POLYFLUORO-COMPOUNDS BASED ON THE CYCLOHEPTANE

RING SYSTEM.   PART 4.   REACTIONS OF NUCLEOPHILES

WITH DODECA- AND WITH 1H-UNDECA- FLUOROCYCLOHEPT-

1-ENE;   DECAFLUOROCYCLOHEPTYNE AS A REACTIVE

INTERMEDIATE

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SUMMARY

    Dodecafluorocycloheptene exchanged its vinylic fluorines with nucleo-
philes; it gave 1H-undeca- and 1H,2H-deca- (with sodium borohydride), and
1-methylundeca- and 1,2-dimethyldeca-   -fluorocycloheptene (with methyl
lithium). No isomeric products were detected. 1 Methylundecafluorocyclo-
heptene and lithium aluminium hydride afforded 1H-2-methyldecafluorocyclo-
hept-1-ene. Dodecafluorocycloheptene and ammonia gave a little 1-amino-
undecafluorocycloheptene, and 1-amino-3-iminononafluorocyclohept-1-ene,
the latter being easily hydrolysed to the 3-one. 1H-Undecafluorocyclohept-
1-ene did not give simple addition-elimination with methyl lithium; 1,2-
dimethyloctafluorocyclohepta-1,3-diene was the product generally isolated,
with 1,2,4-trimethylheptafluorocyclohepta-1,3-diene if methyl lithium was
in excess. Methyl lithium in the presence of furan gave a Diels-Alder
adduct in good yield, 8,11-epoxy-2,2,3,3,4,4,5,5,6,6-decafluorobicyclo-
[5,4,0]undeca-1(7), 9(10)-diene. Oxidation of this gave decafluoropimelic
acid. This is clear evidence for exchange of hydrogen by lithium in the
starting olefin, followed by loss of lithium fluoride, to give decafluoro-
cycloheptyne as a transient intermediate.

INTRODUCTION

As part of our programme on fluorinated cycloheptanes [1], some
addition reactions to mono-olefins were studied. Perfluorocycloheptene (1)
had been converted [2] into 1- and 3-methoxy-undecafluorocyclohept-1-ene,
in a standard nucleophilic addition-elimination sequence, and with lithium
aluminium hydride had given [2] 1H-undecafluorocyclohept-1-ene (2; see 1st
Scheme for structures). The reaction of the latter with methyl lithium
proved to be of special interest and is now described. At the same time,
some methyl-substituted derivatives were made from the perfluoro-ene (1)
also, to provide reference compounds. Also described, is the reaction of
the perfluoro-ene (1) with ammonia.

RESULTS AND DISCUSSION

(A) Additions to Dodecafluorocyclohept-1-ene (1)

In the present work, dodecafluorocycloheptene (1) was converted into
the 1H-1-ene (2) using sodium borohydride in diglyme (the yield was little
improved over the reaction with lithium aluminium hydride [2]). A second
product isolated in small amount was the 1H,2H-ene (3). No isomers of
either product, with different double bond positions, could be detected,
and if present, could only have been in very small amount (cf. the
isolation of isomers from similar reactions with decafluorocyclohexene [3])

Lithium methyl and the perfluoro-olefin (1) afforded 1-methyl-undeca-
fluorocyclohept-1-ene (4); twice the proportion of organo-metallic gave
the 1,2-dimethyl-ene (5). Again no isomers were detected: however, this
reagent also gave individual products from decafluorocyclohexene [4].

The 1-methyl-olefin (4) was treated with lithium aluminium hydride to
give 1H,2-methyldecafluorocyclohept-1-ene (6). Two very minor glc peaks
could have represented isomers, but only in trace amounts: in contrast,
the comparable reaction with 1-methylnonafluorocyclohexene gave [5]
1H-2-methyl- and 6H-1-methyl-octafluorocyclohex-1-ene, in ratio 3:1.

The proportions of 1- and 3-methoxy products mentioned above obtained
from perfluorocycloheptene (1) were 5.7:1 respectively [2], and of
analogous products from perfluorocyclohexene were 2.4:1 [6].

