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POLYFLUOROCYCLOALKENES PART XI* PERFLUORO - BICYCLO(3,3,0) OCT-7(8)-ENE, - BICYCLO(4,3,0)-NON-8(9)-ENE AND - BICYCLO (4,4,0)-DEC-9(10)-ENE AND SOME DERIVATIVES

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SUMMARY

Tetradecafluorobicyclo (4,3,0) non-8(9)-ene has been prepared by cobaltic fluoride fluorination of decafluoro indane. The reactivities of the double bonds in dodecafluoro-bicyclo (3,3,0) oct-7(8)-ene and hexadecafluorobicyclo (4,4,0) dec-9(10)-ene have been studied qualitatively by the use of chlorine, methanol, cobaltic fluoride, ammonia and dimethylamine and the derivatives so obtained have been characterised.

INTRODUCTION

The reactions of polyfluorocycloalkenes have been extensively studied in many places (for our work see earlier parts in this Series) and the facile reactions with nucleophiles rationalised as addition -elimination sequences at the electron deficient double bonds. This paper describes an extension of this study completed some years ago to a new class of perfluorobicyclo-alkenes in which the double bond is not directly attached to fluorine but which still demonstrate a high susceptibility to nucleophilic substitution. Steric hindrance does not appear to play a significant role in these reactions. The addition -elimination process so clearly established in our earlier

* For Part X, see ref.1.

studies has been used as a guide to the structures of the products obtained.

RESULTS AND DISCUSSION

Three fluorocarbon bicyclo-enes were available, having 8 - 10 carbon atoms. The new tetradecafluorobicyclo (4,3,0) non-8(9)-ene (I) was prepared by cobaltic fluoride fluorination [2] of decafluoro indane at 150°; dodecafluorobicyclo (4,3,0)-nona-di-2(3),8(9)-ene (II) was also produced; both olefins were characterised by NMR spectroscopy. However, the relative inaccessibility of them has so far precluded a study of their reactions.

Dodecafluorobicyclo (3,3,0) oct-7(8)-ene (III) was known from defluorination of tetradecafluorobicyclo (3,3,0) octane and as used in this study contained small amounts of this fluorocarbon precursor; however, it should not interfere with any of the reactions reported.

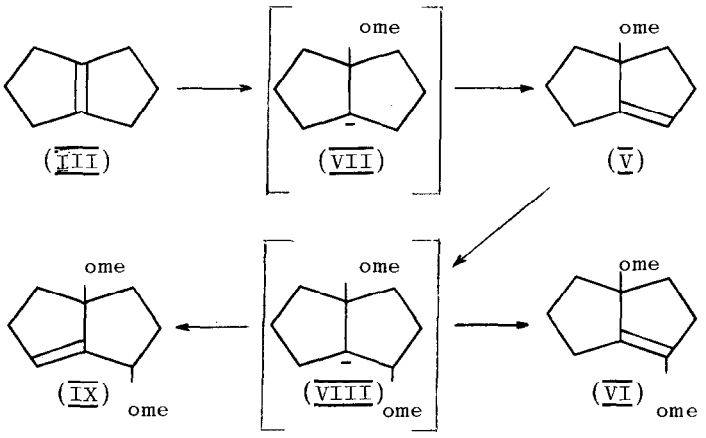
The addition of chlorine to the olefin (III) was typical of that of a highly fluorinated olefin and gave, after 22hr. in a u.v. irradiated Carius tube, a crystalline, probably cis-, 7,8- dichloride (IV).

Olefin (III) reacted exothermically with methanol and potassium hydroxide to give predominantly 8-methoxy-undecafluorobicyclo (3,3,0) oct-1(7)-ene (V) or 1,8-dimethoxy decafluorobicyclo (3,3,0) oct-1(7) ene (VI), depending on the proportions of the reactants; equimolar proportions giving predominantly (V) and a two fold excess of methanol giving predominantly (VI).

The reaction can be rationalised in terms of an addition - elimination sequence [3] as depicted in Fig. 1. A minor unidentified component may have been product (IX) predicted in the scheme.

In analogous reactions of monocyclic enes such as octafluorocyclopentene, eliminations involving loss of fluoride ion from $>CF_2$, though unfavourable, usually proceed to a limited extent.

The known [2] hexadecafluorobicyclo (4,4,0) dec-9(10) ene (X) used in this work contained a very small amount of the inert octafluorodecalin.



