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POLYFLUOROCYCLOALKENES. PART XIX. SOME REACTIONS AND COMPOUNDS FROM 1,2-BIS(TRIFLUOROMETHYL)OCTAFLUOROCYCLOHEXENE

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SUMMARY

The title compound (A) gave a dichloro-adduct (D), which with lithium aluminium hydride yielded a complex mixture, from which a trace of *trans* 1H,2H-1,2-bis(trifluoromethyl)octafluorocyclohexane (E) was isolated. Catalytic hydrogenation of olefin (A) afforded *cis* 1H,2H-1,2-bis(trifluoromethyl)octafluorocyclohexane (C), and a small amount of 6H-1,6-bis(trifluoromethyl)heptafluorocyclohexene (B). Dehydrofluorination of the *cis* dihydride (C) by aqueous potash gave olefin (B) and 2,3-bis(trifluoromethyl)hexafluorocyclohexa-1,3-diene (G); fluorination of (G) by cobalt(*III*) fluoride gave back (A). Fluorination of compounds (C) and (B) afforded *cis* and *trans* 1H-1,2-bis(trifluoromethyl)nonafluorocyclohexane (J and H respectively). Both (H) and (J) were dehydrofluorinated to give olefin (A) exclusively, i.e. fluorine was lost preferentially from the tertiary ⋟C-F group. Ammonia and (A) gave 1,3-diamino-2-cyano-3-trifluoromethylhexafluorocyclohexene (K). Some hydro-polyfluoro-cyclohexanes took up small proportions of deuterium during dehydrofluorinations in the presence of deuterium oxide, but no interconversions of pairs of stereoisomers were observed.

INTRODUCTION

This work was part of our programme [1] on reactions of fluorocycloalkenes. Though done many years ago, it has several features of interest, not covered elsewhere in the meantime. In particular, olefin-forming dehydrofluorinations by aqueous potassium hydroxide were carried out on compounds where fluorine could be lost from the groups ⋟CF, $>CF_2$ or $-CF_3$, all being adjacent to the same hydrogen atom.

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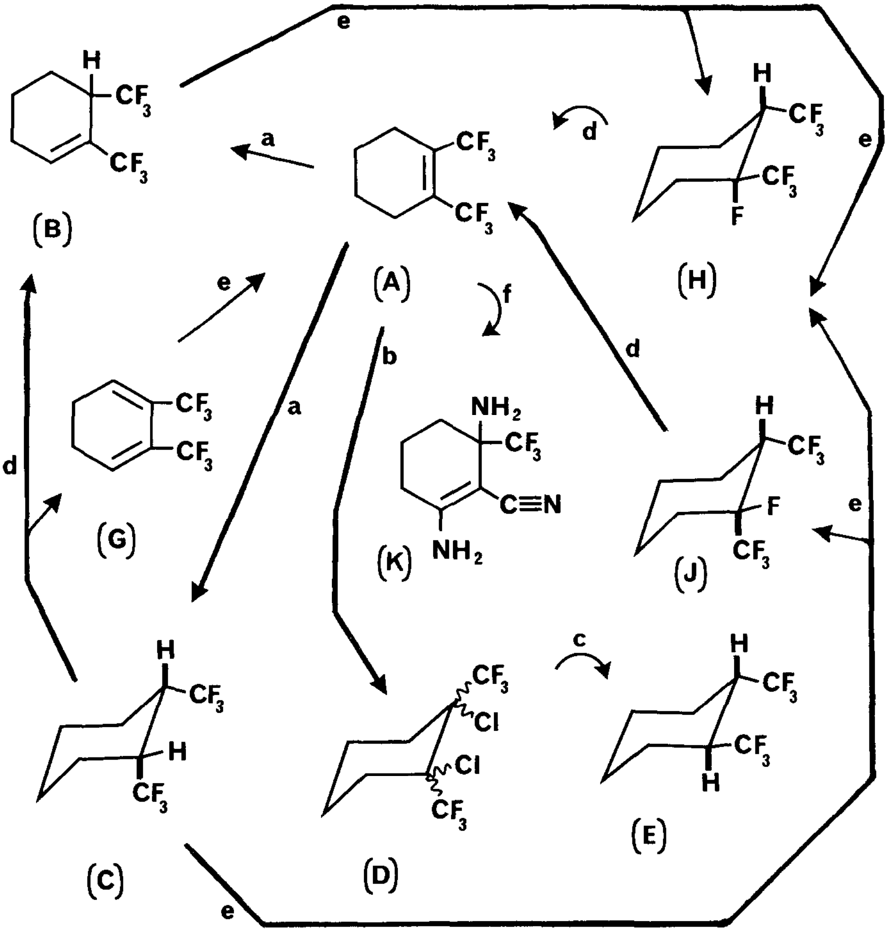
RESULTS AND DISCUSSION

