

Polyfluoroheterocyclic Compounds. Part XXIII.¹ Monoenes and Dienes Derived by the Fluorination of Hexafluorobenzene and of Perfluoro- and Chlorofluoro-heteroaromatic Compounds. A Mechanism for Fluorination by Cobalt Fluorides

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Hexafluorobenzene, pentafluoro-, 3- and 4-chlorotetrafluoro-, and 3,4- and 3,5-dichlorotrifluoro-pyridines have been fluorinated with a mixture of cobalt(III) and calcium fluorides. Reaction conditions can be adjusted so that hexafluorobenzene gives only octafluorocyclohexa-1,4-diene and decafluorocyclohexene. Pentafluoro-, 3-chloro-tetrafluoro-, and 3,5-dichlorotrifluoro-pyridines give only perhalogeno-1-azacyclohex-1-enes together with small amounts of acyclic aza-alkenes when fresh fluorinating agent is used. When there is a chlorine atom on position 4 of the ring system, cyclic dienes are also produced and may be the main products. If a much depleted fluorinating agent is used, pentafluoropyridine gives a trace of heptafluoro-1-azacyclohexa-1,3-diene. The latter can also be prepared from the 4-chloro- and 3,4-dichloro-cyclic aza-monoenes by dechlorination or by the action of fluoride ion on the 4-chloro-diene.

When tetrafluoropyrazine is fluorinated, the only product is hexafluoro-1,4-diazacyclohexa-1,3-diene.

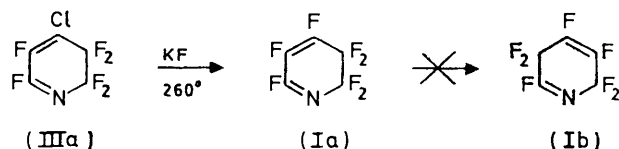
Calculations of the charge and spin densities on the atoms in the ring system at various stages in the fluorination have been made and a mechanism for the process involving, at each stage, the quenching of the first formed radical cation by fluoride ion and then by a fluorine atom, is suggested. The mechanism is supported by the isolation of a dimer from the fluorination of tetrafluoropyrimidine.

WE describe in this paper the results of the fluorination of hexafluorobenzene, pentafluoropyridine, and tetrafluorodiazabenzene by a mixture of cobalt trifluoride and calcium fluoride. This work was initiated with a view to producing fluorinated cyclic aza-alkenes and -alkadienes and to discovering a new route to octafluorocyclohexa-1,3- and -1,4-dienes but, as will be seen, the systems have also provided a valuable test of the possible mechanisms for fluorination by transition metal fluorides. We have carried out a theoretical feasibility study of these same mechanisms and it is now possible to propose a process for fluorination by transition metal fluorides which will embrace the results of both these approaches.

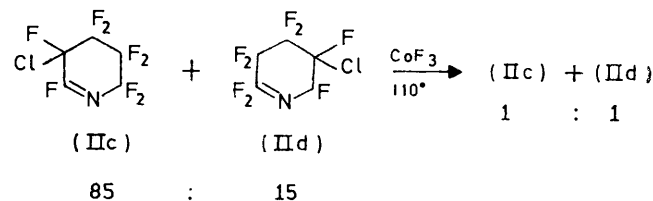
The fluorinations were carried out mainly at temperatures between 100 and 150 °C in a nickel reactor,² the reagent, stirred by a nickel paddle, being an intimate mixture of equal weights of calcium fluoride and cobalt trifluoride. Calcium fluoride was originally introduced to dilute the cobalt trifluoride and prevent the development of hot-spots but it is possible that several cycles in which the fluorinating agent was exhausted and regenerated may have resulted in its conversion into a complex calcium fluorocobaltate³ so that the exact composition of the fluorinating mixture is uncertain. Products obtained from typical experiments with hexafluorobenzene, pentafluoropyridine, and the chlorofluoropyridines are shown in Table 1.

Of the two possibilities (1,4- and 1,3-dienes), hexafluorobenzene gave exclusively the 1,4-diene, but the only case in which even a trace of a 1,4-diene was obtained from a perhalogenopyridine was in the fluorin-

ation of 4-chlorotetrafluoropyridine and it is possible that aza-1,3-dienes are generally isolated because of thermodynamic control. In the pyridine series the derived 1,3-dienes are demonstrably more stable thermodynamically than the 1,4-dienes: dehalogenation of 4-chloro-octafluoro-1-azacyclohex-1-ene (IIIc) over hot iron filings⁴ gave only heptafluoro-1-azacyclohex-1,3-diene (Ia). Similarly, dehalogenation of the mixture of



3,4- and 4,5-dichloroheptafluoro-1-azacyclohex-1-enes (IVc and d) by zinc⁵ gave only this same 1,3-diene (Ia). Nor did the heptafluoro-1-azacyclohex-1,3-diene (Ia) give, by isomerization, any trace of the 1,4-diene (Ib) on heating with caesium fluoride⁶ and, as would be expected from this, heating the 4-chloro-1,3-diene (IIIa) with potassium fluoride also gave only the perfluoro-1,3-diene (Ia) and none of the corresponding 1,4-diene (Ib). An



indication that equilibrium conditions may obtain in some of the reactions is illustrated by the equilibration of the azacycloalkene (IIc) with its isomer (IId). The same equilibration can be achieved by heating with caesium fluoride but not with calcium or cobalt(II)

¹ Part XXII, R. D. Chambers, R. P. Corbally, T. F. Holmes, and W. K. R. Musgrave, preceding paper.

² M. Stacey and J. C. Tatlow, 'Advances in Fluorine Chemistry,' vol. I, eds. M. Stacey, J. C. Tatlow and A. G. Sharpe, Butterworths, London, 1960, p. 166 and refs. therein.

³ J. C. Tatlow and R. G. Plevy, University of Birmingham, personal communication; A. J. Edwards, R. G. Plevy, I. J. Salomi, and J. C. Tatlow, *J.C.S. Chem. Comm.*, 1972, 1028.

⁴ P. L. Coe, C. R. Patrick, and J. C. Tatlow, *Tetrahedron*, 1960, 9, 240.

⁵ A. M. Lovelace, D. A. Rausch, and W. Postelnek, 'Aliphatic Fluorine Compounds,' Reinhold, New York 1958, p. 104.

⁶ J. A. Young, 'Fluorine Chemistry Reviews,' ed. P. Tarrant, Dekker, New York, 1967, p. 359.

fluoride. Fluoride ion-induced rearrangements of olefins are well known^{6,7} but we consider that, with cobalt trifluoride, the radical-cation process described later is more likely.

Fluorination of diazabenzene led to a contrasting and significant result. At 80 °C, tetrafluoropyrazine gave a

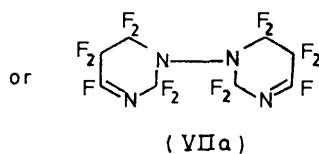
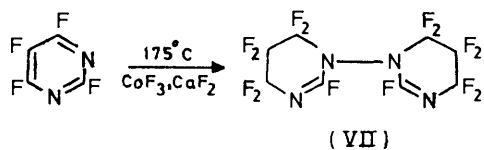
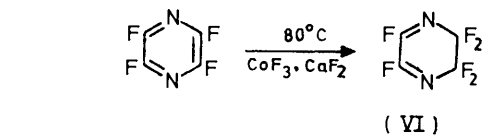
it is useful to emphasize the particular experimental observations which the proposed mechanism must accommodate. They are as follows: (a) in the products C=N is retained; (b) 1,3-dienes are obtained almost exclusively in preference to 1,4-dienes from the heterocyclic systems, whereas 1,4-dienes are preferred in the

TABLE I

Heterocycle (mmol)	Products (mmol)				
	(a)	(b)	(c)	(d)	(e)
					$\text{XCF}_2 \cdot \text{YCF} \cdot \text{ZCF} \cdot \text{CF} = \text{N} \cdot \text{CF}_3$
(I) {	X = Y = Z = F pentafluoropyridine (17.7) pentafluoropyridine (77.2) *	(Ia) (1.7)		(Ic) (11.1) (Ic) (47.4)	(Ie) (1.7)
(II) {	X = Cl, Y = Z = F 3-chlorotetrafluoropyridine (86.2)			(IIc) and (IIId) (30.2)	(IIe) (26.4)
(III) {	X = Z = F, Y = Cl 4-chlorotetrafluoropyridine (79.6)	(IIIa) (35.8)	(IIIb) (1.8)	(IIIc) (9.6)	
(IV) {	X = Y = Cl, Z = F 3,4-dichlorotrifluoropyridine (74.3)	(IVa) (12.1)		(IVc) and (IVd) (21.6)	(IVe) (5.2)
(V) {	X = Z = Cl, Y = F 3,5-dichlorotrifluoropyridine (79.2)			(Vc) (28.8)	(Ve) (10.6)
Homocycle					
hexafluorobenzene (26.0) at 50 °C	(0)	(6.7)	(11.4)	(0)	

* Using a much depleted fluorinating agent. No attempt has been made to investigate the structural isomerism of the heterocyclic ring compounds.

