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THE THERMAL ISOMERIZATION OF HEPTAFLUOROCYCLOHEXADIENES

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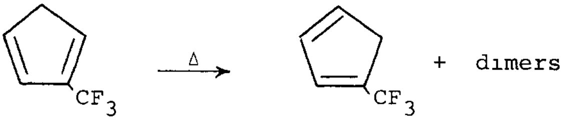
SUMMARY

The evidence for the involvement of sigmatropic fluorine migrations in the isomerizations of fluorinated polyenes is reviewed and the difficulties inherent in providing satisfactory rationalizations are discussed. The thermal isomerizations of heptafluorocyclohexadienes under various reaction conditions are described. It is established that such isomerizations occur by a mechanism which does not involve catalysis by fluoride ion, however the exact mechanistic pathway remains uncertain.

INTRODUCTION

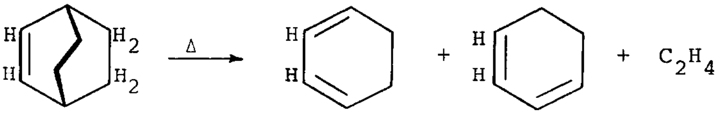
It has been known for many years that highly fluorinated cyclohexadienes undergo thermal isomerizations. The first workers in this field used a flow system incorporating an unpacked 'aged' nickel tube, it was established that at 450° octafluorocyclohexa-1,4-diene was isomerized to the -1,3-diene (40% conversion) and that at 260° 1H-heptafluorocyclohexa-1,3-diene gave a mixture of starting material and its isomers the 2H-1,3- and 1H-1,4-dienes in the proportions 6:1:4.5 respectively [1]. The isomerization of the two perfluorocyclohexadienes has been the subject of a more recent study which established that the 1,4-diene is slightly more stable than the 1,3-diene and that with rising temperature its relative stability decreases; thus, K = [1,3-diene]/[1,4-diene] has a value of 0.299 at 250° and 0.405 at 450° [2]. These equilibration studies were carried out in the presence of fluoride ion to reduce the time required for equilibrium to be reached and it seems likely that the interconversion involves a fluoride ion promoted process, similarly the "aged" nickel tube used in the initial studies [1] is consistent with a mechanism involving a fluoride ion initiated isomerization at a surface. In the diene equilibration study [2] it was reported that interconversion also occurs, albeit very slowly, in the absence of added fluoride ion and this allows alternative mechanistic rationalizations to be considered including schemes involving fluorine atom migrations. Several other reactions have been reported which could be rationalized in terms of the migration of a fluorine atom and some of these are briefly reviewed below.

Perfluoro-(2-methylcyclopentadiene) isomerized to perfluoro-(1-methylcyclopentadiene) when heated at 80° for two days (Scheme 1) [3].



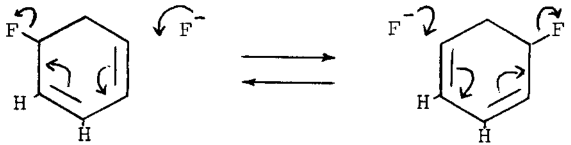
Scheme 1 (unmarked bonds to fluorine)

In an earlier report from this department it was shown that pyrolytic elimination of ethylene from 1,4,5,5,6,6-hexafluorobicyclo[2,2,2]oct-2-ene gave a mixture of 1H,2H- and 2H,3H-hexafluorocyclohexa-1,3-dienes rather than the 1H,2H-isomer exclusively (Scheme 2) [4]. Subsequently, it was shown



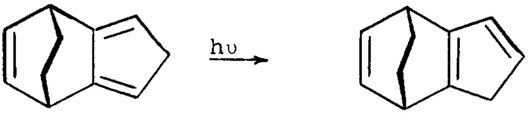
Scheme 2 (unmarked bonds to fluorine)

that either of the dihydrohexafluorocyclohexa-1,3-dienes was isomerized on pyrolysis to a mixture consisting predominantly of the two diene isomers shown in Scheme 2. It seems unlikely that this isomerization was catalysed by traces of fluoride ion, that is via the process indicated in Scheme 3, for two reasons; in the first place reaction conditions (flash pyrolysis, silica tube, low pressure) are unlikely to have resulted in the presence of significant quantities of fluoride ion and,



