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THE ACTION OF ELEMENTAL FLUGRINE OF POLYFLUGRO-OLEFINS AND -AROMATIC COMPOUNDS. PART I. THE FLUGRIMATION OF HEXAFLUGROBENZENE

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SUMMARY

Hexafluorobenzene has been fluorinated at 0° with elemental fluorine of low oxygen content to give mainly tetradecafluorobicyclohex-2.2',5,5'-tetra-enyl and a glassy oligomer based mainly on the hexafluoro-1:4-dienyl unit together with smaller amounts of hexadecafluorobicyclohex-2,2',5-tri-enyl, decafluorocyclohexene, dodecafluorocyclohexane and fragmentation products.

INTRODUCTION

It is now nearly forty years since Bigelow's classic work on vapour phase fluorination of hydrocarbons; the paper (1) indicated the need for fluorine containing a minimum of oxygen. Indeed it is nearly twenty years since Miller and Dittman (2) reported the oxidation of tetrachloroethylene with a mixture of fluorine and oxygen. Since then numerous fluorinations using elemental fluorine have been described and reviewed (3) but the influence of oxygen in the fluorine used has not always been closely examined. Early work in this Department (4) showed that aromatic compounds could be "polymerised" to short-chain oligomers when dilute fluorine was bubbled through solutions of them in fluorocarbons. This type of process has now been examined further using hexafluorobenzene as substrate.

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RESULTS AND DISCUSSION

In an earlier study (5) we found that the fluorination of hexafluorobenzene in the liquid phase at 0° using fluorine diluted with nitrogen gave substantial amounts of acid fluorides. However, the fluorine used was generated from an electrolyte melt made with hydrogen fluoride of unknown water content without special provisions to exclude moisture.

In the present study a conveniently modified electrolysis cell



Figure 1 (not to scale) Fluorine Generator

(Fig. 1) was used that produced fluorine of low oxygen content, as demonstrated by the absence of acid fluorides in its reaction product with hexafluorobenzene at 0° . However, an independent measure of the oxygen content of the fluorine generated was not made.

136

Hexafluorobenzene reacted smoothly in the liquid phase with a mixture of fluorine and nitrogen in the approximate ratio of 1:10. The glass reaction vessel permitted some measure of control over the vigour of the fluorination. The slow production of fluorine oxide and silicon tetrafluoride by attack of fluorine on glass was not considered significant in this study.

The fluorination was continued until fluorine was detected in the exit gases in appreciable quantities. The reaction vessel then contained a clear, slightly viscous liquid and the cold trap a clear mobile liquid; both materials were free of acid fluorides. When subjected to a combination of distillation and GLC these combined liquids afforded hexafluorobenzene (I) (20%), dodecafluorocyclohexane (II) contaminated with perfluorinated fragmentation products (7%), decafluorocyclohexene (III) (8%), tetradecafluorobicyclohex-2,2',5,5'-tetra-enyl (IV) (20%), hexadecafluorobicyclohex-2,2',5-tri-enyl (V) (5%) and a mixture of oligomers based on $(C_6F_6)_n$ (VI) (40%).

The triene (V) and tetra-ene (IV) were characterised by elemental analysis, mass spectrometry and U.V.-, IR- and ¹⁹F NMR - spectroscopy. The glassy oligomeric material (VI) was difficult to analyse because of combustion problems. The carbon and fluorine content $(C_6F_{7.5})$ suggested a higher degree of saturation than the linear structure (VI) $(C_6F_{6.2-6.6})$ shown in Fig. 2. However, pyrolytic defluorination to hexafluorobenzene (70%) is good evidence for a substantial proportion of hexafluorocyclohexal:4-dienyl units in oligomer (VI).

Pyrolytic defluorinations of some of these products were interesting and structurally useful. Thus, when the tetra-ene (IV) was passed over iron oxide or glass helices at 450° it gave hexafluorobenzene as the sole product. This result is consistent with the structure allocated to (IV) whether the process of defluorination is ionic or free-radical in character. Thus, iron oxide might elicit the synchronous ω -elimination depicted by (VII), or act as a "sink" for fluorine atoms generated in the





homolytic sequence derived from (VIII). This process is essentially the reverse of its formation from hexafluorobenzene and parallels the known (6) cleavage of saturated fluorocarbons with C-C bonds involving tertiary carbons. The fact that the defluorination is observed over glass is slight evidence for the operation of a homolytic process.

On the basis of such a defluorination process, a purely linear oligomer of the type depicted by (VI) would be expected to give entirely hexafluorobenzene when passed over iron oxide at 450° . However, when the oligomer (VI) was so treated it gave hexafluorobenzene (7 parts) together with a complex mixture of suspected perfluoro - ter - and quater - phenyls (3 parts). The latter could arise either from branching points in the oligomer (VI) or from oligomeric species containing saturated or partially saturated cyclo hexyl- units both of which might break down to hexafluorobenzene less readily.

