

Received: October 31, 1977

PYROLYSIS OF TETRADECAFLUOROTRICYCLO[6,2,2,0^{2,7}]DODECA-2,6,9-
TRIENE AND RELATED COMPOUNDS. THERMAL ISOMERIZATIONS
INVOLVING FLUORINE SHIFTS

W.J. FEAST*, R.R. HUGHES and W.K.R. MUSGRAVE

Department of Chemistry, University of Durham, South Road,
Durham, DH1 3LE.

SUMMARY

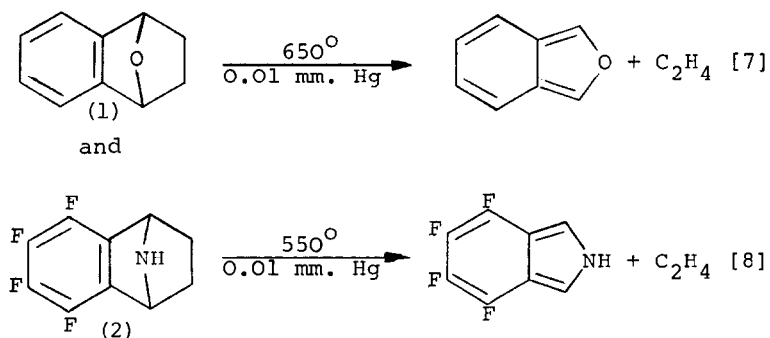
The vacuum pyrolysis of tetradecafluorotricyclo-[6,2,2,0^{2,7}]dodeca-2,6,9-triene (6) results in initial isomerization to perfluorotricyclo[8,2,0,0^{2,7}]dodeca-2,6,8-triene (7) followed by elimination of tetrafluoroethylene and formation of perfluoro-1,2-dihydronaphthalene (8), perfluoro-1,4-dihydronaphthalene (9), perfluoroindene (10) and perfluoro-(2 or 3)-methylindene (11); the expected primary product of elimination of tetrafluoroethylene from (6) or (7), namely perfluoro-2,3-dihydronaphthalene, was not detected. The formation of the observed products can be accounted for in terms of fluorine migrations, further examples of such migrations are described.

INTRODUCTION

Pyrolytic elimination of bridging units from polycyclic compounds has found widespread use in synthesis, being a particularly effective method when the product is an aromatic compound. The elimination of the one carbon bridge from norbornadienes and related systems is a typical example of the process; although it often provides a good route to benzenoid aromatics [1,2,3], the outcome is not always predictable and is sensitive both to the structure and substitution pattern of the substrate and to the pyrolysis

conditions [1,4]. For example, the Diels-Alder adduct of tetrafluorobenzynes and cyclopentadiene loses methylene on pyrolysis in a sealed tube to give 1,2,3,4-tetrafluoro-naphthalene [5], whereas pyrolysis of its non-fluorinated analogue in a flow system gives benzocycloheptatriene [6].

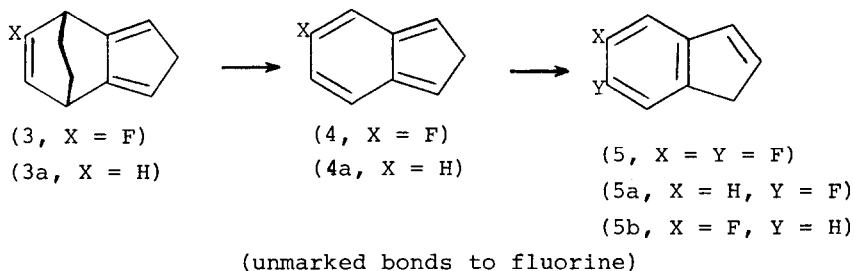
In recent years the experimental technique generally known as flash vacuum pyrolysis has been successfully applied in synthesis and has been particularly useful in the preparation of unstable or reactive compounds not otherwise easily accessible. In this technique the substrate passes at a low pressure through a pyrolysis zone and is then rapidly quenched in a cooled trap. The elimination of ethylene from compounds (1) and (2) to yield isobenzofuran [7] and tetrafluoroisobenzofuran [8] respectively (Scheme 1) provides illustration of the application of this technique.



Scheme 1

During the last few years we have been using flash vacuum pyrolysis to eliminate difluorocarbene and/or tetrafluoroethylene from various polyfluoropolycyclic compounds [9,10]. In the majority of cases we have reported the elimination has been either of tetrafluoroethylene from a bicyclo[2,2,2]octa-2,5-diene unit or of difluorocarbene from a norbornadiene unit, and in most cases the reaction proceeds smoothly and virtually quantitatively to give the expected aromatic product. In some cases, however, the expected primary product of extrusion of the bridging unit was not

isolated. Thus, the flash vacuum pyrolysis of perfluoro-tricyclo[5,2,2,0^{2,6}]undeca-2,5,8-triene (3) yields perfluoro-indene (5) and not the anticipated primary product perfluoroisindene (4) (Scheme 2) [10]. Although a full



