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THE SYNTHESIS AND DEHYDROFLUORINATION OF SOME POLYFLUOROALKANES

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SUMMARY

trans-1,2-Bis-(heptafluoro-n-propyl)- and *trans*-1,2-bis-(pentadecafluoro-n-heptyl)-ethylene were made from copper perfluoroalkyls. Fluorination over CoF_3 afforded perfluoro- and polyfluoro-n-octanes and -n-hexadecanes. Dehydrofluorinations of 4*H*-heptadeca- and 4*H*,5*H*-hexadecafluoro-n-octane are much slower than those of undeca- and 1*H*/2*H*-deca-fluorocyclohexane.

INTRODUCTION

This paper describes the syntheses of some polyfluoro-n-octanes and -n-hexadecanes and their dehydrofluorinations by aqueous KOH solution to give olefins.

RESULTS AND DISCUSSION

One sequence started from *trans*-1,2-bis-(pentadecafluoro-n-heptyl)ethylene, prepared as described[1] by the reaction at 110–130° of pentadecafluoro-n-heptyl iodide and *trans*-di-iodo-ethylene in DMF containing copper-bronze. The second sequence utilised *trans*-1,2-bis-(heptafluoro-n-propyl)ethylene made by an analogous reaction using C_3F_7I. *Trans* configurations were assigned to each olefin on the basis of the large H–H coupling constants ($J = 8.0$ Hz; *cf. cis*- and *trans*-difluoroethylene (J(H–H) = 2.0 and 8.0 Hz respectively[2]).

Each fluoro-olefin was fluorinated over CoF_3 to yield a mixture of products, the proportions of which depended upon the temperature of reaction. Fluorination of *trans*-1,2-bis-(heptafluoro-n-propyl)ethylene at 210–220° gave a five-component mixture which was separated by preparative-scale GLC into perfluoro-n-octane, starting material, and three new compounds. The latter were identified as 4*H*-heptadecafluoro-n-octane and two different compounds, boiling points 111–2° and

114–5°, each analysing correctly for $C_8H_2F_{16}$, which were identified as the diastereoisomers of 4*H*,5*H*-hexadecafluoro-n-octane. However, definite assignments of the DL or *meso* structures could not be made.

The polyfluoro-n-octane derivatives were then dehydrofluorinated using aqueous KOH. From 4*H*-heptadecafluoro-n-octane was obtained a two-component mixture, inseparable by preparative-scale GLC, with an analysis corresponding to C_8F_{16}. This was identified by IR and NMR spectroscopy as a mixture of hexadecafluoro-oct-4- and 3-ene, although it proved impossible from ^{19}F NMR spectra to assign configurations. These two products arise from elimination of HF from starting material in either possible direction.

Dehydrofluorinations of the 4*H*,5*H*-hexadecafluoro-n-octane isomers gave rise, in each case, to *trans*-4*H*-pentadecafluoro-oct-4-ene, identified as such by IR and NMR spectroscopy. The *trans* configuration was assigned on the basis of the large H–C=C–F coupling constant ($J = 27.5$ Hz), since coupling constants for analogous *cis* olefins are in the range 0–20 Hz[2]. All these dehydrofluorinations were difficult, with much unchanged starting material, even though drastic conditions were used.

Fluorination of *trans*-1,2-bis-(pentadecafluoro-n-heptyl)ethylene over CoF_3 at 125–50° gave a product containing four components in addition to starting material. A partial separation of the components was achieved by co-distillation with n-hexyl-methyl-ketone, followed by treatment of the appropriate fraction with $KMnO_4$ in acetone, to remove starting material. The first fraction afforded perfluoro-n-hexadecane m.p. 125° (cited 115°[3]), which was the only product obtained by fluorination at 200°. The second fraction obtained from the co-distillation was identified as 8*H*-tritriacontafluoro-n-hexadecane, and from a third fraction an inseparable mixture of two components resulted, which were identified as DL- and *meso*-8*H*,9*H*-dotriacontafluoro-n-hexadecane in the ratio 6:4.

