Fluoro-olefins. Part VII.[1] Some Thermal Diels–Alder Reactions of Perfluorocyclohexa-1,3-diene

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Perfluorocyclohexa-1,3-diene acts as both a diene and a dienophile in its thermal reactions with cyclopentadiene (to give 1,7,8,9,10,10,11,11-octafluorotricyclo[5,2,2,$0^{2,6}$]undeca-3,8-diene and 2,3,4,5,5,6,6,7-octafluorotricyclo[6,2,1,$0^{2,7}$]undeca-3,9-diene) and cyclohexa-1,3-diene (to give 1,8,9,10,11,11,12,12- and 2,3,4,5,5,6,6,7-octafluorotricyclo[6,2,2,$0^{2,7}$]dodeca-3,9-diene), but when it is heated with perfluorocyclopentadiene only the dimer of the latter is obtained. Thermal reaction of perfluorocyclohexa-1,3-diene with *N*-allyltrifluoroacetamide gives a Diels–Alder adduct, *N*-(1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]oct-5-en-2-ylmethyl)trifluoroacetamide; the corresponding amine, generated *via* reaction of the amide with methanolic hydrogen chloride, slowly isomerises to 1,2,3,7,8,8,9,9-octafluoro-4-azatricyclo[4,3,1,$0^{3,7}$]decane, thus indicating that the original adduct is predominantly or even exclusively the *endo*-isomer.

THIS work stemmed from a detailed study of Diels–Alder reactions of perfluorocyclopentadiene,[2] and was carried out at a time when published information on cycloaddition reactions of perfluorocyclohexa-1,3-diene was restricted to a brief report[3] of the formation of 1,4-adducts with monosubstituted ethylenes [type (I)] and maleic anhydride, of an undefined adduct with anthracene, and of three adducts [(II)—(IV)] with butadiene. Recently the formation of Diels–Alder adducts from perfluorocyclohexa-1,3-diene and alkynes[4] and nitriles[5] has been described in detail.

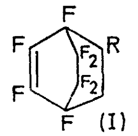
^{19}F N.m.r. (56·46 MHz) spectral parameters of Diels–Alder adducts of perfluorocyclohexa-1,3-diene and derived compounds

	Chemical shift assignments (p.p.m. to high field of trifluoroacetic acid)[b]		
Compound[a]	$-CF_2-$	$=CF-$	$\geqslant CF$
(XIV)[c]	51·0	73·5	123·3
		74·4	128·5
(XV)	50·0	72·0	122·4
		73·2	126·7
(XVI)	50·4	73·4	122·8
		76·6	129·2
(XVII)	46·8	*d*	120·0
	54·4		121·4
(VI)	49·0	73·3	127·4
	49·6	74·0	
(XI)	49·8	72·4	128·0
	50·3	74·2	128·9
(VII)	40·0	62·8	90·7
	45·4	78·0, 78·4	
(VIII)	38·6	60·2	82·7
	44·0	73·8, 73·8	
(XII)	42·2	64·3	87·8
	42·9	77·1	99·1

[a] The following samples were examined (% refers to w/w): (XIV), 25% in MeCN; (XV), 25% in Me_2CO; (XVI), neat (>95%); (XVII), *ca.* 50% mixture with (XVI); (VI), 20% in $CDCl_3$; (XI), neat; (VII), 60% in $CDCl_3$; (VIII), <10% in $CDCl_3$; (XII), *ca.* 25% mixture with (XI). [b] Correct relative intensities of absorptions were observed. [c] δ_{CF_3} $-0·8$ p.p.m. (s). [d] $\delta_{N\cdot CF}$ 60·4; δ_{CHF} 136·0 p.p.m. ($|J_{H,F\text{-}gem}|$ 53·6 Hz).

