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Polyhalogenoallenes. Part VI.¹ Some Addition Reactions of Perfluoropenta-1,2-diene

By R. E. Banks, A. Braithwaite, R. N. Haszeldine,* and D. R. Taylor, Chemistry Department, University of Manchester Institute of Science and Technology, Manchester 1

Perfluoropenta-1,2-diene is inert towards chlorine, hydrogen chloride, and hydrogen bromide at room temperature in the dark, but combines quantitatively with anhydrous hydrogen fluoride under these conditions to give *cis*- and *trans-2H*-nonafluoropent-2-ene. The latter is also obtained by treatment of perfluoropenta-1,2-diene with caesium fluoride in formamide; reaction of the diene with caesium fluoride alone provides perfluoropent-2-yne. Anhydrous methanol readily attacks perfluoropenta-1,2-diene to give *trans-2H*-octafluoro-1-methoxypent-2-ene and heptafluoro-1-methoxypent-2-yne. Photochemical hydrobromination of perfluoropenta-1,2-diene gives 3H-2-bromo-octafluoropent-1-ene and 1H-2-bromo-octafluoropent-2-ene (probably both as *cis*- and *trans*-isomers), while photochemical chlorination with an excess of chlorine gives 1,2,2,3-tetrachloro-octafluoro-n-pentane. The n.m.r. spectra of the reaction products are presented, and possible reaction mechanisms are discussed.

TETRAFLUOROALLENE is exceptionally susceptible to ionic attack,² and when treated with either 'electrophilic' (chlorine, hydrogen halides) or 'nucleophilic'

¹ Part V, R. E. Banks, A. Braithwaite, R. N. Haszeldine, and D. R. Taylor, J. Chem. Soc. (C), 1968, 2593.

(water, methanol) reagents under extremely mild conditions in the dark it rapidly yields 1:1 adducts, $CF_2:CX:CF_2Y$ (X = Y = Cl or X = H, Y = F, Cl, Br, ² R. E. Banks, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc.*, 1965, 978.

OH, or OMe), some of which undergo spontaneous elimination³ or rearrangement reactions (Scheme 1).⁴

$$\begin{array}{c|c} CF_2; C:CF_2 \\ XY & -76 \text{ to } 20^\circ \\ CF_2; CX \cdot CF_2Y & \xrightarrow{X = H, Y = OH} \\ CF_2; CX \cdot CF_2Y & \xrightarrow{X = H, Y = OH} \\ CF_2; CH \cdot COF + HF \\ CF_3 \cdot CH; CF \cdot OMe \\ SCHEME 1 \end{array}$$

In marked contrast, the only reaction detected when perfluoropenta-1,2-diene is treated with an excess of chlorine, hydrogen chloride, or hydrogen bromide at 20° in the dark is formation of the allene dimers.¹ However, perfluoropenta-1,2-diene does combine with hydrogen fluoride at 20° , to give a 65:35 mixture of the isomeric pentenes (I) and (II) in 99% yield [equation (1)]. Nevertheless, the result of a qualitative competition reaction, in which an approximately 1:1:1 molar mixture of perfluoropenta-1,2-diene, tetrafluoroallene, and anhydrous hydrogen fluoride was kept at 20° in the dark for 2 hr., shows that the lower homologue is the more reactive towards hydrogen fluoride [equation (2)].

$$C_{2}F_{5} \cdot CF:C:CF_{2} \xrightarrow{HF' (in excess)} \longrightarrow C_{2}F_{5} \cdot C:C \xrightarrow{CF_{3}} (65\%) + F \xrightarrow{C_{2}F_{5}} C:C \xrightarrow{H} (35\%) (1)$$
(I)
(I)
(II)

 $C_3F_4 + C_5F_8 + HF \xrightarrow{20^\circ} C_3F_4(19\%)$, CF3. CH:CF2 (81%), C5F8 (42%), cis- and trans- $C_2F_5 \cdot CF \cdot CH \cdot CF_3 (37\%), (C_5F_8)_2 (20\%)$ (2)

