THE ACTION OF ELEMENTAL FLUORINE ON POLYFLUORO-OLEFINS AND -AROMATIC COMPOUNDS. PART II* THE FLUORINATION OF DECAFLUORO-CYCLOHEXENE AND OCTAFLUOROCYCLOHEXA-1,4- AND -1,3-DIENE

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SUMMARY

The title compounds have been fluorinated with elemental **fluorine** of low oxygen content to give products derived from fluorine addition, accompanied by dimerisation and oligomerisation of radical intermediates in the case of the dienes. The 1,4-diene is relatively unreactive towards fluorine and polymerisation did not occur. Acid fluorides, of the type formed using fluorine produced without precautions to minimise oxygen-containing species, were not produced in these reactions.

INTRODUCTION

Reactions of elemental fluorine diluted with nitrogen with hexafluorobenzene in the liquid phase have been described [1]. Analogous reactions of perfluorocyclohexene and -cyclohexadienes are now reported.

RESULTS AND DISCUSSION

Reactions of decafluorocyclohexene (I) so far reported (e.g. chlorine and bromine [2], iodotrifluoromethane [3] chlorodifluoromethyl radicals [4], bromine-bromine trifluoride mixtures [5], cobaltic fluoride [6]) indicated that reaction with fluorine would be relatively sluggish. Nevertheless, it was surprising that virtually no reaction occurred between

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fluorine/nitrogen and this olefin at 0° , although reaction proceeded smoothly at 25° to give only dodecafluorocyclohexane (II) and starting material, in the ratio of 2:1.

Octafluorocyclohexa-1,4-diene (III) appeared to be slightly more reactive than decafluorocyclohexene. Thus, with fluorine in nitrogen at 21° after 4hr., the diene gave dodecafluorocyclohexane (30%), decafluorocyclohexene (37%), octafluorocyclohexa-1,4-diene (25%) and extended species (8%). Thus, the 1,4-diene is not as reactive towards fluorine as might be expected and does not polymerise with the great vigour suggested by Grakauskas [7].

In an early study [8] of the reaction of fluorine (produced without precautions to minimise oxygen containing species) with octafluorocyclohexa-1,3-diene (IV), the predominant products were acid fluorides. In the present work, a vigorous reaction was observed, similar to that reported with hexafluorobenzene $\begin{bmatrix} 1 \end{bmatrix}$ and the reaction mixture was shown to be devoid of acid fluorides by infrared spectroscopy. The products isolated from a typical fluorination at 0° were those of simple addition of fluorine (40%) and those produced by dimerisation (45%) and oligomerisation (15%) of radical intermediates. The "dimeric" fraction contained five components; the major one (V) was a diene with a symmetrical structure that displayed one double bond stretching frequency in the infrared at 1730 cm⁻¹ (cf. hexadecafluorobicyclohex-2,2¹,5tri-enyl [1], tetradecafluorobicyclohex-2,2¹,5,5¹-tetra-enyl [1] and eicosafluorobicyclohex-2-enyl (VI) which all show IR absorption maxima at 1730 cm^{-1}). Compounds (V) and (VI) were produced together with docosafluorobicyclohexyl and hexadecafluorobicyclohex- $2, 2^{1}, 5$ -trienyl by cobaltic fluoride fluorination of tetradecafluorobicyclohex-2, 2^1 ,5,5¹-tetraenyl at 100°. The latter tetra-ene and the mixed "dimeric" species from the 1,3-diene and fluorine all gave docosafluorobicyclohexyl with cobaltic fluoride at 180°. Permanganate oxidation of octadecafluorobicyclohex-2,2¹-bi-enyl (V) gave hexafluoroglutaric acid as the major product; this is consistent with the structure allocated.

The other diene isolated, octadecafluorobicyclohex-2,3 - bi-enyl (VII.), had a complex NMR spectrum that displayed some

double peaks consistent with the presence of the anticipated diastereoisomers [9]. Two vinylic (CF=CF) absorptions occurred in the IR spectrum at 1730 and 1755 cm⁻¹; this trend in absorption maxima is consistent with that observed in related compounds; thus trifluoromethylnonafluorocyclohex-2- and -3-enes display maxima at 1742 and 1757 cm⁻¹ respectively [10]; the analogous pentafluoroethyl derivatives display maxima at 1728 and 1749 cm⁻¹ respectively [11]. The permanganate oxidation of compound (VII) gave a mixture of acids as anticipated but the normal derivatives were intractable.

The structural allocations so derived for compounds (V - VII) were all supported by elemental analysis, IR, NMR, and UV spectroscopy and mass spectroscopy.