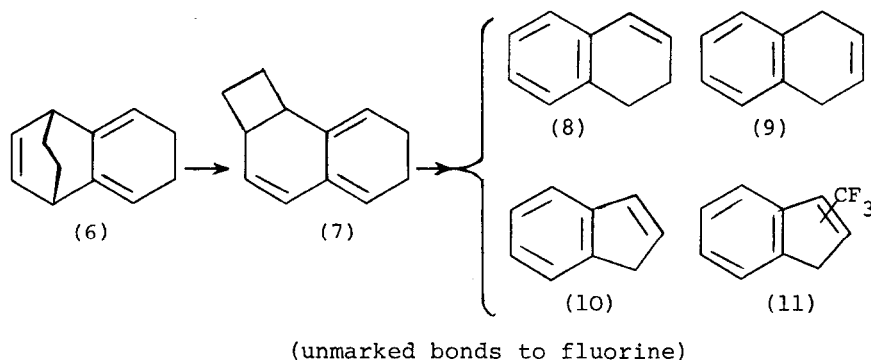
Scheme 2

correlation diagram for the cheletropic reaction involving the elimination of tetrafluoroethylene from (3) cannot be constructed, since there is no appropriate symmetry element, consideration of the HOMO/LUMO [11] interactions involved reveals that symmetry allowed mixing can occur and the proposed elimination is therefore symmetry allowed. Further reasons to anticipate the formation of isoindene were the observation that tetrafluoroisindole is significantly more stable than its non-fluorinated analogue [8], and the expectation that the isomerization of perfluoroisindene to perfluoroindene would be less easy than that of the analogous non-fluorinated system, involving as it must either a fluorine migration or a reorganization via an initial symmetry forbidden closure to a benzobicyclo[2,1,0]-pentene. The failure to detect perfluoroisindene (4) and the results of pyrolysis of 8H-undecafluorotricyclo[5,2,2,-0^{2,6}]undeca-2,5,8-triene (3a) (see below) bring the mechanism assuming initial extrusion of tetrafluoroethylene into question. When compound (3a) (Scheme 2) is pyrolysed it might be expected that the hydrogen in the six membered ring of the postulated primary product, the isoindene (4a), would be sufficiently remote from the site of the isomerization to have little or no effect on its course; if this were so, the expected product would be a 50:50 mixture of 5H- (5a)

and 6H-heptafluoroindene (5b), in practice a 20:80 ratio of these compounds is the product observed [12]. Attempts to detect intermediates in the pyrolysis of compounds (3) and (3a) were unsuccessful. We subsequently examined the pyrolysis of the closely related compound perfluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene (6) (Scheme 3) in the hope that the perfluorinated orthoxylylene derivative, perfluoro-2,3-dihydronaphthalene, which would be formed as the primary product of extrusion of the tetrafluoroethylene bridge might be more stable and consequently easier to isolate than perfluoroisoidene, we now report the results of this investigation.

RESULTS AND DISCUSSION

The preparation and some reactions of perfluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene (6) have been described previously [9,13,14], as have both the apparatus and technique of pyrolysis used in this work [9]. Pyrolysis of (6) at temperatures in the range 580° to 680° and a pressure at the exit of the pyrolysis apparatus of 10⁻³ mm. Hg gave mixtures from which tetrafluoroethylene and the compounds shown in Scheme 3 were isolated (see experimental section).



Scheme 3

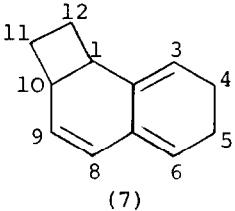
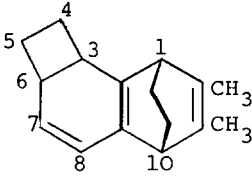
The relative concentrations of compounds (8), (9), (10) and (11) in the pyrolysis product over the temperature range

580° to 680° were constant within experimental error at 14:2:6:1 respectively; this observation was true whether the compound pyrolysed was (6) or (7). When (6) was pyrolysed (7) formed upto 30% of the product at 580° but its concentration decreased with increasing temperature and it was not present in the product in detectable amounts at 680°. The final products (8) → (11) were not appreciably inter-converted on re-pyrolysis at 680°; no other compounds were detected in the gas chromatographic analysis of the product of any pyrolysis experiment, and in all cases the mass balance was good (> 97%). The most likely explanation of these observations being that (7) is an intermediate on the route to (8), (9), (10) and (11).

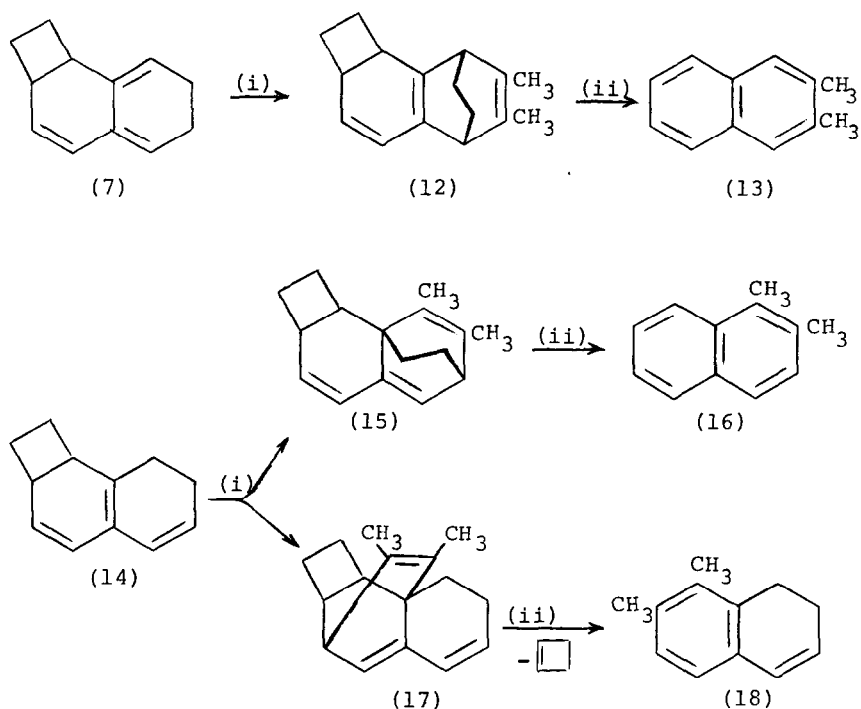
Compound (7) was identified as an isomer of (6) by mass spectroscopy and elemental analysis. The i.r. (bands at 1710 and 1645 cm^{-1}) and u.v. spectra were consistent with a system of conjugated double bonds but gave no indication of benzenoid aromaticity. The ^{19}F n.m.r. spectrum of (7) was complicated by coincidences of shifts and overlapping multiplets, but could be assigned (Table 1) as the sum of resonances arising from: two difluoromethylenes, coincident in shift; two difluoromethylenes, as separate AB systems ($J_{\text{AB}} \sim 220$ Hz), consistent with their being located in a cyclobutane ring [15]; four vinylic fluorines, two of which were mutually coupled with a coupling constant value, 57 Hz, typical of a 'peri' interaction [15]; and two tertiary fluorines, the shifts of which were rather low and similar to those recorded for perfluorobicyclo[4,2,0]oct-2-ene (187.6 and 198.0) [16]. These data are consistent with both (7) and the alternative (14) (Scheme 4), and a Diels-Alder reaction was carried out to distinguish between the two possibilities. As a consequence of the possible dispositions of the various bridges in adducts (12), (15) and (17), the expected products of 1:1 Diels-Alder addition between but-2-yne and either (7) or (14) would be mixtures. Fortunately, gross changes in the ^{19}F n.m.r. spectra on going from either (7) or (14) to the various possible 1:1 adducts serve to distinguish the isomeric trienes