Addition of hydrogen fluoride across the 1,2-bond in perfluoropenta-1,2-diene can also be effected with caesium fluoride in the protic solvent formamide at 20° (cf. ref. 5 and the formation of CF₃·CH:CF₂ from tetrafluoroallene and moist caesium fluoride²), but only the trans-pentene (II) appears to be formed. Presumably doubtedly involves a nucleophilic mechanism [equation (3), coupled with the resistance shown by perfluoropenta-1,2-diene towards attack by hydrogen halides except for hydrogen fluoride, expected to be the most



powerful proton donor, leads us to suspect that the reaction between the allene and hydrogen fluoride may proceed by an electrophilic mechanism (see Scheme 2). The transient carbonium ions (IVa or b) are not allylic, because of the initially mutually perpendicular orientation of the two π -bonds in the allene; they will only gain the resonance stabilization characteristic of an allylic carbonium ion if the final attack by fluoride is sufficiently delayed to permit a 90° rotation about the 1,2-bond (see Scheme 2).6 Rapid conversion of the carbonium ions into products is supported by the failure to detect 2H-nonafluoropent-1-ene (V) as a product of the reactions:

$$C_{2}F_{5} \cdot CF:C:CF_{2} + H^{+} \Longrightarrow C_{2}F_{5} \cdot CF:CH \bigoplus C_{2}F_{5} \cdot CF:CH \cdot CF_{2} \longrightarrow C_{2}F_{5} \cdot CF:CH:CF_{2}$$

$$cis - and \ trans - C_{2}F_{5} \cdot CF:CH \cdot CF_{3} \ (I \ and \ II) \longleftarrow C_{2}F_{5} \cdot CF_{2} \cdot CH:CF_{2} \ (V)$$
Scheme 3

this addition reaction owes its stereospecificity to preferential formation of an intermediate carbanion (III) with a *trans*-configuration [equation (3)]. The reaction does not appear to proceed by initial fluoride-catalysed rearrangement of the perfluoropenta-1,2-diene to perfluoropent-2-yne (see later), since a sample of this acetylene was recovered in 93% yield after treatment with caesium fluoride in formamide at room temperature.

The stereospecificity of the formation of 2H-nonafluoropent-2-ene when the method employed un-

Rapid collapse of an ion pair of carbonium ion (IV) and fluoride should also result in cis-addition of HF across the allene 1,2-double bond; 7 such addition could give rise either to cis-2H-nonafluoropent-2-ene (I) or to its trans-isomer (II), depending on the direction of approach of the reagent to the reaction site. Preferential formation of the *cis*-product is ascribed to partial shielding of one side of the 1,2-bond by the pentafiuoroethyl group (a Courtauld molecular model

⁵ W. T. Miller, J. H. Fried, and H. Goldwhite, J. Amer. Chem. Soc., 1960, 82, 3091. ⁶ D. R. Taylor, Chem. Rev., 1967, 67, 317.

7 M. J. S. Dewar, Angew. Chem. Internat. Edn., 1964, 3, 245.

 ³ R. E. Banks, W. R. Deem, R. N. Haszeldine, and D. R. Taylor, J. Chem. Soc. (C), 1966, 2051.
 ⁴ D. R. Taylor, unpublished results.

reveals the distinct possibility of such hindrance to attack).



Protonation of the central allenic carbon in perfluoropenta-1,2-diene is expected from consideration of resonance effects involving release of electron density from the vinylic fluorines $^{2}[(A) \leftrightarrow (B) \leftrightarrow (C) \leftrightarrow (D)].$ If the stability of perfluoroalkylcarbonium ions decreases in the order $CF_3 > R_F CF_2 > (R_F)_2 CF > (R_F)_3 C$ owing to overlap of filled 2p orbitals of α -fluorine substituents with a vacant sp^2 carbon orbital,⁸ the orientation of HF addition to the pentadiene can be explained in terms of the greater stability ofC₂F₅·CF:CH·CF₂ (IV) compared with that of C_2F_5 ·CF·CH:CF₂. (As explained above, these are not canonical forms of the same carbonium ion, owing to the geometry of the allenic system.) Replacement of the electron-withdrawing vinylic perfluoroethyl group in perfluoropenta-1,2-diene by fluorine would lower the energy of the transition state involved in protonation of the central carbon and account for the difference in reactivity shown towards hydrogen fluoride by perfluoropenta-1,2-diene and tetrafluoroallene.

