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POLYFLUORO-COMPOUNDS BASED ON THE CYCLOHEPTANE RING SYSTEM.

PART 5. OCTAFLUOROCYCLOHEPTA-1,3,5-TRIENE AND HEXAFLUOROTROPONE

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SUMMARY

Decafluorocyclohepta-1,3-diene underwent reductive addition-elimination with sodium borohydride to give mainly 1H-nonafluorocyclohepta-1,3-diene, together with minor products, the 1H,4H-octafluoro-analogue and, most significantly, 5H-nonafluorocyclohepta-1,3-diene. Decafluorocyclohepta-1,4-diene similarly gave mainly a mixture of 1H- and 2H-nonafluorocyclohepta-1,4-diene, together with some 6H-nonafluorocyclohepta-1,4-diene and a trace of the 5H-1,3-diene. These last two dienes were important products, having hydrogen on allylic carbons. They could be dehydrofluorinated, either by bubbling through molten potassium hydroxide or, better, with powdered alkali in an inert medium. Unless special precautions were taken, such reactions yielded hexafluorotropone. With care however the primary product, octafluorocyclohepta-1,3,5-triene, could be isolated, but it was hydrolysed rapidly, even by water, to give the tropone. Isomerisations and pyrolytic dehydrofluorinations of the major reduction products were carried out, but none yielded the triene or the tropone. It seemed that the triene was probably formed but decomposed to give perfluoroarenes. An interesting defluorination pathway was also operating, to give pentafluorobenzene. 2H-Nonafluorocyclohepta-1,3-diene was an isomerisation product. Hexafluorotropone reacted with sodium methoxide in methanol to give 3,6-dimethoxytetrafluorotropone.

INTRODUCTION

The work reported in this paper is a natural extension of our previous studies on fluorocycloheptane chemistry [1], being the first synthesis of the most highly unsaturated members with this ring system. In earlier investigations on 6-membered rings, the fluorination of benzene by cobalt (III) fluoride gave ranges of nonafluorocyclohexanes [2] and octafluorocyclohexanes [3], isolated relatively readily. These served as precursors for our first syntheses of hexafluorobenzene [4] and pentafluorobenzene [5], respectively, by three-stage dehydrofluorinations with strong alkali. Likewise, octafluorocyclopentanes, available from fluorinations of cyclopentane [6], afforded hexafluorocyclopentadiene [7] by two-stage dehydrofluorinations; pentafluorocyclopentadienes were made analogously [8]. Alternative approaches to polyfluorobenzenes were also developed, in which hydrogen was strategically introduced into polyfluorocyclohexenes via addition-elimination reactions with lithium aluminium hydride, thus permitting the benzene skeleton to be obtained via subsequent dehydrofluorination [2,9].

This present paper describes work completed some ten years ago, but only published previously as a preliminary note [10]. The problem was to obtain polyfluorocyclohept-anes or -enes, with suitably placed hydrogen, which would dehydrofluorinate to give three double bonds. In general, in polyfluorocycloalkane chemistry dehydrofluorinations of compounds having groups of the type $\cdot\text{CF}_2\cdot\text{CHF}\cdot\text{CHF}\cdot\text{CF}_2\cdot$ give much greater proportions of cycloalkenes with vinylic hydrogen, i.e. $\cdot\text{CF}_2\cdot\text{CH}=\text{CF}\cdot\text{CF}_2\cdot$, by loss of fluorine from a >CHF group, than of those with allylic hydrogen or multiple unsaturation [cf. 6, 11]. This applies even when the considerable driving force of the resonance energy of the benzene ring might be expected to favour multiple unsaturation [cf. 3]. Even when the stereochemistry of the cyclohexane ring is also favourable towards aromatisation, significant amounts of non-aromatic products with $\text{CH}=\text{CF}$ bonds are formed [2,3,12]. The electronic effect (F in >CF_2 is more strongly bound than in >CHF) predominates, and where there are stereochemical factors which favour loss of F from >CF_2 rather than >CHF they promote only partial formation of products with entirely $\text{CF}=\text{CF}$ bonds from fluorocyclohexanes, and much less in most cases from cyclopentanes.

Cycloheptanes have more flexible rings than cyclohexanes, and the stereochemistry of the groups being eliminated has not so far appeared to play any major role in polyfluorocycloheptane systems [1]. In fact,

dehydrofluorinations of the two stereoisomeric 1H,2H-dodecafluorocycloheptanes gave exclusively 1H-undecafluorocyclohept-1-ene, as far as could be detected [13]. This then was the background against which the present study was undertaken.

RESULTS AND DISCUSSION

Synthesis of Starting Materials

Two approaches were possible; either (i) isolation of suitable trihydroundecafluorocycloheptanes, the 1H,3H,5H-system being required, or (ii) introduction of hydrogen into olefines of the series with suitable double bond shifts to allow further dehydrofluorination of the products.

In the earlier work [14], fluorinations of cycloheptane by cobalt (III) fluoride at 180-190°C had given fair quantities of dodecafluorocycloheptanes, mainly the 1H/3H- and 1H/4H-stereoisomers, which were isolated without too much difficulty by fractional distillation. However, though there was some material analysing as $C_7H_3F_{11}$, it was not in great quantities, and seemed to be a complex mixture. Only a 1H,2H,4H- and a 1H,2H,5H-stereoisomer were recognised, and there are many possible products.

In the present work, cyclohepta-1,3,5-triene was fluorinated similarly at 160-170°C, to give a generally similar crude product mixture, with 25-30% being readily isolatable as the dodecafluorocycloheptane fraction. Though the proportion of mixture corresponding to $C_7H_3F_{11}$ could be increased a little, glc analysis indicated that it was still highly complex, and that there were no very major constituents. Preliminary separations were not at all encouraging.