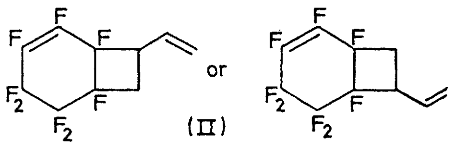
The results presented here show that, like perfluorocyclopentadiene,[2b,c] perfluorocyclohexa-1,3-diene acts as both a diene and a dienophile in its reactions with cyclopentadiene and cyclohexa-1,3-diene. For both perfluoro-dienes this phenomenon possibly arises from the operation of a concerted but non-synchronous mechanism of the type proposed by Woodward and Katz.[6] Full discussion of this is deferred to a later publication.

^{19}F *Nuclear Magnetic Resonance Spectra of the Diels–Alder Adducts from Perfluorocyclohexa-*1,3-*diene.*—The structures of all the compounds reported herein were



(I)

R = Ac, CO_2Me, CN, OEt, or Ph



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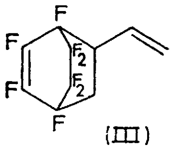
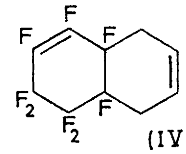


(III)



(IV)

established by a combination of chemical and spectroscopic (particularly ^{19}F n.m.r.) methods. The basic problem was how to distinguish, by ^{19}F n.m.r. spectroscopy, between compounds containing dienic residue (A), *i.e.* that arising from 1,4-addition to perfluorocyclohexa-1,3-diene, and those containing residue (B), *i.e.* that arising from 1,2-addition to the diene. Examination of the ^{19}F n.m.r. spectra of the compounds isolated during this investigation revealed that they fall into two classes having distinct characteristic absorption parameters. By comparing these parameters with those of

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[1] Part VI, R. E. Banks, J. M. Birchall, T. Clarke, R. N. Haszeldine, and M. J. Stevenson, *J. Chem. Soc.* (*C*), 1968, 266.

[2] (*a*) R. E. Banks, L. E. Birks and R. N. Haszeldine, *J. Chem. Soc.* (*C*), 1970, 201 and references quoted therein; (*b*) R. E. Banks, L. E. Birks, M. Bridge, A. C. Harrison, R. N. Haszeldine, P. Hunt, and H. M. E. Steiner, unpublished results; (*c*) R. E. Banks, A. C. Harrison, and R. N. Haszeldine, *Chem. Comm.*, 1966, 338.

[3] R. D. Chambers, W. K. R. Musgrave, and D. A. Pyke, *Chem. and Ind.*, 1965, 564.

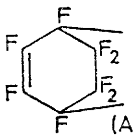
[4] L. P. Anderson, W. J. Feast, and W. K. R. Musgrave, *J. Chem. Soc.* (*C*), 1969, 211.

[5] L. P. Anderson, W. J. Feast, and W. K. R. Musgrave, *J. Chem. Soc.* (*C*), 1969, 2559.

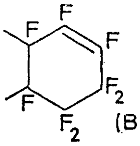
[6] R. B. Woodward and T. J. Katz, *Tetrahedron*, 1959, **5**, 70.

1,2- and 1,4-adducts of perfluorocyclopentadiene [7] and by reference to chemical and other spectroscopic data on the compounds it has been possible to distinguish between those adducts containing residue (A) and those containing (B).

The characteristic parameters are as follows. (i) The

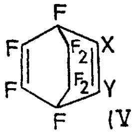


(A)



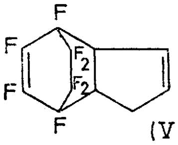
(B)

absorption of the CF$_2$ groups in (A) is centred at *ca.* 50 p.p.m. to high field of external trifluoroacetic acid, whereas in residue (B) it occurs at *ca.* 40—45 p.p.m. (ii) A greater chemical shift difference is observed between the vinylic fluorine absorptions in (B) (>10 p.p.m.) than in (A) (<5 p.p.m.). (iii) The tertiary (bridgehead) fluorines in (A) resonate at much higher applied field (*ca.* 125 p.p.m.) than those in (B) (*ca.* 90 p.p.m.) and a considerable chemical shift difference (*ca.* 10 p.p.m.) is observed between types >*CF*·CF$_2$– and >*CF*·CF= in the latter residue. The parameters assigned to residue (A) are consistent with those reported recently [4] for a series of octafluorobicyclo[2,2,2]-octa-2,5-diene derivatives (V).