Nucleophilic Reactions.—Perfluoropenta-1,2-diene undergoes a retropropargyl rearrangement 6 in the presence of anhydrous caesium fluoride:

$$C_{2}F_{5} \cdot C = C = CF_{2} \quad F^{-} \implies C_{2}F_{5} \cdot C \stackrel{\frown}{=} C \cdot CF_{3} \longrightarrow$$

$$\downarrow \\ F \qquad \qquad \downarrow \\ C_{2}F_{5} \cdot C \equiv C \cdot CF_{3} + F^{-} \qquad (4)$$

The reaction is best carried out in the vapour phase [equation (5)], when the product, perfluoropent-2-yne,

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methanol and the allene at sub-zero temperatures, leading to the quantitative formation of a 77:23 mixture of the two ethers, 2H-octafluoro-1-methoxypent-2-ene and heptafluoro-1-methoxypent-2-yne; both of these products appear to polymerize slowly when stored in glass. The former ether is assigned a transconfiguration on the basis of its strong CH:CF coupling constant (30.0 c./sec.) and weak CF₂·C:C·CF₂ coupling. Formation of these ethers (see Scheme 4) is accounted for by nucleophilic attack of methanol at the terminal diffuoromethylene group of the allene, followed by loss of a proton and formation of a methoxy-carbanion (VI) analogous to the perfluoro-carbanion (III) proposed as the intermediate in reactions between caesium fluoride and perfluoropenta-1,2-diene [cf. equations (3) and (4)]. Two fates are open to the methoxy-carbanion: protonation to give exclusively the sterically favoured transmodification of the allyl ether, or loss of fluoride with formation of the acetylenic ether.



Free-radical Reactions.—The extreme readiness with which tetrafluoroallene homopolymerizes has prevented a study of the orientation of free-radical attack on the allenic system.² Perfluoropenta-1,2-diene, however, does not polymerize readily, and so its photochemical chlorination and hydrobromination have been studied.

Though inert towards chlorine at room temperature in the dark, perfluoropenta-1,2-diene is rapidly converted into the saturated tetrachloride, 1,2,2,3-tetrachlorooctafluoro-n-pentane (95%), and a small amount of mixed dimers, $(C_5F_8)_2$ (4%), when photolysed in the presence of an excess of chlorine. No attempt was made to prepare an unsaturated dichloro-derivative.

$$C_{2}F_{5} \cdot CF:C:CF_{2} \longrightarrow C_{2}F_{5} \cdot C:C \cdot CF_{3} (96\%) + trans - C_{2}F_{5} \cdot CF:CH \cdot CF_{3} (3\%)$$

$$C_{2}F_{5} \cdot CF:C:CF_{2} \longrightarrow C_{2}F_{5} \cdot C:C \cdot CF_{3} (28\%) + (C_{5}F_{8})_{2} (55\%)$$
(5)

is obtained almost quantitatively but is contaminated with trans-2H-nonafluoropent-2-ene (II); presumably the latter arises through reaction of the intermediate carbanion [(III), cf. equation (3)] with traces of moisture in the system. The major product of a liquid-phase reaction is the dimer of perfluoropenta-1,2-diene.

The susceptibility of perfluoropenta-1,2-diene towards nucleophilic attack is revealed by the onset of a vigorous exothermic reaction between an excess of neutral The absence of reaction between hydrogen bromide and perfluoropenta-1,2-diene in the dark permitted the study of a photochemical reaction, carried out in a silica vessel with u.v. irradiation for 6 hr. [equation (6)]. The product consisted of a 1:12:5:2 mixture of

⁸ P. E. Aldrich, E. G. Howard, W. J. Linn, W. J. Middleton, and W. H. Sharkey, *J. Org. Chem.*, 1963, **28**, 184; G. A. Olah, R. D. Chambers, and M. B. Comisarow, *J. Amer. Chem. Soc.*, 1967, **89**, 1268.

$$C_{2}F_{5} \cdot CF:C:CF_{2} \xrightarrow[u.v. light]{HBr} C_{2}F_{5} \cdot CHF \cdot CBr:CF_{2} (44\%) + C_{2}F_{5} \cdot CF:CBr \cdot CHF_{2} (6) (VII) (VIII) (cis, 19\%; trans, 8\%)$$

isomeric hydrobromides C₅HBrF₈ (70%) and a highboiling liquid which was not investigated. By use of a combination of g.l.c., i.r., and n.m.r. techniques, the two major isomeric 1:1 adducts were found to be 3*H*-2-bromo-octafluoropent-1-ene (VII) and 1H-2bromo-octafluoropent-2-ene, probably the cis-isomer (VIII); the third most abundant hydrobromide is possibly trans-1H-2-bromo-octafluoropent-2-ene [equation (6)]. This result indicates that a bromine atom preferentially attacks the central carbon of the allenic system to give an intermediate radical (IX) which exists long enough to permit 90° rotation of the orbital containing the unpaired electron, so that it is transformed into an allylic radical (X) (see Scheme 5).



