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THE SIGMATROPIC MIGRATION OF FLUORINE

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SUMMARY

Pyrolysis of polyfluorocyclohexadienes at 475-480°C over new quartz or Pyrex glass gave products derived from 1,5-sigmatropic migrations of fluorine; 1,3-migrations occurred to only a small degree. As the quartz or glass aged, other processes - 1,3-migrations and defluorinations to aromatics - began to occur; these appear to be due in some way to fluoride ion, since pyrolysis over sodium fluoride gave similar products.

INTRODUCTION

Although sigmatropic migrations of hydrogen and of carbon-centred groups are extremely well-known, there are only a few scattered reports on the related fluorine migrations; it appears [1] that fluorine behaves like hydrogen in preferring the 1,5-process (presumably suprafacial) to the 1,3 in thermal reactions; photochemical reactions are less clear-cut with both 1,5- and 1,3-fluorine migrations being reported [2]. The equilibration of polyfluorocyclohexa-1,3- and -1,4-dienes by heating [3] in aged metal tubes cannot really be classified as 'sigmatropic'. These reactions, which superficially involve 1,3 and perhaps 1,5 fluorine migrations, are very probably

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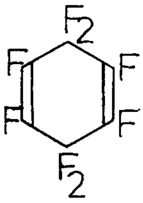
brought about by fluoride ion, itself produced by decomposition of the substrates by the metal. Fluoride ion induced 'migrations' are discussed in more detail later in this paper (see Schemes 4-6).

We now report a systematic study of the thermal sigmatropic migration of fluorine: the polyfluoroyclohexadienes I-V, available from the fluorination products of benzene over cobalt trifluoride [4], were employed for this purpose.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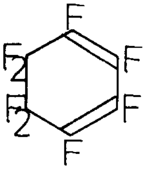
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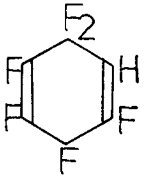
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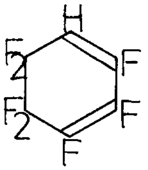
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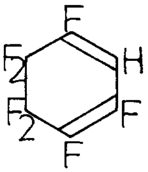
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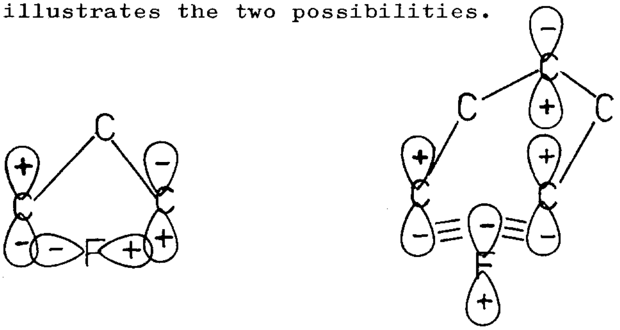
DISCUSSION AND RESULTS

The usual simple models of orbital symmetry conservation may be applied to fluorine migration. For example, the frontier orbital approach shows that, like carbon, fluorine could migrate 1,3 or 1,5. The 1,3-process requires 'inversion' and the 1,5 'retention', and the reactions may be envisaged as fluorine atom movements over allyl or pentadienyl radicals, with only the HOMO playing a significant role; Scheme 1 illustrates the two possibilities.

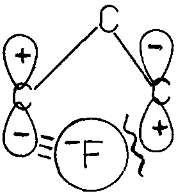


1,3-migration ('inversion')

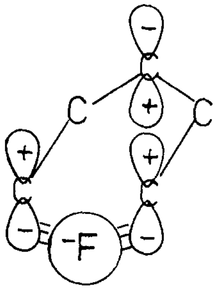
1,5-migration ('retention')

Scheme 1

This ignores the two lone pairs on fluorine and they could perturb this simple picture. It might be better, therefore, to regard the migration as one of a fluoride ion, which is of course spherically symmetrical, over an allyl or pentadienyl cation. Only a 1,5-suprafacial process is now allowed (Scheme 2): the required carbon skeleton orbital is now the LUMO.



1,3-suprafacial
(forbidden)



1,5-suprafacial
(allowed)

Our results bear this out (Table 1). Pyrolysis of the 1,4-dienes (I) and (III) at 475-480°C over new Pyrex glass or new quartz gives little if any reaction; 1,3-sigmatropic fluorine migrations would be required. On the other hand, similar treatment of the 1,3-dienes (IV) and (V) leads to considerable rearrangement; the 1,5-process is now possible and it strongly predominates over the 1,3. In the former, the dienes are converted into each other, and in the latter both give the 1,4-diene (III) (see Scheme 2.) The perfluorodiene (II) of course gives no observable reaction if 1,5-migration occurs, since this merely regenerates the diene (II).