The pathways depicted in Figure 1 assume that the attacking species is either a fluorine atom or molecule. Formation of the localised radical A from octafluorocyclohex-1:4-diene (III) would be expected to lead to compounds (VIII) and (IX). The small quantity of extended species from the 1,4-diene, and the small amounts of any twelve carbon species other than compounds (V), (VI) and (VII) from the 1,3-diene suggests that radical A is much less favourable that its stabilised counterpart B.

The reactivity of the 1,3-diene toward fluorine is greater than that of the 1,4-diene as evidenced by the greater extent of reaction at a lower temperature and by localised flashes of light in the reaction vessel. However, the reactivities of these two dienes toward bromine and bromine trifluoride mixtures are roughly the same [12]; This may well indicate that the fluorine reaction is free radical in nature, whereas other species predominate in the bromine-bromine trifluoride system. It is also of interest that although the reactivities of fluorine toward the 1:4-diene and decafluorocyclohexene are roughly comparable, the diene shows a markedly greater reactivity towards both cobaltic fluoride and bromine-bromine trifluoride than the latter.

The reaction of tetradecafluorobicyclohex- $2,2^{1},5,5^{1}$ tetra-enyl with fluorine gave a glassy oligomer as the main product [1], in contrast to the 1,4-diene; this difference probably arises from their relative volatilities. Thus, whereas



<u>Figure 1</u>. (i) F. or F_2 ; (ii) 1,3-C₆F₈; (iii) 1,4-C₆F₈

the 1:4-diene may well react in the bubbles of gas [13], the much less volatile tetra-ene presumably reacts mainly at the gas-liquid interface.

The glassy material obtained from the 1,3-diene was difficult to characterise. Elemental analysis (mean: C, 25.9; F, 66.5%) was consistent with incomplete combustion of the sample or with the presence of oxygen. However, the latter is unlikely in view of the absence of IR absorptions in the regions characteristic of carbonyl groups.

The photochemical gas phase oxidation of octafluorocyclohexa-1,3-diene has been shown [4] to give mainly volatile products containing ether and acid fluoride groups as the main links both between and within molecules. Physical data on these compounds provided good evidence that neither these nor analogous species were present in this study using purified fluorine.

EXPERIMENTAL

Apparatus

Gas chromatography

Analytical and preparative separations were made with 1.5 m and 9.1 m glass columns (6 mm diam.), respectively, packed with dinomyl phthalate-celite (1:3) (Pye 104 instrument)

·NMR Spectroscopy

Spectra were measured with a Perkin-Elmer R12B Instrument at 56.4 MHz with trichlorofluoro methane as internal reference and chemical shifts are quoted in p.p.m.

<u>Mass Spectra</u>

These were measured on an AE1 MS9 instrument

Fluorination of decafluorocyclohexene

(a) Fluorine [generated by 1.00 A, in the manner described previously [1]] and nitrogen $(3 \text{ dm}^3 \text{h}^{-1})$ were bubbled through decafluorocyclohexene (18.65 g) at 0° for 3 hr in a glass reaction vessel (25 cm³) fitted with a thermometer pocket and a reflux condenser. The condenser was fitted with traps in series held at -78° and -180° . The product (18.51 g)

collected in the first trap was shown by IR spectroscopy to be mainly decafluorocyclohexene; GLC $(95^{\circ}: N_{2}, 1 \text{ dm}^{3}\text{h}^{-1})$ revealed the presence of traces of dodecafluorocyclohexane.

(b) Fluorine (generated by 2.00 A) and nitrogen $(2 \text{ dm}^3 \text{h}^{-1})$ were bubbled for 4 hr. through decafluorocyclohexene (17.78 g) at 25°. A liquid (16.96 g) collected in the first trap and a portion (4.20 g) was separated by GLC (95°; N₂, 3 dm³ h⁻¹) to give dodecafluorocyclohexane (2.60 g) and decafluorocyclohexene (1.40 g); both had correct IR spectra.

Fluorination of octafluorocyclohexa-1,4-diene

Fluorine (generated by 2.00 A) and nitrogen (2 dm³h⁻¹) were bubbled for 4 hr. through octafluorocyclohexa-1,4-diene (III) (15.11 g) at 21°. The product (15.49 g) collected in the first trap was distilled to give a volatile fraction (14.09 g) and a residual glass (0.40 g). The former (7.00 g) was separated by GLC (50°; N₂, $3dm^3h^{-1}$) to give dodecafluorocyclohexane (II) (1.98 g), decafluorocyclohexene (I) (2.45 g) and octafluorocyclohexa-1,4-diene (1.57 g), all with correct IR spectra, and a liquid (0.56 g), shown by GLC (95°; N₂, $3dm^3h^{-1}$) to contain three long retained components in the ratio of 2:2:1, which was not investigated further.