EXPERIMENTAL

Perfluoropenta-1,2-diene was prepared as described previously.¹ Analytical instrumentation included a Perkin-Elmer 21 spectrophotometer (i.r.) with sodium chloride optics, Perkin-Elmer R10 and Varian HA 100 n.m.r. spectrometers (operating at 60 and 100 Mc./sec. for ¹H and 56·46 and 94·10 Mc./sec. for ¹⁹F, respectively), and a MS/2H A.E.I. mass spectrometer. Gas-liquid chromatography was performed with a Perkin-Elmer model 452 (thermistor detectors) or a Pye model 24 (dual-flame ionisation detector) fractometer; g.l.c. separations were carried out with a specially constructed katharometer chromatograph.¹

Reactions of Perfluoropenta-1,2-diene.—(a) With chlorine. No reaction occurred when a mixture of perfluoropenta-1,2-diene (0.22 g., 1.04 mmole) and chlorine (0.089 g., 1.25 mmole) was kept in the dark in a sealed Pyrex tube (300 ml.) at 20° for 15 hr.; only unchanged perfluoropentadiene (0.43 mmole, 41% recovery) and its dimers (0.13 g., 0.31 mmole, 100% yield based on pentadiene consumed), identical (i.r. and g.l.c.) with an authentic sample,¹ were obtained after unchanged chlorine had been removed by shaking the mixture with dry mercury. Irradiation of a mixture of perfluoropenta-1,2-diene (0.71 g., 3.34 mmoles) and chlorine (0.54 g., 7.67 mmoles) in silica tubes (2 imes 350 ml.) placed 15 cm. from a 100 w tungsten filament lamp for 20 min. gave, after unchanged chlorine had been removed by shaking the mixture with dry mercury, perfluoropentadiene dimers (0.06 g., 0.14 mmole, 4%) and 1,2,2,3-tetrachloro-octafluoro-n-pentane (1.12 g., 3.18 mmoles,

95%), isolated by g.l.c. (2 m. silicone–Embacel at 130°) as a colourless liquid (Found: C, 17·3; Cl, 39·9%; M, 352 by mass spectrometry. $C_5F_8{}^{35}Cl_4$ requires C, 17·0; Cl, 39·8%; M, 352), b.p. 152–153°/760 mm. (Siwoloboff), $n_D{}^{20}$ 1·380, λ_{max} (capillary film) 7·55s, 8·12vs, 8·34vs, 8·43vs, 8·64vs, 9·00s, 9·12vs, 9·68vs, 9·76vs, 10·00w, 10·35w, 10·51w, 10·79w, 11·15s, 11·55m, 11·64s, 12·13m, 12·35s, 12·50s, 13·00m, 13·40w, 14·14vs, 14·41s, 14·69s, 15·00m, 15·29sh, and 15·35m μ , ¹⁹F n.m.r. data in Table 1.



N.m.r. data for 1,2,2,3-tetrachloro-octafluoron-pentane (reference internal CFCl₃)

	(1) CE) (2A, 2 FCF	$ \begin{array}{c} (3) \\ (4A, 4B) \\ (4A, 4B)$	
		3 01	2 02 01 0002 02 20	Moduli of spin–spin coupling
		Rel.		constants
F Nuclei	P.p.m.	int.	Multiplicity *	(c./sec.)
1	$\hat{7}9.6$	3	d	1, 13.5
2	116.3	2	AB system ($\Delta \nu$ 120.2	JAB 277.0
			c./sec.): A portion as broad t, B por-	$J_{2A,4A} \approx J_{2A,4I} \approx 10.0$
			tion as dddq	$J_{2B, 4B} 18.0$
				$J_{2B, 4A} = 16.9$
				$J_{2B,3} 6.5$
		-		$\int_{2B,1} 1.5$
3	115.7	1	qtd overlapping with	$J_{3,1} 13.5$
			liner bands of m at	J 3, 4A 9.8
4	57.0	9	AB system (A: 100.9	$J_{3,4B} = 163.0$
Ŧ	01.0	2	c /sec): A portion	$J_{AB} = 1000$
			as dd. B portion as	<i>J</i> _{4A,2B} 10·2
			ddd	J 4A, 2B
				JAB 24 9.7
				J _{4B,2B} 18.0
				$J_{4B,3} 10.9$

