Heterocyclic Polyfluoro-compounds. Part 41.[1] Photochemical Isomerization of 1-Substituted Hexafluoro-1*H*-azepines: Hexafluoro-2-azabicyclo[3.2.0]hepta-3,6-dienes and their Reactions

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Photochemical isomerization of 1-ethoxycarbonyl-, 1-cyano-, or 1-amido-hexafluoro-1*H*-azepine yields the respective 2-substituted hexafluoro-2-azabicyclo[3.2.0]hepta-3,6-diene (92—98%).

The 2-ethoxycarbonylheptadiene undergoes Diels–Alder addition of cyclopentadiene, to give four adducts by *exo*-attack at the CF=CF bonds, and of furan, to give three of the four analogous adducts (attack at the CF=CFN bond is preferred), adds phenyl azide reluctantly to give a 15 : 2 : 2 : 1 mixture of adducts, where addition to the CF=CFN bond predominates, gives a 3 : 1 mixture of *trans*- and *cis-exo*-3,4-dibromides, and is catalytically reduced to 2-ethoxycarbonyl-1,4,5,6,7-pentafluoro-2-azabicyclo[3.2.0]heptane.

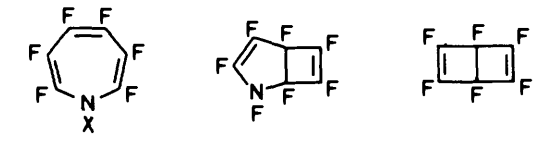
1*H*-AZEPINES undergo ready photoisomerization to 2-azabicyclo[3.2.0]hepta-3,6-dienes.[2,3] Fluorine, and particularly fluoroalkyl group, substitution usually has a beneficial effect upon the stability and ease of formation of strained valence-bond isomers,[4-6] the so-called 'perfluoroalkyl effect',[7] which appears to be largely steric in origin.[8] The availability[1,9] of the three 1-substituted hexafluoro-1*H*-azepines (1)—(3), the last compound being obtained by sulphuric acid hydrolysis of the cyano-compound (2), prompted a study of their isomerization.

U.v. irradiation of the azepine (1) on a small scale (0.18 g) in Pyrex produced the expected 2-azabicyclo-[3.2.0]hepta-3,6-diene (4) in essentially quantitative yield (98%), but on a larger scale both yield and conversion were much reduced. High yields were also obtained in solution (n-hexane or t-butyl alcohol), and acetophenone or benzophenone as triplet sensitizer, or penta-1,3-diene as quencher, had no great affect, indicating that, like that of the corresponding hydrocarbon azepine,[10] the isomerisation is a singlet state reaction. However, large-scale reactions with benzophenone present readily gave the pure diene (4) in high yield (81%). In chloroform, the cyanoazepine (2) yielded the azadiene (5) (92%) and the amide (3) yielded (6) (93%). The azadiene (4) was remarkably thermally stable; it was recovered to the extent of 88% after 3 h at 200 °C, and produced initially largely the parent azepine (1). In contrast, the corresponding non-fluorinated compound has a half-life of *ca.* 15 min at 126.5 °C.[2]

Hexafluoro-Dewar-benzene (7) is reactive in cycloaddition reactions, undergoing ready *exo*-addition of 1,3-dienes[11] and 1,3-dipoles[12] to its strained C=C double bonds. In the azadienes (4)—(6), there is a similar cyclobutene fragment, as well as a C=CN bond in a less strained five-membered ring. The most readily available diene (4) was selected for study.

The heptadiene reacted slowly with cyclopenta-1,3-diene at room temperature over one month [*cf.* dienophile (7) which reacted completely within 12 h] to give a mixture (75% conversion) of four 1 : 1-adducts, two of which could not be separated by g.l.c. These were identified (see below) as the four possible adducts, (8), (9), and a mixture of (10), and (11), obtained by *exo*-addition to (4), in the ratio 22 : 46 : 24 : 8. At 40° C, the same adducts were obtained in the ratio 36 : 48 : 13 : 3. With the less reactive furan at 75 °C for 85 h, a mixture (65% conversion) of three adducts, (12), (13), and (14) or (15), was obtained, in the ratio 9 : 58 : 33.