TABLE 1

 ^{19}F N.m.r. Spectral Parameters^a for (7) and (12)

Compound ^b	Chemical shifts (ppm) (integrated intensity) coupling constants (Hz)	Assignment (Site of F atom)
 <p>(7)</p>	182.3(1)	Tertiary-F (1 or 10)
	185.4(1)	
	127.4(4)	-CF ₂ CF ₂ - (4 and 5)
	120.8(1)	-CF ₂ CF ₂ - (11 and 12)
	122.3(1)	
	125.6(1)	
	127.3(1)	
	129.0(1) d, J = 16	Vinylic-F (3)
	134.6(1)	Vinylic-F (6)
	117.6(1)	Vinylic-F (8)
	143.2(1)	Vinylic-F (9)
 <p>(12)</p>	205.5(1)	Tertiary-F (1)
	205.3(1) d, J = ~35	Tertiary-F (10)
	176.0(1)	Tertiary-F (3 or 6)
	189.7(1) dd, J = ~25, J = ~25	Tertiary-F (3 or 6)
	120.9(3)	-CF ₂ CF ₂ - (4, 5, 11 and 14)
	123.8(5)	
	151.1(1)	Vinylic-F (7)
124.0(1) d, J = ~35	Vinylic-F (8)	

^a Shifts w.r.t. external CFC1₃.^b Unmarked bonds to fluorine atoms, (7) neat, (12) a low melting solid was liquified by addition of one drop CHCl₃.



Key (i) Diels-Alder addition of $\text{CH}_3\text{C}\equiv\text{CCH}_3$; (ii) vacuum pyrolysis.

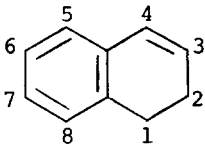
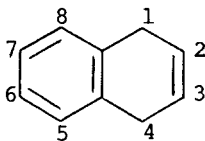
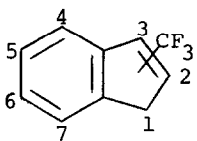
(unmarked bonds to fluorine)

Scheme 4

without recourse to a possibly complicated separation of isomers. Thus, in going from (7) to (12) two vinylic fluorine resonances will be lost and two new tertiary fluorine resonances will be found, as was in fact observed (Table 1); whereas in going from (14) to either (15) or (17) only one vinylic fluorine resonance will be replaced by a tertiary fluorine resonance. Further, pyrolysis of adduct (12) gave 2,3-dimethylhexafluoronaphthalene (13), a known compound [17]; neither (15) nor (17) could reasonably be expected to give (13) on pyrolysis, the former would be expected to give 1,2-dimethylhexafluoronaphthalene (16) and the latter 7,8-dimethyl-1,1,2,2,3,4,5,6-octafluorodihydro-

TABLE 2

 ^{19}F N.m.r. Spectral Parameters^a for (8), (9) and (11).

Compound ^b	Chemical shifts (ppm) (integrated intensities) coupling constants Hz	Assignment
 (8)	125.5 (2)	-CF ₂ - (2)
	117.1 (2)	
	135.7 (1)	Aromatic-F (8)
	138.5 (1)	
	140.6 (1)	Aromatic-F (6 and 7)
	146.2 (1)	
	148.3 (1)	
158.6 (1)		
 (9)	99.5 (4)	-CF ₂ - (1 and 4)
	137.2 (2)	Aromatic-F (5 and 8)
	147.7 (2)	Aromatic-F (6 and 7)
	155.5 (2)	Vinyllic-F (2 and 3)
 (11)	67.7 (3) (d,12)	CF ₃ - (3 or 2)
	117.3 (2)	-CF ₂ - (1)
	112.9 (1)	Vinyllic-F (2 or 3)
	145.5 (1)	Aromatic-F (4 or 7)
	147.7 (1)	Aromatic-F (7 or 4)
154.3 (2)	Aromatic-F (5 and 6)	

^a Shifts w.r.t. external CFCl₃.^b Unmarked bonds to fluorine atoms, (8) and (11) neat, (9) liquified by addition of one drop CHCl₃.

naphthalene (18). A detailed examination of the ^{19}F n.m.r. spectrum of (12) showed it to be a 50:50 mixture of the expected stereoisomers, the spectrum is complex and mostly unresolved but one of the tertiary resonances of the cyclobutane unit exists as a doublet of doublets (both $J = 25$ Hz), the analogous resonance in the starting triene (7) is a simple doublet ($J = 25$ Hz) and the observed signal is interpreted as arising from two overlapping signals from two closely related stereoisomers present in equal concentrations. Similar conclusions can be drawn from detailed examination of one of the tertiary fluorine resonances of the bicyclo-[2,2,2]octa-2,5-diene unit in (12); unfortunately we were unable to resolve the isomers on any of the gas chromatography columns available to us.

