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Thermal reactions of hexafluoro-1,3-butadiene. Part II. Synthesis and thermal transformations of $C_{12}F_{18}$ trimers*

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Abstract

Hexafluoro-1,3-butadiene reacts at ⩾150 °C with its cyclodimers containing trifluorovinyl groups to give all the trimers expected for [2+2]- and [2+4]-cycloadditions. The ratios of the products formed depend on the temperature and are determined by the stabilities of the dimers and trimers concerned. All those trimers which contain a cyclobutane moiety take part in thermal transformations, such as ring expansion, dimerization and retrocycloaddition reactions. Hexafluoro-1,3-butadiene and its dimers, which are formed in retrocycloaddition reactions, undergo secondary thermal transformations. The latter include the previously unknown insertion of a hexafluorobutadiene molecule into the four-membered ring of one of the dimers.

Introduction

Non-catalytic thermal reactions of conjugated dienes are characterized by a low degree of oligomerization, their main products being the cyclodimers of 1,3-dienes [2] although 1,3-butadiene also gives small quantities of a trimer [3]. Earlier work has shown that *F*-1,3-butadiene[†] gives dimers and trimers of an unknown structure [4].

The application of modern research methods as a means of studying the thermal reactions of *F*-1,3-butadiene has allowed us to determine the structures of its various dimers **2**–**6** [1]. We have also shown that the formation of the [2+2]- and [2+4]-cycloadducts **2**–**4** at temperatures ⩾150 °C is accompanied by secondary processes. As previously described [1], these include the isomerization of dimers **3** and **4** into dimers **1** [5], **2**, **5** and **6**, and the formation of trimers **7**–**11** which is studied further in the present work. This paper also provides proofs for the structures of the trimers obtained as well as descriptions of their thermal transformations as shown in Scheme 1.

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*For Part I, see ref. 1.

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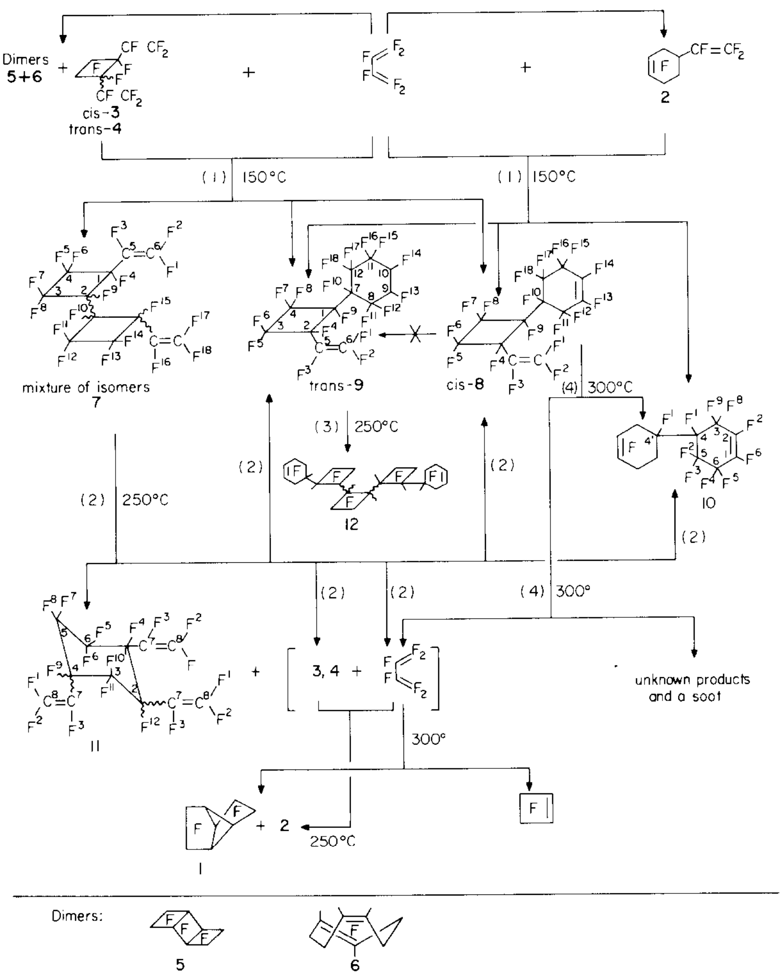
[†] *F*- corresponds to perfluoro-.



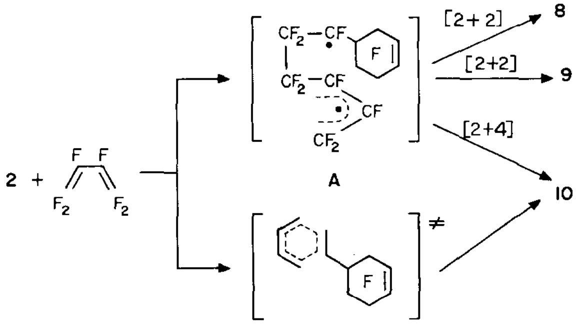
Scheme 1.

Results and discussion

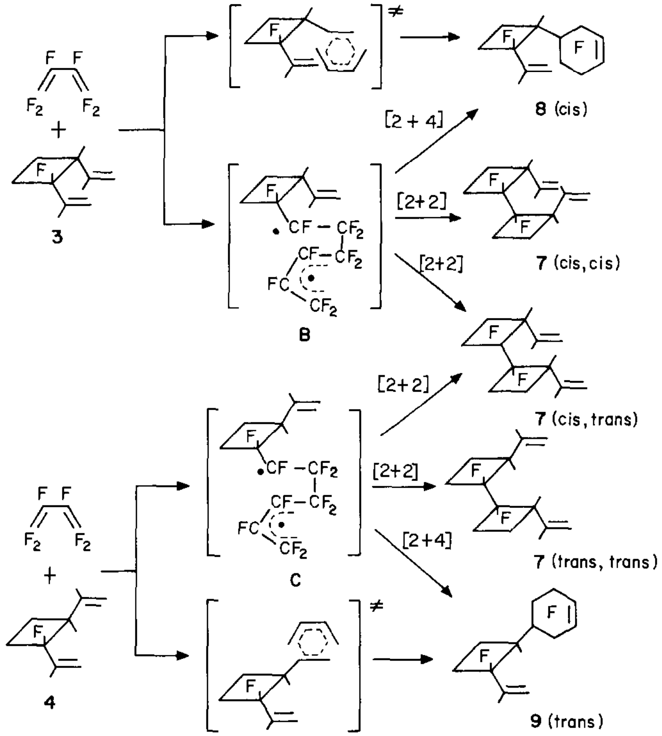
The formation of trimers

When *F*-butadiene is heated (at 150 °C) with its dimers **3** and **4**, it simultaneously produces dimers **2–5** and the trimers **7–10** [Scheme 1, reaction (1)]. Since the formation of products via trimolecular collisions is highly improbable, trimers **7–10** are obviously generated as a result of the reaction of *F*-butadiene with its dimers (cf. ref. 3).

Of the two competing processes, i.e. *F*-butadiene dimerization and reaction with its dimers, the former has proved to be considerably more rapid [at 150 °C, the dimer/trimer ratio was 95:5 after 28 h and 80:20 after 128 h]. All the trimers found have structures corresponding to the [2+2]- or [2+4]-cycloadducts of *F*-butadiene and its dimers, including dimer **2** generated directly via reaction (1). Both [2 + 2]- and [2 + 4]-cycloadditions of *F*-butadiene to dimer **2** can produce trimers **8–10** (Scheme 2) while its cycloaddition to dimers **3** and **4** can result in the formation of trimers **7–10** (Scheme 3). As can be seen from Schemes 2 and 3, trimers **8** and **9** can either be the [2 + 4]-cycloadducts of *F*-butadiene and dimers **3** and **4** or the [2 + 2]-cycloadducts of *F*-butadiene and dimer **2**. Trimers **7** can only be derived from dimers **3** and **4**, while trimer **10** can only be derived from dimer **2**.