The reactions are summarised in the Scheme. The starting point was the known [2] 1,2-bis(trifluoromethyl)octafluorocyclohexene (A), made by mild fluorination of decafluoro-*o*-xylene using cobalt (III) fluoride. Catalytic hydrogenation of compound (A) [cf. 3] was not straightforward, reaction being negligible at atmospheric pressure or in solvents. Though hydrogen uptake started steadily in an autoclave reaction using a palladium/charcoal catalyst at 16°C and a pressure of 100 atmospheres, there was gradual evolution of some hydrogen fluoride, which poisoned the catalyst and eventually stopped the reaction. After 24 hours, less than half the starting material had reacted, and further uptake was very slow. Besides unreacted (A) there were two products present. The minor one, compound (B), emerged first on gas chromatographic separation, and analysed as C_8HF_{13}. There was an infrared peak at 1709 cm^{-1}, and the ^{19}F nmr spectrum had peaks at 60.1 and 61.9 for $-CF_3$, 3 AB quartets from $>CF_2$ groups, and a signal ascribed to a lone vinylic fluorine (cf. 1-trifluoromethylnonafluorocyclohexene, with an ir double bond peak at 1710 cm^{-1} [4], and a ^{19}F nmr peak from $-CF_3$ at 61.25 [5]). The structure of (B) therefore was 6H-1,6-bis(trifluoromethyl)heptafluorocyclohexene.

The major product (C) analysed as $C_8H_2F_{14}$, and it showed a poorly resolved ^{19}F nmr spectrum, with broad signals, at 16°C. At -60°C, there were two signals due to $-CF_3$ at 59.5 and 61.4, and 4 AB quartets from $>CF_2$ groups; however at +70°C, there was only one $-CF_3$ signal at 59.8, and two AB quartets from $>CF_2$ groups. Taken in conjunction with the spectrum from the stereo-isomer (E) (see later), this showed the structure of (C) to be 1H,2H/1,2-bis-(trifluoromethyl)octafluorocyclohexane, the *cis* isomer of this species. Having a *cis* arrangement of groups on C(1) and C(2), one (relatively bulky) $-CF_3$ group must occupy an axial and one an equatorial position in a fixed conformation of compound (C). This is the case at -60°C, and the ^{19}F nmr spectrum distinguishes them, the four different $>CF_2$ groups present being registered also. At room temperature, some ring inter-conversion is occurring, but relatively slowly, whereas at +70°C there is rapid interchange, and only an averaged $-CF_3$ signal, and those from the two sets of $>CF_2$ groups of different positional significance, are registered.

Olefin (B) may be formed in the hydrogenation reaction by dehydrofluorination of compound (C). It is even possible that some of the *trans* isomer (E) is formed initially and is then dehydrofluorinated completely to give olefin (B). A more likely explanation than either, however, is that the initial



ALL UNMARKED BONDS ARE TO FLUORINE

REAGENTS : a, H_2/Pd ; b, Cl_2/uv ; c, $LiAlH_4/Et_2O$;
d, KOH/H_2O ; e, CoF_3 ; f, NH_3/Et_2O .

SCHEME

attack by hydrogen (adsorbed on the catalyst surface) on position 1 of the double bond of the starting olefin (A) gives an intermediate species (a radical at C(2) ?) which can react in two ways: (i), a suitably-placed adjacent hydrogen can react at C(2) to give the saturated product, the *cis* addition giving exclusively compound (C): (ii), a differently-positioned hydrogen can remove a fluorine from C(3) as hydrogen fluoride, the fluorine substituents at C(3) being activated by the adjacent reactive centre at C(2). A new double bond will then form between C(2) and C(3). What is surprising is that no products of further reduction of olefin (B) were detected, since the double bond in this compound is less sterically hindered than that in (A).