Three of the four final products of pyrolysis have been reported previously. The perfluorodihydronaphthalenes (8) and (9) have been described by Russian workers [18, 19 and 20] and, apart from some minor differences in the values of chemical shifts and coupling constants (our values in Table 2, literature values ref. 19), the spectroscopic data recorded by us is substantially in agreement with that published previously. Perfluoroindene (10) has been described by us [10].

Mass spectroscopy and elemental analysis identify (11) as an isomer of (8) and (9), the ^{19}F n.m.r. (Table 2) demonstrates the presence of trifluoromethyl and difluoromethylene units together with four aromatic fluorine resonances and a single low field fluorine suggesting a trifluoromethyl substituted indene. The presence of the indene skeleton is confirmed by the characteristic u.v. spectrum (Figure 1) and the remaining problem is that of assigning the site of the trifluoromethyl substituent as C-2 or C-3. The strong absorption in the infrared spectrum at 1695 cm.^{-1} ($-\text{CF}=\text{C}(\text{CF}_3)-$) as compared to 1754 cm.^{-1} ($-\text{CF}=\text{CF}-$) in perfluoroindene confirms that the substituent is on the double bond. The multiplicity of small couplings in this system results in a general broadening of all the ^{19}F n.m.r. resonances with the result that only one splitting

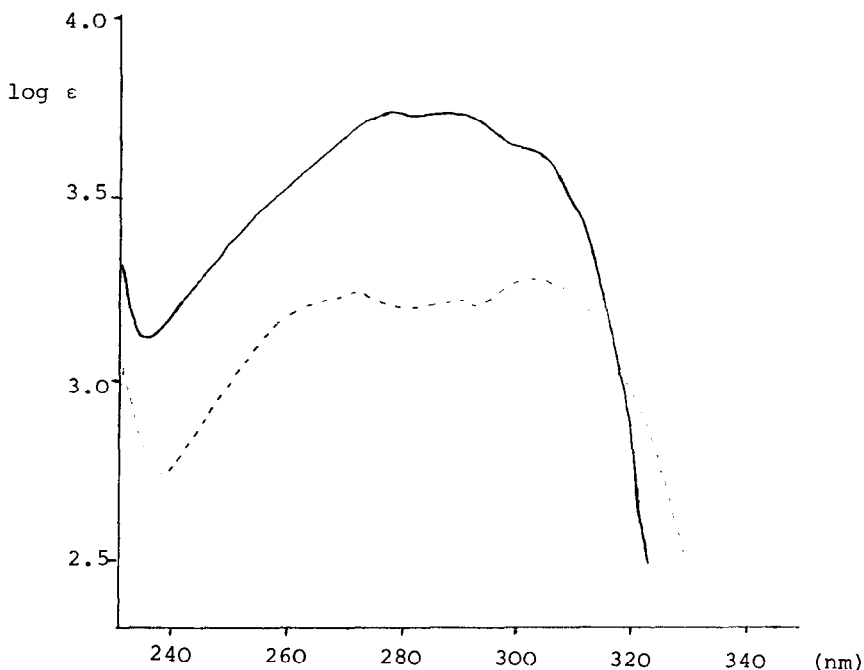
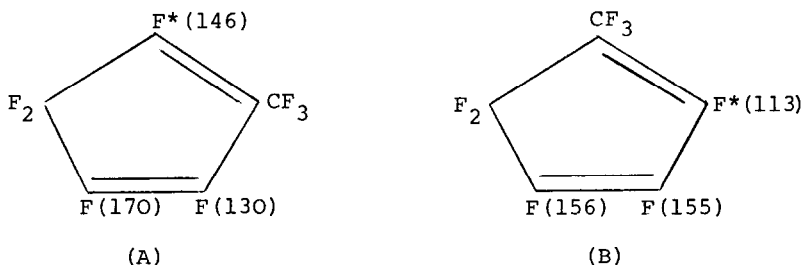


Figure 1. U.V. spectra of perfluoroindene (10) (-----) and perfluoromethylindene (11) (—).

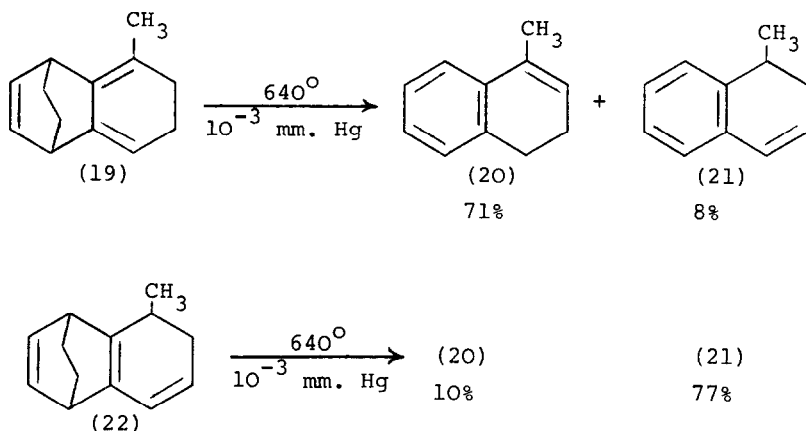
can be resolved; it also proves difficult to construct a convincing assignment based on the analysis of observed chemical shifts and substituent shift effects in closely related systems since the detailed assignments of the spectra of the relevant parent systems, namely perfluoroindene [21] and perfluorocyclopentadiene [22], remain uncertain. The assignment of the resonance at 112.9 (Table 2) as the vinyl fluorine is in agreement with the observed large downfield shifts for vinylic fluorines on trifluoromethylsubstituted double bonds in four [23], five [24,25] and six membered rings [26]. If an attempt is made to extrapolate from the data reported for the known perfluoromethylcyclopentadienes [25] it may be argued that a vinylic fluorine interposed between a difluoromethylene and vinylic trifluoromethyl does not experience a large downfield

