Journal of Fluorine Chemistry, 15 (1980) 129–138
© Elsevier Sequoia S.A., Lausanne – Printed in the Netherlands

Received: August 31, 1979

POLYCYCLIC FLUORO-AROMATIC COMPOUNDS PART VIII. [1] THE PREPARATION OF PERFLUOROCHRYSENE AND SOME RELATED COMPOUNDS

JAMES BURDON*, IAN W. PARSONS and HARPAL S. GILL

Chemistry Department, University of Birmingham, P. O. Box 363,
Birmingham B15 2TT (Great Britain)

SUMMARY

Fluorination of chrysene over cobalt trifluoride gives perfluoro-perhydrochrysene, and over potassium tetrafluorocobaltate a mixture of perfluorohexadecahydro(IV)- and perfluorotetradecahydro(V)- chrysene. Defluorination of perfluoroperhydrochrysene over iron oxide at 400–530°C gives a mixture of three partially aromatized compounds (VI, VIII, and IX) and perfluorochrysene(VI) (3%).

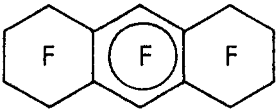
INTRODUCTION

Several of the basic perfluoropolynuclear carbocyclic aromatic compounds are known: perfluoronaphthalene [2,3],-anthracene [4],-phenanthrene [4,5], -biphenylene [6], -pyrene [1,4,7], and -acenaphthylene [4]. They have been prepared by two main methods: (i) fluorination of the parent hydrocarbon, for example with cobalt trifluoride to the corresponding

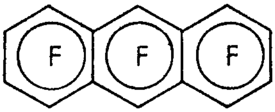
---

*Author to whom correspondence should be addressed.

perfluoroperhydro-compound, followed by defluorination over nickel, iron, or iron oxide to the perfluoro-aromatic[1, 2, 4, 5]; (ii) chlorination of the parent hydrocarbon to the perchloro-compound, followed by replacement of chlorine by fluorine by treatment with a source of fluoride ion[2,7]. The first route normally gives small amounts of partially aromatised compounds[1, 2, 4, 5] (e.g. perfluorotetralin is obtained[2] as well as octafluoro-naphthalene from the defluorination of perfluorodecalin) in addition to the major, completely aromatised, product, except in the case of anthracene where the reverse obtains: the major product in the preparation of decafluoro-anthracene is (I), and not (II) which was obtained in very poor yield[4, 5].



I

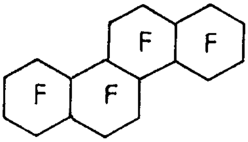


II

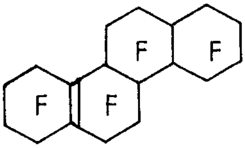
We now report the preparation of perfluorochrysene(VI), and some partially aromatized compounds related to it, by the fluorination/defluorination route.

RESULTS AND DISCUSSION

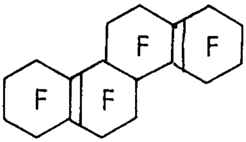
Chrysene was fluorinated at 460-510°C over cobalt trifluoride to give what was clearly a mixture of perfluoro-perhydro-chrysene isomers(III); there were at least 20 tertiary fluorine peaks in the ^{19}F nmr spectrum and six is the most a single isomer can give.



III



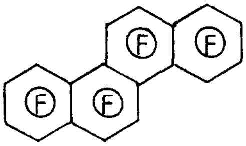
IV



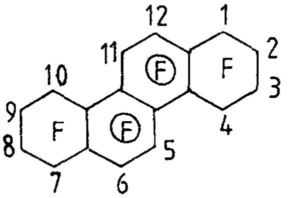
V

Fluorination of chrysene over potassium tetrafluorocobaltate at 460-520°C gave two major product types: mixed mono-ene isomers (stereoisomers of structure IV, and of its regioisomers with the double bond between the central rings) and mixed diene isomers (stereoisomers of structure V, and of its conjugated isomer). Neither compound type showed any IR absorption between 1700 and 1800 cm^{-1} and so double bonds of the $-CF{=}C<$ or $-CF{=}CF-$ type were absent[8]: this is what would be expected both on the basis of the existing theory[9] of fluorination by high-valency transition metal fluorides, and by comparison with the fluorinations of naphthalene[10], anthracene [5], and phenanthrene[5] over $KCoF_4$ in which virtually the only double bonds in the products were those at ring junctions.

