroalkyl Olefins [2]

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Photochemical addition of iodopolyfluoroalkanes [R_FI; R_F = n-C_3F_7, $(CF_3)_2$CF, CF_2ClCF_2, CF_2ClCFCl] to perfluorobut-2-yne gives mixtures of the (E)- and (Z)-1 : 1-adducts [R_F(CF_3)C=ClCF$_3$]. With potassium fluoride at 220 °C, the vinylic iodine is replaced by fluorine and partial or complete rearrangement of the double bond takes place. The allylic chlorine of 4,5-dichloro-2-iodo-3-trifluoromethylhexafluoropent-2-ene is also replaced by fluorine to give a mixture of (E)- and (Z)-1-chloro- and 5-chloro-perfluoro(3-methylpent-2-enes), identical with that prepared from 5-chloro-2-iodoperfluoro(3-methylpent-2-ene).

Ultraviolet irradiation of perfluoro-2-methylhex-2-ene or -3-ene results initially in cis-trans-isomerisation, and under more vigorous conditions mixtures of two terminal olefins are formed by migration of fluorine or a perfluoroalkyl group to the =CFR$_F$ group; no migration from the =CFCF$_3$ group to RR'C= or interconversion of the methylhexenes (6) and (7) takes place. Perfluoro(2,3-dimethylpent-2-ene) showed 1,3-fluorine shifts from (CF$_3$)$_2$C= CF$_3$C=, and CF$_3$CF$_2$C=, and also CF$_3$ group migration from the CF$_3$CF$_2$C= moiety, but migration of F and CF$_3$ from the (C$_2$F$_5$)$_2$C= group were the only detectable reaction of perfluoro(3-ethyl-2-methylpent-2-ene); no product corresponding to migration from the (CF$_3$)$_2$C= group was observable. Interconversion of the trialkyl chlorodecafluoro-(10) and undecafluoro-olefins (11) takes place under mild conditions, but the products formed under more vigorous conditions were not positively identified. The migrations appear to involve symmetry-allowed 1,3-sigmatropic shifts of fluorine or fluoroalkyl groups.

In a previous paper in this series, the rearrangement, on u.v. irradiation, of perfluoro(2,3-dimethylbut-2-ene) to perfluoro(2,3-dimethylbut-1-ene) was reported. Under similar conditions, perfluoro(2-methylbut-2-ene) (3a) and perfluoro(2-methylpent-2-ene) (3b) underwent 1,3-fluorine migration regiospecifically, but more slowly, to give exclusively the perfluoro(2-methylalk-1-enes) (4a and b).[1]

Scheme 1
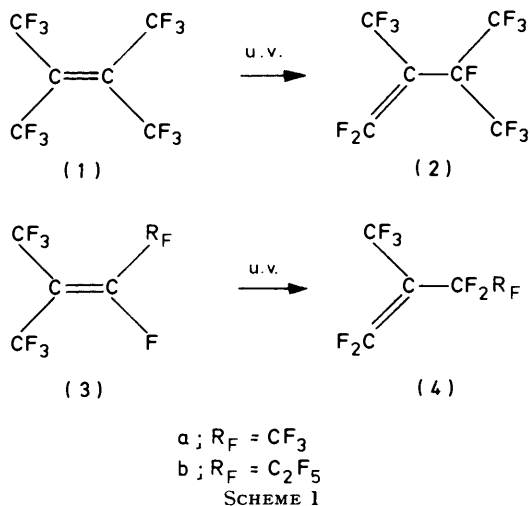
We now report the preparation and photochemical rearrangement of a further series of perfluoro- and chloropolyfluoro-olefins designed to test the scope of this novel reaction.

Preparation of the Olefins.—Perfluorobut-2-yne underwent thermally initiated free-radical addition reactions with heptafluoro-1- and -2-iodopropane to give the 2-iodoperfluoro-olefins (5a and b) as mixtures of the (E)- and (Z)-isomers.[3] The yield of compound (5a) was
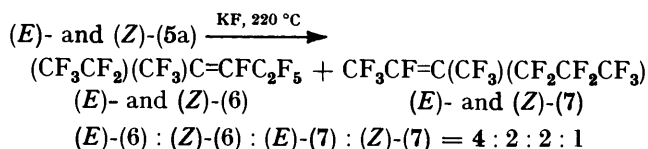
good, but telomerisation was more extensive when the 2-iodopropane was used, as expected, and the pentene (5b) was obtained in only 25% yield.
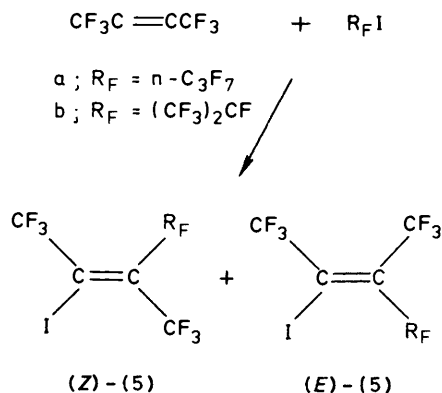

The geometrical isomers were readily distinguished (see Table) by the presence of large couplings between the three fluorines at C-1 and the fluorines at C-4 in the (Z)-(5) compounds and between the fluorines at C-1 and the CF$_3$ group attached to C-3 in the (E)-(5) compounds {J[(Z)-CF$_3$C=CCF] is known to be much larger than J[(E)-CF$_3$C=CCF]}.[4]

Replacement of the iodine by fluorine using potassium fluoride at 220 °C [cf. the preparation of perfluoro(2-methylbut-2-ene) (3a)] [5] was accompanied by fluoride-ion induced rearrangement of the double-bond position, so that the product mixture resulting from compound (5a), formed in 79% yield, consisted of the (E)- and (Z)-isomers of perfluoro(3-methylhex-3-ene) (6) as well as the expected (E)- and (Z)-perfluoro(3-methylhex-2-ene)