shift (F^* in isomer A below) whereas when the vinylic fluorine and trifluoromethyl are interchanged a large downfield shift is observed (F^* in isomer B below), this



would favour assigning the substituent in (11) to C-2; other but essentially similar approaches to an analysis of substituent shift effects favour assigning (11) as perfluoro-2-methyl indene, however assignments based on such arguments can, at best, only be regarded as provisional. Never-the-less, the ^{19}F n.m.r. spectrum provided good evidence that (11) was either perfluoro-2-methylindene or the 3-isomer and not a mixture of both. An attempt to resolve the question by oxidative degradation failed and was not repeated for lack of material.

In the pyrolysis of (6) it is clear that fairly extensive reorganization occurs between the initial isomerization to (7) and the formation of the final products (8) \rightarrow (11) (Scheme 3). It was thought that an examination of the pyrolysis of related structures might provide an insight into the actual course of this reaction, to this end methyl substituted derivatives of triene (6) were prepared. Reaction of triene (6) with lithium methyl in diethyl ether gives a complex mixture of mono-, di- and tri-methyl substituted trienes. The separation and characterization of the components of this mixture is described elsewhere [27]. Sufficient of two monomethyl-trienes (19) and (22) was obtained to allow a study of their flash vacuum pyrolysis and the results are summarized on the following page (Scheme 5). The mass balance in both

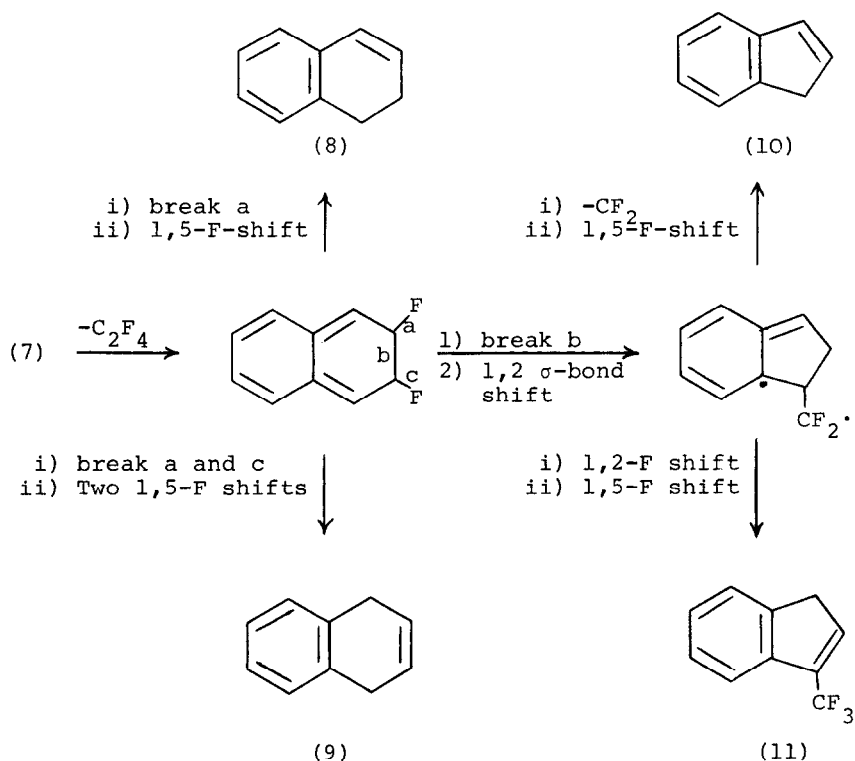
Scheme 5

cases was excellent ($\sim 100\%$), the materials not recorded in Scheme 5 being starting trienes; two trace products in each case (all four being identified as isomers of the starting monomethyl trienes (19) and (22) by gas chromatography/mass spectroscopy), and perfluoronaphthalene formed by elimination of methyl fluoride; as with the products of pyrolysis of (6), neither (20) nor (21) was appreciably interconverted on re-pyrolysis; however, by contrast with the pyrolysis of (6), no products of ring contraction or substituted 1,4-dihydronaphthalenes were detected, the absence of the latter is not unreasonable since such compounds might reasonably be expected to undergo a 1,4-elimination of methyl fluoride yielding perfluoronaphthalene. The structures of (20) and (21) are unambiguously assigned on the basis of elemental analysis, mass, infrared and ^{19}F n.m.r. spectroscopy; the diagnostic large $J_{\text{F}_4, \text{F}_5}$ and $J_{\text{F}_1, \text{F}_8}$ coupling constants observed in (8) make these assignments particularly straightforward and the spectroscopic details are reported elsewhere [27].

