AN UNEXPECTED REACTION BETWEEN PERFLUOROISOBUTYLENE, CAESIUM FLUORIDE AND HALOFORMS

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Abstract—$(CF_3)_2C=CF_2$ reacts with CHCl, $CHBr_3$ and CHI_3 in the presence of CsF in diglyme, giving 3,3 - difluoro - 2 - halogeno - 4,4,5,5 - tetrakis(trifluoromethyl)cyclopent - 1 - enes. In the case of $CHCl_3$ the intermediate is shown to be 1,1 - dichloro - 3,3 - bis - (trifluoromethyl)allene (identified as an adduct with furan). 3,3 - Difluoro - 2 - chloro - 4,4,5,5 - tetrakis(trifluoromethyl)cyclopent - 1 - ene eliminates HCl under the action of CsF, giving a trimer of 3,3 - difluoro - 4,4,5,5 - tetrakis(trifluoromethyl)cyclopent - 1 - yne, namely, perfluorocarbon $C_{27}F_{42}$ (a Dewar benzene derivative).

Earlier the perfluoro - t - butylanion $(CF_3)_3C^-$ generated from $(CF_3)_2C=CF_2$ and CsF in aprotic dipolar solvents was shown to be capable of substituting halogen at carbon by the group $(CF_3)_3C^{1-3}$. Trying to extend this reaction, we investigated the interaction of the system $(CF_3)_2C=CF_2 + CsF$ with a number of geminal polyhalogen derivatives, namely, $C_6H_5CHCl_2$, $C_6H_5CCl_3$, $(C_6H_5)_2CCl_2$, CCl_4 and $CHCl_3$. Even though the reaction conditions were varied, none of the above-listed compounds could be introduced into the reaction, with the exception of chloroform which reacted exothermally with perfluoroisobutylene and caesium fluoride in diglyme or other similar solvents. The result proved to be unexpected: perfluorocarbon $C_{27}F_{42}$ was isolated, which fact prompted us to investigate this reaction in greater detail, as well as to study corresponding reactions with bromoform and iodoform.

RESULTS AND DISCUSSION

The interaction of $(CF_3)_2C=CF_2$ with CsF and $CHCl_3$, besides perfluorocarbon $C_{27}F_{42}$, gives 2 - H - 2 - trifluoromethylperfluoropropane (monohydroperfluoroisobutane) $(CF_3)_3CH$, CCl_4 and a compound $C_9HF_{14}Cl$. The reaction with $CHBr_3$ led to $(CF_3)_3CH$, CBr_4 and a compound $C_9HF_{14}Br$. In the case of CHI_3 a compound $C_9HF_{14}I$ was obtained together with $(CF_3)_3CH$ and perfluoro - t - butyliodide $(CF_3)_3CI$. In the case of $CHBr_3$ and CHI_3 perfluorocarbon $C_{27}F_{42}$ was not isolated.
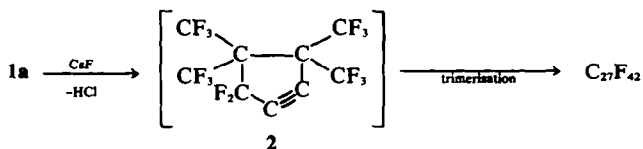
There are two points essential for the elucidation of the reaction picture. Firstly, all compounds of the structure $C_9HF_{14}X$ where X = Cl, Br or I have analogous IR-, mass-, NMR ^{19}F and ^{1}H spectra, whence it follows that they all have the same structure. These spectral data in combination with those of F–F double nuclear magnetic resonance
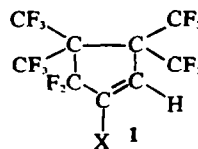

a: X = Cl
b: X = Br
c: X = I

unambiguously show that these compounds are 3,3-difluoro - 2 - halogeno - 4,4,5,5 - tetrakis(trifluoromethyl)cyclopent - 1 - enes (**1, a-c**). Secondly, one cannot fail to observe that perfluorocarbon $C_{27}F_{42}$ is a threefold fragment C_9F_{14} which can be obtained by elimination of hydrogen halide from compounds of type **1**. It is logical to suppose perfluorocarbon $C_{27}F_{42}$ to be a trimer of 3,3 - difluoro - 4,4,5,5 - tetrakis(trifluoromethyl)cyclopent - 1 - yne (**2**). Indeed, with the aid of GLC, we succeeded to show that the reaction of CsF in diglyme with cyclopentene (**1a**) gives perfluorocarbon $C_{27}F_{42}$, CsF behaving as a dehydrochlorinating agent.