(7). The isomers were again readily distinguished

$$(E)\text{- and }(Z)\text{-(5a)} \xrightarrow{\text{KF, 220 °C}}$$

$(CF_3CF_2)(CF_3)C=CFC_2F_5$ + $CF_3CF=C(CF_3)(CF_2CF_2CF_3)$
(E)- and (Z)-(6)   (E)- and (Z)-(7)

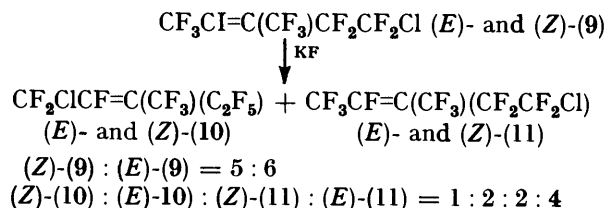(E)-(6) : (Z)-(6) : (E)-(7) : (Z)-(7) = 4 : 2 : 2 : 1

spectroscopically (Table), and g.l.c. allowed the separation of the hex-3-enes (6) from the hex-2-enes (7), and also the preparation of samples of each in which the (E)-isomer predominated. Estimation of the isomer ratios by integration of appropriate peaks in the ^{19}F n.m.r. spectra allowed calibration of the g.l.c. peaks. Double-bond migration was complete in the reaction of (E)- and (Z)-(5b) with fluoride ion (see Scheme 2), and only per-

(5b)

(8)
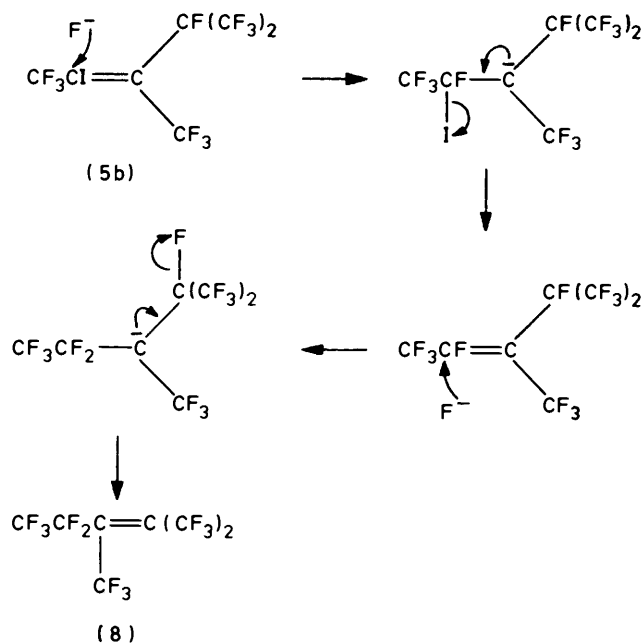
SCHEME 2

fluoro(2,3-dimethylpent-2-ene) (8), identical with a sample prepared by the reaction of caesium fluoride and tetrafluoroethylene with the butene (3a), was obtained; this illustrates the greater ease of departure of the tertiary fluorine of the $CF(CF_3)_2$ group compared with the secondary fluorine of the CF_2CF_3 group.
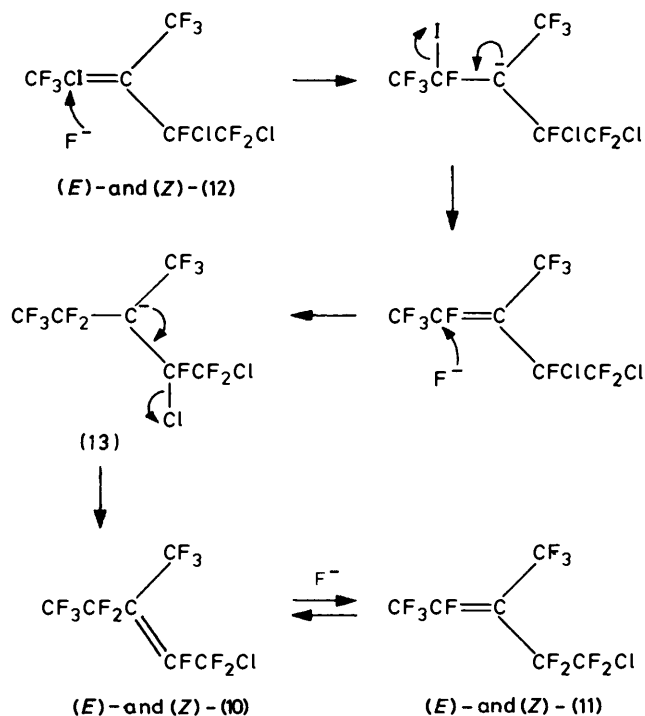
In order to introduce chlorine as a label in an otherwise completely fluorinated alkyl olefin, 1-chloro-2-iodotetra-fluoroethane, readily prepared by the reaction of iodine monochloride with tetrafluoroethylene,[6] was heated with perfluorobut-2-yne. The resulting mixture of (E)- and (Z)-5-chloro-2-iododecafluoro(3-methylpent-2-ene) (9), formed in 49% yield, was heated with potassium fluoride; again fluoride ion induced migration of the double bond to an appreciable extent, to give a mixture of the (E)- and (Z)-isomers of 1-chloroundecafluoro(3-methylpent-2-ene) (10) in addition to the expected (E)- and (Z)-5-chloro-compound (11).