Scheme 2.



Scheme 3.

Since only [2 + 4]-cycloaddition is allowed as a concerted process for thermal reactions, the formation of [2 + 2]-cycloadducts in reaction (1) evidently proceeds via a stepwise radical mechanism, while [2 + 4]-cycloadducts can be products both of Diels–Alder concerted reactions or of stepwise reactions with the biradical intermediates **A–C**, which are common to both [2 + 4]- and [2 + 2]-cycloadditions (Schemes 2 and 3).

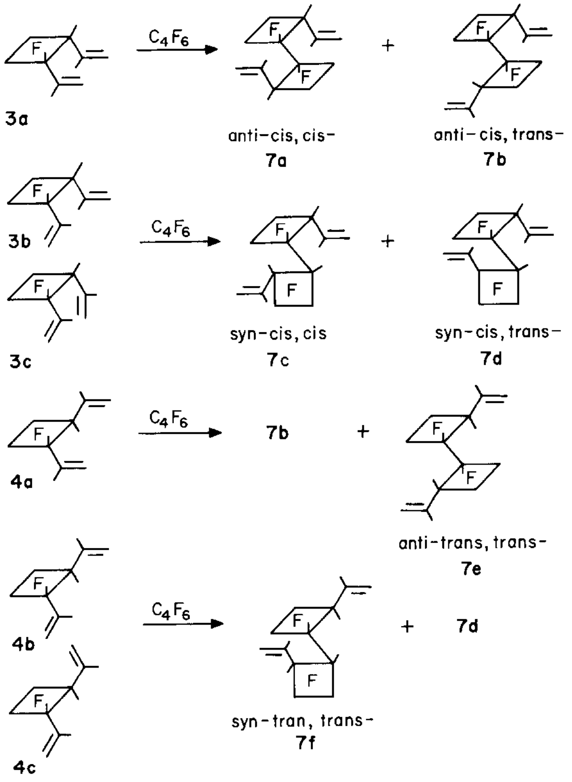
Comparison of the composition of trimers **7–10** generated in reaction (1) [at 150 °C and after 28 h, the ratio **7**/(**8** + **9**)/**10** = 4.5:8:1] and in the thermal reaction of *F*-butadiene [at 150 °C and after 56 h, the ratio **7**/(**8** + **9**)/**10** = 1.2:6:1] enables an approximate evaluation of the relative contribution of [2 + 2]- and [2 + 4]-processes. This shows that [2 + 4]-cycloaddition amounts to *c.* 15% of the reactions of dimer **2** and *c.* 35% of the reactions of dimers **3** and **4**. Hence, in reaction (1), *c.* 25% of trimers **8** and **9** are derived from dimers **3** and **4** as a result of [2 + 4]-cycloaddition and *c.* 75% arise from dimer **2** due to [2 + 2]-cycloaddition.

All the expected [2 + 2]- and [2 + 4]-cycloadducts of *F*-butadiene and dimers **2–4** were found among the products of reaction (1) (Schemes 2 and 3). In addition, according to GLC and NMR spectroscopy data, the mixture of [2 + 2]-cycloadducts (**7**) contains six isomers instead of the expected three, viz. *cis,cis*-, *cis,trans*- and *trans,trans*- (Scheme 3). In order to explain this fact, it is apparently necessary to suppose that dimers **3** and **4** exist as the conformers **3(a–c)** and **4(a–c)**, respectively [1], and that these afford in [2 + 2]-cycloaddition reactions with *F*-butadiene both *syn* and *anti* adducts (Scheme 4) which are incapable of mutual transformation. Hence the total number of theoretically possible isomers for **7** increases to six, as indeed observed experimentally.

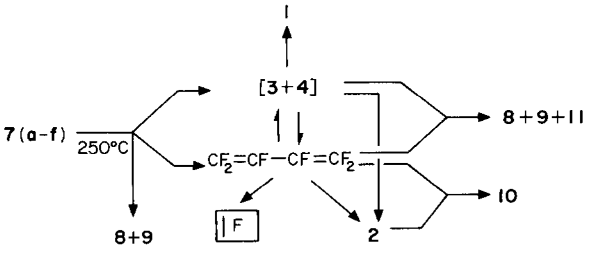
The thermal reactions of trimers 7

A study of the thermal reactions of trimers **7** has shown that all the isomers are stable up to 200 °C. At higher temperatures (⩾ 250 °C), retrocycloaddition reactions accompanied by secondary processes are observed [Scheme 1, reaction (2)]. Even at 250 °C trimers **7** react almost completely (the extent of conversion is *c.* 95%). The formation of all the products of reaction (2) can readily be explained if the transformation of trimers **7** is assumed to start with a retrocycloaddition reaction, yielding *F*-butadiene and the dimers **3** and **4** (Scheme 5). Thus, dimer **1** can be derived from dimers **3** and **4**, dimer **2** from *F*-butadiene or from dimer **4** [1], *F*-cyclobutene from *F*-butadiene [6], and trimers **8–11** can be adducts of *F*-butadiene and dimers **2–4** (Scheme 5). In addition, trimers **8** and **9** can be formed as a result of the isomerization of trimers **7** competing with retrocycloaddition. Just like direct cycloaddition, retrocycloaddition must proceed via a stepwise reaction which starts with a C(1)–C(2) bond breaking in a ring leading to the formation of intermediates **D** and **E** from conformers **7(A, B)** (Scheme 6).

Stabilization of these intermediates, which differ in the structure of their allylic radicals (**D**, *trans*: **E**, *cis*) can result in different products. Both biradicals are capable of eliminating an *F*-butadiene molecule to form dimers



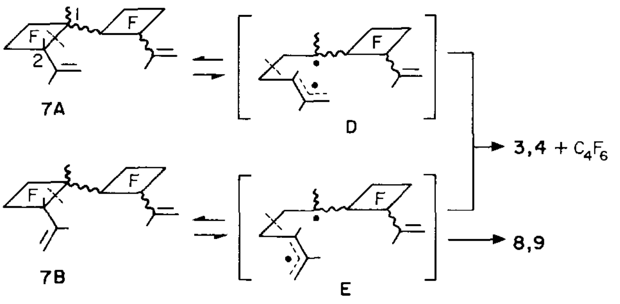
Scheme 4.



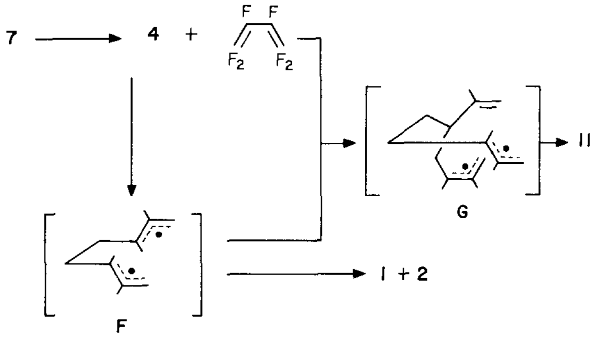
Scheme 5.

3 and **4** (retrocycloaddition) or to recombine yielding the initial trimers **7**. In addition, biradical **E**, which has the *cis* structure for its allylic radical, can be closed to form a six-membered ring and to yield trimers **8** and **9** (isomerization). Thus, trimers **8** and **9** can arise as products of the isomerization of trimers **7** (Scheme 6) or of the [2+4]-cycloaddition of *F*-butadiene to dimers **3** and **4** (Scheme 5). Both processes can be achieved via reaction (2) either as competing or excluding reactions.

Trimer **11** (Scheme 5, cf. refs. 7 and 8) was not found among the products of reaction (1) or of the thermal reaction of *F*-butadiene at

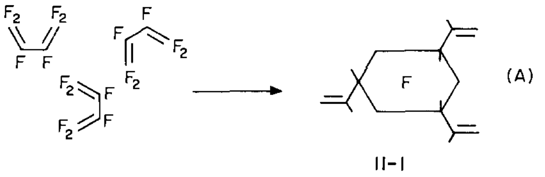


Scheme 6.