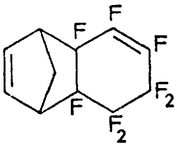


(V)

Reactions of Perfluorocyclohexa-1,3-*diene with Other Cyclic Dienes*.—(i) *With perfluorocyclopentadiene and cyclopentadiene*. The rapid self-dimerisation of perfluorocyclopentadiene [8] prevents the formation of an adduct between this diene and perfluorocyclohexa-1,3-diene, but the ' electron rich '–' electron poor ' system



(VI)

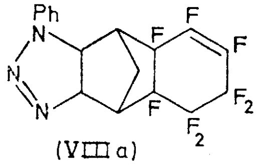


(VII)

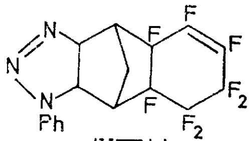
cyclopentadiene–perfluorocyclohexa-1,3-diene gives a 19 : 81 mixture of two 1 : 1 adducts in 86% total yield during 24 hr. at 75°. Structures (VI) and (VII), respectively, are assigned to these adducts on the basis of i.r. and n.m.r. spectroscopic analyses; *endo*-configurations are proposed since reactions between cyclopentadiene and cyclic conjugated dienophiles normally obey Alder's ' *endo* ' rule [9] and the same can reasonably be expected to hold for reactions of perfluorocyclohexa-1,3-diene on the basis of the work with *N*-allyltrifluoroacetamide described later.

The i.r. spectrum of the minor adduct (VI) shows a strong CF:CF str. absorption at 5·69 μm., *i.e.*, within the range quoted [3] for the 1,4-adducts (I) (5·67—5·69 μm.) and close to that absorption shown by 1,4-adducts of type (V) (5·63—5·67 μm.),[4] whereas that of the major adduct (VII) displays strong CF:CF absorption at 5·75 μm., compatible with values reported for perfluorocyclohexene (5·73 μm.) [10] and the 1,2-adducts (II) (5·75) and (IV) (5·73 μm.).[3]

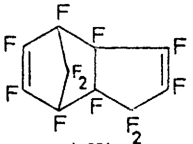
The ^{1}H n.m.r. spectrum of the major adduct (VII) is characteristic of a 1,4-adduct of cyclopentadiene,[7,11] showing three systems of approximately equal intensities at τ 3·85 (s, =CH–), 6·74br (s, >CH), and 7·72 (AB, $|J_{gem}|$ 9·0 Hz, internal chemical shift 0·3 p.p.m., >CH$_2$); similarly the spectrum of the minor adduct (VI) is consistent [7,11] with a structure derived from 1,2-addition to cyclopentadiene and shows a broadened doublet centred at τ 4·10 (possibly an AB pattern with undetected outer members, =CH–), two broad bands at τ 6·42 and 6·72 (>CH) and a broad singlet at τ 7·83 (>CH$_2$) of approximate relative intensities 2 : 1 : 1 : 2.



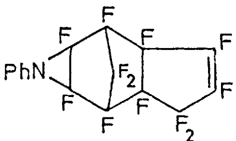
(VIIIa)



(VIIIb)



(IX)



(X)

The major adduct reacts readily with phenyl azide at room temperature to give triazoline (VIII) in 94% yield. This provides chemical support for structure (VII), since ready addition of phenyl azide is an established diagnostic test for a bicyclo[2,2,1]heptene residue [13] and perfluorotricyclo[5,2,1,0^{2,6}]deca-3,8-diene (IX), which contains a strained CF:CF bond, does not appear to combine with phenyl azide at room temperature during 1 month but reacts at 70° to yield the aziridine (X).[12] In view of the complexity of the fine structure in its ^{19}F n.m.r. spectrum, the triazoline (which retains CF:CF str. absorption in the i.r. at 5·75 μm.) is believed to be a mixture of isomers (VIIIa) and (VIIIb); as in the ^{19}F n.m.r. spectrum of (VII) (see later), one of the olefinic

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[7] R. E. Banks, A. C. Harrison, R. N. Haszeldine, and K. G. Orrell, *J. Chem. Soc.* (*C*), 1967, 1608.