It was decided therefore to attempt the synthesis of octafluorocycloheptatriene via the decafluorocyclohepta-1,3-(I) and -1,4-diene (II) (See Scheme) both readily available [14] from dehydrofluorinations of the dodecafluorides. It was confirmed that these dehydrofluorinations worked on a larger scale; the proportions of products being ca. 2.5:1 in favour of the 1,3-diene (I). It was hoped to introduce hydrogen into these using metal hydrides, as had been done earlier with fluorocyclohexenes [e.g. 2,9] and to obtain products with allylic hydrogen via double bond rearrangement.

Previously, few reactions of this type had been done with fluorocyclohexadienes. There was one report [15] of a reaction of octafluorocyclohexa-1,4-diene with lithium aluminium hydride, 1H-heptafluorocyclohexa-1,4-

diene being the only product isolated. Such a reaction with octafluorocyclohexa-1,3-diene had not been reported, but with some nucleophiles it gave [16] a preponderance of 2-substituted products, though a little material arising from the desired type of double bond shift was isolated.

As a preliminary, the reaction of octafluorohexa-1,3-diene with sodium borohydride in diglyme was carried out (this is milder than LiAlH_4 in this type of reaction [17]). Major products were hexa- and penta-fluorobenzene and 1H,4H-hexafluorocyclohexa-1,3-diene, with a trace of 1H-heptafluorocyclohexa-1,3-diene. A reaction run for a shorter time gave the last as the major product. Clearly, in this reduction by far the major point of attack was at C_1 , in contrast to the earlier reactions with other nucleophiles [16]. All the products found could have arisen from attack at C_1 , the arenes deriving from products formed by double bond rearrangements, though similar rearrangements could have given them following attack at C_2 also. It was of course this type of reaction that was required from the seven carbon systems, and the proportion of arene product was encouraging, whatever the point of attack.

Preparation of Hydrogen-containing Diene Precursors

Decafluorocyclohepta-1,3-diene (I) was treated with sodium borohydride in diglyme at -5°C and afforded one major (III) and two minor products (IV and V). The major product (III) analysed as C_7HF_9 , and the ultraviolet spectrum indicated a 1,3-diene structure. The ^{19}F and ^1H nmr spectra showed a low-field >CF_2 group, adjacent to vinylic hydrogen, and no major coupling by the hydrogen (See the Table for nmr spectra of all new compounds; peak positions have been reported for dienes I and II [14], and other useful compounds [1].) Compound III was therefore 1H-nonafluorocyclohepta-1,3-diene. Subsequently, compound III was isomerised to the 2H-1,3-diene (IX) (see later) and this completely confirmed the structure. Also, photoisomerisation of diene III gave a bicyclo(3,2,0)heptene with bridgehead hydrogen [18].

The minor product IV was of the type sought. Isomeric with III and having conjugated unsaturation, its ^{19}F and ^1H nmr spectra showed a >CHF group with the typical coupling of 50 mHz, and specifically located alongside the double bond system. Compound IV was therefore 5H-nonafluorocyclohepta-1,3-diene. The other minor product V had the formula $\text{C}_7\text{H}_2\text{F}_8$ and a 1,3-diene system. The nmr spectra clearly showed the structure to be 1H, 4H-octafluorocyclohepta-1,3-diene (V).

The pathway for this reaction with diene I is clear. The first attack by the nucleophilic reagent is (as for the cyclohexa-1,3-diene) at C₁ to give an intermediate such as IA. This can lose F⁻ from the original C₁ to give product III. Alternatively, the allylic carbanion in IA can rearrange to lose F⁻ from the original C₅ to give product IV. The proportion of this is much less than that of hexafluorobenzene in the cyclohexadiene case, not perhaps surprisingly. A second attack on the 1H-diene III, at the more electron-deficient double bond, gives the disubstituted diene V.

Decafluorocyclohepta-1,4-diene (II) was treated with sodium borohydride to give two major and two minor products with smaller unidentified species. The two major products (VI and VII) were separable by glc only with difficulty. Both had formulae C₇HF₉ with vinylic hydrogen and showed no double bond conjugation. Nmr spectroscopy showed VI to be the 1H-1,4-diene (two >CF₂ absorptions at ca. 105 and one at 118) and VII the 2H-1,4-isomer (one >CF₂ at ca. 89 and two at ca. 118). The third product (VIII) was an isomeric 1,4-diene. It had typical nmr peaks for a >CHF group, and other appropriate peaks, so that its structure was clearly shown as 6H-nonafluorocyclohepta-1,4-diene (VIII). The fourth, very minor, product was found to be the 5H-1,3-diene (IV).

With diene II therefore the attack of the nucleophile occurs at each end of the double bond, and no significant directional effects would be expected here. Attack at position 1 gives an intermediate like IIA, which loses F⁻ predominantly to give VI, but to some extent to give IV via double bond shift. Likewise, attack at position 2 gives IIB, which decomposes chiefly to VII but also to VIII as well.

Octafluorocycloheptatriene and Hexafluorotropone

The two dienes IV and VIII were each subjected to dehydrofluorination studies. Aqueous potassium hydroxide caused extensive decomposition, but a small amount of a new product was isolated, which behaved as a polyene but appeared to be unstable. The first practicable dehydrofluorinations were carried out by bubbling a stream of nitrogen containing diene IV or diene VIII through molten potash. On glc analysis the liquid product showed two new peaks, besides that due to starting material. However, the peak due to the longest-retained component grew rapidly with time, at the expense of the other product peak, and crystals were deposited in the liquid. After a day or so these were isolated, and found to be hexafluorotropone (X). This had the expected uv and ir spectral characteristics, and the mass spectrum had a large peak corresponding to loss of carbon monoxide.