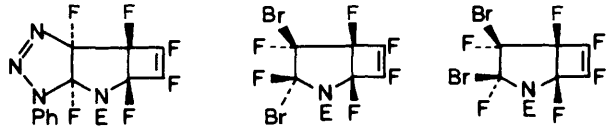
With phenyl azide at 70 °C for 27 days, the azadiene



(1) X = CO_2Et (4) X = CO_2Et (7)
(2) X = CN (5) X = CN
(3) X = $CONH_2$ (6) X = $CONH_2$

(8) Y = CH (9) Y = CH
(12) Y = O (13) Y = O

(10) Y = CH (11) Y = CH
(14) Y = O (15) Y = O

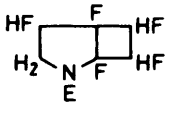


(16) (17) (18)

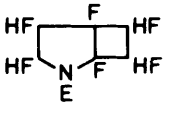
E = CO_2Et

(4) produced a mixture of 1 : 1-adducts in low conversion, in which adduct (16) appeared to predominate (75%) (the direction phenyl azide addition is not completely certain), ^{19}F n.m.r. spectroscopy indicated the presence of two further adducts (10%), and the ^{1}H n.m.r. spectrum indicated the presence of a fourth OEt group (5%), although the corresponding fluorine absorptions were not detected.

The azadiene added bromine in the dark; only the CF=CFN bond was attacked and the isomers (17) and (18) were obtained in 3 : 1 ratio. Upon catalytic reduction with palladium on carbon in ethanol at room temperature, the azadiene (4) gave a 3 : 1 mixture of isomeric 1,4,5,6,7-pentafluoro-2-azabicyclo[3.2.0]heptanes (19), where the fluorine adjacent to the nitrogen had been lost. An attempt on a small scale to limit the hydrogenolysis produced a mixture in which the presence of the tetrahydride (20) and olefin (21), in addition to (19) was indicated by g.l.c. coupled-mass spectrometry. With powdered potassium hydroxide at 120 °C in a flow system, the pentafluoro-compound (19) produced a mixture of olefins (22) and (23) in low yield.



(19)



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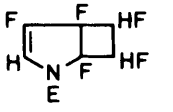
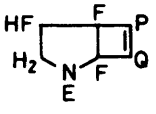
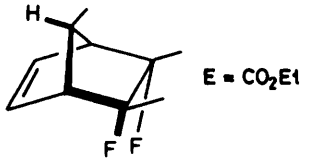


(21)



(22) P = H, Q = F

(23) P = F, Q = H



(24)

Noteworthy in all these reactions in the greater reactivity of the CF=CFN double bond, despite it being part of a less strained five-membered ring. However, overall, the reactivity is much reduced compared with hexafluoro-Dewar-benzene (7),[11-14] although, like the latter, the azadiene shows a preference for *exo*-addition, presumably for steric reasons.

Structure of the Products.—All the products obtained had consistent i.r. and mass spectra. N.m.r. spectroscopy, particularly ^{19}F, was more useful in defining the detailed structure.

All the isomers obtained by photochemical isomerization of the 1*H*-azepines showed two C=C stretching frequencies around 1 770 cm^{-1}, and in their ^{19}F n.m.r. spectra, two high-field bands indicative of fluorines attached to a saturated carbon atom. One occurred rather to low field of the other, suggesting it was adjacent to nitrogen rather than carbon. For the four remaining olefinic fluorine absorptions, two occurred in the range (−38.7 to −48.4 p.p.m.) associated with a four-membered ring,[13] while the remainder fell into two groups around −51 and −62 p.p.m. The high-field band was tentatively assigned to the fluorine adjacent to the quadrupolar nitrogen, since it appeared much broader than the remaining absorptions in compounds (4) and (6). On this evidence, the structures (4) to (6) seem assured.

In the products obtained from compound (4), the presence or absence of ^{19}F n.m.r. absorptions around −40 to −50 p.p.m. (see Table), assignable to olefinic fluorines in a four-membered ring, indicated which double bond had undergone addition. Molecular models suggested that *endo*-addition to compound (4) was subject to severe steric crowding, both in the transition state and in the product, where steric crowding should result in a substantial downfield shift of the absorptions of the remaining olefinic fluorines.[15] The absence of any great shift argues against *endo*-addition. Among the cyclopentadiene adducts (8)—(11), only two of them, (9) and (11), showed substantial coupling of one of the bridgehead methylene protons to two fluorine nuclei. This may be ascribed to the four-bond coupling constant in the fragment (24), which has the necessary 'converging vector' path.[16] On this basis, the structures of the adducts are obtained. Addition to the CF=CFN double bond results in an appreciable chemical-shift difference of methine protons in the cyclopentene fragment, which is not seen in the adducts from addition to the other, more symmetrical double bond.

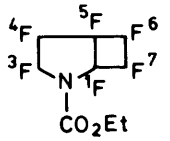
The furan adducts (12), (13), and (14) or (15) are assigned largely by analogy with the cyclopentadiene adducts.

