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FLUOROCYCLOHEXANES. PART XVI.

THE SIX H-TRIFLUOROMETHYLDECAFLUORO- AND TWO OF THE 2H,4H-TRIFLUOROMETHYLNONAFLUORO-CYCLOHEXANES

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SUMMARY

Fluorination of benzotrifluoride by cobaltic fluoride at 260-280° gave, besides the fluorocarbon, the six possible tridecafluoromethylcyclohexane isomers, and two 2H,4H-dodecafluorides. Of the C_7HF_{13} compounds, only the cis-2H-, and the cis- and trans-4H-isomers could be isolated pure. The two 3H-isomers were made by pyrolysis of perfluoro(1-methyl-3-isopropylcyclohexane) in the presence of toluene. The trans-2H-isomer was made by further fluorination of one of the 2H,4H-dodecafluorides. Aqueous potash and the cis-2H-tridecafluoride gave 1-trifluoromethylnonafluorocyclohex-1-ene, which with stronger alkali hydrolysed to 1-carboxynonafluorocyclohex-1-ene. The cis- and trans- 2H and 4H-tridecafluorides were dehydrofluorinated by sodium fluoride at 320-380° (the cis-isomer of each pair reacted faster than the trans- : axial versus equatorial hydrogen) to give, respectively, the 1-trifluoromethylnonafluoro-ene and the 4-trifluoromethyl-isomer. The latter was isomerised to the former by sodium fluoride at 500-600°. The 1-CF_3-ene gave hexafluoroglutaric acid on oxidation with alkaline potassium permanganate.

INTRODUCTION

This paper briefly describes work done almost 20 years ago on trifluoromethylpolyfluorocyclohexanes. Following our systematic study of the polyfluorocyclohexanes themselves [1], we had intended to carry out a similar investigation of methylcyclohexanes. However, this was never taken beyond the first stage now described.

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Since the methyl group does not fluorinate very readily, benzotrifluoride was chosen as the starting material. Later work from our group on the fluorination of benzotrifluoride by cerium(IV) fluoride has been reported already [2].