Scheme 7.

150 °C. Its formation in reaction (2) can be considered to be the result of a process which competes with the isomerization **4** → **1** + **2**. As described earlier [1], the isomerization of dimer **4** (⩾ 200 °C) starts with cyclic C(1)–C(2) bond breakage and generation of biradical *F* (Scheme 7). Apparently, under the conditions of reaction (2), biradical **F** is trapped by an *F*-butadiene molecule. Then, closure of biradical **G** occurs, giving rise to trimer **11** having a non-symmetrical structure. The alternative trimolecular reaction (A) is highly unlikely and, in addition, should yield the symmetrical trimer **11-1** which was not found among the products of reaction (2).



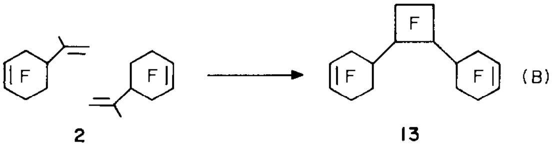
The thermal reactions of trimer 9

The existence of trimers **8** and **9** in the mixture arising from reaction (2) (Scheme 1) demonstrates their relative stability at 250 °C. On prolonged heating (250 °C, 40 h), however, the slow formation of the *F*-butadiene hexamer (**12**) occurred while the mixture of unreacted trimers became enriched with trimer **8**. Thus, even at 250 °C, trimer **9** undergoes [2+2]-cyclodimerization [Scheme 1, reaction (3)]. At 300 °C, reaction (3) proceeds more rapidly but is accompanied by tar formation.

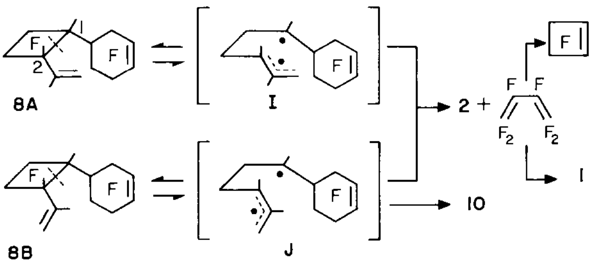
The thermal reactions of trimer 8

In contrast to trimer **9**, the corresponding isomer **8** does not take part in reaction (3). This inability to undergo [2+2]-cycloaddition is obviously explained by steric hindrance, arising from the *cis* arrangement of the trifluorovinyl and cyclohexenyl substituents in the molecule of trimer **8**. Trimer **8** proved to be stable up to 250 °C. At higher temperatures, a reaction occurred which yielded *F*-cyclobutene, dimers **1** and **2**, trimer **10**, a tar and a soot [Scheme 1, reaction (4)]. This shows that there are at least two competing processes, i.e. retrocycloaddition and the isomerization **8**→**10**, participating in reaction (4). As seen in Scheme 8, trimer **8**, which exists as the conformers **8A** and **8B**, can lead to the biradical intermediates **I** and **J**. The latter can be stabilized by decomposition to *F*-butadiene and dimer **2** (retrocycloaddition) or by closure to the initial trimer **8**. In addition, intermediate **J**, which has the *cis* structure for its allylic radical, can be closed to yield a six-membered ring and to generate trimer **10** (isomerization). It should be noted that the absence of trimer **9** and hexamer **12** from amongst the products of reaction (4) must exclude the isomerization **8**→**9**, although this could also proceed via the biradical intermediates **I** and **J**.

According to Scheme 8, the ratio of dimers **1** and **2** in the products of reaction (4) must be ≤ 1, which contradicts the observed value of *c*. 13. Incidentally dimer **2** is stable at 300 °C [1] and its possible [2+2]-cyclodimerization [reaction (B)] must afford the *F*-butadiene tetramer **13**, which



was not found among the products of reaction (4). It follows, therefore, that Scheme 8 depicts only a part of the transformations which occur, while reaction (4) also involves processes which affect cyclohexene along with the



Scheme 8.

cyclobutane moieties of molecule **8** and result in the formation of noticeable quantities of tar and soot. Trimer **10** is also stable at 300 °C.

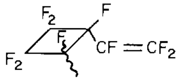
Thus, a study of the thermal stability of trimers **7–10** has shown that all of them are stable up to 200 °C and hence cannot be the source of dimers **1** and **5** at 150 °C (cf. ref. 1).

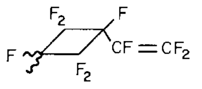
Spectral characteristics and proofs of structures

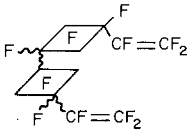
According to elemental analyses and mass spectrometric data, the products **7–11** are *F*-butadiene trimers. Trimers **7–10** were isolated in the pure state by preparative GLC methods, trimer **7** being obtained as a mixture of isomers while trimer **8** was obtained after heating the mixture of trimers **8**+**9** at 300 °C. Trimer **11** could not be obtained in the pure state. Chromatographic mass spectrometric and NMR spectroscopic methods demonstrated that trimer **11** was contaminated by *c*. 25% of trimers **7**.

*Mixture of octadecafluoro[2,2′-divinyl-bicyclobutyl] isomers **7(a–f)***

The IR spectrum of the trimer with a boiling point of 163–164 °C exhibited an intense $\nu(C{=}C)$ band at a frequency of 1786 cm^{-1} characteristic of the trifluorovinyl group. The ^{13}C NMR spectrum consisted of five resonances with the relative intensity ratio 1:1:2:1:1 demonstrating the identity of the two ‘halves’ of the trimer molecule. Two of the four resonances of unit intensity corresponded to tertiary C atoms, two others to the C atoms of the trifluorovinyl groups, while the peak of double intensity corresponded to the carbon atoms of the CF_2 groups. The spectrum described conforms with a molecule which consists of two identical ‘halves’ **K** (structure **7**) or **L** (structure **7-1**).


K


L


7-1

The choice between structures **7** and **7-1** in favour of the former was made in the following way. Since the trimer can only be derived from dimers **3** and **4**, for which the structure **L** was rejected earlier [1], one of the ‘halves’ of the trimer must have structure **K** while the molecule which consists of two identical ‘halves’ must be structure **7**. The ^{19}F NMR spectrum exhibited several groups of uniform signals having different intensities, and demonstrated the presence of several $C_{12}F_{18}$ isomers. A more detailed study of the ^{19}F NMR spectrum became possible after separation of the isomer mixture into three fractions consisting of two isomers each with impurities. This revealed that the mixture contained six isomers, one being present in negligible quantity. A tentative assignment of isomers **7** (Table 1) was achieved by ^{19}F NMR spectroscopy.