Phenyl azide gives largely one adduct, but ^{19}F n.m.r. spectroscopy indicated the presence of *ca.* 10% of two other adducts whose absorptions could not be individually assigned, and ^{1}H n.m.r. spectroscopy, which, in particular, showed four types of OEt group, suggested the presence of a further adduct (*ca.* 5%) not detected by ^{19}F n.m.r. spectroscopy. The major adduct appeared to result from addition to the CF=CFN double bond, with olefinic absorptions at −40.7 and −49.7 p.p.m. Apart from the two dibromides (17) and (18), and this azide adduct, all the remaining compounds showed OEt absorptions in the ranges 1.26—1.34(CH_3) and 4.15—4.27 p.p.m. (OCH_2). The upfield shift seen for this adduct (0.99 and 3.94 p.p.m.) suggested that the phenyl group was close, as in structure (16).

In both the dibromides (17) and (18), the absorptions of the bridgehead fluorine nucleus not adjacent to nitrogen were substantially deshielded, indicating an adjacent *exo*-bromine [*cf.*,[13] the dibromide of (7)], and in isomer (17), the CFBrN absorption, with a low-field value of 16.3 p.p.m., should have an adjacent bromine *cis* to the fluorine nucleus. The low-field shift of the OEt absorptions (1.26 and 4.53 p.p.m.) was presumably also a consequence of a near bromine atom.

Catalytic reduction produced two pentafluoro-compounds (19) with rather similar chemical shifts of fluorine nuclei. The bridgehead fluorine (5-F) was deshielded

^{19}F Chemical shifts of 2-ethoxycarbonylhexafluoro-2-azabicyclo[3.2.0]hepta-3,6-diene derivatives



Compound	Chemical shifts (p.p.m.) [a]					
	δ_1	δ_3	δ_4	δ_5	δ_6	δ_7
(4)	−95.2	−62.4	−51.6	−112.3	−45.9	−47.7
(8) [b]	−87.6	−55.9	−65.5	−98.1	−44.1	−51.5
(9) [c]	−85.8	−55.1	−61.8	−101.4	−43.4	−51.3
(10) [d]	−98.2	−77.7	−51.0	−111.9	−106.0	−107.9
(11) [e]	−98.2	−77.7	−51.4	−111.9	−106.0	−107.9
(12) [f]	−92.1	−51.4	−62.3	−99.2	−45.6	−47.2
(13) [g]	−89.9	−56.0	−63.0	−100.5	−43.3	−51.4
(14) or (15) [h]	−102.9	−82.0	−50.3	−112.3	−108.9	−109.3
(17) [i]	−56.7	16.3	−31.2	−82.6	−35.8	−48.4
(18)	−62.8	−12.9	−34.7	−83.2	−38.6	−48.1
(19) [j]	−50.4		−144.9	−101.8	−129.7	−130.3
	−53.8		−144.9	−102.3	−130.2	−130.6

[a] For 15—30% solutions in CCl_4, with +ve values to low field of ext. CF_3CO_2H. [b] δ_H 2.05 and 2.31 (CH_2, ^2J 10 Hz), 3.12, 3.49 (CH), and 6.12 (CH=CH) p.p.m. [c] δ_H 1.53 and 1.80 (CH_2, ^2J 11 and $^4J_{HF}$ 7 Hz), 3.23, 3.69 (CH), and 6.22 p.p.m. (CH=CH). [d] 3 : 1 Mixture of (10) and (11) with δ_H 1.95 and 2.11 (CH_2, ^2J 15 Hz), 3.31 (CH), and 6.33 p.p.m. (CH=CH). [e] Approximate values, since a mixture with (10) and masked, with δ_H 1.46 and 1.56 (CH_2, ^2J 10 and $^4J_{HF}$ 8 Hz), 3.12 (CH), and 6.09 p.p.m. (CH=CH). [f] Mixture with (13) and (14) or (15). [g] δ_H 5.13, 5.37 (CH—O), and 6.55 p.p.m. (CH=CH). [h] δ_H 5.20 (CH—O) and 6.63 p.p.m. (CH=CH). [i] Mixture with (18). [j] Two isomers, where the upper values refer to the major isomer.

(compare *exo*-5*H*,6*H*-hexafluorobicyclo[2.2.0]hex-2-ene [13]) indicating an adjacent *exo*-hydrogen, and the similarity of chemical shifts suggested that the isomerism arose from restricted rotation about the N–CO bond, rather than ring substitution, although this type of isomerism was not seen in the remaining compounds. The individual assignment of the olefins (22) and (23), obtained by dehydrofluorination, rests upon the tentative assignment of a lower-field fluorine or proton absorption to a nucleus nearest to the N–CO_2Et group.