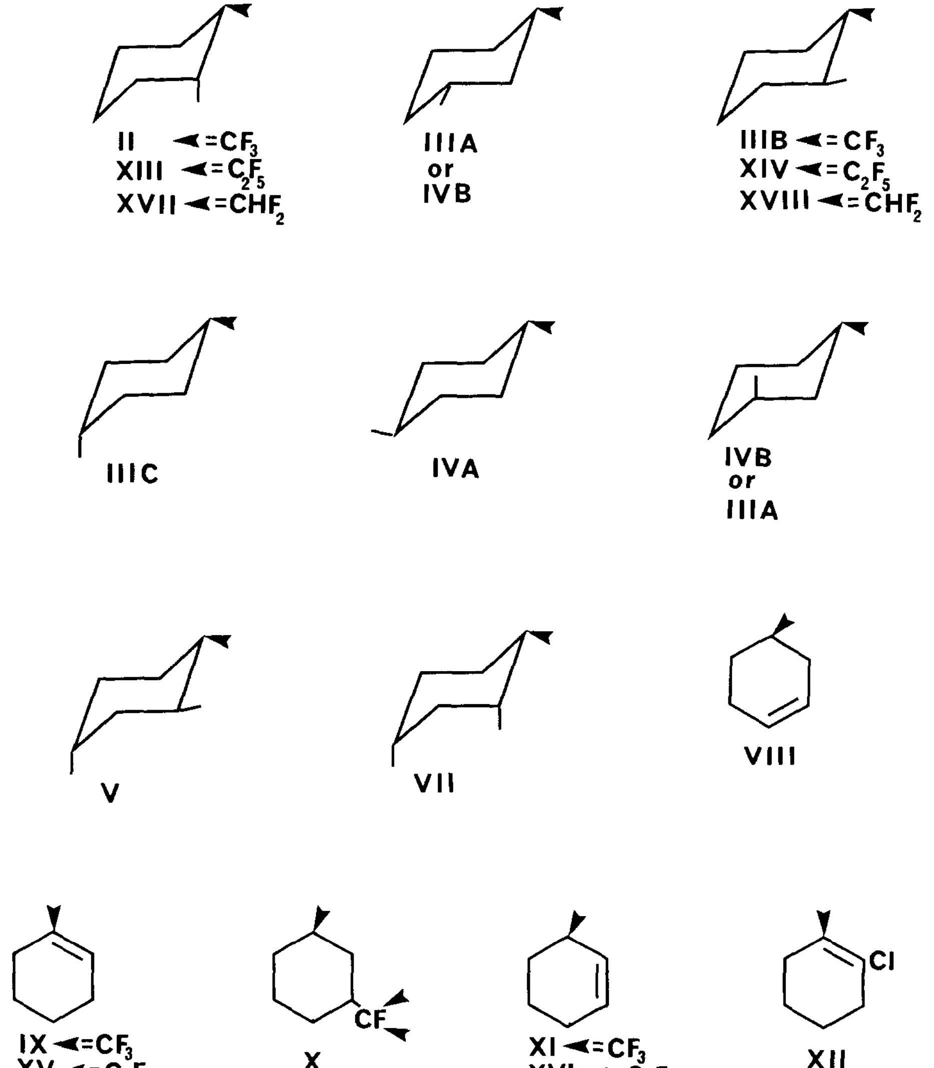
RESULTS

Separations

Fluorination of benzotrifluoride by cobaltic fluoride at 260-280° using standard procedures gave a mixture which showed seven major peaks (I-VII) by glc analysis. Fractional distillation separated the mixture into a range of fractions (1-8). Preparative scale glc showed that only peaks I, II, V and VII were pure compounds.

By far the major product (fractions 1 and 2) was perfluoromethylcyclohexane (Peak I). Fraction 4, mainly peaks II and III, yielded a pure trifluoromethyldecafluorocyclohexane isomer(II), later shown to be the cis-2H-compound (see Scheme for structures). Peak III contained 3 components, all analysing as C_7HF_{13}: IIIA and IIIB could not be separated further, and were respectively, one of the 3H-isomers, and the trans-2H-isomer. Compoun IIIC, obtained pure, was the cis-4H-isomer. Fraction 6 contained peaks IV and V. Peak IV consisted of the other two C_7HF_{13} structures; one (IVA) predominated, and was the trans-4H-isomer, which could be obtained pure with some difficulty, although the minor component, IVB the other 3H-isomer could not. Peak V was a $C_7H_2F_{12}$-compound with a 2H,4H-structure. Fraction 7 was mainly peaks VI and VII. Peak VI was a mixture of $C_7H_2F_{12}$ isomers which could neither be separated nor fully characterised. Peak VII was pure, a second 2H,4H-$C_7H_2F_{12}$ compound.

4H-Tridecafluorides Compounds IIIC and IVA were known products, respectively, cis- and trans- 4H-trifluoromethyldecafluorocyclohexane. These had been made previously [3] as a mixture, from $4CF_3.C_6F_{10}.Cl$/lithium aluminium hydride, and from the pyrolysis of mixtures of $4CF_3.C_6F_{10}.CF(CF_3)_2$ and toluene. Pure isomers now shown to be identical to IIIC and IVA were subsequently made [2] by glc separation of the products of the former reaction. Characterisation was by nmr [4], and by their relative rates of dehydrofluorination [2] by aqueous potash to the known olefin 4-trifluoromethylnonafluorocyclohex-1-ene(VIII) [3]. The trans-isomer reacted more slowly, having equatorial hydrogen in a rigid conformation [4].