* s = Singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

(b) With anhydrous hydrogen fluoride. A mixture of perfluoropenta-1,2-diene (0.49 g., 2.32 mmoles) and an excess of anhydrous hydrogen fluoride [obtained by heating anhydrous potassium hydrogen difluoride (0.5 g., 6.4 mmoles) at 600° in vacuo] was kept in a copper tube (12 ml.) for 2 hr. at 20° to give, after the excess of hydrogen fluoride had been removed by passing the volatile products over anhydrous sodium fluoride, a 65:35 mixture (0.53 g., 2.29 mmoles, 99%) of cis-2H-nonafluoropent-2-ene (Found: C, 25.7; H, 0.5%; M, 232 by mass spectrometry. C₅HF₉ requires C, 25.9; H, 0.4%; M, 232), b.p. 32.8° (isoteniscope), λ_{max} (vapour) 3.24m, 5.59m, 5.68s, 5.80vs (C.C str.), 6.80m, 7.08s, 7.29vs, 7.45vs, 7.70vs, 7.91vs, 8.10vs, 8.33vs, 8.47vs, 8.96vs, 9.69vs, 10.25m, 11.21vs, 11.83vs, 12.60m, 13.05vs, 14.10s, and 15.02w µ, and trans-2H-nonafluoropent-2-ene (Found: C, 25.9; H, 0.5%; M, 232 by mass spectrometry. C_5HF_9 requires C, 25.9; H, 0.4%; M, 232), b.p. 28.8° (isoteniscope), $\lambda_{max.}$ (vapour) 5.79vs (C.C str.), 7.19vs, 7.47vs, 7.70vs, 7.80sh, 7.87vs, 8.12vs, 8.52vs, 9.10vs, 9.70m, 9.90vs, 11.50s, 12.15vs, 12.60s, 13.40vs, and $14.50s \mu$. The isomeric pent-2-enes were isolated by g.l.c. (4 m. Kel-F 10 oil-Embacel at 20°) and identified by ¹H and ¹⁹F n.m.r. analysis (data in Table 2); they are easily distinguishable by n.m.r. spectroscopy since the CH:CF coupling constant for the trans-isomer $(|J_{3,5}|)$ is larger than the corresponding value for the *cis*-compound $(|J_{4,5}|)$, and the CF C:C CF coupling constant is nearly ten times greater for the *cis*-isomer $(|J_{2,3}|)$ than for the *trans* $(|J_{2,4}|)$.

(c) With anhydrous hydrogen fluoride, in the presence of tetrafluoroallene. A mixture of perfluoropenta-1,2-diene (0.186 g., 0.88 mmole), tetrafluoroallene² (0.102 g., 0.91

TABLE 2

N.m.r. data for *cis*- and *trans*-2*H*-nonafluoropent-2-ene (references external CF_3 · CO_9H and benzene)

> (3) CF₃

(1) (2) CF₂—CF₂

			·	
		(4) F	H ⁽⁵⁾	Moduli of spin-spin
Nuclei 1	P.p.m. 8·6	Rel. int. 3	Multiplicity dqt	$\begin{array}{c} \text{constants} \\ \text{(c./sec.)} \\ J_{1.4} 7.9 \end{array}$
2	46.2	2	qdqd	$\begin{array}{c} J_{1,3} 2.8 \\ J_{1,2} 1.9 \\ J_{2,3} 15.0 \\ J_{2,4} 10.5 \end{array}$
3	20.0	3	tddq	$\begin{array}{c} J_{2,1} 1.9 \\ J_{2,5} 0.5 \\ J_{3,2} 15.0 \\ J_{3,4} 11.4 \end{array}$
4	35.2	1	dqtq	$\begin{array}{c} J_{3,5} & 7.8 \\ J_{3,1} & 2.8 \\ J_{4,5} & 19.2 \\ J_{4,3} & 11.4 \end{array}$
5	0·93 (7)		dq	$\begin{array}{c} J_{4,2} \ 10.5 \\ J_{4,1} \ 7.9 \\ J_{5,4} \ 19.2 \\ J_{5,3} \ 7.8 \end{array}$
	Ċ	$CF_{3} - CF_{2}$	$C = C \xrightarrow{(5)}_{H} CF_{3}(4)$	
				Moduli of spin–spin coupling constants
Nuclei 1	P.p.m. 7·8	Rel. int. 3	Multiplicity dt	(c./sec.) J _{1.3} 6·6
2	46.2	2	dseptet	$\begin{array}{c} J_{1,2}^{1,0} \ 1.9 \\ J_{2,3} \ 12.6 \end{array}$
3	36.9	1	dqtq	$\begin{array}{c} J_{2,1} \approx J_{2,4} 1.9\\ J_{3,5} 28.8\\ J_{3,4} 18.0\\ J_{3,4} 19.0 \end{array}$
4		3	ddt	$J_{3,2} \ 12.0 \\ J_{3,1} \ 6.6 \\ J_{4,3} \ 18.0 \\ J_{4,5} \ 7.0$
5	1·04 (τ)		dq	$J_{4,2} = 1.9 \\ J_{5,3} = 28.8 \\ J_{5,3} = 7.0$
	A	bbreviatio	ns as Table 1.	J 5.4 · V