At first sight, the presence of some 1,3-migration product in these reactions suggests that they are less specific than the corresponding hydrogen migrations, where only the 1,5-process has been observed [5]. This could be so, but it may not be. First, the 1,3-migrations might occur by the mechanism which intrudes as the quartz or glass ages (see later). Secondly, the ratio of 1,5- to 1,3-migrations - between 6:1 and 30:1 - translates into between 20:1 and 400:1 at 150-200°C, the temperature range in which hydrogen sigmatropic reactions are carried out; such small amounts of 1,3-hydrogen migration could possibly have escaped detection.

TABLE 1

Pyrolyses[a] in new[b] tubes

Starting Material	Tube[c]	Products[d]				
		I	II	III	IV	V
I	G	99.1	0.9			
II	G	1.2	97.4			
III	G			99.6	0.1	0.3
IV	G			2.6	73.4	23.8
V	G			6.3	34.3	59.2
I	Q	99.1	0.9			
II	Q	0.5	98.8			
III	Q			100		
IV	Q			0.9	69.9	29.1
I(47.7%) + II(52.3%)	Q	46.1	53.7			

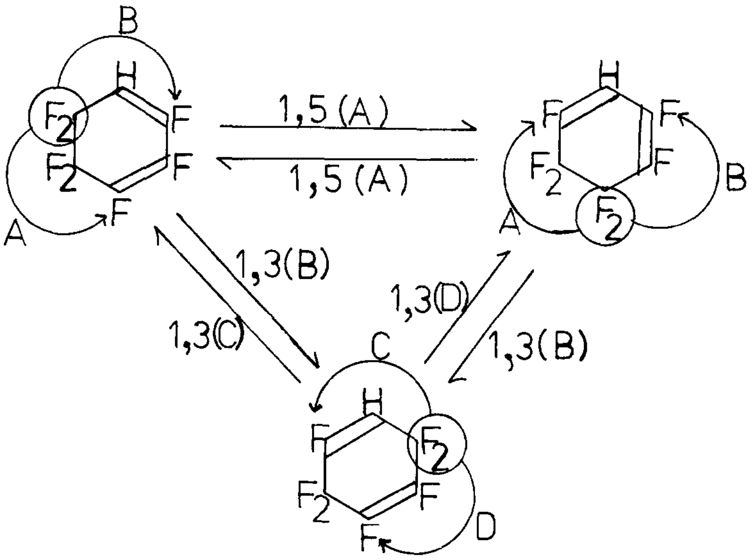
[a] At 475-480°C; input, 0.3g; recovery 0.13-0.14g. [b] Less than 20 pyrolyses. [c] G=Pyrex glass; Q=Quartz. [d] % Composition, determined from glc peak area ratio; in some cases very small quantities of short retained materials were observed.

TABLE 2

Pyrolyses[a] in old[b] tubes

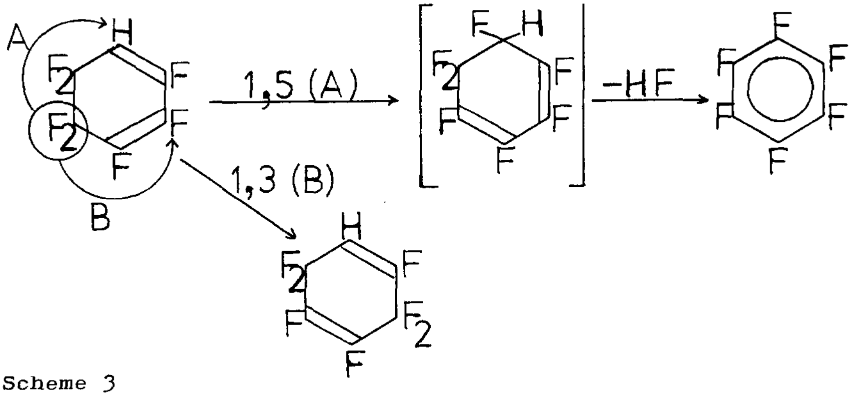
Starting Material	Tube[c]	Products[d]						
		I	II	III	IV	V	C_6F_6	C_6F_5H
II	G	2.4	96.9					
II[e]	G	4.6	86.0				8.0	
III	G			89.6	5.3	1.4		
IV	G			3.5	87.9	3.7		
IV[e]	G			10.9	44.9	22.1	0.5	21.5
I	Q	94.9	4.7					
II	Q	7.1	91.9					
III	Q			81.4	13.5	5.1		
III[e]	Q			40.5	24.4	22.9	2.0	9.2
IV	Q			27.3	60.2	9.9		

[a] At 475°C; input 0.3g; recovery 0.1-0.14g. [b] More than 20 pyrolyses. [c],[d] As Table 1. [e] The tubes used here had been aged much more than in other experiments, and a black deposit was clearly visible.