A useful method we introduced for conversion of >C=C< to >CH-CH< in fluorocarbon chemistry, is addition of chlorine followed by selective replacement of it by hydrogen, using lithium aluminium hydride [6,3]. With olefin (A), chlorine addition was sluggish, but some dichloro-adduct (D) was formed. Treatment of this adduct (D) with lithium aluminium hydride, even under mild conditions, gave a very complex mixture, containing many olefinic species and resembling that formed by the olefin (A) itself in a similar process. It could well be that partial reduction of (D) gives intermediates which can easily lose hydrogen chloride (see the later discussion) to give back olefin (A), which will react in its own right [see 3], leading to olefinic products. One of the significant components of the mixture from the reaction of (D) with $LiAlH_4$ was probably compound (C), but it could not be isolated pure. Fortuitously the one component that was isolated (though in traces only) was the stereoisomer of (C), *trans* 1H,2H-1,2-bis(trifluoromethyl)octafluorocyclohexane (E). It had an ir spectrum very similar to that of compound (C), but a much simpler ^{19}F nmr spectrum, with no special temperature variations: there was one signal from $-CF_3$ at 70, and two due to $>CF_2$, a singlet at 130 and an AB quartet. In this case, the conformation with equatorial $-CF_3$ groups and axial hydrogens should be by far the most stable. Sadly, insufficient of compound (E) was available to allow further investigations.

Compound (C) was dehydrofluorinated very readily with aqueous potassium hydroxide. Qualitatively, it reacted much faster and with more dilute alkali than most hydrofluorocarbons studied previously. Two products were formed, the same mono-ene (B) as arose in catalytic hydrogenation, and a new diene (G). This analysed as C_8F_{12}, and its ultraviolet absorption indicated a 1,3-diene. The quite simple ^{19}F nmr spectrum showed a symmetrical structure; it comprised 3 singlets; at 60.3 (CF_3-C=C), 113.0 ($\underline{F}C=CCF_3$; [cf. 5]) and 133 ($>CF_2$). Diene

(G) was therefore 2,3-bis(trifluoromethyl)hexafluorocyclohexa-1,3-diene. A low temperature reaction of diene (G) with cobaltic fluoride afforded olefin (A), by a 1,4- addition of fluorine.

There was a small mixed fraction also isolated from the dehydrofluorination of (C), half of which was olefin (B), and the rest another olefin, which could not be purified. It had an ir band at 1740 cm^{-1}.

Fluorinations of both the *cis* dihydride (C) and its dehydrofluorination product, the mono-olefin (B), using cobaltic fluoride at 215°C, gave a mixture of perfluorodimethylcyclohexane and two new compounds (H and J). Each analysed as C_8HF_{15}, and they had very similar ^{19}F nmr spectra, showing the presence of two $-CF_3$ groups ($>CH-CF_3$ and $>CF-CF_3$) and four $>CF_2$ groups (4 AB quartets), comparable peaks for both compounds being at virtually identical positions. The remaining peaks, one in each spectrum, due to the tertiary $\geqslant CF$ were distinct. That from the predominant product (H) was at 176, and that from the minor product (J) at 185. From previous nmr studies, equatorial fluorines absorb at higher field than axial fluorines in polyfluorocyclohexanes [7], so that (H) had an axial fluorine and (J) an equatorial one. Thus (H) was the *trans* stereoisomer of 1H-1,2-bis(trifluoromethyl)octafluorocyclohexane and (J) the *cis* , this allocation being in line with the results of comparative dehydrofluorinations (see later).

Though the formation of both stereoisomers (H and J) from the olefin (B) is as expected, their production from the saturated compound (C) shows the non-stereospecificity of fluorination by cobaltic fluoride, in this particular case. In much of our work on polyfluorocyclo-hexanes [8], -pentanes [9], and -heptanes [10], such fluorinations have been widely used in structural allocations. The self-consistency and completeness of the results, within specific series, ensured their correctness, leaving aside conclusive alternative evidence based on nmr spectroscopy and dehydrofluorination studies, and on X-ray crystallography in one or two cases [11]. The result with compound (C) is abnormal therefore, though it is a somewhat different type of compound. Our earlier work involved retention of stereochemistry in $>CHF$ groups, whilst an adjacent $>CHF$ was converted to $>CF_2$: with compound (C), both groups are $>CH-CF_3$. The most probable explanation is a much greater carbon acidity of the hydrogens in (C), leading to rapid loss of hydrogen fluoride (from $>CF_2$) to give the mono -ene (B). The easy dehydrofluorination by alkali found for (C) would be paralleled by that promoted by heated metal fluorides, known [12,4] to give olefins from polyfluorocyclohexanes. Compound (C) would meet hot metal fluoride in the reactor before fluorination by the cobaltic fluoride could be begun, much less completed. Once formed, olefin (B) would give rise to a preponderance of the *trans* isomer (H) of the pentadecafluoride structure, since, with two equatorial $\mathrm{-CF_3}$ groups, this is a less strained system than the *cis* form (J). The relatively high proportion of perfluorodimethylcyclohexane formed in a fluorination at only 215°C was noteworthy. It arose most probably *via* diene (G), formed in a second dehydrofluorination stage, and thence fluorination to (A), which survived at 75°C, but not at 215°C.