The possibility of branch-points arising from linear oligomers (VI) in the fluorination of hexafluorobenzene was indicated by the variation in yield of the tetra-ene (IV) indicated in Figs. 3 and 4. It will be noted





from these experiments that in both stirred and unstirred reaction mixtures there is an optimisation of the yield of the tetra-ene (IV). This would suggest a participation of (IV) in the generation of higher molecular weight compounds. Indeed, when the tetra-ene (IV) was fluorinated in the manner of hexafluorobenzene it gave a clear glass (IX) as the major product. When this $C_{12}F_{14}$ - oligomer (IX) was pyrolysed over iron oxide at 450° it gave hexafluorobenzene (1 part) and a complex mixture containing suspected perfluoro - ter - and - quater - phenyls (1 part). The latter material displayed the same IR spectrum as that of the analogous material from the defluorination of the C_6F_6 - oligomer (VI).

The high proportion of tetra-ene (IV) and oligomer (VI) is consistent with the initial formation of a radical intermediate from hexafluorobenzene, either by reaction with a fluorine atom (3) or a fluorine molecule (7). The processes giving rise to the products isolated are devicted in Fig. 2. The absence of products derived from ortho-attack is surprising but could



nossibly be anticipated from electron spin resonance studies (8). A similar orientation effect has been noted in other free radical reactions of hexafluorobenzere (9).

It is of interest to compare the present study with that of Grakauskas (10) who reacted hexafluorobenzene in 1,1,2-trichloro-1,2,2-trifluoroethane at 20° with 3 mol. of fluorine to give perfluorobicyclohexyl and a polydecafluorocyclohexene. Presumably this could be the ultimate fate of our products in a protracted fluorination. The difference is unlikely to be a consequence of the presence of trichloro-trifluoroethane. In none of our fluorinations of hexafluorobenzene did we observe violent reactions comparable to those reported by Grakauskas (10). Further, our fluorination studies on octafluorocyclohexa-1,3- and -1,4-diene do not support his suggestion (10) that octafluorocyclohexadiene can polymerise with great vigour.

Arparatus

Gas chromatography

Analytical work was carried out using 1.5 m class columns (6 mm diam.) packed with dimonyl phthalate-celite (1:3) (Pye 104 instrument). For preparative work a 9.1 m class column (6 mm diam.) was macked with dimonyl phthalate-celite (1:3) (Pye 104 instrument).

NMR spectroscopy

Spectra were measured with a Perkin-Elmer R12B instrument at 56.4 MH with trichloroflueromethane as internal reference and chemical shifts are quoted in ppm.

Mass spectra

These were measured on an AEI MS9 instrument.

Fluorine generator

Fluorine was generated by the standard electrolysis of rotassium fluoride - hydrogen fluoride (3:2) at 85° in a mild steel cell fitted with a porcus carbon anode and illustrated in detail in Fig. 1.

The teflen disc in the base of the cell permitted an initial electrolysis of the totally molten electrolyte without hydrogen entering the anode compartment. This procedure was followed in an attempt to preferentially remove as much water from the system as possible. Mixing of the electrolyte was promoted by the convection currents generated by the geometry of the cell. The electrolyte composition was periodically restored with hydrogen fluoride containing 260 ppm of water. At all other times electrolysis was maintained at <u>ca</u>. 0.5 amp with a continuous small flow of dry nitrogen (2 ℓ h⁻¹) over the electrolyte surface within the anode compartment. A long outlet tube for bydrogen minimised back diffusion of air into the cell.

The gas stream from the anode compartment passed through a 23 cm copper cylinder (6.5 cm diam.) packed with sodium fluoride pellets and two glass traps in series at -180° to ensure removal of hydrogen fluoride and condensation of oxides of fluorine produced by attack on the binding agent of the anode.

Fluorination of hexafluorobenzene with excess of fluorine

Fluoring (generated by 2.0 amp) and nitrogen $(6-8 \ \text{l} \ \text{h}^{-1})$ were bubbled for 4 h through hexafluorobenzene (29.05 g) at 0° in a class reaction vessel (25 cm³) carrying a thermometer pocket and reflux condenses A temporary reduction in the gas flow-rate was found adequate to moderate the reaction if small localized flashes of light were observed in the reactor. The condenser was "backed" by glass trans held at -28° and -180° .

A clear slightly viscous liquid (23.79 g) remained in the reaction vessel after 4 h and a clear liquid (7.76 g) collected in the tran at -78° . The total product was shown to be devoid of acid fluorides using IR spectroscopy and was distilled to give a volatile fraction (19.78 g) and a residual clear glass (11.71 g).