[8] R. E. Banks, A. C. Harrison, and R. N. Haszeldine, *J. Chem. Soc.* (*C*), 1966, 2102.

[9] J. G. Martin and R. K. Hill, *Chem. Rev.*, 1961, **61**, 537.

[10] J. K. Brown and K. J. Morgan, *Adv. Fluorine Chem.*, 1965, **4**, 269.

[11] P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Amer. Chem. Soc.*, 1964, **86**, 616.

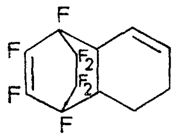
[12] R. E. Banks, M. Bridge, R. Fields, and R. N. Haszeldine, *J. Chem. Soc.* (*C*), in the press.

[13] R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 565.

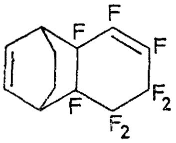
fluorine absorptions coincides (at 73·8 p.p.m.) with that of one tertiary nucleus.

Nine bands appear in the ^{19}F n.m.r. spectrum of the major adduct (VII), four of which form an AB pattern (J_{gem} 278 Hz, internal chemical shift 11·1 p.p.m., integrated intensity 1·9) centred at 40·0 p.p.m. and assigned to one CF$_2$ group; a singlet at 45·4 p.p.m. (intensity 2·0) is assigned to the other. The other bands appear at 62·8, 78·0, 78·4, and 90·7 p.p.m.; the first and last of these (integrated intensities 1·0 and 0·9) are assigned to one olefinic and one tertiary fluorine nucleus, respectively, but specific assignment of the 78·0 and 78·4 p.p.m. bands has not been possible.

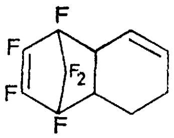
(ii) *With cyclohexa*-1,3-*diene*. Treatment of perfluorocyclohexa-1,3-diene with its hydrocarbon analogue at 60° gives an unidentified white solid, which does not melt below 360° and is insoluble in common solvents, and a *ca*. 10 : 1 mixture (61% yield) of two 1 : 1 adducts; these are formulated as (XI) and (XII), respectively, on the basis of i.r. and n.m.r. spectroscopic analyses and are presumed to possess *endo*-configurations.



(XI)



(XII)



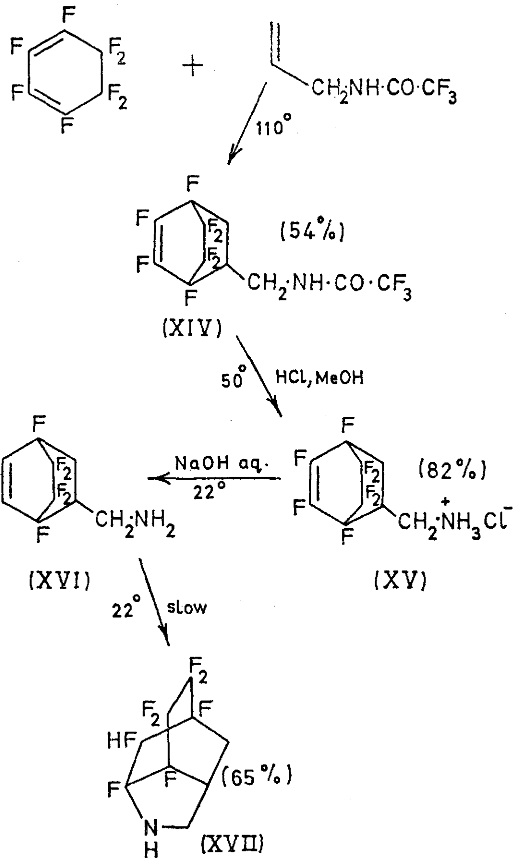
(XIII)

The i.r. spectrum of the major adduct (XI) exhibits olefinic absorptions at 5·68s (CF:CF str.) and 6·04w µm. (CH:CH str.) and its ^{19}F n.m.r. spectrum displays absorptions characteristic of a residue of type (A) (see Table). A pure sample of the minor component (XII) could not be isolated, so it was examined spectroscopically as a mixture (*ca*. 1 : 3) with (XI). The i.r. spectrum contains CF:CF str. absorption at 5·72 µm. [which appeared as a shoulder on the 5·68 µm. absorption of (XI)], typical of a 1,2-adduct of perfluorocyclohexa-1,3-diene (see before), and the ^{19}F n.m.r. spectrum (see Table) also contains absorptions characteristic of such an adduct.