(all unmarked substituents are fluorine)

Fig. 1

The level of steric hindrance associated with approach to the double bond of (X) probably explains its failure to undergo photochemical chlorination even after one week in a Carius tube (cf. successful chlorinations of olefin (III) and perfluoro-2,3-dimethylbut-2-ene [4]). Similarly, (X) was unaffected by hydrogen over palladised charcoal at pressures up to 120 atmospheres (cf., perfluoro-2,3-dimethylbut-2-ene, which was unaffected by H_2/Pd/alumina [4]).

The addition of fluorine to olefin (X) was achieved with cobaltic fluoride at 350°; this was a sluggish reaction requiring two passages over cobaltic fluoride to approach complete saturation of (X). Both stereoisomers of octadecafluorodecalin were produced but the proportion of cis-isomer was slightly higher than in the octadecafluorodecalin produced by cobaltic fluoride fluorination of tetralin [5].

The resistance of (X) to cobaltic fluoride and the formation of both cis- and trans- perfluoro-decalins is in keeping with current theories of fluorination by high valency metal fluorides [6].

Inspite of the high level of steric impedance implied in the above addition processes, the olefin (X) reacted with a range of nucleophiles in keeping with the electron deficiency of its double bond.

The reaction of (X) with methanol and potassium hydroxide was markedly more sluggish than the analogous reaction of olefin (III) and this may reflect the greater accessibility of the double bond in (III). However, methoxidation of (X) with sodium in methanol occurred readily to give a mixture containing 4 principal and 3 minor components possessing large and closely similar retention volumes. Nevertheless, three of the main products were separated by preparative GLC and identified as 1,10-dimethoxy-tetradecafluorobicyclo (4,4,0)dec-1(9)ene (XI), the suspected cis- and/or trans- 8,10-dimethoxytetradecafluorobicyclo (4,4,0)dec-1(9)ene (XII) and cis- and/or trans-1,8,10-trimethoxy tridecafluorobicyclo (4,4,0)dec-1(9)ene (XIII).

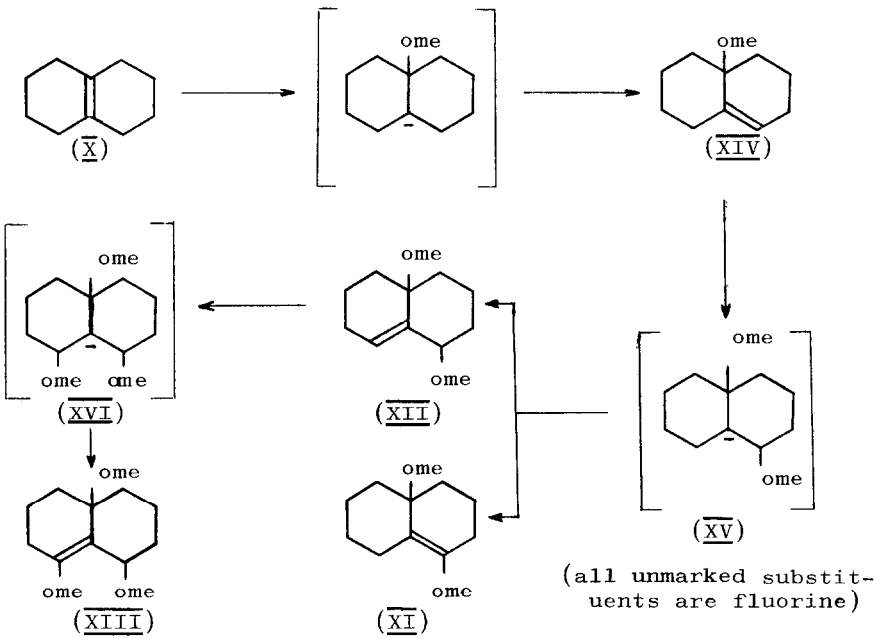


Fig. 2.

Variation of the temperature of reaction between -40° and 20° affected only the proportions of the products. Thus, the proportion of (XIII) increased and that of (XI) and (XII) decreased with increase in temperature and the ratio of (XII) to (XI) decreased with increase in the proportion of (XIII); these changes are consistent with the addition-elimination sequence depicted in Fig. 2. Attempts to isolate the mono-methoxide (XIV) failed, even when 1:1:1 molar proportions of reactants, reverse addition and dilution of the reaction mixture with an inert solvent was used. Under these conditions a higher proportion of starting material was recovered; this is consistent with the higher reactivity anticipated for the double bond in (XIV).