The relative rates of dehydrofluorination of the three polyfluoro-octanes were investigated by measurements of the extent of dehydrofluorination of mixtures. Preliminary experiments showed that the rate of dehydrofluorination of undecafluorocyclohexane followed pseudo first-order kinetics for over 90% of reaction so that a pseudo first-order rate constant could be calculated. Relative rates were then obtained from dehydrofluorinations of mixtures and expressed in terms of the ratio of rate constants.

Direct comparisons of the rate of elimination of HF from undecafluorocyclohexane with those from 4*H*-heptadecafluoro-n-octane and 4*H*,5*H*-hexadecafluoro-n-octane (b.p. 111°) were not possible since the difference between the rates were too great. However, it is known[4] that 1*H*/2*H*-decafluorocyclohexane is more resistant to attack by aqueous alkali than undecafluorocyclohexane and measurements confirmed this, the relative rate being 55, so that the former compound could be used to relate the reactivities of open chain and cyclic compounds.

The relative rates of dehydrofluorination of 1*H*/2*H*-decafluorocyclohexane and of 4*H*,5*H*-hexadecafluoro-n-octane, whose two isomers boil at 111° and 114° respectively, were measured with respect to 4*H*-heptadecafluoro-n-octane and were found to be 120, 14 and 4.5 respectively. Thus the rates of dehydrofluorination of undecafluorocyclohexane with respect to 4*H*-heptadecafluoro-n-octane and to the two isomers of 4*H*,5*H*-hexadecafluoro-n-octane of respective b.p. 111° and 114° are 6600, 471 and 1467 respectively, and the rate for 4*H*,5*H*-hexadecafluoro-n-octane, b.p. 111°, relative to that for the isomer b.p. 114°, is 3.

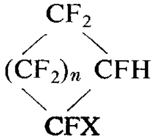
8*H*-Tritriacontafluoro-n-hexadecane was treated with aqueous alkali and gave a new GLC peak arising presumably from the expected olefin mixture. Assuming this, the relative rate with respect to 4*H*-heptadecafluoro-n-octane was measured and found to be 1.9, showing the two monohydro derivatives to react similarly. Complete identification of the olefin was not possible, since preparative-scale separation from starting material was not achieved.

The much greater ease of dehydrofluorination of undecafluorocyclohexane with respect to the linear analogue (C_8HF_{17}) is, at first sight, surprising. Inspection of models of the two compounds shows that there is considerably greater steric hindrance to the approach of base in the case of the linear fluorocarbon, even with the molecule in its lowest-energy staggered conformation, and some conformations show even greater steric hindrance.

The more rapid loss of fluorine from the 4*H*,5*H*-hexadecafluoro-n-octane isomers than from 4*H*-heptadecafluoro-n-octane is in agreement with previous work [5] which indicated that with alkanes, as with cycloalkanes, fluorine is more readily eliminated from a –CFH– group than a $>CF_2$ group. It is of interest that elimination from the 4*H*,5*H*-hexadecafluoro-n-octane isomers gives only one product, the more stable *trans* olefin, and this must arise by a *trans*–co-planar elimination from the DL pair and by a *cis* elimination from the *meso* isomer. The similarity in the rates of elimination then suggests that the reaction could well proceed *via* a carbanion mechanism. For a concerted mechanism a staggered conformation for *trans* and a partly eclipsed conformation for *cis* elimination is required. If in the latter case there was an energy difference between the most stable (staggered) and the eclipsed conformers corresponding to the barrier to rotation in 1,1,1-trifluoroethane [6], (*ca.* 3.3 kcal mole^{-1}) and if the staggered forms of the DL and *meso* isomers had identical energies this would give a ratio of rates at 60°, $k_{trans}/k_{cis} = 150$. However, the different energy contents of the two isomers in their varying conformers may be influenced by H–F interactions. It has been found that 1*H*,2*H*/- and 1*H*/2*H*-octafluorocyclopentane isomers [7] dehydrofluorinate at approximately the same rate, though *trans* and *cis* eliminations must be involved here as well, but, being cyclic, rotational barriers are unimportant.

