Tetrahedron Vol. 36, pp. 1423 to 1433
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0040-4020/80/0515-1423/$02.00/0

THE CONSEQUENCES OF CATION-RADICAL FLUORINATION THEORY—II

FLUORINATION PATHWAYS WITH LESS-REACTIVE REAGENTS

JAMES BURDON* and IAN W. PARSONS
Chemistry Department, University of Birmingham,
P.O. Box 363, Birmingham B15 2TT

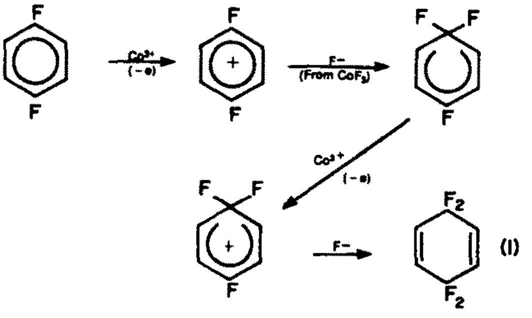
(*Received in UK* 13 *August* 1979)

Abstract—The fluorination of benzene with caesium tetrafluorothallate and of pyridine or benzo[b] furan with caesium tetrafluorocobaltate gives sequences of *polyfluoroaromatics with vicinal fluorines*. Polynuclear aromatics are fluorinated by caesium or potassium tetrafluorocobaltate to give products containing little or no hydrogen, whereas the stronger fluorinating agent cobalt trifluoride gives products which contain much hydrogen. These two previously unexplained features are rationalized by a mechanism which involves 1,2-migrations of fluorine in cyclohexadienyl-type radicals or cations, and is backed up by CNDO/2 calculations. This rationalization implies significantly different rates of atom or ion migrations through the lattices of the different solid fluorinating agents.

Fluorination of organic compounds with high valency transition metal fluorides (HVMFs) has long been studied.[2,3] Much early effort[3] went into the study of fluorination products from benzene, and in particular the reaction with cobalt trifluoride was carefully investigated. Even in this simple case, about 20 products are commonly found. An early rationalization[3] of these products postulated that the major fluorination pathway went via repeated 1,4-additions of fluorine atoms to the benzene ring, and later evidence,[4,5] including the isolation[4] of 1,1,4,4-tetrafluorocyclohexa-1,4-diene (I), supported this.

Extensions of this work to the fluorinations of various substrates, e.g. tetrahydrofuran,[6] thiophen,[7] and 1,3-bis(trifluoromethyl)benzene,[8] and to the use of different reagents, e.g. cerium(IV) fluoride,[9] manganese(III) fluoride,[3,10] potassium tetrafluorocobaltate(III)[4,11] and the related lithium salt all suggested,[11] or now suggest, the generality of this phenomenon in fluorinations of aromatic substrates.

More recently,[1,12] the proposal that such reactions go via an electron abstraction from the aromatic π-system, leading to cation-radical species which are postulated to be important product determining intermediates, has led to a rationale for this sequence of 1,4-reactions, at least for mono-cyclic aromatic substrates and reactive reagents, and has provided a theoretical framework for the study of fluorination mechanisms, drawing on analogies with well-understood reactions such as aqueous oxidations with high oxidation state transition metal species and electrochemical oxidations.

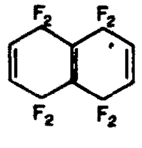


Scheme 1. Reaction of p-difluorobenzene and cobalt trifluoride.

DISCUSSION

In the first paper[1] of this series, we presented several possible mechanisms within the cation-radical framework for the fluorination of aromatic compounds with HVMFs. The route that fitted the experimental data most closely is exemplified with p-difluorobenzene and cobalt trifluoride in Scheme 1. In this and similar fluorination pathways, fluoride ion always attacks the radical-cations and cations at the carbons with the highest positive charge densities, as calculated by the CNDO/2 method.

There was, however, a major feature that neither this nor any of the other routes could accommodate: polynuclear aromatics—naphthalene,[11,13] anthracene,[14,15] phenanthrene,[14,15] pyrene[14,15]—gave little, if any, H-containing products when fluorinated with reagents such as $KCoF_4$ and $CsCoF_4$, but gave large quantities of such compounds when treated with the apparently *stronger* fluorinating agent, cobalt trifluoride. It was as if the $KCoF_4$ and $CsCoF_4$ fluorinations were proceeding largely via the corresponding perfluoro-aromatics.[14] None of our pathways permitted this and most involved the intermediacy of compounds of, for example, type I or II.