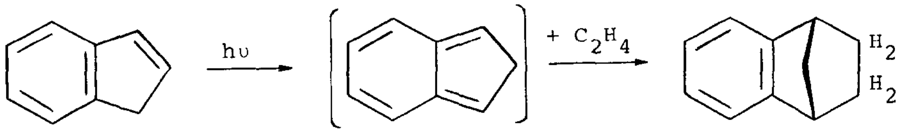
Scheme 3 (unmarked bonds to fluorine)

although the site of attack by F^- is not readily predicted for this system, it would seem likely that attack would be at both terminal and non-terminal diene carbons and would lead to a more complex mixture than the predominant 1,3-diene interconversion observed. In particular a fluoride ion promoted process would be expected (see later) to yield significant quantities of pentafluorobenzene. We have also shown, while investigating the chemistry of some fluorinated polycyclic polyenes, that dodecafluorotricyclo[5,2,2,0]-undeca-2,5,8-triene is isomerized photochemically to dodecafluorotricyclo-[5,2,2,0]-undeca-2,3,8-triene (Scheme 4) [5]. Vacuum pyrolysis



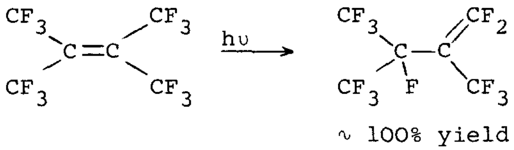
Scheme 4 (unmarked bonds to fluorine)

of the same triene yielded perfluoroindene. It was suggested that plausible explanations for both observations could be provided by a [1,5]sigmatropic migration of fluorine. Further work on perfluoroindene indicated that it was photochemically isomerized to perfluoroisoindene [6], the latter being postulated as an intermediate since irradiation of perfluoroindene in the presence of ethylene gives rise to the Diels-Alder adduct of perfluoroisoindene as shown in Scheme 5. This was considered, at that time, to be an unambiguous example of a sigmatropic fluorine shift. Haszeldine and co-workers have reported fluorine shifts when highly fluorinated olefines are



Scheme 5 (unmarked bonds to fluorine)

irradiated with ultra-violet light. For example, Scheme 6 shows the result of irradiating perfluoro-2,3-dimethylbut-2-ene for approximately seven days. No rearrangement was detectable in

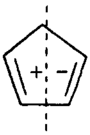


Scheme 6

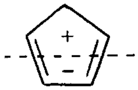
the dark at temperatures up to 300°C. It was suggested that this possibly represents a suprafacial [1,3] sigmatropic shift of fluorine, and it was stated that this would be symmetry allowed for the photochemically excited state [7].

The examples reported above can all be rationalized in terms of a process which involves the migration of a fluorine atom, although in some cases alternative rationalizations are possible, in particular fluoride ion catalysed isomerizations. Attempts to construct a straightforward theoretical rationalization for isomerizations apparently involving fluorine shifts, are frustrated by the fact that several of the systems for which observations are available involve cyclopentadienyl as the framework radical, and because of orbital degeneracy there is some ambiguity in defining the symmetries of the orbitals involved. A further complication exists in the nature of the migrating group in that the fluorine atom might conceivably use either one end of a p-atomic orbital or both ends. Anastassiou has discussed the question of establishing the cyclopentadienyl HOMO and LUMO symmetries [8], he contends that the expected distortion and degeneracy splitting will be accentuated by the presence of the migrating group and further suggests that the frontier orbital of interest can be identified on the basis of first order perturbational theory. This requires that splitting of a pair of degenerate molecular orbitals upon partial bond fixation (distortion) occur in such a way as to increase the energy of the molecular orbital with the largest number of nodes crossing formal double bonds, and to decrease the energy of the alternate molecular orbital. Thus for the two initially degenerate cyclopentadienyl molecular orbitals depicted below, this approach predicts that ψ_3 will move to higher energy than ψ_2, and consequently, for the cyclopentadienyl radical ψ_3 should be considered as the HOMO. However,