TABLE 1

^{19}F NMR spectra of hexafluoro-1,3-butadiene trimers **7(a–f)**

Compound	Chemical shifts − δ (ppm)																	
	F(1)	F(2)	F(3)	F(4)	F(5)	F(6)	F(7)	F(8)	F(9)	F(10)	F(11)	F(12)	F(13)	F(14)	F(15)	F(16)	F(17)	F(18)
7a	8.96	27.0	110.8	105.0	44.2	49.0	44.5	49.3	107.0									
7b	10.1	26.45	~111	93.7	44.6	49.6	44.6	49.6	107.4	108.0	44.6	49.6	44.6	49.6	105.1	~111	26.45	10.4
7d	7.7	24.8	112.6	91.9	42.3	48.6	48.0	49.0	107.7	111.4	44.2	52.6	45.4	52.2	106.8	110.3	27.5	10.7
7e	9.95	27.75	110.9	98.1	41.2	47.6	44.4	49.26	107.4									
7f	8.3	25.25	111.6	89.8	44.4	50.2	48.1	49.6	107.8	110.1	48.2	49.9	44.5	52.2	105.9	110.9	25.4	8.7

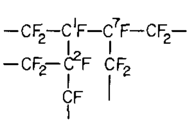
Compound	Coupling constants J(F–F) (Hz)																	
	1–2	1–3	2–3	5–6	7–8	11–12	13–14	15–17	16–17	16–18	17–18	2–?	2–?	2–?	17–?	17–?	17–?	17–?
7a				224	224	224	224											
7b			113	226	226	226	226		113									
7d[a]	45	36	113	230	228	228	237	48.5	112.5	34.5	57.5	25.0	21.5	9.5	21.5	4.5	3.5	
7e	57	35	112	232	232	232	232		112	35	57	47	12	6.6	47	12	6	6
7f[b]	46	37	113	244	233	233	233		114	36	49	35	8.8		38	6	6	

[a] Other constants: J(3–?), 41, 21.6, 17, 4, 4, 3; J(4–?), 22, 22, 15, 15, 8, 5.5, 5.5; J(5–?), 29, 23, 5.5, 5.5, 5.5; J(6–?), 5.3, 2.7, 2.7, 2.7; J(8–?), 6, 6, 6, 3, 3, 3; J(10–?), 37, 7, 22.8, 21.6, 15.6, 14.4; J(11–?), 22, 4, 4, 4, 4; J(12–?), 22, 6.6, 4.8, 2; J(13–?), 30, 21.6, 5, 5, 2.6, 2.6, 2.6; J(14–?), 18.6, 6, 4.8; J(15–?), 41, 41, 15.6, 7.7, 4.5, 4; J(16–?), 41, 24, 16.8; J(18–?), 3.2 Hz.

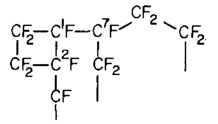
[b] Other constants: J(3–?), 52, 23.5, 17, 13, 4; J(10–?), 46, 23, 23, 23; J(18–?), 7 Hz.

cis- *and* trans-*Dodecafluoro[1-(4-cyclohexenyl)-2-vinylcyclobutanes] (8) and (9)*

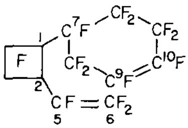
The ^{19}F NMR spectra of the trimers exhibited resonances of 18 F atoms each and were of the same type, thus demonstrating that the trimers are not structural isomers. The ^{13}C NMR spectrum of one isomer included resonances corresponding to 12 C atoms, four being atoms, three being tertiary C atoms and the remaining four being in CF_2 groups. The spin–spin coupling of the C and F atoms, observed in the spectrum, allowed the establishment of the carbon framework of the molecule in the following manner. The J(C–F) constants demonstrate that the tertiary C(1) and C(2) atoms are each bonded to two CF and one CF_2 groups, while the C(7) atom is bonded to one CF and two CF_2 groups (fragment **M**). In contrast, at least four of the five CF_2 groups are bonded to one CF and to one CF_2 group each (fragment **N**). Two of the four sp^2 atoms [C(5) and C(6)] are involved in a $-CF{=}CF_2$ group while the other two [C(9), C(10)] are in a $-CF{=}CF-$ group. Total combination of the ^{13}C NMR data corresponds solely to structure **O**. The vibrational spectra of both products did not contradict structure **O** and indicated that the trimers in question were not structural isomers. Thus, the Raman spectrum of the first trimer exhibited two intense polarized bands due to $\nu(C{=}C)$ vibrations with frequencies at 1781 and 1709 cm^{-1}, respectively. These correspond to the intense band at 1781 cm^{-1} and the band of medium intensity at 1710 cm^{-1} in the IR spectrum.



M



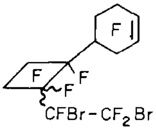
N



O

A similar picture was observed in the vibrational spectrum of the second trimer, where intense polarized Raman bands at 1781 and 1708 cm^{-1} conformed with the intense band at 1780 cm^{-1} and the band of medium intensity at 1711 cm^{-1} in the IR spectrum. The existence of a band at 1780 cm^{-1} in the vibrational spectra of trimers **O** may be due to the $\nu(C{=}C)$ vibration of the $CF{=}CF_2$ groups, while a band at 1710 cm^{-1} may be attributed to vibration of the $CF{=}CF$ groups. The correctness of this assignment has been confirmed by the results of the bromination of the trimers. It is known that bromination of the $CF{=}CF_2$ group occurs readily and is often accompanied by the evolution of heat, whereas bromination of the $CF{=}CF$ group only occurs under more severe conditions. This allows the selective bromination of the $CF{=}CF_2$ groups in the presence of $CF{=}CF$ groups which remain unchanged [9].

On the basis of the above considerations it is possible to assign the



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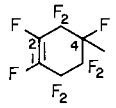
band at 1710 cm^{-1}, which is present in the IR spectra of the trimers and their bromination products **14**, to the ν(C=C) vibration of the CF=CF groups. In turn, the band at 1780 cm^{-1}, observed in the spectra of the trimers but absent from the spectra of bromides **14**, corresponds to the ν(C=C) vibrations of the $CF=CF_2$ groups. The frequency of the CF=CF group vibration (1710 cm^{-1}) is lower than that observed in the vibrational spectrum of *F*-cyclohexene (1749 cm^{-1}) [10]. There is no clear explanation for this observation since a similar decrease is not observed in the spectrum of dimer **2** [1].

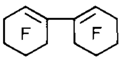
The ^{19}F NMR spectrum of each trimer exhibited resonances corresponding to three F atoms [F(1)–F(3)] being in a $CF=CF_2$ group, three F atoms [F(4), F(9), F(10)] being bonded to tertiary C atoms, two F atoms [F(13), F(14)] being located with a C=C double bond and 10 F atoms forming pairs of AB-systems and being located in five CF_2 groups (some of these exhibit a coupling constant $J(AB) \approx 220$ Hz while part exhibit a coupling constant $J(AB) \approx 290$ Hz). In the spectra of both trimers, four of the five AB-systems exhibit closely similar chemical shifts and consequently the spectra provide little further information in this region. When the spectra of the two trimers were compared, a noticeable difference in the chemical shifts of the tertiary atoms F(4) and F(9) as well as the proximity of the chemical shifts for the other F atoms was observed. This suggests that since the trimers are not structural isomers they differ in the mutual arrangement of the F(4) and F(9) atoms and, accordingly, in the arrangement of the trifluoromethyl and cyclohexenyl groups. Hence, they are the *cis* and *trans* isomers **8** and **9** having the **O** structure. Since the *cis* isomer is both sterically hindered and unfavourable, we have assigned its structure (**8**) to the trimer which is formed in smaller quantities and does not produce the [2+2]-cyclodimer **12**.

*Octadecafluoro[4-(4-cyclohexenyl)cyclohexene] (**10**)*

The ^{13}C NMR spectrum of the trimer exhibited six resonances due to 12 equivalent C atoms in pairs and indicated that the two 'halves' of the molecule are identical. Two of the six signals corresponded to C(1) and C(2) atoms of the CF=CF groups having different substituents at their ends, one to the tertiary C(4) atoms and three others to the carbon atoms of the CF_2 groups, one of which is bonded to two CF groups while the other two are bonded to CF and CF_2 groups. The 'half' of the molecule for which these conditions are fulfilled must have structure **P**, whilst the trimer molecule which consists of two identical 'halves' must correspond to structure **10**.



P



10 - 1

The ^{19}F NMR spectrum exhibited nine resonances, showing that 18 F atoms are in equivalent pairs and that the 'halves' of the molecule are identical. Two of the nine resonances are due to F(6) and F(7) atoms in CF=CF group, one is due to an F(1) atom bonded to a tertiary C atom, while the remaining six resonances are due to F atoms forming AB-systems consisting of three CF_2 groups. The values of the J(AB) constants, which lie in the range 275–280 Hz, indicate that all three CF_2 groups occur in a six-membered ring, while total combination of the ^{19}F NMR data agrees with the trimer possessing structure **10** which contains two **P** fragments.