Thus, compared with polyfluorocyclohexenes, in the polyfluorocyclo-
heptene series addition-elimination reactions with nucleophiles proceed
to a greater extent by elimination of the original vinylic fluorine at the
point of initial attack ('inwards' elimination [cf. 7,3-6]) rather than

1　　2　　2a　　2b

2c　　3　　4　　5

6　　7　　8　　9

10　　11　　12　　13

14

All unmarked bonds
are to
FLUORINE
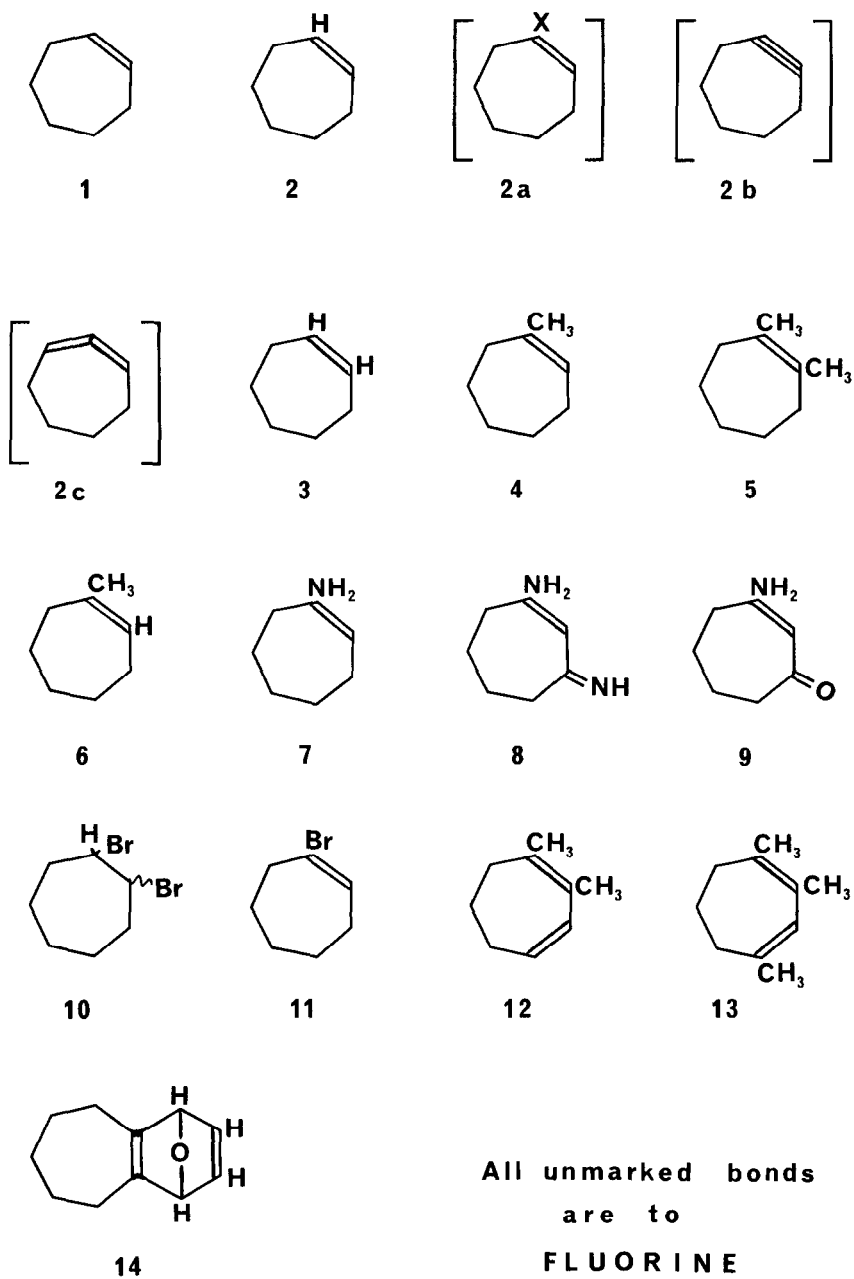
SCHEME 1

fluorine from an adjacent CF_2 group ('outwards' elimination). This is due to the greater flexibility of the C_7 ring as compared to the C_6. "Inwards" elimination is usually favoured electronically, and 'outwards' elimination arises because of opposing stereochemical factors in the rigid C_6 ring system. With the C_7 ring, these stereochemical factors are less pronounced. The bigger ring can accommodate more readily to give intermediates with coplanarity of groups to be eliminated, which are required for these processes.