Perfluorocycloalkenes and ammonia give imino-amines [13,14] and there was an interesting variant in the process with the perfluoro-ene (A). The product was mainly 1,3-diamino-2-cyano-3-trifluoromethylhexafluorocyclohexene (K), as shown by analysis and spectroscopic parameters. There was a minor closely-related component which could not be isolated, but appeared to contain similar functional groups. The reaction sequence from (A) presumably involved loss of both fluorines at the original C(3) at fairly early stages, leaving a carbanionic centre at C(2). This could lose fluorine only from the adjacent $\mathrm{-CF_3}$ group, giving rise to $\mathrm{=CF_2}$, further attack on which by ammonia would eventually lead to a $\mathrm{-C{\equiv}N}$ substituent at C(2).

DEHYDROFLUORINATIONS OF 1-H-1,2-BIS(TRIFLUOROMETHYL)NONAFLUOROCYCLOHEXANES (H and J) AND RELATED COMPOUNDS

Dehydrofluorination of the dihydride (C) was very rapid, fluorine being lost from the $\mathrm{>CF_2}$ groups at positions 3 and 6 to give the products isolated (B) and (G). A very minor by-product may have had an exocyclic $\mathrm{=CF_2}$ group, but this could not be established firmly. That loss of fluorine from $\mathrm{-CF_3}$ in these compounds was possible however was shown by the formation of the cyano-diamine (K) from olefin (A). With the monohydro-compounds (H and J), loss of fluorine was possible from →C-F, $\mathrm{>CF_2}$ or $\mathrm{-CF_3}$ groups.

The *trans* isomer (H) was dehydrofluorinated extremely readily by aqueous potassium hydroxide, probably faster even than compound (C). There was only one product detectable, bis(trifluoromethyl)octafluorocyclohexene (A). The *cis* isomer (J) also reacted very readily, though rather more slowly than isomer (H), confirming the structural allocations based on nmr. Again, the olefin (A) was the only product detected. Clearly therefore the tertiary fluorine (→C-F) is the one lost most readily from both isomers.

The *trans* isomer (H) having axial hydrogen and fluorine would be expected to react by the classical *anti-periplanar* E2 process [cf. 6]. The *cis* isomer

(J) could react by a *syn-clinal* E2 process from a boat-type intermediate conformation of an equilibrating system :
1-H *ax*, 2-F *eq* / 1-CF_3 *eq*, 2-CF_3 *ax* ⇔ 1-H *eq*, 2-F *ax* / 1-CF_3 *ax*, 2-CF_3 *eq*
Ready eliminations of H and F arranged *cis* have been found in dehydrofluorinations of polyfluorocyclopentanes [9]. An alternative is a mechanism with a carbanionic-type intermediate having no special steric demands. Whatever the process, stereochemical requirements do not override the lower stability of the tertiary →C-F bond.

In earlier work [6], dehydrofluorinations were conducted in basic media containing deuterium oxide, and the recovered, supposedly unreacted, hydrofluorocarbons were found to contain small proportions of deuterium in some cases. This device is well known as an indicator of carbanionic character in a reaction process. With the 1H,2H-decafluorocyclohexanes, the one slower to dehydrofluorinate, the 1H/2H- *(trans)* stereoisomer, gave 3% deuteriation of the recovered starting material, but with the other, the 1H,2H/- *(cis)*, no exchange was detectable [6]. However, there was a surprisingly high deuteriation of recovered undecafluorocyclohexane.

In the present study, similar experiments were carried out on several fluorocyclohexanes. The surprising earlier [6] result with undecafluorocyclohexane was essentially confirmed; under the conditions now used there was up to 23% deuteriation. With the 4H-1-trifluoromethyldecafluorocyclohexanes [15,4], the faster dehydrofluorination of the *cis* isomer was confirmed, and in both cases, some deuteriation of the recovered fluorohydrocarbon had occurred.

Of the compounds first made in the present work, very mild conditions were required to permit the recovery of a 'starting-material' fraction. The *cis* dihydro-compound (C) was treated with a deficiency of KOH / D_2O, and the recovered hydrofluorocarbon was 1.6% deuteriated. The *trans* monohydro-compound (H) was allowed to react for a few seconds only; the recovered starting material (ca 10%) was indeed that, no deutero-content being detected. The *cis* isomer (J) was given a slightly longer reaction time, and the recovered 'starting-material' was 8.7% deuteriated.