The lower boiling 4*H*,5*H*-hexadecafluoro-n-octane isomer eliminates three times faster than the higher boiling isomer, suggesting that the former is the DL pair. Of all the conformers of these diasterioisomers one would expect the staggered form of the DL pair to have lowest energy and this form has both hydrogen atoms with an anti-periplanar β-fluorine atom, favouring more rapid elimination even if a carbanion mechanism were operating. However, if the structures are assigned from these dehydrofluorination arguments, the lowest energy rotamers of the DL pair have a higher dipole moment than those of the *meso* isomer, and hence the DL isomer should have the higher boiling point. In similar stereoisomeric pairs of fluorocyclo-hexanes and -pentanes higher dipole moments are associated with higher boiling points, and the same is true with the DL- and *meso*-2*H*,3*H*-octafluoro-n-butane isomers[5]. Thus, the boiling points of the polyfluoro-n-octane isomers appear to be anomalous, although this may be due to the change in population of rotamers of only slightly higher energy for which the dipole moments of the DL and *meso* forms are different from those in the ground state, or to the shape of the relatively long n-alkane chain, with many fluoro substituents, sterically hindering the close alignment of fluorine and hydrogen from neighbouring molecules necessary for interaction.

It has long been known that dehydrofluorinations involving terminal hydrogens on primary carbon atoms in compounds of the type $R_fCF_2CF_2H$ are very slow compared with those involving hydrogen on secondary carbons in cyclic polyfluorides



($n = 1$–4; X = H or F)

which lose HF fairly readily with strong aqueous bases. However, it is now apparent that non-terminal hydrogen from >CHF groups in polyfluoro-n-alkanes also eliminates only sluggishly with aqueous base, faster than from $-CF_2H$ groups, but much slower than from >CHF groups in cyclic systems, and this result is of considerable interest.

EXPERIMENTAL

General

NMR spectra were measured on a Perkin–Elmer R10 Spectrometer. The ^1H spectra were measured at a frequency of 60 MHz with TMS (tetramethylsilane) as internal standard and chemical shifts are given in τ values ($0.0\ \tau = 10$ ppm downfield from TMS). Except where stated, ^{19}F spectra were measured using CCl_3F as internal standard and results quoted in ppm to high field of $CCl_3F(\phi^*)$.

Preparative GLC separations were done using two columns: column 1, 5 m × 35 mm i.d. packed with dinonyl phthalate on celite = 1:2 and column 2, 9 m × 10 mm i.d. packed with Ucon oil 50 HB-2000 on Chromosorb P = 1:9. Quantitative analytical GLC was done using a capillary column 100 m × 0.25 mm i.d. coated with polypropylene glycol (Ucon oil LB 550X) operating at room temperature with detection by means of flame ionisation.

Relative rates of dehydrofluorination were determined in a round-bottomed flask fitted with a high-frequency vibro stirrer, the amplitude of motion being adjusted to give good mixing. The reaction mixtures were analysed by GLC, the area under the peaks being used as a quantitative measure of composition. Rate measurements using undecafluorocyclohexane/aq. KOH mixtures showed that the dehydrofluorination reaction was pseudo first order. Thus pseudo first-order rate constants may be calculated from the extent of decomposition and the ratio of constants used as a measure of the relative rate.

Trans-*1,2-bis-(heptafluoro-n-propyl)ethylene*

A mixture of *trans*-di-iodoethylene[8] (7.0 g), and activated copper-bronze (10 g) was stirred with DMF (20 ml) under N_2 and heated (120°). Heptafluoro-n-propyliodide (15 g) in DMF (10 ml) was added with rigorous exclusion of air, and the mixture refluxed for 24 h, cooled and distilled to yield *trans*-1,2-bis-(heptafluoro-n-propyl)ethylene (nc) (6.55 g), b.p. 92–3°/753 mm Hg. (Found: C, 26.1; H, 0.4; F, 73.4. $C_8H_2F_{14}$ requires C, 26.4; H, 0.5; F, 73.1%.) The IR spectrum showed a weak absorption at 3100 cm^{-1} (=C–H); the mass spectrum was consistent with the proposed structure. The ^1H NMR spectrum consisted of one signal at 3.55 τ (triplet $J = 8$ Hz), typical of =C–H, and the ^{19}F spectrum of three signals with chemical shifts ϕ^* 81.5, 115.9 and 128.5, and of intensity ratio 3:2:2 respectively, which were assigned to the CF_3– and two –CF_2– groups respectively.