II ◄ = CF_3
XIII ◄ = C_2F_5
XVII ◄ = CHF_2

IIIA
or
IVB

IIIB ◄ = CF_3
XIV ◄ = C_2F_5
XVIII ◄ = CHF_2

IIIC

IVA

IVB
or
IIIA

V

VII

VIII

IX ◄ = CF_3
XV ◄ = C_2F_5
XIX ◄ = CHF_2

X

XI ◄ = CF_3
XVI ◄ = C_2F_5
XX ◄ = CHF_2

XII

◄ = CF_3 ; except where stated : / = H :

All unmarked bonds are to FLUORINE

SCHEME

2H-Tridecafluorides Product II was a new 2H-trifluoromethyldecafluorocyclohexane, different from one mentioned earlier [2]. Dehydrofluorination with aqueous alkali was troublesome, since very dilute base was ineffective and the product was destroyed by more concentrated solutions. A compromise was found which gave a moderate yield of a single olefinic product, 1-trifluoromethylnonafluorocyclohex-1-ene(IX). This was our first synthesis of IX: its nmr parameters have been recorded [5], and it was isolated by us subsequently from octafluorotoluene/CoF_3 [6], and from benzotrifluoride/CeF_4 [2].

On oxidation with permanganate in acetone [7], olefin IX gave a mixture of acids, but alkaline permanganate afforded hexafluoroglutaric acid, isolated as known salts [7]. If the keto-acid, $CF_3CO(CF_2)_4COOH$, were an intermediate in this oxidation, it should have given $H(CF_2)_4COOH$, or possibly $HOOC(CF_2)_2COOH$, if fluoride ion were lost from the intermediate carbanion. Hydrolysis/oxidation of the stable $-CHF_2$ group does not seem very likely [cf. 3]. Hydrolysis of the CF_3 group of IX prior to oxidation also seems unlikely, since the concentration of base was much less than that used to generate IX, and 1-carboxynonafluorocyclohex-1-ene should give $HOOC(CF_2)_4COOH$ on oxidation. The likeliest route to hexafluoroglutaric acid seems therefore to be nucleophilic attack on the double bond by an anion containing manganese (probably at position 2), followed by loss of fluoride ion at position 6 of the resultant carbanion, before a cyclic species can form, due to steric hindrance by CF_3. Oxidation of the alkene so produced would give $HOOC(CF_2)_3COOH$.

When $2H.C_6F_{10}.CF_3$(II) was attacked by stronger base decomposition occurred, but in one case it was possible to isolate in small yield 1-carboxynonafluorocyclohex-1-ene as its S-benzylthiouronium salt. The CF_3 group of IX is sensitive to alkaline hydrolysis, as are some other CF_3 groups located on double bonds [8].

The second 2H-isomer of the C_7HF_{13} series was in fact that isolated earlier [2], although not then characterised completely. In that work, inter alia 1-trifluoromethyl-2H,4H-pentafluorocyclohexa-1,4-diene had been obtained. Mild fluorination of this (CoF_3) had given, as the major but not exclusive product, a 2H,4H-trifluoromethylnonafluorocyclohexane. This was found to be identical with the $C_7H_2F_{10}$ compound, V, isolated in the present work. Further fluorination of V gave the cis-4H-C_7HF_{13}(IIIC), and a 2H-isomer, which was not compound II, and must therefore have been the trans-2H-isomer(IIIB). It was shown spectroscopically that this sample was the same compound as that present in sub-fraction 4(ii)a of the product from the fluorination of benzotrifluoride.

Following the difficulties of dehydrofluorinating the cis-2H-isomer (II) with aqueous base, it was decided that for the less readily available trans-isomer (IIIB) the process using heated sodium fluoride [9] would be used. To test the method, the cis- and trans-4H-compounds, respectively IIIC and IVA, were each passed through a tube containing sodium fluoride pellets heated to 320°C. The sole product from each was the 4-CF_3-ene(VIII), but the cis-isomer (IIIC) reacted much more extensively (> 75%) than the trans (IVA) (ca 37%), in general agreement with the process using aqueous base [2]. Reactions were then carried out using the cis-(II) and the trans-(IIIB)-2H isomers. Compound II dehydrofluorinated to ca. 75% at 320-340°, whilst compound IIIB at 320-380° had reacted to less than 30%.