The addition steps giving rise to the carbanionic intermed-iates depicted in Fig. 2 should be trans-processes [3] and such addition can occur from either side of the double bonds in (XIV) and (XII) giving rise to cis- and/or trans- forms of (XII) and (XIII) *via* the carbanionic intermediates (XV) and (XVI). No attempt was made to establish the stereochemical configuration of (XII) and (XIII). None of the products arising by protonation of the carbanionic intermediates were detected, but by analogy with related work [3] these should be very minor components.

The proportions of the two products arising from elimination of fluoride ion from intermediate (XV) should be similar to those observed in the analogous reaction of decafluorocyclohexene [3]. In reactions that did not go to completion, (XI) and (XII) were isolated in the ratio of 60:40 respectively. The higher proportion of elimination involving loss of F from $>CF_2$, compared with the decafluorocyclohexene methoxidation, may stem from the greater geometrical constraints in the bicyclodecene system.

Hexadecafluorobicyclo (4,4,0)dec-1(9)ene (X) and dimethylamine in ether, whilst reacting rather more sluggishly than hindered perfluoro olefins like perfluoro-2,3-dimethylbut-2-ene [4], gave tetradecafluoro-1,10-bis(dimethylamino)bicyclo (4,4,0)dec-1(9)-ene (XVII) at a low temperature. The formation of (XVII) in a standard addition-elimination pathway is depicted in Fig. 3.

The failure to isolate the monosubstitution product (XVIII), like the monomethoxy analogue (XIV) presumably stems from the lower reactivity of the symmetrical double bond of the starting

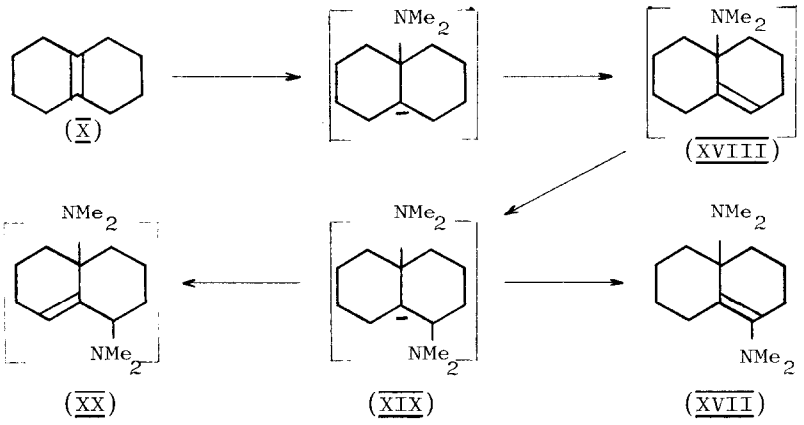


Fig. 3. (all unmarked substituents are fluorine)

material (X). The exclusive direction of elimination of fluoride ion from the carbanionic intermediate (XIX), reflected in the failure to isolate (XX) or its derivative 1,8,10- tris (dimethyl amino) tridecafluorobicyclo (4,4,0)dec-1(9)ene, parallels the reaction of dimethylamine with decafluorocyclohexene which gives only 1-dimethylamino nonafluorocyclohexene [7]. Presumably the dimethylamino group greatly weakens the attached C-F bond in comparison with the analogous methoxide situation.

Olefin (X) also reacted readily with dry ammonia in ether to give dodecafluoro-1,10-diamino-8-imino-bicyclo(4,4,0)dec-1 (9)ene (XXI). The exact sequence of the elimination steps in Fig. 4 is not clear. However eliminations giving either the N=C or to the C=C group in the intermediates (XXII) and (XXIII) lead to the same final product (XXII), since equilibration of tautomers can occur.

The presence of a conjugated system in the diamino-imine (XXI) was clearly indicated by selective absorption in the ultraviolet region similar to that given by 1-aminoheptafluoro-

3-iminocyclohex-1-ene [8]. Like the latter compound, the diamino-imine (XXI) was readily hydrolysed with dilute mineral acid; this gave dodecafluoro-1,10-diamino-8-keto-bicyclo(4,4,0) dec-1(9)-ene (XXIV).