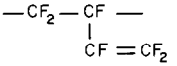
The vibrational spectrum of trimer **10** should include only one $\nu(C=C)$ band, presumably with the frequency at *c.* 1750 cm^{-1}, as occurs in the spectrum of *F*-cyclohexene [10]. In reality, however, the $\nu(C=C)$ vibration in the Raman spectrum of the trimer corresponds to two polarized bands of medium intensity with frequencies of 1775 and 1721 cm^{-1} (cf. bands at 1778 and 1727 cm^{-1} of medium intensity in the IR spectrum). Evidently, both bands are due to $CF=CF$ group vibrations. Indeed, although the frequency of the band at 1775 cm^{-1} is close to the $\nu(C=C)$ vibration of the $CF=CF_2$ group, ^{13}C and ^{19}F NMR spectral data as well as the inability of the trimer to react with bromine (characteristic of the trifluorovinyl group) exclude its presence from the trimer molecule.

It should be noted that the Raman bands at 1775 and 1721 cm^{-1} form a doublet, symmetrical relative to the expected frequency at *c.* 1750 cm^{-1}. Generally, such splitting arises from the presence of conformers in the trimer molecule, from interaction between the two $C=C$ bonds or from Fermi resonance. The considerable difference between the 1775 and 1721 cm^{-1} frequencies, and the retention of their intensity ratio when a sample of **10** was frozen, shows that such splitting was not due to the existence of conformers of trimer 10. The polarization of both Raman bands excludes interaction between the $C=C$ bonds in the trimer molecule, since in the Raman spectrum of a molecule containing conjugated $C=C$ bonds one of the bands, i.e. that arising from ν_{as}, must be depolarized. In addition, the vibrational spectrum of isomer **10-1** containing conjugated $C=C$ bonds was observed to be different from the spectrum of trimer **10** [11]. Thus, only one possible explanation remains; the above splitting arises from Fermi resonance between a double-bond vibration and an overtone of the intense band of frequency ~ 890 cm^{-1} which is present in the vibrational spectrum of trimer **10**.

It is important to note that both $\nu(C=C)$ bands in the vibrational spectrum of the liquid trimer at room temperature possessed strongly pronounced shoulders. A study of the temperature dependence of the Raman spectrum in the double-bond vibrational region has revealed that the intensity of each shoulder decreased when the temperature was decreased. Indeed, such shoulders virtually completely disappeared in the spectrum of crystalline **10**. These observations demonstrate that an equilibrium exists between the conformers of trimer **10** in the liquid state, such conformers differing in the mutual arrangement of the cyclohexene 'halves' as a result of restricted rotation around the C(4)–C(4′) bond.

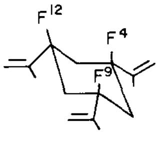
Octadecafluoro[1,2,4-trivinylcyclohexane] (11)

The IR spectrum of the trimer contained an intense band at 1775 cm^{-1} characteristic of the trifluorovinyl group. The ^{13}C NMR spectrum exhibited four resonances corresponding to 12 C atoms with a relative intensity ratio of 1:1:1:1, indicating the presence of three identical fragments each containing four atoms. One of the signals is due to tertiary C atoms, another to the carbon atoms of CF_2 groups and two further signals due to sp^2 atoms involved in $CF{=}CF_2$ groups. The whole spectrum corresponds to fragment **R**. Combinations of three **R** fragments correspond to two possible trimer structures,

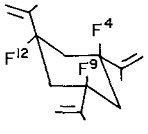


$$-CF_2-\underset{CF=CF_2}{\underset{|}{CF}}-$$

R



11-1a



11-1b

i.e. **11** and **11-1**. The choice in favour of structure **11** has been made on the basis of the ^{19}F NMR spectrum.

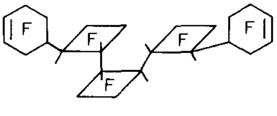
This spectrum exhibited 12 resonances, three being characteristic of the $CF{=}CF_2$ group and having threefold intensity. This indicates that three trifluorovinyl groups are present in the molecule. The remaining nine signals corresponded to isolated F atoms, six forming three AB-systems of three CF_2 groups in a pairwise fashion and the remaining three being bonded to tertiary C atoms. The spectrum was in agreement with structure **11** but contradicted structure **11-1**.

The above conclusion is true for both possible isomers, i.e. **11-1a** and **11-1b**. Indeed, in the spectrum of trimer **11-1a** the tertiary F atoms, being equivalent, must exhibit one resonance of threefold intensity, while the three CF_2 groups must correspond to one AB-system. In the case of isomer **11-1b**, its spectrum is likely to include two resonances with a relative intensity ratio of 1:2 corresponding to tertiary F atoms, as well as two AB-systems with the same intensity ratio corresponding to CF_2 groups. The presence of three signals of tertiary F atoms with similar but not identical chemical shifts in the spectrum of the trimer, with an analogous picture being observed for the AB-systems of the three CF_2 groups, unambiguously indicates that since these atoms and groups are non-equivalent they are contained in a molecule with a non-symmetrical structure.

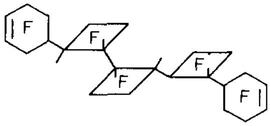
Hexatridecafluoro{1,2-bis[trans-2-(4-cyclohexenyl)cyclobutyl] cyclobutane} (12)

This is formed from trimer **9**. According to elemental analysis and mass spectrometric data, this arises as a product of the dimerization of the trimer. A comparison of the vibrational spectra of hexamer **12** and trimer **9** showed that of the two $\nu(C{=}C)$ stretching bands of the trimer at 1708 and 1783 cm^{-1}, only a band of medium intensity with a frequency of 1709 cm^{-1} is exhibited in the Raman spectrum of the hexamer (cf. medium intensity band at 1710 cm^{-1} in the IR spectrum) which is assigned to the vibration of the $CF{=}CF$ bond of the cyclohexene moiety. The disappearance of the intense band at *c.* 1780 cm^{-1}, characteristic of the $CF{=}CF_2$ group, provides further evidence for the participation of this group in the dimerization. On the other hand, the absence of any vibrational bands arising from new C=C bonds excludes linear dimerization and suggests [2+2]-cyclodimerization leading to hexamer **12**.

The ^{19}F NMR spectrum of the hexamer was complicated and included three signal regions corresponding to fluorine atoms associated with CF_2 (30–50 ppm), CF=CF (53–57 ppm) and CF (93–113 ppm) groups. An equality between the observed and expected intensity ratio $CF_2/(CF=)/CF = 6:1:2$, together with the absence of any other resonances in the spectrum, supports the existence of structure **12**. It should be noted, however, that dimerization of trimer **9** may result in the formation of two isomers (**12**)



12-cis (exo, exo)



12-trons (exo, exo)

with a *cis* and *trans* arrangement of the substituents in the central cyclobutane ring. Each of these isomers is capable of existing as three conformers (*exo,exo-*, *exo,endo-* and *endo,endo-*). The complexity of structure **12** and the variety of forms in which it can exist make it impossible to interpret the ^{19}F NMR spectrum of the hexamer in any detail.

Experimental

Mass spectra were recorded on a VG 7070E spectrometer employing an ionizing electron energy of 70 eV, an ionic source temperature of 150 °C and a lap system of 110 °C. The results are given in terms of m/z, (% intensity), [tentative assignment]. IR spectra over the range 400–4000 cm^{-1} were measured as a thin layer on an UR-20 spectrophotometer, while Raman spectra over the range 10–4000 cm^{-1} were measured on a Ramanor HG-2S spectrometer using 100 mW power Ar^+ laser excitation at the 5145 Å spectral band. ^{19}F and ^{13}C NMR spectra were recorded on a Bruker WP-200 SY spectrometer (working frequencies of 188.3 and 51.31 MHz, respectively) in deuteroacetone or carbon tetrachloride. Chemical shifts (in ppm) are quoted relative to external trifluoroacetic acid ($-\delta_F$) or tetramethylsilane (δ_C). Mathematical narrowing of the peaks was used in the primary treatment of the spectra.