$CF_3CI=C(CF_3)CF_2CF_2Cl$ (E)- and (Z)-(9)

$\downarrow$ KF

$CF_2ClCF=C(CF_3)(C_2F_5)$ + $CF_3CF=C(CF_3)(CF_2CF_2Cl)$
(E)- and (Z)-(10)   (E)- and (Z)-(11)

(Z)-(9) : (E)-(9) = 5 : 6
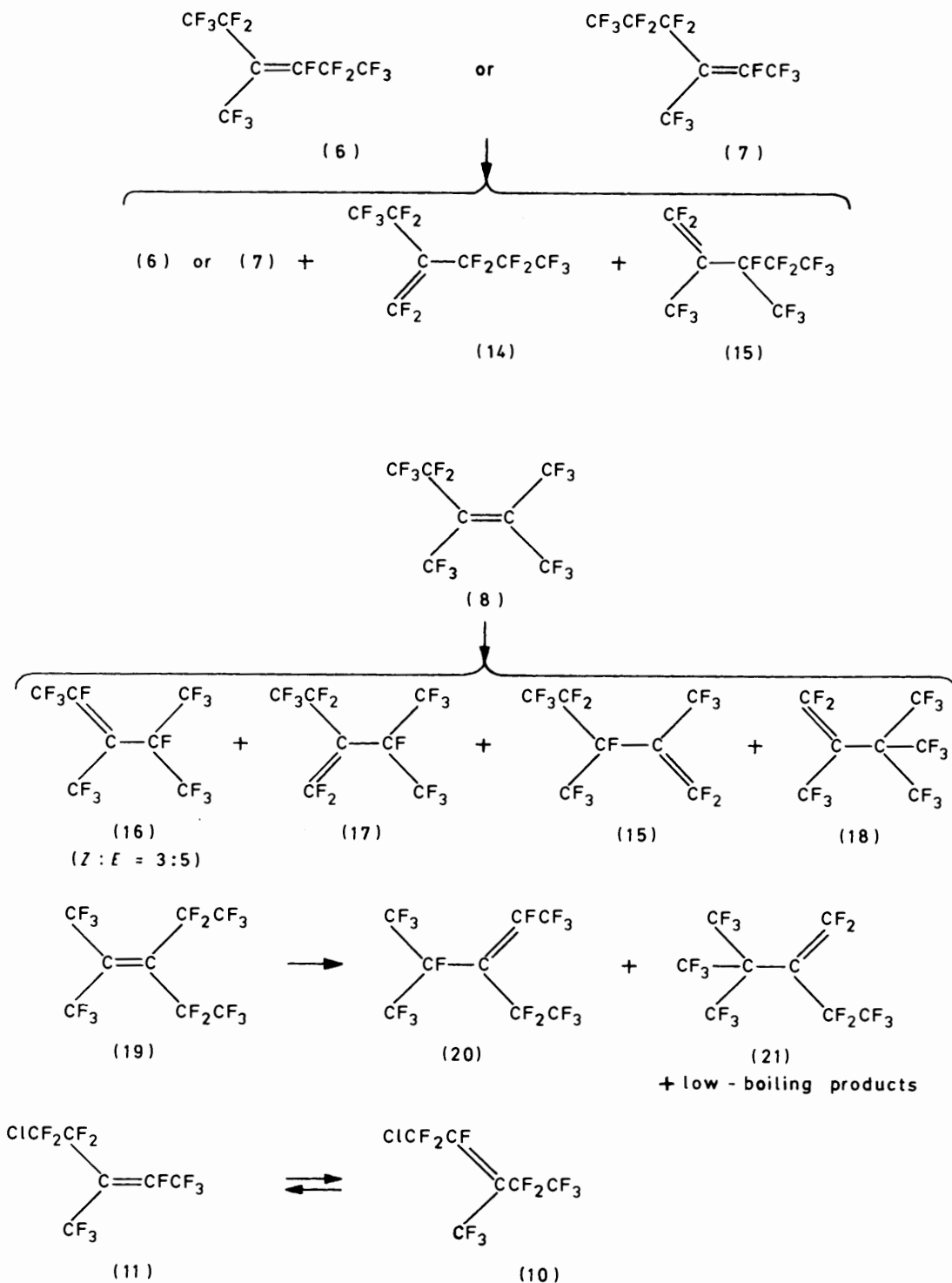(Z)-(10) : (E)-10) : (Z)-(11) : (E)-(11) = 1 : 2 : 2 : 4

1,2-Dichloro-1,2,2-trifluoro-1-iodoethane also reacted with perfluorobut-2-yne at 160 °C to give the 1 : 1-adducts (12) [(E)- and (Z)-isomers] in good yield. The reaction with potassium fluoride, however, led to the formation of a mixture of the monochloro-compounds (10) and (11) in proportions which were essentially identical with those obtained from compound (9); two minor products observed may have been the expected dichloro-compounds, but characterisation was not possible. Presumably initial displacement of iodide ion from compound (12) is followed by further attack by fluoride ion, present in excess, leading to the carbanion (13); elimination of chloride ion from this gives the internal olefins (E)- and (Z)-(10). Fluoride-ion attack can then give the isomeric olefins (E)- and (Z)-(11) in equilibrium with compound (10) (Scheme 3).

Fluoride-ion attack on the initial products is evidently faster than on the chloro-compounds (9) or (12), since reactions which were carried out so that up to 70% of the starting material was recovered gave the same mixtures of compounds (10) and (11).