ψ_2

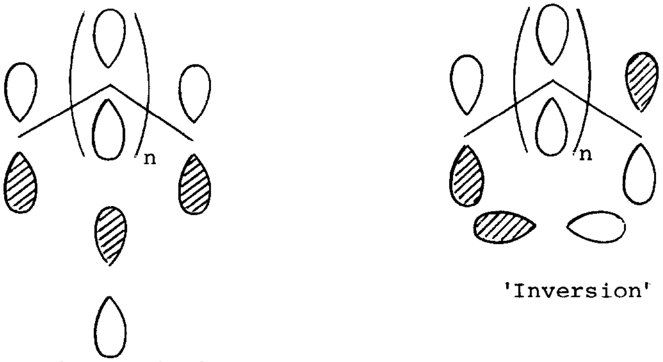


ψ_3



even if the ambiguity over which orbital of the framework radical is to be considered as the HOMO can be resolved in this way, there remains the ambiguity over how the migrating fluorine will interact with the relevant framework orbital. This latter point is illustrated below. In the situation where fluorine uses one face of a p-atomic orbital to interact with the framework orbital we have an analogy with migration of carbon with retention of configuration, and in the case where both ends of

Fluorine Migration Possibilities



Using one end of a p-lobe

'Retention'

Using both ends of p-lobes

'Inversion'

the p-atomic orbital are used in the interaction we have an analogy with inversion at a migrating carbon centre. These terms are used below, although of course, there is no stereochemical significance attached to them in the case of fluorine migrations. Further it should be noted that this simplistic approach ignores the question of whether the p-atomic orbital on fluorine is able to interact effectively with the termini as indicated; even assuming such interaction occurs, no account of the inevitable interactions between the filled orthogonal p-atomic orbitals on fluorine and the framework orbitals is included.

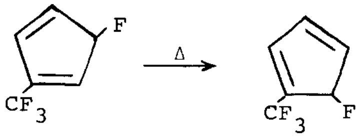
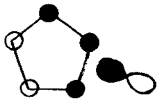
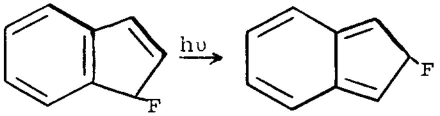
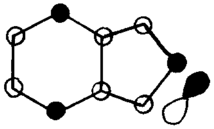
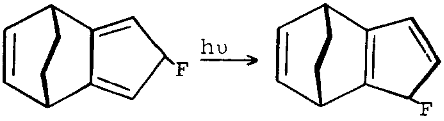
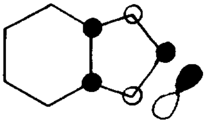
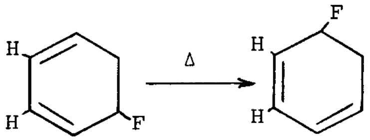
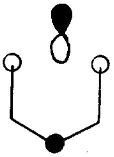
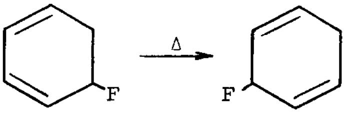
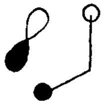
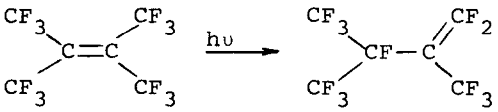
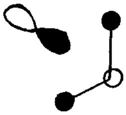
At this point, it seems appropriate to examine how the fluorine atom interacts with the framework radical in the previously reported fluorine isomerizations to see whether or not some pattern emerges with respect to 'retention' or 'inversion'. The results of previous investigations are summarized in Table 1.

It can be seen that the migration of the fluorine atom with respect to 'inversion' or 'retention' occurs in a seemingly random manner, although some reservations should be made about placing too much reliance on the cyclopentadienyl assignments. It would appear that earlier assertions were somewhat premature [6,7], and it seemed appropriate to attempt a detailed examination of the isomerization of cyclohexa-1,3-dienes, since in this case the ordering of the π-molecular orbitals in the framework radical is completely unambiguous. It might therefore be possible to establish whether the migrating fluorine atom displays a marked tendency to use one lobe or both lobes of the p-atomic orbitals. All of the above arguments presuppose a concerted migration process. If a systematic rationalization in terms of orbital symmetry control emerged from this work, the observations could be taken as evidence supporting a concerted (or nearly concerted) fluorine migration; however, the absence of a satisfactory theoretical rationalization in these terms would leave the mechanism of such migrations open to further question.