40% conversion into perfluoro-1,4-diazacyclohexa-1,3-diene (VI); tetrafluoropyrimidine was considerably less reactive. However, at 175 °C tetrafluoropyrimidine was

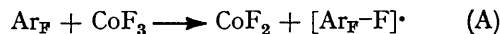


converted into a dimer [(VII) or (VIIa)], together with some by-products. The bulk of spectroscopic evidence suggests (VII) rather than (VIIa). No identifiable product was obtained from reactions with tetrafluoropyrimidine.

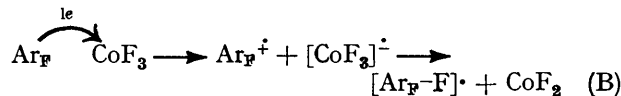
Before we attempt to rationalize these various results,

products from fluorinated benzenes;² (c) the position of chlorine in chlorofluoropyridines is important since chlorine at the 4-position leads to considerably more diene in the product; (d) formation of a dimer (VII) from tetrafluoropyrimidine is *compelling evidence for the intermediacy of radicals*, with coupling occurring exclusively through nitrogen; and (e) isomeric azacycloalkenes can be equilibrated under the conditions of the reactions.

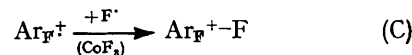
We may consider the formation of radicals by either of two processes: (A) direct fluorine atom transfer, or



(B) formation of a radical cation, followed by transfer of



fluoride ion. Once the radical cation is formed, a further possibility is fluorine atom transfer (C). It

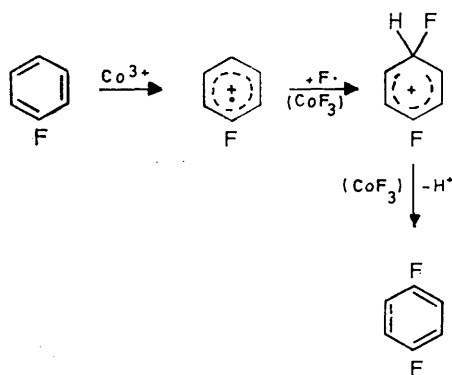


should be emphasized that the net result of both steps in (B) is fluorine atom transfer, as in (A) and, in fact,

² P. H. Ogden and R. A. Mitsch, *J. Amer. Chem. Soc.*, **1967**, **89**, 5007.

processes (A) and (B) represent extremes of a possible mechanism belonging to the same manifold. Although some of the subsequent species involved are common to both pathways, important differences may still arise, depending on where, between (A) and (B), the mechanism lies.

The intermediacy of radical cations in fluorination processes was suggested first by Filler and his co-workers⁸ in relation to fluorinations involving xenon difluoride, and has subsequently been advanced by Burdon, Parsons, and Tatlow⁹ to account for reactions involving cobalt trifluoride. It was also proposed⁹ that fluorine atom transfer from cobalt trifluoride to the radical cation occurs, and this particular sequence was pursued in order to relate the formation of *p*-difluorobenzene in cobalt trifluoride reactions to electrophilic aromatic substitution (Scheme 1).



SCHEME 1

In order to shed some light on the possible mechanisms for these reactions we have performed a crude theoretical analysis of some of the major features of the relevant reaction pathways. Since, however, we are only interested in interpreting relative reactivities, some of the simplifying approximations which are necessary to carry out any sort of theoretical analysis are not quite as severe as might otherwise have been the case. All-valence-electron SCFMO calculations have therefore been carried out in the CNDO/2 formalism.

Theoretical Considerations.—In future publications the theoretical basis of proposed mechanisms for fluorination of hydrocarbon and lightly fluorinated aromatic and heteroaromatic compounds by both high valency metal fluorides and hydrogen-fluoride-catalysed xenon difluoride reactions will be examined in some detail. We content ourselves here with a discussion of possible mechanisms for fluorination of perhalogenopyridines by high valency metal fluorides to produce perhalogenoazacyclo-hexenes and -hexadienes. The further reaction involving ring fission will also be discussed at a later stage.

Although it is convenient in performing a theoretical analysis to analyse the mechanisms in terms of discrete

⁸ M. J. Shaw, H. H. Hyman, and R. Filler, *J. Amer. Chem. Soc.*, 1969, **91**, 1563; *J. Org. Chem.*, 1971, **36**, 2917.

⁹ J. Burdon, I. W. Parsons, and J. C. Tatlow, *Tetrahedron*, 1972, **28**, 43.

steps, it seems probable that the electron transfer and the transfer of fluorine atom (C), or fluoride ion (B), between aromatic or heteroaromatic system and lattice is concerted. There is a whole spectrum of possibilities; however the major part of our discussion envisages that electron transfer is well developed before fluorine atom or fluoride ion transfer becomes important. In the case of fluoride ion addition one can argue that this must be the case since CoF_3 itself is a poor fluoride ion source whereas electron transfer to cobalt should considerably enhance the facility for fluoride ion transfer.

[Standard geometries¹⁰ have been used as follows. For the discussion of the radical cations and derived hexadienyl cations for perfluorobenzene and the halogenopyridines the ring geometries used were those appropriate to the parent ring systems with C-F and C-Cl bond distances taken as 1.33 and 1.70 Å, respectively. For the hexadienyl species the F-C-F angles at the site of substitution were taken to be $109^\circ 28'$ with the plane bisecting the internal angle. In the reaction sequence involving the dienes the ring geometry was taken to be that for the appropriate diene derived from standard tables,¹⁰ and the substituted species was treated in a similar manner to that described for the hexadienyl species.]

(1) *Production of radical cations.* In this particular section of the work we have investigated in detail perfluoropyridine and, for comparison, perfluorobenzene. In the flow systems employed, the reactions obviously take place at the gas-solid interface and it is of interest to consider the energetics of the initial processes. For both molecules the lowest ionization potential corresponds to removal of a π -electron. For the isolated molecules this process is *endothermic* to ca. 230 kcal mol⁻¹ (10 eV)¹¹ and it is clear therefore that for the initial steps (B) or (C) to be energetically feasible extensive interaction must occur at the gas-solid interface. [For perfluoropyridine the lowest energy radical cation corresponds to a ${}^2A_{2(\pi)}$ state whilst for perfluorobenzene the radical cation is orbitally degenerate and subject to a first-order Jahn-Teller distortion. On the time scale involved in the fluorination however the unpaired spin and charge densities at each carbon atom will be statistically equal.] The calculated unpaired spin and charge densities for the ring atoms in perfluorobenzene and perfluoropyridine radical cations are given in Figure 1.

For the perfluoropyridine radical cation the charge and spin densities are largest at C-2(C-6) and C-3(C-5), respectively, and at both sites the relevant figures are larger in absolute magnitude than for the carbon atoms in the perfluorobenzene radical cation. [In the light of the large amount of energy required to produce the radical cations it is of interest to confirm that, on an order of magnitude basis, interaction with an ionic lattice is likely to yield sufficient stabilization energy for

¹⁰ L. E. Sutton, ed., 'Interatomic Distances,' The Chemical Society, London, 1958.