Next, the dehydrofluorination of diene VIII was carried out using powdered potassium hydroxide in dry benzene. After about 2 hours, the major glc peak was at a maximum (it corresponded with the original trace product from the reactions with aqueous alkali, and with the second peak from those with molten potash). Isolation by glc gave octafluorocyclohepta-1,3,5-triene(XI). The uv and ir spectroscopic parameters were as expected, and the mass spectrum showed peaks at $C_7F_7^+$ due to loss of a fluorine, and at $C_6F_6^+$ due to loss of CF_2 . This triene (XI) was very susceptible to bases and even to water. Prolonging the reaction as outlined above to 3 hours duration gave mainly the tropone (X) and very little of the triene (XI) survived, whilst exposure of XI to moist air in a cooled trap led to rapid formation of X.

5H-1,3-Diene (IV) also afforded the triene (XI) with KOH/benzene, the reaction being a little faster than for the 1,4-diene (VIII). The best system tried for the dehydrofluorination was powdered sodium hydroxide in perfluorodimethylcyclohexane, the glc separation being easier than with benzene. Again, if such a system was left in contact with the triene (XI) for 2 hours or so, almost complete conversion to the tropone (X) occurred.

Though the triene (XI) would be expected to hydrolyse to the tropone (X), the extreme rapidity of the reaction is surprising. Double bonds activate the normally inert $>CF_2$ group, particularly if it is sandwiched between two of them, but hitherto strong acids have been used for these hydrolyses (cf. octafluorocyclohexa-1,4-diene [15]). In the fluorocycloheptane series, such a reaction with the diene (II) did not stop at hydrolysis of the lone $>CF_2$, but attack on the double bond system occurred also to give hexafluoro-1,5-dihydroxy-8-oxabicyclo(3,2,1)octan-3-one [19].

The mechanism of the hydrolytic attack on the triene (XI) is not certain. It could involve direct replacement at the allylic $>CF_2$ group, but, perhaps more likely, is addition to the double bond system. Attack by a water molecule at position 1 followed by HF loss to give carbonyl, and a double bond shift with loss of a fluorine from the $>CF_2$, would give the tropone (X) directly. It appeared that the triene (XI) reacted readily with nucleophiles; it should be a precursor of many new compounds.

Both the tropone (X) and the triene (XI) appeared to decompose at about 200°C, but despite the obvious peaks in their mass spectra corresponding to loss of CO and CF_2 respectively, no arene-type products could be isolated from pyrolysis reactions (see later for indications of this type of decomposition however).

The tropone (X) did not show the ready hydration characteristic of perfluoroketones generally. The uv spectrum in water was not much changed from that in cyclohexane, in accord with this. Compound X however was quite susceptible to nucleophilic attack, and sodium methoxide in methanol gave a mixture from which the predominant product (XII) could be isolated. This analysed as a dimethoxytetrafluorotropone, and its ^{19}F and ^1H nmr spectra immediately suggested the 3,6-dimethoxy-structure (triplet splitting of the CH_3 signal). Though this was far too simplistic an interpretation of the nmr spectra, the structural allocation was in fact correct. There are close similarities between the mass spectra of tropones and those of the related benzene derivatives formed by loss of carbon monoxide [20]. The mass spectrum of the dimethoxytetrafluorotropone (XII) was compared with those of the three isomeric dimethoxytetrafluorobenzenes [21]. There was a significantly closer relationship between the mass spectra of the tropone (XII) and that of 1,4-dimethoxytetrafluorobenzene, than between those of the others. However, some extra peaks in that of XII compared with all of the others suggested that loss of CO is not the sole fragmentation process. Subsequently, 3,6-di-methoxytetrafluorotropone (XII) was synthesised [22] by further substitution on a monomethoxypentafluorotropone, the major product of a one-stage methoxylation of X [22]. The structure of this monomethoxide was established absolutely by X-ray crystallography [23]. Both this analysis [23], and X-ray crystallographic study of hexafluorotropone itself [24], showed that there was little bond delocalisation in the π -electron systems, and that the structures corresponded largely to conjugated polyene systems, as with hydrocarbon tropones.

Attempted Isomerisations of Polyfluorocycloheptadienes

Dehydrofluorinations of the 6H-1,4-diene (VIII) and the 5H-1,3-diene (IV) were attempted by passage over heated sodium fluoride powder contained in a vertical glass tube heated to around 400°C . This technique has effected dehydrofluorinations of polyfluorocyclohexanes [25], and offered the possibility of generating triene (XI) in the absence of water. However the only products isolated (apart from recovered VIII or IV) were hexafluorobenzene together with traces of pentafluorobenzene and octafluorotoluene. It seems that dehydrofluorination only occurred at temperatures ($\sim 400^\circ\text{C}$) at which any octafluorocycloheptatriene (XI) produced

was decomposed to give fluoroaromatic species, chiefly by loss of CF_2 . The conditions were generally similar to those used for isomerisations of the parent dienes (I and II) [26] (smaller tube here, but more finely-divided packing). It seemed appropriate therefore to compare the reaction with that of diene I which was passed through the tube at 460°C , the temperature used previously [26]. The isomerisation to decafluorobicyclo-(3,2,0)hept-6-ene and a trace of 1,4-diene (II) was confirmed, but small amounts of hexafluorobenzene and of octafluorotoluene were detected in the present reaction, though not previously. These can only arise by a defluorination process. Recovery of only octafluorotoluene, following its passage under similar conditions, suggested that hexafluorobenzene arises from these cycloheptene systems by direct loss of CF_2 and not via octafluorotoluene.

Pyrolytic isomerisation/dehydrofluorinations of the major monohydrodiene isomers (III, VI and VII) were attempted next, being much more available sources of the triene (XI). Isomerisations to one another occurred, but there was no detectable triene XI or tropone X. There was also however a trace of hexafluorobenzene, and significant amounts of pentafluorobenzene.