The system we chose to study was the monohydroheptafluorocyclohexa-1,3-dienes, since these are all relatively easily available, have quite distinct g.p.c. retention volumes, and

TABLE 1

(Unmarked bonds to fluorine)

Ref.	Reaction	Interaction of the fluorine atom with the framework radical
3	 [1,5] shift with 'retention'	 HOMO
6	 [1,5] shift with 'inversion'	 LUMO
5	 [1,5] shift with 'inversion'	 LUMO
4	 [1,5] shift with 'retention'	 HOMO
2	 [1,3] shift with 'inversion'	 HOMO
7	 [1,3] shift with 'retention'	 LUMO

mixtures could therefore be readily analysed. Furthermore, the likely products of reaction, other than those from isomerization, namely pentafluorobenzene and hexafluorobenzene (produced by defluorination and dehydrofluorination respectively), are also well known and characterized. The presence of the hydrogen atom allows one to detect isomerization processes and the early reports of Patrick et al. [1,2] and Weston [4] had already established that such processes do occur in analogous systems.

RESULTS AND DISCUSSION

The objectives of the work to be described were two-fold. In the first place it was expected, in the light of established results with closely analogous systems, that the heptafluorocyclohexadienes would interconvert thermally, hence to establish the interconversion pathways was the first objective. Secondly, it was important to establish whether we are observing a pure thermal isomerization or one involving another agent such as: a fluoride ion, a surface effect, or traces of hydrogen fluoride from the decomposition of the starting material. Having established the isomerization processes which occur and their relative ease, assuming there is more than one observed process, it was hoped a mechanistic rationalization might then be constructed.

Chromatographically pure samples of 1H- and 2H-heptafluorocyclohexa-1,3-diene and 1H-heptafluorocyclohexa-1,4-diene were obtained by established literature routes [9,10]. The first attempts to study their thermal isomerization were carried out by heating small amounts of thoroughly degassed dry samples of the respective isomers in small, carefully flamed out pyrex ampoules which had been sealed from a vacuum line. This approach proved to be unsuitable since under conditions severe enough to initiate any reaction there was always some decomposition of the starting diene, except in the case of the 1,4-isomer. Thus on opening the sealed tubes, after a period of heating, both of those originally containing the 1,3-diene isomers contained hydrogen fluoride. In the light of our stated objectives, the presence of hydrogen fluoride in the product invalidated this experiment and hence this approach was abandoned.

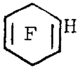
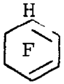
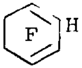
The next experimental procedure adopted was that of pyrolysis in a flow system. The apparatus used in these experiments consisted of a silica tube, 1.4 cm. int. diam. x 59 cm. lightly packed with silica wool to one end of which a pyrex reservoir containing the compound to be pyrolysed was attached, with a pyrex trap at the other end. Both reservoir and trap could be cooled in liquid air and all connections were through ground glass joints. The inlet to the reservoir was connected via a needle valve and a Dreschel bottle containing concentrated sulphuric acid to a nitrogen supply, and the outlet from the trap was connected to a vacuum system incorporating a mercury manometer. The middle 44 cm. of the silica tube was heated in a tubular electric furnace, the latter being insulated with a surrounding pyrex glass tube packed with Vermiculite. The temperature at the outer surface of the silica tube was measured using a Chromel-Alumel thermocouple. The sample to be pyrolysed was weighed into the reservoir, approximately 1 g of P_2O_5 was added, the reservoir was then connected to the pyrolysis apparatus and cooled in liquid air. The apparatus was evacuated (approximately 10^{-3} mm Hg) and the tarred trap was cooled in liquid air whilst the reservoir was allowed to warm up to room temperature. When all the material had evaporated from the reservoir the contents of the trap were allowed to reach atmospheric pressure, by bleeding in dry nitrogen, and then to warm up. Finally the trap was weighed and the contents analysed by g.l.c. (di-n-decyl phthalate/celite (1:2), 125^{o}, GDB detector). For pyrolyses carried out above a pressure of 10^{-3} mm dry nitrogen was bled into the system to the required pressure, the pressure being measured by the mercury manometer or Vacustat gauge at a point close to the outlet of the trap. The results are recorded in Table 2.