Photochemical Rearrangement Reactions.—The photochemical rearrangements of the olefins prepared as described in the previous section, together with some

(E)-and (Z)-(12)

(13)

(E)-and (Z)-(10)   (E)-and (Z)-(11)

SCHEME 3

$$
\underset{(6)}{\overset{CF_3CF_2}{\underset{CF_3}{\diagdown}}C{=}CFCF_2CF_3} \qquad \text{or} \qquad \underset{(7)}{\overset{CF_3CF_2CF_2}{\underset{CF_3}{\diagdown}}C{=}CFCF_3}
$$

(6) or (7) + $\underset{CF_2}{\overset{CF_3CF_2}{\diagdown}}C{-}CF_2CF_2CF_3$ + $\underset{CF_3}{\overset{CF_2}{\diagdown}}C{-}CFCF_2CF_3$

(14)   (15)

$$
\underset{(8)}{\overset{CF_3CF_2}{\underset{CF_3}{\diagdown}}C{=}C\overset{CF_3}{\underset{CF_3}{\diagup}}}
$$

$\underset{CF_3}{\overset{CF_3CF}{\diagdown}}C{-}\underset{CF_3}{\overset{CF_3}{\diagup}}CF$ + $\underset{CF_2}{\overset{CF_3CF_2}{\diagdown}}C{-}\underset{CF_3}{\overset{CF_3}{\diagup}}CF$ + $\underset{CF_3}{\overset{CF_3CF_2}{\diagdown}}CF{-}\underset{CF_2}{\overset{CF_3}{\diagup}}C$ + $\underset{CF_3}{\overset{CF_2}{\diagdown}}C{-}\underset{CF_3}{\overset{CF_3}{\diagup}}C{-}CF_3$

(16)   (17)   (15)   (18)

($Z : E = 3 : 5$)

$\underset{CF_3}{\overset{CF_3}{\diagdown}}C{=}\underset{CF_2CF_3}{\overset{CF_2CF_3}{\diagup}}C$ → $\underset{CF_3}{\overset{CF_3}{\diagdown}}CF{-}C{=}\underset{CF_2CF_3}{\overset{CFCF_3}{\diagup}}$ + $CF_3{-}\underset{CF_3}{\overset{CF_3}{\diagdown}}C{-}\underset{CF_2CF_3}{\overset{CF_2}{\diagup}}C$

(19)   (20)   (21)

+ low – boiling products

$\underset{CF_3}{\overset{ClCF_2CF_2}{\diagdown}}C{=}CFCF_3$ ⇌ $\underset{CF_3}{\overset{ClCF_2CF}{\diagdown}}C{=}\underset{CF_2CF_3}{}C$

(11)   (10)

SCHEME 4

others available to us from other work,[7] are summarised in Scheme 4.

The results obtained showed marked dependence on the age of the lamp used. Thus lamp A (an old lamp, presumably emitting less of the high-energy radiation) caused rapid geometrical isomerisation of samples of compounds (6) or (7), previously enriched in the (E)-isomer by g.l.c., giving, in each case, an $E : Z$ ratio of ca. 1 : 1 after 40—70 h; no further change took place on prolonged irradiation with lamp A, but this ready cis-trans isomerisation precluded investigation of the geometrical requirements of the migrations observed subsequently. Irradiation of these mixtures with lamp B (a new lamp) for 10 days resulted in each case in the formation of the terminal olefins (14) and (15) as major products, identified by their ^{19}F n.m.r. spectra; minor products included perfluoroethane, perfluoropropane, and silicon tetrafluoride, as well as several others which could not be identified.

^{19}F N.m.r. coupling constants in fluoro-olefins [a]

Compound	$^4J_{cis}$[b]	$^5J_{cis}$[c]
(E)-(5a)		16
(Z)-(5a)		23.2
(E)-(5b)		16.8
(Z)-(5b)		59
(E)-(6)	33	20
(Z)-(6)	20	
(E)-(7)	31.0	13.0
(Z)-(7)	23	20
(8)		14
(Z)-(9)		22.4
(E)-(10)	31.5	18
(E)-(11)	29.2	14.5
(Z)-(11)	22.4	21
(E)-(12)		18
(Z)-(12)		48
(E)-(16)		15
(Z)-(16)		47
(17)	39	
(E)-(20)		21
(Z)-(20)		52
(21)	38	

[a] In Hz. Full parameters are given in Supplementary Publication (SUP No. 23326, 7 pp.). [b] $J(CF_xC=CF)$. [c] $J(CF_3C=CCF_x)$.

Formation of the terminal olefin (14) is readily explained by migration of an allylic fluorine from the CF_3 group of either hexene (6) or (7) to the $=CFR_F$ group (Scheme 5), in accordance with the previous observation of fluorine migrations in this direction [1] shown in Scheme 1. The formation of the terminal olefin (15) clearly requires a different reaction. Migration of an allylic CF_3 group in compound (6), or a C_2F_5 group in (7), would give the observed product (Scheme 5).
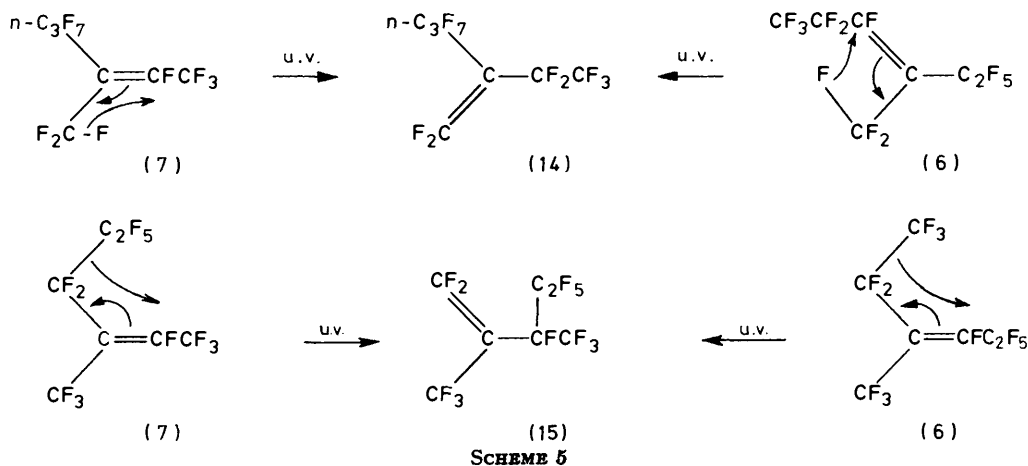
The hex-3-enes (6) were converted into compounds (14) and (15) somewhat less rapidly (70% in 150 h) than the hex-2-enes (7) (100% in 150 h under identical conditions), and the ratio of (14) : (15) obtained was 5 : 1 with compound (6) as starting material and 3 : 2 with (7). Under these conditions, therefore, it appears that C_2F_5 migration is more efficient than that of CF_3, but both are found to be comparable to fluorine migration when the number of fluorines correctly sited for migration is taken into consideration.