EXPERIMENTAL

Techniques used were similar to those described previously.[1]

Preparation of 1-*Amidohexafluoro*-1H-*azepine*.—1-Cyanohexafluoro-1*H*-azepine [9] (0.75 g, 3.32 mmol) and concentrated sulphuric acid (7.00 g), sealed in a Pyrex ampoule (17 cm^3) and heated at 60 °C for 15 min, gave, after addition to crushed ice (25 g), diethyl ether extraction (4 × 25 cm^3), and removal of the solvent under reduced pressure, a brown solid (0.60 g), which was sublimed at 20 °C and 0.001 mmHg to give an unidentified yellow solid, and at 60 °C and 0.001 mmHg to give 1-*amidohexafluoro*-1H-*azepine* (3) (0.26 g, 1.07 mmol, 32%) (Found: C, 34.5; H, 1.0; F, 46.8; N, 11.6%. $C_7H_2F_6N_2O$ requires C, 34.4; H, 0.8; F, 46.7; N, 11.5%), m.p. 102—103 °C, with $\nu_{max.}$ 3 520m, 3 360m (N-H str.), 1 760m, 1 730s (C=C str.), and 1 710s cm^{-1} (C=O str.); $\lambda_{max.}$ (ethanol) 210 and 250 nm (ε 3 230); δ_F* (15% w/v in $CDCl_3$) −11.9 (2,7-F), −64.3 (3,6-F), and −73.2 (4,5-F) and δ_H 5.57 p.p.m. The mass spectrum showed *m/e* 201 ($C_6HF_6N^{+\bullet}$, 100%), 200 ($C_6F_6N^+$, 23.2), 174 ($C_5F_6^{+\bullet}$, 36.6), 155 ($C_5F_5^+$, 26.6), 151 ($C_5HF_4N^+$, 20.0), 44 ($CONH_2^+$, 98.7), and 43 ($CONH^+$, 27.4).

Photochemical Isomerization of 1-*Substituted Hexafluoro*-1H-*azepines*.—(a) 1-*Ethoxycarbonylazepine*. 1-Ethoxycarbonylhexafluoro-1*H*-azepine (0.18 g, 0.64 mmol), sealed *in vacuo* in a Pyrex ampoule (17 cm^3) and irradiated with u.v. light for 125 h, gave after sublimation *in vacuo* 2-*ethoxycarbonylhexafluoro*-2-*azabicyclo*[3.2.0]*hepta*-3,6-*diene* (4) (0.17 g, 0.63 mmol, 98%) (Found: C, 39.5; H, 1.7; F, 41.9; N, 5.2%; $M^{+\bullet}$, 273. $C_9H_5F_6NO_2$ requires C, 39.6; H, 1.8; F, 41.8; N, 5.2%; *M*, 273), m.p. 31—33 °C. An involatile residue (0.01 g) was washed out with chloroform and shown by t.l.c. analysis to be a complex mixture which was not further examined. The azediene showed $\lambda_{max.}$ (n-hexane) 218 nm (ε 3 460); $\nu_{max.}$ (liq. film) 1 784s, 1 763s (C=C str.), 1 741s (C=O str.), and 1 708 cm^{-1}; δ_F (30% w/v in carbon tetrachloride) −45.9 (7-F or 6-F), −47.7 (6-F or 7-F), −51.6 (4-F), −62.4 (3-F), −95.2 (1-F), and −112.3 (5-F); δ_H 1.34 (CH_3) and 4.27 p.p.m. (CH_2); *m/e* (>15%) 228 ($C_7F_6NO^+$, 17.5), 201 ($C_6HF_6N^{+\bullet}$, 97.0), 200 ($C_6F_6N^+$, 100.0), 181 ($C_6F_5N^{+\bullet}$, 16.9), 174 ($C_5F_6^{+\bullet}$, 96.8), 155 ($C_5F_5^+$, 30.8), 93 ($C_3F_3^+$, 15.7), 69 (CF_3^+, 25.9), 46 ($CH_2O_2^{+\bullet}$, 18.6), 44 ($CO_2^{+\bullet}$, 16.3), 32 ($CHF^{+\bullet}$, 97.6), and 31 (CF^+, 31.8).