Separation and purification of the products obtained were achieved via a preparative GLC method [Tzvet 4-67 chromatograph with a catharometer detector, 4000×13 mm column, Craitex (25%) on Chromaton W carrier, helium as the carrier gas and column temperatures of 110 and 150 °C].

The reaction of hexafluoro-1,3-butadiene with cis *and* trans-*1,2-bis(trifluorovinyl)-1,2,3,3,4,4-hexafluorocyclobutanes (3) and (4) [Reaction (1), Scheme 1]*

A homogeneous mixture consisting of 8.1 g of *F* butadiene dimers **3** (33.5%) and **4** (66.5%) and 8 g of *F*-butadiene was heated in a stainless-steel bomb at 150 °C. The reaction time, composition and yields of products (GLC, ^{19}F NMR methods) are listed in Table 2.

The thermal reactions of hexafluoro-1,3-butadiene

Reaction a

F-Butadiene (115 g) was heated in a stainless-steel bomb at 150 °C for 56 h. The following fractions were distilled from the reaction mixture: (a) *F*-butadiene (b.p., 5–10 °C, 14 g ($\sim$90% conversion)); (b) dimer **1** (b.p., 70–80 °C, 1 g (1%)); (c) dimers **3–5** (b.p., 90–106 °C, 69.4 g (69%)); (d) trimers **7–10** (b.p., 170–180 °C, 17.5 g [ratios **7**/(**8**+**9**)/**10** $\sim$ 1.2:6:1 and **8**/**9** $\sim$ 1:2, GLC, ^{19}F NMR methods]). The residue amounted to 11.1 g. Trimer yields (%): **7**, 2.5; **8**, 4.3; **9** 8.0; **10**, 2.

Reaction b

F-Butadiene (72 g) was heated in a stainless-steel bomb at 150 °C for 120 h. The following fractions were distilled from the reaction mixture: (a) *F*-butadiene (b.p., 5–10 °C, 10.1 g (86% conversion)); (b) dimer **1** (b.p., 63–85 °C, 0.5 g (0.8%)); (c) dimers **3–5** (b.p., 90–110 °C, 37.7 g (52.3%)); (d) trimers **7–10** (b.p., 165–185 °C, 16.1 g [ratio **7**/(**8**+**9**)/**10** $\sim$ 1.1:5.8:1]). The residue amounted to 5 g. Trimer yields (%): **7**, 3.6; (**8**+**9**), 19; **10**, 3.2 (GLC, ^{19}F NMR methods).

Reaction c

F-Butadiene (105.6 g) was heated in a stainless-steel bomb at 300 °C for 64 h. The following fractions were distilled from the reaction mixture: (a) *F*-cyclobutene (b.p., 5–10 °C, 51 g (47%)); (b) dimer **1** (b.p., 80–83 °C, 20.5 g (19.4%)); (c) dimer **2** (b.p., 87–103 °C, 9.9 g (9.5%)); (d) trimers **7–11** (b.p., 148–195 °C, 13 g [ratio (**7**+**11**)/(**8**+**9**)/**10** = 1:7.3:1.1]). The residue amounted to 4.7 g. The conversion of *F*-butadiene was $\sim$100%. Trimer yields (%): (**7**+**11**), 1.3; (**8**+**9**), 9.5; **10**, 1.4 (GLC, ^{19}F NMR methods).

The thermal reactions of F-*butadiene trimers* ***7(a–f)***

Reaction a

A mixture of trimers **7(a–f)** was heated in a sealed glass ampoule at 150 °C for 50 h and then at 200 °C for 50 h. The mixture composition was not changed (^{19}F NMR spectroscopy).

Reaction b [Reaction (2), Scheme 1]

A mixture of trimers **7(a–f)** (5 g) was heated in a sealed glass ampoule at 250 °C for 30 h. The composition of the mixture obtained was (mol%): *F*-cyclobutene, 10; *F*-butadiene, 21; dimer **1**, 18.8; dimer **2**, 14.5; trimers (**7**+**11**), 15.3 (ratio **7**/**11** $\sim$ 1:3); trimers (**8**+**9**), 11; trimer **10**, 2; unidentified products, $\sim$7 (^{19}F NMR spectroscopy).

The thermal reactions of F-*butadiene trimer* ***9***

Reaction a [Reaction (3), Scheme 1]

A mixture (1:1) of trimers **8** and **9** (7.6 g) was heated in a stainless-steel bomb at 250 °C for 40 h. After removal of the unreacted trimer mixture

TABLE 2

Reaction of hexafluoro-1,3-butadiene with dimers **3** and **4**. Reaction time, product composition and yields

Reaction time (h)	Composition of product mixture (%)[a]						*F*-Butadiene conversion (%)	Yield (%) (based on *F*-butadiene)			
	F-Butadiene	**1**	**3** + **4**[b]	**7**	**8** + **9**	**10**		**3** + **4**	**7**	**8** + **9**	**10**
28	35.5	0.6	60.5	0.8	1.4	0.2	29	94	1.7	3.0	0.4
128	7.5	7.2	61.5	2.4	18.5	2.5	85.5	75.5[c]	1.9	14.5	2.0

[a] According to ^{19}F NMR data.

[b] Mixture of dimers **3** and **4** containing *c.* 5–10% of dimer **5**.

[c] Dimer **4**.

(5.3 g, ratio **8**/**9** ~ 3:2) by vacuum distillation (58–66 °C/2 mmHg), the raw hexamer **12** (1.4 g, 82%) was obtained. The conversion of trimer **9** was 45%.

Reaction b

A mixture containing trimer **9** (40%) and trimer **8** (60%) (4.7 g) was heated in a stainless-steel bomb at 300 °C for 15 h. A soot (1.1 g) was filtered off and the filtrate distilled at 52–53 °C/1 mmHg) affording a mixture (2.1 g) with the following composition (mol%): trimer **10**, 7; trimer **9**, 15.5; trimer **8**, 77.5; traces of dimers **1** and **2** and of *F*-cyclobutene. The residue (1.4 g) consisted of a tar containing hexamer **12** (^{19}F NMR spectroscopy). The conversion of trimer **9** was 83%.

The thermal reactions of F-*butadiene trimer* **8**

Reaction a

See above, experiment a [Reaction (3), Scheme 1]. The conversion of trimer **8** was 0%.

Reaction b [Reaction (4), Scheme 1]

Trimer **8** (1.2 g) was heated in a stainless-steel bomb at 300 °C for 15 h. A soot (0.2 g, 22%) and mixture (0.9 g) of the following composition (mol%) were obtained: *F*-cyclobutene, 3; dimer **1**, 33; dimer **2**, 2.5; trimer **8**, 33; trimer **10**, 16.5; unidentified products, ~ 12 (^{19}F NMR spectroscopy). The conversion of trimer **8** was 75%.

The thermal stability of F-*butadiene trimer* **10**

Trimer **10** was heated in a stainless-steel bomb at 300 °C for 50 h. The conversion of trimer **10** was 0% (GLC, ^{19}F NMR methods).