Scheme 2

A minor point arises concerning the regio-selectivity of the migrations. If the CF_2- groups which are not circled in Scheme 2 were the origin of the migrating fluorine, then products other than those observed would arise. Scheme 3 shows the possibilities for the 1,3-diene (IV).

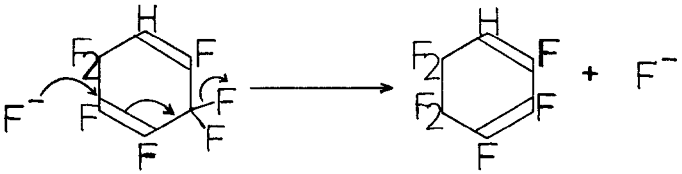


Scheme 3

Similar situations arise with the other dienes, and our <u>tentative</u> conclusions are that: (i) fluorine migrates most easily when it is on a CF_2-group adjacent to a hydrogen; and (ii) hydrogen-bearing carbon is not favoured as a migration terminus. We defer a full discussion on these points until we have carried out experiments which are better designed to explore them.

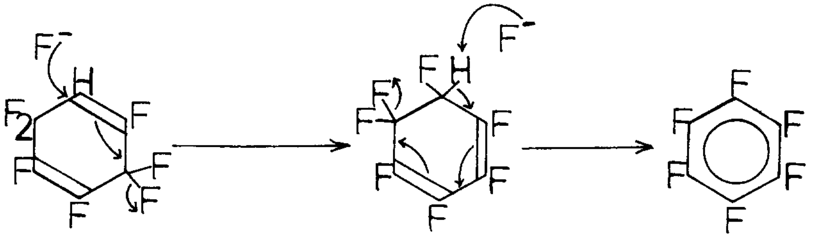
Our results are not as clear-cut as the foregoing discussion suggests. As the quartz and glass pyrolysis tubes 'aged' with use, the reactions, still at 475-480°C, became less selective, and what superficially appear to be 1,3-fluorine migrations took place to an increasing extent, in addition to the 1,5 migrations mentioned above (Table 2); the 1,4-dienes, for example, which had been unreactive in the new tubes - 1,5-migration being impossible - isomerised to some extent to 1,3-dienes. Still further aging brought about another reaction: aromatization. This mainly occurred by formal loss of F_2, and to a lesser extent by loss of HF (Table 2).

Both these reactions with 'aged' tubes - apparent 1,3-fluorine migrations and aromatization - also took place in a new Pyrex glass tube which contained some sodium fluoride pellets. It is therefore tempting to suppose that they were both brought about in some way by fluoride ion, which is somehow deposited on the surface of the tube and its packing by complete degradation of some of the diene starting materials (recoveries were in the range 40-50%). Fluoride ion catalysed 'migrations' are well-known in fluorine chemistry and can here be exemplified as shown in Scheme 4,



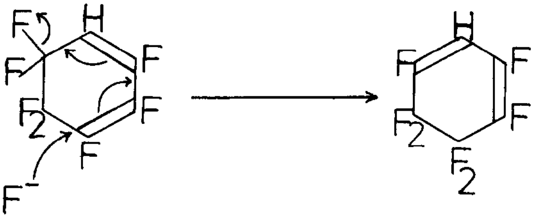
Scheme 4

that is, an apparent 1,3-fluorine migration. Octafluorocyclohexa-1,3-(II) and -1,4-(I)-diene have, in fact, been interconverted by extended heating with fluoride ion and the equilibrium constant has been determined[6]: similar pathways to those shown in Schemes 4-6 can obviously be drawn. Scheme 5 shows how attack at a hydrogen-bearing carbon could give rise to hexafluorobenzene, the minor aromatic product.



Scheme 5

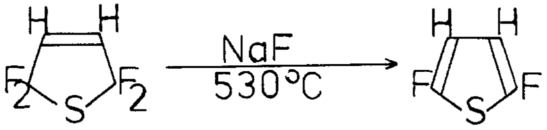
Fluoride ion could, of course, catalyse 1,5-rearrangements, and it probably does (Scheme 6).