It is quite obvious that the "building blocks" for the 5-member cycles constituting the basis of the structures of compounds (**1**) and perfluorocarbon $C_{27}F_{42}$ are two molecules of perfluoroisobutylene and one molecule of the haloform. With a view to throwing light on a possible pathway in which these cycles are formed, we attempted to trap the active intermediates participating in the process. To this end, the reaction of $(CF_3)_2C=CF_2$, CsF and $CHCl_3$ was conducted in the presence of cyclohexene, styrene and furan. In the latter case 5 - dichloromethylene - 6,6 - bis - (trifluoromethyl) - 7 - oxabicyclo/2,2,I/hept - 2 - ene (**4**) was obtained in a fair yield, this compound being a Diels-Alder

$$1a \xrightarrow[-HCl]{CsF} \left[\begin{array}{c} \text{(structure 2)} \end{array} \right] \xrightarrow{\text{trimerisation}} C_{27}F_{42}$$

2

adduct of furan and 1,1 - dichloro - 3,3 - bis(trifluoromethyl)allene (**3**). With cyclohexene and styrene no intermediates could be trapped, to say nothing of traces of dichloronorcarane obtained with cyclohexene. It should also be pointed out that CHCl₃ undergoes no changes when treated with CsF in diglyme under the same conditions as those under which its reaction with perfluoroisobutylene takes place.
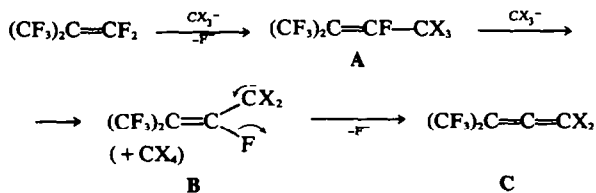

3   **4**
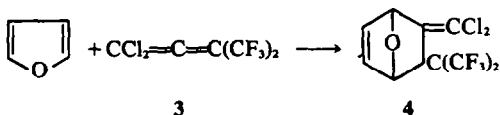
Taking the above-stated into account, it can be concluded that the main active intermediate of this reaction is a trihalogen methyl anion which is formed, evidently, as a result of exchange between perfluoro - t - butylanion and the haloform:

$$(CF_3)_2C=CF_2 + CsF \rightleftharpoons (CF_3)_3C^-Cs^+$$

$$(CF_3)_3C^- + CHX_3 \rightleftharpoons (CF_3)_3CH + {}^-CX_3$$
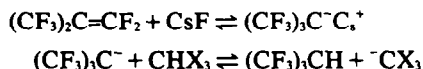
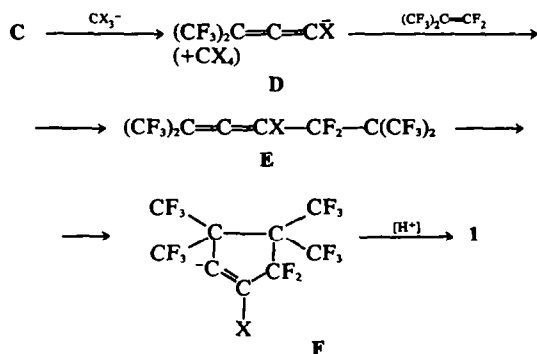This explains the formation of monohydroperfluoroisobutane $(CF_3)_3CH$ as well.