mmole), and anhydrous hydrogen fluoride [obtained by heating dry potassium hydrogen fluoride (0.081 g., 1.03 mmole) at 600° in vacuo] gave, after 2 hr. in a copper tube (12 ml.) at 20°, tetrafluoroallene (0.019 g., 0.17 mmole, 19% recovery), perfluoropenta-1,2-diene (0.077 g., 0.37 mmole, 42% recovery), 2H-pentafluoropropene (0.097 g., 0.74 mmole, 100% on C_3F_4 lost), a 58 : 42 mixture (0.068 g., 0.33 mmole, 65% on C_5F_8 lost) of cis- and trans-2H-nonafluoropent-2-ene, and dimers of perfluoropenta-1,2-diene (0.039 g., 0.09 mmole, 35% on C_5F_8 lost). Products were identified by i.r. and g.l.c., by comparison with authentic samples, and the composition was determined by g.l.c. (7 m. D.N.P.-Embacel at 20°). The conditions employed would favour reaction of the hydrogen fluoride with the pentadiene, since the hydrogen fluoride would have been

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mainly in the liquid phase with the higher-boiling allene (HF, b.p. $19\cdot5^{\circ}$; C_3F_4 , b.p. $-37\cdot6^{\circ}$; C_5F_8 , b.p. $22\cdot9^{\circ}$).

(d) With anhydrous hydrogen chloride. Dimerisation of the allene was the only reaction observed when a mixture of dry hydrogen chloride and perfluoropenta-1,2-diene was (i) kept for 3 days at 20° in the dark, (ii) kept for 0.5 hr. at 100° in diffused daylight, or (iii) exposed to direct sunlight for 4 days in a Pyrex tube.

(e) With anhydrous hydrogen bromide. Dimerisation of the allene was the only reaction observed when a mixture of perfluoropenta-1,2-diene and anhydrous hydrogen bromide was kept in a sealed Pyrex tube for 12 hr. at 20° in the dark. A mixture of perfluoropenta-1,2-diene (0.445 g., 2·1 mmoles) and anhydrous hydrogen bromide (0·186 g., 2.3 mmoles) was therefore photolysed for 6 hr. in a silica tube (300 ml.) placed 15 cm. from a 500 w Hanovia lamp. Volatile products were passed in vacuo through a -22° trap and condensed in a -78° trap, to give a mixture of C_5 HBrF₈ isomers (0.462 g., 1.6 mmole, 70%) (Found: M, 292 by mass spectrometry. Calc. for $C_5H^{79}BrF_8$: M, 292) as a colourless liquid, b.p. 85-88°/760 mm., shown by g.lc. (2 m. Silicone-Embacel at 105°) to consist of four components, (i)—(iv), in the ratio 1:12:5:2. A high boiling residue (0.12 g.) was not investigated. G.l.c. separation of the mixture of C_5HBrF_8 isomers (on 4 m. D.N.P.-Embacel at 64°) gave i.r. samples of component (ii), shown to be 3H-2-bromo-octafluoropent-1-ene (44%), $\lambda_{max.}$ (vapour) 3.36w, 5.74vs (C.C str.), 7.22s, 7.52s, 7.62vs, 7.96vs, 8.12vs, 8.20sh, 8.38sh, 8.59vs, 8.80s, 9.17vs, 9.62vs, 10.04vs, 12.13s, 12.88w, 13.42vs, 13.95m, 14.40m, and 14.72s μ , and component (iii), believed to be cis-1H-2bromo-octafluoropent-2-ene, (19%), $\lambda_{max.}$ (vapour) 3.31w, 5.61w, 5.76vs (C.C str.), 5.88s (C.C str.), 5.98s, 7.23s, 7.38s, 7.53vs, 7.69vs, 8.00m, 8.14vs, 8.40vs, 8.6-8.7 (doublet) vs, 8.92m, 9.21m, 9.78vs, 10.05s, 10.22sh, 11.70m, 12.15m, 12.35m, and 13.60s μ , and component (iv), possibly trans-1H-2-bromo-octafluoropent-2-ene (8%), ¹⁹F n.m.r. bands at 6.9 (CF₃), 39.0 (CF₂H), and 42.7 (CF₂) p.p.m. upfield from CF₃·CO₂H (interchange).