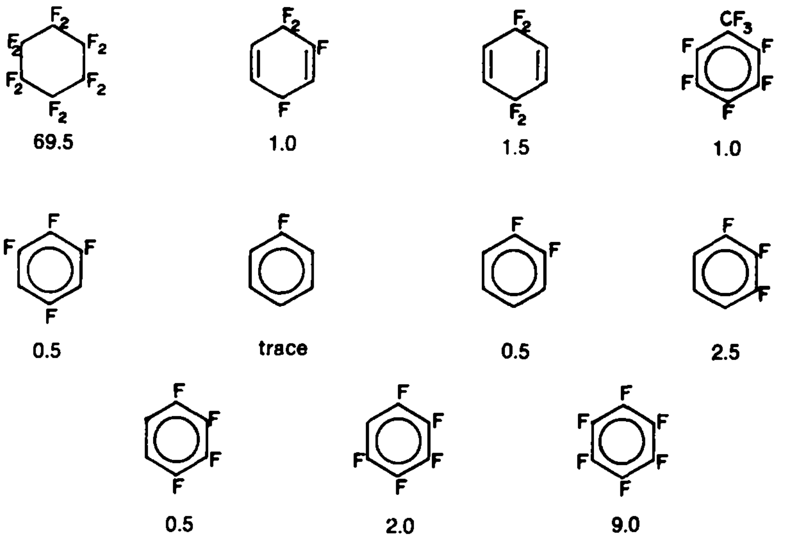


II

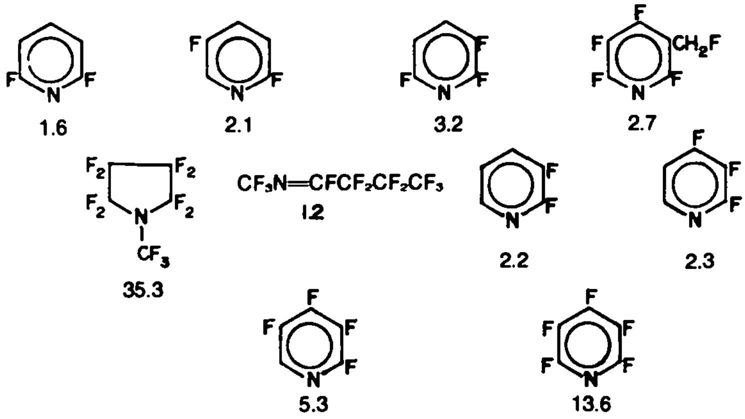
Removal of all the hydrogens from these would be quite difficult, and it is likely that fluorinations with cobalt trifluoride proceed via such compounds: indeed, fluorination of diene I with cobalt trifluoride gives the same product distribution as fluorination of benzene itself.[5]

In this paper we offer a possible rationalization for the paucity of H-containing products in the $KCoF_4$/$CsCoF_4$-polynuclear aromatic reactions.

Before doing this, we present three examples of another apparent anomaly which also cannot be accommodated by any of the mechanisms we discussed ear-



Scheme 2. Products (wt. %) from the benzene/CsTlF$_4$ reaction (remaining unidentified products were all minor).

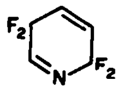


Scheme 3. Products (wt.%) from the CsCoF$_4$/pyridine reaction (the remaining unidentified products were all minor).

lier,[1] but which is rationalizable within the framework described later in this paper.

The first example is the benzene/CsTlF$_4$ reaction.[16] At 500°, the products were those shown in Scheme 2: all are known compounds. The most striking feature here concerns the polyfluorobenzenes, the majority of which form a pattern in which *ortho*-fluorines are successively introduced (mono-fluoro → 1,2-difluoro → 1,2,3-trifluoro → 1,2,3,4-tetrofluoro → pentafluoro → hexafluoro). There seems to be little formation of aromatics which lie outside this pattern. This is to be contrasted with the cobalt trifluoride/[3] and KCoF$_4$/benzene[4] reactions, which gave smaller amounts of polyfluoro-aromatics and which appeared to proceed mainly via compound I, in accord with the favoured fluorination mechanism.[1]

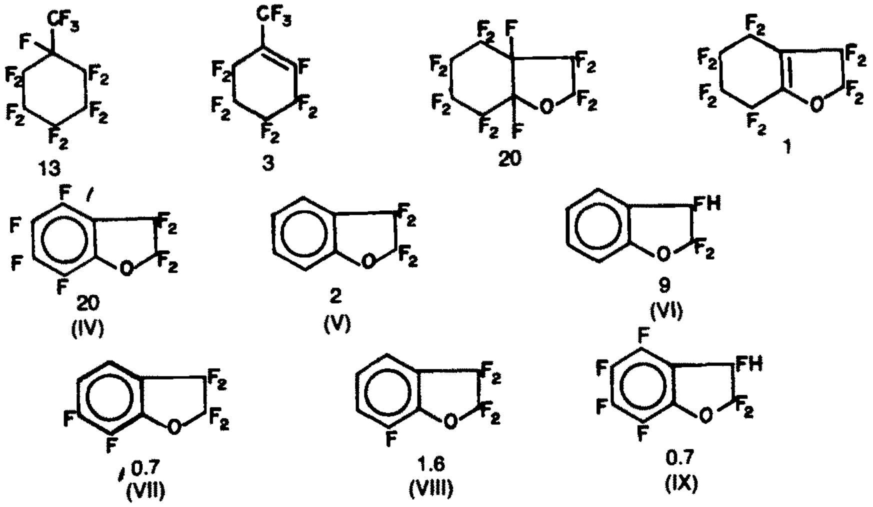
The second example is the pyridine/CsCoF$_4$ reaction.[14] At 310°, the products were those shown in Scheme 3: most are known compounds and the structures of the rest followed quite straightforwardly from their ^{19}F and ^{1}H NMR spectra. It is possible to rationalize the formation of the perfluoro (N-methylpyrrolidine) and the open chain azine by the routes described in our first paper:[1] the major intermediate is the diene (III):