Further, a number of transformations can be pictured, whose sequence leads to 1,1 - dihalogeno - 3,3 - bis(trifluoromethyl)allenes (**C**). The trihalogenomethyl anion reacts with perfluoroisobutylene according to the conventional scheme of vinylic substitution, giving 1,1,1 - trihalogeno - 3 - trifluoromethylperfluorobut - 2 - ene (**A**) which interacts with the trihalogenomethyl anion with the formation of anion **B** and tetrahalogenomethane; elimination of the fluoride ion from anion **B** leads to allene **C** (if X = Cl this is the identified compound **3**). The formation of CCl₄ and

of the haloform, the perfluoroisobutylene molecule having already lost two fluorine atoms at the CF₂-group. Evidently, the reaction of allene C with the second molecule of perfluoroisobutylene gives the arrangement of atoms constituting the cycle in question. This process can be interpreted as follows. Allene **C** interacts with the anion CX_3^- giving CX_4 and anion **D**; the latter reacts with perfluoroisobutylene and cyclization of the resulting anion **E** with subsequent reaction of the cyclic anion **F** with any source of proton (haloform, caesium bifluoride) gives cyclopentene (**1**). The

$$C \xrightarrow[(+CX_4)]{CX_3^-} (CF_3)_2C=C=C\bar{X} \xrightarrow{(CF_3)_2C=CF_2}$$

D

$$\longrightarrow (CF_3)_2C=C=CX-CF_2-C(CF_3)_2 \longrightarrow$$

E

$$\longrightarrow \text{(structure F)} \xrightarrow{[H^+]} 1$$
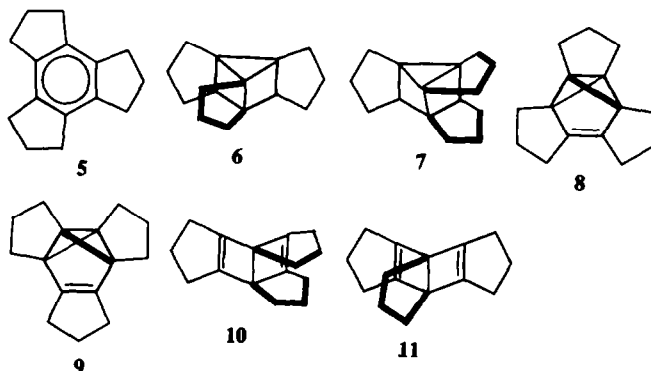
F

stage of conversion of anion **E** to cyclic anion **F** is not evident, since usually allene systems are attacked by nucleophiles at the central C atom. It may be supposed that there exist certain factors which favour this cyclization; anyway, the fact that no products were isolated corresponding to the linear anion **E** is noteworthy.

As has been stated above, compound **1a** when interacting with caesium fluoride in diglyme under mild conditions eliminates HCl giving perfluorocarbon $C_{27}F_{42}$. In the case of the reaction of $(CF_3)_2C=CF_2 + CsF$ with CHBr₃ and CHI₃ the

$$(CF_3)_2C=CF_2 \xrightarrow[-F^-]{CX_3^-} (CF_3)_2C=CF-CX_3 \xrightarrow{CX_3^-}$$

A

$$\longrightarrow (CF_3)_2C=C\underset{(+CX_4)}{\overset{CX_2}{\diagdown}} F \xrightarrow{-F^-} (CF_3)_2C=C=CX_2$$

B   **C**

CBr₄ can be thus explained. As to the reaction with CHI₃, $(CF_3)_3CI$ is formed due to iodination of the anion $(CF_3)_3C^-$ by the action of polyiodocompounds.

Allene **C** is a product of interaction of one molecule of perfluoroisobutylene with a molecule

formation of this perfluorocarbon is not observed. This may be attributable to the difficulty of proton abstraction from compounds **1b** and **1c** due to the unshared electron pair of the neighbouring halogen atom which repels the attacking fluoride ion the stronger the larger the atomic radius of the halogen;
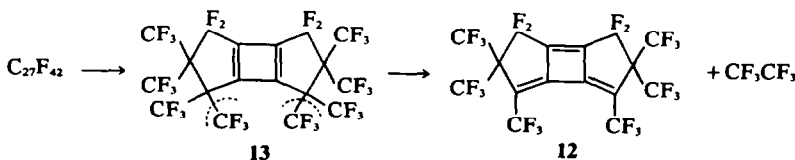
two CF$_3$-groups at the neighbouring C atom make the proton abstraction stage rather sensitive to steric effects.