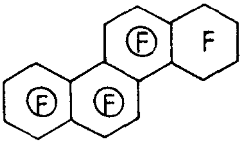
Defluorination of perfluoro-perhydrochrysene over iron oxide at 400-530°C gave perfluorochrysene(VI) and the three partially aromatized compounds (VII, VIII, and IX) as major products. Their structures followed fairly straightforwardly from elemental analyses, IR, UV, mass, and nmr spectroscopy, but some comments on the ^{19}F nmr spectra are perhaps appropriate.



VI

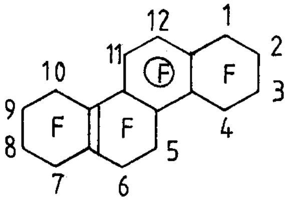


VII

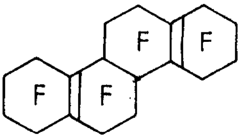


VIII

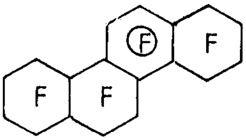
Perfluorochrysene(VI) showed three pairs of signals: an AB spectrum with J_{AB}=63Hz which is typical[11] of peri-coupling in polyfluoro-naphthalenes and so must arise from F_6 and F_7 (=F_1 and F_{12}); an AB spectrum with J_{AB}=153Hz, a magnitude which is known[12] to arise between fluorines on the 'inside' (positions 4 and 5) of fluorophenanthrenes - these corresponds to F_4 and F_5 (=F_{10} and F_{11}) of perfluorochrysene; and two other signals whose chemical shifts suggest[13] that they each have two ortho-fluorine neighbours and so are F_2 and F_3 (=F_8 and F_9). The signals within each pair were easily distinguished by decoupling studies.



IX



X



XI

The ^{19}F nmr spectrum of compound(VII) has two features to which we draw attention. First, a triplet and a doublet, in intensity ratio 1:2, with a coupling constant of 82Hz. These could be due either to F_6 and F_7, or to F_4 and F_5: we reject the first possibility on the grounds that such a large coupling is not present in the spectra of either perfluorotetralin or compound(I), where fluorines related like F_6 and F_7 are to be found. Secondly, the signals at 133.8 and 134.6 are in the position expected[14] for CF_2 groups flanked by CF_2 groups in six-membered rings (i.e. F_2 and F_3).

The ^{19}F spectrum of compound(VIII) is obviously more complex but it does show some of the features more easily seen in (VI) and (VII): an AB spectrum with J_{AB}=166Hz (F_{10}, F_{11}); an AB spectrum with J_{AB}=68Hz (F_6, F_7); a doublet and a triplet in intensity ratio 2:1 with J=78Hz (F_4, F_5); and signals at 134.0 and 134.4 due to CF_2 groups flanked by CF_2 groups (F_2, F_3).

Several of the peaks in the ^{19}F nmr spectrum of (IX) cannot be definitely assigned, but enough features are obvious to make the structure certain. The triplet (J= 64Hz) can be assigned to F_{11} [by comparison with compounds (VI) and (VIII)] and irradiation of it allows F_{12} and F_{10} to be located; irradiation of the resonance due to F_{12} in turn locates F_1; F_8, F_9, F_2, and F_3 are in the expected positions (134) for such CF_2 groups; the other signals have been assigned by comparison with compounds (VI) and (VIII). Double bond isomers of (IX) cannot be entertained since there is no IR absorption between 1700 and 1800 cm^{-1} (no $-CF=C<$ or $-CF=CF-$ [8]).

That the one-ring-aromatic compound(XI) is not among the major products is perhaps surprising. It could well be present in minor amounts as could the remaining two- and three-ring aromatic compounds, as some twelve small glc peaks were unidentified. It is possible that either the main defluorination route proceeds by loss of all tertiary fluorines to give triene(X) before any aromatisation occurs, or that loss of the two tertiary fluorines from(XI) to give the conjugated double bond in (IX) is so easy that a significant amount of (XI) never builds up.

The defluorination of perfluoro-perhydrochrysene resembles that of perfluoro-perhydroanthracene more than that of the other perfluoro-perhydro-polycyclics in that the partially aromatized compound(VII) is by far the major product [compound (I) is the major product[5] in the anthracene case]. Why this should be so, we do not understand. Because of it, the fluorination/defluorination route is a very poor way of preparing perfluorochrysene, as it is for perfluoro-anthracene.

Many perfluoro-polynuclear aromatics have UV spectra which strongly resembles those of the parent hydrocarbons[4]: the resemblance between the spectra of perfluorochrysene and chrysene is not nearly as great as between, for example, pyrene and perfluoro-pyrene, but there are clear similarities. Interestingly, perfluorochrysene is pale yellow, whereas chrysene itself is colourless.