Fluorination of trans-*1,2-bis-(heptafluoro-n-propyl)ethylene*

The olefin (71 g) was fluorinated in portions (10 g) over CoF_3 (100 g) at 210–220° in the usual way[9], and the mixture from the reactor washed with water and dried ($MgSO_4$) to a liquid product (57 g). An aliquot (52 g) of this was separated by preparative scale GLC (Column 1, 50–55°, 15 l/h N_2) to yield five components. These were:

(i) Perfluoro-n-octane (nc) (3.5 g), b.p. 101–3°/753 mmHg. (Found: C, 22.0; F, 78.2. C_8F_{18} requires C, 21.9; F, 78.1%.) The ^{19}F NMR spectrum consisted of three signals ϕ^* 81.7, 122.6 and 126.5, intensity ratio 3:4:2 respectively, due to the two CF_3– and six –CF_2– groups.

(ii) Starting material (2.8 g).

(iii) 4*H*-Heptadecafluoro-n-octane (nc) (18.9 g), b.p. 106–7°/753 mmHg. (Found: C, 23.1; H, 0.2; F, 77.1. C_8HF_{17} requires C, 22.9; H, 0.2; F, 76.9%.) The IR spectrum showed a very weak absorption at 2960 cm^{-1} (aliphatic C–H). The ^1H NMR spectrum consisted of one signal at 4.72 τ (doublet $J = 45$ Hz) and ^{19}F spectrum of five signals ϕ^* 81.4, 123.4, 126.6, 127.5 and 213.1 in the intensity ratio 6:6:2:2:1 respectively, the first of which was assigned to the CF_3– groups, the last to the –CHF– group and the remainder to the –CF_2– groups.

(iv) 4*H*,5*H*-Hexadecafluoro-n-octane (nc) (10.0 g), b.p. 111–2°/753 mmHg. (Found: C, 23.6; H, 0.7; F, 75.2. $C_8H_2F_{16}$ requires C, 23.9; H, 0.5; F, 75.6%.) The ^1H NMR spectrum consisted of a complex signal at 4.72 τ and the ^{19}F spectrum contained signals at ϕ^* 81.3, 127.3, 211.5 in the intensity ratio 3:2:1 and an AB system at 121.3 and 127.3 ($J = 316$ Hz) with intensity ratio 2 consistent with the proposed structure.

(v) 4*H*,5*H*-Hexadecafluoro-n-octane (nc) (9.5 g), b.p. 114–5°/753 mmHg. (Found: C, 23.4; H, 0.75; F, 76.0. $C_8H_2F_{16}$ requires C, 23.9; H, 0.5; F, 75.6%.) The ^1H NMR spectrum consisted of one signal at 4.74 τ and the ^{19}F spectrum of signals at ϕ^* 81.2, 127.3, 218.6 in the intensity ratio 3:2:1 with an AB system at 121.0 and 127.0 ($J = 315$ Hz) with intensity ratio 2.

Fluorination of trans-*1,2-bis-(pentadecafluoro-n-heptyl)ethylene*

The title compound[1] (52.7 g), was fluorinated over CoF_3 at 125–150° to yield a solid product (37.8 g) containing five components. Fluorination of a sample (3.1 g) at 200° gave only one component (3.0 g), and at 150–200° three components were found in the reaction mixture.

Separation of components

A sample (19.4 g) of the fluorocarbon mixture, obtained by fluorination at 125–150°, was mixed with n-hexyl-methyl-ketone (30 ml) and fractionally distilled, four fractions being taken. On cooling, solid fluorocarbon separated from the ketone and was filtered, washed with cold acetone (0°) and dried. The fractions were analysed by GLC (composition estimated from peak areas), the samples being injected as saturated solutions in perfluoromethylcyclohexane. The results are given in the Table 1.