A portion (8.00 c) of the volatile fraction was separated by GLC $(95^{\circ}; N_{0} 6 \text{ lh}^{-1})$ to give: (i) a liquid (4.28 g) shown by GLC (50°: N_{0} 1 k h^{-1}) to contain 4 components; (ii) hexadecafluorobicyclohex-2,2',5-tri-enyl (V) nc (0.63 g) b.p. 169-120° shown by GLC (50°: N₂ 1 l h⁻¹) to be one peak (Found: C, 32.5; F, 67.6 C₁₂F₁₆ requires C, 32.1; F. 67.8%) γ_{max} 1730 cm⁻¹. (CF=CF), m/e 247 (C₆F₉⁺) 205 (C₆F₉⁺), its 19 F NMR spectrum consisted of nine bands at 112.2 (multiplet) (C_L), 140.5 (multiplet) (C₂,), 145.1 (multiplet) (C₃,), 148.5 (multiplet) (C2 and C6), 152.5 (triplet J 19 Hz) (C2), 153.9 (triplet, J 19 Hz) (C5), 164.3 (Broad band) (C1,), 166.3 (Broad band) (C1) and 106-146 (complex AB overlap) (C41, C51 and C61) in the relative intensity ratio of 2:1:1:2: 1:1:1:1:6, respectively; (iii) tetradecafluorobicyclohex-2.2',5,5'-tetraenvl (IV) nc (2.49 g) b.p. 172° shown by GLC (50° , N₂ 1 l h⁻¹) to be one peak (Found: C, 34.8; F, 64.55 $C_{12}F_{14}$ requires C, 35.1: F. 64.9%). $V_{\text{max.}}$ 1730 cm⁻¹ (CF=CF), m/e 205 ($C_{6}F_{7}^{+}$) its ¹⁹F NMR spectrum consisted of 4 bands at 109.3 ($\delta_{\rm A}$), 112.9 ($\delta_{\rm B}$) (AB, J 315 Hz) ($C_{\rm L}$, $C_{\rm L}$), 153.2 174.0 (singlet) (C1,C1) in the relative intensity ratio of 2:2:2:1. respectively.

A portion (3.60 g) of component (i) was separated by GLC (50°; N_p 6 \pm h⁻¹) to give: (a) a liquid (0.65 g) shown by IR- and ¹⁰F NMR-spectroscopy to be mainly dodecafluorocyclohexane (II) containing fragmentation products; (b) decafluorocyclohexene (III) (0.80 g) with a correct IR spectrum; (c) hexafluorobenzene (I) (2.00 g) with a correct IR spectrum. The glassy product was difficult to characterise (Found: C, 31.6; F, 63.8%).

Optimisation of the yield of tetradecafluorobicyclohex 2,2',5,5'-tetraenyl (IV) from hexafluorobenzene and fluorine

Hexafluorobenzene (8 g) at 0° was treated with fluorine and nitrogen in the manner described previously. Two such fluorinations were conducted; one with a stirred reaction vessel, the other unstirred. Both fluorinations were stopped at intervals and the product analysed for the volatile components, the tetra-ene (IV), the oligomer (VI) and hexafluorobenzene. The results are expressed in Figs. 3 and 4.

Fluorination of tetradecafluorobicyclohex-2,2',5,5'-tetra-enyl (IV)

Fluorine (generated by 2.2 amp) and nitrogen $(4 \ t \ h^{-1})$ were bubbled through the tetra-ene (IV) (5.72 g) at 8° in the apparatus described previously. After 1½ h a very viscous liquid (4.85 g) was recovered which was distilled to give: (i) a volatile liquid (1.82 g) shown by GLC .(95°; N₂ 2 t h⁻¹) and IR spectroscopy to contain mainly the tetra-ene (IV) and the triene (V) in the ratio of (1:4); (ii) a clear glass (IX) (2.90 g) (Found: C, 31.7, 32.3; F, 68.7, 69.7 $C_{12}F_{16}$ trequires C, 30.7; F, 69.3%).

Defluorination of tetradecafluorobicyclohex-2,2',5,5'-tetra-enyl (IV)

This compound (IV) (2.00 g) was passed over iron oxide in a 30 cm copper tube (30 mm diam.) at 450° in nitrogen (1 g h⁻¹) to give hexafluorobenzene (1.19 g) with a correct IR spectrum.

Likewise, compound (IV) (1.60 g) was passed through a 30 cm glass tube (30 mm diam.) containing glass helices at 450° in nitrogen (1 l h⁻¹) to give hexafluorobenzene (0.88 g) with a correct IR spectrum

Defluorination of oligomer (VI)

This material (6.94 g) was passed over iron oxide in the manner previously described to give a liquid (4.06 g). A portion (3.88 g) of the latter was distilled to give hexafluorobenzene (2.63 g) with a correct IR spectrum and a yellow oil (X) (1.05 g) shown by GLC $(95^\circ;$

 $N_{2}4 \pm h^{-1}$) to contain several components (Found: C, 34.1, 34.9; F, 63.3, 62.5%) \sum_{max} 1500 cm⁻¹ (strong) (polyfluoroaromatic).

Defluorination of the oligomer (IX)

This material (2.10 g) was passed over iron oxide in the manner previously described to give a liquid (1.18 g) which was distilled to give hexafluorobenzene (0.58 g) with a correct IR spectrum and a yellow oil (0.57 g) with an IR spectrum identical to that of (X).

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