We have not defluorinated the $KCoF_4$ fluorination products (IV and V) but on the basis of results obtained[5] on analogous phenanthrene- and anthracene-like compounds, they would be expected to give a very similar product mixture to that obtained from perfluoroperhydrochrysene.

EXPERIMENTAL

Fluorination of Chrysene over Cobalt Trifluoride

Chrysene (3.0g) was introduced over 60 minutes as a solid in a nitrogen stream (0.2 dm^3/h) into a heated (460-510°C) and stirred bed of cobalt trifluoride (150g) in a reactor of the type described before[15]. The products were collected in a trap cooled in liquid air. After the addition, the nitrogen flow-rate was increased to 10 dm^3/h for a further 45 minutes. The outlet from the reactor was heated with a Bunsen burner at intervals during the fluorination to avoid condensation of solids and high-boiling liquids. Highly volatile products (CF_4, C_2F_6, SiF_4, and COF_2 by IR) were allowed to escape and the less volatile viscous material (3.4-3.9g) was washed with aqueous sodium hydroxide and water, and dried over phosphoric oxide.

The combined products (33.1g) from several such fluorinations were fractionally distilled under reduced pressure (0.1 mm Hg) through a vacuum-jacketed column packed with glass helices. The fraction, b.p. 65-72°C/0.1 mm Hg (22.0g) was perfluoro-perhydrochrysene (III), b.p. 283-290°C [lit.[16], b.p. 135°C/10 mm Hg] (Found: C, 27.6; F, 72.7. $C_{18}F_{30}$ requires C, 27.5; ; F, 72.5%). Glc displayed several broad peaks; ^{19}F nmr showed a large number (>20) of peaks in the tertiary C—F region (170-190), but the ratio of the combined intensities of these peaks to those attributable (107-144) to CF_2-groups was 1:4 - correct for perfluoroperhydrochrysene isomers.

On standing, a fraction b.p. 68°/0.1 mm Hg (3.3g from 33.1g of total crude) deposited crystals (0.8g), m.p. 70-70.5°C, which, since they showed a single sharp peak on glc, are probably a single stereoisomer of perfluoroperhydrochrysene (Found: C, 27.3; F, 72.7%) (they were not sufficiently soluble for a satisfactory ^{19}F nmr to be obtained).

Fluorination at 200-450°C gave only small yields of highly volatile products (CF_4, etc.), presumably because the perfluoroperhydrochrysene isomers were too involatile at these temperatures to emerge from the reactor in a reasonable time.

Fluorination of Chrysene over Potassium Tetrafluorocobaltate

This was carried out at 460-520°C on chrysene (3.0g) in a similar manner to the cobalt trifluoride fluorination. The yields of crude product were 2.3-2.8g.

A portion (1.0g) of such a product was separated by glc [Pye-Unicam 104 instrument; column 9m x 10mm; packed with

Silicone gum SE30 on Universal B (1:40); temp. 170°C; N_2 inlet pressure 30 psi] into: (i) *perfluorohexadecahydrochrysene* nc (0.40g IV) (Found: C, 28.8; F, 71.2; top mass peak 748. $C_{18}F_{28}$ requires C, 28.9; F, 71.1%; $M^{+\cdot}$ 748); and (ii) *perfluorotetradecahydrochrysene* nc (0.32g V) (Found: C, 30.8; F, 69.2; top mass peak 710. $C_{18}F_{26}$ requires C, 30.4; F, 69.6%; $M^{+\cdot}$ 710). Neither product showed IR absorption in the 1700-1800 cm^{-1} region, and in the ^{19}F nmr spectra the ratios of the intensities of CF_2 peaks (94-142) to CF (174-188) were in accord with isomers of the types (IV) and (V), respectively.

Defluorination of perfluoroperhydrochrysene(III)

Perfluoroperhydrochrysene(III) (2.0g) was introduced dropwise in a stream of nitrogen (0.1 dm^3/h) into a heated (400-530°C) vertical nickel tube (45 cm x 2.5 cm), packed with iron(III) oxide, over a period of about 30 minutes. Nitrogen (2.5 dm^3/h) was passed for a further hour after the addition and the product was collected in a trap cooled in liquid air; the outlet was heated occasionally to avoid blocking. The reddish-yellow semi-solid product was treated with acetone when a colourless lower layer of unchanged perfluoroperhydrochrysene separated. Evaporation of the acetone layer left a solid (0.08-0.56g; optimum temp. of defluorination, 440°C) which, according to glc, contained four major and about twelve minor components.