The formation in these reactions of hexafluorobenzene and octafluorotoluene from decafluorocyclohepta-1,3-diene (I) and particularly, of pentafluorobenzene from all the hydrodienes, means that quite significant proportions of the reactants must be diverted into a pathway involving defluorination, rather than dehydrofluorination, though there is no obvious fluorine acceptor. This issue has been raised recently by colleagues [27]. Most previous examples of defluorinations of this type are explicable as disproportionation processes [28], but, as with our colleagues heterocyclic example [27], this does not seem to be the case here. The expected cycloheptene products (formed in equimolar proportions to cycloheptatrienes which decomposed to arenes) would surely have been found in some of the reactions. All are known [13,14], and even if they subsequently dehydrofluorinated, the cycloheptadienes (I and II) would have shown up. It seems therefore that some direct defluorination pathway afforded cycloheptatrienes, which then decomposed to the fluoro-arenes.

Because isomerisation of the dienes clearly did occur, reactions were attempted by passage over aluminium fluoride heated to about 400°C , to optimise this type of process. 1,3-Dienes interconverted, and the 1,4-dienes (VI + VII) gave some of the 1,3-dienes (III + IX) but no very advantageous results emerged, and no dienes of types IV or VIII were found.

Likewise, the 1,4-dienes (VI + VII) were converted to 1,3-dienes (III + IX) by liquid phase reactions involving caesium or potassium fluorides in dimethylformamide, but there was some polymer formation, though no detectable IV or VIII.

The only useful synthetic result from this part of the work was the isolation of the hitherto unknown 2H-nonafluorocyclohepta-1,3-diene (IX) from the isomerisations. It had the expected spectroscopic parameters, confirming its own structure and that of the isomer III. Its total absence (by analytical glc) from the products of the original reaction of I with borohydride was established. A sample of IX was made by passage of III over glass helices at 480°C, a minor product being 1H-nonafluoro-bicyclo(3,2,0)hept-6-ene [18] (via cross-ring bond formation in diene III).

In work done later but already published [29], 1,3-dienes (I, III and V) were converted into iron tricarbonyl complexes, which were pyrolysed at 440°C as a possible route to fluorocycloheptatrienes. However, respectively, hexa-, penta-, and tetra-fluorobenzene were the only products obtained. Here of course there is an obvious fluorine acceptor.

CONCLUSIONS

This work achieved its main objective in providing the first samples of hexafluorotropone (X) and octafluorocycloheptatriene (XI). The formation of even small proportions of the precursor dienes (IV and VIII) by pathways involving "outwards" elimination of F⁻, particularly unfavourable in polyfluorocycloheptane chemistry [cf. 1], is noteworthy. However, real progress in the perfluorotropone field will only come when a route from much more readily accessible compounds has emerged. In view of the relatively low decomposition temperatures and high reactivity of octafluorocycloheptatriene the obvious approach from a reaction between a polyfluoroarene and a carbene may prove difficult to realise (none has been published yet). Isolation of suitable nonafluorocycloheptanes, despite the lack of promise mentioned earlier, should obviously be considered again, perhaps using different fluorinating agents. The interconversions of dienes of the cycloheptane series and bicyclo(3,2,0)heptanes may perhaps be used to rearrange structures of readily-available precursors, and provide an approach to polyfluorotropones.

EXPERIMENTAL

General

Gas-liquid chromatographic separations (glc) were carried out preparatively using columns 4.8m x 75mm internal diameter packed with silicone gum Si301 on Celite (1:5) (Column A), dinonyl phthalate on Celite (1:2) (Column B) and dinonyl phthalate on Chromosorb P (1:5) (Column C). Semi-preparative separations were done on columns (9m x 10mm) used in a Pye series 104 unit: packings were Ucon oil (LB550X) on Chromosorb P (1:4) (Column D), dinonyl phthalate on Celite (1:2) (Column E) and silicone gum Si301 on Chromosorb P (1:5) (Column F). Given for each separation are the column used, temperature ($^{\circ}\text{C}$) and nitrogen flow rate (1 h^{-1}).

Infrared spectra (ir) were measured on a Perkin Elmer 257 machine and ultraviolet spectra on a Unicam SP800.

Mass spectra were recorded on an A.E.I. MS9 instrument.

Nuclear magnetic resonance spectra (nmr) were done on a Varian HA100 machine (^1H at 100, ^{19}F at 94.1 MHz respectively) or on a Perkin Elmer R10 machine (^1H at 60, ^{19}F at 56.4 MHz respectively). ^1H chemical shifts are quoted in τ units using tetramethylsilane, and ^{19}F in ppm to high field of trichlorofluoromethane, both internal references. Solutions (ca. 10%) in carbon tetrachloride were used unless otherwise stated. Results are recorded in the Table (c = complex, b = broad, d = doublet, t = triplet, q = quartet, AB = AB quartet, p = pentet).

Reduction of Octafluorocyclohexa-1,3-diene

To a suspension of the diene [30] (22.5g) in dry diglyme (85 cm^3), cooled to -5°C , a stirred suspension of sodium borohydride (2.88 g), in diglyme (100 cm^3), was added dropwise during 45 minutes. The mixture was stirred for a further 75 minutes at -5°C , sulphuric acid (4M) was added cautiously and, when effervescence had ceased, the fluorocarbon layer was separated off, washed thrice with water, and dried (MgSO_4). The yellow liquid (14.5 g) gave by glc (A, 89° , 65):- (i) a mixture (0.03 g) including unreacted starting material; (ii) 1H-heptafluorocyclohexa-1,3-diene (trace) [31]; (iii) 1H,4H-hexafluorocyclohexa-1,3-diene (2.4 g) [32]; (iv) hexafluorobenzene (5.2 g) [4]; (v) pentafluorobenzene (3.2 g) [5]; (vi) a mixture (1.17 g).

A smaller-scale reaction (proportional quantities) on the diene (2.0 g), carried out for 15 minutes only, gave 1H-heptafluorocyclohexa-1,3-diene as the major product, all the others being present.