¹¹ G. H. King, J. N. Murrell, and R. J. Suffolk, *J.C.S. Dalton*, 1972, 564.

overall electron transfer to become a feasible proposition. As a reasonable speculative model we have considered an octahedral hole in a CoF_3 lattice corresponding to a lattice defect at the surface. With a perfluorobenzene molecule located at the octahedral site with the molecular plane parallel to the base of the remaining square pyramid and at a distance appropriate to the Co-F distance¹² in the CoF_3 lattice it is gratifying to note that electron transfer from the aromatic system to the metal ion and the resultant electrostatic interaction of the radical cation with neighbouring ions is such that the production of the radical cation becomes energetically much more favourable (*ca.* 50 kcal mol⁻¹; *ca.* 2 eV). We

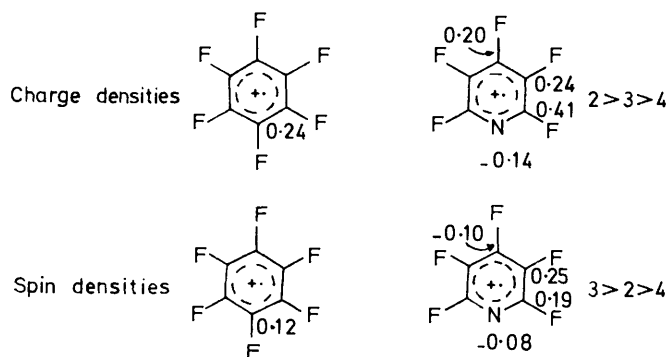


FIGURE 1

quote these results not as a definite study of the likely gas-solid interface interactions but merely to show that a substantial lowering of the energy required to produce the radical cation is likely to arise from such interactions. In the light of the subsequent processes however it would seem reasonable to assume that the rate-determining step in high valency metal fluoride fluorination is still production of the radical cations.]

If the rate-determining step for the fluorinations corresponds to production of the radical cations the overall reactivities of the perhalogenopyridines and perfluorobenzene should be roughly comparable. The available experimental data suggest that this is reasonable. The differences in ionization potential for the perhalogenopyridines with respect to perfluorobenzene are shown in Table 2. When the interactions with the

TABLE 2

Relative ionization potentials (eV)	
Perfluorobenzene	(0)
Perfluoropyridine	-0.1
3-Chlorotetrafluoropyridine	-0.5
4-Chlorotetrafluoropyridine	
3,4-Dichlorotrifluoropyridine	-0.8
3,5-Dichlorotrifluoropyridine	

lattice are considered the differences in energy for production of the radical cations should be quite small.

(2) *Reactions of radical cations; production of dienes.* With a radical cation held at the gas-solid interface there are two likely processes to be considered for the next stage in the reaction: transfer of (i) a fluorine atom or (ii) fluoride ion from the lattice to the radical cation to produce, respectively, substituted hexadienyl cations

or radicals; the latter can, of course, also be produced by route (A). Further reaction involving transfer of a fluoride ion (to the cationic species) or fluorine atom (to the radical species) can then produce dienes which are the first isolable products in the fluorination. The reaction schemes in the particular cases of perfluorobenzene and perfluoropyridine are shown in Schemes 2 and 3.

It has been implied^{8,9} that in the case of lightly fluorinated aromatic species the orientation of substituents in the initial products can best be understood in terms of initial addition of fluorine atoms to the aromatic radical cations to produce substituted hexadienyl cations, *i.e.* route (C). An analogy may then be drawn with substituent effects in electrophilic aromatic substitution. On the basis of such substituent effects the alternative initial reaction of the radical cation with fluoride ion, route (B), to produce a substituted hexadienyl radical has been considered a less likely process.⁹ An analogy drawn between the processes involved in these fluorinations on the one hand, and in electrophilic and radical substitutions on the other, is not necessarily valid, however, since the potential energy surfaces involved are so different. Thus for electrophilic and radical aromatic substitution the surfaces are such that the substituted hexadienyl cations or radicals are reasonable approximations to the respective transition states. In the case of reactions involving aromatic radical cations it seems much more likely that the transition states would be relatively 'early' in which case the selectivities of the processes are likely to be controlled by the charge and spin densities in the radical cations rather than the relative energies of the hexadienyl species.

Table 3, for example, shows the calculated relative energies for hexadienyl cations and radicals in the cases of perfluorobenzene and perfluoropyridine. If the transition states for reaction of the radical cations with fluorine atoms or fluoride ions resembled, respectively, the substituted hexadienyl cations or radicals, the results in Table 3 clearly show the greater selectivity of the pathway involving the cationic intermediates.

TABLE 3

Calculated relative energies to produce substituted hexadienyl radicals and cations from perfluorobenzene and pyridine radical cations and fluorine atoms or fluoride ions (kcal mol⁻¹)

Radicals		Cations	
(1a)	(0)	(1b)	(0)
(2a)	-2.7	(2b)	+9.9
(3a)	+3.8	(3b)	-3.2
(4a)	+1.5	(4b)	+25.9

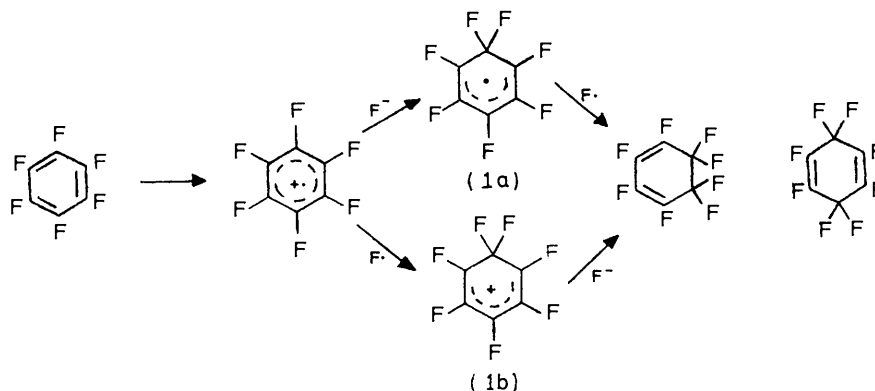
For the isolated species, however, the reactions of both fluorine atoms and fluoride ions with the respective aromatic or heteroaromatic radical cations is predicted to be strongly exothermic. For the possible reactions

¹² Cf. R. Hoppe, 'Advances in Fluorine Chemistry,' vol. 6, eds. J. C. Tatlow, R. D. Peacock, and H. H. Hyman, Butterworths, London, 1970, p. 387.

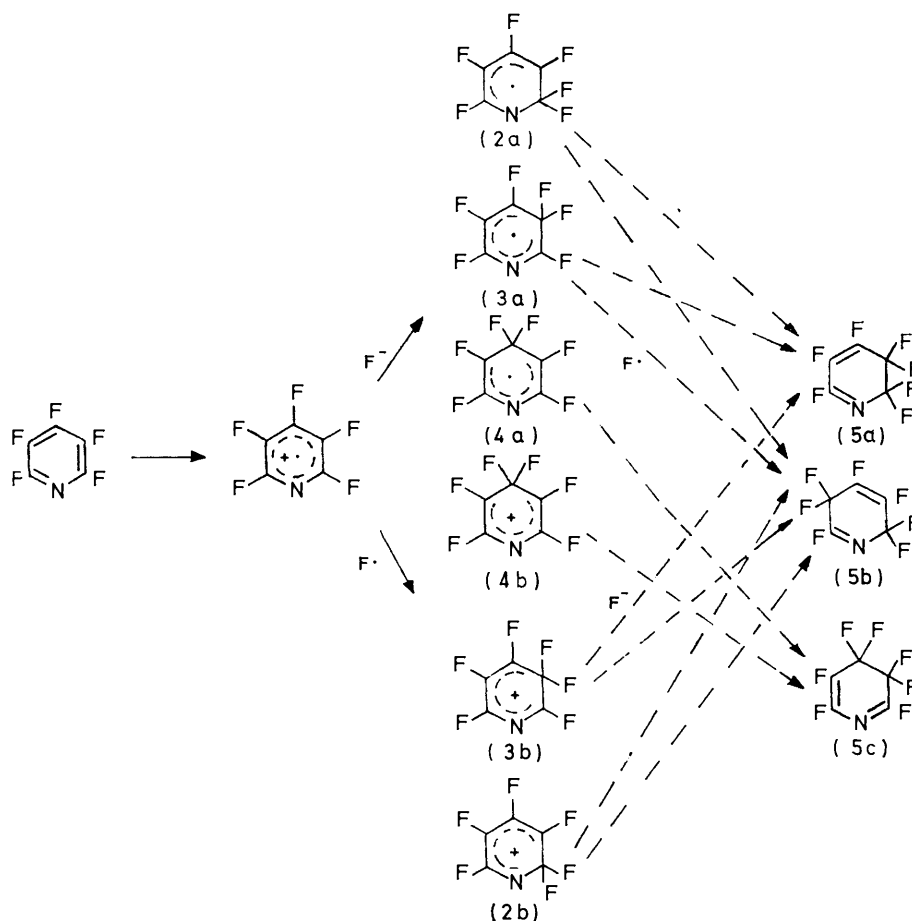
occurring at the gas-solid interface the potential energy surface will undoubtedly be modified. It still seems likely, however, that the rate-determining step will be production of the initial radical cations, and the Ham-

mond Polanyi postulate¹³ should take into account the initial interactions rather than the relative energies of the hexadienyl species.