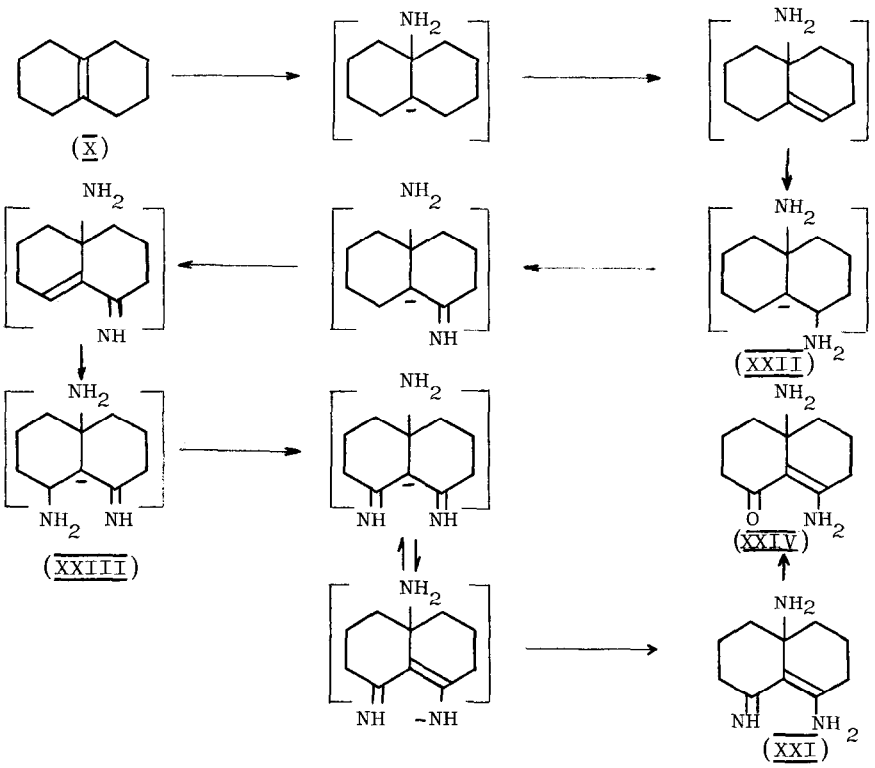


Fig.4. (all unmarked substituents are fluorine)

It was of interest to compare the ultraviolet absorption spectra of (XXI) and (XXIV) with those of the analogous products derived from decafluorocyclohexene (table 1). The difference between the two series probably reflects the fact that the bicyclodecene conjugated system is hetero-annular with an S-cis-configuration, whereas the cyclohexene conjugated system is homo-annular with an S-trans-configuration. The lower extinction coefficient for the bicyclodecene compounds results from the diminished delocalisation associated with their non-coplanar conjugated systems.

TABLE 1

	λ_{max}	ε_{max}*
1-Aminoheptafluoro-3-iminocyclohexene [8]	2910	2.25
1-Aminoheptafluorocyclohexen -3-one [8]	3010	2.80
Dodecafluoro-1,10-diamino-8-imino-bicyclo (4,4,0)dec-1(9)ene	3185	0.79
Dodecafluoro-1,10-diamino-8-keto-bicyclo (4,4,0)dec-1(9)one	3200	1.11

* $\times 10^{-4}$

Attempts to form N-acetyl and -benzoyl derivatives of (XXI) failed, in distinction to 1-amino-heptafluoro-3-iminocyclohexene which gave a diacetate [8]. A Courtaulds model of (XXI) indicates that the amino group at C_{10} is largely shielded from attack by adjacent ring carbon and fluorine atoms and that both hydrogens could be strongly hydrogen-bonded to fluorines at C_3 and C_6. However, there is ro apparent obstruction to the reaction of the aminoimine system.

EXPERIMENTAL

Apparatus

Gas chromatography

Analytical work was carried out using 2m. glass columns (3-4mm. diam.) packed with dinonyl phthalate-celite (1:2) (unit A), and silicone-gum-Celite (1:5) (unit B). For preparative work copper columns (4.9m. long, 35 and 75mm. diam.) were used packed with silicone-gum-celite (1:5) (35mm. diam.) (Col. A) silicone-gum-celite (1:2) (75mm. diam.) (Col. B) and dinonyl phthalate-celite (1:4) (Col. C).