When larger amounts of the liquid azepine were irradiated in Pyrex, the conversion was incomplete even after prolonged irradiation, and substantial amounts of involatile material were obtained. For example, the azepine (6.87 g, 25.2 mmol), sealed *in vacuo* in a Pyrex ampoule (35 cm^3) and irradiated for 19 days, gave after fractionation *in vacuo*, recovered azepine (2.87 g, 10.5 mmol, 42%), the azadiene (4) (2.35 g, 8.6 mmol, 59%), and an involatile residue (1.65 g). In solution (n-hexane or t-butyl alcohol), yields of the azadiene were comparable with those obtained from similar scale irradiations of the liquid azepine. Acetophenone and benzophenone appeared to accelerate the conversion of the azepine, thus avoiding the necessity for g.l.c. separation of the azepine from its isomer. For example, on a preparative scale, the azepine (3.92 g, 14.36 mmol), benzophenone (0.81 g, 4.43 mmol) and n-hexane (28.72 g), sealed *in vacuo* in a Pyrex ampoule (100 cm^3) and irradiated (Hanovia UVS 500 lamp at a distance of 2.5 cm) at 20 °C for 6 days, gave after fractionation *in vacuo*, the azadiene (4) (3.18 g, 11.63 mmol,

* Positive values to low field of ext. trifluoroacetic acid.

81%) which condensed at −10 °C, n-hexane which condensed at − 78 °C, and an involatile residue (1.55 g).

The isomerisation in t-butyl alcohol was little affected by the addition of penta-1,3-diene.

(*b*) 1-*Cyanoazepine*. 1-Cyanohexafluoro-1*H*-azepine [9] (0.39 g, 1.71 mmol) and chloroform (22 g), sealed *in vacuo* in a Pyrex ampoule (17 cm^3) and irradiated with u.v. light for 82 h gave, after fractionation *in vacuo*, 2-*cyanohexafluoro*-2-*azabicyclo*[3.2.0]*hepta*-3,6-*diene* (5) (0.36 g, 1.58 mmol, 92%) (Found: C, 37.3; F, 50.0; N, 12.6. $C_7F_6N_2$ requires C, 37.2; F, 50.4; N, 12.6%), as a white solid, m.p. 19—21 °C, which condensed at −15 °C and recovered chloroform (22 g) which condensed at −78 °C. A trace (0.03 g) of involatile residue remained in the ampoule. The azadiene showed $\lambda_{max.}$ (n-hexane) 212 nm (ε 4 100); $\nu_{max.}$ (liq. film) 2 262vs (C≡N str.) 1 775s sh and 1 766s cm^{-1} (C=C str.); δ_F (15% w/v in CCl_4) −38.7 (7-F or 6-F) −48.4 (6-F or 7-F) −50.2 (4-F), −63.9 (3-F) −87.0 (1-F) and −105.6 p.p.m. (5-F); *m/e* (>15%) 226 ($M^{+\bullet}$, 42.4,) 200 ($C_6F_6N^+$, 37.5), 186 ($C_6F_6^{+\bullet}$, 100.0), 181 ($C_6F_5N^{+\bullet}$, 22.7), 174 ($C_5F_6^{+\bullet}$, 17.7), 155 ($C_5F_5^+$, 54.4), 131 ($C_3F_5^+$, 26.4), 124 ($C_4F_4^{+\bullet}$, 34.2), 117 ($C_5F_3^+$, 21.9), 105 ($C_4F_3^+$, 18.8), 100 ($C_2F_4^{+\bullet}$, 15.6), 93 ($C_3F_3^+$, 53.2), 83 ($C_3N_2F^+$, 21.4), 74 ($C_3F_2^{+\bullet}$, 23.7), 69 (CF_3^+, 49.7), and 31 (CF^+, 80.3).

(*c*) 1-*Amidoazepine*. 1-Amidohexafluoro-1*H*-azepine (0.42 g, 1.70 mmol) and chloroform (21.1 g), sealed *in vacuo* in a Pyrex ampoule (17 cm^3) and irradiated for 82 h, gave, after fractionation *in vacuo*, 2-*amidohexafluoro*-2-*azabicyclo*-[3.2.0]*hepta*-3,6-*diene* (6) (0.39 g, 1.58 mmol, 93%) (Found: C, 34.2; H, 0.7; F, 46.2; N, 11.8. $C_7H_2F_6N_2O$ requires C, 34.4; H, 0.8; F, 46.7; N, 11.5%), as a white solid, m.p. 121—123 °C, which condensed at −5 °C, and recovered chloroform (21.2 g). An involatile residue (0.03 g) remained. The azadiene showed $\lambda_{max.}$ (ethanol) 222 nm (ε 5 940); $\nu_{max.}$ (mull) 1 769s, 1 754vs (C=C str.), and 1 711s cm^{-1} (C=O str.); δ_F (15% w/v in EtOH) −44.1 (6-F or 7-F), −47.1 (7-F or 6-F), −51.3 (4-F), −59.7 (3-F), −92.0 (1-F), and −114.7 p.p.m. (5-F); *m/e* (>15%) 201 ($C_6HF_6N^{+\bullet}$, 36.4), 174 ($C_5F_6^{+\bullet}$, 100.0), 155 ($C_5F_5^+$, 17.8), 46 ($CHFN^+$, 18.4), and 44 (CH_2NO, 45.0).