Deuteriations of various substrates were then attempted in simple heterogeneous mixtures with deuterium oxide in the absence of any added base: catalysis by glass is of course possible. After five days, (C) was deuteriated to the extent of 0.6%, and, after 9 days, (H) to 0.25% (considered just detectable), and (J) to 3.4%. Undeca- and the two 4H-trifluoromethyldecafluorocyclohexanes had no detectable deuterium contents after similar treatment.

Since these deuteriations suggested that carbanionic species might be intermediates in some dehydrofluorinations, possible optical inversions were investigated. Both members of each of three stereoisomeric pairs were subjected to dehydrofluorinations using aqueous potash, and the recovered hydrofluorocarbon 'starting-materials' examined carefully by the best glc systems to determine whether any of the related stereoisomer was present. 1H,2H-Decafluorocyclohexanes, 4H-1-trifluoromethyldecafluorocyclohexanes, and 1H-1,2-bis(trifluoromethyl)nonafluorocyclohexanes (H and J) were used, and in no case was any of the inverted stereoisomer detected, though quite small proportions showed up if added deliberately. It was also shown that compound (C), recovered from incompleted dehydrofluorinations, contained no detectable amounts of the *trans* stereoisomer (E).

Thus, the formation of discrete free carbanionic intermediates which can undergo stereochemical inversion, does not seem to occur in these dehydrofluorination systems. The most likely dehydrofluorination pathways still seem to be E2 *anti-periplanar* ones for most of the reactions involving fluorocyclohexanes. The deuteriation that occurs to an extent with undecafluorocyclohexane, and with the less reactive members of various stereoisomeric pairs, could be due to more carbanion-like transition states in those cases, because the equatorial hydrogens give rise to stereochemistry unfavourable for E2 eliminations. It is also possible that equatorial hydrogens are more acidic than axial, though some of the latter can be deuteriated. The carbanionic species may re-protonate (or deuteriate) back to 'hydrofluorocarbons' faster than they lose fluoride ion to give olefins, leaving the dehydrofluorinations to proceed by E2-type reactions from higher-energy conformations, which have the groups that are to be lost carried in *trans* or in *cis* coplanar arrangements.

Where the potential carbanionic centre carries no fluorine substituent directly, as in compounds (C), (H) and (J), the carbon acidity is clearly much higher than where >CHF groups are involved [cf. 16,17], and a little H-D exchange occurs even in a neutral medium. Even with such relatively strong carbon acids however, the extent of deuteriation occurring in basic media was still small. The ready dehydrofluorinations of compounds (C), (H) and (J) could depend on acidic (weak) C-H bonds being adjacent to relatively weak tertiary →C-F bonds. This would ensure very facile E2 processes when the stereochemistry is correctly arranged for coplanarity; directly with (H) and during ring rearrangements for (C) and (J). Finally, another factor is that olefins with the minimum numbers of vinylic fluorine substituents (minimising I-π interactions) are the most stable isomers [see e.g.18]. Both effects operate in the same direction: the order of carbon-fluorine bond stability is $-CF_3$ > $>CF_2$ > $\rightarrow$CF; the structures arising from such bond breakings are, respectively, $R_2C{=}CF_2$, $R_2C{=}CFR$ and $R_2C{=}CR_2$.

EXPERIMENTAL

General

Preparative gas liquid chromatography (glc) was carried out in copper tubes (4.88 m × 35 mm i.d.) packed with tricresyl phosphate on celite (1:3) [column 1], or with dinonyl phthalate on celite (1:4) [column 2]. Smaller-scale separations were done on Pye model 104 machines using a column (8 m × 5 mm) packed with dinonyl phthalate on celite 1:3 [column 3].

Ultraviolet spectroscopy was done on a Unicam SP 800 instrument. Infrared spectra were measured by a Perkin Elmer 257 machine using liquid films, and significant peak positions, in cm^{-1}, are given. Mass spectra (ms) were run on an AEI MS 9 spectrometer. For each compound, only the mass peak representing the molecular weight (except where stated) is cited, but in every case the fragmentation pattern was entirely consistent with the structure.

Nuclear magnetic resonance spectra (nmr) were measured with a Varian HA 100 instrument, using carbon tetrachloride solutions. ^{19}F results were at 94.1 MH$_z$: values given are chemical shifts in p.p.m. from trichlorofluoromethane as internal reference (values in parentheses are relative intensities; s = singlet, b = broad). ^1H (δ) values (at 100 MH$_z$) are in p.p.m. from tetramethylsilane. Only the basic chemical shift data necessary in structural determinations are given.

Identities of products and authentic specimens were established by glc retention times and infrared spectroscopy.