TABLE 1

Peak No.	Composition (wt. (g))			
	b.p. 158–60° (7.1)	b.p. 160–62° (1.4)	b.p. 163–65° (5.0)	b.p. 165–68° (2.9)
I	59	4	—	—
II	13	5	—	—
III	28	83	60	7
IV	—	8	36	32
V	—	—	4	61

A second co-distillation of the fraction b.p. 158–60° with the ketone gave a fraction (2.9 g) consisting of peak I containing only a trace of peak II (starting material). The sample was purified by refluxing with $KMnO_4$ in acetone for 4 h when the mixture was filtered and the solid washed with acetone, dried and sublimed to yield perfluoro-n-hexadecane, m.p. 125°, b.p. 238–9° (cited[3] 115° and

240°). (Found: C, 22.8; H, 0.3; F, 76.7. $C_{16}F_{34}$ requires C, 22.9; H, 0.0; F, 77.1%.) The ^{19}F NMR spectrum was done using C_6F_6 as solvent and internal standard, and consisted of three signals with chemical shifts (ppm low field of C_6F_6) 82.9, 43.0 and 38.2 in the intensity ratio 3:12:2 consistent with the proposed structure.

Co-distillation of the fraction b.p. 160–62° with n-hexyl-methyl-ketone gave a sample (1.1 g) consisting of peak III containing only traces of peaks I and IV. This was identified as 8*H*-tritriacontafluoro-n-hexadecane (nc) m.p. 103–6°. (Found: C, 23.4; H, 0.4; F, 76.0. $C_{16}HF_{33}$ requires C, 23.4; H, 0.1; F, 76.5%.) The ^1H NMR spectrum consisted of a doublet ($J\sim45$ Hz) at 4.5 τ. The ^{19}F NMR spectrum consisted of three signals at ϕ^* 81.6, 121.9 and 126.3, the first of which was assigned to the CF_3– group, and the remainder to $>CF_2$ groups: these peaks had acceptable intensity ratios. A fourth signal was observed at ϕ^* 212.3 due to the remaining (tertiary) fluorine atom, although the intensity of the signal was too low for accurate measurement. Co-distillation of the fraction b.p. 163–65° with the ketone gave a sample (0.6 g) which consisted of peaks IV and V in the ratio 6:4. The sample was identified as a mixture of DL- and *meso*-8*H*,9*H*-dotriacontafluoro-n-hexadecane (nc) m.p. 92–7°. (Found: C, 23.5; H, 0.5; F, 76.2. $C_{16}H_2F_{32}$ requires C, 23.9; H, 0.3; F, 75.8%.) The ^1H NMR spectrum consisted of a doublet ($J\sim$ 45 Hz) at 4.55 τ. The ^{19}F NMR consisted of four signals at ϕ^* 81.5, 122.1, 124.7 and 126.3. The first of these was assigned to the CF_3– groups and the remaining signals to $>CF_2$ groups: the intensity ratios of these signals were acceptable. Two other signals were observed at ϕ^* 210.9 and 219.2 (of relative intensity 3:1) which were due to the tertiary fluorine atoms of the DL- and *meso*-isomers.

Dehydrofluorination of 4H-*heptadecafluoro-n-octane*

The title compound (3.2 g) was mixed with 50% aq. KOH (15 ml) at 75° and stirred using a vibro mixer for 10 h. The product was separated, washed with water and dried ($MgSO_4$). Analysis by GLC showed that it consisted of starting material (67%) and a product (33%). Separation by preparative-scale GLC (Column 2, 40°) gave (i) starting material and (ii) a two-component mixture (0.6 g) identified as hexa-decafluoro-oct-4-ene and hexadecafluoro-oct-3-ene. (Found: C, 23.7; F, 75.7. C_8F_{16} requires C, 24,0; F, 76.0%.) The ^{19}F NMR spectrum consisted of signals at ϕ^* 81.7, 84.2 and 85.3 with a total intensity ratio of 3 (CF_3– groups), at ϕ^* 115.8–134.9 with a total intensity ratio of 4 (–CF_2– groups) and at ϕ^* 155.1 with an intensity ratio of 1 (vinylic fluorine atoms). This is consistent with the proposed structure. The IR spectrum showed a weak absorption at 1710 cm^{-1} (–C=C–).

