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THE PHOTOCHEMICAL ISOMERIZATION OF SOME FLUORINATED POLYCYCLICPOLYENES

A POSSIBLE PHOTOCHEMICAL 1,5-SIGMATROPIC MIGRATION OF A FLUORINE ATOM

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Abstract—Irradiation of tetradecafluorotricyclo[$6,2,2,0^{2,7}$]-dodeca-2,6,9-triene (**4**) and dodecafluorotricyclo[$5,2,2,0^{2,6}$]-undeca-2,5,8-triene (**7**) in the vapour phase with UV light results in their isomerization to tetradecafluorotetracyclo-[$6,2,2,0^{2,7},0^{5,7}$]-dodeca-2,9-dienes (**5** and **6**) and dodecafluorotricyclo[$5,2,2,0^{2,6}$]-undeca-2,3,8-triene (**8**) respectively. The mechanisms of the isomerizations are discussed and it is concluded that **8** arises from **7** by way of a photochemical 1,5-sigmatropic migration of a fluorine atom. Vacuum pyrolysis of **7** and **8** gives perfluoroindene in a good yield.

THE PRIMARY PRODUCTS of the two symmetry allowed photochemical isomerizations of cyclohexa-1,3-diene are hexa-1,3,5-triene and bicyclo[2,2,0]hexene. In the absence of steric constraints the predominant mode of reaction observed in hydrocarbon cyclohexa-1,3-dienes and their derivatives is the electrocyclic ring opening leading initially to the triene which may then undergo further reactions giving rise to a variety of products.[1] We recently reported the photochemical isomerization of perfluorocyclohexa-1,3-diene (**2**).[2] When irradiated in the vapour phase this diene gives perfluorobicyclo[2,2,0]hexene (**1**) quantitatively; the absence of any products derived from the alternative electrocyclic ring opening to the triene (**3**) can be ascribed to the strengthening of the C5—C6 σ bond by fluorine substitution[3] and/or the well known aversion of fluorine for vinylic sites.[4]

We have recently synthesized two perfluoropolycyclic compounds which contain cyclic conjugated diene systems and studied their photochemical isomerization. Tetradecafluorotricyclo[$6,2,2,0^{2,7}$]dodeca-2,6,9-triene (**4**) and dodecafluorotricyclo[$5,2,2,0^{2,6}$]undeca-2,5,8-triene (**7**) were synthesized by dehydrofluoroination of the Diels–Alder adducts of perfluorocyclohexa-1,3-diene with 1H,2H-octafluorocyclohexene and 1H,2H-hexafluorocyclopentene respectively.[5]

When triene **4** was irradiated in the vapour phase with 2537 Å UV light the product consisted of a mixture of approximately equal amounts of the two isomers of tetradecafluorotetracyclo[$6,2,2,0^{2,7},0^{5,7}$]dodeca-2,9-diene (**5** and **6**). These isomers had very similar gas chromatographic retention times and were obtained pure in only small quantities after repetition of the separation cycle. The separated products were shown to be single components on analytical gas chromatography; they were characterized unambiguously by spectroscopy and vacuum pyrolysis to perfluoroindene. The mass spectra (Table 1) establish that **4**, **5** and **6** are isomeric, all three having the same parent and major fragment ions. However, a fragmentation sequence involving an early expulsion of :CF_2 can be detected in the spectra of **5** and **6** which is not present in the spectrum of **4**. Expulsion of :CF_2 from the parent leads to a fragment at *m/e* 360 present