The relevant charge and spin densities have been presented in Figure 1. On the basis that for the lowest



SCHEME 2



SCHEME 3

mond Polanyi postulate¹³ would then indicate relative 'early' transition states for subsequent reactions with fluorine atoms or fluoride ion. On this basis therefore, arguments concerning the product determining steps

energy pathways involving fluorine atom or fluoride ion, attack will be determined initially by the favourable interactions with local spin or charge densities, re-

¹³ G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

spectively, it is clear from Figure 1 that the orientation of initial attack for perfluoropyridine radical cation is predicted to be

C-3 > C-2 > C-4 for fluorine atom attack

and

C-2 > C-3 > C-4 for fluoride ion attack

The striking feature evident from Figure 1 is that for 'early' transition states, fluoride ion attack leading to substituted hexadienyl radicals might well be more selective than the corresponding process with fluorine atoms leading to cations. The favoured products for fluoride ion attack and fluorine atom attack should therefore be (2a) and (3b), respectively which also correspond to the most stable species (*cf.* Table 3). In the subsequent quenching of these intermediates it may also be argued that the transition states should be early, and the spin and charge densities at the ring atoms for the species (1a)—(4a) and (1b)—(4b) are given in Figure 2.

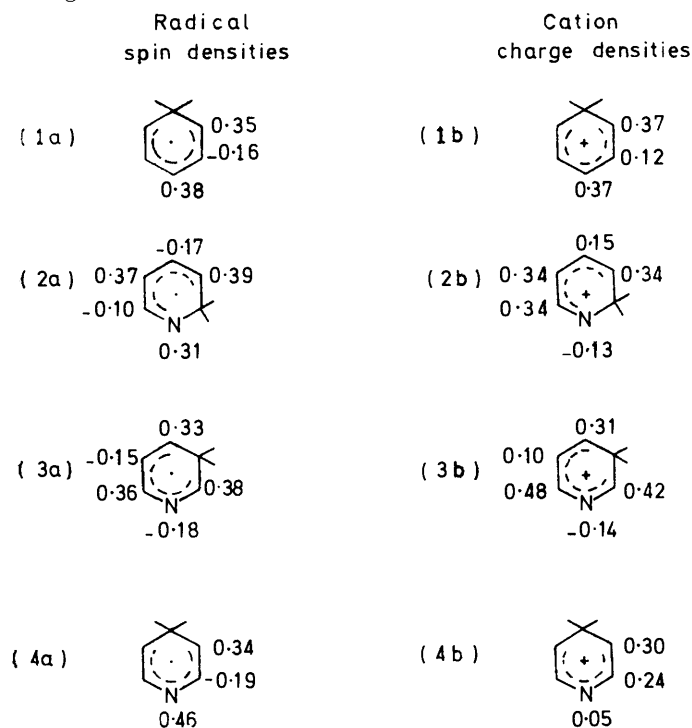


FIGURE 2

Considering first the reactions involving perfluorobenzene, if initial fluorine atom addition is followed by fluoride ion addition the charge distributions in (1b) suggest that formation of 1,3- and 1,4-dienes might be competitive (*n.b.* these dienes have been shown to be of comparable stability¹⁴). If on the other hand fluoride ion addition is followed by fluorine atom addition the spin densities for (1a) suggest a slight preference for overall 1,4-addition, as is observed experimentally.

In the case of perfluoropyridine the favoured intermediates (2a) and (3b) for the two possible mechanisms

¹⁴ A. M. Doyle, C. R. Patrick, and A. E. Pedler, *J. Electroanal. Chem.*, 1971, **33**, 23.

would be expected to yield (5a) and (5b) (Scheme 3), respectively.

From this discussion the most we can say is that preference for production of 1,3-diene rather than 1,4-diene in the case of perfluoropyridine and for 1,4-diene

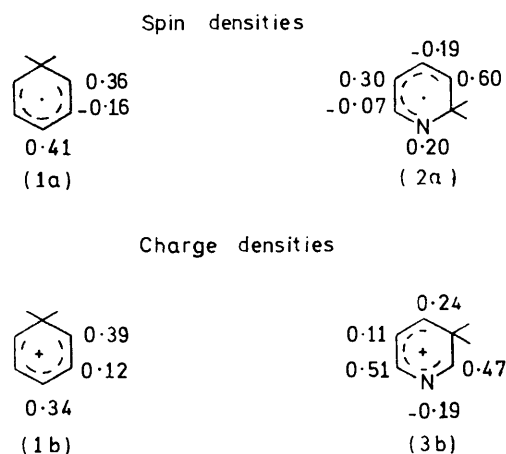


FIGURE 3

rather than 1,3-diene in the case of perfluorobenzene is at least understandable in terms of fluoride ion quenching of the respective radical cations. (The very nature of the reaction does not lend itself to definitive kinetic studies which might produce results amenable to more detailed theoretical scrutiny.) In carrying out the calculations it is convenient on computational grounds to consider formation of radical cations (from aromatic or heteroaromatic precursors), and subsequent fluorine atom or fluoride ion quenching (to hexadienyl cations and radicals respectively), to be a vertical process as far as the nuclear framework of the initial ring system is concerned. In interpreting relative trends this is an entirely reasonable approximation. However, in proceeding from the initial reactants to substituted hexadienyl species (σ -complexes) the nuclear framework will undoubtedly distort. It is therefore of interest to make some allowance for this, and calculations have been carried out on (1a) and (1b) and on (2a) and (3b) to see if the trends discernible from the calculations for the vertical processes are reinforced for adiabatic processes. The results are shown in Figure 3.

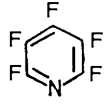
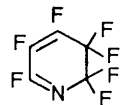
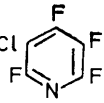
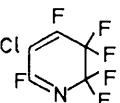
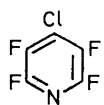
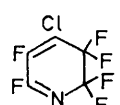
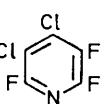
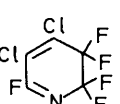
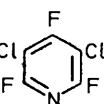
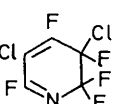
For quenching of the favoured hexadienyl radicals by fluorine atoms the predicted trend for perfluorobenzene to produce predominantly 1,4-diene and perfluoropyridine to produce 1,3-diene is clearly reinforced. For the cationic species the opposite trend is maintained. Within the limits of the theoretical framework, therefore, the model proposed for the initial stage of the fluorination process seems to be in tolerable agreement with the experimental data if initial reaction of the radical cation involves fluoride ions rather than fluorine atoms. Such a mechanism would not necessarily produce any coupling products since the spin densities are considerably delocalized in all species.

(3) *Reactions of dienes.* We now consider the further

reaction of the dienes. The isolation of dienes in some cases and monoenes in others could be rationalized in several ways. First, if there were major differences in reactivities of the heteroaromatic compounds themselves in the first step leading to dienes, this could mean widely differing residence times for the dienes in the reactor. Even if the reactivities of the dienes were independent of the substitution pattern this could lead to differing ratios of monoene to diene in the isolated products. Alternatively the proportion of monoene with respect to diene isolated as product may merely reflect differences in reactivity of the dienes themselves. The third possibility is that both factors are important and need to be taken into account. The available experimental evidence seems to suggest that the final product distributions do represent predominantly differences in reactivities of dienes. The following discussion is therefore based on this premise. Thus for 3- and 4-chloro-tetrafluoropyridine, with comparable *overall* conversion ratios of starting material into products, the former yields predominantly monoene products whereas the latter yields predominantly dienes.

The postulated mechanism for fluorination of dienes follows closely that already discussed for the aromatic and heteroaromatic species. The rate-determining step may again correspond to production of the corresponding radical cations. In this connection it is interesting to compare the relative ionization potentials for the dienes and precursors. The calculated differences are shown in Table 4.