The ^{1}H n.m.r. spectrum of the major adduct (XI) is similar to that of the corresponding Diels–Alder adduct of perfluorocyclopentadiene with cyclohexa-1,3-diene (XIII),[2b] showing an AB pattern ($|J|$ 9·3 Hz, internal chemical shift 0·6 p.p.m.) centred at τ 3·98 (=CH–) and two broad bands at τ 7·13 ($\geq$CH) and 8·05 (>CH$_2$) (relative intensities 1 : 1 : 2). The spectrum of the 1 : 3 mixture of (XII) and (XI) contains additional absorption at *ca*. τ 3·8 (=CH–) [visually obscured by the low-field branch of the AB system of (XI) but detected by integration], a broad singlet at τ 6·84 ($\geq$CH) and complex absorption centred at *ca*. τ 8·5 (>CH$_2$). These parameters are not inconsistent with published data on bicyclo[2,2,2]octene derivatives.[14]

Reaction of Perfluorocyclohexa-1,3-*diene with* N-*Allyltrifluoroacetamide*.—This reaction was studied to provide information about the stereochemistry of Diels–Alder reactions of perfluorocyclohexa-1,3-diene. The method follows exactly that used in the case of perfluorocyclopentadiene,[2a] and, as in the case of the pentadiene, reveals that the adduct (XIV) formed with *N*-allyltrifluoroacetamide is predominantly, or even exclusively, the *endo*-isomer (see Scheme).

The Diels–Alder adduct (XIV) of perfluorocyclohexa-1,3-diene with *N*-allyltrifluoroacetamide was obtained in 54% yield (based on 70% consumption of the diene, which, unlike perfluorocyclopentadiene,[2a,8] does not undergo competitive dimerisation [5] at 110°). The free amine (XVI) cycloisomerises much less rapidly than the corresponding compound derived from perfluorocyclopentadiene, in keeping with a less strained double bond and (as revealed by a study of Framework models) a greater distance between the amino nitrogen and the proximate –CF= group. ^{19}F N.m.r. spectroscopy was used to follow the isomerisation of the primary amine (XVI) into the azatricyclodecane (XVII), and the half-life of the free amine was found to be *ca*. 24 hr. at 35°.



SCHEME

Compounds (XIV), (XV), and (XVI) each display a CF:CF str. absorption in the i.r. at 5·67 µm., as expected for adducts containing the dienic residue (A); ^{19}F n.m.r. spectral assignments for compounds (XIV)—(XVII) are listed in the Table.

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[14] *E.g.*, K. Tori, H. Kitahonoki, Y. Takano, and T. Tsuji, *Tetrahedron Letters*, 1964, 559.

EXPERIMENTAL

I.r., mass, and n.m.r. spectra were recorded with a Perkin-Elmer 257 (grating) spectrophotometer, an A.E.I. MS902 spectrometer (ionising electron beam energy 70 ev), and a Perkin-Elmer R10 spectrometer (56·46 MHz for ^{19}F spectra, 60·00 MHz for ^{1}H), respectively. G.l.c. was performed with Perkin-Elmer Fraktometer model 116 and Pye model 104 chromatographs.

Perfluorocyclopentadiene was prepared by dechlorination of tetrachlorohexafluorocyclopentane with zinc.[15] Perfluorocyclohexa-1,3-diene (Imperial Smelting Corp., Avonmouth) was distilled under nitrogen before use.