The reaction of dodecafluorocycloheptene with ammonia gas was also studied. Comparable reactions on perfluorocyclo -hexene and -pentene have given 1-amino-3-imino- -heptafluorocyclohex-1-ene [8] and -pentafluoro-cyclopent-1-ene [9], respectively. 1-Trifluoromethylnonafluorocyclohex-1-ene reacted similarly [9], and primary amines afforded analogous products [8,9]. The imino-groups of all were readily hydrolysed by acid, affording 1-amino-perfluorocycloalk-1-ene-3-ones [8,9]. Perfluorocycloheptene (1) gave an interesting result in the reaction with ammonia. The major product was not eluted from the glc tube used for isolation, but the small amount of a minor product (7) was. It was quite volatile, had ir bands attributable to NH_2 and $-C = CF$, but the absence of appropriate uv absorption showed there was no conjugation. Though there was insufficient for elemental analysis, and the top mass was 289, corresponding to loss of HF, it seems probable that compound 7 was 1-amino-undecafluorocyclohept-1-ene. This is the expected primary product of attack by ammonia on olefin 1, and this is the first occasion that such a product has been found from olefins of this type. The major reaction product was isolated as a syrup by distillation, and was the expected 1-amino-3-iminononafluoro-cyclohept-1-ene (8). Hydrolysis of 8 with dilute hydrochloric acid gave the corresponding 1-amino-3-one (9).

B   Reactions with 1H-undecafluorocyclohex-1-ene (2)

The 1H-1-ene (2) reacted normally with bromine to give a mixed dibromo-adduct (10), which, with aqueous base, gave exclusive dehydro-bromination to the 1-bromo-1-ene (11). Again, both stereoisomers of the dibromide (10) reacted in the manner favoured electronically, i.e. loss of F from $>CBrF$ rather than $>CF_2$.

Several types of pathway were possible for reactions between the 1H-1-ene (2) and methyl lithium:- (I), simple addition-elimination, like that with olefin 1, to give compound 6 : (II), formation of an organo-lithium compound (2a; X=Li); this could then remain as a stable species

(pathway IIA), or decompose in some way (pathway IIB). If IIA operated, further addition across the double bond was possible, if unlikely. If such addition was slow however, species with electrophilic character could react with the organo-lithium (2a; X=Li) , e.g. methyl iodide, present from the original preparation of methyl lithium and/or equilibria in the system, could give compound 4, and thence 5 with more methyl lithium. Even if methyl iodide was not involved, reagents could be added subsequently, to give a synthetic route to products of type 2a. If pathway IIB operated, products with more unsaturation were to be expected.

In the event, the products already isolated (4-6) were not found in the reaction mixtures, but useful spectroscopic parameters, to help identify the actual products,were obtained from them. The 1H-1-ene (2) and methyl lithium (made from methyl iodide and lithium metal in a medium of diethyl ether) at -70°, gave off methane, showing that metallation of the =CH position was occurring. However, there was only around 25% of the volume of methane corresponding to complete exchange. The only product isolated, apart from recovery of almost half of the starting material (2), was a dimethyl-compound (12). A four-fold excess of methyl lithium only increased the evolution of methane to around 70% of the theoretical, and afforded still some recovered 2, a trace of the same compound (12), and a new trimethyl-compound (13). Since metallation of olefin 2 (pathway II) was clearly occurring, the incipient acidity of its hydrogen was checked: with deuterium oxide in the presence of potassium hydroxide, there was some 75% uptake of deuterium into olefin 2. This uptake is comparable to that with 1H-nonafluorocyclohex-1-ene and several other hydrofluorocarbons [10]. Attempts were made therefore to use the lithium derivative (2a; X=Li), formed from olefin 2 and methyl lithium, synthetically, i.e. to produce derivatives of type 2a by reaction with electrophiles (pathway IIA). This can be done with analogous 1H-polyfluoro-olefins in the cyclohexene, cyclopentene and cyclobutene series [11]. However, when iodine or acetaldehyde was added to a mixture of 1H-1-ene (2) and methyl lithium in slight excess at -70°, only the same dimethyl-product (12) was obtained, as had been produced in the absence of added reagents. From a reaction at a rather lower temperature involving iodine, besides compound 12, another product, a minor one, was isolated. Though impure, the spectroscopic properties suggested that it was largely the 1-iodo-olefin (2a; X=I) . However, no further success could be achieved in making derivatives of type 2a.