In all these cyclohexanes the conformations of the rings are dominated by the trifluoromethyl group, which takes up an equatorial position in a ring form locked at room temperature, as shown by nmr [4].

With the pairs of 2H- and 4H-compounds, the isomer in each pair which dehydrofluorinates the faster will be the cis-compound (II and IIIC). In these, the hydrogen atoms are disposed axially, and antiperiplanar elimination of axial H and axial F on adjacent carbon atoms can occur. The stereoisomers (IIIB and IVA) reacting more slowly will be trans where the H is equatorial. This is in accord with much previous work on fluorocyclohexanes (cf. [10] and earlier papers cited therein). These stereochemical allocations were supported by nmr spectroscopy, where the appropriate axial and equatorial F substituents on the CHF positions could be identified in the spectra [4, 11].

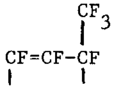
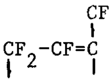
3H-Tridecafluorides To identify the 3-H.C_6F_{10}.CF_3 isomers, the earlier approach [3] was used. A standard fluorination of 2-(3'-tolyl)propene [12] afforded perfluoro-1-methyl-3-isopropylcyclohexane(X). Passage of this through a hot tube in the presence of excess toluene [3] gave a complex mixture from which small quantities of two compounds, D and E, were isolated by glc, each analysing as C_7HF_{13}. Compound D was shown by spectroscopy and glc to be identical with the C_7HF_{13} isomer IIIA, present in peak III, but which could not be isolated therefrom. Compound E had a glc retention time very close to that of peak IV, which was mainly the trans-4H-compound. However, spectroscopy showed that E was the same as the minor compound IVB present in peak IV. The stereochemistry of IIIA and IVB could not be established with certainty.

2H,4H-Dodecafluorides Two were isolated, the first (V), as explained above, being fluorinated further to give IIIB and IIIC. Its stereochemistry was not fully worked out before [2], but clearly V was 2H/-4H-1-trifluoromethylnonafluorocyclohexane. Compound VII was similarly fluorinated to II and IIIC. The ^{19}F nmr spectrum showed two equatorial fluorines in CHF groups and dehydrofluorination over heated sodium fluoride afforded two of the olefinic products that had been obtained from compound V [2]. Therefore, compound VII was 2H,4H-1-trifluoromethyl/-nonafluorocyclohexane.

Trifluoromethylnonafluorocyclohexenes It was of interest to see whether the olefins VIII and IX could be interconverted by heated sodium fluoride, which can effect isomerisations [9]. Nothing occurred at temperatures below 420°, showing that the above dehydrofluorination results were not invalidated. However, at temperatures from 420-600° the 4-CF_3 -ene(VIII) was converted, to systematically increasing extents, to the 1-CF_3-ene(IX). However, this was not affected itself, i.e. no equilibrium could be detected. Compound IX is clearly significantly more stable than compound VIII at least at higher temperatures. Presumably steric factors (more room for the CF_3) and the presence of one rather than two vinylic fluorines, both contribute to this stabilisation of IX relative to VIII.

Unfortunately, compounds IIIA and IVB were made in quantities sufficient only to characterise them. It was not possible to separate pure isomers by glc from the benzotrifluoride fluorination product. The dehydrofluorinations of these 3H-isomers could not therefore be studied, to see whether both the 4-CF_3-(VIII) and 3-CF_3-(XI)-enes were formed. In this work, the 3-isomer (XI) could not be isolated or detected from any source. Dehydrofluorinations of mixtures such as sub-fractions 4(ii) or 6(i) gave either the known olefins VIII and IX, or a mixture of those two compounds only. The product from one such dehydrofluorination of a sub-fraction 4(ii), gave, by analytical glc, an additional peak, but a compound different from VIII could not be isolated or identified. Despite many attempts, the presence of three glc product peaks from this dehydrofluorination could never be repeated. Further, there was no evidence for a third fluorocarbon olefin in any of the dehydrofluorination or isomerisation experiments involving compounds VIII and IX.