Preparation of Polyfluorocycloheptane Starting Materials

Cyclohepta-1,3,5-triene (3,000 g total; in individual fluorination runs of ca. 150 g each) was passed in the vapour phase through a standard [13] stirred reactor containing CoF_3 (10 Kg) at 160-170°C. The product (6,300 g total) on distillation as before [14] and monitored by glc analysis, afforded a fraction b.r. 101°-108.5°C (1648 g) very largely 1H/3H and 1H/4H-dodecafluorocycloheptane.

This fraction (125 g) was refluxed with potassium hydroxide (175 g) in water (350 g) for 24 hours. The organic layer (101 g) was separated, washed twice with water, and dried (MgSO_4). Separation by glc (B, 70°, 35; done in three portions) gave:- (i) decafluorocyclohepta-1,4-diene (II) (23.1 g), b.p. 82-83°C; (ii) decafluorocyclohepta-1,3-diene (I) (56.3 g), b.p. 86-87°C; (iii) 5H-undecafluorocycloheptene (3.5g); (iv) 4H-undecafluorocycloheptene (2.1 g); all were identified by glc and ir [14].

Reduction of Decafluorocyclohepta-1,3-diene (I)

To a suspension of diene I (40 g) in dry diglyme (80 cm³), cooled to -5°C, a suspension of sodium borohydride (1.7 g) in diglyme (140 cm³) was added dropwise and with stirring during 30 minutes. Stirring was continued for 100 minutes further at -5°C. Sulphuric acid (4M) was added cautiously until effervescence ceased. The lower layer was separated off, and washed with water (3 x 50 cm³). Glc separation (B, 85°, 35) of the dried (MgSO_4) product (35.6 g) gave:- (i) recovered diene I (8.7 g) (glc and ir); (ii) 1H-nonafluorocyclohepta-1,3-diene (III) (nc) (15.0 g), b.p. 98°C (Found: C, 32.6; H, 0.4. C_7HF_9 requires C, 32.8; H, 0.4%); M/e 256(M); ir 3100, 3040 (w; C-H), 1690 (shoulder 1710) (s; C=C); λ_{max} 243 nm (ϵ 2850); (iii) a mixture (3.2 g). Further glc (F, 67°, 6) on fraction (iii) (2.0 g) afforded:- (iiia) the 1H-1,3-diene (III) (0.1 g) (glc and ir); (iiib) 5H-nonafluorocyclohepta-1,3-diene (IV) (nc) (1.1 g), b.p. 107-108°C (Found: C, 32.3; H, 0.6%); M/e 256 (M); ir 2950 (w), 1720 (shoulder 1700) (s); λ_{max} 244 nm (ϵ 5010); (iiic) 1H,4H-octafluorocyclohepta-1,3-diene (V) (nc) (0.35 g), b.p. 115°C (Found: C, 34.2; H, 0.8; F, 64.3. $\text{C}_7\text{H}_2\text{F}_8$ requires C, 35.3; H, 0.8; F, 63.8%); M/e 238 (M); ir 3080, 3040 (w), 1680 (s; CH=CF); λ_{max} 238 nm (ϵ 3950); (iv) a mixture of at least two further components (0.1 g).

Reduction of Decafluorocyclohepta-1,4-diene (II)

To a solution of diene II (12 g) in dry diglyme (25 cm³), cooled to 0°C, was added, dropwise and with stirring during 30 minutes, sodium borohydride (0.4 g) in dry diglyme (25 cm³). After being stirred for 2 h further at 0°C, the mixture was processed as above to give a crude product (9.0 g). Glc (C, 85°, 50) afforded:- (i) recovered diene II (3.2 g); (ii) a mixture of 1,4-dienes VI and VII (2.4 g) (see later); (iii) 6H-nonafluorocyclohepta-1,4-diene (VIII) (nc) (1.2 g), b.p. 93-94°C (Found: C, 33.0; H, 0.5%); M/e 256 (M); ir 2960 (w), 1735 (s); uv, no strong selective absorption above 200 nm; (iv) a mixture (0.3 g). Fraction (ii) (7.75 g) on further glc (F, 75°, 3) gave:- (iia) 1H-nonafluorocyclohepta-1,4-diene (VI) (nc) (3.75 g), b.p. 90-91°C (Found: C, 32.8; H, 0.6%); M/e 256 (M); ir 3100, 3050 (w), 1725 (shoulder 1740); uv, no strong selective absorption above 200 nm; (iib) 2H-nonafluorocyclohepta-1,4-diene (VII) (nc) (3.1 g), b.p. 91-92°C (Found: C, 32.7; H, 0.7%); M/e 256 (M); ir 3100, 3060 (w), 1735 (m), 1720 (s); uv, as for diene VI. Fraction (iv) (2.23 g) on further glc (D, 80°, 4) gave:- (iva) a mixture (0.4 g) (5 components); (ivb) the 5H-1,3-diene (IV) (0.88 g) (glc and ir); (ivc) a mixture (0.35 g).

Dehydrofluorination of the 5H-1,3-Diene (IV) and the 6H-1,4-diene (VIII) using Molten Potash

Diene IV (1.0 g) was vapourised in a nitrogen stream (3.5 lh⁻¹) which was bubbled just below the surface (ca. 5 mm) of molten potassium hydroxide (commercial grade; 10-15% H₂O) (18 g) at 200°C. Care was necessary as violent frothing occurred, and the rate of vapourisation was governed by this. The system was purged with nitrogen for 15 min. and the liquid product (0.3 g) was collected in a trap cooled by liquid nitrogen. Analytical glc showed the presence of three components; the first corresponded to starting material (IV), and the third increased, as the mixture was kept, at the expense of the second. After 24 hours the liquid had deposited a mass of needle crystals. The trap contents were extracted with ether and dried (MgSO₄), and the extract evaporated. The solid residue was sublimed (80°/15 mm Hg) and the sublimate recrystallised from

n-hexane to give hexafluorotropone (X) (nc) (0.2 g), m.p. 102-103°C (sealed tube) (Found: C, 39.0; F, 53.6. C_7F_6O requires C, 39.3; F, 53.3%); M/e 214 (M), 186 (s; M-CO); ir, 1625 (shoulders 1660, 1610) (s); 1540, 1520 (double peak) (s); λ_{max} (in nm) in cyclohexane, 225, 309, 315 (ϵ 24000, 7650, 5800 respectively); in water, 230, 262, 320 (ϵ 21800, 4560, 6420 respectively); in hydrochloric acid (4M), 231, 323 (ϵ 28800 and 9000 respectively).