Reactions of Perfluorocyclohexa-1,3-*diene*.—(a) *With perfluorocyclopentadiene.* An equimolar mixture of perfluorocyclohexa-1,3-diene (3·14 g.) and perfluorocyclopentadiene (2·45 g.) was heated at 110° for 2 days in a Pyrex ampoule (300 ml.). Fractionation of the product gave perfluorocyclohexa-1,3-diene (2·97 g., 95% recovery), perfluorocyclopentadiene dimer (2·39 g., 98%) (both identified by i.r. and g.l.c. analysis), and traces of an insoluble white solid that was not investigated.

(b) *With cyclopentadiene.* An equimolar mixture of perfluorocyclohexa-1,3-diene (4·48 g., 20·0 mmoles) and cyclopentadiene (1·32 g., 20·0 mmoles) was heated at 75° for 24 hr. in a Pyrex ampoule (300 ml.). The involatile product (5·10 g.), a pale yellow oil, was shown by g.l.c. (4 m. silicone oil MS550, Celite; 175°) to contain two components (ratio 19 : 81), samples of which were isolated by preparative g.l.c. and shown to be 1,7,8,9,10,10,11,11-*octafluorotricyclo*[5,2,2,$0^{2,6}$]*undeca*-3,8-*diene* (estimated yield 16%) [Found: C, 45·8; H, 2·2%; *M* (mass spec.), 290. $C_{11}H_6F_8$ requires C, 45·5; H, 2·1%; *M*, 290], m.p. 40—41°, b.p. (Siwoloboff) 179—180°, and 2,3,4,5,5,6,6,7-*octafluorotricyclo*[6,2,1,$0^{2,7}$]*undeca*-3,9-*diene* (estimated yield 70%) [Found: C, 45·5; H, 2·1%; *M* (mass spec.), 290. $C_{11}H_6F_8$ requires C, 45·5; H, 2·1%; *M*, 290], b.p. (Siwoloboff) 181—182°, respectively.

A mixture of 2,3,4,5,5,6,6,7-octafluorotricyclo[6,2,1,$0^{2,7}$]-undeca-3,9-diene (1·36 g., 4·69 mmoles) and phenyl azide (0·56 g., 4·71 mmoles) solidified during 3 days storage at room temperature. The product was sublimed *in vacuo* (105° bath) to yield an approximately equimolar mixture (by n.m.r. analysis) of 2,3,4,5,5,6,6,7-octafluoro-10-phenyl-10,11,12-triazatetracyclo[6,5,1,0,$^{2,7}0^{9,13}$]tetradeca-3,11-diene and 2,3,4,5,5,6,6,7-octafluoro-12-phenyl-10,11,12-triazatetracyclo[6,5,1,0,$^{2,7}0^{9,13}$]tetradeca-3,10-diene (1·80 g., 4·40 mmoles, 94%) (Found: C, 49·9; H, 3·0; N, 10·2. $C_{17}H_{11}F_8N_3$ requires C, 50·0; H, 2·7; N, 10·3%) as a white solid that decomposed slowly when heated above 110°.

(c) *With cyclohexa*-1,3-*diene.* An approximately equimolar mixture of perfluorocyclohexa-1,3-diene (3·60 g., 16·06 mmoles) and cyclohexa-1,3-diene (1·29 g., 16·12 mmoles) was heated at 60° for 24 hr. in a Pyrex ampoule (300 ml.). The involatile product (4·75 g.), a mixture of a colourless oil and a white solid, was filtered and the solid, which discoloured without melting when heated to 360°, was discarded; the oil (3·14 g.) (Found: C, 47·4; H, 2·8. A 1 : 1 adduct of C_6F_8 and C_6H_8 requires C, 47·4; H, 2·6%), b.p. (Siwoloboff) 208—210°, was shown by g.l.c. to contain two components in the ratio of *ca.* 10 : 1. G.l.c. separation (2 m. silicone SE30, Celite; 145°) of the oil gave 1,8,9,10,11,11,12,12-octafluorotricyclo[6,2,2,$0^{2,7}$]dodeca-3,9-diene (estimated yield 40%) and a *ca.* 3 : 1 mixture (by n.m.r. analysis) of this diene (total yield *ca.* 55%) and 2,3,4,5,5,6,6,7-octafluorotricyclo[6,2,2,$0^{2,7}$]dodeca-3,9-diene (yield *ca.* 6%).