It is perhaps somewhat surprising, particularly in view of the previously reported successful isolations of

derivatives of orthoxylylenes [7,8], that no polyfluoro-2,3-dihydronaphthalenes were isolated in this work. The elimination of tetrafluoroethylene from (6), (19) and (22) is, in each case, a symmetry allowed process however the evidence suggests that in practice the tetrafluoroethylene bridge is not directly expelled but first undergoes an isomerization via a 1,3-migration of a sigma bond to yield an intermediate polyfluorotricyclo[8,2,0,^{2,7}]dodeca-triene (proved for the pyrolysis of (6), consistent with the evidence for the pyrolysis of (19) and (22)), the elimination of tetrafluoroethylene from these intermediates is then likely to be a non-concerted process and is accompanied by

pyrolysis of the methyl substituted derivatives (19) and (22) that the aromatic ring in the products derives from the bicyclo[2,2,2] units of the starting materials and consequently the isomerizations occur in what were initially the cyclohexadiene units of (6), (7), (19) and (22), such isomerizations can most easily be accommodated in terms of processes involving breaking of allylic carbon-fluorine or carbon-carbon bonds, with the former process predominating. Thus, if we assume that the eventual expulsion of tetrafluoroethylene from (7) (Scheme 3) leads to a structure on the reaction surface closely resembling perfluoro-2,3-dihydronaphthalene, then a series of isomerizations each involving an allylic bond cleavage at some stage allows a provisional rationalization of the outcome of the reaction to be constructed (Scheme 6). This scheme accounts for all the products of pyrolysis of (6) and (7) and suggests the trifluoromethyl group in (11) should be at C-3 rather than C-2. The formation of (20) as the major product in the pyrolysis of (19) (Scheme 5) can be accommodated by the rationalization advanced in Scheme 6, the fluorine migration in this case proceeding predominantly in the direction favouring formation of $-\text{CF}_2-$ (20) rather than $>\text{CFCH}_3$ (21) and an alkylated olefin (20) rather than a fluorine substituted one (21); However, the absence of ring contraction products remains a puzzle. Perhaps the



(unmarked bonds to fluorine)

Scheme 6

most surprising result of those reported here is the pyrolysis of (22), in this case a symmetry allowed expulsion of tetrafluoroethylene would lead directly to a stable aromatic product rather than the inherently reactive 2,3-dihydronaphthalenes expected as primary products from (6) and (19), nevertheless only 77% of the reaction proceeds by the expected route there being a substantial amount of isomerization involving fluorine migration.

CONCLUSIONS

The original aim of this work, the synthesis of perfluoro-2,3-dihydronaphthalene, was not achieved. The results reported add further examples to the list of reactions whose

outcome can be explained in terms of fluorine migrations [10, 25, 28-30]. The growing list of such reactions implies that fluorine shifts may well be relatively common and merit closer investigation, although alternative explanations have been advanced in some cases [31]. The compounds described here were not designed for an investigation of fluorine migrations and the complexity of their reactions makes them unsuitable for such a purpose, in future publications we shall describe studies of simpler and consequently less ambiguous systems.

EXPERIMENTAL

General.- Techniques and apparatus were as described previously [9, 13 and 14]. Perfluorotricyclo[6,2,2,0^{2,7}]-dodeca-2,6,9-triene [13, 14] was prepared as described previously.

Pyrolyses of Perfluorotricyclo[6,2,2,0^{2,7}]-dodeca-2,6,9-triene (6)

Using the apparatus described previously [9], triene (6) was pyrolysed at different temperatures and throughput rates, and a pressure at the exit of the pyrolysis apparatus of 10^{-3} mm. Hg. The product consisted of tetrafluoroethylene, identified by its infrared spectrum, and a liquid fraction which was analysed by gas chromatography (2-cyanoethylmethylsilicone (17%) on Chromosorb P, 100⁰, N₂ carrier, gas density balance detector). The components of the mixture were, in order of increasing retention time: (i) unreacted triene (6); perfluorotricyclo[8,2,0,0^{2,7}]-dodeca-2,6,8-triene (7); (iii) perfluoroindene (10); (iv) perfluoro-1,4-dihydronaphthalene (9); (v) perfluoro-2 or 3-methylindene (11); and (vi) perfluoro-1,2-dihydronaphthalene (8). The results of a series of runs are tabulated on the following page, the total mass balance for each run was better than 97%. Compounds (9) and (11) had

very similar gas chromatographic retention volumes and are presented together in the table; however from the shape of the overlapping peaks the constancy of the ratio of (9):(11) could be seen.

Run	Pyrolysis Rate (g. hr. ⁻¹)	Temp. (°C)	Product Composition (% by weight)				
			(6)	(7)	(8)	(9) + (11)	(10)
1	8	580	65.0	11.0	15.0	3.2	5.7
2	8	620	19.0	7.0	47.0	9.7	17.0
3	6	650	9.0	2.0	56.0	12.3	19.9
4	15	650	17.0	8.0	48.0	10.1	17.1
5	4	680	~1.0	0.0	63.0	13.2	22.4

The combined products from runs 1 to 5 were fractionally distilled (Fischer Spaltrohr-System, Column MMS 200) to give (i) perfluoroindene, b.p. 45°/10 mm., with correct i.r. spectrum; (ii) triene (6), b.p. 53°/10 mm.; (iii) a fraction b.r. 58-60°/10 mm. containing (9) (ca. 25%), (11) (ca. 25%) together with (6), (7) and (8); and (iv) a fraction b.r. 61-62°/10 mm. containing (10) (ca. 10%) and (8) (ca. 90%).