From one batch of runs, a small extra glc peak was found, but isolation showed that this was due to a chloro-olefin, shown by mass spectrometry and infrared to have structure XII, formed by exchange of vinylic F for Cl. The batch of sodium fluoride used for these experiments was found to contain a chloride, and passage of compound IX over heated sodium chloride gave small amounts of olefin XII. Strangely, however, the proportion could not be increased very much beyond that obtained using the contaminated sodium fluoride.

Thus, despite false leads, no evidence at all for the presence of the 3-CF_3-ene(XI) could be found in any of our products. It is not surprising that the cis-2H-isomer(II) gave exclusively olefin IX on dehydrofluorination. Antiperiplanar HF elimination occurs, with F lost from a less stable tertiary position, and the most stable olefin (IX) is produced. The position with the trans-2H-isomer(IIIB) is uncertain. Formation of olefin IX would require a less favourable stereochemical pathway, but the above stability factors still apply and exclusive formation of IX is possible. It is surprising, however, that olefin XI was not found in the products of dehydrofluorination of mixtures containing the 3H-isomers (IIIA and IVB). It seems therefore that olefin XI must be less stable than its isomers VIII and IX, and, if so, presumably it is the 1-CF_3-isomer(IX) into which it must isomerise. Perfluoro-olefins with the least number of vinylic fluorines are usually formed preferentially [13], and it is possible that the group  $\underset{|}{\mathrm{CF}}{=}\mathrm{CF}{-}\underset{|}{\overset{\mathrm{CF_3}}{\overset{|}{\mathrm{CF}}}}$ (as in XI) rearranges especially readily to  $\underset{|}{\mathrm{CF_2}}{-}\mathrm{CF}{=}\underset{|}{\overset{\mathrm{CF_3}}{\overset{|}{\mathrm{C}}}}$ (as in IX).

However, it was found that in analogous reactions [14], involving the cis- and trans-2H-1-pentafluoroethyldecafluorocyclohexanes(XIII and XIV; which however could not be completely separated from each other), dehydrofluorinations gave two olefins, XV and XVI. The latter 3-ene, although the minor product, was isolated and characterised [14]. The pair of cis- and trans-2H-1-difluoromethyldecafluorocyclohexanes(XVII and XVIII respectively) could be isolated pure [15]. Compound XVII dehydrofluorinated the faster, to give exclusively the 1-CHF_2-olefin(XIX). The trans-compound (XVIII) dehydrofluorinated more slowly, to give olefin XIX, and the 3-difluoromethyl-isomer(XX), in proportions roughly 2:1, respectively; again, the 3-isomer (XX) was isolated and characterised [15]. In general, therefore, olefins with polyfluoroalkyl groups adjacent to double bonds are not especially labile.

It is not clear whether the 3-trifluoromethyl-olefin(XI) is relatively less stable than olefins XVI and XX for specific reasons, e.g. because the trifluoromethyl group exercises a special effect, or whether only small amounts were formed in our reactions and were not detected.

EXPERIMENTAL

General

Fluorinations. A standard stirred reactor [16] was used: 1.2 m x 150 mm i.d. containing ca. 7 Kg of CoF_3.

Gas liquid chromatography. Preparative work [17] was done in two columns; A, 4.88 m x 35 mm diam; B, 4.88 m x 75 mm; each packed with dinonyl phthalate/Kieselguhr (1:2). Figures quoted are tube, temperature and nitrogen flow rate ($\ell\ h^{-1}$).

Spectroscopy. ^{19}F nmr was done on a Mullard SL 44 Mark 1 instrument at 30.1 Mc./sec. Values are quoted in p.p.m. from trifluoroacetic acid which was used as external reference. Carbon tetrachloride was the solvent employed.