We shall now consider the structrue of perfluorocarbon C$_{27}$F$_{42}$. Leaving the problem of orientation of the 5-membered cycles alone for a while, we can picture the following trimers of cyclopentyne: benzene (**5**), prismanes (**6**) and (**7**), benzvalenes (**8** and **9**), Dewar benzenes (**10** and **11**),

and by the formation of CF$_3$I when the reaction is carried out in the presence of iodine. In the latter case C$_2$F$_6$ is also formed, iodine being a less effective trapper of free radicals than bromine. Compound (**12**) does not react with iodine; as to bromine, according to the data of combined GLC-mass spectrometry, a small amount of a product of substitution of one of trifluoromethyl groups by the bromine atom is formed.


The choice between these structures can be made on the basis of the chemical and physico-chemical properties of perfluorocarbon C$_{27}$F$_{42}$. The benzene and prismane structures are in contradiction with the spectral data (see below). As regards benzvalenes and Dewar benzene (**10**), they must under heating easily transform to benzene (**5**) while for structure (**11**) such a transformation is impossible, since the resulting benzene should contain a 5-membered bridge to link two *para*-positions.

Perfluorocarbon C$_{27}$F$_{42}$ proved to be stable when heated in a sealed glass ampoule. Only at 270–290° conversion takes place which after several hours is practically quantitative, to 3,3,10,10 - tetrafluoro - 4,4,5,8,9,9 - hexakis(trifluoromethyl)tricyclo-(5.3.0.0) - 1,5,7 - decatriene (**12**) and hexafluoroethane. Evidently, cyclopentyne fragments undergo recombination with the formation of a dimer, i.e. cyclobutadiene (**13**) which is stabilized through the elimination of two trifluoromethyl groups. Deep

Heating of perfluorocarbon C$_{27}$F$_{42}$ with chlorine leads to a very deep transformation accompanied by the chlorinolysis of C–C bonds, this reaction starting at a somewhat lower temperature than decomposition of the pure compound or its decomposition in the presence of bromine or iodine.

The reaction gives hexachlorobenzene in an amount clearly exceeding that which could be expected from any structure (**5–11**) should C$_6$Cl$_6$ be formed only from the fragment containing the 6-membered carbon cycle. Among other reaction products CF$_3$Cl, CF$_2$Cl$_2$, CCl$_4$, C$_3$F$_6$Cl$_2$, C$_4$F$_9$Cl are identified. This reaction naturally, gives no indication regarding the structure of the initial perfluorocarbon C$_{27}$F$_{42}$.

The above data give grounds for considering perfluorocarbon C$_{27}$F$_{42}$ to be a trimer of cyclopentyne (**2**) with a structure of type **11**. Taking into account the asymmetry of cyclopentyne (**2**) and the

conversion of such kind and not isomerization to a compound of benzene type can hardly be explained as proceeding from structures **8**, **9** and **10**.

Elimination of trifluoromethyl groups occurs in the form of free trifluoromethyl radicals, which is substantiated by the formation of CF$_3$Br when the reaction is carried out in the presence of bromine

possibility of different orientation of the 5-membered rings in the formation of the trimer, three structures of type **11** can be considered.

There are no reasons for making a particular choice between these structures. Though in all the investigated cases this substance behaved as a chromatographically homogeneous one (GLC), yet

11a

11b

11c
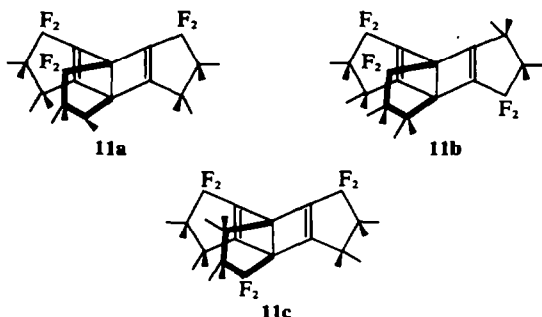
its being a mixture of compounds **11a-c** is not ruled out.