Fraction (iii) from the above distillation was separated by preparative gas chromatography (Perkin-Elmer F21, di-n-decylphthalate/Chromosorb P, 125°, N₂ carrier) to give: (a) perfluoro-1,4-dihydronaphthalene (9), ca. 0.2 g. (Found: F, 61.3%, M⁺, 310. Calculated for C₁₀F₁₀, F, 61.3%, M, 310), a colourless solid, m.p. 34° (lit.¹⁸ 30-31°); ν_{\max} 1770 (-CF=CF-), 1505 and 1535 cm.⁻¹ (fluorinated benzene ring); λ_{\max} 275 (1,700) and 270(s) nm (ϵ , 1600); and (b) perfluoro-2 or 3-methylindene (11), ca. 0.2 g., (Found, F, 61.2%, M⁺, 310), a colourless liquid; ν_{\max} 9695 (-CF=C(CF₃)-) and 1510 cm.⁻¹ (Fluorinated benzene ring); λ_{\max} 285 (5500), 275 (5400), 305(s) (4000) and 295(s) nm (ϵ -5000).

Fraction (iv) from the above distillation was separated by preparative gas chromatography (Varian Autoprep, di-n-decylphthalate/Chromosorb P, 150°, H₂ carrier) to give:

(c) perfluorotricyclo[8,2,0,0^{2,7}]dodeca-2,6,8-triene (7), ca. 1.5 g. (Found: F, 65.3%, M⁺, 410. C₁₂F₁₄ requires F, 64.9%, M, 410) a colourless liquid; ν_{\max} 1710 and 1645 cm.⁻¹; λ_{\max} 325 (200), 300 (800), 280 (1900), 250 (3000) and 230 nm (ϵ -7400); and (d) perfluoro-1,2-dihydronaphthalene (8), (Found: F, 61.5%, M⁺, 310. Calculated for C₁₀F₁₀: F, 61.3%, M⁺, 310) a colourless liquid, b.p. 168^o, ν_{\max} 1730 (-CF=CF-), 1522 and 1495 cm.⁻¹ (fluorinated benzene ring); λ_{\max} 260 (8300), 267(s) (7200), 293 (6300), 301(s) nm (ϵ -5300).

Pyrolysis of Perfluorotricyclo[8,2,0,0^{2,7}]dodeca-2,6,8-triene (7)

Triene (7) (0.054 g., 0.135 mmoles) was pyrolysed at 680^o/5 x 10⁻³ mm. Hg to give: (i) a gas fraction consisting of tetrafluoroethylene and traces of silicon tetrafluoride, by i.r.; and (ii) a liquid fraction shown by gas chromatographic analysis to consist of (8), (9), (10) and (11). The ratio of the products was 22:13:63 as (10):((9) + (11)): (8) respectively.

Pyrolysis of Compounds (8), (9) and (11)

Small quantities of (8), (9) and (11) were pyrolysed individually at 640^o/5 x 10⁻³ mm. Hg. Gas chromatographic analysis revealed that the products from (8) and (11) were unchanged starting materials, the product from pyrolysis of (9) contained ca. 1% of (8).

Diels-Alder Reaction of Perfluorotricyclo[8,2,0,0^{2,7}]dodeca-2,6,8-triene (7) with But-2-yne

A mixture of triene (7) (0.5 g., 1.22 mmoles) and but-2-yne (0.071 g., 1.29 mmoles) was sealed in vacuo in a Pyrex ampoule (70 ml.), which was heated at 120^o for 72 hrs. The contents of the ampoule appeared considerably charred but gas chromatographic analysis of the recovered volatile materials indicated a single component (ca. 80%) in addition to starting materials. The product was purified by preparative gas chromatography (Varian Autoprep, Silicone

oil (30%)/Chromosorb P, 150^o, H₂ carrier) to give: 11,12-dimethyl tetradecafluorotetracyclo[8,2,2,0^{3,6},0^{2,9}]tetradeca-2,7,11-trienes (12) (0.22 g., 0.47 mmoles, 39%), (Found: C, 41.3%; H, 1.5%; M⁺, 464. C₁₆H₆F₁₄ requires C, 41.4%; H, 1.3%; M, 464), a white solid m.r. 65-72^o, ν_{\max} 2940 (CH₃-), 1710 and 1620 (conjugated fluorinated diene) and 1680(w) cm.⁻¹ (-C(CH₃)=C(CH₃)-); and λ_{\max} 263 nm (4500).

Pyrolysis of 3-Methyltridecafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,6,9-triene (19).

Triene (19) (0.261 g., 0.65 mmoles) was pyrolysed, 640^o/10⁻³ mm. Hg, to give: (i) a gaseous fraction (0.60 mmoles), shown by i.r. and mass spectroscopy to consist primarily of tetrafluoroethylene with a trace of fluoromethane; and (ii) a liquid fraction (0.195 g.) which was shown by analytical gas chromatography (di-n-decylphthalate/Chromosorb P, He carrier, 150^o, coupled with a V.G. Micromass 12B) to consist of: (i) starting triene (19), ca. 6%; (ii) two isomers of (19), both ca. 7%; (iii) 1,1,2,2,3,5,6,7,8-nonafluoro-4-methyl-1,2-dihydronaphthalene (20), 71%; (iv) 1,2,2,3,4,5,6,7,8-nonafluoro-1-methyl-1,2-dihydronaphthalene (21), 8.1%; and (v) perfluoronaphthalene, ca. 2.0%.

Compounds (20) and (21) were separated from the liquid mixture by preparative gas chromatography and identified by their correct infrared spectra.