Fluorination of octafluorocyclohexa-1,3-diene

Fluorine (generated by 2.00 A) and nitrogen $(3 - 5 \text{ dm}^3 \text{h}^{-1})$ were bubbled for 4 hr. through octafluorocyclohexa-1,3-diene (IV) (10.03 g) at 0°. The product (9.87 g) collected from the first trap and reaction vessel (4:1 by weight) was distilled to give a volatile fraction (8.29 g) and a residual glass (1.43 g). A portion (8.00 g) of the volatile fraction was separated by GLC (95°; N₂, 5 dm³h⁻¹) to give sub-fractions (i) - (vii), all liquids: (i) (3.16 g) was shown by GLC (50°; N₂, 1 dm³h⁻¹) to contain three components, separated by GLC (50°; N₂, 3 dm³h⁻¹) to give (a) dodecafluorocyclohexane (II) and fragmentation products (1.56 g) in the ratio of 2:1 (by IR and NMR spectroscopy and GLC retention volumes) and (b) decafluorocyclohexene (I) (1.60 g) with a correct IR spectrum: (ii) was octafluorocyclohexa-1,3-diene (0.34 g) with a correct IR spectrum:

(iii) was an unidentified liquid (0.10 g): (iv) was eicosafluorobicyclohex-2-enyl (VI) nc (0.78 g) b.p. 179 - 180° (one peak on GLC at 95° and N_2 , 3 dm³h⁻¹) (Found: C, 27.4; F, 72.1 $C_{12}F_{20}$ requires C, 27.5; F, 72.5%) γ_{MAX} 1730 cm⁻¹ (CF=CF) m/e 243 ($C_6F_9^+$) [no peak at 281 ($C_6F_{11}^+$)], its ¹⁹F NMR spectrum consisted of five bands at 136.4 (multiplet) (C_2 or C_3), 146.9 (multiplet) (C_2 or C_3), 162.5 (multiplet) (C_1), 182.1 (multiplet) (C_1^{-1}) and 106 - 146 (complex AB overlap) (C_2^{-1}) , c_3^{1} , c_4^{1} , c_5^{1} , c_6^{1} , $c_4^{}$, $c_5^{}$, and $c_6^{}$) in the relative intensity ratio 1:1:1:1:16, respectively: (v) was an unidentified liquid (0.06 g): (vi) was octadecafluorobicyclohex-2,2¹-bienyl (V) nc (1.45 g) b.p. 180 - 181° (one peak on GLC at 95° and N_2 , 3 dm³h⁻¹) (Found: C, 29.4; F, 70.8. $C_{12}F_{18}$ requires C,29.6; F, 70.4%), γ_{MAX} 1730 cm⁻¹ (CF=CF), m/e 243 ($C_6F_9^+$), its ¹⁹F NMR spectrum consisted of four bands at 139.7 (multiplet) (C_2 , C_2^1 or C_3 , C_3^1), 147.9 (multiplet) (C_2 , C_2^1 or C_3 , C_3^1),161.5 (broad band) (C_1 and C_1^1) and 106 - 146 (complex AB overlap) (C_4 , C_5 , C_6 , C_4^1 , C_5^1 , C_6^1) in the relative intensity ratio of 1:1:1:6, respectively: (vii) was octadecafluorobicyclohex-2,3¹-bi-enyl (VII) nc (1.00 g) b.p. 183 -184° (one peak on GLC at 95° and N₂, 3 dm³h⁻¹) (Found: C, 29.4; F, 70.6%), γ_{MAX} 1730 cm⁻¹ (CF=CF) and 1755 cm⁻¹ (CF=CF) m/e 243 (C₆F₉⁺), its ¹⁹F NMR spectrum consisted of seven bands at 138.3, 140.7 (multiplet) (C2 or C3), 146.9, 148.3 (multiplet) (C or C₃), 152.1 (multiplet) (C¹₃ or C¹₄), 155.1 (multiplet) (C¹₃ or C¹₄), 163.1 (multiplet) (C₁), 173.5, 175.3 (multiplet) (C¹₁) and 106 - 146 (complex AB overlap) (C¹₂, c_5^{1} , c_6^{1} , c_4^{-} , c_5^{-} , c_6^{-}) in the relative intensity ratio of 1(1:1) :1(1:1):1:1:1:1(1:1): 2, respectively.