Separation of Defluorination Product

(a) *By gas-chromatography* The product (3.90g) was separated (same column, etc., as in the chrysene/$KCoF_4$ experiment; temp. 220-275°C) in batches to give: (i) *perfluoro-1,2,3,4,5,6,7,8,9,10-decahydrochrysene* nc (0.45g, 4%, IX), m.p. 125°C (from perfluro-1,4-dimethylcyclohexane) (Found: C, 34.1; F, 66.3; top mass peak, 634. $C_{18}F_{22}$ requires C, 34.1; F, 65.9%; $M^{+\cdot}$, 634); λ_{max} (c, 0.043 mg/ cm^3 in EtOH) at 214 (ε, 18700), 241 (ε, 8550), and 274 nm (ε, 3540); ν_{max}, at 1582, 1610, and 1657 cm^{-1}: (ii) *perfluoro-1,2,3,4,7,8,9,10-octahydrochrysene* nc (1.42g, 15%, VII), m.p. 169-170°C (from perfluoro-1,4-dimethylcyclohexane) (Found: C, 36.0; F, 64.1; top mass peak 596. $C_{18}F_{20}$ requires C, 36.3; F, 63.7%; $M^{+\cdot}$, 596); λ_{max} (c, 0.017 mg/cm^3 in EtOH) at 230 (ε, 58 800), 269 (ε, 4580), 279(ε, 5640), 290 (ε, 4930), 323 (ε, 1760), 341 (ε, 3520), and 355 nm (ε, 4230); ν_{max} at 1488, 1508, and 1625 cm^{-1}: (iii) perfluoro-1,2,3,4-tetrahydrochrysene nc (0.21g, 2%, VIII), m.p. 101-102°C (from perfluoro-1,4-dimethylcyclohexane) (Found: C, 42.3; top mass peak, 520. $C_{18}F_{16}$ requires C, 41.6; $M^{+\cdot}$, 520); λ_{max} (c, 0.017 mg / cm^3 in EtOH) at 225 (ε, 27500), 260 (ε, 51700), 307 (ε, 11800), 318 (ε, 13500), 366 (ε, 3530), and 384 nm (ε, 3400); ν_{max} at 1497, 1510, 1580, 1610, 1630, and 1657 cm^{-1}: and (VI) perfluorochrysene nc (0.28g, 3% VI) as pale yellow crystals from perfluoro-1,4-dimethylcyclohexane, m.p. 100°C (Found: C, 48.3; top mass peak 443.986. $C_{18}F_{12}$ requires C, 48.7; $M^{+\cdot}$, 443.981); λ_{max} (c, 0.012 mg/cm^3 in EtOH) at 207 (ε, 23700), 243 (ε, 21800), 273 (ε, 73500), 332 (ε, 12200), 345 (ε, 12900), 376 (ε, 2870), and 396 nm (ε, 2680); ν_{max} at 1495, 1545, 1628 and 1645 cm^{-1}.

(b) By column chromatography Crude product (3.78g) was separated on a column of silica gel (50 cm x 2.5 cm) with light petroleum (b.p. 40-60°C) as eluent. Four fractions were collected: (i) perfluoro-1,2,3,4,5,6,7,8,9,10-decahydrochrysene (0.49g X) (ii) perfluoro-1,2,3,4,7,8,9,10-octahydrochrysene (1.15g VII); (iii) a mixture (0.72g) of fraction (ii) and perfluoro-1,2,3,4-tetrahydrochrysene(VIII); and (IV) a mixture (0.45g) of perfluoro-1,2,3,4-tetrahydrochrysene(VIII) and perfluorochrysene(VI). These fractions were analysed by a combination of glc and IR.

^{19}F NMR Spectra of Fluoro-aromatics

These were run on a Varian XL 100 instrument at 94.1 MHz in CD_3COCD_3 at 34°C. Chemical shifts are in ppm upfield from internal $CFCl_3$. Couplings are in Hz; all signals contained smaller splittings (often very many) in addition to those given below. Relative intensities are indicated thus: / /

(a) Perfluorochrysene(VI) Six signals of equal intensity: an AB system [δ_A = 130.0 (F_4, F_{10}); δ_B = 133.3 (F_5, F_{11}); J_{AB} = 153.0]; another AB system[δ_A = 144.8 (F_6, F_{12}); δ_B = 145.9 (F_1, F_7); J_{AB} = 63.0] ; and two triplets ($J \sim 18$) at 154.8 (F_3, F_9) and 152.9 (F_2, F_8). Irradiation of the 152.9 signal affected those at 154.8 and 145.9 most markedly, and irradiation of the 154.8, those at 152.9 and 130.0.