Reactions of 2-*Ethoxycarbonylhexafluoro*-2-*azabicyclo*-[3.2.0]*hepta*-3,6-*diene*.—(*a*) *Thermal decomposition*. The title diene, heated in a sealed Pyrex ampoule at 180 °C for 3 h, was largely (96%) recovered. At 200 °C, the diene underwent 12% decompositon after 3 h and gave the parent azepine (11% on the diene taken). After 7 h, the recovery of diene was 34%, and the azepine (42%) was formed, the remainder being involatile material. After 16 h, 11% of diene was recovered and 28% of the azepine formed.

(b) *With cyclopenta*-1,3-*diene*. The heptadiene (1.09 g, 4.00 mmol) and cyclopentadiene (0.34 g, 5.15 mmol), sealed in a Pyrex ampoule (30 cm^3) and shaken at room temperature for 1 month, gave unchanged heptadiene (0.28 g, 1.01 mmol, 25%) and dicyclopentadiene (0.14 g, 2.17 mmol), volatile at room temperature and estimated by i.r. spectroscopy and g.l.c. (2 m SE30 at 85 °C), and a residue (1.01 g) which distilled at 70 °C and 0.001 mmHg. This residue, which appeared as three components on 4 separate g.l.c. columns, was separated by g.l.c. (5 m SE30 at 120 °C) to give (1RS, 2SR, 3SR, 6SR, 8SR, 9SR)-7-*ethoxycarbonyl*-2,3,4,5,6,8-*hexafluoro*-7-*azatetracyclo*[7.2.1.$0^{2,8}$.$0^{3,6}$]*dodeca*-4,10-*diene* (8) (0.22 g, 0.66 mmol, 22%) (Found: C, 49.9; H, 3.3; F, 33.7; N, 4.0%; $M^{+\bullet}$, 339. $C_{14}H_{11}F_6NO_2$ requires C, 49.6; H, 3.3; F, 33.6; N, 4.1%; *M*, 339), m.p. 64—65 °C, its (1RS, 2RS, 3RS, 6RS, 8RS, 9SR)-*isomer* (9) (0.46 g, 1.37 mmol, 46%) (Found: C, 50.0; H, 3.3; F, 34.0; N, 4.4%; $M^{+\bullet}$, 339), m.p. 67.9 °C, and a 3 : 1 mixture of (1*RS*, 2*RS*, 3*SR*, 7*RS*, 8*SR*, 9*SR*)- and (1*RS*, 2*SR*, 3*RS*, 7*SR*, 8*RS*, 9*SR*)-isomers (10) and (11) of 4-ethoxycarbonyl-2,3,5,6,7,8-hexafluoro-4-azatetracyclo[7.2.1.$0^{2,8}$.$0^{3,7}$]dodeca-5,10-diene (0.32 g, 0.95 mmol, 32%) (Found: C, 49.9; H, 3.3; F, 33.7; N 4.0%; $M^{+\bullet}$ 339. Calc. for $C_{14}H_{11}F_6NO_2$: C, 49.6; H, 3.3; F, 33.6; N, 4.1%; *M*, 339).

The heptadiene (1.50 g, 5.51 mmol) and cyclopentadiene (1.44 g, 21.88 mmol), heated at 40 °C for 20 days, gave unchanged heptadiene (1%), dicyclopentadiene (1.08 g, 8.22 mmol), and a mixture (1.80 g) of the above dodecadienes in the ratio 36 : 48 : 13 : 3.