The glassy product was difficult to characterise (Found: C, 26.5, 25.4; F, 67.8, 65.3%), its IR spectrum contained strong absorption maxima at 1730 and 1755 cm^{-1} (CF=CF)

Cobaltic fluoride fluorination of the mixed "dimeric" species from the elemental fluorine fluorination of octafluorocyclohexa-1,3-diene

A portion (1.01 g) of the mixed "dimeric" compounds [sub-fractions (iv - vii) above] (5 components on GLC at 95° and

 N_2 , 2 dm³h⁻¹) was added in a stream of nitrogen (0.5 dm³h⁻¹) to a stirred reactor containing cobaltic fluoride (200 g) at 180° during 1 hr. After the addition, nitrogen (2 dm³h⁻¹) was passed for a further 2 hr and the product (1.10 g), collected in a glass trap at -180°, was shown by GLC (95°; N_2 , 2 dm³h⁻¹) and IR spectroscopy to be docosafluorobicyclohexyl.

Cobaltic fluoride fluorination of tetradecafluorobicyclohex- $2,2^{1},5,5^{1}$ -tetra-enyl

(a) The title compound (1.20 g), prepared from the elemental fluorine fluorination of hexafluorobenzene as previously described [1], was fluorinated with cobaltic fluoride in the above manner at 200° and the product (1.45 g) shown by IR spectroscopy and GLC (95°; N_2 , 2 dm³h⁻¹) to be docosafluorobicyclohexyl containing a trace of eicosofluorobicyclohex-2-enyl (VI).

(b) The title compound (1.34 g) was fluorinated in the same way at 100° and the liquid product (1.64 g) shown by GLC $(95^{\circ}, N_2, 2 \text{ dm}^3 \text{h}^{-1})$ to contain four main components which were separated by GLC $(95^{\circ}; N_2, 5 \text{ dm}^3 \text{h}^{-1})$ to give: (i) a mixture (0.05 g) of components thought to be fragmentation products; (ii) docosafluorobicyclohexyl (0.36 g) with a correct IR spectrum; (iii) eicosafluorobicyclohex-2-enyl (VI) (0.52 g) with an IR spectrum identical to that of the compound (VI) obtained from the 1:3-diene and fluorine; (iv) octadecafluorobicyclohex-2,2¹-bi-enyl (V) (0.52 g) with an IR spectrum identical to that of the light an IR spectrum identical to the from the 1:3-diene and fluorine; (iv) octadecafluorobicyclohex-2,2¹-bi-enyl (V) (0.52 g) with an IR spectrum identical to that of the compound (VI) obtained from the 1:3-diene and fluorine; (v) hexadecafluorobicyclohex-2,2¹,5-trienyl (0.13 g) with a correct IR spectrum [1].

Oxidation of octadecafluorobicyclohex-2,21-bi-enyl

The olefin (V) (0.30 g) was added to a solution of potassium permanganate (1.05 mol.per double bond) in acetone (50 cm³; dried over $MgSO_4$) and the dianilinium salt (0.24 g) prepared by the standard method [14]. Recrystallisation (ethanol/chloroform) was unsuccessful. The ¹⁹F NMR spectrum of the crude salt in DMSO consisted of singlets at 116.1 and 123.4 in the relative intensity ratio of 2:1 [an authentic specimen of dianilinium hexafluoroglutarate displayed singlets at 115.8 and 122.8 of relative intensity ratio 2:1 [15]] and a singlet at 117.5 consistent with the presence of <u>ca</u>. 10% of dianilinium tetrafluorosuccinate [an authentic specimen displayed a singlet at 117.0 [15]].

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REFERENCES

- 1 I. J. Hotchkiss, R. Stephens and J. C. Tatlow, J. Fluorine Chem., 6, 135 (1975).
- 2 T. J. Brice and J. H. Simons, J. Amer Chem. Soc., <u>73</u>, 4017 (1951); J. C. Tatlow and R. E. Worthington, J. Chem. Soc., 1251 (1952).
- 3 R. N. Haszeldine and J. E. Osborne, J. Chem. Soc., 61 (1956).
- 4 H. Derbyshire, Ph.D. Thesis, University of Birmingham (1959).
- 5 R. D. Chambers, W. K. R. Musgrave and J. Savory, J. Chem. Soc., 3779 (1961).
- 6 J. Ricra and R. Stephens, Tetrahedron, 22, 2555 (1966).
- 7 V. Grakauskas, J. Org. Chem., <u>34</u>, 2835 (1969).
- 8 R. Stephens, unpublished work.
- 9 J. Burdon, personal communication.
- 10 D. J. Alsop, Ph.D. Thesis, University of Birmingham (1959).
- 11 B. R. Letchford, Ph.D. Thesis, University of Birmingham (1963).
- 12 T. W. Bastock, Ph.D. Thesis, University of Birmingham (1973).
- 13 J. M. Tedder and P. C. Anson, J. Chem. Soc., 4390 (1957).
- 14 J. Burdon and J. C. Tatlow, J. Appl. Chem., <u>8</u>, 293 (1958).
- 15 G. E. Ditchfield, Ph.D. Thesis, University of Birmingham (1971).