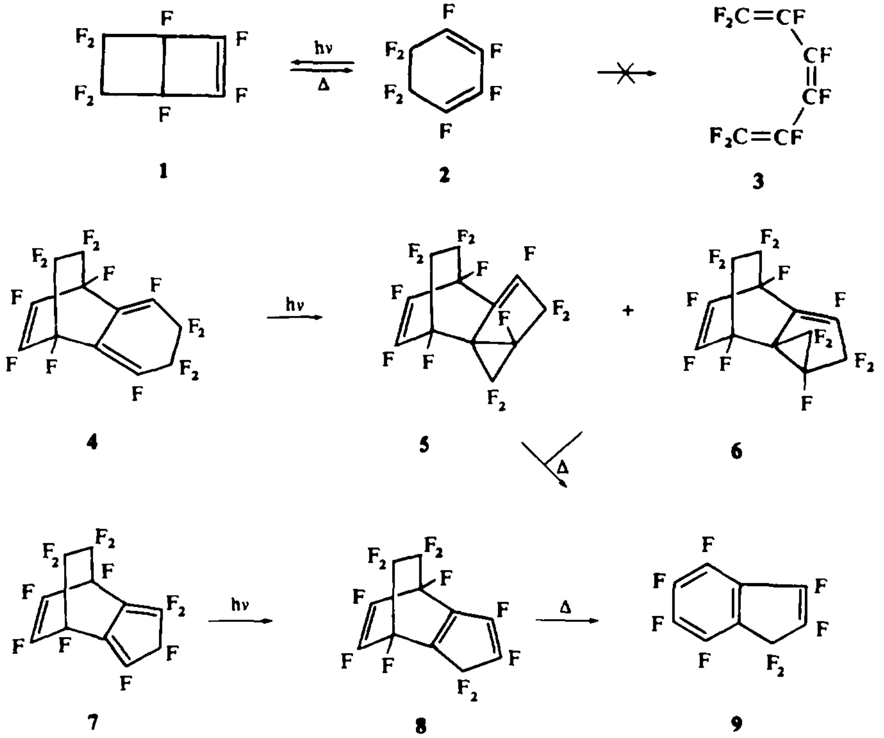


FIG 1

in **5** and **6** but absent from **4**; the greater abundance of the ion at *m*/*e* 341 in **5** and **6** as compared to **4**, and the presence of *m*/*e* 322 in **5** and **6** can be attributed to either an easy expulsion of :CF_2 from P-F and P-2F or successive losses of one fluorine from *m*/*e* 360. Similar consideration of the relative abundances of ions at *m*/*e* 310 and 260 are consistent with the presence of a CF_2 unit in **5** and **6** which is relatively easily expelled.

The ^{19}F NMR spectra (Table 2) of **5** and **6** proved conclusive in assigning their gross structure. The five structures listed in Table 2 have in common the bicyclo[2,2,2] unit (labelled α, Table 2) for which the recorded shift values for vinylic, tertiary and bridging —CF_2—CF_2— fluorines are in good agreement with the spectra of a large number of related compounds which contain this structural element.[6, 7] It has also been found that where the substituents on this structure are sufficiently different the bridging —CF_2—CF_2— unit may be split into separate signals for each difluoromethylene;[7] this occurs in the case of the photoisomers **5** and **6** giving a quartet (Integrated Intensity 2, J_{AB} 215 Hz) and a complex multiplet (Intensity 2) for one isomer and a system of two overlapping quartets (J_{AB} ~230) for the other; whereas for their symmetrical precursor (**4**) all the —CF_2— groups occur as one complex multiplet. The two other difluoromethylene units in the spectra of **5** and **6** appear as AB quartets, which from their chemical shifts and coupling constants can be assigned to a CF_2 in a five-membered ring and adjacent to a double bond (J_{AB} 274 and 273 Hz),[8] and a CF_2 in a three membered ring

TABLE 1. MASS SPECTRA[a]

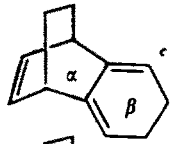
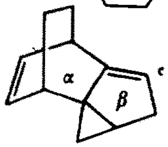
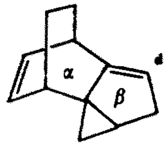
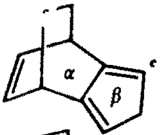
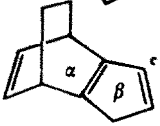
m/e		4	5	6	7	8	9
410	$C_{12}F_{14}$	9·4	1·2	2·7			
391	$C_{12}F_{13}$	4·0	2·4	2·5			
360	$C_{11}F_{12}$		0·9	1·2	18·0	11·3	
341	$C_{11}F_{11}$	4·7	10·1	7·5	2·5	4·7	
322	$C_{11}F_{10}$		4·0	2·8			
310	$C_{10}F_{10}$	45·0	26·9	28·7			
291	$C_{10}F_{9}$	19·0	18·9	15·5	11·8	10·0	
272	$C_{10}F_{8}$	9·9	9·9	16·8	4·9	6·0	
260	$C_{9}F_{8}$	11·0	21·7	19·9	100·0	100·0	64·0
241	$C_{9}F_{7}$	100·0	100·0	100·0	61·2	66·7	100·0
222	$C_{9}F_{6}$	4·0	4·6	4·9	3·1	4·7	
210	$C_{8}F_{6}$	5·3	11·1	10·0	21·2	27·3	43·7
203	$C_{9}F_{5}$	3·9			2·7	4·0	
191	$C_{8}F_{5}$				2·9	4·7	6·9
179	$C_{7}F_{5}$				2·2	4·7	
172	$C_{8}F_{4}$				2·2	4·0	
168					7·8		
160	$C_{7}F_{4}$				3·7	6·0	9·4
141	$C_{7}F_{3}$	4·7	9·1	7·3	8·6	12·0	20·0
122	$C_{7}F_{2}$					4·3	6·3
117	$C_{3}F_{4}$	4·8	9·3	7·7	8·5	8·0	8·1
100	$C_{2}F_{4}$				2·7	7·3	
93	$C_{3}F_{3}$	3·9	6·5	5·8	5·9	7·3	6·5
81	$C_{2}F_{3}$					4·0	
69	CF_{3}	3·9	7·6	6·6	3·9	6·0	