Migration of fluorine from the allylic CF_2 group of compound (7) to the $=CFCF_3$ group would give the isomer (6), and a similar migration in (6), from CF_2 to $=CFC_2F_5$, would give (7), but no evidence for such interconversion of the trisubstituted olefins was found. Neither migration nor geometrical isomerisation had taken place in compound (6) ($Z : E = 1 : 3$) after 7 days at 220 °C.

In contrast to the slow reaction of the trialkyl olefins (6) and (7), perfluoro(2,3-dimethylpent-2-ene) (8) was completely converted, on irradiation for 3 days with lamp A, into a mixture of compounds (15), (16), (17), and (18) (ratio 10 : 10 : 15 : 8 respectively). Allylic fluorine migration from the $(CF_3)_2C=$, from the $CF_2C=$, and from the $CF_3C=$ group account for the formation of the products (15), (16), and (17), respectively, and CF_3 migration from the $CF_3CF_2C=$ group gives compound (18). The observed ratio of (Z)- and (E)-isomers of the pentene (16) may be due to photochemical geometrical isomerisation of the initially formed isomers rather than to any stereoselectivity of this migration. Migration from the individual CF_3 groups of the $(CF_3)_2C$ group cannot be distinguished; in spite of the number of such fluorines apparently correctly placed for migration, the terminal olefin (15) was formed in similar yield to the internal olefin (16) and the other terminal olefin (17). When account is taken of the number of groups available for migration, CF_3 migration to form compound (18) is the most favourable process, and this is enhanced when lamp B is used [observed ratio (15) : (16) : (17) : (18) = 2 : 1 : 1 : 2 giving a ' per group ' mobility of 1 : 6 : 2 : 12 for the three different fluorine migrations and the CF_3 migration]. This change is again presumed to be related to the difference in the proportion of low-wavelength radiation emitted by each lamp.
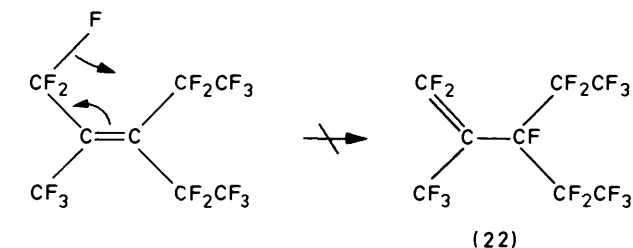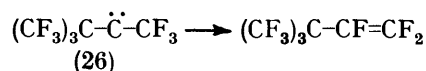
Perfluoro(3-ethyl-2-methylpent-2-ene) (19), available from other work,[7] was also isomerised completely on irradiation with lamp A for 3 days, giving compound (20), by fluorine migration from the CF_2 groups, and the isomer (21) by CF_3 group migration in the ratio 3 : 2. A separated sample of compound (20) showed no change on further irradiation under these conditions. When the pentene (19) was irradiated with lamp B, CF_3 migration was again more favourable, the ratio of (20) : (21) obtained being 8 : 7. Under these conditions, low-boiling material (perfluoro-ethane, -propane, and several other components of similar b.p.) was also produced with this olefin. No evidence was found in this case for migration of fluorine from the CF_3 groups, which would have been expected to give the terminal olefin (22).

Irradiation of the chloro-olefin (11) led to the formation of its isomer (10) by fluorine migration from the $CF_2C=$ group, but irradiation of a mixture enriched in compound (10) caused only a small decrease in the proportion of the starting compound (11). This is, so far, the only observation of interconversion of one trialkyl olefin to another [cf. the reactions of (6) and (7) above], the usual reactions being tetra-alkyl olefin ⟶ trialkyl or terminal olefin, and trialkyl olefin ⟶ terminal olefin,

Scheme 5 structures:

$$n\text{-}C_3F_7\text{-}C(F_2C\text{-}F)=CFCF_3 \quad (7) \xrightarrow{u.v.} \quad n\text{-}C_3F_7\text{-}C(F_2C=)\text{-}CF_2CF_3 \quad (14) \xleftarrow{u.v.} \quad CF_3CF_2CF(F/)(CF_2)C\text{-}C_2F_5 \quad (6)$$

$$C_2F_5/CF_2 \backslash CF_3\text{-}C=CFCF_3 \quad (7) \xrightarrow{u.v.} \quad CF_2=/C_2F_5/CF_3\text{-}C\text{-}CFCF_3 \quad (15) \xleftarrow{u.v.} \quad CF_3/CF_2\backslash CF_3\text{-}C=CFC_2F_5 \quad (6)$$
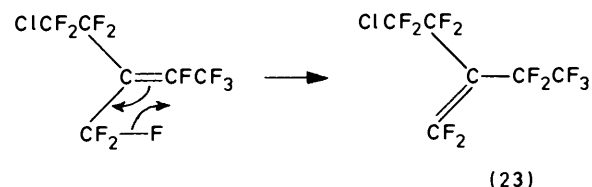
Scheme 5

the latter reaction requiring more forcing conditions. After irradiation of (10) or (11) for 3 weeks using lamp B, the n.m.r. spectra showed that a complex mixture had been formed, with (10) and (11) present only as minor components. A relatively strong band in the complex [19]F n.m.r. spectra at δ —37.5 suggested the presence of a CF_2CF_3 group, and hence fluorine migration from the

$$\begin{array}{l} F\backslash CF_2/CF_3\text{-}C=C(CF_2CF_3)(CF_2CF_3) \end{array} \xrightarrow{\times} CF_2=/CF_3\text{-}C\text{-}CF(CF_2CF_3)(CF_2CF_3)$$