Hydrogenation of 1,2-Bis(trifluoromethyl)octafluorocyclohexene (A)

The title compound (20.0 g) and palladium-charcoal (10%; ca. 0.5 g) were shaken at ca. 16°C for 24 hours in an autoclave (capacity 60 cm^3), charged with purest-grade hydrogen at 100 atm. pressure. The pressure fell to ca. 80 atm., and hydrogen fluoride was present when the vessel was vented. The liquid product (17.0 g) was distilled, and separated by glc (1, 60°, 20) to give:-

(i), unreacted A (8.0 g): (ii), *6H-1,6-bis(trifluoromethyl)heptafluorocyclohexene* (B) *nc* (1.0 g), b.p. 100°C (Found: C, 27.8; H, 0.6. C_8HF_{13} requires C, 27.9; H, 0.3%): (iii), *1H,2H/1,2-bis(trifluoromethyl)octafluorocyclohexane (cis* isomer) (C) *nc* (5.0 g), b.p. 114°C (Found: C, 26.4; H, 0.5. $C_8H_2F_{14}$ requires C, 26.4; H, 0.6%). The reaction was not entirely reproducible, and some experiments gave lower yields of total products, and/or higher proportions of the olefin (B).

Compound (B) had ir peaks at 2960 (C-H), and 1709 ($FC=CCF_3$): M/e, 344: ^{19}F nmr, 60.1 (3), 61.9 (3), 108-138 (analysed as three AB quartets (3×2) and a signal (1) due to =CF).

Compound (C) had an ir band at 2960: M/e, 364: ^{19}F nmr peaks; at 16°C, very broad, fine structure not resolved; at -60°C, 59.5 (3), 61.4 (3), 103-149 (analysed as four AB quartets (4×2)); at +70°C, 59.8 (3), two AB quartets at 113-139 (2×2).

Chlorine Addition to Compound (A)

Compound (A) (30.0 g) and chlorine (5.5 g) were sealed in a Pyrex glass tube and irradiated with uv light for 150 hours at ca 16°C. The liquid product was washed with water and sodium metabisulphite solution, dried ($MgSO_4$) and separated by glc (1, 100°, 25) to give :- (i), unreacted (A) (20.0 g); (ii), *1,2-dichloro-1,2-bis(trifluoromethyl)octafluorocyclohexane* (D) *nc* (7.0 g) m.p. 67°C (Found: C, 22.2; Cl, 16.7. $C_8Cl_2F_{14}$ requires C, 22.2; Cl, 16.4%): M/e, 432 (^{35}Cl).

Reaction of Lithium Aluminium Hydride with the Dichloride (D)

Dichloride (D) (60 g) in diethyl ether (50 cm^3) was added dropwise to a stirred suspension of lithium aluminium hydride (1.5 g) in diethyl ether (150 cm^3) at -65°C. Apparatus and reagents were scrupulously dried. Stirring was continued for 1 hour at -65°C. Water was then carefully added at 0°C, followed by hydrochloric acid, and the ether layer was washed with water, dried ($MgSO_4$), and most of the ether distilled off through a 1' distillation column. Glc analysis showed the presence of at least nine components. A significant component had glc retention times identical to those of the *cis* dihydro-isomer (C). From the product mixture, only two components could be isolated pure by glc (2, 60°, 20):- (i), ether; (ii), *1H-2-trifluoromethyl/-2H-1-trifluoromethyloctafluorocyclohexane (trans* isomer) (E) *nc* (0.2 g): ir 2980: M/e, 364: ^{19}F nmr, 70 (3,s), 130 (2,s), 133-157 (2, AB quartet): ^1H nmr, 4.3 (b).

Dehydrofluorination of the Cis *Dihydride (C)*

Compound (C) (11.0 g) was shaken with a solution of potassium hydroxide (1.5 g) in water (10 cm^3) for 10 min., the aqueous layer being then essentially neutral. Glc separation (1, 60°, 20) afforded:- (i), *2,3-bis(trifluoromethyl)hexafluorocyclohexa-1,3-diene* (G) *nc* (0.9 g), b.p. 75°C (Found: C, 29.8. C_8F_{12} requires C, 29.6%): (ii), 6H-1,6-bis(trifluoromethyl)heptafluorocyclohexene (B) (1.0 g): (iii), a mixture (0.2 g): (iv), starting material (C) (4.3 g). No *trans* dihydride (E) could be detected by glc, though this experiment was done under conditions to favour generation of it. Use of higher ratios of base gave increased yields of (B) and (G), with complete consumption of (C).