Fluorination of benzotrifluoride. This (300 cm^3) was passed at a rate of 90 $cm^3\ h^{-1}$ through the reactor at 260-280°C; the reactor was then swept with nitrogen (10 $\ell\ h^{-1}$) for 2 h. The product was washed with water and dried (recovery 740-770 g).

Fractional distillation of product (2800 g) through a 4 ft. column packed with Dixon gauzes gave fractions (no., b.r., weight):- (1), 70-75°, 193 g; (2) 75-77°, 597 g; (3), 77-80°, 172 g; (4), 80-87°, 547 g; (5), 87-92°, 233 g; (6), 92-97°, 299 g; (7), 97-102°, 350 g; (8), still residue, 94 g.

Analytical glc (packing as above) on the original mixture showed 7 major peaks (I-VII) of which III and IV were complex.

Fractions (1) and (2) were mainly peak I; this was perfluoromethylcyclohexane. The first fraction contained an azeotrope of I and a little unchanged benzotrifluoride.

Fraction (3) contained peaks I-IV but was not separated.

Fraction (4), showed peaks II and III with some IV and V. It was separated by glc (B, 80°, 50: 107 g in 6 runs) to give 4(i) (24.0 g), *2H-1-trifluoromethyl/-decafluorocyclohexane* (cis-2H; II) nc, b.p. 86-87° (Found: C, 25.1; H, 0.5. C_7HF_{13} requires C, 25.3; H, 0.3%): 4(ii) (39.6 g a mixture: 4(iii) (18.6 g), a mixture. Sub-fraction 4(ii) (35.0 g in 6 runs) was further separated (A, 70°, 15) to give 4(ii)a (12.7 g), a mixture of a 3H-(IIIA) and trans-2H(IIIB) $-C_7HF_{13}$ isomers (Found: C, 25.6; H, 0.4%), identified by ir, and with IIIA the major component; ^{19}F nmr showed 2 sets of CF_3 peaks, a doublet of quintets centred at -7 (IIIA), and a doublet of quartets at -5 (IIIB): 4(ii)b (14.4 g), a mixture: 4(ii)c (3.3 g), 4H-1-trifluoromethyl/-decafluorocyclohexane (cis-4H; IIIC) b.p. 89° (Found: C, 25.5; H, 0.4%) [2].

Fraction 5, containing peaks II-V was not separated.

Fraction 6 contained peaks II-VI mainly IV and V. Separation (B, 85°, 50: 35.0 g in 2 runs) gave 6(i) (8.6 g), mainly the trans-4H(IVA), containing a little 3H-isomer(IVB); ^{19}F nmr showed a broad set of CF_3 peaks centred at ca. -5, distinguishable as two overlapping doublets of quintets: 6(ii) (4.4 g), 2H/4H-1-trifluoromethylnonafluorocyclohexane(V), b.p. 95-96° (Found: C, 26.9; H, 0.7; F, 72.4. Calc. for $C_7H_2F_{12}$: C,26.8; H, 0.6; F, 72.6%) [2]: 6(iii) (13.5 g), a mixture. From one sample of fraction 6, with an optimised glc separation, fraction 6(i) contained no detectable 3H-compound(IVB), being pure 4H/-1-trifluoromethyldecafluorocyclohexane (trans-4H; IVA) b.p. 92-93° (Found: C, 25.0; H, 0.5%) [2].

Fraction 7 contained peaks III-VII and separation (B, 100°, 52) gave: 7(i), a mixture of di-H-trifluoromethylnonafluorocyclohexanes(VI), b.p. 98° (Found: C, 27.0; H, 0.6; F, 72.2%): 7(ii), 2H,4H-1-trifluoromethyl/-nonafluorocyclohexane(VII) nc, b.p. 100° (Found: C, 27.0; H. 0.6; F, 72.7%); ^{19}F nmr, total intensity 12, including peaks at -3.9 (CF_3), 122.4 (axial F on C_1), 156.1 (equ. F on C_2), 162.8 (equ. F on C_4).