Spectral characteristics of compounds obtained

3,3 - *Difluoro* - 2 - *halogeno* - 4,4,5,5 - *tetrakis(trifluoromethyl)cyclopent* - 2 - *enes* (**1, a-c**). Spectral characteristics of these compounds are given in Table 1. Without quenching, signals $CF_3(4)$ and $CF_3(5)$ are multiplets. CF_2 and H are heptets. F–F double resonance spectrum has been investigated for compound **1b**. With the signal $CF_3(5)$ quenched, the signal $CF_3(4)$ becomes a triplet; with the signal $CF_3(4)$ quenched, the signal $CF_3(5)$ appears as a doublet; with CF_2 quenched, the signal $CF_3(4)$ becomes a heptet, and with $CF_3(4)$ quenched, the signal CF_2 becomes a singlet. Characteristic peaks in mass spectra: **1a** (for ^{35}Cl)—410 (M), 391 (M-F), 375 (M-Cl), 341 (M-CF₃); **1b** (for ^{79}Br)—454 (M), 435 (M-F), 385 (M-CF₃), 375 (M-Br); **1c** − 502 (M), 483 (M-F), 375 (M-I), 355 (M-H-F-I), 306 (M-I-CF₃).
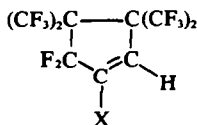
1a: X = Cl
b: X = Br
c: X = I

5 - *Dichloromethylene* - 6,6 - *bis(trifluoromethyl)* - 7 - *oxabicyclo* - */2.2.1/* - *hept* - 2 - *ene* (**4**). Ir spectrum: a weak absorption band at 1575 cm⁻¹, characteristic of the bicyclo/2.2.1/hept - 2 - ene

system[4] and a more intensive absorption band of another double bond at 1650 cm⁻¹. In the ^{19}F NMR spectrum signals of *exo* - CF₃ - group (− 12·8, quartet) and *endo* - CF₃ - group (− 17·4, quartet with additional splitting on the proton) are present.

Signals in ¹H NMR spectrum: H(I) 5·34, H(2) 6·51, H(3) 6·80, H(4) 5·53; $J_{H(2)-H(3)} = 6$, $H_{H(3)-H(4)} = 1·8$, $J_{H(1)-H(2)} = 1·2$, $J_{H(2)-CF_3} \approx 1$ (constants are determined by the NMR ¹H spectrum with quenching of ¹⁹F and ¹H). Mass spectrum (for ^{35}Cl): 312 (M), 283 (M-CHO), 249 (C₇F₆ClO), 229 C₈H₃F₆O, 217 C₉HF₃ClO, 213 C₇H₂F₃Cl₂, 195 C₇H₃F₂Cl₂, 179 C₇H₃F₃Cl, 163 C₈H₄F₄O, 145 C₈H₂F₅, 68 C₄H₄O. The character of fragmentation can be explained by that compound **4** under an electron impact isomerizes with the formation of compounds containing an aldehyde group. Rearrangement of such type for compounds of the 7 - oxabicyclo/2.2.1/ - 2,5 - heptadiene series in the presence of Rh(CO)₄Cl₂ is known.[5]

Compound **4** easily forms an adduct with phenylazide, this being characteristic of olefines with a double bond in a strained cyclic system.[6] The adduct has been obtained as two isomers. IR spectrum: high-melting isomer 1650 (C=C), 1600 (N=N), 1520, 1490, 1450 (aromatic C=C) cm⁻¹; low-melting isomer 1650 (C=C), 1600 (N=N), 1500, 1460 (aromatic C=C) cm⁻¹.