The diene (G) had λ_{max} 2,770 (ϵ = 6.5 × 10^4; solvent ethanol): ir bands were present at 1660 and 1695: ^{19}F nmr peaks were at 60.3 (3,s), 113.0 (1,s) and 133.0 (2,s): M/e, 324.

Mixture (iii) consisted of mono-ene (B), as in fraction (ii) (ca 50%), and another olefin with an ir band at 1740, but which could not be isolated pure.

Fluorination of 2,3-Bis(trifluoromethyl)hexafluorocyclohexa-1,3-diene (G)

The title compound (G) (1.6 g) was passed in a nitrogen stream (ca. 4 l/h) through a small stirred reactor [19], made from nickel tube (46 cm × 4.4 cm i.d.) and fitted with a co-axial stirrer shaft with paddles, rotated at ca. 4 revs / min. It contained cobalt(III) fluoride (ca. 120 g), and the reactor temperature was 75°C.

Removal by glc of a trace of shorter-retained impurity from the liquid product (1.4 g), left 1,2-bis(trifluoromethyl)octafluorocyclohexene (A), further identified by ^{19}F nmr spectroscopy.

Fluorination of the Cis *Dihydride (C)*

Compound (C) (7.5 g) was passed through the cobaltic fluoride reactor at 215°C, to give a liquid (7.5 g) which was separated by glc (1, 60°, 20) to give:- (i), 1,2-bis(trifluoromethyl)decafluorocyclohexane (0.2 g) [20] : (ii), a mixture (2.1 g): (iii), unreacted (C) (2.5 g). Mixture (ii) had three components and was further separated by glc (3, 60°, 4) to give:- (ii)a, 1,2-bis(trifluoromethyl)decafluorocyclohexane (0.5 g): (ii)b, *1H-2-trifluoromethyl/-1-trifluoromethylnonafluorocyclohexane (trans* isomer) (H) *nc* (1.0 g), b.p. 98°C (Found : C, 25.6; H, 0. C_8HF_{15} requires C, 25.15; H, 0.25%): (ii)c, *1H/-1,2-bis(trifluoromethyl)nonafluorocyclohexane (cis* isomer) (J) *nc* (0.2 g), b.p. 98°C.

No *trans* dihydride (E) was detected.

Compound H had an ir band at 2953: M/e, 363 (M-F): ^{19}F nmr, 58.5 (3,s), 71.0 (3,s), 118-144 (8, 4×AB quartets), 176.0 (1,s). Compound J had an ir band at 2962: M/e, 363 (M-F): ^{19}F nmr, 58.5 (3,s), 71.0 (3,s), 118-144 (8, 4×AB quartets), 185.0 (1,s).

Fluorination of 6H-1,6-Bis(trifluoromethyl)heptafluorocyclohexene (B)

Compound (B) (2.0 g), fluorinated as before at 150°C, gave a liquid product (1.7g) containing starting material (B). The *trans* and *cis* 1H- compounds (H and J, respectively) were present in roughly the same proportions as from the saturated dihydro-compound (C).

Reaction of Ammonia with 1,2-Bis(trifluoromethyl)octafluorocyclohexene (A)

A slow stream of dry ammonia gas was passed for 4 hours through a stirred solution of compound (A) (6.6 g) in dry diethyl ether (60 cm^3) A yellow colour developed and much solid was deposited. Water was added, the water layer extracted with ether, and the combined ether extracts dried ($MgSO_4$), filtered and concentrated to a partly crystalline yellow syrup (5.0 g) containing two components. The main one was isolated after several recrystallisations from carbon tetrachloride. Obtained were white crystals of *1,3-diamino-2-cyano-3-trifluoromethylhexafluorocyclohexene* (K) *nc* (2.0 g), m.p. 65°C (Found : C, 30.3; H, 1.3; N, 13.6. $C_8H_4F_9N_3$ requires C, 30.7; H, 1.3; N, 13.4%): M/e, 313: λ_{max} 2,690 (ϵ 6300; in ethanol): ir (nujol mull) 3400; 3330; 3250; 3210; 2215; 1660; 1600: ^{19}F nmr, 73.7 (3), 110-142 (6, 3×AB quartets); ^{1}H nmr, 6.4 (b).

The minor component could not be isolated pure; from its ir spectrum, it appeared to contain >C=C<, $-NH_2$ and $-C{\equiv}N$ groups.