(22)

CF_3 group of compound (11) (Scheme 6) to give the terminal olefin (23); a band at δ —92 suggested a tertiary CF, and thus migration of a CF_2Cl group from the pentene (11) or of a CF_3 group from its isomer (10) to give the same product (24) (Scheme 6). These products could not, however, be positively identified.
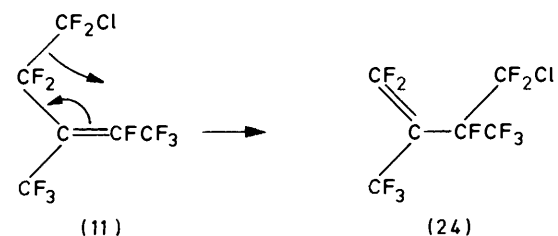
As with the earlier results obtained with perfluoro-(2,3-dimethylbut-2-ene), perfluoro(2-methylbut-2-ene), and perfluoro(2-methylpent-2-ene),[1] the results reported here are consistent with suprafacial 1,3-sigmatropic shifts of either a fluorine or a fluoroalkyl group, which would be symmetry-allowed for the photochemically excited state. The reactivity order (tetra-alkyl- > tri-alkyl- > dialkyl-olefin) suggests that the relief of steric crowding is important, but this seems to contrast with the observation that fluorine migration from the CF_2CF_3 groups of compounds (8) and (19), with consequent formation of the trialkyl olefins (16) and (20), is more efficient (per available fluorine) than migration from the CF_3 groups to give terminal olefins.
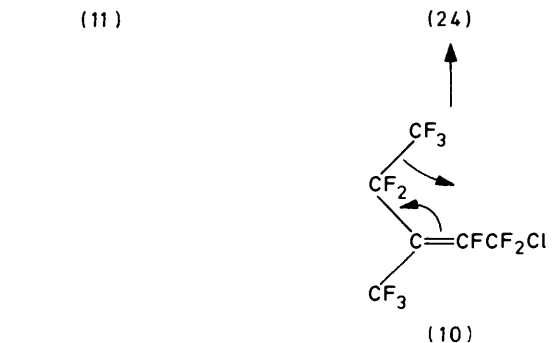
Photochemical rearrangement of hydrocarbon olefins has been shown to involve the formation of carbene intermediates such as (25) as the major reaction path, with a parallel hydrogen migration presumed to involve a 1,3-sigmatropic shift.[8] Although the perfluoroalkyl

carbene (26), analogous to (25), would not be expected to undergo intramolecular C–F insertion to give the cyclopropane, it would give perfluoro(3,3-dimethylbut-1-ene) which is readily distinguishable from the observed
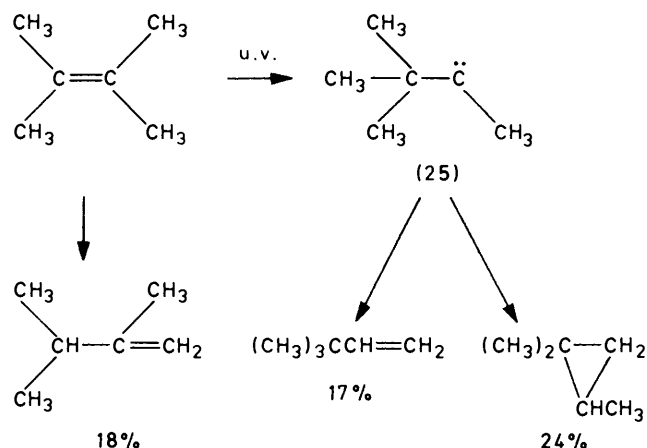
$$(CF_3)_3C\text{-}\ddot{C}\text{-}CF_3 \longrightarrow (CF_3)_3C\text{-}CF=CF_2$$

(26)

product (2). Similarly, although a product containing the $(CF_3)_3C$ group could be generated via carbene form-

$$ClCF_2CF_2\text{-}C(CF_2\text{-}F)=CFCF_3 \longrightarrow ClCF_2CF_2\text{-}C(CF_2=)\text{-}CF_2CF_3$$

(23)

$$CF_2Cl/CF_2\backslash CF_3\text{-}C=CFCF_3 \quad (11) \longrightarrow CF_2=/CF_2Cl\backslash CF_3\text{-}C\text{-}CFCF_3 \quad (24)$$

$$\uparrow$$

$$CF_3/CF_2\backslash CF_3\text{-}C=CFCF_2Cl \quad (10)$$

Scheme 6

ation from the pentene (8), the resulting olefin would be perfluoro(4,4-dimethylpent-2-ene) rather than the observed terminal olefin (18). In no case can the products observed in the present work be derived by formation

and rearrangement of a carbene intermediate, and such a path can thus account, at most, only for the relatively small amounts of unidentified products.

CH₃
 \   CH₃
  C=C   /
 /   \
CH₃   CH₃

  u.v.
  ———→

CH₃
  \   ..
   CH₃—C—C
        /   \
      CH₃   CH₃
       (25)

CH₃   CH₃
  \   /
   CH—C=CH₂
  /
CH₃
  18%

(CH₃)₃CCH=CH₂
   17%

(CH₃)₂C—CH₂
         \ /
          CHCH₃
   24%

EXPERIMENTAL

I.r. spectra were recorded on Perkin-Elmer 257 or 621 spectrophotometers, and ¹⁹F n.m.r. spectra on Perkin-Elmer R 10, R 20A (56.46 MHz), or Varian HA 100 (94.1 MHz) spectrometers. Chemical shifts have positive values to low field of external trifluoroacetic acid. Complete ¹⁹F n.m.r. parameters are available as a Supplementary publication (SUP. No. 23326, 7 pages).* Mass spectra were obtained on an A.E.I. MS 902 spectrometer. Irradiations were carried out with Hanovia 500 medium-pressure mercury arc lamps, with the reactants sealed *in vacuo* in silica tubes. Lamp A was an old lamp (used previously for *ca.* 1 000 h); lamp B was new.