(*c*) *With furan*. The heptadiene (0.48 g, 1.77 mmol) and furan (1.51 g, 22.22 mmol), sealed in a Pyrex ampoule (17 cm^3) and heated at 75 °C for 85 h, gave recovered heptadiene (0.17 g, 0.62 mmol, 35%) and furan (1.46 g, 21.47 mmol, 97%), which were removed *in vacuo*, and a residue (0.36 g) which was flash distilled at 70 °C and 0.001 mmHg to give a liquid (0.34 g), separated by g.l.c. (5 m SE30 at 110 °C) to give (1*RS*, 2*SR*, 3*SR*, 6*SR*, 8*SR*, 9*SR*)-7-ethoxycarbonyl-2,3,4,5,6,8-hexafluoro-12-oxa-7-azatetracyclo[7.2.1.$0^{2,8}$.$0^{3,6}$]dodeca-4,10-diene (12) (0.03 g, 0.10 mmol, 9%) (Found:* C, 45.6; H, 2.6; F, 33.1; N, 4.0%; $M^{+\bullet}$, 341. Calc. for $C_{13}H_9F_6NO_3$: C, 45.8; H, 2.6; F, 33.4; N, 4.1%; *M*, 341) (1RS, 2RS, 3RS, 6RS, 8RS, 9SR)-7-*ethoxycarbonyl*-2,3,4,5,6,-8-*hexafluoro*-12-*oxa*-7-*azatetracyclo*[7.2.1.$0^{2,8}$.$0^{3,6}$]*dodeca*-4,10-*diene* (13) (0.21 g, 0.62 mmol, 55%) (Found: C, 45.5; H, 2.5; F, 33.2; N, 4.2%; $M^{+\bullet}$, 341. $C_{13}H_9F_6NO_3$ requires C, 45.8; H, 2.6; F, 33.4; N, 4.1%; *M*, 341), and either (1RS, 2RS, 3SR, 7RS, 8SR, 9SR-(14) or (1RS, 2SR, 3RS, 7SR, 8RS, 9SR)-4-*ethoxycarbonyl*-2,3,5,6,7,8-*hexafluoro*-12-*oxa*-4-*azatetracyclo*[7.2.1.$0^{2,8}$.$0^{3,7}$] *dodeca*-5,10-*diene* (15) (0.12 g, 0.35 mmol, 31%) (Found: C, 46.0; H, 2.7; F, 33.6; N, 4.2%; $M^{+\bullet}$, 341. $C_{13}H_9F_6NO_3$ requires C, 45.8; H, 2.6; F, 33.4; N, 4.1%; *M*, 341). The distillation residue (0.02 g) was a complex mixture by t.l.c.

The heptadiene (0.70 g, 2.57 mmol) and furan (0.83 g, 12.22 mmol), heated at 95 °C for 18 h, gave recovered heptadiene (0.05 g, 0.19 mmol) and furan (0.61 g, 8.97 mmol) and the above three adducts (0.83 g, 2.43 mmol, 100% based on heptadiene consumed) in the ratio 8 : 58 : 35.

A reaction carried out at 85 °C for 4 days using a large excess of furan gave an inseparable mixture of 2 : 1-adducts of furan and the diene, identified by mass spectrometry ($M^{+\bullet}$, 409. Calc. for $C_{17}H_{13}F_6NO_4$: *M*, 409), and containing at least 4 components by ^{19}F n.m.r. spectroscopy (7 absorptions in the range −60 to −76 and 12 in the range −95 to −118 p.p.m.).

(*d*) *With phenyl azide*. The heptadiene (1.42 g, 5.20 mmol) and phenyl azide (3.16 g, 26.55 mmol), sealed in a Pyrex ampoule (100 cm^3) and heated at 70 °C for 27 days, gave nitrogen (0.16 g, 4.51 mmol), volatile material fractionated *in vacuo* to give a mixture (by i.r. spectroscopy) of carbon dioxide, ethylene, and silicon tetrafluoride (10 mg), and of recovered heptadiene (1.26 g, 4.63 mmol, 89%) and phenyl azide (2.67 g, 22.44 mmol, 84%). The involatile residue (0.49 g) was flash distilled at 80 °C and 0.001 mmHg to give a 15 : 2 : 2 : 1 mixture of 1 : 1-adducts (0.10 g, 0.26 mmol, 46% based upon heptadiene consumed) (Found: C, 45.7; H, 2.3. Calc. for $C_{15}H_{10}F_6N_4O$: C, 45.9; H, 2.6%). The major adduct (16) showed δ_F (15% in CCl_4) −38.6 (N–CF–N), −40.7, −49.7 (=CF), −59.7 (CF–N=), −71.1 (CF–NCO), and −103.8 (CF) p.p.m., and the two adducts each present to

* For a 1 : 1-mixture with the major adduct.

the extent of 10% showed δ_F −36.1, −45.5, −47.2, −48.1, −51.4, −58.5, −60.1, −62.5, −91.8, −102.9, and −112.4 p.p.m. The distillation residue (0.39 g) was a complex mixture by t.l.c.

(*e*) *With bromine.* The heptadiene (1.12 g, 4.10 mmol) and bromine (0.89 g, 5.53 mmol) sealed in a Pyrex ampoule and shaken at room temperature for 19 h in the dark, gave volatile product which was fractionated to give recovered bromine (0.22 g, 1.39 mmol, 25%), and traces of ethyl bromide (10 mg), condensing at −78 °C, and carbon dioxide (10 mg), condensing at −196 °C. The residue (1.77 g) was flash distilled *in vacuo* to give a 3 : 1 mixture of isomeric 3,4-dibromo-2-ethoxycarbonylhexafluoro-2-azabicyclo[3.2.0]-hept-6-enes (17) and (18) (1.69 g, 3.90 mmol, 95% based upon heptadiene consumed) (Found: C, 24.9; H, 1.2; F, 26.3; N, 3.2. Calc. for $C_9H_5Br_2F_6NO_2$: C, 25.1; H, 1.3; F, 25.9; N, 3.1%), which was not resolved by g.l.c. (2 m SE30, APL, PEGA, or TXP at 130 °C). The unidentified distillation residue (0.08 g) contained at least three components by t.l.c.