3,3,10,10 - *Tetrafluoro* - 4,4,5,8,9,9 - *hexakis(trifluoromethyl)tricyclo* /5.3.0.0/ - 1,5,7 - *decatriene* (**12**). IR spectrum: weak absorption bands at 1525 and 1545 (shoulder at 1565) cm⁻¹; UV spectrum (hexane as solvent): two absorption maxima $\lambda_1 = 272$ nm, $\epsilon_1 = 1700$; $\lambda_2 = 280$ nm, $\epsilon_2 = 2700$. ^{19}F NMR spectrum (in acetone): three signals at −15·7 (a), −11·4 (b) and +22·8 (c), the ratio of intensities 3:6:2. The signals appear as multiplets; with quenching of F(a), the signal F(b) becomes a triplet, F(c) becomes a heptet; with F(c) quenched, F(a) becomes a heptet and F(b), a quartet; $J_{F(A)-F(C)} = 3·5$,

Table 1. Spectral characteristics of 3,3 - difluoro - 2 - halogeno - 4,4,5,5 - tetrakis(trifluoromethyl)cyclopent - 1 - enes (**1a-c**)

Compound	Chemical shifts				Spin–spin interaction constants				Frequencies in IR spectrum, cm⁻¹	
	CF₃(5)	CF₃(4)	CF₂	H	CF₃(5)–H	CF₃(4)–CF₂	CF₃(5)–CF₃(4)		C=C	C–H
1a	− 13·1	− 10·1	+ 37·8	3·65	7·3	9·7			1655	2985
1b	− 14·3	− 11·4	+ 34·8	3·70	7·3	9·8	8·5		1650	2980
1c	− 15·7	− 11·4	+ 33·7	3·85	7·3	9·7			1620	2980

Constant $J_{CF_3(5)-CF_3(4)}$ is obtained from the F–F double resonance spectrum investigated only for compound (**1b**)
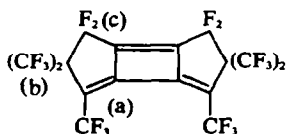
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$J_{F(A)-F(B)} = 6\cdot2$, $J_{F(B)-F(C)} = 10$. The mass spectrum contains intensive peaks with $m/e = 610$ (M), 591 (M-F), 541 (M-CF$_3$), 472 (M-2CF$_3$), 453 (M-2CF$_3$-F).

Perfluorocarbon $C_{27}F_{42}$. IR spectrum: absence of absorption maxima above $1500\,cm^{-1}$; in the QR spectrum a medium-intensity band $1683\,cm^{-1}$, indicative of the presence of a double bond. UV spectrum has no absorption maxima above 200 nm. ^{19}F NMR spectrum: three broad signals at $-12\cdot0$, $-11\cdot4$ and $+29\cdot4$ with the ratio of intensities $3:3:1$, which corresponds to $2CF_3:2CF_3:CF_2$. The spectrum changes but little with temperature; the structure of the signals could not be revealed by the F–F double resonance method. The character of the ^{13}C NMr spectrum corresponds to the molecule being based on the structural unit of 3,3 - difluoro - 4,4,5,5 - tetrakis(trifluoromethyl)cyclopent - 1 - yne (2). The spectrum has been measured on a "Bruker HX-90" in SO$_2$FCl and CFCl$_2$CFCl$_2$ with quenching ^{19}F and without quenching it (more than 220,000 stored records) (Table 2).
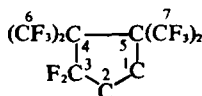

Table 2. ^{13}C NMR spectrum of perfluorocarbon $C_{27}F_{42}$

Atom ^{13}C	1	2	3	4[b]	5[b]	6, 7
Chem. shifts[a]	$-12\cdot0$	$-19\cdot2$	$+26\cdot6$	$+59\cdot0$	$+76\cdot7$	$+18\cdot0$
	(s)	(tr)	(tr)			$+18\cdot5$
						(quartets)
						287
$J_{^{13}C-^{19}F}$		22	286			290

[a] From internal standard CFCl$_2$CFCl$_2$.
[b] These signals can be seen only when ^{19}F is quenched.

One has to admit that though in structure of type 11 one of the rings (containing no double bond) differs from the other two rings, this difference contributes little to the electron shielding of the atoms, however, broadened the character of ^{19}F signals may be explained by this difference and by the different orientation of the 5-membered cycles.

The mass spectrum of perfluorocarbon $C_{27}F_{42}$

contains an intensive peak with $m/e = 69$ (CF$_3$), the heaviest of the observed fragments has $m/e = 748$, which corresponds to the dimer of cyclopentyne (2); but in the whole the picture of decay conveys little information, since it consists of a great number of low-intensity peaks.