It seemed therefore that pathway IIB was operating predominately. The structures of products 12 and 13 were clear from analytical and spectroscopic data as having extra unsaturation. Compound 12 analysed as a dimethyl octafluorocycloheptadiene. Selective absorption in the uv indicated a 1,3-diene, and ir bands at 1730 and 1650 (very weak) cm^{-1} suggested the structure 1,2-dimethyloctafluorocyclohepta-1,3-diene (12). Nmr data supported this, there being only one peak for methyl in the ^1H spectrum, whilst there were two ^{19}F peaks for vinylic fluorine in a CF=CF group, one at 153.6 (next to CF_2) and one at 126.1 (next to $-\overset{\text{\tiny \textbardbl}}{C}-CH_3$). Peaks for two CF_2 groups, one at 118.9 (next to $F\overset{\text{\tiny |}}{C}=C$) and one at 113.8 (next to $CH_3\overset{\text{\tiny |}}{C}=C$) were also present. The background data for identification of these positions came from olefins 1 and 2 [2], perfluorocyclo-hepta-1,3- and -1,4-dienes [12], and the methylheptenes (4-6).

The other product (13) analysed as a trimethylheptafluorocyclohepta-diene, and the uv and ir spectra suggested a 1,3-structure with all methyl groups on the double bond positions. A ^{19}F nmr band at 101.4 indicated a vinylic fluorine between two methyl groups ($CH_3 \cdot \overset{\text{\tiny |}}{C}=CF -\overset{\text{\tiny \textbardbl}}{C}\cdot CH_3$), whilst two bands at 111.0 and 111.5 were due to two CF_2 groups, each next to vinylic methyl. Compound 13 was therefore 1,2,4-trimethylheptafluorocyclohepta-1,3-diene.

An intermediate in the decomposition of the 1H-1-ene (2) was identified by carrying out the reaction with methyl lithium in the presence of furan. This is a well-known device for trapping reactive unsaturated intermediates, in a Diels-Alder reaction, and we have used it successfully in fluorocarbon chemistry to isolate adducts from tetrafluorobenzyne [13] and from an anti-Bredt bridgehead "olefin"in the polyfluorobicyclo(2,2,1)heptane series [10].

The reaction with olefin 2 in fact proceeded much better than those in the absence of furan. More methane was evolved (over 90% theoretical), and the major product (14) was isolated in 60% yield (glc analysis suggested around 90% was present). Compound 14 analysed as an adduct of furan and a C_7F_{10} unit, and ir and nmr spectroscopy suggested a symmetrical molecule with two double bonds. Final structure proof was provided by permanganate oxidation; salts of decafluoro pimelic acid [2] were obtained.

Clearly therefore, decomposition of the lithium derivative (2a; X=Li) in the presence of furan proceeded primarily via decafluorocycloheptyne (2b) as an intermediate, the alternative, decafluorocyclohepta-1,2-diene (2c), not being detected as a furan adduct. The comparable reaction with 1H-nonafluorocyclohex-1-ene went mainly via octafluorocyclohexyne, but product

due to octafluorocyclohexa-1,2-diene was isolated (product ratio 3.5 : 1)
[11]. Further, unlike the present one, this decomposition did not go too
readily, and the lithium compound was useful synthetically, to give
products analogous to 2a. It seems that, again, the C_7 ring can adapt
distinctly better than the C_6 to ring strain, this time that necessary to
accommodate highly unsaturated centres. Perfluorocycloheptyne, though
obviously strained, is formed fairly readily, so that lithium compound 2a
(X=Li) has only a short lifetime.