(b) Perfluoro-1,2,3,4,7,8,9,10-octahydrochrysene(VII) Six signals at 100.8 (d, J = 82)/2/ (F_4, F_{10}), 105.8/2/ (F_1, F_7), 117.2 (t, J = 82) /1/ (F_5, F_{11}), 133.8 /2/ and 134.6 /2/ (F_2, F_3, F_8, F_9), and 136.0 /1/ (F_6, F_{12}).

(c) Perfluoro-1,2,3,4-tetrahydrochrysene(VIII) Twelve signals at 100.3 (d, J = 78) /2/ (F_4), 104.4 (d, $J \sim$ 20-25) /2/ (F_1), an AB spectrum [δ_A = 115.3 (additional d, $J \sim 16$); δ_B = 125.7; J_{AB} = 166] /2/ (F_{10}, F_{11}), 134.0 /2/ and 134.4 /2/ (F_2, F_3), 134.6 (t, J = 78) /1/ (F_5), 138.2 (approx. quartet, $J \sim$ 15-20) /1/ (F_{12}), an AB spectrum [δ_A = 141.0; δ_B = 1 44.7; J_{AB} = 68] /2/ (F_6, F_7), 150.4 (t, $J \sim 20$) /1/ and 153.4 (t, $J \sim 20$) /1/ (F_8, F_9).

(d) Perfluoro-1,2,3,4,5,6,7,8,9,10-decahydrochrysene (IX) Twelve signals at 102.4 /2/ (F_4); 105.2 /2/ (F_1), 111.2 /4/ F_7, F_{10}), 114.0 (dt, J = 18,64 - the 64 triplet is very distorted in intensity because of the nearness of its partner at 111.2) /1/ (F_{11}), 121.5 /2/ and 123.7 /2/ (F_5, F_6), 123.0 (q, $J \sim 18$) /1/ (F_{12}), 133.9 /4/ and 135.3 /4/ (F_2, F_3, F_8, F_9). Irradiation of the 114.0 signal markedly affected those at 111.2 and 123.0, and irradiation of 123.0, those at 114.0 and 105.0.

REFERENCES

1 Part VII is : J. Burdon, I. W. Parsons, and H. S. Gill, J.Chem.Soc. Perkin I, (1979) 1351.

2 B. Gething, C. R. Patrick, M. Stacey, and J. C. Tatlow, Nature, 183, (1959) 588; B. Gething, C. R. Patrick, and J. C. Tatlow, J.Chem.Soc., (1962) 186.

3 G. Fuller, J.Chem.Soc., (1965) 6264.

4 D. Harrison, M. Stacey, R. Stephens, and J. C. Tatlow, Tetrahedron, 19 (1963) 1893.

5 J. Burdon, J. R. Knights, I. W. Parsons, and J. C. Tatlow, Tetrahedron, 30 (1974) 3499.

6 D. V. Gardner, J. F. W. McOmie, P. Albriktsen, and R. K. Harris, J.Chem.Soc (C), (1969) 1994; P. Sartori and A. Golloch, Chem.Ber., 101, (1968) 2004.

7 G. G. Yakobson, V. M. Vlasov, and N. N. Vorozhtsov, Dokl. Akad.Nauk SSSR, 169, (1966) 855.

8 J. Burdon and D. H. Whiffen, Spectrochim.Acta, 12 (1958) 139.

9 J. Burdon, I. W. Parsons, and J. C. Tatlow, Tetrahedron, 28, (1972) 43; J. Burdon and I. W. Parsons ibid., 31 (1975) 2401.

10 P. L. Coe, R. M. Habib, and J. C. Tatlow, J. Fluorine Chem., 5 (1975) 19.

11 D. Price, H. Suschitsky, and J. I. Hollies, J.Chem.Soc. (C), (1969) 1967; R. A. Fletton, R. D. Lapper and L. F. Thomas, Chem.Comm., (1969) 1049.

12 K. L. Servis and K-N Fang, J.Amer.Chem.Soc., 90 (1968) 6712.

13 M. I. Bruce, J.Chem.Soc., (A), (1968) 1459.

14 J. Homer and L. F. Thomas, Trans.Faraday.Soc., 59, (1963) 2431.

15 M. Stacey and J. C. Tatlow, Adv.Fluorine Chem., 1 (1960) 166.

16 A. V. Grosse and G. H. Cady, Ind.Eng.Chem., 39 (1947) 367.