EXPERIMENTAL

IR spectra have been recorded on an "UR-20" spectrophotometer; Raman spectrum has been recorded on a "Coderg PHO" spectrometer, and UV spectra have been recorded on a "Hitachi EPS-3T". NMR spectra have been investigated on spectrometers "Bruker HX-90" (working frequency for ^{19}F, $84\cdot6$ MHz, for ^{13}C, $22\cdot635$ MHz); "NMR-100 JEOL" (working frequency for ^{1}H, 100 HMz); "Perkin-Elmer R-12" (working frequency for ^{1}H, 60 MHz); and "Hitachi H-60" (working frequency for ^{19}F, $56\cdot4$ HMz). Chemical shifts are given in PPM: ^{1}H from the external standard TMS in δ-scale, ^{19}F from the external standard CF$_3$COOH; constants of spin-spin interaction J are given in Hz. Mass spectra and combined GLC-mass spectra have been obtained on a "CH-8 Varian", electron energy, 70 eV.

Interaction of perfluoroisobutylene with chloroform and caesium fluoride. Into a suspension of freshly calcined finely comminuted caesium fluoride ($15\cdot2$ g; 100 mmol) in 30 ml anhyd diglyme perfluorisobutylene (20 g; 100 mmol) was slowly introduced while stirring (weakly exothermal reaction). Then, under stirring, anhyd chloroform ($11\cdot9$ g; 100 mmol.) was added dropwise; the mixture became yellow and the temp rose to 40°. Stirring was continued at room temp for 3 h, then under heating to 40–50° for 1 h; after that the mixture was cooled, the ppt separated and extracted with hexafluorobenzene or 1,1,2 - trifluoro - 1,2,2 - trichloroethane. The solvent was evaporated and perfluorocarbon $C_{27}F_{42}$ obtained in the form of colourless crystals, m.p. 96–98° (from hexane). The yield in separate experiments varied from 0·6 to 1·4 g. (Found: C, 28·90; F, 71·18; mol.wt. (precision ebullioscopy, solvent - hexafluorobenzene), 1121 ($\pm2\%$)*. Calc for $C_{27}F_{42}$: C, 28·88; F, 71·12%. mol.wt., 1122·27). The substance was readily soluble in hexafluorobenzene, freons, perfluoropiperidine, sulphurylfluorochloride, but poorly soluble in conventional organic solvents. Under ordinary conditions it did not react with bromine, potassium permanganate or sulphuric acid.

The filtrate was subjected to distillation, gathering fractions with a b.p. from 30 to 120°. In the lower-boiling fractions, perfluoroisobutylene, (CF$_3$)$_3$CH, CHCl$_3$ and CCl$_4$ were identified by GLC, NMR and mass spectrometry. From a fraction with b.p. 80 to 120° compound 1a b.p. 118° (micromethod) was isolated by preparative GLC. (Found: C, 26·29; H, 0·28; F, 64·67; Gl, 7·92. Calc. for C$_5$HF$_{14}$Cl: C, 26·31; H, 0·24, F, 64·79; Cl, 8·65%).

Interaction of perfluoroisobutylene with bromoform and caesium fluoride. To a mixture of perfluoroisobutylene, (20 g; 100 mmol) and caesium fluoride (15·2 g; 100 mmol) (50 ml) bromoform (20 g; 79 mmol) was added gradually under stirring. The mixture became very dark and the temp rose to 60°. On completion of the reaction the mass was poured into water, the aqueous layer was decanted, and the organic layer was separated into the crystalline and liquid fractions. The crystals (about 15 g) proved to be carbon tetrabromide; their m.p., as well as that of a mixture with authentic sample, was 92–94°. The liquid part

was dissolved in ether, the solution was dried with MgSO₄, the ether was distilled off and the residue was distilled. A fraction (1·6 g) with b.p. 127–130° was obtained, according to GLC data mainly consisting of compound **1b** (the yield about 17%). The substance was separated by preparative GLC; b.p. 138° (micromethod). (Found: C, 24·18; H, 0·30; F, 53·87; Br, 17·40. Calc. for C₉HF₁₄Br: C, 23·74; H, 0·22; F, 58·48; Br, 17·78%). Among volatile products (CF₃)₃CH was identified.