From these results certain generalizations can be drawn. When either 1H- or 2H-heptafluorocyclohexa-1,3-diene is pyrolysed in this manner the concentration of the other 1,3-diene isomer first increases and then decreases, in all cases, with rise in the pyrolysis temperature. The other compounds in

TABLE 2

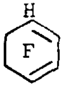
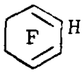
Analysis of products from flash pyrolysis

1H-heptafluorocyclohexa-1,3-diene

Pressure in mm.	Temp. °C	Weight loss in material %	Composition of product (percentages)										
										?	?	?	?
10^{-3}	550	6.5	Trace	0.7	5.7	69.1	13.4	1.0	9.1	Trace	0.8		0.2
	600	17.7	0.1	1.0	10.7	46.0	23.2	3.2	8.7	1.7	3.2	0.4	1.8
	650	17.2	0.6	2.2	18.7	33.6	17.0	6.9	10.5	0.3	5.4	2.0	2.5
	700	46.7	1.2	3.7	17.0	15.8	8.5	23.2	13.5	0.7	9.2	2.9	4.0
10^{-1}	550	10.9	0.1	0.5	6.4	69.6	10.4	1.1	6.5	0.3	3.3	0.8	1.0
	600	11.3	0.2	1.0	10.3	41.1	20.7	4.8	8.2	2.2	7.3	1.7	2.3
	650	14.2	0.4	1.6	17.8	32.6	18.9	6.5	8.0	0.9	8.9	2.6	1.7
	700	47.6	1.2	3.1	14.8	12.2	7.3	24.5	12.4	5.7	12.3	1.3	2.6
10^{1}	550	38.2	0.1	0.5	4.9	68.7	5.1	0.3	17.3	3.2			Trace
	600	42.3	0.2	0.6	5.9	55.0	13.7	0.9	13.9	9.6			0.3
	650	52.8	0.3	1.4	12.4	28.5	16.1	6.5	13.2	20.7			0.8
	700	62.7	0.6	2.6	17.7	21.0	11.7	14.0	12.0	14.8	3.5		2.1

2H-heptafluorocyclohexa-1,3-diene

Composition of product (percentages)

										?	?
10^{-3}	550	4.6			4.3	29.0	59.2	3.0	2.1	1.8	0.6
	600	16.5		0.2	7.7	40.1	38.1	6.2	2.8	3.3	1.7
	650	21.6	0.1	1.4	23.0	28.5	20.7	14.9	4.9	4.8	1.6
	700	42.6	0.3	3.8	19.2	13.1	9.2	35.4	12.8	6.3	
10^{-1}	550	12.9			2.6	23.6	69.1	1.1	1.7	2.0	Trace
	600	13.8		Trace	9.1	38.2	41.6	3.7	3.6	3.2	0.6
	650	24.0		0.5	18.7	30.2	24.6	9.7	7.3	6.9	2.2
	700	33.5	0.2	0.9	23.6	22.9	16.5	19.3	8.1	5.3	3.2
10^{1}	550	44.7			1.0	10.1	83.8	0.9	4.2		Trace
	600	48.3			4.3	28.8	59.7	2.4	2.2	2.2	0.5
	650	51.9			12.6	38.2	30.1	9.1	3.1	6.2	0.8
	700	59.3	0.1	0.7	18.2	28.5	18.8	16.6	6.1	7.5	3.6

1H-heptafluorocyclohexa-1,4-diene

10^{1}	700	65.6	0.5	1.7	18.4	12.8	6.6	28.6	11.6	18.1	1.7

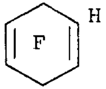
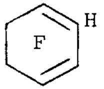
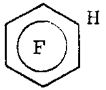
Increasing order of G.P.C. retention volume the product mixture, namely, 1H-heptafluorocyclohexa-1,4-diene, hexafluorobenzene and pentafluorobenzene also generally increase in concentration with temperature rise. On some occasions there were some relatively small quantities of higher molecular weight materials. Coupled gas chromatography mass spectrometric analyses of these mixtures indicated that these products corresponded to di and trimers of the starting material from which some hydrogen fluoride and/or fluorine had been eliminated; they were not present in appreciable amounts in all the experiments and have not been properly characterized, hence they are omitted from further consideration. The results of the experiments outlined above are consistent with the hypothesis that the first outcome of these pyrolyses is the interconversion of the two conjugated isomers. Under only marginally more severe conditions both of these are then further isomerized to the 1,4-diene and/or lose either hydrogen fluoride or fluorine to yield hexa- and penta-fluorobenzene respectively.