[a] Obtained on an M.S.9 Spectrometer (A.E.I.) operating at 70 eV and a source temperature of 200°. Spectra are tabulated by abundances measured w.r.t. the base peak taken as 100%.

(J_{AB} 173 and 176 Hz).[9] Further evidence for the assigned structures is that the tertiary fluorines of the bicyclic unit (α) are split into two separate signals for both **5** and **6** whereas in the symmetrical precursor (**4**) there is a single signal; also photoisomers **5** and **6** both have a third tertiary fluorine resonance discreet from these other signals and ascribable to the cyclopropyl fluorine.[9] Although there are significant differences between the NMR spectra of **5** and **6** it is not possible to make an unambiguous assignment of stereochemistry.

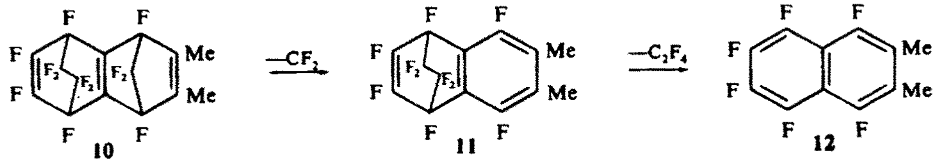
The IR spectra are compatible with the above assignments, in particular the absorptions in the double bond region; thus **4** shows three absorptions arising from the isolated double bond (1767 cm^{-1}) and the conjugated diene (1742 and 1703 cm^{-1}) whereas only two absorptions occur in the photoisomers, in one case a poorly resolved pair (1751 and 1747 cm^{-1}) and in the other two distinct peaks (1750 and 1738 cm^{-1}). Finally isomers **5** and **6** were subjected to vacuum pyrolysis. We hoped to isolate **7** by expulsion of the CF_2 unit from the three membered ring; however, in the event it was found that under comparatively mild conditions (340°/10^{-3} mm) isomers **5** and **6** were interconverted and under conditions where breakdown occurred both CF_2 and C_2F_4 units were expelled

TABLE 2. ^{19}F NMR SPECTRAL PARAMETERS[a]

Compound[b]	Tertiary F α	Tertiary F β	Vinylic F α	Vinylic F β	Difluoromethylene α	Difluoromethylene β
4  [c]	215·9(2)	—	152·4(2)	134·3(2)	129·2(4)[e]	129·2(4)[e]
5  [c]	214·5(1) 215·4(1)	229·6(1)	152·5(2)	131·5(1)	δ_A 125·0(1) δ_B 135·3(1) J_{AB} 215 133·0(2)	δ_A 105·4(1) δ_B 119·8(1) J_{AB} 274[f] δ'_A 143·4(1) δ'_B 150·3(1) J_{AB} 173[g]
6  [d]	213·4(1) 214·2(1)	229·9(1)	147·8(1) 148·5(1)	133·6(1)	δ_A ~ 110(1) δ_B ~ 133(1) J_{AB} ~ 230 δ'_A ~ 126(1) δ'_B ~ 132(1) J_{AB} ~ 230	δ_A 104·2(1) δ_B 124·2(1) J_{AB} 273[f] δ'_A 146·0(1) δ'_B 155·7(1) J_{AB} 176[g]
7  [c]	216·5(2)	—	152·8(2)	143·4(2)	δ_A 127·7(2) δ_B 129·5(2) J_{AB} 228[h]	δ_A 132·2(1) δ_B 139·2(1) J_{AB} 309
8  [c]	219·4(2)	—	154·9(1)[i] 156·0(1)[i]	151·5(1)[i] 152·4(1)[i]	133·2(4)[e]	δ_A 133·0 δ_B 137·6 J_{AB} 304