The 6H-1,4-diene (VIII) (0.9 g) was treated in the same way to give hexafluorotropone (0.15 g).

Dehydrofluorination of the 6H-1,4-Diene (VIII) using Potassium Hydroxide in Benzene

(a) Diene VIII (0.7 g), powdered potassium hydroxide (0.2 g), and dry benzene (3 cm³) were stirred together at 80°C for ca. 2 hours, the reaction being monitored by glc. When the product peak was maximised at the expense of the peak due to VIII the liquid was distilled out at 15 mm Hg, and separated by glc (D, 90°, 5.7) to give:- (i) recovered VIII (trace); (ii) octafluorocyclohepta-1,3,5-triene (XI) (nc) (0.25 g), b.p. 110-111°C (Found: M, 235.9881. C_7F_8 requires M 235.9872); M/e 236 (M), 217 (M-F), 186 (M-CF₂); ir 1690 (s, C=C); λ_{max} in cyclohexane, 231, 246 nm (ϵ 6740 and 6850 respectively); (iii) benzene. Fractions (i) and (iii) were identified by glc and ir. The solid left in the original reaction flask was extracted with ether, but no tractable product could be isolated.

(b) In a similar reaction to (a), on diene VIII (0.9 g) using potassium hydroxide (0.45 g) and continued for 3 hours, there was formed a crystalline deposit. Isolation as before gave diene VIII (0.03 g) and triene XI (0.08 g); and, from the ether extracts, after sublimation of the residue at 70°C/15 mm Hg, tropone X (0.44 g), all identified by glc and ir.

Dehydrofluorination of the 5H-1,3-Diene (IV) using Caustic Bases in Inert Media

(a) Diene IV (0.9 g) was stirred with powdered KOH (0.5 g) in dry benzene (3 cm³) at 75°C for 1 hour (XI formation at its optimum by glc). Isolation as before gave:- (i) triene XI (0.58 g); (ii) benzene; and from the ether extracts, tropone X (0.01 g).

(b) A repeat of experiment (a) but using powdered sodium hydroxide and perfluoro-(1,4-dimethylcyclohexane) gave triene XI (0.62 g).

(c) Diene IV (0.08 g), KOH (0.5 g) and C_8F_{16} (3 cm^3) were stirred at 85°C for 1.5 hours. Glc showed a good yield of triene XI comparable to that in experiments (a) and (b). The reaction was continued for 2 hours further, the glc peak due to triene XI then having disappeared, and a mass of colourless crystals having been deposited. Work up as before gave, from the ether extract, tropone X (0.39 g).

(d) When triene XI (0.07 g) in a cooled trap was left exposed to moist air, crystalline tropone X (0.06 g) was formed rapidly.

Attempted Pyrolysis Reactions of the Tropone X and Triene XI

(a) When the tropone X was sealed under nitrogen in a hard glass tube which was heated at 185°C for 10 min., a good recovery of unchanged X was achieved. A repeat experiment at 200°C for 20 minutes caused considerable decomposition. By glc analysis there were present at least four new components besides starting material, but no hexafluorobenzene could be detected.

(b) Pyrolysis of triene XI (1:2 solution in dry cyclohexane) at 190°C by passage through a tube packed with glass helices gave only recovered triene XI with some tropone X. When triene XI (0.5 g) in dry benzene (2 cm^3) was sealed in a tube under N_2 and heated at 190°C for 2 hours the products contained tropone X (0.12 g) together with an unidentified polymeric mixture (0.23 g). No hexafluorobenzene or octafluorotoluene could be detected.

Reaction of Hexafluorotropone (X) with Sodium Methoxide

Sodium methoxide in dry methanol (8.0 cm^3 , 0.45 M) was added dropwise during 30 minutes to a stirred solution of tropone X (0.7 g) in dry methanol (50 cm^3) at ca. 15°C . After 12 hours further, methanol was evaporated at 15 mm Hg and the residue (ca. 10 cm^3) was poured into water (80 cm^3). Extraction with ether in the usual way gave a yellow solid (0.6 g). Separation of a chloroform solution on a silica gel column using chloroform as eluant gave:- (i) recovered hexafluorotropone X (0.17 g); (ii) a mixture (0.24 g) of X and XII; (iii) a mixture (0.06 g) of XII and a third product; (iv) a residue (0.1 g). Progressive sublimation of fraction (ii) at $70\text{--}85^\circ\text{C}/15\text{ Hg}$ afforded 3,6-dimethoxytetrafluorotropone (XII) (nc) (0.095 g) m.p. $83\text{--}85^\circ\text{C}$ (sealed tube) (Found: C, 45.8; H, 2.8. $C_9H_6F_4O_3$ requires C, 45.4; H, 2.5%); M/e 238 (M), 210 (M-CO), 195 (M-C₂H₃O); ir 2960 shoulder 3010, 2840 (m, CH), 1600, 1505; λ_{max} in cyclohexane, 248, 335 nm (ϵ 36000 and 7900 respectively).