Dehydrofluorinations and Deuteriations of Cis *and* Trans *1H-1,2-Bis(trifluoromethyl)nonafluorocyclohexane (J and H respectively)*

(a) The *trans* isomer (H) (0.5 g) was shaken for one minute with a solution of potassium hydroxide (1.0 g) in deuterium oxide (1.0 g). The sole compound present was 1,2-bis(trifluoromethyl)octafluorocyclohexene (A).

Isomer (H) (0.1 g) was shaken for a few seconds with a solution of potassium hydroxide (0.1 g) in deuterium oxide (1.0 g). Glc separation (3, 60°, 4) gave two products :- (i), starting material (H) (ca 10%) : (ii), olefin (A) (ca 90%). No isomer (J) could be detected (glc), and isomer (H) showed no detectable deuterium content (ms).

(b) Isomer (J) (0.1 g) was shaken for ca. 30 seconds with a solution of potassium hydroxide (0.05 g) in deuterium oxide (1.0 g). Glc (3, 60°, 4) showed starting material (J) (ca. 40%) and olefin (A) (ca. 60%). No isomer (H) was detected (glc), but the recovered (J) had a deuterium content of 8.7% (ms).

(c) Identical experiments showed the *trans* isomer (H) to be dehydrofluorinated faster than the *cis* (J).

(d) After being left in contact with deuterium oxide for nine days in the absence of base, the *trans* isomer (H) had a deuterium content of 0.25% (ms). Treated similarly, the *cis* isomer (J) showed a deuterium content of 3.4% .

Deuteriation of the Cis *dihydride (C)*

When compound (C) (2.0 g) was shaken with a solution of potassium hydroxide (0.2 g) in deuterium oxide (2.0 cm^3), as in the previous experiment, the recovered starting material was shown (by ms) to contain 1.6% of the deuteriated analogue.

When (C) (0.3 g) was left in contact with deuterium oxide (0.8 g) in the absence of base for 5 days, there was 0.6% deuteriation (ms).

Dehydrofluorinations and Deuteriations of Polyfluorocyclohexanes

(a) *Undecafluorocyclohexane.* This (1.0 g), was shaken with a solution of KOH (1.0 g) in D_2O (1.0 g). After 20 minutes, there was present decafluorocyclohexene (75%) and starting material (13.9% deuteriated by ms) : after two days, the small amount of hydrofluorocarbon remaining was 23% deuteriated (ms).

When undecafluorocyclohexane (0.5 g) and deuterium oxide (0.9 g) were left in contact for 8 days, no deuteriation could be detected (ms).

(b) *1H,2H/-Decafluorocyclohexane* (cis) [6]. This (1.0 g), and KOH (1.0 g) in water (1.0 g) were shaken together for 10 minutes at 16°C. There was 50% conversion to 1H-nonafluorocyclohexene, but by glc the recovered 1H,2H/-decafluoride contained no 1H/2H-stereoisomer *(trans)* (0.1% detectable).

(c) *1H/2H-Decafluorocyclohexane* (trans) [6]. This (2.0 g) was heated at 100°C in a sealed tube with KOH (2.0 g) and water (2.0 g). The expected -enes [21] were present, but no 1H,2H/-stereoisomer *(cis)* (glc).

Dehydrofluorinations and Deuteriations of Trifluoromethyldecafluorocyclohexanes

(a) *4H-1-Trifluoromethyl/-decafluorocyclohexane* (cis). This (0.5 g), and KOH (0.5 g) in water (0.5 g) at 16°C were shaken together. Product composition was as follows (respectively, time (min.); recovered *cis* isomer (%);

4-trifluoromethylnonafluorocyclohexene [4] formed (%)) :- 8, 39, 61; 26, 27, 73; 53, 11, 89; 78, 6, 94. By glc, no *trans* isomer was present in the recovered C_7HF_{13} (0.4% was easily detectable).

This compound (0.5 g) was shaken with KOH (0.9 g) in D_2O (1.0 g) at 16°C for 4 min.; there was ca 25% olefin formation (glc), and 2.7% deuteriation (ms).

(b) *4H/-1-Trifluoromethyldecafluorocyclohexane* (trans) From an experiment on this, done as for (a), the figures were :- 23, 92, 8; 33, 54, 46; 43, 46, 54; 53, 37, 63; 68, 32, 68; several days, 12, 88. No *cis* isomer was present in the recovered C_7HF_{13} (glc). This compound (0.5 g), KOH (1.0 g) and D_2O (1.0 g) were shaken together at 16°C for 30 min.: there was ca 40% olefin formation (glc) and 15.3% deuteriation (ms).

(c) In separate experiments, the *cis* and *trans* isomers (1.0 g) were left with D_2O (1.0 g) for 7 days. In neither case could any deuteriation be detected (by ms).

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