At this point, the question arises as to whether these observations were the result of a thermal isomerization of the diene or an alternative process. One clear candidate for the alternative process was a catalysed isomerization by the presence of adventitious traces of fluoride ion; this could arise from the decomposition of some pyrolysed material on the silica wool or tube walls. To examine this possibility the dienes were submitted to pyrolysis in a flow system over sodium fluoride. The experimental procedure was similar to that used before except sodium fluoride pellets replaced silica wool in the pyrolysis tube. The products from the pyrolysis of 1H-heptafluorocyclohexa-1,3-diene contained starting material, 1H-heptafluorocyclohexa-1,4-diene and pentafluorobenzene but no 2H-heptafluorocyclohexa-1,3-diene or perfluorobenzene. In all previous pyrolyses of the 1H-1,3-diene the 2H-isomer was a major component in the product, and the perfluorobenzene content, although small, rose significantly with rise in pyrolysis temperature. Thus the composition of the products from the pyrolysis over sodium fluoride pellets differs both qualitatively and quantitatively from those obtained in the pyrolysis over silica wool, and is strong evidence that the processes observed in the latter case were not initiated by traces of adventitious fluoride ion. However, the question of a surface effect still remains and to examine this the reactions were investigated in systems with a minimum surface area. The experimental technique involved sealing under vacuum, a small dry sample of 1H-perfluorocyclohexa-1,3-diene in a ten litre, essentially spherical, pyrex flask carrying a small side arm to allow vacuum transfer of starting diene and isomerization products. The vessel was then heated for a set period in a thermostated oven, the products were recovered and analysed by g.l.c., as before. The results of these experiments are shown in Table 3. Unfortunately, only a restricted series of experiments could be carried out using this technique since the only oven large enough to accommodate the ten litre flask was the glassblowers' annealing oven, and this was available on limited occasions only. Smaller flasks did not allow samples to be used of a size which would exert only a low pressure at the isomerization temperature and yet at the same time yield an amount of material sufficient for analysis by the available techniques. The results of these experiments supported the earlier conclusions drawn on the vacuum pyrolysis experiments in that the first process observed, and therefore the easiest accomplished, was the interconversions of the 1,3-isomers, subsequently, these isomerized to the 1,4-isomer. In this work no dehydrofluorinated product was detected and it seems possible that this reaction may be dependent upon surface effects. However small amounts of the defluorination product, pentafluorobenzene, were detected.

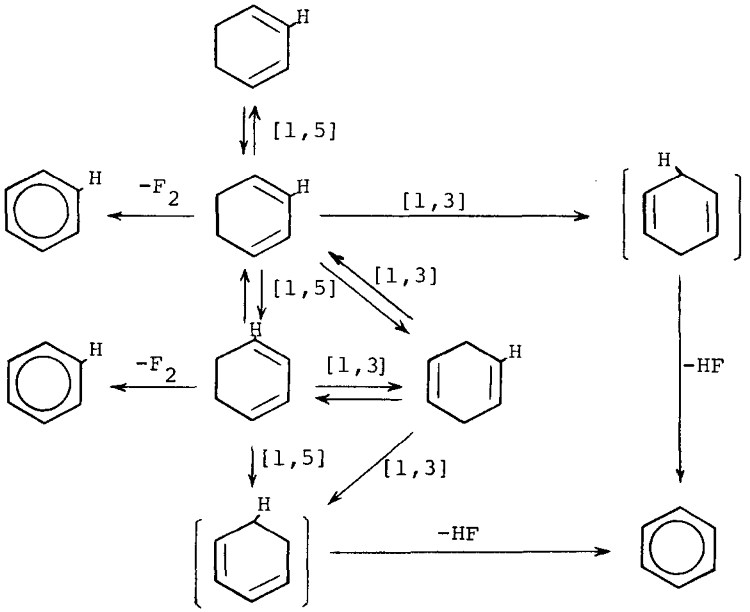
It is of particular interest to note, that the interconversion of the conjugated dienes occurs before their conversion to the non-conjugated isomer. The results of Patrick, referred to earlier [12], indicate that for the perfluorocyclohexadiene case the non-conjugated isomer is the most stable, and it seems quite likely that the heptafluorocyclohexadiene system will be more analogous to that of the perfluoro than to that of the hydrocarbon system, where the conjugated diene is the most stable.