[a] Chemical shifts in p.p.m. upfield from external $CFCl_3$ (unless otherwise stated), integrated intensities in parentheses, coupling constants Hz; [b] unmarked valencies to F; [c] neat liquid; [d] solution in CCl_4 (internal $CFCl_3$); [e] complex multiplet; [f] five membered ring; [g] three membered ring; [h] pseudo AB; [i] assignment based on signal shape by analogy with related systems, vinylic F in α-rings are sharp singlets whereas in β-rings they are extensively coupled.

giving perfluoroindene (**9**). Insufficient material was available to optimize conditions for expulsion of only CF_2, although achieved with other systems; for example, 4,5-dimethyldodecafluorotetracyclo[6,2,2,1^{3,6},0^{2,7}]trideca-2,4,9-triene (**10**) gives a quantitative yield of the expected dimethyldecafluorobenzobicyclo[2,2,2]octa-2,5-diene (**11**) (expulsion of CF_2) under mild conditions and the dimethylhexafluoronaphthalene (**12**) (expulsion of CF_2 and C_2F_4 bridges) under vigorous conditions.[10]



10 **11** **12**

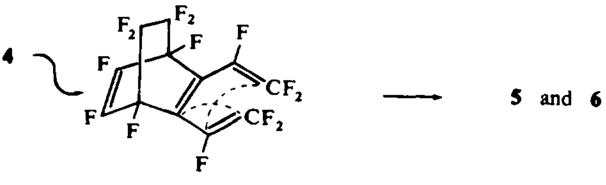
FIG 2

Vapour phase irradiation of **7** gave **8** as the only product. elemental analysis and mass spectroscopy (Table 1) confirm that **7** and **8** are isomeric. The ^{19}F NMR spectra (Table 2) showed that the symmetric triene **7** was isomerized to an unsymmetrical product since the single vinyl signals for α and β rings in **7** become split into two resonances for the two different vinyl fluorines in each ring of **8**. However, the chemical shifts, integrated intensities, and coupling constant for the AB quartet arising from the difluoromethylene in ring β, are in very close agreement as expected for compounds with the structural similarity of **7** and **8**. The IR spectra support this assignment; **7** shows absorption at 1765 cm^{-1} due to the isolated double bond, and peaks at 1755 and 1735 cm^{-1} for the diene system; the analogous absorptions for **8** occur at 1761, 1738 and 1629 cm^{-1} the low frequency peak being assigned to the double bond at the ring junction. The UV spectrum confirms the conjugated diene structure with peaks at 3050 Å (ε −1100) and 2770 Å (ε −2800) for **8** and **7** respectively. Vacuum pyrolysis of **7** and **8** resulted in expulsion of tetrafluoroethylene and gave perfluoroindene in good yield.

Perfluoroindene has previously been difficult to prepare. Pyrolytic defluorination of perfluoroperhydroindane giving only perfluoroindane[11] and pyrolysis of perfluorotricyclo[5,2,$0^{2,6}$]-deca-3,8-diene (i.e. the dimer of perfluorocyclopentadiene) over a metal surface gave predominantly perfluoroindane together with traces of material tentatively assigned as perfluoroindene.[12]

We are able to confirm that the product isolated by Banks *et al.* was predominantly perfluoroindene, thus our IR and mass spectral data are substantially the same as those reported, the ^{19}F NMR spectrum, elemental analysis and mode of synthesis confirming the assignment. The chemistry of this interesting aromatic is the subject of a separate publication.

The comparison of the course followed in the photochemical isomerizations of trienes **4** and **7** together with that previously reported for **2** leads to some interesting conclusions. Clearly the 'bond strengthening by fluorine substitution'[3] and 'aversion of fluorine for vinylic sites'[4] invoked to account for the isomerization of diene **2** are over-ruled in the case of triene **4** since the only route which can account for products **5** and **6** is an initial ring opening to tetraene **13** followed by a photochemical Diels–Alder reaction, i.e. the allowed $\pi 2s + \pi 4a$ addition.