Attempted Pyrolytic Dehydrofluorinations of Polyfluorocycloheptadienes

A vertical Pyrex tube (0.3 m x 26 mm diam.) was packed carefully with coarse sodium fluoride powder, obtained by crushing pellets. The tube was heated electrically and swept with a slow stream of nitrogen throughout the experiments, and this was continued for 1 hour after the completion of each addition. In all cases, except where stated, products were identified by having correct glc retention times and infrared spectra.

(a) 6H-1,4-diene (VIII)

This (0.5 g) at 400°C (N₂ 0.8 lh⁻¹) gave a product separated by glc (D, 120⁰, 4.5; product from three runs) to give:- (i) recovered VIII (0.18 g); (ii) hexafluorobenzene (0.53 g); (iii) pentafluorobenzene (trace). Fraction (ii) contained, besides C₆F₆, a small proportion of octafluorotoluene.

(b) 5H-1,3-diene (IV)

Done as above, glc (D, 120⁰, 4.2) gave:- (i) hexafluorobenzene (0.14 g); (ii) octafluorotoluene (trace); (iii) pentafluorobenzene (glc only) (trace); (iv) recovered IV (0.03 g).

(c) Decafluorocyclohepta-1,3-diene (I)

Pyrolysis (1.1 g) at 460°C (glc, D, 75⁰, 4.2) gave:- (i) decafluoro-bicyclo(3,2,0)hept-6-ene [26] (0.25 g); (ii) the decafluoro-1,4-diene (II) (trace); (iii) recovered I (0.5 g); (iv) mixture (0.02 g); (v) hexafluorobenzene (0.035 g); (vi) octafluorotoluene (0.025 g).

(d) Octafluorotoluene

Treated as in (c) this was recovered (> 80%) with no other materials detected.

(e) 1H-1,4-diene (VI)

Diene (0.4 g) at 460°C (glc D, 110⁰, 4.5; product from four runs), afforded:- (i) a mixture (0.31 g) of 1H-(VI) and 2H-(VII)-1,4-dienes in roughly equal proportions; (ii) a mixture (0.09 g), largely 1H-1,3-diene (III) but probably with some 2H-1,3-diene (IX) present (glc only); (iii) a mixture (trace) largely hexafluorobenzene; (iv) pentafluorobenzene (0.22 g).

(f) 2H-1,4-diene (VII)

Done as in (e), there resulted from three runs:- (i) as (e)(i), (0.3 g); (ii) diene III (0.05 g); (iii) hexafluorobenzene (0.02 g); (iv) pentafluorobenzene (0.09 g).

(g) 1H-1,3-diene (III)

Done as in (e), compound III (1.4 g) afforded:- (i) recovered III (0.26 g) containing hexafluorobenzene (ca. 5%); (ii) 2H-1,3-diene (IX) (0.04 g); (iii) pentafluorobenzene (0.2 g).

2H-Nonafluorocyclohepta-1,3-diene (IX)

The 1H-1,3-diene (III) (1.5 g) was pyrolysed as above at 480°C through a tube packed with Fenske glass helices. The product (1.25 g) was separated by glc (E, 90°, 5.3) to give:- (i) 1H-nonafluorobicyclo(3,2,0)-hept-6-ene [18] (0.06 g); (ii) unidentified (trace); (iii) recovered III (0.73 g); (iv) 2H-nonafluorocyclohepta-1,3-diene (IX) (nc) (0.15 g), b.p. 101-102°C (Found: C, 33.0; H, 0.8; F, 66.4%); M/e 256 (M); ir 3040 (w), 1720 (shoulder 1700) (s); λ_{\max} 249 nm (ϵ 6100).

Isomerisations of Polyfluorocycloheptadienes

Experiments (a-c) were done in the tube mentioned above, but packed with aluminium fluoride powder.

(a) Decafluorocyclohepta-1,4-diene (II) (0.9 g) at 400°C gave, after glc (E, 80°, 5), decafluorocyclohepta-1,4-(II) (0.37 g) and -1,3-diene (I) (0.16 g).

(b) The 1H-1,3-diene (III) (1.2 g) afforded (glc, E, 95°, 7.3) dienes III (0.74 g) and IX (0.10 g).

(c) A mixture of 1H- and 2H-nonafluorocyclohepta-1,4-dienes (VI + VII) (1.5 g) at 420°C afforded (glc, E, 90°, 5):- (i) the starting mixture (0.18 g); (ii) the 1H-1,3-diene (III) (0.28 g); (iii) the 2H-1,3-diene (IX) (0.14 g).

(d) A mixture of dienes VI + VII (4.0 g), anhydrous caesium fluoride (1.8 g) and dry dimethylformamide (8 cm³) was heated at 150°C for 1½ hours. The mixture was diluted with ether, washed with water, dried (MgSO₄), and most of the ether distilled off. Further distillation gave a liquid (2.1 g) and a black polymeric solid. The liquid (1.0 g) by glc (E, 85°, 7.2) gave ether, the 1H-1,3-diene (III) (0.55 g) and the 2H-1,3-diene (IX) (0.24 g).

TABLE

Nmr Spectra of New Compounds

Compound Number	Chemical Shift	Relative Intensity	Position in Formula	Type of Signal and Coupling	
III	F	107.6	2	7	c
		109.8	1	2	c
		117.4	2	5	c
		126.3	2	6	c
		137.8	1	3	c
		141.5	1	4	c
	H	4.12	-	1	b
IV	F	113.5	2	6	AB, J = 290
		126.0	2	7	AB, J = 290
		132.4	1	1	c
		ca. 146	2	2,3	c
		150.7	1	4	c
		204.7	1	5	cd, J = ca. 50
	H	5.04	-	5	cd, J = ca. 50
V	F	110.2	2	5,7	c
		112.5	1	2,3	c
		131.4	1	6	c
H	4.09	-	1,4	b	
VI	F	104.1	2	} 3,7	c
		105.5	2		c
		113.1	1	2	c
		117.6	2	6	c
		146.5	1	} 4,5	c
		148.0	1		c
	H	3.92	-	1	b
VII	F	89.2	2	3	c
		112.7	1	1	c
		117.6	4	6,7	c
		142.7	1	4	c
		148.3	1	5	c
	H	4.02	-	2	b