III

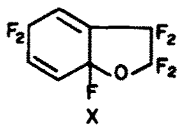
This same intermediate can also lead to almost all the products from the KCoF$_4$ and cobalt trifluoride fluorinations of pyridine.[18] Similar calculations have been carried out by Durham workers[19] on pentafluoro- and polyfluorochloro-pyridines; their conclusions were similar to ours. Once again, however, *most* of the aromatic products from the CsCoF$_4$ reaction do not fit this pattern; instead they appear to belong to a sequence (2-F → 2,3-F$_2$ → 2,3,4-F$_3$ → 2,3,4,5-F$_4$ → 2,3,4,5,6-F$_5$) where fluorines have been successively introduced into positions *ortho* to existing fluorines; the reaction begins with fluoride ion attack on the pyridine cation-radical at C$_2$, which is calculated to be the position of highest positive charge.

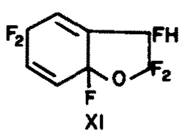
The third example is the benzo[b]furan/CsCoF$_4$ reaction.[20,21] At 380°, the products were those shown in Scheme 4. Here again, as with the first two examples, most or all of the aromatic products show the pattern of



Scheme 4. Products (wt.%) from the $CsCoF_4$/benzo(b)furan reaction (remaining unidentified products were minor).

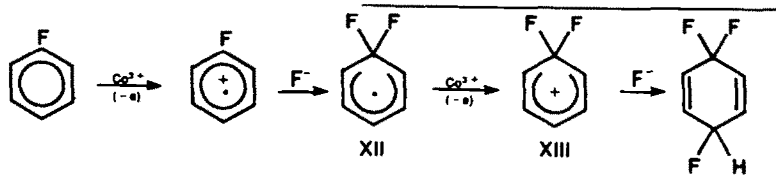
ortho-fluorination (V→VIII→VII→→IV). If the fluorination first gives V and VI, and CNDO/2 calculations of the type given in our first paper[1] certainly support initial attack on the furan ring, then subsequent "*ortho*-fluorination" would lead to VIII (F *ortho* to 0) and so on. Fluorinations with $KCoF_4$ and cobalt trifluoride[21] follow the same pathway up to V and VI; after this the paths divide and *all* the CoF_3 and $KCoF_4$ products can be rationalized if the dienes X and XI are intermediates, and formation of these is wholly in accord with the favoured mechanism.[1]


X

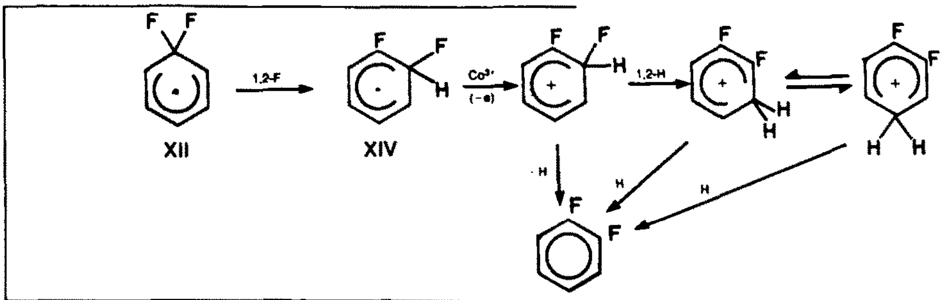

XI

To summarize then, the second feature we will discuss occurs with at least two caesium-containing fluorinating agents and shows itself in the production of sequences of fluoro-aromatic compounds with successive fluorines introduced vicinally.

To exemplify the central point of our rationalization of these two anomalous features, we turn to the fluorination of fluorobenzene. In the favoured mechanism,[1] this proceeded thus:



We now suggest that, besides being oxidized, the cyclohexadienyl radical (XII) can, in circumstances to be discussed later, rearrange by 1,2-migration of fluorine, followed by oxidation and loss of a proton, either before or after further proton migrations, to give 1,2-difluorobenzene:-



Continuation of this—attack of F^- on a F-bearing carbon in the cation-radical of *o*-difluorobenzene, followed by 1,2-F migration—would lead to 1,2,3-trifluorobenzene and so on. Analogous reactions might also, or alternatively, occur with the cyclohexadienyl cation (XIII). We will now justify this suggestion and then show how it can account for the two anomalies described above.

Arguments for 1,2-fluorine migrations in *both* radicals (e.g. XII) and cations (e.g. XIII) can be sustained for all the fluorinations discussed in this paper, except for one pyridine case [marked with an asterisk in Scheme 5], where the cation route is perhaps doubtful.

The arguments can be divided into two parts: the thermodynamics of 1,2-migrations, and their kinetics.