A 12:5:2 mixture of components (ii)—(iv) was also obtained by g.l.c. separation (column as above), and used for ¹H and ¹⁹F n.m.r. analysis (CFCl₃ solution at 56.46 and 60 Mc./sec., data in Table 3), on which the structural assignments are based.

(f) With methanol. A mixture of methanol (distilled from magnesium, 0.2 g., 6.25 mmoles) and perfluoropenta-1,2-diene (0.7 g., 3.33 mmoles) was sealed in vacuo in a Pyrex tube (10 ml.) at -196° . A vigorously exothermic reaction occurred immediately the mixture melted; the temperature rose to ca. 40° after 1 min., whereupon the mixture was chilled, and separated by g.l.c. (4 m. Kel-F 10 oil-Embacel at 60°) to give heptafluoro-1-methoxypent-2-yne (0.172 g., 0.77 mmole, 23%) (Found: C, 32.4; H, 1.5%; M, 224 by mass spectrometry. C₆H₃F₇O requires C, 32.2; H, 1.3%; M, 224) as a colourless liquid, b.p. 49·1° (isoteniscope), λ_{\max} (vapour) 3·28w, 3·34m, 3·46w, 4·24w, 4·34w, 4·53w, 4·70w, 4·86w, 5·02w, 5·70w, 5·77w, 6.50w, 6.86m. 7.42s, 7.78vs, 8.10vs, 8.69vs, 9.09vs, 9.36vs, 10.05vs, 12.14m, 13.37m, 14.38vs, and 14.85m μ , ¹H and ¹⁹F n.m.r. data in Table 4, and trans-2H-octafluoro-1-methoxypent-2-ene (0.62 g., 2.54 mmole, 76%) (Found: C, 29.5; H, 1.9%; M, 244 by mass spectrometry. $C_6H_4F_8O$ requires C, 29.5; H, 1.6%; M, 244) as a polymerisable, colourless liquid, b.p. 72.3° (isoteniscope), λ_{max} (vapour) 3·18w, 3·21w, 3·30m, 3·34m, 3·40w, 3·47m, 5·78s (C.C

str.), 5.87sh, 6.88s, 7.20vs, 7.48vs, 7.80vs, 8.14vs, 8.45vs, 8.64vs, 8.85vs, 9.10vs, 9.40vs, 10.07vs, 11.95s, 12.40s, 13.40s, 14.38s, and 15.14s μ , ¹H and ¹⁹F n.m.r. data in Table 5.

TABLE 3

N.m.r. data for 3H-2-bromo-octafluoropent-1-ene and cis-1H-2-bromo-octafluoropent-2-ene (references internal tetramethylsilane and CF_3 · CO_2H interchange) obtained for a 25% solution in trichlorofluoromethane



^a The resonance due to nucleus 3 was not observed in the range (-40 to 70 p.p.m.) scanned, and is expected to occur at >90 p.p.m.