Spectroscopy

Except as otherwise stated the following instruments were used: Perkin-Elmer 257 infra-red grating spectrophotometer,

Unicam SP800 ultraviolet spectrophotometer using a deuterium lamp and 1cm. path length Silica Cell, a Varian A60 NMR instrument at 60mc/sec. for proton NMR spectra with TMS as external standard, and an A.E.I. MS9 instrument for mass spectrometry.

Tetradecafluorobicyclo (4,3,0) non-8(9)-ene. -

Decafluoroindane (5.0g), prepared by pyrolytic defluorination of perfluoroperhydroindane over iron gauze at 490° [9], was passed in nitrogen (81 hr.$^{-1}$) over cobaltic fluoride (150g.) at 150° to give a liquid (5.55g.) which was shown by GLC (unit A; 100°; N_2, 1ℓ hr.$^{-1}$) to contain 3 components. Further fluorinations of batches of decafluoroindane (3.0g.) at 50°, 80° and 110° gave products which were shown by GLC (unit A; 100°; N_2, 1ℓ hr^{-1}) to contain the same components in varying proportions; the product formed from decafluorindane (10.0g.) at 80° contained all three components in reasonable yield. The combined product (13.0g.) from all the fluorinations of decafluoroindane (24.0g.) so conducted was separated by GLC (col. B; 130°; N_2, 55ℓ hr.$^{-1}$) to give a mixed fraction (7.6g.) and deczfluoroindane (4.5g.). The former was then separated by GLC (col. C; 90°; N_2, 15ℓ hr^{-1}) to give: (i) tetradecafluorobicyclo (4,3,0) non-8(9)-ene (I) nc (4.4g.) b.p. 98.5° (Found: C, 28.8. C_9F_{14} requires C, 28.9%), m/e 374 ($C_9F_{14}^+$), ν max. 1700cm^{-1} (v.w.), its ^{19}F NMR spectrum (Perkin Elmer R10 at 56.4 mc/sec. with CCl_3F as internal standard) consisted of bands at 112.5, 114.9, 132.4 and 134.8 ϕ^* in the relative intensity ratio of 2:2:1:2, respectively; (ii) dodecafluorobicyclo (4,3,0)-nona-di-2(3) 8(9)-ene (II) nc (2.2g.), b.p. 108.5°, λ max 2420 Å (ε , 1170 in ethanol) m/e 336 ($C_9F_{12}^+$), ν max. 1760cm^{-1} (s), its ^{19}F NMR spectrum (Perkin Elmer R10 at 56.4 mc/sec, with $C\ell_3F$ as internal standard) consisted of bands at 109.0, 113.1, 132.6 and 153.7 ϕ^* in the relative intensity ratio of 2:2:1:1, respectively.

Dodecafluorobicyclo (3,3,0) oct-7(8)-ene. -

This olefin (III) was prepared by the defluorination of tetradecafluorobicyclo (3,3,0) octane with iron gauze at

400° [10]. However, since the GLC separation of the olefin from the starting material was very difficult, the majority of the reactions reported in this study employed olefin containing small amounts of the fluorocarbon. Since perfluorobicyclooctane forms an azeotrope with both ether and acetone, the normal isolation procedures often remove it.

1,5-Dichloro dodecafluorobicyclo (3,3,0) octane. - Dodecafluorobicyclo (3,3,0)oct-7(8)-ene (III) (0.85g.) and chlorine (2 g.) were sealed in a Carius tube and irradiated with U.V. light for 22hr. to give a volatile waxy solid (0.80g.) which was sublimed to give suspected cis-7,8-dichlorododecafluorobicyclo (3,3,0) octane (IV) nc m.p. 129-130° (sealed tube) (Found: C, 23.9; Cl, 17.6. $C_8Cl_2F_{12}$ requires C, 24.3; Cl, 18.0%).

8-Methoxy-undecafluorobicyclo (3.3.0) oct-1(7)-ene. - Methanol (0.32g.) in ether (10ml) was added dropwise over 1hr. to a stirred mixture of dodecafluorobicyclo (3,3,0) oct-1(5)-ene (3.26g.) and KOH (0.66g.) at 20°. Water (50ml) was then added and the solution extracted with ether (3 x 10ml). The dried ($MgSO_4$) extract was then filtered and distilled through a vacuum jacketed column (6") packed with glass helices, and the residue (ca. 2ml) was separated by GLC (col. A; 84°; N_2, 21ℓ $hr.^{-1}$) to give: (i) ether (ca. 1.0g.); (ii) 8-methoxy undecafluorobicyclo(3,3,0)oct-1(7)-ene (V) nc (0.7g.) b.p. 125-126° (Found: C, 32.1; H, 0.9. $C_9H_3F_{11}O$ requires C, 32.1; H, 0.9%), ν max. 1740cm^{-1}. (Perkin Elmer 21), its ^1H NMR (Mullard SL44 instrument at 30MC/S) consisted of a singlet at 3.43 p.p.m.