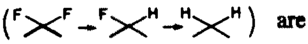
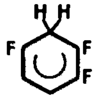
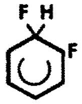
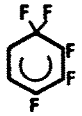
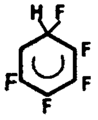
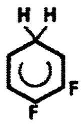
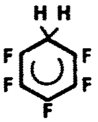
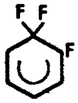
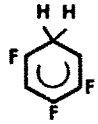
There is no direct experimental evidence for the relative stabilities of cyclohexadienyl radicals of the XII and XIV types. CNDO/2 calculations, however, indicate that both migration steps  are *always* exothermic for a variety of F-containing ben-

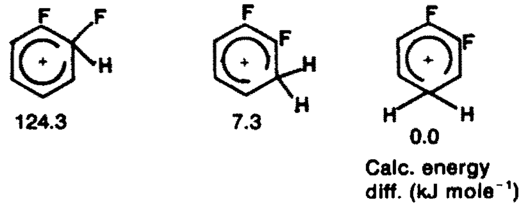
Table 1. Energies (Hartree) of polyfluoro-benzenium ions and radicals

	Cation	Radical		Cation	Radical
	101.4168	101.7714		128.4953	128.8000
	101.4646	101.7836		182.3593	182.7278
	101.5092	101.8108		182.3825	182.7351
	101.5120	101.8107		182.4389	182.7615
	128.4061	128.7594		128.4565	128.7740
	128.4308	128.7676		128.4815	128.7994
	128.4938	128.7958		128.4990	128.8004
	128.4793	128.7951			

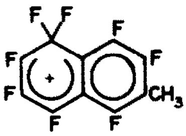
zenes and naphthalenes (Tables 1 and 3), and usually so, or only slightly (< 66 kJ mole^{-1}) endothermic for fluorine containing pyridines and anthracenes (Tables 2 and 4).

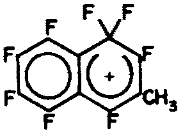
For the cations, there seems to be no doubt that, in solution, F-containing cyclohexadienyl cations are most stable when the tetrahedral carbon is a CH_2-group rather than a CHF. Olah *et al.*[22-24] have reported many examples of the protonation of polyfluoro-aromatics and the proton is always added at a H-bearing carbon and never at a F-bearing. CNDO/2 calculations indicate that as with the radicals, both migration steps () are *always* exothermic for benzenes and naphthalenes (Tables 1 and 3) and usually so for pyridines and anthracenes (Tables 2 and 4). It is in the pyridines that the difference between migrations in radicals and migrations in cations may be investigated; some of the 1,2-fluorine shifts that would be required by our reaction paths are endothermic for radicals and not for cations, and some *vice-versa*.

Some support for the reliability of the CNDO/2 calculations is afforded by results on protonated 1,2-difluorobenzene where the 4-protonated form is calculated to be slightly more stable than the 3, in accord with the experimental result[23]—observable amounts of both forms are present at −50° in superacid solution with the 4-form being favored (protonation at the *F*-bearing position is not observed and would not be expected on the basis of CNDO/2 calculations):



1,2,4-Trifluorobenzene is predicted to protonate at the 5-position, which is what occurs in superacid medium,[24] and in a more complex example, the naphthalene derived cation XV is calculated to be less stable than its isomer XVI by 10.9 kJ mole^{-1}: Russian workers[25] have shown that XV isomerises to XVI on being treated with SbF_5 at 40°.


XV


XVI

We conclude that the *directions* of the postulated migration (e.g. XII → XIV and the cation analogue) are almost always thermodynamically favoured for both radical and cationic species; the few exceptions are only slightly endothermic (≤ 50 kJ $mole^{-1}$) for the radicals, but may be strongly so (> 130 kJ $mole^{-1}$) for the cations.

We now turn to the kinetics of 1,2-migrations. General 1,2-migrations of Br and Cl in radical species have been widely reported,[26] and examples in cyclohexadienyl systems are known; there is a recent claim[27] for a similar migration of F, although on a simplistic view of orbital symmetry rules, such a migration is forbidden. 1,2-Migrations of H atoms are unknown; indeed they are definitely forbidden by orbital symmetry rules. However, they are not necessary to the success of the mechanism discussed in this paper: migration of F (from  to ), followed by hydrogen loss is all that is required—no hydrogen migrations are needed.

The situation with cationic species is rather more difficult. 1,2-Proton migrations are well-known and their kinetics need not be discussed further; they are not, in fact, essential to our mechanism, as discussed above. There are no clear examples of 1,2-F migration in cations and so it might be argued that although the migrations of this type that we require are usually thermodynamically favourable, their rates may be too small to render them observable. There has been a claim[28,29] for a 1,2-F shift or for a 1,2-fluoronium ion, but the experimental data can be more easily explained[30] in a way which avoids such features. Furthermore, there is no evidence for rate enhancement by neighbouring fluorine in solvolytic reactions, whereas this is well-known with the other halogens.[31] It therefore seems that fluorine forms 1,2-fluoronium ions—which are necessarily intermediates or transition states in 1,2-fluorine migrations—either not at all or only with great difficulty.