From the glc traces, rough proportions of peak areas 11-VII were 1:3:1.5:2:2:2, respectively.

Fluorination of 2-(3'-tolyl)propene. This [12] (50 g; input rate 38 g h^{-1}) was passed through the reactor at 270-300° to give product (86 g). Distillation through a 1 ft. column (Dixon gauzes) followed by glc (B, 104°, 50) on the fraction b.r. 140-156° (30 g) gave perfluoro-1-methyl-3-isopropylcyclohexane(X) nc, b.p. 144° (Found: C, 23.8; F, 75.5. $C_{10}F_{20}$ requires C, 24.0: F, 76.0%).

3H-Trifluoromethyldecafluorocyclohexanes from fluorocarbon X. X (17.0 g; input rate 22 g h^{-1}) and toluene (70 cm^3) were passed through a tube [3] at 570° to give a crude product. Distillation through a 1 ft column (Dixon gauzes) followed by glc (A, 85°, 13) on the fraction b.r.

57-110° (7.0 g) afforded (i) 3H-1-trifluoromethyldecafluorocyclohexane(D) nc (0.5 g), b.p. 87-89° (Found: C, 25.0; H, 0.4%): (ii) 3H-1-trifluoromethyldecafluorocyclohexane(E) nc (0.5 g), b.p. 93° (Found: C, 25.8; H, 0.4%).

Fluorination of the 2H/-4H-1-CF_3-nonafluoride(V). This was as described earlier [2]. The tridecafluorides isolated were 2H/-1-trifluoromethyldecafluorocyclohexane (trans-2H; IIIB) nc, b.p. 88°, see also [2]; and the cis-4H(IIIC).

Fluorination of the 2H,4H-1-CF_3/-nonafluoride(VII). Fluorination as abov at 170°, followed by glc (A, 100°, 15) gave perfluoromethylcyclohexane(I), the cis-2H(II), the cis-4H(IIIC), and starting material (VII), all identified by ir.

Dehydrofluorination of the cis-2H-tridecafluoride(II) with aqueous potassium hydroxide. II (12.0 g), potassium hydroxide (3.0 g) and water (16 cm^3) were heated together (bath temp 104-105°) for 13 h. The fluorocarbon layer was separated and distilled from P_2O_5 to give 1-trifluoromethylnonafluorocyclohex-1-ene(IX) (7.0 g), b.p. 70° (Found: C, 27.1. Calc. for C_7F_{12} C, 26.9%); ir 1710 cm^{-1} ($-CF{=}C(CF_3)-$); first reported by Haszeldine and Osborne [18].

After II (3.0 g), KOH (2.5 g), and water (4 cm^3) had been refluxed together vigorously for 3 h, there was no fluorocarbon layer. The aqueous layer was extracted with ether (3 x 20 cm^3), then acidified (HCl: 2M) and extracted again with ether. Evaporation of the ether, take-up of the residue in a little water, neutralisation (KOH; 0.1M) and addition of aqueous S-benzylthiouronium chloride gave (recrystallised from water 3 times) S-benzylthiouronium nonafluorocyclohex-1-ene-1 carboxylate nc, m.p. 165° (Found: C, 39.7; H, 2.4 $C_{15}H_{11}F_9N_2O_2S$ requires C, 39.7; H, 2.4%).

Oxidation of the 1-CF_3-1-ene(IX). IX (3.0 g), potassium permanganate (10.0 g), potassium hydroxide (10.0 g) and water (150 cm^3) were refluxed together for 12 h. Work up as usual afforded dianilinium hexafluoroglutarate (44%) converted into bis S-benzylthiouronium hexafluoroglutarate (70%), both with correct m.p. and C and H analyses [7].