TABLE (continued)

Compound Number	Chemical Shift	Relative Intensity	Position in Formula	Type of Signal and Coupling	
VIII F	99.8 & 104.3	2	3	AB, J = 290	
	99.5 & 114.2	2	7	AB, J = 290	
	125.8	1	5	c	
	144.7	1	} 3,4,5	c	
	145.2	1		c	
	147.9	1		c	
	185.5	1	6	d, J = ca. 50	
H	5.06	-	6	d, J = ca. 50	
IX F	116.7	1	1	c	
	120.5	2	7	c	
	122.9	2	5	c	
	125.6	1	1	cq	
	132.7	2	6	cp	
	151.7	1	4	cq	
H	3.75	-	2	dt, $J_d = 16.5$, $J_t = 6.0$	
X F (CDCl ₃)	126.0	1	2,7	c	
	137.5	1	3,6	c	
	142.9	1	4,5	c	
XI F (CCl ₄ + C ₆ D ₆)	90.3	1	7	c	
	146.7	1	} 3,4	c	
	150.0	1		} 2,5	c
	152.0	1			1,6
XII F (CDCl ₃)	124.2	1	2,7	ct, $J_t = 11$	
	138.9	1	4,5	ct, $J_t = 11$	
H	5.9	-	3,6 (OCH ₃)	t, $J_t = 1.0$	

REFERENCES

- Part 4 of this Series; A. E. M. M. Khalil, R. Stephens and J. C. Tatlow, *J. Fluorine Chem.*, 22 (1983) 133.
- J. A. Godsell, M. Stacey and J. C. Tatlow, *Tetrahedron*, 2 (1958) 193.
- E. Nield, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, (1959) 159.
- J. A. Godsell, M. Stacey and J. C. Tatlow, *Nature*, 178 (1956) 199.
- R. Stephens and J. C. Tatlow, *Chemistry and Industry*, (1957) 821;
E. Nield, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, (1959) 166.

- 6 R. J. Heitzman, C. R. Patrick, R. Stephens and J. C. Tatlow, *ibid.*, (1963) 281.
- 7 J. Burdon, T. M. Hodgins, D. R. A. Perry, R. Stephens and J. C. Tatlow, *ibid.*, (1965) 808.
- 8 A. Bergomi, J. Burdon and J. C. Tatlow, *Tetrahedron*, 22 (1966) 2551.
- 9 E. Nield, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, (1960) 3800.
- 10 D. J. Dodsworth, C. M. Jenkins, R. Stephens and J. C. Tatlow, *J. Chem. Soc. Chem. Comm.*, (1972) 803.
- 11 R. P. Smith and J. C. Tatlow, *J. Chem. Soc.*, (1957) 2505.
- 12 P. L. Coe, A. W. Mott and J. C. Tatlow, *J. Fluorine Chem.*, 20 (1982) 167.
- 13 J. A. Oliver, R. Stephens and J. C. Tatlow, *ibid.*, 22 (1983) 21.
- 14 A. E. M. M. Khalil, R. Stephens and J. C. Tatlow, *ibid.*, 22 (1983) 31.
- 15 E. Nield and J. C. Tatlow, *Tetrahedron*, 8 (1960) 38.
- 16 A. B. Clayton, W. J. Feast, D. R. Sayers, R. Stephens and J. C. Tatlow, *J. Chem. Soc. (C)*, (1971) 1183.
- 17 F. J. Mettillie and D. J. Burton, *Fluorine Chem. Reviews*, 1 (1967) 315.
- 18 Part 6 of this Series; D. J. Dodsworth, C. M. Jenkins, R. Stephens and J. C. Tatlow, *J. Fluorine Chem.*, in the press.
- 19 M. J. Hamor, T. A. Hamor, C. M. Jenkins, R. Stephens and J. C. Tatlow, *J. Fluorine Chem.*, 10 (1977) 605.
- 20 H. Budzikiewicz, C. Djerassi and D. H. Williams, *Mass Spectrometry of Organic Compounds*, (1967) Holden-Day, San Francisco, p.539.
- 21 J. Burdon, W. B. Hollyhead and J. C. Tatlow, *J. Chem. Soc.*, (1965) 5152.
- 22 M. E. Allen, R. Stephens and J. C. Tatlow, unpublished work.
- 23 M. J. Hamor and T. A. Hamor, *Acta. Crystallog.*, B32 (1976) 2475.
- 24 J. J. Guy, T. A. Hamor and C. M. Jenkins, *J. Fluorine Chem.*, 5 (1975) 89.
- 25 M. Stacey, R. Stephens and J. C. Tatlow, *Brit. Pat.* 1,017,814 (1966).
- 26 A. E. M. M. Khalil, R. Stephens and J. C. Tatlow, *J. Fluorine Chem.*, 22 (1983) 43.
- 27 J. Burdon and I. W. Parsons, *J. Fluorine Chem.*, 13 (1979) 159.
- 28 B. Gething, C. R. Patrick, J. C. Tatlow, R. E. Banks, A. K. Barbour and A. E. Tipping, *Nature*, 183 (1959) 586.
- 29 P. Dodman and J. C. Tatlow, *J. Organometallic Chem.*, 67 (1974) 87.
- 30 D. E. M. Evans and J. C. Tatlow, *J. Chem. Soc.*, (1954) 3779.
- 31 R. Stephens, J. C. Tatlow and E. H. Wiseman, *ibid.*, (1959) 148.
- 32 A. G. Hudson, A. E. Pedler and J. C. Tatlow, *Tetrahedron*, 25 (1969) 4371