13

FIG 3

Examination of molecular models clarifies the reasons for this difference in preferred mode of allowed isomerization of the analogous diene units in structures **2** and **4**; thus, during ring closure in **2** leading to **1** it is clear from models that the C—F sigma bonds at C-2 and C-3 describe an outward rotary motion which would be sterically impossible for the analogous sigma bonds in **4** and consequently rules out the 4π electrocyclic ring closure for the triene (**4**). This observation is relevant to the isomerization of **7**, for which two explanations may be postulated. An initial electrocyclic ring closure to structure **14** followed by a thermally allowed $\sigma 2s + \sigma 2a$ isomerization[13] (involving the bonds marked x of this highly strained intermediate) would seem a reasonable rationalization in the absence of the evidence from the isomerization of **4**; however, in the light of this evidence such a route seems unlikely. The only plausible alternative is a 1,5-sigmatropic migration of fluorine, as indicated in **15**.

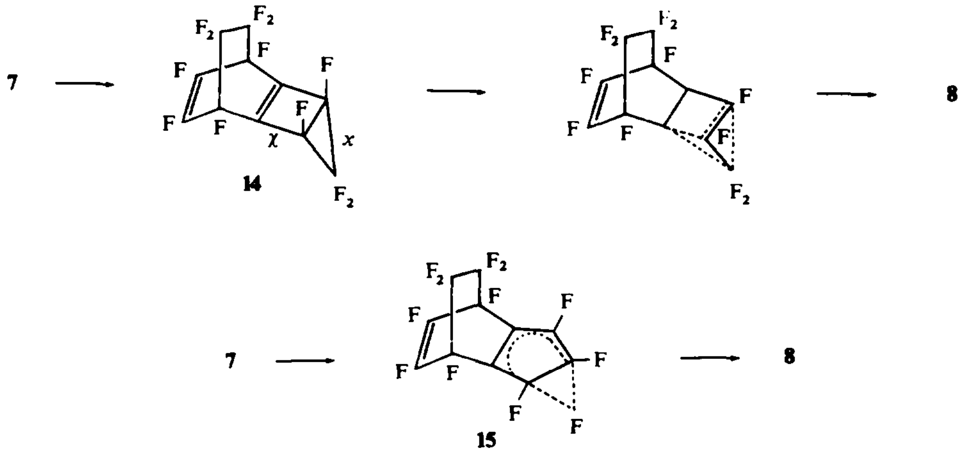


FIG 4

Orbital symmetry arguments become ambiguous when considering cyclopentadienyl systems, although attempts to resolve the ambiguity have been published,[14] since the two anti-bonding and two bonding orbitals of highest energy occur as degenerate pairs with different symmetry characteristics; however, INDO SCF MO calculations on the 1,5-suprafacial shift of a fluorine in hexafluorocyclopentadiene (taken as a model for this reaction) indicate a considerable energy barrier for the ground state isomerization whereas the excited state isomerization experiences no such energy barrier.[15] Since triene **7** was formed in a reaction run at 180° and was recovered unchanged after heating at 100° for 48 hr, we believe that the photochemical isomerization of **7** and **8** is best accounted for in terms of a 1,5-suprafacial sigmatropic fluorine migration. We are attempting to test the validity of this proposition by labelling experiments.

EXPERIMENTAL

Techniques and apparatus were as described previously[7] unless otherwise specified.

Irradiation of tetradecafluorotricyclo[6,2,2,0^{2,7}]*dodeca-2,6,9-triene* (**4**). The triene (**4**) (0·82 g, 2·0 mmoles) was introduced into a quartz ampoule 25 cm × 2·7 cm diam by vacuum transfer from phosphoric oxide. The top of the ampoule was connected *via* a graded seal to a pyrex constriction to enable it to be easily sealed under vacuum. The bottom 10 cm of the sealed ampoule was covered with opaque paper to shield the liquid and the vapour was irradiated (2537 Å lamps, Rayonet 208 photochemical reactor, 25°) for 120 hr. The volatile liquid recovered (0·69 g) was shown by analytical gas chromatography to consist of two components of very similar retention time in approximately equal proportions; each component was obtained pure by repeated prep GLC (1·1 cm diam. × 7·62 m; di-n-decylphthalate–Chromosorb P (1:4); N_2; at 48°) giving the two isomers of tetradecafluorotetracyclo[6,2,2,$0^{2,7}$,$0^{5,7}$]-dodeca-2,9-diene (**5** and **6**) (*ca.* 150 mg and 100 mg). (Found: F, 64·3. $C_{12}F_{14}$ requires F, 64·9% for the shorter retained isomer **5**).