Pyrolysis of 6-Methyltridecafluorotricyclo[6,2,2,0^{2,7}]dodeca-2,3,9-triene (22)

Using the same procedure and conditions as above triene (22) (0.44 g., 1.08 mmoles) was pyrolysed to give: (i) a gaseous fraction (1.01 mmoles), consisting of tetrafluoroethylene containing a trace of fluoromethane; and (ii) a liquid fraction (0.339 g.) consisting of: (i) triene (22), ca. 4%; (ii) two isomers of (22), each ca. 3%; (iii) compound (20), 10%; (iv) compound (21), 77%; and (v)

perfluoronaphthalene, ca. 3%. Compounds (20) and (21) were isolated by preparative gas chromatography and identified by

Pyrolysis of 1,1,2,2,3,5,6,7,8-Nonafluoro-4-methyl-1,2-dihydronaphthalene (20) and 1,2,2,3,4,5,6,7,8-Nonafluoro-1-methyl-1,2-dihydronaphthalene

Compounds (20) and (21) were pyrolysed, $640^{\circ}/10^{-3}$ mm. Hg, and the product analysed by gas chromatography and i.r. spectroscopy. Compound (20) was recovered essentially (98%) unchanged, the residue of the mass balance consisting of a mixture of unidentified volatile compounds. Compound (21) was largely recovered (96%) unchanged, the residue of the mass balance consisted of perfluoronaphthalene and a number of unidentified volatile compounds.

ACKNOWLEDGEMENTS

We thank S.R.C. for a studentship (RRH), and Dr. R.S. Matthews for helpful discussion of some aspects of the n.m.r. spectroscopy reported.

REFERENCES

- 1 R.W. Hoffmann, *Ang. Chem. Int. Ed. Eng.*, (1971) 10, 529.
- 2 E.T. McBee, D.K. Smith and H.E. Ungnade, *J. Amer. Chem. Soc.*, (1955) 77, 387.
- 3 R.E. Banks, A.C. Harrison, R.N. Haszeldine and K.G. Orrell, *J. Chem. Soc. (C)*, (1967), 1608.
- 4 H.E. Ungnade and E.T. McBee, *Chem. Revs.*, (1958) 58, 249.
- 5 D.P. Callender, P.L. Coe, J.C. Tatlow and A.J. Uff, *Tetrahedron*, (1969) 25, 25.
- 6 S.J. Cristol and R. Caple, *J. Org. Chem.*, (1966) 31, 585.
- 7 V.E. Wiersum and W.J. Mijs, *J. Chem. Soc. Chem. Comms.*, (1972) 347.
- 8 J. Bornstein, D.E. Remy and J.E. Shields, *Tet. Lett.*, (1974) 4247.
- 9 W.J. Feast, R.R. Hughes and W.K.R. Musgrave, *J. Fluorine Chemistry*, (1977) 9, 271. Part VIII of a series, which summarizes earlier results.
- 10 W.J. Feast and W.E. Preston, *Tetrahedron*. (1972) 28, 2805.

- 11 Values for the coefficients of the π -M.O.s of orthoxylylene are available from, C.A. Coulson and A. Streitwieser, 'Dictionary of π -Electron Calculations', Pergamon Press (1965).
- 12 W.E. Preston, unpublished.
- 13 W.J. Feast, R.R. Hughes and W.K.R. Musgrave, J. Chem. Soc. Perkin I, (1977), 152.
- 14 W.J. Feast, W.K.R. Musgrave and W.E. Preston, J. Chem. Soc., Perkin I, (1972) 1527.
- 15 J.W. Emsley, J. Feeney and L.H. Sutcliffe 'High Resolution Nuclear Magnetic Resonance Spectroscopy', (1966), Volume 2, Pergamon Press.
- 16 L.P. Anderson, Ph.D. Thesis, Durham University (1969).
- 17 W.J. Feast, W.K.R. Musgrave and W.E. Preston, J. Chem. Soc., Perkin Trans. I, (1972) 1830.
- 18 V.D. Shteingarts, G.G. Yakobson and N.N. Vorozhtsov, Dok. Akad. Nauk. SSSR, (1966) 170, 6, 1348.
- 19 V.D. Shteingarts and B.G. Okseneko, Zh. Org. Khim., (1970) 6, 8, 1611 (English Translation 1623).
- 20 T.V. Chuikova and V.D. Shteingarts, Izv. Sib. Otdel. AN SSSR, (1973) (9)/Ser. Khim. Nauk. 4, 83.
- 21 R.S. Matthews - private communication.
- 22 R.E. Banks, A.C. Harrison, R.N. Haszeldine and K.G. Orrell, J. Chem. Soc. (C), (1967) 1608.
- 23 R.E. Banks, M.G. Barlow, W.R. Deem, R.N. Haszeldine and D.R. Taylor, J. Chem. Soc., (1966) 981.
- 24 J. Feeney, L.H. Sutcliffe and S.M. Walker, Trans. Faraday Soc., (1966) 62, 11, 2969.
- 25 G. Camaggi and F. Gozzo, J. Chem. Soc. (C), (1971) 925.
- 26 S.F. Campbell, A.G. Hudson, E.F. Mooney, A.E. Pedler, R. Stephens and K.N. Wood, Spectrochimica Acta, (1967) 28A, 2119
- 27 W.J. Feast, R.R. Hughes and W.K.R. Musgrave, in preparation; and R.R. Hughes, Ph.D. Thesis, Durham University (1975).
- 28 W.J. Feast, W.K.R. Musgrave and R.G. Weston, J. Chem. Soc. (C), (1971) 937.
- 29 W.J. Feast and W.E. Preston, J. Chem. Soc., Chem. Comm., (1974) 985.
- 30 A.N. Bell, R. Fields, R.N. Haszeldine and I. Kumadaki, J. Chem. Soc., Chem. Comm., (1975) 866.
- 31 F.J. Palensky and H.A. Morrison, J. Amer. Chem. Soc., (1977) 99, 3507.