Before postulating a reaction pathway from the 1H-1-ene (2) to the
methyl dienes 12 and 13, several possibilities need to be considered.
Either methyl lithium itself, or lithium iodide, could add to reactive
intermediates (cf. bridgehead 'olefins', to which the latter adds [10,14]).
The absence of stereochemical control of elimination processes in fluoro-
cycloheptane chemistry (see earlier) suggests that addition of lithium
iodide to a cycloheptyne would be followed by its immediate elimination.
However, this need not be so with a cyclohepta-1,2-diene. If a lithium
iodide adduct had a finite existence, the equilibria existing in the
species generated could effect interchange of both lithium and iodine for
each other, and a lithio-derivative could react with methyl iodide to give
a methyl compound.

The isolation of compound 14 from the decomposition in the presence
of furan, strongly suggests that the cycloheptyne (2b) is the most
probable reactive intermediate in all decompositions of the lithio-
derivative of olefin 2. Hence the likliest pathway is the addition to
cycloheptyne 2b of methyl lithium, and the route to dienes 12 and 13 would
be as represented in Scheme 2. However, the first-formed adduct (2d) must
decompose to a cyclohepta-1,2-diene intermediate (2e). There is no
precedent to indicate the preferred direction of addition to such an allene-
type intermediate (2e). The reaction represented, leading to adduct 2f, is
that required to give the orientation found in diene 12.

It is possible to postulate plausible pathways to diene 12 via the
cyclohepta-1,2-diene (2c), but these seem less likely than primary decom-
position to give the cycloheptyne (2b).

Diene 13 presumably arises via nucleophilic addition-elimination to
diene 12, and no special intermediates need to be invoked.

More work is merited on these interesting systems.
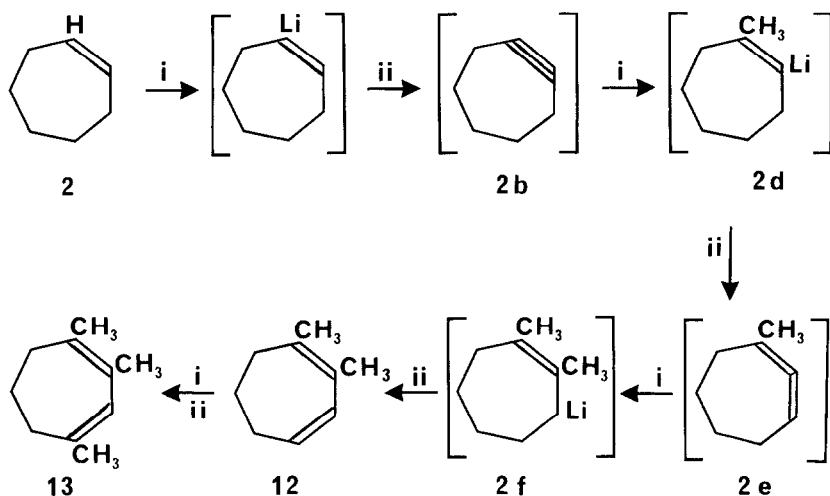
REACTIONS :- i with CH₃Li ; ii loss of LiF

All unmarked bonds are to **FLUORINE**

SCHEME 2

EXPERIMENTAL

General

    Spectroscopic data were measured as in Part 2 [12]. Gas liquid chromatography was also as done there [12], with the use of a further semi-preparative tube, F, packed with silicone gum/celite (1:5).

Reactions of dodecafluorocycloheptene (1)

(a) With sodium borohydride A suspension of sodium borohydride (4.0 g) in dry diglyme (120 cm³) was added to well-stirred dodecafluorocyclo-heptene (1) (60.0 g) in diglyme (60 cm³) held at -40°. When most of 1 had reacted (glc), the mixture was allowed to warm to 0°, water (150 cm³) was added cautiously, and the lower layer was separated off. It was washed well with cold water and dried (MgSO₄) (41.2 g). Separation by glc (B, 70°, 40; 10 g portions) gave:- (i) unreacted 1 (9.3 g) (ir) : (ii) 1H-undecafluorocyclohept-1-ene (2) [2] (16.9 g) (ir) : (iii) a mixture (2.3 g mainly (2) : (iv) 1H,2H-decafluorocyclohept-1-ene (3) nc (1.9 g) b.p.