Dehydrofluorinations with heated sodium fluoride. A nickel tube was used (0.75 m x 2.5 mm i.d.) packed with pellets of sodium fluoride, and heated electrically. Fluorohydrocarbon was dropped into a vapouriser held at 20° above its b.p., and then swept into the tube in a stream of nitrogen (1 ℓ h^{-1}). Products were collected in a glass trap cooled in liquid nitrogen.

(a) Cis-4H-tridecafluoride(IIIC). A total of 8.0 g was passed in 6 runs at 320° giving combined products (6.9 g). Glc (A, 70°, 15) gave: (i), 4-trifluoromethylnonafluorocyclohex-1-ene(VIII) [3] (4.0 g) (ir 1760 cm^{-1}; -CF=CF-), ^{19}F nmr -5.9 (CF_3),32.3, 33.2, 41.5, 41.7, 52.2, 58.4, 77.8 (-CF=CF-), 107.5: (ii), starting material (IIIC) (1.2 g).

(b) Trans-4H-tridecafluoride(IVA). In 9 runs 21.7 g was passed at 320° giving products (18.1 g). Glc (A, 72°, 15) gave the 4-CF_3-ene(VIII) (6.2 g), and unchanged trans-4H(IVA) (10.6 g).

(c) Cis-2H-tridecafluoride(II). In 8 runs (1 x 300°, 5 x 320°, 2 x 340°) 25.0 g gave products (23.4 g), glc (A, 75°, 15) affording the 1-CF_3-1-ene(IX) (16.4 g) and unchanged II (5.4 g).

(d) Trans-2H-tridecafluoride(IIIB). In 6 runs (1 x 320°, 1 x 340°, 1 x 350°, 2 x 360°, 1 x 380°) 4.7 g gave products (3.3 g), glc (A, 100°, 16) affording the 1-CF_3-1-ene(IX) (0.8 g) and unchanged IIIB (2.1 g).

(e) 2H,4H-1-Trifluoromethyl/-nonafluorocyclohexane(VII). In 5 runs (1 x 360°, 3 x 380°, 1 x 400°), 5.0 g gave products (3.1 g); glc (A, 75°, 15) gave: (i), 1-trifluoromethylheptafluorocyclohexa-1,3-diene (0.7 g) [2]: (ii), 4H-1-trifluoromethyloctafluorocyclo-hex-1-ene (0.4 g) [2]: (iii), starting material (1.1 g): (iv), octafluorotoluene (0.3 g) [19] [also found in the analagous dehydrofluorination of V]: all identified by ir.

Isomerisations of trifluoromethylnonafluorocyclohexenes(VIII and IX).

(a) 4-CF_3-1-ene(VIII). A series of runs through the apparatus used for dehydrofluorination (above) was done between 300° and 600°. Glc and ir showed no change below 420°, but an increasing proportion of the 1-CF_3-1-ene(IX) present from 420-600°.

From 6 runs (2 x 420°, 2 x 430°, 2 x 520°), VIII (21.0 g) gave products (14.5 g) which by glc (A, 80°, 15) gave the 1-CF_3-ene(IX) (9.1 g) and the 4-CF_3-ene(VIII) (4.1 g). From 5 runs at higher temperatures (18 g VIII) the product was repassed (4 runs at 420°) to give pure 1-CF_3-ene(IX) (11.2 g).

(b) 1-CF_3-1-ene(IX). Similar experiments to the above gave only unreacted IX in 69% recovery, with no other compounds detectable by glc.

(c) From one series of runs of types (a) and (b), a minor component of significantly longer retention time was present in the olefinic products (ca. 4%). Isolation (glc as before) gave 1-trifluoromethyl-2-chloro-octafluorocyclohex-1-ene(XII) nc (Found: m/e 330 [$C_7{}^{37}ClF_{11}$], 328 [$C_7{}^{35}ClF_{11}$], 311 [$C_7{}^{37}ClF_{10}$], 309 [$C_7{}^{35}ClF_{10}$]: ir 1650 cm^{-1} ($-CCl=CCF_3-$; cf. [10]).

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