Table 2. Energies (Hartree) of polyfluoropyridinium ions and radicals

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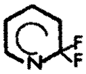
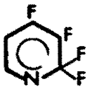
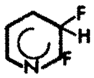
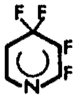
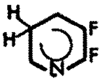
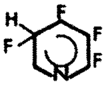
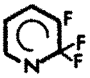
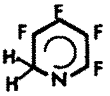
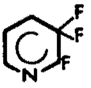
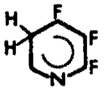
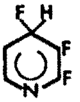
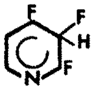
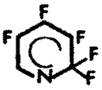
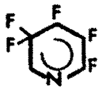
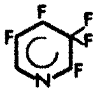
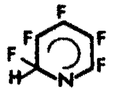
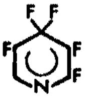
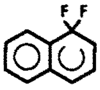
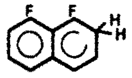
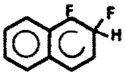
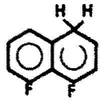
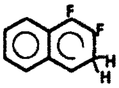
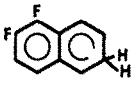
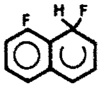
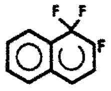
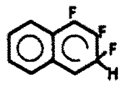
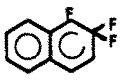
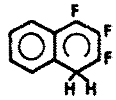
	105.1895	105.5693		159.1420	159.5384
	105.2437	105.5660		159.1690	159.5267
	105.2646	105.5956		159.1176	159.5252
	105.2886	105.5912		159.1908	159.5315
	132.1780	132.5558		159.2224	159.5654
	132.1844	132.5411		132.2700	132.5765
	132.1826	132.5511		132.2292	132.5568
	186.1269	186.5214		186.1308	186.5049
	186.1295	186.5060		186.1527	186.5297
	186.0996	186.5067			

Table 3. Energies (Hartree) of polyfluoronaphthalenium ions and radicals

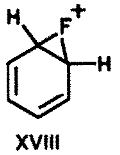
	Cation	Radical		Cation	Radical
	131.4428	131.6804		131.5312	131.8322
	131.4848	131.6938		131.5431	-
	131.4998	131.8225		131.5216	-
	131.4801	131.6863		158.4449	158.7700
	158.4583	158.7840		158.4588	158.7880
	158.5129	158.8035			

Nevertheless, there can be no overpowering objection in principle to 1,2-F migration or bridging in cations. Bridging does occur with other halogens[31]—the same group—and neighbouring group participation is known with oxygen[32]—the same period. Furthermore, it is difficult to avoid Peterson and Bopp's conclusion[33] that a 1,4-fluoronium cation occurs during the solvolysis of 5-fluoropent-1-yne, so that fluorine bridging, albeit not of the 1,2-type, can occur.

Rough calculations on the basis of existing data show that 1,2-F migrations in cations could conceivably occur under the rather high temperatures (200–500°) of fluorination, even though they may not be observable under more usual laboratory conditions. For example, the neighbouring group accelerations, in a particular SN1-type reaction, due to iodine, bromine, and chlorine were[31] 3×10^6, 810, and 3, respectively. These figures can be taken as measures of the ease with which these halogens form bridging halonium species. A figure of 10^{-6} for fluorine on the same scale would not seem to us to be unreasonably high (this 10^{-6} has, of course, no meaning in terms of neighbouring group participation rates; it is merely a measure of the ease of 1,2-bridging by fluorine compared to the other halogens). Russian workers[34] have measured a half-life of about 10^{-1}–10^{-2} sec. at −60° for a 1,2-Cl migration in a phenanthrene-based cyclohexadienyl-type system. This leads to a half-life of about 10^5–10^6 sec. for the equivalent 1,2-F migration; this is much longer than experiments are usually run for, and therefore could explain why Russian workers have never reported F migrations in their extensive work[35] on polyfluoro-naphthalenium and -anthracenium ions, even on species that might have been expected to undergo such isomerisations. Now, if for the purposes of rough calculation, the rate of 1,2-F migration is taken to double for every 10° rise in reaction temperature, then at the temperatures of fluorination the half-life for migration drops to well below the millisecond range, which is quite fast enough to accommodate our needs (the residence time of a molecule in a fluorination reactor is of the order of hours).

In addition to this, there are some *ab initio* calculations on a fluoronium species of the type we are discussing. Hehre and Hiberty[36] have calculated that the ion XVIII lies about 170 kJ mole^{-1} above the ion XVII:


XVII


XVIII

These calculations give too high an energy difference between the corresponding protonated species[37] (i.e. replace F by H in XVII and XVIII)—about 85 kJ mole^{-1} compared to the experimental value [38] of about 40—and so 170 is probably too high for the difference between XVII and XVIII. However, even this figure of 170 might just about do for our purposes: at about 400°, this gives the half-life for a fluorine migration of less than a second.

There is a further and alternative possibility which may be available for 1,2-F migrations: the metal ions of the fluorinating agent might intervene in some way to facilitate migrations. Metal ions are known[39] to bring about carbon skeletal rearrangements which do not otherwise occur.

Nevertheless, whatever the mechanistic background is, the *facts* of the fluorination experiments seem clear—abnormally large amounts of aromatic products with vicinal fluorines are formed with caesium-containing fluorinating agents. In these cases some sort of process whereby fluorine can migrate around a ring from a F-bearing carbon until it reaches a H-bearing one seems to us to be inescapable. In this paper we elaborate both likely pathways—radical and cation—and, while both may occur, the former can involve much higher energy barriers than the latter in at least one case—pyridine.

Our views on the major routes by which pyridine and benzo[b]furan are fluorinated to aromatic products are outlined in Schemes 5 and 6.