TABLE 4
Calculated ionization potential differences (eV)

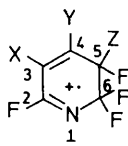
	-		-0.52
	-		-0.50
	-		-0.30
	-		-0.30
	-		-0.50

For the isolated molecules the formation of the radical cations is uniformly more favourable for the dienes. When interactions with the lattice are considered, however, it is not clear that such an energetic preference will be maintained. *A priori* therefore it is not possible

on the basis of these calculations to analyse the relative reactivities of the heteroaromatics and dienes. It is interesting that the lowering of ionization potential in going from heteroaromatic to diene is largest for those heteroaromatic species which give very little diene in the overall fluorination. However the absolute magnitudes of the ionization potentials for the dienes are in the order perfluoro > 4-chloro \approx 3-chloro > 3,4-dichloro \approx 3,4-dichloro systems.

The spin and charge densities for the radical cations are shown in Table 5. The isolation of monoene products with only carbon-nitrogen double bonds suggests that in subsequent reactions involving either fluorine atom or fluoride ion that initial attack will be at C-3 or C-4.

TABLE 5
Diene radical cation charge and spin densities

				Spin densities				Charge densities			
X	Y	Z		N	C-2	C-3	C-4	N	C-2	C-3	C-4
F	F	F		0.67	0.02	0.04	-0.01	-0.04	0.49	0.13	0.24
Cl	F	F		0.63	0.03	0.03	-0.01	-0.06	0.50	-0.02	0.27
F	Cl	F		0.61	0.02	0.04	-0.01	-0.05	0.48	0.06	0.07
Cl	Cl	F		0.56	0.03	0.03	-0.01	-0.07	0.49	0.02	0.10
Cl	F	Cl		0.66	0.02	0.04	-0.01	-0.06	0.50	-0.04	0.29

We consider first a reaction sequence involving initial fluorine atom attack. If the transition state is 'early' the site of attack and relative reactivities should be determined by unpaired spin distributions. It is clear from Table 5 that most of the unpaired spin density is at nitrogen and the spin densities at ring carbon atoms are small, which might suggest very little difference in reactivity. From bond energy data¹⁵ it is evident that the stabilities of the resulting cations are such as to favour initial attack of fluorine atoms in the order C-4 > C-3 > C-2 > N. (This basically hinges on the relative energies of C=N vs. C=C and C-F vs. N-F.) Under the experimental conditions, reaction at C-2 or N might be reversible. These possible side reactions are only important however insofar as reaction at C-2 could lead to elimination from C-6, which effectively provides a further mechanism for isomerization of 1,3- and 1,4-dienes (see Scheme 4, later). To put matters in perspective however, the CNDO/2 calculations give relative energy differences in the range 40–50 kcal mole greater (*i.e.* less stable) for the cations derived from fluorine atom attack at C-2 than for attack at C-4, for the diene radical cations in Table 5.

If the transition state is 'early,' therefore, the spin density distributions do not suggest great differences in the reactivities of the dienes, whilst a later transition state would suggest that reaction at C-4 would be the most favourable. The calculated relative energies for the corresponding cations are shown in Table 6. This

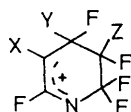
¹⁵ T. L. Cottrell, 'The Strength of Chemical Bonds,' Butterworths, London, 2nd edn., 1958.

suggests that the 4-chloro- and 3,4-dichloro-dienes should be the most reactive. It appears therefore that consideration of possible transition states for an initial reaction involving fluorine atom attack on the diene radical cations does not lead to a clear-cut picture of the relative reactivities of the dienes.

We now consider a mechanism in which initial reaction involves attack by fluoride ion on the diene radical cations. The charge densities in Table 5 clearly show that if the transition state for the reaction is relatively early then initial attack at C-4 may well lead to con-

TABLE 6

Relative energy differences for cations produced by addition of a fluorine atom to C-4 in the radical cations of the dienes



(6a)

X	Y	Z	Intermediate (6a) relative energy (kcal mol ⁻¹) from dienes [e.g. (5a)]
F	F	F	0
Cl	F	F	-1.6
F	Cl	F	-10.0
Cl	Cl	F	-10.4
Cl	F	Cl	-2.5

siderable differences in reactivity between the dienes. Thus the 4-chloro- and 3,4-dichloro-compounds might be expected to be considerably less reactive. The highest positive charge densities however are associated with C-2 in each case and it is interesting that the calculations now suggest that the energies for the radical intermediates corresponding to attack at C-2 and C-4 are comparable. For reaction at C-2, elimination from C-6 would also lead to isomerization to 1,4-diene (see Scheme 4).

It seems probable therefore that the distribution in terms of diene *versus* monoene or ring-opened products is explicable in terms of the decreased reactivity of the C-4 relative to the C-2 position on replacing fluorine by chlorine (at C-4). The most likely process resulting from attack at C-2 would be elimination of a fluorine atom to regenerate 1,3-diene or possibly give a small amount of 1,4-diene (see Scheme 4).

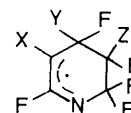
The calculated relative energy differences for production of a radical are given in Table 7. The sequence of energies is in striking contrast with those for the cationic species (Table 6). If the transition states for the reactions of fluoride ions with diene radical cations are 'late,' the relative energies for the intermediates (6b) suggest that the perfluoro-compound should be the most reactive (with respect to production of monoene), and the 3,5-dichloro-compound the least reactive. The reactivity sequence is therefore most readily interpreted in terms of initial reaction of the diene radical cation with a *fluoride ion*, rather than a fluorine atom, with a relatively 'early' transition state. Further reaction of (6b) with a fluorine atom leads directly to the monoene

product. The calculated spin densities are shown in Table 8, and for comparison those for the radicals corresponding to initial attack at C-2 are also given.

TABLE 7

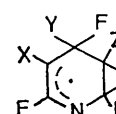
Relative energy differences for radicals produced by addition of a fluoride ion to C-4 in the radical cations of the dienes

X	Y	Z	Intermediate (6b) relative energy (kcal mol ⁻¹) from dienes [e.g. (5a)]
F	F	F	0
Cl	F	F	5.0
F	Cl	F	1.4
Cl	Cl	F	5.5
Cl	F	Cl	7.0



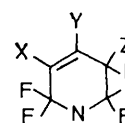
(6b)

TABLE 8



(6b)

X	Y	Z	Unpaired spin densities		
			N	C-2	C-3
F	F	F	0.40	-0.17	0.64
Cl	F	F	0.39	-0.17	0.65
F	Cl	F	0.40	-0.17	0.62
Cl	Cl	F	0.38	-0.16	0.63
Cl	F	Cl	0.39	-0.17	0.65

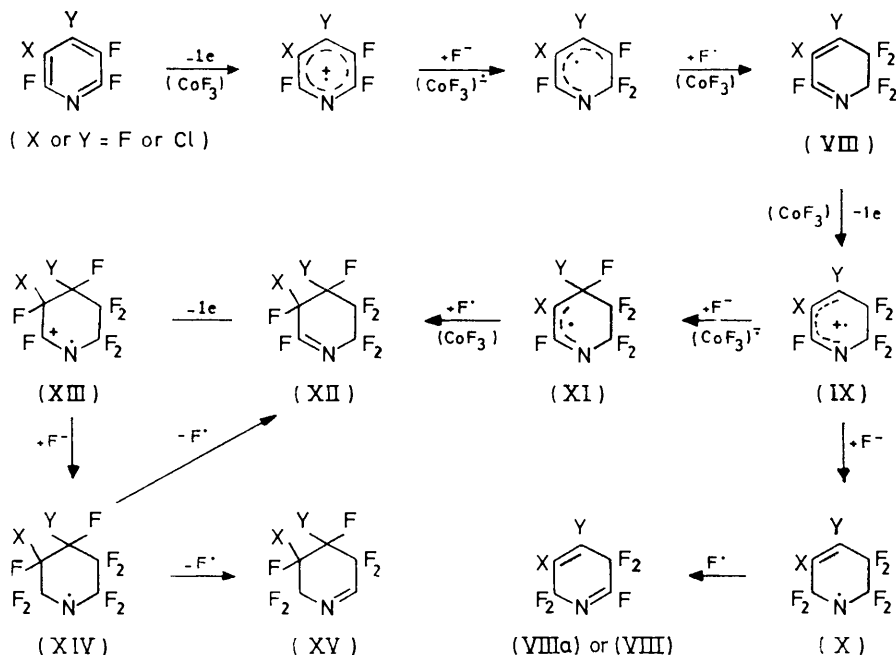


X	Y	Z	Unpaired spin densities		
			N	C-3	C-4
F	F	F	0.75	0.03	0.00
Cl	F	F	0.74	0.03	0.00
F	Cl	F	0.75	0.03	-0.01
Cl	Cl	F	0.74	0.02	-0.01
Cl	F	Cl	0.75	0.03	0.00