(*f*) *With hydrogen.* The heptadiene (0.56 g, 2.05 mmol), ethanol (4.32 g), and palladium on carbon (0.24 g), were sealed *in vacuo* in a Pyrex ampoule (300 cm^3), which was pressurised with hydrogen (1.4 atm) at −196 °C. The ampoule was then shaken at room temperature for 7 days, when the volatile condensable product comprised ethanol, unchanged heptadiene (0.04 g, 0.14 mmol, 7%), and, by titrimetric analysis, hydrogen fluoride (0.04 g, 2.00 mmol). The residue was extracted with chloroform, filtered, and the solvent removed to give a 3 : 1 mixture of isomeric 2-ethoxycarbonyl-1,4,5,6,7-pentafluoro-2-azabicyclo[3.2.0]-heptanes (19) (0.49 g, 1.89 mmol, 100%) (Found: C, 42.3; H, 4.2; F, 36.6; N, 5.7%; $M^{+\bullet}$, 259. Calc. for $C_9H_{10}F_5NO_2$: C, 41.7; H, 3.9; F, 36.7; N, 5.4%; *M*, 259), δ_H 1.26 (CH_3), 3.6 (CH_2N, major isomer), 4.1 (CH_2N), 4.17 (OCH_2), and *ca.* 5.7 p.p.m. (CHF).

The heptadiene (0.14 g, 0.49 mmol), ethanol (1.26 g), and palladium catalyst (30 mg), similarly shaken with 1 atm of hydrogen at room temperature for 22 h, gave after chloroform extraction a product (0.10 g) which g.l.c. (2 m SE30 at 95 °C) coupled mass spectrometry indicated to be a 3 : 4 : 6 mixture of 2-ethoxycarbonyl-1,3,4,5,6,7-hexafluoro-2-azabicyclo[3.2.0]heptane (20), with *m/e* 277 ($M^{+\bullet}$, 4.0) and 185 ($C_6H_4F_5N^{+\bullet}$, 100%), 2-ethoxycarbonyl-1,4,5,6,7-pentafluoro-2-azabicyclo[3.2.0]hept-3-ene (21), with *m/e* 257 ($M^{+\bullet}$, 15.8) and 121 ($C_4H_2NF_3^{+\bullet}$, 100%), and the above pentafluoroheptane. An attempt to repeat this reaction on a larger scale gave only the pentafluoroheptane and unchanged heptadiene.

2-Ethoxycarbonyl-1,4,5,6,7-pentafluoro-2-azabicyclo-[3.2.0]heptane (0.26 g, 1.00 mmol) was passed *in vacuo* through a Pyrex tube containing dried (by fusion) potassium hydroxide (*ca.* 15 g in *ca.* 5 mm pieces) and heated to 120 °C. The volatile product (0.10 g) was separated by g.l.c. (1m PEGA at 120 °C) to give unchanged heptane (0.07 g, 0.27 mmol, 26%) and a 55 : 45 mixture of 2-ethoxycarbonyl-1,4,5,6- (23) and -1,4,5,7-tetrafluoro-2-azabicyclo[3.2.0]hept-6-enes (22) (0.03 g, 0.13 mmol, 13%) (Found: C, 45.5; H, 4.1; F, 31.6; N, 5.9. Calc. for $C_9H_9F_4NO_2$: C, 45.2; H, 3.8; F, 31.2; N, 5.9%), $\nu_{max.}$ 1 728vs br (C=O str.) and 1 659s cm^{-1} (C=C str.); δ_F (25% in CCl_4) −23.1 (6-F), −58.0 (1-F), −93.1 (5-F), and −110.8 (4-F) for the major isomer, and −14.9 (7-F), −57.1 (1-F), −89.3 (5-F), and −114.6 p.p.m. (4-F) for the minor isomer; δ_H 1.29 (CH_3), 4.15 (OCH_2), 3.3—4.5 (CH_2-N) 5.09 (4-H, minor isomer), 5.21 (4-H, major isomer), 5.56 (7-H), and 5.90 p.p.m. (6-H); *m/e* 194 ($C_7H_4F_4NO^+$, 1.1) and 44 (C_2HF, 100%).

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