Interaction of perfluoroisobutylene with iodoform and caesium fluoride. To a mixture of perfluoroisobutylene, (10 g; 50 mmol) caesium fluoride (7·6; 50 mmol) and diglyme (40 ml), a soln of iodoform (10 g; 25 mmol) in diglyme (10 ml) was added under stirring. There was intensive darkening and the temp rose to 40°. The stirring was continued for 1 h while heating to 40°, then the volatile part of the mixture was distilled off under a slight vacuum and moderate heating into a trap cooled down to −78°, the remaining part of the mixture was poured into water, the organic layer was dissolved in ether, dried (MgSO₄), and the ether was distilled off. From the residue by the method of preparative GLC, **1c** was isolated, b.p. 156° (micromethod). (Found: C, 22·02; Calc for C₉HF₁₄I: C, 21·51%). The contents of the trap were (CF₃)₃Cl with an admixture of (CF)₃CH.

Interaction of perfluoroisobutylene, chloroform, caesium fluoride and furan

5 - Dichloromethylene - 6,6 - bis(trifluoromethyl) - 7 - oxabicyclo/2.2.1/hept - 2 - ene (**4**). To a mixture of perfluoroisobutylene, (20 g; 100 mmol) caesium fluoride (15·2 g; 100 mmol) and diglyme (50 ml) prepared as described above, furan (19 g; 280 mmol) was added and then, gradually and under stirring, CHCl₃ (17 g; 142 mmol.) The mixture became yellow and the temp rose to 35°. Then the mixture was heated under stirring for 2 h at 35°, after which 10 g of unreacted perfluoroolefine were distilled off. The mixture was poured into water, the lower layer separated, dissolved in ether, the solution was dried (MgSO₄) and the ether was distilled off. The residue crystallized yielding 9 g (57·5%) of compound **4**, m.p. 52–53° from 90% alcohol. (Found: C, 34·69; H, 1·34; F, 36·70; Cl, 22·56; mol.wt. (cryoscopically in benzene),

306·5. Calc for C₉H₄F₆Cl₂O: C, 34·50; H, 1·28; F, 36·42; Cl, 22·68%; mol.wt., 313·03). Among volatile reaction products (CF₃)₃CH and CCl₄ were identified.

To phenylazide (0·5 g; 5 mmol) compound **4** (1·5 g; 5 mmol) was added. The mixture was first liquid, then after 1·5 h it crystallized. Another 0·5 g of phenylazide were added, after a period of 24 h the crystals were filtered off and washed with hexane yielding 1·6 g (76·1%) of an adduct with m.p. 172–174° from dimethylformamide. (Found: C, 41·56; H, 2·83; F, 26·09; Cl, 16·44; N, 9·77%). By evaporation of hexane 0·2 g (9·5%) of an adduct were obtained with m.p. 123–125° from hexane. (Found: C, 41·76; H, 2·22; F, 26·59; Cl, 16·94, N, 9·46%. Calc for C₁₅H₉F₆Cl₂N₃O: C, 41·69; H, 2·10; F, 26·38; Cl, 16·43 N, 9·72%).

3,3,10,10 - Tetrafluoro - 4,4,5,8,9,9 - hexakis(trifluoromethyl)tricyclo (5.3.0.0) - *1,5,7 - decatriene* (**12**). Perfluorocarbon C₂₇F₄₂ (1·0 g) was heated for 6 h in a sealed glass ampoule at 280 ± 10°. Compound **12** (0·89), m.p. 78–79° from hexane were obtained. The yield was practically quantitative. (Found: C, 31·51; F, 68·65; mol.wt. (cryoscopically in CFCl₂CFCl₂), 605. Calc. C₁₆F₂₂: C, 31·48; F, 68·50; mol.wt., 610·16). The substance was soluble in many of organic solvents; it instantly decolorized a soln of KMnO₄ in acetone.

In gaseous phase hexafluoroethane, CO₂, CF₄, CHF₃ were identified. The walls of the ampoule were coated with carbon and noticeably corroded.

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