Polyfluorocyclopentadienes. Part V.[1] Reaction of Perfluorocyclopentadiene with *N*-Allyltrifluoroacetamide

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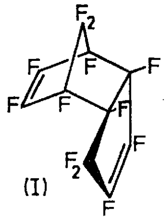
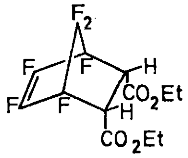
Reaction of perfluorocyclopentadiene with *N*-allyltrifluoroacetamide at 50° gave a Diels–Alder adduct, *N*-(1,4,5,6,7,7-hexafluorobicyclo[2,2,1]hept-5-en-2-ylmethyl)trifluoroacetamide. The corresponding amine, generated by hydrolysis of the amide, isomerised spontaneously to 1,2,3,7,8,8-hexafluoro-4-azatricyclo[4,2,1,0^{3,7}]nonane, thus indicating that the amide adduct was predominantly, or even exclusively, the *endo*-isomer.

THE thermal dimer of perfluorocyclopentadiene[2] has been assigned an *endo*-configuration (I) on the basis of a detailed analysis of its ^{19}F n.m.r. spectrum[3] and the formation of the same saturated fluorocarbon, $C_{10}F_{16}$, when the dimer and *endo*-tricyclo[5,2,1,0^{2,6}]decane are treated with cobalt trifluoride.[4] Otherwise, no absolute stereochemical assignments have been made for Diels-Alder adducts obtained by thermal 1,4-addition of appropriate olefins to perfluorocyclopentadiene, although the problem has received some attention. Thus, an adduct prepared from perfluorocyclopentadiene and diethyl maleate has been tentatively assigned the *endo*-configuration (II) on the basis of a comparison of its ^{19}F n.m.r. spectrum with that of the corresponding *trans*-isomer;[1] and inconclusive attempts have been made[5] to determine the configurations of two stereoisomers of the perfluorocyclopentadiene–norbornadiene adduct (III) by use of the photo-cycloisomerisation method.[6] Attempts to apply the photochemical technique to the adduct (IV) have been frustrated by the isolation of only the isomeric compound (V) from the product of thermal reaction between perfluorocyclopentadiene and *p*-benzoquinone.[7]


(I)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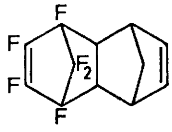
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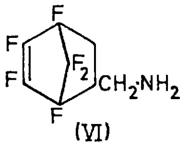
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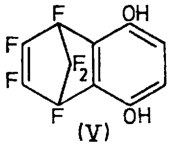
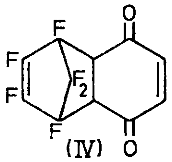
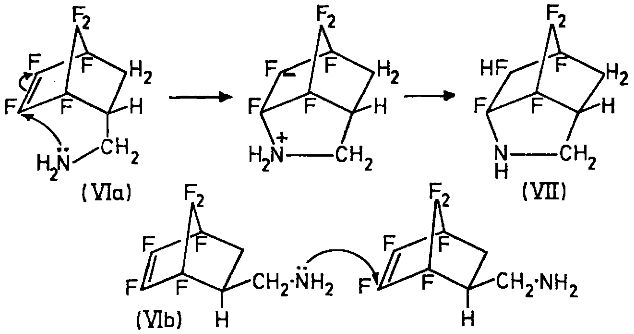

(V)


(IV)

The object of the present work was to prepare an adduct that could be examined by chemical methods in a manner analogous to the classical bromo- or iodo-lactonisation technique, applicable to Diels-Alder adducts derived from cyclopentadiene.[8] Since perfluoro-olefins readily undergo nucleophilic addition reactions with primary alkylamines,[9] adduct (VI), derived theoretically from perfluorocyclopentadiene and allylamine, seemed ideal for study: the *endo*-isomer (VIa) was expected to isomerise *via* ring closure to the amine (VII) and the *exo*-isomer (VIb) to undergo intermolecular addition (see Scheme 1).