Irradiation of dodecalfuorotricyclo[5,2,2,$0^{2,6}$]*undeca*-2,5,8-*triene* (**7**). Using the procedure for triene **4** triene **7** (2·28 g, 6·33 mmoles) was irradiated in the vapour phase for 160 hr, a volatile liquid (2·16 g) was recovered leaving a trace of a viscous brown oil in the ampoule. Prep GLC (0·95 cm diam × 4·5 m; di-n-decylphthalate—Chromosorb P (1:4); N_2; at 75°) separation gave (i) triene **4** (0·25 g), identified by IR spectrum and (ii) *dodecafluorotricyclo*[5,2,2,$0^{2,6}$]*undeca*-2,3,8-*triene* (**8**) (1·0 g). [Found: C, 36·4; F, 63·5; M (mass spectroscopy) 360. $C_{11}F_{12}$ requires C, 36·7; F, 63·3%; M, 360.]

Vacuum pyrolyses. The apparatus consisted of a silica tube (62 cm × 1·2 cm int. diam.) lightly packed with silica wool, the middle 45 cm were heated in an electric furnace, temperatures quoted were measured at the outside surface of the pyrolysis tube in the middle of the furnace by a chrome–alumel thermocouple. Samples to be pyrolysed were vacuum transferred through the hot zone, and collected in a glass trap cooled in liquid air.

(a) *Dodecafluorotricyclo*[5,2,2,$0^{2,6}$]*undeca*-2,5,8-*triene* (**7**). Triene **7** (12·0 g, 33·3 mmoles) was pyrolysed at 620°/10^{-3} mm and yielded (i) tetrafluoroethylene, identified by IR and mass spectra and (ii) a liquid (9·28 g) which was distilled to give a colourless liquid perfluoroindene (**9**) (7·25 g, 27·9 mmoles, 84%) b.p. 149°. [Found: C, 41·3; F, 58·1; M (mass spectroscopy), 260. C_9F_8 requires C, 41·6; F, 58·4%; M. 260]; the ^{19}F NMR showed six multiplets at 127·3 (2F), 141·3 (F), 148·2 (2F), 150·9 (F), 155·5 (F) and 162·0 (F) p.p.m. upfield from $CFCl_3$; the IR and mass spectra (Table 1) were substantially the same as reported previously.[12]

(b) *Dodecafluorotricyclo*[5,2,2,$0^{2,6}$]*undeca*-2,3,8-*triene* (**8**). Triene **8** (0·368 g, 1·02 mmoles) was pyrolysed at 540°/10^{-3} mm to give (i) tetrafluoroethylene and (ii) perfluoroindene (**9**) (0·231 g, 0·90 mmoles, 88%), with correct IR spectrum.

(c) *Tetradecafluorotetracyclo*[6,2,2,$0^{2,7}$,$0^{5,7}$]*dodeca*-2,9-*dienes* (**5**) *and* (**6**). (i) The isomer, (**5** or **6**), with the shorter retention time on analylitical gas chromatography (0·113 g) was pyrolised at 340°/10^{-3} mm, no gas was evolved and examination of the liquid product (0·110 g) by analytical GLC and IR spectroscopy showed it a mixture of isomers (**5** and **6**) in approximately 4:1 ratio with the material having the shorter gas chromatographic retention time predominating. This liquid mixture was repyrolysed 600°/10^{-3} to give a gas (discarded) and perfluoroindene (0·062 g) contaminated with an unidentified more volatile material (< 10%).

(ii) The isomer, (**5** or **6**), with the longer retention time on gas chromatography (0·057 g) was pyrolysed at 600°/10^{-3} mm to give a gas (discarded) and perfluoroindene (0·018 g) containing approximately the same proportion of the same impurity as the product of pyrolysis c(i).

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