Scheme 6

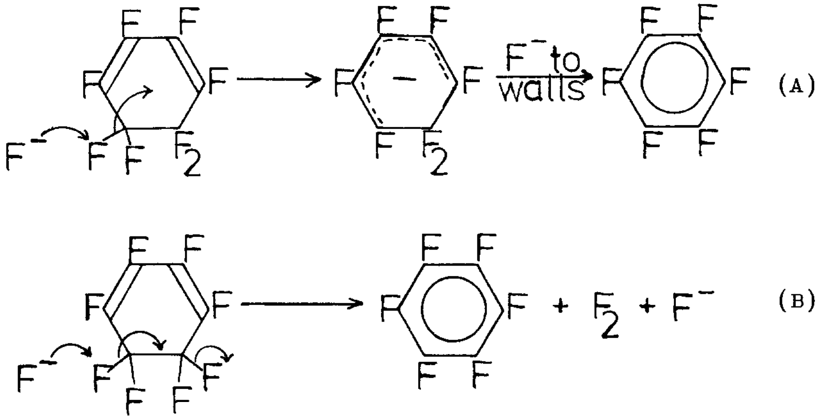
This can be dismissed as the explanation of the 1,5-migrations in the <u>new</u> tubes for two reasons: first, there is little, if any, fluoride ion in a new tube, and secondly, since fluoride ion certainly brings about apparent 1,3-migrations, these too would be observed in new tubes and they are not, or only to a small extent. Indeed, when they are observed in new tubes, this <u>could</u> be due to a very slight amount of fluoride ion deposited in the early stages of aging: if this is so then 1,5-migration is even more preferred over 1,3 than the figures in Table 1 suggest.

The other aging reaction, aromatization by apparent loss of F_2, is much more difficult to rationalize. It cannot be due to simple loss of fluorine or to disproportionation (diene + diene ⟶ mono-ene + aromatic); in connection with this, there may have been some mono-enes formed in the reactions which gave aromatics - there were one or two unidentified components with the correct glc retention times for mono-enes - but the quantities were much too small to allow disproportionation as a major mechanism. We have therefore to conclude, reluctantly, that aromatization is also brought about by fluoride ion. Indeed, there is an example in the literature [7] of aromatization brought about by fluoride; a polyfluorothiolen was converted into a difluorothiophen by passage over sodium fluoride at 530°C (Scheme 7). At that time, however, it was not thought that fluoride ion would function as an aromatizing agent, and the experiments were interpreted as showing thermal loss of molecular fluorine.



Scheme 7

Two possibilities are tentatively suggested for the aromatization (Scheme 8).



Scheme 8

(B) is essentially a one-step version of (A). Both proposals involve evolution of fluorine, but at the reaction temperature this would react with the Si-O bonds in the glass or quartz to give Si-F units.

Simple thermodynamic considerations (bond strengths, translational entropy) militate against the one-step process (B), but just about permit the two-step process (A).

It is possible to see, in outline, how fluoride ion might occur in the glass tubes: pyrolytic breakdown of the dienes could give carbonaceous material and fluoride ion, with the $K^+/Ca^{2+}/Al^{3+}$ ions in the glass providing the counter ion. It is difficult to see how anything analogous could occur in quartz; Si-F units are unlikely to be sources of F^-, and there are no counter ions available. After long aging, the tubes are black, so perhaps some C/Si or C- alone species can act as a repository of F^-, but this is not really a satisfactory explanation. Alternatively, of course, the aromatization in aged tubes may not be brought about by fluoride ion, but by some other species produced through aging, and the similarity of the reactions in aged tubes with those in sodium fluoride packed tubes may be co-incidental.

One unsatisfactory feature of all our reactions is the low recovery (40-50%): this must leave a small doubt as to the generality of our conclusions.

TABLE 3
Pyrolyses[a] over sodium fluoride/Pyrex glass

Starting Material	Products[b]						
	I	II	III	IV	V	C_6F_6	C_6F_5H
I	94.1	2.6				3.0	
II	3.0	94.1				2.7	
III			70.9	11.1	3.6	0.8	12.6
IV			6.4	67.2	16.2	0.2	3.1

[a] At 475° in a new Pyrex glass tube; input 0.2g; recovery 0.08-0.12g. [b] As d, Table 1.

EXPERIMENTAL

Apparatus

This consisted of a vertical tube (Pyrex, 1.0 cm int. dia. x 50 cm long; quartz 1.6 cm int. dia. x 70 cm long) packed with shards of Pyrex glass or quartz, or in the NaF experiments, a mixture of glass and NaF pellets. The inlet system was a pressure-equalised dropping funnel, and the outlet was via a cooled glass trap to atmosphere. The apparatus was connected to an N_2 supply via a flow-meter and a Dreschel bottle (conc. H_2SO_4). The central 45 cm of tube was heated by a furnace (to 475-480°C in all experiments), and temperatures were measured on the outside of the heated section by pyrometer.

Pyrolysis

A diene (0.2-0.3g) was placed in the inlet funnel and the whole system was flushed with N_2 (1 dm^3/h) for 30 min. before running the diene (1 drop/3 min) through the tube. When all the diene had entered the system, the N_2 flow was continued for 15 min before removal of the trap, warming to room temperature, and analysis (by relative glc peak areas; stationary phase, dinonylphthalate/Celite 1:3; temperature 85°C; flame ionization detection). The products (40-50% weight yields) were identified by glc retention time, and in a few cases, by separation, collection and infrared spectroscopy.

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