SCHEME 1

Owing to the susceptibility of perfluorocyclopentadiene towards nucleophilic attack,[10] it was considered impractical at the outset to prepare (VI) directly from the diene and allylamine (this was verified later when the two components were found to interact below room temperature and to give a tar when heated together under conditions appropriate[5] to the formation of a Diels-Alder adduct); accordingly, the hydrochloride of (VI) was synthesised indirectly, in 26% yield, from perfluorocyclopentadiene and *N*-allyltrifluoroacetamide (see Scheme 2). The structures of the Diels-Alder adduct from perfluorocyclopentadiene and *N*-allyltrifluoroacetamide (VIII) and the derived hydrochloride (IX) were established by elemental analysis and spectroscopic methods; in particular, their ^{19}F n.m.r. spectra

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[1] Part IV, R. E. Banks, M. Bridge, and R. N. Haszeldine, *J. Chem. Soc.* (*C*), 1970, 48.

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

[3] R. Fields, M. Green, and A. Jones, *J. Chem. Soc.* (*B*), 1967, 270.

[4] J. Burdon, T. M. Hodgins, D. R. A. Perry, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 808.

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

[6] See J. Sauer, *Angew. Chem. Internat. Edn.*, 1967, **6**, 16, and references cited therein.

[7] R. E. Banks, M. Bridge, and R. N. Haszeldine, unpublished results.

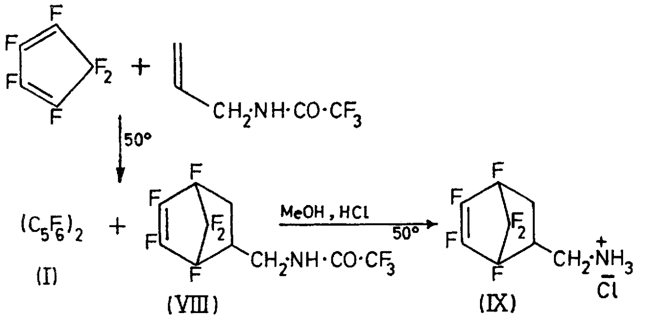
[8] See. H. Stockmann, *J. Org. Chem.*, 1961, **26**, 2025 and references cited therein.

[9] R. E. Banks, 'Fluorocarbons and their Derivatives,' Oldbourne, London, 1964.

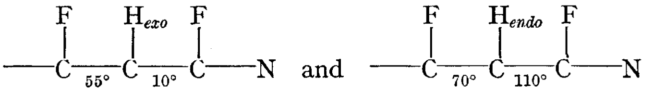
[10] F. L. Bowden, R. N. Haszeldine, and A. D. Hulme, publication in preparation dealing with reactions between perfluorocyclopentadiene and metal carbonyl anions; R. E. Banks, L. E. Birks, and R. N. Haszeldine, other work in progress.

were fully consistent with the presence of the 1,4,5,6,7,7-hexafluoro[2,2,1]hept-5-en-2-yl group.[5]

The free amine (VI) was released by titration of its hydrochloride (IX) against sodium hydroxide, but although the solid product isolated (68%) had a molecular formula corresponding to (VI), its i.r. spectrum showed only a single weak band in the N–H str. region at 2·92 µm. and extremely weak absorption in the CF⁚CF str. region at 5·70 µm. that disappeared after the product had been stored at room temperature for several weeks [the bicycloheptenes (VIII) and (IX) exhibit strong permanent absorptions at 5·70 and 5·71 µm., respectively]. Neither the 56·46 nor the 94·10 MHz ^{19}F n.m.r. spectrum of the product (25% w/v in acetone) showed an AB pattern characteristic[5] of a 1,4,5,6,7,7-hexafluoro[2,2,1]hept-5-enyl group, but comprised five band absorption systems of relative intensities 1·0 : 2·0 : 1·0 : 1·0 : 1·0 at 56·3 (CF·NH), 59·3 (CF_2; $W_{\frac{1}{2}}$ *ca.* 14 Hz at both 56·46 and 94·10 MHz), 126·8, 131·0, and 133·1 (CHF) p.p.m. to high field of external trifluoroacetic acid; the last absorption showed a doublet ($|J|$ 56 Hz) characteristic of a geminal CHF group. Thus the final product of removal of the amine-protecting group from the Diels-Alder adduct of perfluorocyclopentadiene and *N*-allyltrifluoroacetamide formed at 50° is assigned the tricyclononane structure (VII), presumably formed *via* the *endo*-amine (VIa) (Scheme 1); this implies that the adduct is predominantly or even exclusively the *endo*-isomer. The i.r. evidence quoted indicates either that ring closure of (VIa) was not complete when the product was isolated or that some *exo*-amine (VIb) was present and was lost slowly *via* an intermolecular process (see Scheme 1), or both. The 100 MHz ^1H spectrum of a solution of (VII) in carbon tetrachloride shows a band system at τ 4·90 caused by the proton of the CHF group, and highly complex absorption in the range τ 6·4—8·0; the τ 4·90 band appears as a doublet ($|J_{HF\text{-}gem}|$ 56 Hz) of poorly resolved triplets ($|J|$ *ca.* 10 Hz) showing additional fine structure. The latter fairly substantial couplings, in the light of recent proposals regarding the dihedral angle dependence of vicinal proton–fluorine couplings in cyclic systems,[11] suggest that the hydrogen of the CHF group in compound (VII) lies in the *exo*-position; the approximate values of the dihedral angles in question, estimated by use of Framework molecular models, are:



SCHEME 2



On the basis of the work described, Diels-Alder reactions of perfluorocyclopentadiene are expected to comply with Alder's '*endo*' rule fairly closely, as do those of cyclopentadiene.[6]

EXPERIMENTAL

I.r. spectra were recorded with a Perkin–Elmer model 257 grating instrument, mass spectra with an A.E.I. MS902 spectrometer (ionising electron beam energy 70 ev), and n.m.r. spectra with a Perkin–Elmer R10 instrument operated at 60 (^1H) or 56·46 MHz (^{19}F) or a Varian HA-100 spectrometer operated at 100 (^1H) or 94·10 MHz (^{19}F). G.l.c. analyses were performed with a Pye 104 chromatograph.

Perfluorocyclopentadiene was prepared by dechlorination of tetrachlorohexafluorocyclopentane with zinc in bis-(2-methoxyethyl) ether.[1] *N*-Allyltrifluoroacetamide [Found: C, 39·0; H, 3·9; N, 9·3%; *M* (mass spec.), 153. Calc. for $C_5H_6F_3NO$: C, 39·2; H, 3·9; N, 9·15%; *M*, 153], b.p. 87·5°/29 mm., $\lambda_{max.}$ (film) 3·02br (bonded N–H str.), 5·85 (amide I band), 6·06 (C=C str.), 6·42 (amide II band), and 8·25, 8·44, and 8·60 µm. (triplet, C–F str.), was prepared in conventional fashion from trifluoroacetic anhydride and allylamine.

Reactions of Perfluorocyclopentadiene.—(a) *With allylamine.* Perfluorocyclopentadiene (4·66 g., 26·8 mmoles) was condensed, *in vacuo*, on to allylamine (1·59 g., 27·8 mmoles) at −196° in a Pyrex tube (250 ml.). The tube was sealed and allowed to warm to room temperature; the mixture turned brown, and after being heated at 70° for 18 hr. had changed into a viscous tar, which was not examined.

(b) *With* N-*allyltrifluoroacetamide.* Perfluorocyclopentadiene (4·02 g., 23·1 mmoles) was heated with *N*-allyltrifluoroacetamide (2·06 g., 13·5 mmoles) at 50° for 64 hr. in a Pyrex ampoule (90 ml.). Volatile product (2·14 g., shown by i.r. and g.l.c. to be mainly perfluorocyclopentadiene dimer containing some perfluorocyclopentadiene) was pumped out of the tube, leaving an oil (3·35 g.) which was distilled *in vacuo* to yield a mixture (by i.r.) of perfluorocyclopentadiene dimer and *N*-allyltrifluoroacetamide (1·78 g.) and a white solid, b.p. 74—75°/10^{-4} mm., which was sublimed *in vacuo* at 45° to give N-(1,4,5,6,7,7-*hexafluorobicyclo*[2,2,1]*hept-5-en-2-ylmethyl*)*trifluoroacetamide* (1·30 g., 4·0 mmoles, 30%) [Found: C, 36·6; H, 1·8; N, 4·2%; *M* (mass spec.), 327. $C_{10}H_6F_9NO$ requires C, 36·7; H, 1·8; N, 4·3%; *M*, 327], m.p. 47°, $\lambda_{max.}$ (film from soln. in $CHCl_3$) 3·02br (bonded N–H str.), 5·70 (CF⁚CF str.), 5·78 (amide I band), and 6·38 (amide II band) µm., δ (25% w/v in $CHCl_3$; interchange CF_3·CO_2H) −1·2 (s, CF_3; *cf.* CF_3·CO·NH·CH_2·CH⁚CH_2, −1·2), +65·4 (AB pattern, CF_2; $|J_{gem}|$ 178 Hz), +77·4 (⁚CF), +79·8 (⁚CF), +131·2 (⋛CF), and +133·8 (⋛CF) p.p.m.