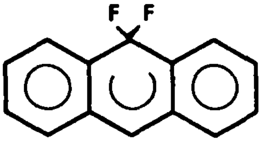
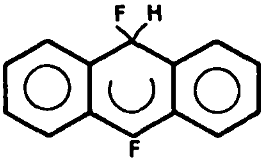
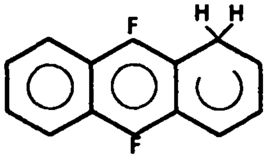
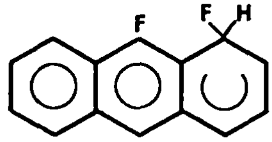
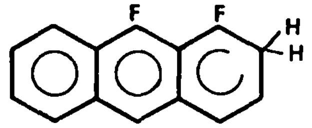
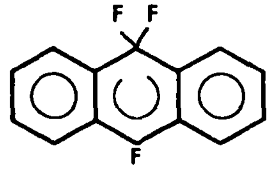
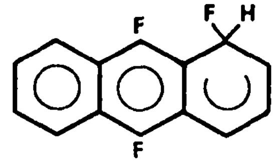
All the migration steps (fluorines or hydrogens) are, according to CNDO/2 calculations (Table 2), exothermic or slightly endothermic in the pyridinium radical case. In the analogous sequence of steps with cationic intermediates, one of the steps (*) is markedly endothermic. The initial additions of the extra F atoms are predicted, by the methods elaborated in our previous paper,[1] to take place as shown.

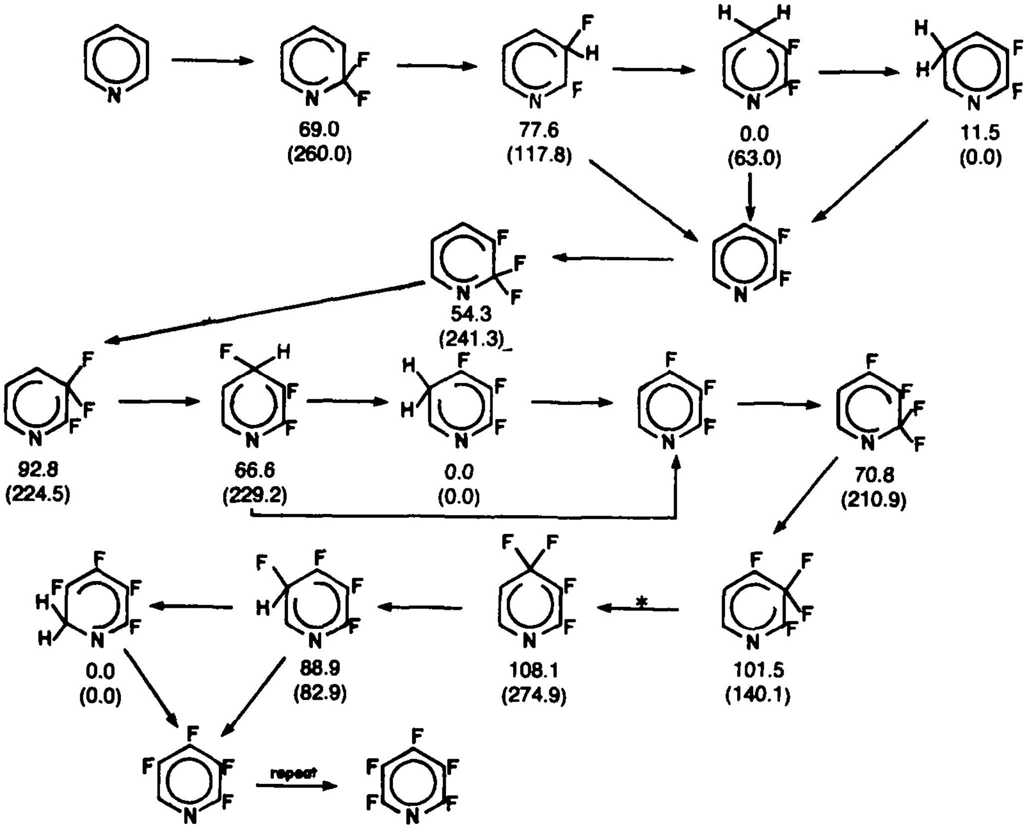
The benzo[b]furan route is based on analogy with the benzene and pyridine cases; the only calculation we have carried out shows that attack of fluorine begins in the furan ring.

The first anomaly mentioned in this paper—the higher degree of fluorination of polynuclear aromatics with the apparently weaker fluorinating agents—can also be resolved by a mechanism involving 1,2 shifts of F and H.