Preparation of 2-Iodotridecafluoro(3-methylhex-2-ene) (5a). —Perfluorobut-2-yne (9.72 g, 0.060 mol) and 1-iodohepta-fluoropropane (17.76 g, 0.060 mol) were kept *in vacuo* (3 × 300 ml Pyrex tubes) at 220 °C for 7 d to give perfluoro-but-2-yne (0.50 g, 5%), a trace of iodoheptafluoropropane, and a mixture of (Z)- and (E)-2-iodotridecafluoro(3-methylhex-2-ene) (5a) (15.5 g, 68%) (Found: C, 18.6; F, 53.6; I, 27.3. Calc. for C₇F₁₃I: C, 18.3; F, 54.0; I, 27.7%), b.p. 130—133 °C. The ¹⁹F n.m.r. spectrum showed the isomers to be in the ratio (Z) : (E) = 3 : 4. G.l.c. (4-m column, dinonyl phthalate, 110 °C) allowed separation of the (E)- and (Z)-isomers which were identified spectroscopically.

Reaction of 2-Iodotridecafluoro(3-methylhex-2-ene) (5a) *with Potassium Fluoride.*—2-Iodotridecafluoro(3-methylhex-2-ene) (15.0 g, 32.7 mmol) and potassium fluoride (30.0 g, 0.52 mol) were kept *in vacuo* at 220 °C for 7 d. The volatile products were shaken with mercury and distilled to give a mixture (9.0 g, 79%) (Found: C, 24.1; F, 75.5. Calc. for C₇F₁₄: C, 24.0; F, 76.0%), b.p. 65—68 °C, of (Z)- and (E)-perfluoro(3-methylhex-2-ene) (7) and (Z)- and (E)-perfluoro-(3-methylhex-3-ene) (6), from which traces of unknown impurities were removed by g.l.c. (4-m column, dinonyl phthalate, 40 °C). Further g.l.c. (10-m SE-30 column, 30 °C) gave a 1 : 2 mixture of (Z)- and (E)-perfluoro (3-methylhex-3-enes), a 4 : 1 mixture of (E)- and (Z)-perfluoro(3-methylhex-2-enes), and a *ca.* 1 : 1 mixture of

* For details of the Supplementary publications scheme see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1981, Index issue.

the (E)- and (Z)-hex-2-enes, which were identified spectro-scopically.

Preparation of 2-Iodotridecafluoro(3,4-dimethylpent-2-ene) (5b).—Perfluorobut-2-yne (12.96 g, 0.080 mol) and 2-iodo-heptafluoropropane (23.68 g, 0.080 mol) were kept *in vacuo* (4 × 300-ml Pyrex tubes) at 220 °C for 7 d. The resultant liquid was shaken with mercury and distilled to give a mixture of (Z)- and (E)-2-iodotridecafluoro(3,4-dimethylpent-2-ene (5b) (9.0 g, 25%) (Found: C, 18.5; F, 54.4; I, 27.4 Calc. for C₇F₁₃I: C, 18.3; F, 54.0; I, 27.7%), b.p. 130—132 °C, and a fraction (10.0 g), b.p. 172 °C, which appeared (¹⁹F n.m.r. spectrum) to be a mixture of iodoperfluoro-(tetramethylheptadienes).

Reaction of 2-Iodotridecafluoro(3,4-dimethylpent-2-ene) (5b) *with Potassium Fluoride.*—2-Iodotridecafluoro(3,4-di-methylpent-2-ene) (8.0 g, 17.4 mmol) and potassium fluoride (10.0 g, 0.17 mol) were kept *in vacuo* at 220 °C for 7 d. The iodine was then removed, and the residue distilled and purified further by g.l.c. to give perfluoro(2,3-dimethylpent-2-ene) (8) (4.0 g, 65%) (Found: C, 24.2; F, 76.0. Calc. for C₇F₁₄: C, 24.0; F, 76.0%), b.p. 68—70 °C, v̄ 1 750 cm⁻¹ (C=C); *m/e* 331 [(M − F)⁺, 33%] and 281 [(M − CF₃)⁺, 21].

Preparation of 5-Chloro-2-iododecafluoro(3-methylpent-2-ene) (9).—A mixture of 1-chloro-2-iodotetrafluoroethane (10.5 g, 0.040 mol), prepared by the reaction of iodine mono-chloride and perfluoroethylene,⁶ and perfluorobut-2-yne (6.5 g, 0.040 mol) was kept in Pyrex tubes (2 × 300 cm³) at 220 °C for 7 d and then distilled to give a 5 : 6 mixture of (Z)- and (E)-5-chloro-2-iododecafluoro(3-methylpent-2-ene) (9) (8.3 g, 49%) (Found: C, 17.0; F, 44.7. Calc. for C₆Cl-F₁₀I: C, 17.0; F, 44.8%), b.p. 142—144 °C, and an oily residue.

Reaction of 5-Chloro-2-iododecafluoro(3-methylpent-2-ene) (9) *with Potassium Fluoride.*—5-Chloro-2-iododecafluoro(3-methylpent-2-ene) (8.3 g, 19.5 mmol) and potassium fluoride (15 g, 0.26 mol) were kept in a 300-cm³ Pyrex tube at 230 °C for 6 d. The crude product (6.2 g) was then distilled to give a mixture of compounds, b.p. 75—78 °C (4.5 g, 73%) (Found: C, 22.5; F, 66.4. Calc. for C₆ClF₁₁: C, 22.4; F, 66.0%). The n.m.r. spectrum of the mixture and those of samples enriched in the various isomers by preparative g.l.c. (10-m S.E. 30, room temp.) showed it to consist of (Z)- and (E)-5-chloroundecafluoro(3-methylpent-2-ene) (11) and (Z)-and (E)-1-chloroundecafluoro(3-methylpent-2-ene) (10) in the ratio 2 : 4 : 1 : 2.