113-114° (Found: C, 30.0; H, 0.9. $C_7H_2F_{10}$ requires C, 30.4; H, 0.7%);
m/e 276 (M); ir 3070 (w) (C-H), 1670 (vw) (CH=CH); nmr, ^{1}H, 3.59, t,
J=8; ^{19}F, 105.9 s (2) 3 and 7, 127.4 c (1) 5, 129.3 s (2) 4 and 6.

(b) With methyl lithium A solution of methyl lithium in diethyl ether
(0.83 M; 30 cm^3) was added dropwise to a stirred solution of 1 (5.0 g) in
ether (50 cm^3) at -70°. After 20 min at -70°, the mixture was allowed to
attain room temperature during 45 min. Dilute hydrochloric acid was added
cautiously, and the ether layer, together with ether extracts of the
aqueous layer, were dried (MgSO$_4$) and concentrated (short fractionating
column) to small volume (8 cm^3). Glc (A, 70°, 15) gave:- 1 (0.9 g) (ir) :
(ii) ether : (iii) 1-methylundecafluorocyclohept-1-ene (4) nc (1.9 g) b.p.
117-118° (Found: C, 31.0; H, 1.1. $C_8H_3F_{11}$ requires C, 31.2; H, 1.0%);
m/e 308 (M); ir 3020-2860 (vw) (C-H), 1700 (m) (C=C); nmr, ^{1}H, 7.89 (c);
^{19}F, 107.1 (2) 7, 111.6 (1) 2, 114.5 (2) 3, 127.7 (2) 5, 128.5 (2) 4,
129.0 (2) 6, all complex.

(c) With methyl lithium in excess The above reaction was repeated using
twice the amount of methyl lithium solution. Glc (C, 100°, 15) gave:-
(i) 1 + ether (2.9 g) : (ii) 1,2-dimethyldecafluorocyclohept-1-ene (5) nc
(1.6 g) b.p. 156-157°, m/e 304 (M); ir 3030-2860 (w) (C-H), 1650 (w) (C=C);
^{1}H, 7.94, pentet, J=2.5; ^{19}F, 105.5 s (2) 3 and 7, 127.9 c (1) 5, 128.8 s
(2) 4 and 6.

Reaction of 1-methylundecafluorocyclohept-1-ene (4) with
lithium aluminium hydride To well-stirred LiAlH$_4$ (4.5 g) in dry diethyl
ether (100 cm^3) at -70°, olefin (4) (10.0 g), in ether (30 cm^3), was added
during 1 h. After 20 min further, the mixture was warmed to 15° during
30 min. After being cooled to 0°, excess sulphuric acid (50% v/v) was
added very cautiously. The ether layer was separated, dried (MgSO$_4$) and
concentrated. Glc (A, 70°, 14) gave:- (i) ether : (ii) olefin 4 (0.9 g)
(ir) : (iii) 1H-2-methyldecafluorocyclohept-1-ene (6) nc (5.1 g) b.p.
138-139° (Found: C, 33.1; H, 1.2. $C_8H_4F_{10}$ requires C, 33.1; H, 1.4%) :
(iv) a mixture (0.6 g) containing 50% of 6, and two unidentified components.
Compound 6 had m/e 290 (M); ir 3060-2940 (w) (C-H), 1675 (w) (C=C);
nmr, ^{1}H, 3.7 t, J=12 of quartets, J=2 (1) 1, 7.8 c (3) 2; ^{19}F, 104.8 (1) 7,
109.0 (1) 3, 128.0 (1) 5, 129.8 (2) 4 and 6.