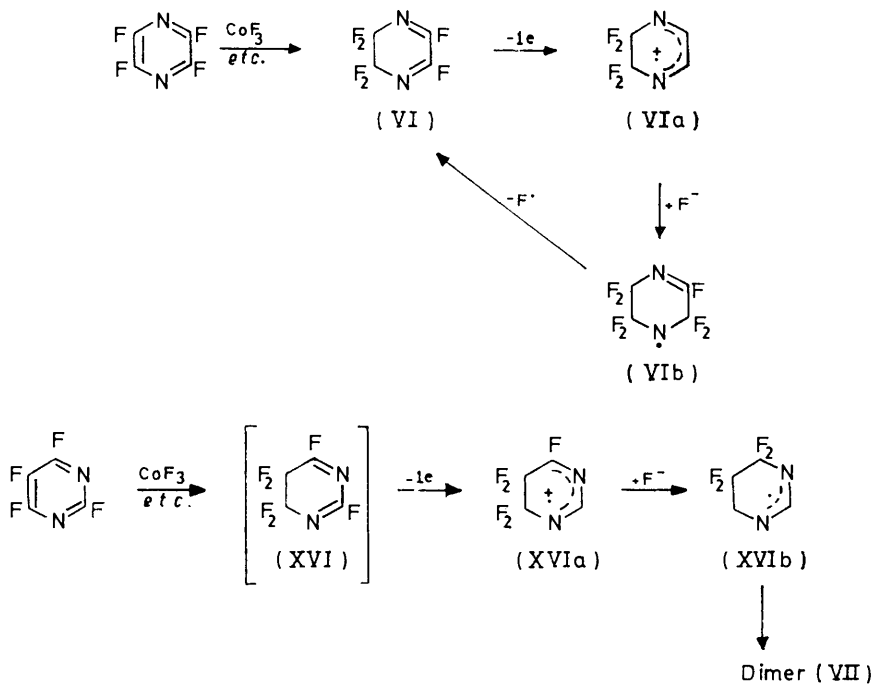
The quenching of (6b) by fluorine atoms to yield monoene products should proceed straightforwardly at C-3 where there is a high unpaired spin density. It is not unreasonable that dimers are not major products in any of the reactions involving the perhalogenopyridines since the steric interactions coming into play for close approach of two radicals through C-3 would be expected to be substantial. [For species (6b) in Table 8 it is clear that the unpaired spin density is larger at C-3 than at N. For the pyrimidine system, however, in the corresponding species (10b) (see Scheme 5) the unpaired spin densities will be shared between the two nitrogens. It is reasonable that the dimer (VII) should thus be formed.] By contrast, if initial reaction of the radical cation at C-2 is a competitive process, as well as the possibility of leading to isomerized diene, the large

unpaired spin density at nitrogen and the much more favourable steric interactions might well lead to dimer formation [for the pyrimidine system (VIIa)]. In this

ring. This reaction is, interestingly enough, fairly specific and the interpretation of these results will form the subject of a further paper.



SCHEME 4



SCHEME 5

connection it may well be significant that in the fluorination of perfluoropyrimidine the corresponding dimer product (VII) has been isolated.

The further reaction of monoene by processes analogous to those already discussed leads to fragmentation of the

Conclusions and Summary.—On the basis of the foregoing discussion it is clear that the selectivity arising from the position of chlorine in the chlorofluoropyridines cannot be satisfactorily accounted for on the basis of either route (A) or (C), while route (B) does provide a

useful framework for accommodating all the evidence both from experiment and theory.

The mechanism which we propose, therefore, is summarized in Scheme 4. The radical cation (IX) could be quenched at the 2-position by fluoride ion but the resultant radical (X) is probably short-lived and loses a fluorine atom to return to the diene (VIII) or (VIIIa). In contrast, attack by fluoride ion at the 4-position in the radical cation (IX) could lead to an aza-allyl system (XI) of sufficient life-time to be quenched by abstracting a fluorine atom from cobalt trifluoride, giving the aza-alkene (XII). The equilibration between aza-alkenes (XII) and (XV) probably involves the radical cation (XIII), which in turn could give the short-lived radical (XIV), which loses a fluorine atom to give either (XII) or (XV). When Y = Cl, much more diene (VIII) is isolated. The scheme which we have proposed involves further reaction of the diene (VIII) *via* (IX) followed by attack by fluoride ion at the 4-position in (IX). It is well established that nucleophilic attack occurs much faster at carbon, in an olefin or an aromatic ring, which is attached to fluorine rather than to chlorine.⁹ Therefore, if the 4-position in (IX) is inhibited to nucleophilic attack by replacement of fluorine by chlorine, preferential attack at the 2-position will occur, giving (X), and hence the system will revert to the 1,3-diene (VIII) or the 1,4-diene (VIIIa).

The formation of products from tetrafluoro-pyrazine and -pyrimidine is rationalized in a similar way (Scheme 5). Further reaction of the diene (VI), from tetrafluoro-pyrazine, would give the radical cation (VIa) which, on reaction with fluoride ion would lead to a relatively short-lived radical (VIb) which loses a fluorine atom rather than dimerizing. In contrast, the radical cation (XVIa) from the diene (XVI) leads to a more stable diaza-allyl radical (XVIb) which, in this case, is able to dimerize giving (VII).

EXPERIMENTAL

I.r. and u.v. spectra were measured with a Perkin-Elmer 137 spectrophotometer and a Unicam SP 800 spectrophotometer, respectively. An A.E.I. MS9 instrument was employed for mass spectrometry. The n.m.r. results were obtained with Perkin-Elmer R10 and Varian A56/60 spectrometers. Samples were run as neat liquids with hexafluorobenzene as an internal reference unless otherwise stated; chemical shifts are quoted in p.p.m. (negative values to low field). Analytical g.l.c. was carried out with a 6 ft \times $\frac{1}{8}$ in (diam.) column packed with di-isodecyl phthalate on crushed firebrick (column A) in a Perkin-Elmer 452 gas chromatograph. Preparative scale g.l.c. was carried out with a Perkin-Elmer F21 automatic gas chromatograph fitted with a 4.5 in \times 9.5 mm (diam.) column packed with di-isodecyl phthalate on Chromosorb P (1 : 4) (column B).

Fluorinations.—All fluorinations were carried out in a small stirred reactor constructed from nickel, which was 44 cm long \times 4.4 mm in diameter. Unless otherwise stated, the reactor contained cobalt(III) fluoride (150 g) and calcium fluoride (150 g). The reactant was dropped from a suitably modified burette directly into the reactor, through

which a steady stream of nitrogen gas was flowing, and the products were collected at liquid air temperature.

(a) *Hexafluorobenzene.* (i) For this fluorination, the reactor contained only cobaltic fluoride (600 g). Hexafluorobenzene (6.4 g, 34 mmol) was fluorinated in a steady stream of nitrogen (4.8 l h⁻¹) at 100–106° to give a mixture (6.0 g) shown by g.l.c. (column A at room temperature) to consist of two components: (a) perfluorocyclohexane (1.9 g, 6.3 mmol) and (b) perfluorocyclohexene (4.1 g, 15.6 mmol). The components were separated by preparative scale g.l.c. and identified spectroscopically.

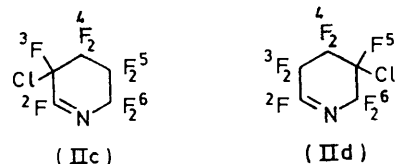
(ii) For this and all subsequent reactions, the reactor contained a mixture of cobalt(III) fluoride (150 g) and calcium fluoride (150 g). Hexafluorobenzene (6.4 g, 34 mmol) was fluorinated at 50°, to give a mixture (6.0 g) of three components: (a) perfluorocyclohexene (3.0 g, 11.4 mmol), (b) perfluorocyclohexa-1,4-diene (1.5 g, 6.7 mmol), and (c) hexafluorobenzene (1.5 g, 8.5 mmol). The components were separated by preparative scale g.l.c. and identified spectroscopically.

(b) *Pentafluoropyridine* (I). (i) Pentafluoropyridine (3.0 g, 17.7 mmol) was fluorinated at 120° to give a mixture (3.2 g). Quantitative g.l.c. examination revealed two known compounds: (a) perfluoro-1-azacyclohex-1-ene (Ic) (2.72 g, 11.1 mmol)¹⁶ and (b) perfluoro-2-azahex-2-ene (Ie) (0.48 g, 1.7 mmol),¹⁵ identified spectroscopically.