TABLE 3

Analysis of products from the pyrolysis of 1H-heptafluorocyclohexa-1,3-diene at low pressure

Experiment	1	2	3	4	5	6	7	8
Volume bulb	10 1	10 1	10 1	10 1	10 1	10 1	10 1	10 1
Wt. material (g)	0.242	0.246	0.25	0.264	0.244	0.248	0.245	0.225
Pressure in mm. at temp. T^oC	3.46	4.41	4.83	5.16	4.82	4.90	4.99	4.58
T^oC	200	320	365	380	380	380	400	400
Time in hours	31	24	24	24	48	100	24	100
Analysis								
				2.3	4.5	20.0	7.4	
		NO REACTION		76.1	54.8	51.6	50.2	COMPLETE DECOMPOSITION
				21.6	35.1	21.5	36.0	
?					3.32	5.2		
					2.3	1.7	6.3	

The question to be considered at this point is whether or not these experimental results fit into a convenient theoretical rationale. In Scheme 7 the possible processes which may be occurring during thermolysis of the heptafluoro-1,3-diene system are summarized schematically, the structures shown in parenthesis have not been isolated.



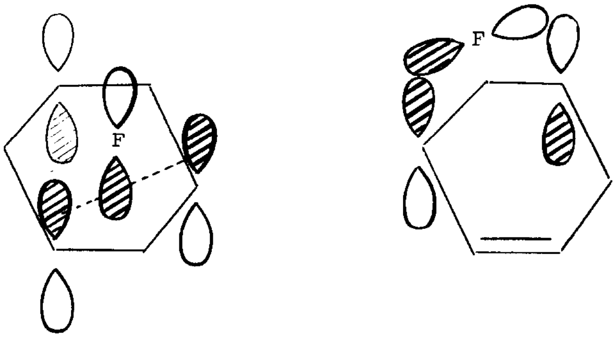
Scheme 7 (unmarked bonds to fluorine)

Since it has been shown that fluoride ion catalysed processes do not provide a satisfactory explanation of the thermal isomerization results, it seems reasonable to claim that this work establishes the following:

(i) Thermal isomerizations occur in the cyclohexadiene series which are most conveniently accounted for in terms of sigmatropic fluorine shifts.

(ii) The easiest process available is apparently that of a (1,5] shift followed by a [1,3] shift; of necessity, both of these processes must be suprafacial. Unfortunately, the difference in activation energy for the two processes cannot be estimated from these results, but it would appear that it is not large.

It is apparent that if the observed migrations are concerted, a shift in which the fluorine migrates with 'retention' is preferred over one involving 'inversion' at the fluorine, as shown below, although the degree of preference observed is not marked.



The work reported here leaves the overall picture no clearer since the previous cases where the framework radicals π-molecular orbitals ordering is unambiguous are both photochemical isomerizations [5,7], one of which would appear to favour retention and the other inversion. What does emerge from this work is that thermal isomerizations of cyclohexadienes do occur and by a mechanism which does not involve catalysis by fluoride ion at a surface. Whether the observed fluorine migrations are concerted sigmatropic shifts or whether alternative mechanisms involving discrete C-F bond homolysis or heterolysis and recombination of the resulting species occur cannot be ascertained. It will require more sophisticated studies to solve this particular problem.

REFERENCES

1 B. Gething, C.R. Patrick, J.C. Tatlow, R.E. Banks, A.K. Barbour and A.E. Tipping, Nature, 183 (1959) 586.

2 A.M. Doyle, C.R. Patrick and A.E. Pedlar, J. Electroanal. Chem., 33 (1971) 23.

3 G. Camaggi and F. Gozzo, J. Chem. Soc. (C), (1971) 925.

4 W.J. Feast, W.K.R. Musgrave and R.G. Weston, J. Chem. Soc. (C), (1971) 937.

5 W.J. Feast and W.E. Preston, Tetrahedron, 28 (1972) 2805.

6 W.J. Feast and W.E. Preston, J. Chem. Soc. Chem. Comm., (1974) 985.

7 A.N. Bell, R. Fields, R.N. Haszeldine and I. Kumadaki, J. Chem. Soc. Chem. Comm., (1975) 866.

8 A.G. Anastassiou, J. Chem. Soc. Chem. Comm., (1968) 15.

9 J.A. Godsell, M. Stacey and J.C. Tatlow, Tetrahedron, 2 (1958) 193.

10 R. Stephens, J.C. Tatlow and E.H. Wiseman, J. Chem. Soc., (1959) 148.