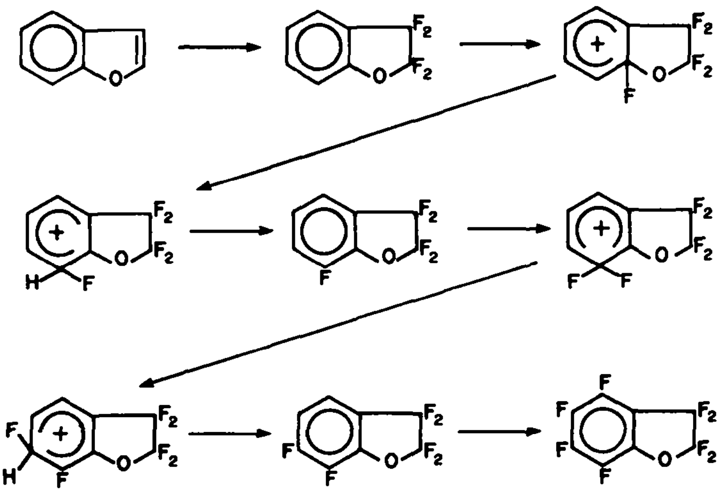
The sequence for naphthalene is outlined in Scheme 7; once again all the suggested migrations amongst the manifold of possible isomers are calculated (Table 3) to be exothermic, this time for all radical and all cationic steps. A *peri*-migration also seems possible and this is indicated in the Scheme. Experimentally, $KCoF_4$ and naphthalene gave[13] XX, XXI, and XXII, whereas $CsCoF_4$ gave only the last two.[11] As mentioned earlier, the CoF_3 fluorination appears to take a different course[1] with the difluoronaphthalenium cation XIX reacting with

Table 4. Energies (Hartree) of polyfluoroanthracenium ions and radicals

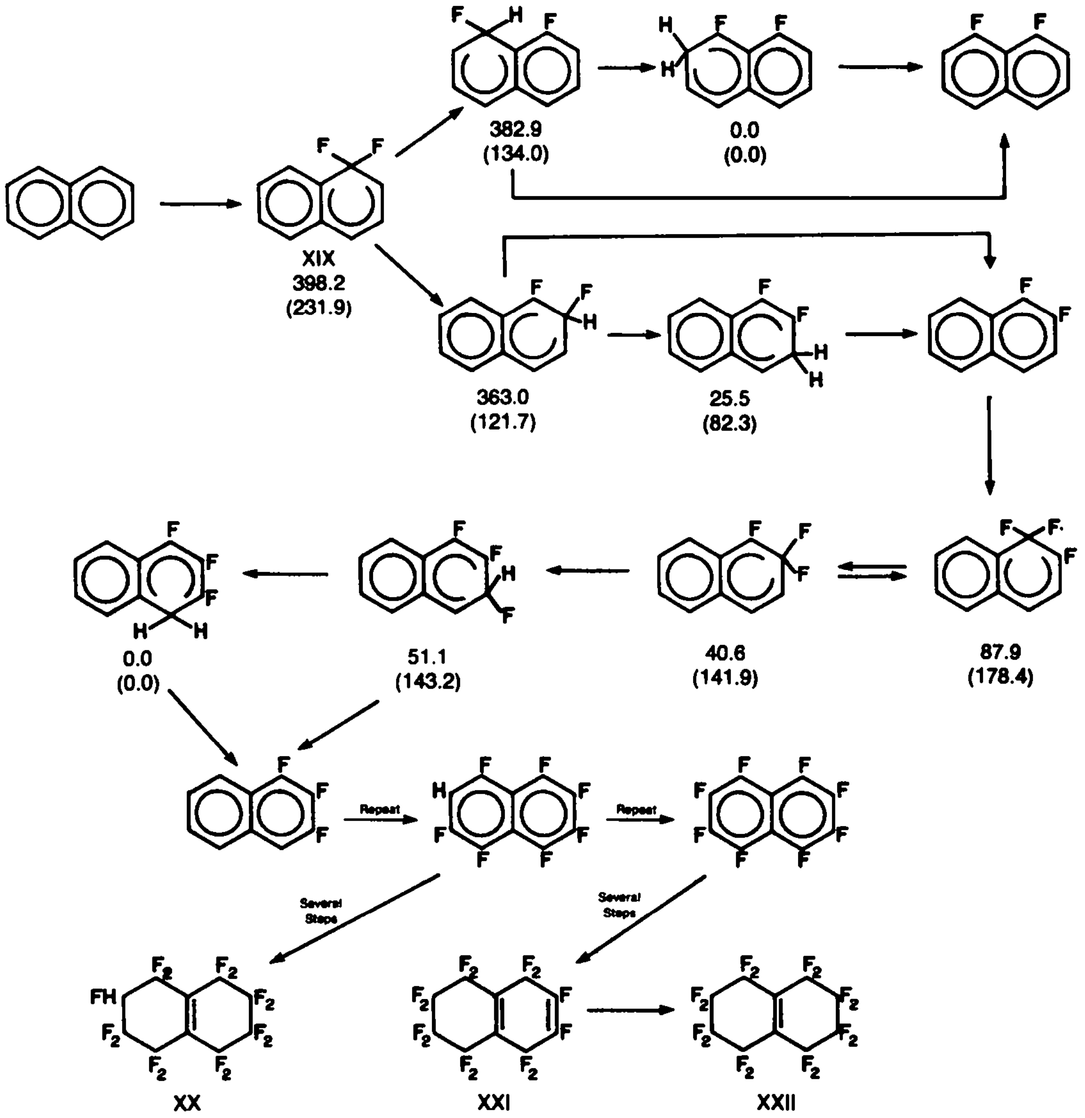
	Cation	Radical
	161.4736	161.7860
	161.5042	161.7917
	161.5111	161.7887
	161.4541	161.7668
	161.5123	161.7922
	188.4768	188.7843
	188.4473	188.7594



Scheme 5. Major routes for aromatic formation in the pyridine/$CsCoF_4$ reaction. Figures are energy differences (kJ mol^{-1}) between radical isomers with the most stable isomer being placed at 0.0. Figures in parentheses are for the corresponding cations.