Reaction of dodecafluorocycloheptene (1) with ammonia (a) A slow stream
of ammonia gas, dried by passage over calcium oxide, was passed during
40 min through a solution of the olefin (1) (2.0 g) in dry diethyl ether

(30 cm^3) at room temperature. The colour became yellow and a solid was deposited. Water was added, the ether layer and ether extracts of the aqueous phase were washed with water, dried ($MgSO_4$), and the bulk of the ether evaporated off. Glc separation (F, 100°, 4) gave:- (i) ether : (ii) 1-amino-undecafluorocyclohept-1-ene (7) (0.3 g) b.p. 72°, m/e 289 (M-HF); ir 3200 (m) NH_2, 1700 (m) (C=C), 1640 (m) (NH); no selective absorption in the uv above 225 nm. Longer retained components did not emerge from the column.

(b) The experiment was repeated, ammonia being passed for 5 h. Distillation of the product at 0.2 mm pressure gave:- (i) (0.1 g) a mixture of 3 components : (ii) 1-amino-3-iminononafluorocyclohept-1-ene (8) nc (0.9 g) an orange syrup b.p. 50°/0.2 mm (Found: C, 29.0; H, 1.2; N, 8.9. $C_7H_3F_9N_2$ requires C, 29.4; H, 1.1; N, 9.8%); m/e 286 (M); ir 3500-3200 (s) (NH), 1650 (s) (C=C), 1600 (s) (NH); uv band at 306 nm (ε 1340 in ethanol).

When the imino-amine (8) (0.6 g) and dilute hydrochloric acid (25 cm^3; 2 M) were kept at ca 15° for 2 h, a precipitate was formed. This was filtered off and recrystallised from carbon tetrachloride to give 1-amino-nonafluorocyclohept-1-ene-3-one (9) nc (0.3 g) m.p. 61° (Found: C, 29.0; H, 0.8; N, 5.0. $C_7H_2F_9NO$ requires C, 29.3, H, 0.7; N, 4.9%); m/e 287 (M); ir (nujol) 3340-3200 (s) (NH), 1650-1550 (s;b) (C=O, C=C, NH); uv band at 319 nm (ε, 1350 in ethanol); nmr, ^1H, 4.4 (bs); ^{19}F, 111.1 (2), 117.5 (2), 128.0 (2), 128.2 (2) 4, 5, 6 and 7, 151.9 (1) 2.

1H-Undecafluorocyclohept-1-ene (2) and bromine   Bromine (3.5 cm^3) and the 1H-1-ene (2) (5.0 g), in a sealed tube at 15°, were irradiated with uv light for 140 h. The products were washed with sodium metabisulphite solution, water, dried ($MgSO_4$) (5.2 g). Glc (C, 100°, 15) gave:- (i) 1H-1-ene (2) (1.2 g) (ir) : (ii) 1H,1,2-dibromodecafluorocycloheptane (10) 2.1 g; 2 isomers by glc; ir 3000 (w); ^1H nmr, 6.5 (t, J=6.5).

Mixture (10) (2.0 g) potassium hydroxide (2.0 g) and water (3 cm^3) were shaken in a sealed tube at 15° for 21 h. The organic layer was separated washed with water dried ($MgSO_4$) and separated by glc (F, 90°, 3.5) to give 1-bromoundecafluorocyclohept-1-ene (11) nc (0.8 g) b.p. 120-121° (Found: C, 22.7; Br 21.5. C_7BrF_{11} requires C, 22.5; Br, 21.4%); m/e 373 (M); ir 1670 (shoulder 1695) (s) (C=C); ^{19}F nmr, 89.8 pentet, J=14 (1) 2, 99.4 (2) 7, 113.6 (2) 3, 127.4 (4) 4 and 6, 129.8 (2) 5, all complex.