Hydrolysis of N-(1,4,5,6,7,7-*Hexafluorobicyclo*[2,2,1]*hept-5-en-2-ylmethyl*)*trifluoroacetamide.*—The amide (0·444 g., 1·358 mmole) was heated at 50° for 10 hr. with methanol

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[11] K. L. Williamson, Y-F Li Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *J. Amer. Chem. Soc.*, 1968, **90**, 6717.

(10 ml.) saturated with hydrogen chloride. The product was evaporated under reduced pressure and the white solid residue was washed with chloroform, leaving 1,4,5,6,7,7-*hexafluorobicyclo*[2,2,1]*hept-5-en-2-ylmethylammonium chloride* (0·271 g., 1·014 mmole, 86% based on amide converted) (Found: C, 35·6; H, 3·1; N, 5·35. $C_8H_8ClF_6N$ requires C, 35·9; H, 3·0; N, 5·2%), m.p. 251° (decomp.), $\lambda_{max.}$ (mull) 3·43br ($\overset{+}{N}H_3$ asym. and sym. str.), 5·71 (CF⁝CF str.), 6·18, 6·25, and 6·37 (broad, poorly-resolved triplet, $\overset{+}{N}H_3$ asym. bending), and 6·63 ($\overset{+}{N}H_3$ sym. bending) μm., δ (25% w/v in D_2O; interchange $CF_3\cdot CO_2H$), +63·6 (AB pattern; $|J_{gem}|$ 183 Hz), +75·2 (⁝CF), +75·6 (⁝CF), +128·8 ($\geqslant$CF), and +130·6 ($\geqslant$CF) p.p.m. As expected,[12] the top-mass peak in the mass spectrum of the ammonium salt appeared at *m*/*e* 231 (9%), corresponding to the parent ion of the free amine, $[C_8H_7F_6N]^{\cdot+}$; the base peak corresponded to the product of α-fission of the parent ion, *viz.* $CH_2{=}\overset{+}{N}H_2$. Work-up of the chloroform washings provided *N*-(1,4,5,6,7,7-hexafluorobicyclo[2,2,1]hept-5-en-2-ylmethyl)-trifluoroacetamide (0·057 g., 13%).

A vigorously stirred mixture of ether (10 ml.) and a solution of the ammonium chloride (0·250 g., 0·935 mmole) in water (5 ml.) was titrated (phenolphthalein) against 0·0932M-sodium hydroxide (10·0 ml.) (Found: Equiv. wt., 266·5. Calc. for $C_8H_8ClF_6N$: Equiv. wt., 267·5). The ether layer was dried ($MgSO_4$), filtered, and evaporated, to provide 1,2,3,7,8,8-*hexafluoro-4-azatricyclo*[4,2,1,0^{3,7}]*nonane* (0·146 g., 0·632 mmole; 68%) [Found: C, 41·6; H, 3·2; N, 6·1%; *M* (mass spec.), 231. $C_8H_7F_6N$ requires C, 41·6; H, 3·0; N, 6·1%; *M*, 231], m.p. 172°.

We thank Dr. M. G. Barlow of this Department for a report on the ^1H n.m.r. spectrum of compound (VII).

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[12] K. Biemann and J. A. McCloskey, *J. Amer. Chem. Soc.*, 1962, **84**, 3192.