Octadecafluoro[1-vinyl-2-(1-vinyl-2-cyclobutyl)cyclobutane][mixture of isomers **7(a–f)**]

This was isolated by preparative GLC methods from a mixture of *F*-butadiene trimers (b.p., 163–164 °C). Mass spectrum: 485 (5) $[M]^+$; 417 (0.8) $[M-CF_3]^+$; 367 (0.7) $[M-C_2F_5]^+$; 348 (0.5) $[M-2CF_3]^+$; 317 (0.8) $[M-CF_3-C_2F_4]^+$; 305 (4.6) $[M-C_4F_7]^+$; 255 (8.7) $[M-C_5F_9]^+$; 236 (2.5) $[M-CF_3-C_4F_7]^+$; 224 (8) $[1/2M]^+$; 217 (2) $[M-C_4F_7-CF_4]^+$; 205 (4.4) $[M-C_5F_9-CF_2]^+$; 193 (4.8) $[1/2M-CF_2]^+$; 186 (2.8) $[M-C_5F_9-CF_3]^+$; 181 (3.9) $[M-C_8F_{11}]^+$; 174 (3) $[M-C_7F_{12}]^+$; 162 (100) $[M-C_8F_{12}]^+$; 155 (7.5) $[M-C_7F_{12}-F]^+$; 131 (9.7) $[M-C_4F_7-C_5F_6]^+$; 93 (18) $[C_3F_3]^+$; 69 (17) $[CF_3]^+$. IR (cm^{-1}): 1786 (s). For ^{19}F NMR spectrum of isomers **7(a–f)**, see Table 1. ^{13}C NMR δ (J(C–F) in Hz): 92.6 (d, C(1), J(1–4), 242); 92.5 (d, C(2), J(2–9), 228); 113.5 (tm, C(3), C(4), J(3–7, 8)=J(4–5, 6), 292); 120.5 (d, C(5), J(5–3), 212); 156.2 (dt, C(6), J(6–1, 2), 295, J(6–3), 35) ppm; ratio of isomers **7c** < **7a** < **7d** < **7b** < **7f** < **7e**. Analysis: Found: C, 29.76; F, 70.48%. $C_{12}F_{18}$ requires: C, 29.63; F, 70.37%.

cis-*Dodecafluoro[1-(4-cyclohexenyl)-2-vinylcyclobutane (8)*

This was isolated in the pure state by preparative GLC methods after heating a mixture of trimers **8** and **9** at 300 °C for 2 h (b.p., 175–176 °C). Mass spectrum: 486 (4) $[M]^+$; 417 (1.5) $[M-CF_3]^+$; 367 (2.5) $[M-C_2F_5]^+$; 317 (1.5) $[M-C_3F_7]^+$; 305 (3) $[M-C_4F_7]^+$; 298 (1) $[M-C_2F_5-CF_3]^+$; 279 (1) $[M-C_2F_5-CF_4]^+$; 267 (1.3) $[M-C_2F_5-C_2F_4]^+$; 255 (3.5) $[M-C_5F_9]^+$; 243 (1.7) $[M-C_6F_9]^+$; 236 (1.3) $[M-C_4F_7-CF_3]^+$; 217 (1.8) $[M-C_4F_7-CF_4]^+$; 212 (0.7) $[M-C_7F_{10}]^+$; 205 (3.5) $[M-C_4F_7-C_2F_4]^+$; 193 (9) $[M-C_7F_{11}]^+$; 186 (2.5) $[M-C_4F_7-C_2F_5]^+$; 181 (4) $[M-C_6F_9-C_2F_2]^+$; 162 (100) $[M-C_8F_{12}]^+$; 155 (4) $[M-C_5F_9-C_2F_4]^+$; 143 (7) $[M-C_6F_9-C_2F_4]^+$; 131 (15) $[M-C_9F_{13}]^+$; 112 (3.5) $[M-C_7F_{10}-C_2F_4]^+$; 93 (19) $[C_3F_3]^+$; 69 (19) $[CF_3]^+$. IR (cm^{-1}): 1781 (s); 1770 (m). Raman (cm^{-1}): 1781 (vs, p)*; 1709 (s, p). ^{19}F NMR $-\delta$: 8.6 (ddddd, F(1)); 26.3 (ddddddd, F(2)); 111.8 (ddddddd, F(3)); 91.25 (ddddddd, F(4)); 38.12 and 42.82 (F(5) and F(6), AB-system with additional coupling of F(5) into ddddd and F(6) into dddddd); 38–45 (m, F(7), F(8), F(11), F(12), F(15), F(16), F(17), F(18)); 102.35 (m, F(9)); 107.75 (dddddd, F(10)); 55.25 (m, F(13)); 54.35 (m, F(14)) ppm. Coupling constants: *J*(1–2), 47.2; *J*(1–3), 38; *J*(1–?), 8.5, 3.5, 2.5; *J*(2–4), 18; *J*(2–6), 28; *J*(2–?), 12, 6, 6; *J*(3–2), 117; *J*(3–4), 25, *J*(3–?), 30, 14.5, 5; *J*(4–6), 6; *J*(4–?), 59, 7, 6, 6; *J*(5–6), 222; *J*(5–?), 10, 5, 5, 5; *J*(6–8), 6; *J*(6–?), 27.5, 27.5, 27.5, 6, 6; *J*(10–?), 38.5, 30.5, 25.5, 14.5, 5, 5 Hz. Analysis: Found: C, 29.58; F, 70.59%. $C_{12}F_{18}$ requires: C, 29.63; F, 70.37%.

trans-*Dodecafluoro[1-(4-cyclohexenyl)-2-vinylcyclobutane] (9)*

This compound containing ~10% of the *cis* isomer was obtained from their mixture by preparative GLC repeated three times (b.p., 174–175 °C). Mass spectrum: 486 (2.5) $[M]^+$; 417 (1) $[M-CF_3]^+$; 367 (2) $[M-C_2F_5]^+$; 317 (1.5) $[M-C_3F_7]^+$; 305 (1.5) $[M-C_4F_7]^+$; 298 (1) $[M-C_2F_5-CF_3]^+$; 293 (0.5) $[M-C_5F_7]^+$; 279 (1) $[M-C_2F_5-CF_4]^+$; 267 (1) $[M-C_2F_5-C_2F_4]^+$; 255 (3) $[M-C_5F_9]^+$; 212 (0.5) $[M-C_7F_{10}]^+$; 205 (3.5) $[M-C_5F_9-CF_2]^+$; 193 (7) $[M-C_7F_{11}]^+$; 193 (7) $[M-C_7F_{11}]^+$; 162 (100) $[M-C_8F_{12}]^+$; 131 (14) $[M-C_9F_{13}]^+$; 112 (4) $[M-C_7F_{10}-C_2F_4]^+$; 93 (20) $[C_3F_3]^+$; 69 (19) $[CF_3]^+$. IR (cm^{-1}): 1780 (s); 1711 (m). Raman (cm^{-1}): 1783 (vs, p); 1708 (s, p). ^{19}F NMR $-\delta$: 9.75 (dd, F(1)); 26.25 (ddddd, F(2)); 111.64 (dddddd, F(3)); 102.93 (ddddddd, F(4)); 33.77 (dddddd, F(5)); 47.5 (ddddd, F(6)); 44.7 and 45.9 (m, F(7) and F(8), AB-system); 113.9 (m, F(9)); 110.1 (dddddd, F(10)); 45.1 and 45.9 (m, F(11), F(15) and F(12), F(16), AB-systems); 58.75 (m, F(13)); 58.4 (m, F(14)); 44.5 and 46.5 (m, F(17) and F(18), AB-system) ppm. Coupling constants: *J*(1–2), 54; *J*(2–3), 113; *J*(2–4), 52.5; *J*(2–5), 14.5; *J*(2–?), 2; *J*(3–4), 22; *J*(3–5), 35; *J*(3–?), 40, 30; *J*(4–5), 6; *J*(4–6), 11; *J*(4–10), 5; *J*(4–?), 10, 5; *J*(5–6), 223.5; *J*(5–?), 6, 6; *J*(6–10), 24.5; *J*(6–?), 32.5, 5; *J*(7–8), 220; *J*(10–?), 38.5, 30, 14, 5, 5; *J*(15–16), ~290; *J*(11–12), ~290; *J*(17–18), 292.5 Hz. ^{13}C NMR δ (*J*(C–F) in Hz): 90.4 (dddt, C(1), *J*(1–4, 7, 8), 26, *J*(1–9), 230, *J*(1–10), 26); 93.3 (dddt, C(2), *J*(2–4),

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*p = polarized.