(d) *With* N-*allyltrifluoroacetamide.* Perfluorocyclohexa-1,3-diene (2·82 g., 12·6 mmoles) was heated with *N*-allyltrifluoroacetamide (2·00 g., 13·1 mmoles) at 110° for 2 days in a Pyrex ampoule (60 ml.). The volatile product was pumped out of the reaction vessel and shown by i.r. spectroscopy to be perfluorocyclohexa-1,3-diene (0·86 g., 3·84 mmoles, 30% recovery); the involatile product, a dark brown material, was washed out of the reaction vessel with 1,2-dichloroethane and sublimed *in vacuo* (90° bath) to give a yellowish solid that was re-sublimed to yield N-(1,4,5,6,7,7,8,8-*octafluorobicyclo*[2,2,2]*oct*-5-*en*-2-*ylmethyl*)*trifluoroacetamide* (1·78 g., 4·72 mmoles, 54% based on perfluorocyclohexa-1,3-diene consumed) [Found: C, 35·3; H, 1·9; N, 3·8%; *M* (mass spec.), 377. $C_{11}H_6F_{11}NO$ requires C, 35·0; H, 1·6; N, 3·7%; *M*, 377], a white solid, m.p. 89·5—90·0°, $\lambda_{max.}$ (mull) 3·02br (bonded N–H str.), 5·67 (CF:CF str.), 5·77 and 5·85 (amide I band), and 6·34 μm. (amide II band).

The amide (0·48 g., 1·28 mmole) was heated at 50° for 10 hr. with methanol (10 ml.) saturated with dry hydrogen chloride. The solution was evaporated at 50° under reduced pressure and the yellowish residue was washed with dry chloroform, leaving (1,4,5,6,7,7,8,8-*octafluorobicyclo*-[2,2,2]*oct*-5-*en*-2-*ylmethyl*)*ammonium chloride* (0·33 g., 1·04 mmole, 82%) (Found: C, 34·3; H, 2·8; N, 4·5. $C_9H_8ClF_8N$ requires C, 34·0; H, 2·5; N, 4·4%) as a white solid, m.p. 254° (decomp.), $\lambda_{max.}$ (mull) 3·37vbr ($\overset{+}{N}H_3$ asym. and sym. str.), 5·67 (CF:CF str.), and 6·27br μm. ($\overset{+}{N}H_3$ asym. bending). The highest-mass peak in the mass spectrum of the ammonium salt appeared at *m*/*e* 281 (46%), corresponding to the parent ion of the free amine, $[C_9H_7F_8N]^{+\cdot}$.

A vigorously stirred mixture of ether (20 ml.) and a solution of the ammonium chloride (1·18 g., 3·71 mmoles) in water (25 ml.) was titrated (phenolphthalein) against 0·01M-sodium hydroxide (Found: Equiv., 314. $C_9H_8ClF_8N$ requires Equiv. wt., 317·5). The ether layer was dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give a pale brown oil, $\lambda_{max.}$ (film) 2·92 and 3·04 (doublet N–H str.) and 5·67 μm. (CF:CF str.), shown by ^{19}F n.m.r. spectroscopy to be essentially 1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]oct-5-en-2-ylmethylamine, which slowly solidified when stored in a Pyrex ampoule; after 25 days, the solid was removed from the ampoule and sublimed *in vacuo* (85° bath) to yield 1,2,3,7,8,8,9,9-*octafluoro*-4-*azatricyclo*[4,3,1,$0^{3,7}$]*decane* (0·68 g., 2·42 mmoles, 65%) [Found: C, 38·7; H, 2·6; N, 4·7%; *M* (mass spec.), 281. $C_9H_7F_8N$ requires C, 38·4; H, 2·5; N, 5·0%; *M*, 281], a white solid, m.p. 209°, $\lambda_{max.}$ (mull) 2·93 μm. (sharp, N–H str.).

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