1,8-Dimethoxy decafluorobicyclo(3,3,0)oct-1(7)-ene. - Methanol (1.0ml) was added dropwise to a stirred mixture of dodecafluorobicyclo(3,3,0)oct-1(5)-ene (III) (3.2g.) and KOH pellets (0.65g.). After 40min., water (20ml) was added and the fluorocarbon layer (3.3g.) separated by GLC (col. A, 135°,

N_2 17ℓ hr.$^{-1}$) to give: (i) ether and tetradecafluorobicyclo (3,3,0)octane (0.1g.) with a correct IR spectrum; (ii) 8-methoxy-undecafluorobicyclo(3,3,0)oct-1(7)-ene ($\underline{V}$) (0.2g.) with a correct IR spectrum; (iii) an unidentified component (0.3g.); (iv) 1,8-dimethoxy decafluorobicyclo(3,3,0)oct-1 (7)-ene (VI) nc (1.3g.) b.p. 187-188° (Found: C, 34.5; H, 1.6 $C_{10}H_6F_{10}O_2$ requires C, 34.5; H, 1.7%), ν max. 1680cm^{-1} (C=C) (Perkin Elmer 21), its H NMR spectrum (Mullard SL44) consisted of two bands at 4.05 and 3.16 p.p.m., in the relative intensity ratio of 1:1.

Hexadecafluorobicyclo(4,4,0)-dec-9(10)-ene.

Octafluoronaphthalene (15g.) was passed in a stream of N_2 (8ℓ hr.$^{-1}$) over cobaltic fluoride at 160° in the manner described previously [2] to give hexadecafluorobicyclo(4,4,0) dec-9(10)-ene ($\underline{X}$) (21.1g.) b.p. 126.5°. (Found: C, 28.0. Calc. for $C_{10}F_{16}$ C,28.2%) with a correct IR spectrum. The olefin so obtained contained a very small amount of octadecafluorodecalin which was not removed for the purposes of the following experiments.

Fluorination of hexadecafluorobicyclo(4,4,0)dec-9(10)-ene.

This compound ($\underline{X}$) (4.0g.) was fluorinated over cobaltic fluoride (150g.) in the normal way at 350° and a portion (5.0g.) of the liquid product (5.5g.), shown by IR spectroscopy to be a mixture of cis- and trans- octadecafluorodecalin together with some starting material, was refluorinated at 360° to give a liquid (5.1g.) almost free of the olefin. The latter product was then shaken with KMnO4 (2.5g.) in acetone (100ml.), washed with water and distilled to give a mixture of cis- and trans-octadecafluorodecalin, b.r. 141-143°, in a ratio slightly higher than in the mixture of octadecafluorodecalins obtained by cobaltic fluoride fluorination of tetralin [5].

Dodecafluoro-1,10-diamino-8-imino-bicyclo(4,4,0)dec-1(9)-ene.

Dry (CaO) ammonia was slowly bubbled through hexadeca-fluorobicyclo(4,4,0)dec-9-ene ($\underline{X}$) (35.3g.) in dry ether (400ml.)

for $3\frac{1}{2}$hr., water (ca. 200ml.) then added and the mixture shaken until the ppt. of ammonium fluoride had dissolved. The aqueous phase was extracted with ether (2 x 100ml.) and the combined extracts dried ($MgSO_4$), filtered and evaporated to give a yellow crystalline solid (23.0g.) which was recrystallised from CCl_4, then from EtOH, and then sublimed in vacuo to give pale yellow crystals of dodecafluoro-1,10-diamino-8-imino-bicyclo(4,4,0)dec-1(9)-ene (XXI) nc (16.2g.) m.p. 64-65° (Found: C, 30.6; H, 1.5; N, 10.4. $C_{10}H_5F_{12}N_3$ requires C, 30.4; H, 1.3; N, 10.6%) νmax. 3400 (NH) and 1635cm^{-1}. (C=C), λmax. 3185 Å (ε 7900 in ethanol), m/e 395 ($C_{10}H_5F_{12}N_3^+$).