(ii) For this reaction *ca.* 50% of the available fluorine of the fluorinating agent had previously been used up. Pentafluoropyridine (16.0 g, 95 mmol) was fluorinated at 120–125°, to give a mixture (15.0 g) which was separated by preparative scale g.l.c. (column B at 50°) and fractional distillation to give (a) perfluoro-1-azacyclohex-1-ene (Ic) (11.6 g, 47.4 mmol), identified spectroscopically, (b) perfluoro-1-azacyclohexa-1,3-diene (Ia) (0.37 g, 1.7 mmol), identified spectroscopically (see later), and (c) unchanged pentafluoropyridine (3.0 g, 17.8 mmol).

(c) *3-Chlorotetrafluoropyridine* (II). 3-Chlorotetrafluoropyridine (16.0 g, 86.2 mmol) was fluorinated at 100° and the product (17.5 g) was shown by g.l.c. (column A at room temperature) to consist of three major components.

First was obtained a 1 : 1 mixture of 3-chloro- (IIc) and 5-chloro-octafluoro-1-azacyclohex-1-ene (IIId) (7.9 g, 30.2 mmol), b.p. 74° (Found: C, 22.7; Cl, 13.2%; M, 261. Calc. for C₆ClF₈N: C, 22.9; Cl, 13.6%; M, 261). The mixture could not be separated and structural evidence was based on ¹⁹F n.m.r. spectra of enriched mixtures obtained by g.l.c. fractionation (chemical shifts being upfield with respect to external trichlorofluoromethane). By integration, and by virtue of its low-field shift, the vinylic fluorine (2-F) was readily distinguished [isomer (IIc), 49.20 p.p.m. (d, J 28 Hz); isomer (IIId), 55.47 p.p.m. (t,

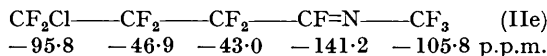


J 23 Hz)], and the multiplet splitting in the case of (IIc) served to locate the chlorine atom. The N·CF₂ groups were also distinguished by their low-field shifts; (IIc) showed a single line at 94.58 p.p.m. (6-F) and (IIId) an AB system [94.98 (6_{ax}-F) and 82.85 p.p.m. (6_{eq}-F)] and the CFCl

¹⁶ R. E. Banks, W. E. Cheng, and R. N. Haszeldine, *J. Chem. Soc.*, 1962, 3407.

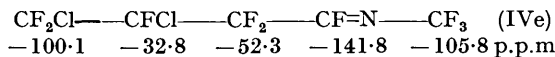
systems appeared in (IIc) at 132.66 (3-F) and in (IId) at 139.12 p.p.m. (5-F). The remaining two sets of geminal nuclei were observed as an overlapping AB system [in (IIc)] [134.08 (4ax-F) and 124.83 p.p.m. (4eq-F)] and a single line [134.52 p.p.m. (5-F)]; and [in (IId)] as two overlapping AB systems [129.53 (3ax-F) and 115.12 (3eq-F), and 137.53 (4ax-F) and 121.06 p.p.m. (4eq-F)].

The other component in the product was 6-chlorodecafluoro-2-azahex-2-ene (IIe) (7.9 g, 26.4 mmol), b.p. 62° (Found: C, 20.05; Cl, 11.7. $C_5ClF_{10}N$ requires C, 20.0; Cl, 11.85%), ν_{\max} 1786s cm^{-1} (C=N) group; ^{19}F n.m.r. as illustrated:

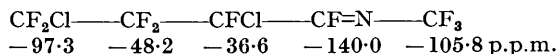


(d) 4-Chlorotetrafluoropyridine (III). 4-Chlorotetrafluoropyridine (14.75 g, 79.6 mmol) was fluorinated at 120–123°; the product consisted of (a) 4-chlorohexafluoro-1-azacyclohexa-1,3-diene (IIIa) (8.0 g, 35.8 mmol), b.p. 96° (Found: C, 26.7; Cl, 15.4; F, 50.6. C_5ClF_6N requires C, 26.8; Cl, 15.9; F, 51.0%), λ_{\max} (cyclohexane) 248 nm (ϵ 9380), ν_{\max} 1705s and 1660s cm^{-1} (C=N and C=C), ^{19}F n.m.r. (1:2:2:1) -114.7 (2-F), -64.7 (6-F), -47.7 (5-F), and -38.7 (3-F) p.p.m.; (b) 4-chlorohexafluoro-1-azacyclohexa-1,4-diene (IIIb) (0.4 g, 1.8 mmol), b.p. 81.5° (Found: C, 26.5; Cl, 15.8%), λ_{\max} (cyclohexane) 217 nm, ν_{\max} 1754s and 1715s cm^{-1} , ^{19}F n.m.r. (1:2:2:1) -110.0 (2-F), -79.8 (6-F), -58.1 (3-F), and -46.5 (5-F) p.p.m.; and (c) 4-chloro-octafluoro-1-azacyclohex-1-ene (IIIc) (2.5 g, 9.6 mmol), b.p. 71.5° (Found: C, 22.9; Cl, 13.8. C_5ClF_8N requires C, 22.9; Cl, 13.8%), ν_{\max} 1749s cm^{-1} (C=N).

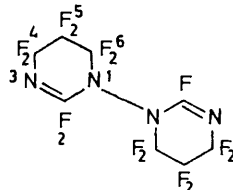
(e) 3,4-Dichlorotrifluoropyridine. 3,4-Dichlorotrifluoropyridine (15.0 g, 74.3 mmol) was fluorinated at 130–135°; the product (13.5 g) consisted of dichloropentafluoro-1-azacyclohexadiene isomers (2.94 g, 12.1 mmol) from which the major component was isolated and identified as 3,4-dichloropentafluoro-1-azacyclohexa-1,3-diene (IVa) (1.9 g, 7.9 mmol), b.p. 127° (Found: C, 24.7; Cl, 29.7; F, 40.8. $C_5Cl_2F_5N$ requires C, 25.0; Cl, 29.6; F, 39.6%), λ_{\max} (cyclohexane) 260 nm (ϵ 6140), ν_{\max} 1718s and 1618s cm^{-1} (C=C and C=N), ^{19}F n.m.r. (1:2:2) -126.3 (2-F), -63.8 (6-F), and -46.3 (5-F) p.p.m. The other products were (b) a dichloroheptafluoro-1-azacyclohex-1-ene isomer mixture (6.0 g, 21.6 mmol) which it was not possible to separate (Found: C, 21.8; Cl, 25.3; F, 49.1; N, 4.8. Calc. for $C_5Cl_2F_7N$: C, 21.6; Cl, 25.5; F, 47.8; N, 5.0%); and (c) 5,6-dichlorononafluoro-2-azahex-2-ene (IVe) (1.65 g, 5.2 mmol), b.p. 86° (Found: C, 19.29; Cl, 22.6; F, 54.6; N, 4.27. $C_5Cl_2F_9N$ requires C, 19.00; Cl, 22.5; F, 54.1; N, 4.40%), ν_{\max} 1770s cm^{-1} (C=N), ^{19}F n.m.r. as illustrated:



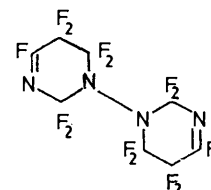
(f) 3,5-Dichlorotrifluoropyridine. 3,5-Dichlorotrifluoropyridine (16.0 g, 79.2 mmol) was fluorinated at 120–130°; the product (12.0 g) consisted of (a) a mixture of isomers of 3,5-dichloroheptafluoro-1-azacyclohex-1-ene (8.0 g, 28.8 mmol) (Found: C, 21.3; Cl, 25.1; F, 47.9; N, 4.95. Calc. for $C_5Cl_2F_7N$: C, 21.6; Cl, 25.5; F, 47.8; N, 5.0%); and (b) 4,6-dichlorononafluoro-2-azahex-2-ene (Ve) (3.36 g, 10.6 mmol), b.p. 92° (Found: C, 19.3; Cl, 21.8; F, 54.3; N, 4.1. $C_5Cl_2F_9N$ requires C, 19.0; Cl, 22.5; F, 54.1; N, 4.4%). ν_{\max} 1764s cm^{-1} (C=N), ^{19}F n.m.r. as illustrated:



(g) Tetrafluoropyrimidine. Tetrafluoropyrimidine (3.5 g, 20 mmol) was fluorinated at 175°; the product (2.0 g) consisted of unchanged starting material (0.8 g, 5.3 mmol) and perfluoro-1,1'-bi-1,3-diazacyclohex-2-enyl (1.2 g, 2.8 mmol), b.p. 145° (Found: C, 23.13; N, 13.7; F, 63.0%; M , 418. $C_8F_{14}N_4$ requires C, 23.0; N, 13.4; F, 63.6%; M , 418), ν_{\max} 1735s cm^{-1} . The ^{19}F n.m.r. assignments are based on structure (VII). Three AB systems (J 192, 233,



(VII)

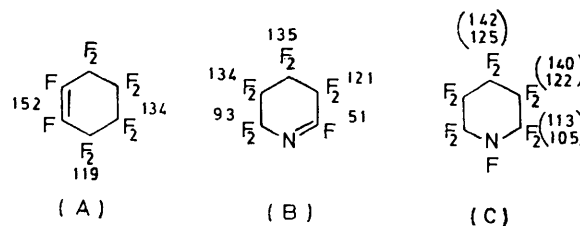


(VIIa)

and 267 Hz) typical of CF_2 resonances were observed and a single absorption to low field was assigned to =CF. The chemical shifts of the neat liquid (upfield of internal

δ in p.p.m.	(Hz)	Assignment	J_{gem}/Hz
62.25	(3520)	2-F ₂	233
96.46	(5464)	4ax-F ₄	
99.08	(5602)	6ax-F ₄	
101.55	(5742)	4eq-F	192
111.07	(6280)	6eq-F	
134.43	(7601)	5ax-F	267
140.87	(7965)	5eq-F	

CCl_3F) are tabulated. Assignments and structure derivation are based on comparisons with the n.m.r. data of the model compounds (A)–(C). It is clear that the chemical



(A)

(B)

(C)

shift of a CF_2 group which is 'isolated' from a C=N or C-N bond, in a six-membered ring, is *ca.* 135 p.p.m. and that fluorine in a $CF_2-N=C$ system resonates at an abnormally low field (*ca.* 93 p.p.m.). Furthermore, the resonance of CF_2 in the situation $-CF_2-N<$ is moved downfield from the 'isolated' position of 135 p.p.m. The tabulated data easily rule out structures other than (VII) and (VIIa). Structure (VIIa) contains a $C=N-CF_2-N<$ system in which both nitrogen atoms should have a 'downfield' influence and a resonance to low field of 96 p.p.m. would be anticipated. Likewise (VIIa) has no 'isolated' CF_2 group and we would not therefore anticipate a resonance as high as 135 p.p.m.

(h) Tetrafluoropyrazine. Tetrafluoropyrazine (2.0 g, 13.2 mmol) was fluorinated in a steady stream of nitrogen (6.0 l h^{-1}) at 80°. The reactant was placed in a flask immersed in an oil-bath at 80° and carried through the reactor by the nitrogen; the product (1.8 g) consisted of unchanged starting material (1.08 g, 7.1 mmol) and perfluoro-1,4-diazacyclohexa-1,3-diene (0.73 g, 3.8 mmol) (Found: C, 25.0; F, 59.4; N, 14.3%; M , 190. $C_4F_6N_2$ requires C, 25.26; F, 60.0; N, 14.7%; M , 190), λ_{\max} (cyclohexane) 211 nm (ϵ 1800), ν_{\max} 1720s cm^{-1} (C=N), ^{19}F n.m.r. (1:2) 58.5 and 100.9 p.p.m. upfield of external CCl_3F .

Dehalogenations.—*Dechlorofluorinations.* These were carried out by passing the reactant in a steady stream of nitrogen gas through a Pyrex reaction tube [30 cm × 2.5 cm (diam.)] packed with coarse iron filings, heated at 350°.

(a) 3-Chloro- and 5-chloro-octafluoro-1-azacyclohex-1-ene isomer mixture (IIc and d). The isomer mixture (IIc and d) (10.0 g, 38.3 mmol) was passed, in a steady stream of nitrogen (3 l h⁻¹), through the reactor tube, at 350°, and the product mixture (6.0 g) was trapped at liquid air temperature. Preparative scale g.l.c. (column B at 70°) showed that it consisted of (a) unchanged starting material (0.95 g, 3.6 mmol); (b) perfluoro-1-azacyclohexa-1,3-diene (Ia) (1.8 g, 8.7 mmol), b.p. 54° (Found: C, 29.2; F, 63.8. C₅NF₇ requires C, 29.0; F, 64.2%), λ_{max.} (cyclohexane) 233 nm (ε 3400), ν_{max.} 1750s and 1700s cm⁻¹ (C=N and C=C), ¹⁹F n.m.r. (1 : 2 : 2 : 1 : 1) —118.4 (2-F), —64.4 (6-F), —42.4 (5-F), —23.3 (3-F), and —13.6 (4-F); (c) pentafluoropyridine (1.75 g, 10 mmol); and (d) unidentified material (1.5 g).

(b) 4-Chloro-octafluoro-1-azacyclohex-1-ene (IIIc). 4-Chloro-octafluoro-1-azacyclohex-1-ene (IIIc) (3.0 g, 11.5 mmol) was passed through the reactor tube, at 350°, and the product mixture (2.2 g) was trapped at liquid air temperature. The mixture consisted of (a) unchanged starting material (1.43 g, 5.5 mmol); (b) perfluoro-1-azacyclohexa-1,3-diene (Ia) (0.46 g, 2.2 mmol); (c) pentafluoropyridine (0.17 g, 1 mmol); and (d) a mixture of unknown materials (0.02 g).

Dechlorinations. These were effected by refluxing the dichloro-compound in a polar solvent, with zinc. Ethanol is normally chosen as solvent for these reactions but dioxan was used with the reactive dichloroheptafluoro-1-azacyclohex-1-ene isomers.

Dechlorination of dichloroheptafluoro-1-azacyclohex-1-ene isomer mixture (IVc and d). The isomer mixture (IVc and d) (3.0 g, 10.8 mmol) in dry dioxan (1 ml) was added to a stirred suspension of activated zinc dust (4.3 g, 66 mmol) in

refluxing dioxan (6.0 ml). The product contained (a) perfluoro-1-azacyclohexa-1,3-diene (Ia) (2.0 g, 9.7 mmol) and (b) unchanged starting material (1.0 g, 3.6 mmol).

Replacement of chlorine by fluorine. A mixture of 4-chlorohexafluoro-1-azacyclohexa-1,3-diene (10 g, 44.7 mmol) and anhydrous potassium fluoride (10 g, 256 mmol) was sealed, under vacuum, in a Carius tube (100 cm³) and heated in a furnace for 4 h at 250°. The product (7.15 g), removed by vacuum transfer, consisted of unchanged starting material (2.65 g, 12 mmol) and perfluoro-1-azacyclohexa-1,3-diene (Ia) (4.4 g, 21.3 mmol), identified spectroscopically.

Isomerizations.—(1) 3-Chloro- (IIc) and 5-chloro-octafluoro-1-azacyclohex-1-ene (IIId) isomer mixture (ratio 85 : 15) (1.0 g, 3.8 mmol) was sealed with caesium fluoride (0.5 g, 3.3 mmol) in a Pyrex tube and heated at 110° for 2 h. The product (0.90 g) was analysed by analytical scale g.l.c. (column A at room temperature) and shown to be a 1 : 1 mixture of the two isomers.

(2) The same isomer mixture (1.0 g, 3.2 mmol) was heated under the same conditions with calcium fluoride (0.5 g, 6.4 mmol); the product (0.85 g) was unchanged starting material.

(3) The same isomer mixture (1.0 g, 3.8 mmol) was heated, under the same conditions, with cobalt(II) fluoride (0.5 g, 10 mmol); the product (0.90 g) was unchanged starting material.

(4) The same isomer mixture (1.5 g, 5.7 mmol) was passed through the fluorinator, at 105°, in a steady stream of nitrogen (4—8 l h⁻¹). The product (1.5 g) was a 1 : 1 mixture of isomers.

(5) 4-Chlorohexafluoro-1-azacyclohexa-1,4-diene (IIIb) (300 mg, 1.3 mmol) was sealed in a Pyrex tube with a small amount of caesium fluoride, and heated for 2 h, at 110°. The product (250 mg) was 4-chlorohexafluoro-1-azacyclohexa-1,3-diene (IIIa).

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