TABLE 4

N.m.r. data for perfluoropent-2-yne and heptafluoro-1-methoxypent-2-yne (references internal tetramethylsilane and external CF₃·CO₂H)

	(1) CF ₃ -	(2) −CF ₂ −−CΞ	≡CCF ₂ O	-CH ₃ Moduli of
Nuclei 1 2 3 4	P.p.m. 8.0 27.6 -16.6 $-6.38 (\tau)$	Rel. int. 3 2 2	Mulitiplicity t sextet t s	spin-spin coupling constants (c./sec.) $J_{1,2} 3 \cdot 3$ $J_{2,1} = J_{2,3} = 3 \cdot 3$ $J_{3,2} 3 \cdot 3$
		$\overset{(1)}{\mathrm{CF}_{3}}-\overset{(2)}{\mathrm{CF}_{2}}$	-C=C-CF ₃	
1 2 3	8.0 28.8 -24.2	3 2 3	t septet t	$\begin{array}{c} J_{1.2} & 3 \cdot 3 \\ J_{2.1} &= J_{2.3} \\ J_{3.2} & 3 \cdot 3 \end{array} = 3 \cdot 3 \end{array}$

Abbreviations as Table 1.

TABLE 5

N.m.r. data for *trans-2H*-octafluoro-1-methoxypent-2-ene (50% solution in CFCl₃) (references internal tetramethylsilane and external CF₃·CO₂H)



(g) With caesium fluoride. (i) Without solvent. Perfluoropenta-1,2-diene (0.221 g., 1.04 mmole) was distilled during 1 hr. from a flask at -45° through a Pyrex tube (3 mm. i.d., 30 cm. long) packed with anhydrous caesium fluoride (dried at 200° in vacuo) and maintained at $100^{\circ}/10^{-1}$ mm. Products were collected in -196° traps and separated by g.l.c. (4 m. D.N.P.-Embacel at 20°) to give perfluoropenta-1,2-diene (0.01 mmole, 1% recovery), trans-2Hnonafluoropent-2-ene (0.03 mmole, 3%) identified by i.r. and g.l.c., and perfluoropent-2-yne (0.211 g., 1.0 mmole, 96% based on C_5F_8 consumed) (Found: C, 28.1%; M, 211 by Regnault's method. Calc. for C_5F_8 : C, 28.3%; M, 212), as a colourless gas, b.p. 3.8° (isoteniscope; lit.,⁹ b.p. 3-4°), λ_{max} (vapour) 4.03w, 4.16w, 4.22w, 4.32w, 4.86w, 6.46w, 6.53w, 6.74w, 6.88w, 7.05w, 7.23m, 7.42s, 7.60s, 7.73vs, 7.85vs, 8.07vs, 8.40vs, 8.63vs, 9.01m, 9.41vs, 9.83m, 11.74s, 13.15s, 14.05w, and 14.60vs µ with the correct ¹⁹F n.m.r. spectrum (Table 4).⁹

(ii) In perfluoro-n-hexane. A solution of perfluoropenta-1,2-diene (0.212 g., 1.0 mmole) and caesium fluoride (anhydrous; 0.24 g., 1.6 mmole) in perfluoro-n-hexane (1.5 ml.) was kept in a sealed Pyrex tube (8 ml.) at 20° for 18 hr., to give perfluoropenta-1,2-diene (0.05 g., 0.24 mmole, 24% recovery), perfluoropent-2-yne (0.45 g., 0.21 mmole, 28% based on allene consumed), the dimers of perfluoropenta-1,2-diene (0.09 g., 0.21 mmole, 55% based on allene consumed), and perfluoro-n-hexane, identified and composition determined by g.l.c. (4 m. D.N.P.-Embacel at 20°).

(iii) In formamide. A solution of perfluoropenta-1,2-diene (0.344 g., 1.62 mmole) and anhydrous caesium fluoride (0.301 g., 2.0 mmoles) in formamide (1.5 ml.) was shaken in a sealed Pyrex tube (8 ml.) at 20°. A rapid colour change through yellow and orange to dark brown occurred during the first 15 min. After a total of 15 hr., trans-2H-nonafluoropent-2-ene (0.255 g., 1.1 mmoles, 68%) was isolated

⁹ W. T. Miller, W. Frass, and P. R. Resnick, J. Amer. Chem. Soc., 1961, **83**, 5582.

and identified by g.l.c., by comparison with an authentic sample.

Attempted Reaction of Perfluoropent-2-yne with Caesium Fluoride.—No reaction occurred when perfluoropent-2-yne (0.123 g., 0.58 mmole), anhydrous caesium fluoride (0.24 g., 1.58 mmole), and formamide (1.5 ml.) were shaken at 20° for 18 hr. in a sealed Pyrex tube (8 ml.). G.l.c. analysis

of the product showed that the perfluor opent-2-yne (0.115 g., 0.54 mmole, 93% recovery) was unchanged.

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