Preparation of 4,5-Dichloro-2-iodo-3-trifluoromethylhexa-fluoropent-2-ene (12).—A mixture of 1,2-dichloro-1-iodo-1,2,2-trifluoroethane (11.2 g, 0.040 mol), prepared by the room temperature addition of iodine monochloride to 2-chloro-1,1,2-trifluoroethylene,⁹ and perfluorobut-2-yne (6.5 g, 0.040 mol) was kept at 160 °C for 7 d in two Pyrex tubes. It was then distilled to give a 3 : 4 mixture of (Z)- and (E)-4,5-dichloro-2-iodo-3-trifluoromethylhexafluoropent-2-ene (12) (10.5 g, 60%) (Found: C, 16.2; F, 38.4. Calc. for C₆Cl₂F₉I: C, 16.3; F, 38.8%), b.p. 65 °C at 18 mmHg.

Reaction of 4,5-Dichloro-2-iodo-3-trifluoromethylhexafluoro-pent-2-ene (12) *with Potassium Fluoride.*—4,5-Dichloro-2-iodo-3-trifluoromethylhexafluoropent-2-ene (8.0 g, 18.1 mmol) and potassium fluoride (15 g, 0.26 mol) were kept at 230 °C for 6 d. A mixture of (Z)- and (E)-1-chloro- and 5-chloro-undecafluoro(3-methylpent-2-enes) was produced, identical with that prepared from 5-chloro-2-iododecafluoro-(3-methylpent-2-ene).

Photochemical Isomerisation Reactions.—(a) *Perfluoro(3-methylhex-2-ene)* (7). The olefin (*ca.* 0.7 g) was sealed in a

silica n.m.r. tube and irradiated (lamp A). The $Z : E$ ratios, measured by integration of the [19]F n.m.r. peaks, were: 0 h, 1 : 5; 40 h, 1 : 2; 110 h, 1 : 1.2. No further change took place on further irradiation with lamp A. Irradiation for 250 h, with lamp B gave perfluoro(2-ethyl-pent-1-ene) (14) (45%) and perfluoro(2,3-dimethylpent-1-ene) (15) (30%) which were identified by their n.m.r. and mass spectra, and at least twenty minor components, including perfluoroethane, perfluoropropane, and silicon tetrafluoride.

(b) *Perfluoro(3-methylhex-3-ene)* (6). Irradiation (lamp A) of the olefin (*ca.* 0.7 g) gave the following $Z : E$ ratios: 0 h, 1 : 2; and 40 h, 1 : 1, with no further change. Further irradiation with lamp B, for 150 h gave perfluoro(2-ethyl-pent-1-ene) (14) (45%), perfluoro(2,3-dimethylpent-1-ene) (15) (9%), starting material (30%), and minor products with the same retention times as those formed in (*a*) above, but in different ratios.

(c) *Perfluoro(2,3-dimethylpent-2-ene)*. The olefin (8) (*ca.* 1.0 g) was irradiated (lamp A, 72 h) to give a mixture of (Z)-perfluoro(3,4-dimethylpent-2-ene) [(Z)-(16)] (9%), the (E)-isomer [(E)-(16)] (14%), perfluoro(2-ethyl-3-methylbut-1-ene) (17) (35%), perfluoro(2,3-dimethylpent-1-ene) (15) (23%), and perfluoro(2,3,3-trimethylbut-1-ene) (18) (19%), identified spectroscopically. Irradiation with lamp B, for 72 h of the olefin (8) (3 g, 8.6 mmol) gave a low-boiling mixture (0.3 g) of perfluoroethane and perfluoropropane, and a mixture (2.7 g, 90%) of the above olefins in the ratio (16) : (17) : (15) : (18) = 2 : 1 : 1 : 2.

(d) *Perfluoro(3-ethyl-2-methylpent-2-ene)* (19). The olefin (*ca.* 1.0 g) was irradiated (lamp A, 68 h) to give a mixture of (Z)-perfluoro(3-ethyl-4-methylpent-2-ene) [(Z)-(20)] (20%), the (E)-isomer [(E)-(20)] (40%), and perfluoro(2-ethyl-3,3-dimethylbut-1-ene) (21) (40%), separated by g.l.c. and identified spectroscopically. Irradiation with lamp B, for 7 d of the olefin (19) gave olefins (20) and (21) in a 1 : 1 ratio.

(e) *5-Chloroundecafluoro(2-methylpent-2-ene)* (11). A mixture of (Z)- and (E)-isomers (*ca.* 1.0 g, ratio 1 : 3.2) was irradiated (lamp A) to give mixtures of the same isomers (65 h, 1 : 3.1; 135 h, 1 : 2.8) together with increasing amounts of (E)-1-chloroundecafluoro(3-methylpent-2-ene) (10) (65 h, 17%; 135 h, 20%). Further irradiation with lamp B for 3 weeks resulted in the formation of a complex mixture containing only a small amount of starting material or of compound (10).

(f) *1-Chloroundecafluoro(3-methylpent-2-ene)* (10). The olefin [*ca.* 1.0 g, mainly the (E)-isomer], containing 35% of the 5-chloropentene (11), was irradiated with lamp A to give the following (10) : (11) ratios: 65 h, 7 : 3; and 240 h, 7 : 3. After irradiation with lamp B for 3 weeks a mixture with essentially the same [19]F n.m.r. spectrum as that in (e) above was obtained.

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