Dehydrofluorination of 4H,5H-*hexadecafluoro-n-octane (b.p. 111°)*

The compound (1.65 g) was stirred with an excess of 50% aq. KOH at 60–70° for 4.5 h. The organic layer was separated, washed with water and dried ($MgSO_4$) to yield a product (0.93 g) which was shown by GLC to consist of starting material (70%) and two new compounds (30%) in the ratio 100:1. Separation by preparative-scale GLC (Column 2, 40°) gave *trans*-4*H*-pentadecafluoro-oct-4-ene (nc) (0.2 g), b.p. 95°/752 mmHg. (Found: C, 24.9. C_8HF_{15} requires C, 25.1%.) The IR spectrum showed a strong absorption at 1720 cm^{-1} ($>C=C<$) and a weak absorption at 3110 cm^{-1} ($=CH-$). The ^1H NMR spectrum consisted of a one signal at 4.22 τ, which was a doublet of triplets ($J_D = 27.5$ Hz), due to the vinylic proton. The ^{19}F spectrum contained four signals ϕ^* 81.3 (CF_3–), 110.8 (–CF_2–), 120.7 (=CF–, a doublet of triplets), and 128.7 (–CF_2–) in the intensity ratio 6:4:1:4, consistent with the proposed structure.

Dehydrofluorination of 4H,5H-*hexadecafluoro-n-octane (b.p. 114°)*

The compound (1.83 g) was stirred with an excess of 50% aq. KOH at 60–70° for 6 h. The organic layer was separated, washed with water and dried ($MgSO_4$) to yield a product (0.9 g) containing starting material (89%) and two other components in the ratio 50:1 (11%), the larger of which was shown by analytical GLC to be identical with the principal product obtained from the dehydrofluorination of 4*H*,5*H*-hexadecafluoro-n-octane (b.p. 111°).

Relative rates of dehydrofluorination

(a) 4H-*Heptadecafluoro-n-octane and undecafluorocyclohexane*

A mixture (2.0 g) of the title compounds in equal proportions was heated with 50% aq. KOH at 60° for 1 h. The product (1.1 g) was separated and shown by GLC to be decafluorocyclohexane and 4*H*-heptadecafluoro-n-octane, with less than 1% of hexadecafluoro-octenes.

(b) Further dehydrofluorination rate experiments

The comparative rate of dehydrofluorination of pairs of fluorocarbons was studied as above. The results are listed below in the following sequence: names and weights of fluorocarbons, conc. of aq. KOH used, temp. of reaction, time, weight of product, conversion of starting materials.

(i) 4*H*,5*H*-Hexadecafluoro-n-octane b.p. 111° (0.98 g), undecafluorocyclohexane (0.95 g), 20%, 60°, 1 h, 1.0 g, 0%, 100%.

(ii) 1*H*/2*H*-Decafluorocyclohexane (2.0 g), undecafluorocyclohexane (2.0 g), 20%, 75°, 8 min, 2.5 g, 3.2%, 82%.

(iii) 1*H*/2*H*-Decafluorocyclohexane (2.0 g), undecafluorocyclohexane (2.0 g), 20%, 50°, 18 min, 2.8 g, 3.3%, 86%.

(iv) 4*H*-Heptadecafluoro-n-octane (1.0 g), 4*H*,5*H*-hexadecafluoro-n-octane b. p. 111° (1.0 g), 50%, 68°, 6 h, 0.9 g, 6.4%, 60%.

(v) 4*H*-Heptadecafluoro-n-octane (1.0 g), 4*H*,5*H*-hexadecafluoro-n-octane b.p. 114° (1.0 g), 50%, 68°, 6 h, 1.0 g, 5.2%, 20.5%.

(vi) 4*H*-Heptadecafluoro-n-octane (1.0 g), 1*H*/2*H*-decafluorocyclohexane (1.0 g), 50%, 65°, 2 h, 1.1 g, 2.2%, 92%.

(vii) 8*H*-Tritriacontafluoro-n-hexadecane (0.5 g), 4*H*-heptadecafluoro-n-octane (0.5 g), 50%, 68°, 6 h, 0.7 g, 52%, 32%.

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