Dodecafluoro-1,10-diamino-8-keto-bicyclo(4,4,0)dec-1(9)-ene.

Finely powdered dodecafluoro-1,10-diamino-8-imino-bicyclo(4,4,0)dec-1(9)-ene (10.7g.) was stirred with 2N HCl (150ml.) for 2hr. During the stirring the starting material was converted to a more voluminous solid (11.0g.) which was triturated with hot CCl_4, filtered, dried and a portion (ca. 1g.) sublimed in vacuo to give dodecafluoro-1,10-diamino-8-keto-bicyclo(4,4,0)dec-1(9)-ene (XXIV) nc m.p. 162° (Found: C, 30.4; H, 1.1; N, 7.3. $C_{10}H_4F_{12}N_2O$ requires C, 30.3; H, 1.0; N, 7.1%), νmax. 3225 (NH), 1655 (C=O) and 1630cm.$^{-1}$ (C=C), λmax. 3200 Å (ε, 11,100 in EtOH), m/e 396 ($C_{10}H_4F_{12}N_2O^+$).

Tetradecafluoro-1,10-bis(dimethylamino)-bicyclo(4,4,0)-dec-1(9)ene.

Hexadecafluorobicyclo(4,4,0)dec-9-ene (X) (10.0g.) in dry (Na) ether (20ml.) was added dropwise to a stirred solution of dimethylamine (5g.) in ethanol (20ml.) at -78°, then allowed to attain room temperature, stirred for 2hr. and water (ca. 20ml.) added. The aqeous phase was extracted with ether and the combined ether extracts dried ($MgSO_4$), filtered and evaporated. The red liquid residue was twice distilled in vacuo to give an extremely viscous yellow liquid (8.4g.) b.p. 76-77°/0.2mm. Hg. which slowly crystallised; two recrystallisations from CCl_4

and sublimation in vacuo gave tetradecafluoro-1,10-bis (dimethylamino)bicyclo(4,4,0)dec-1(9)-ene (XVII) nc (5.2g.) m.p. 59-60° (Found: C, 35.2; H, 2.4. $C_{14}H_{12}F_{14}N_2$ requires C, 35.4; H, 2.5%), ν max. 2985cm^{-1}. (CH) (there was no absorption in the IR between 1600 and 2000cm^{-1}) m/e 474 ($C_{12}H_{12}F_{14}N_2^+$).

Methoxidation of hexadecafluorobicyclo(4,4,0)-dec-9(10)-ene.

This olefin (X) (5.0g.) was added dropwise over 1hr. to a stirred solution of sodium (0.28g.) in dry methanol (10ml.) at -10°. After 2hr. the mixture was allowed to slowly warm to room temperature then mixed with water (ca. 75ml.) to afford a liquid product (3.6g.) which was shown by GLC (unit B, 180°, N_2, 3ℓ hr.$^{-1}$) to contain 4 major and 3 minor components but no starting material. The combined products (25.9g.) of several methoxidations were separated by GLC (col. B, 130°, N_2, 55ℓ hr.$^{-1}$) with difficulty (very large retention volumes) to give the following major fractions: (i) 1,10-dimethoxy-tetradecafluorobicyclo(4,4,0)dec-1(9)ene (XI) nc (2.3g.) (Found: C, 32.0; H, 1.4. $C_{12}H_6F_{14}O_2$ requires C, 32.1; H, 1.3%), ν max. 2970 (CH) and 1690cm^{-1} (C=C), m/e 448 ($C_{12}H_6F_{14}O_2^+$); (ii) the suspected cis- or trans- 8,10-dimethoxy-tetradecafluorobicyclo(4,4,0)dec-1(9)ene (XII) nc (0.4g.) (containing a trace of the 1,10-dimethoxy-isomer) (Found: C, 32.1, H, 1.3%), m/e 448; (iii) cis- or trans-1,8,10-trimethoxytridecafluorobicyclo(4,4,0)dec-1(9)-ene (XIII) nc (1.2g.) (Found: C, 34.3; H, 2.0 $C_{13}H_9F_{13}O_3$ requires C, 33.9; H, 2.0%). m/e 460 ($C_{13}H_9F_{12}O_3^+$), ν max. 2965 (CH) and 1670cm^{-1} (C=C).

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