260, J(2–3, 5, 6, 9), 25); 107.83 (dtt, C(3), C(11), J(3–4) ~ J(11–4), ~28, J(3–5, 6) ~ J(11–15, 16), ~270, J(3–7, 8) ~ J(11–17, 18), ~30); 111.4 (dtt, C(4), C(12), J(4–5, 6) ~ J(12–15, 16), ~30, J(4–7, 8) ~ J(12–17, 18), ~270, J(4–9) ~ J(12–10), ~30); 118.6 (dm, C(5), J(5–3), 200); 154.8 (dt, C(6), J(6–1, 2), 290, J(6–3), 42.5); 90.8 (ddtt, C(7), J(7–10), 230, J(7–9, 11, 12, 17, 18), 25); 142.1 (d, C(9), C(10), J(9–13) ~ J(10–14), ~280) ppm. Analysis: Found: C, 29.58; F, 70.43%. $C_{12}F_{18}$ requires: C, 29.63; F, 70.37%.

Octadecafluoro[4-(4-cyclohexenyl)cyclohexene] ***(10)***

This was isolated in a pure state from a mixture of *F*-butadiene trimers by preparative GLC methods (b.p., 183 °C). Mass spectrum: 486 (12) $[M]^+$; 417 (3) $[M-CF_3]^+$; 367 (4) $[M-C_2F_5]^+$; 255 (22) $[M-C_5F_9]^+$; 243 (2.5) $[1/2M]^+$; 212 (9) $[M-C_7F_{10}]^+$; 205 (22) $[M-C_6F_{11}]^+$; 193 (62) $[M-C_7F_{11}]^+$; 186 (11) $[M-C_6F_{11}-F]^+$; 181 (15) $[M-C_5F_9-CF_2]^+$; 162 (100) $[M-C_8F_{12}]^+$; 155 (13) $[M-C_6F_{11}-CF_2]^+$; 143 (25) $[M-C_7F_{10}-CF_3]^+$; 131 (36) $[M-C_5F_9-2CF_2]^+$; 119 (7) $[C_2F_5]^+$; 100 (2.5) $[C_2F_4]^+$; 69 (69) $[CF_3]^+$. IR (cm^{-1}): 1778 (m); 1790 (sh); 1727 (m); 1735 (sh). Raman (20 °C, liquid) (cm^{-1}): 1775 (m, p); 1787 (sh); 1721 (m, p); 1731 (sh). Raman (−78 °C, crystal) (cm^{-1}): 1778 (m); 1725 (m). ^{19}F NMR $-\delta$ (J(F–F) in Hz): 95.45 (m, F(1)): 31.95 and 32.66 (m, F(2) and F(3), AB-system, J(2–3), ~280); 30.18 and 32.2 (m, F(4) and F(5), AB-system, J(4–5), ~275); 60.59 (m, F(6)); 76.84 (m, F(7)); 32.93 and 34.65 (m, F(8) and F(9), AB-system, J(8–9), ~275) ppm. ^{13}C NMR δ (J(C–F) in Hz): 141.8 (d, C(1), J(1–6), 277); 137.2 (d, C(2), J(2–7), 285); 111.2 (ddt, C(3), J(3–1, 7), 23, J(3–8, 9), 263); 90.74 (ddtt, C(4), J(4–1), 221, J(4–2, 3, 8, 9, 1), 26); 113.98 (dtt, C(5), J(5–1), 26, J(5–2, 3), 234, J(5–4, 5), 29); 109.2 (dtt, C(6), J(6–2, 3, 6), 27, J(6–4, 5), 242) ppm. Analysis: Found: C, 29.40; F, 70.60%. $C_{12}F_{18}$ requires: C, 29.63; F, 70.37%.

Octadecafluoro[1,2,4-tris(vinyl)cyclohexane] ***(11)***

This compound, containing ~25% of trimers **7** (GLC methods*), was isolated from the mixture of the products of reaction (2) by preparative GLC methods. Mass spectrum: 486 (0.8) $[M]^+$; 417 (0.7) $[M-CF_3]^+$; 367 (0.6) $[M-C_2F_5]^+$; 305 (4.3) $[M-C_4F_7]^+$; 255 (7.5) $[M-C_5F_9]^+$; 236 (2) $[M-C_4F_7-CF_3]^+$; 224 (9) $[M-C_4F_7-C_2F_3]^+$; 205 (4) $[M-C_4F_7-C_2F_4]^+$; 193 (4.5) $[M-C_7F_{11}]^+$; 186 (2.5) $[M-C_5F_9-CF_3]^+$; 181 (3.5) $[M-C_8F_{11}]^+$; 174 (3) $[M-C_7F_{12}]^+$; 162 (100) $[M-C_8F_{12}]^+$; 131 (10) $[M-C_4F_7-C_5F_6]^+$; 93 (18) $[C_3F_3]^+$; 69 (17) $[CF_3]^+$. IR (cm^{-1}): 1781 (s). NMR δ (J(C–F) in Hz): 93.56 (dm, C(1), C(2), C(4), J(1–4) = J(2–12) = J(4–9) = 242); 112.6 (tm, C(3), C(5), C(6), J(3–10, 11) = J(5–7, 8) = J(6–5, 6) = 290); 118.95 (dm, C(7), J(7–3), 231); 155.78 (dt, C(8), J(8–1, 2), 294, J(8–3), 46.8) ppm. ^{19}F NMR $-\delta$: 9.7 (dddd, F(1)); 28.1 (m, F(2)); 109.2 (m, F(3)); 105.0 (m, F(4)); 44.77 and 50.23 (m, F(5) and F(6), AB-system); 44.25 and 49.37 (m, F(7) and F(8), AB-system); 102.3 (m, F(9)); 45.6 and 46.7 (m, F(10)

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*Squalene, glass capillary column (100 m), hydrogen gas carrier at 80 °C.

and F(11), AB-system); 105.2 (m, F(12)) ppm. Coupling constants: *J*(1–2), 51; *J*(1–3), 36.5; *J*(1–?), 37, 5; *J*(2–3), 115; *J*(2–?), 35; *J*(3–?), 36, 18, 18; *J*(5–6), 223; *J*(7–8), 223; *J*(10–11), 223 Hz.

*Hexatridecafluoro{1, 2-bis[*trans*-2-(4-cyclohexenyl)cyclobutyl]-cyclobutane} (**12**)*

This was obtained by heating the mixture of trimers **9** and **8** at 250 °C for 40 h and removing the unreacted trimers. Hexamer **12** was isolated in the pure state by dissolution of the glassy residue in a hexane/trichlorotrifluoroethane (1:1) mixture, followed by filtration through alumina, then evaporation of the solvent and subsequent crystallization from trichlorotrifluoroethane (m.p., 164.5–166.6 °C (Koffler table)). Mass spectrum: 972 (11.7) $[M]^+$; 953 (2.7) $[M-F]^+$; 486 (15.6) $[1/2M]^+$; 324 (1) $[1/2M-C_4F_6]^+$; 255 (7.4) $[1/2M-C_4F_6-CF_3]^+$; 243 (5) $[1/2M-C_6F_9]^+$; 224 (4.5) $[1/2M-C_4F_6-C_2F_4]^+$; 205 (6.6) $[1/2M-C_4F_6-C_2F_5]^+$; 193 (56) $[1/2M-C_4F_6-C_3F_5]^+$; 162 (100) $[C_4F_6]^+$; 131 (41) $[C_3F_5]^+$; 100 (5) $[C_2F_4]^+$; 93 (10) $[C_3F_3]^+$; 69 (29) $[CF_3]^+$. IR (cm^{-1}): 1710 (m). Raman (cm^{-1}): 1709 (m). ^{19}F NMR $-\delta$: 30–50 (CF_2); 53–56 (CF=); 93–113 (CF) ppm (ratio of intensities, 6:2:1). Analysis: Found: C, 29.69; F, 70.34%. $C_{24}F_{36}$ requires: C, 29.63; F, 70.37%.

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