1H-Undecafluorocyclohept-1-ene (2) and methyl lithium

(a) Equimolar proportions To well-stirred olefin 2 (3.0 g), in dry diethyl ether (30 cm^3), at -70°, methyl lithium in ether (0.55 $\underline{M}$; 20 cm^3; made from methyl iodide) was added dropwise. When methane evolution ceased (ca 25% of the theoretical was evolved) the mixture was stirred for a further 30 min at -70°, was then warmed to 15° during 45 min, and was refluxed for 30 min. After being cooled, dilute sulphuric acid (40 cm^3; 2 $\underline{M}$) was added, the ether layer washed with water, dried ($MgSO_4$), concen-trated, and the residue distilled at 0.1 mm pressure. Glc (C, 90°, 14) gave:- (i) a mixture (2.4 g) : (ii) an inseparable mixture of three minor components (0.2 g) : (iii) 1,2-dimethyloctafluorocyclohepta-1,3-diene (12) nc (0.6 g) b.p. 168-169° (Found: C, 40.8; H, 2.6. $C_9H_6F_8$ requires C, 40.6; H, 2.3%); m/e 266 (M); ir, 3030-2860 (w) (C-H), 1730 (m) (CF=CF) 1650 (vw) (CMe=CMe); uv peak at 250 nm (ε 5040 in ethanol); nmr, ^{1}H, 7.98 complex multiplet; ^{19}F, 113.8 bs (2) 7, 118.9 complex multiplet (2) 5, 126.1 complex multiplet (1) 3, 127.2 pentet (2) 6, 153.6 complex triplet of doublets (1) 4.

Mixture (i) was separated (E, 70°, 3.5) to give:- (i)a ether : (i)b recovered 1H-undecafluorocyclohept-1-ene (2) (1.3 g) (ir).

(b) Methyl lithium in excess Olefin (2) (2.0 g) in ether (20 cm^3) was treated with methyl lithium (0.39 M; 70 cm^3). Methane evolution was ca. 70% of the theoretical. Isolation as before followed by glc (F, 90, 3.5) gave:- (i) 2 + ether (1.3 g) (ir) : (ii) diene 12 (0.1 g) (ir) : (iii) 1,2,4-trimethylheptafluorocyclohepta-1,3-diene (13) nc (0.3 g): m/e 262 (M), 247 (M-CH_3), 243 (M-F); ir 3000-2860 (m) (C-H), 1685 (s), 1655 (w) (C=C); uv band at 247 nm (ε 5400 in ethanol); nmr, ^{1}H, 8.05 to 8.20 two close peaks, both complex; ^{19}F, 101.4 (1) 3, 111.0 (2) 7, 111.5 (2) 5, 126.9 (2) 6 all complex.

(c) Methyl lithium in the presence of furan To well-stirred olefin (2) (3.0 g) in freshly-distilled furan (30 cm^3) at -70°, methyl lithium (0.46 $\underline{M}$; 50 cm^3) was added dropwise until methane evolution ceased (92% theoretical). After 20 min at -70°, the mixture was warmed to 15° during 1 h, and was then refluxed for 30 min. After cooling, dilute hydrochloric acid (4 $\underline{M}$; 40 cm^3) was added, the ether layer was washed, concentrated, and the product separated by glc (F, 120°, 3.5), to give (solvents not isolated):- (i) trace of diene 12 (by glc) : (ii) 8,11-epoxy-2,2,3,3,4,4,5,5,6,6-decafluorobicyclo[5,4,0]undeca-1(7),9(10)-diene (14) nc (2.1 g) b.p. 186° (Found: C, 38.7; H, 1.3; F, 55.8. $C_{11}H_4F_{10}O$ requires C, 38.6;

H, 1.2; F, 55.5%); m/e 342 (M); ir, 3100-3040 (w) (C-H), 1685 (m), 1560 (w) (C=C); nmr, ^{1}H, 2.6 (1) 9 and 10, 4.0 (1) 8 and 11, both complex; ^{19}F, 104-133, 2 AB quartets and a broad singlet, ratio 2:2:1 : (iii) fluorine-free material (0.2 g).

Oxidation of the epoxy-bicyclo-compound (14)   The compound (0.2 g), potassium permanganate (1.0 g), and water (10 cm^3), were shaken together in a sealed tube at 100° for 1 h. Work up as usual, afforded dianilinium decafluoropimelate (0.22 g), m.p. 175° (from acetone-chloroform) [2], and thence bis-S-benzylthiouronium decafluoropimelate, m.p. 206° (correct ir).

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