Scheme 6. Major route for aromatic formation in the benzo[b]furan/$CsCoF_4$ reaction. A similar scheme can be written for radical species:

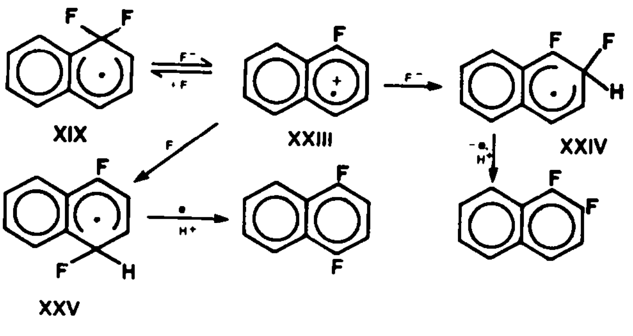


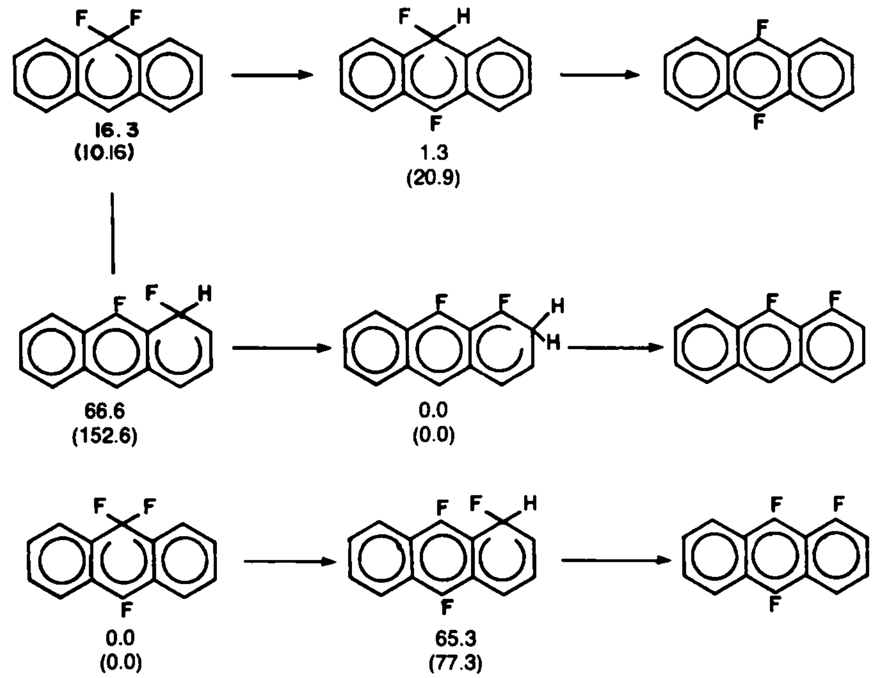
Scheme 7. Major routes for the fluorination of naphthalene over $KCoF_4$ and $CsCoF_4$. Figures as for Scheme 5.

fluoride ion instead of rearranging: this sequence finally leads to the triene (II) and then to saturated H-containing products as elaborated in our earlier paper,[1] where the argument for the formation of difluoronaphthalenium radical (XIX) from naphthalene can also be found.

Calculations on anthracenium species (Table 4) show that *peri*-migrations of fluorines are mildly endothermic for radicals and cations in the early stages of fluorination (Scheme 8) and so a plausible route to perfluoroanthracene, and hence the products actually found[14] in the $KCoF_4$ fluorination, is available via a series of migrations in either species. We have not been able to extend the calculations to more highly fluorinated molecules because of computer limitations.

It is also possible to get the required perfluoropolynuclear aromatics by an extension of the following sequence:





Scheme 8. Early stages in the fluorination of anthracene over $KCoF_4$ or $CsCoF_4$. Figures as for Scheme 5.

There are a number of variations of this which have the same essential feature in common—an equilibration between species like XIX and XXIII. Even if XXIII almost always reacts with fluoride ion to give XIX (and our calculations[1] suggest it should), the reversibility of the step would allow the occasional formation of XXIV or XXV and this would become irreversible by loss of hydrogen. This sequence does not, of course, explain the other anomaly (vicinal fluorines) we have been discussing in this paper, and we abandon it on the argument of Occam's razor, although it is otherwise attractive.

The final point that requires explanation is why the F migrations should take place only with caesium-containing HVMFs for benzenes and pyridines, and with $KCoF_4$ as well for polynuclear aromatics, but not with CoF_3. We believe that this is associated with the structure of the solid fluorinating agent and the migration of ions or atoms through it, and also with the stabilities of the radicals or cations which undergo rearrangement.

In the favoured mechanism of our first paper,[1] we argued that benzenium ions of type XIII would react with a fluoride ion, and that radicals of type XII would be oxidized by electron abstraction. However, in order to do this a fluorine species (ion or atom: even electron abstraction is likely to take place via a F atom bridge between a Co^{3+} ion and the organic radical, although it could occur directly to a Co^{3+} ion) must be available on the surface of the HVMF, and this may not always be so. In the local environment of the radical or cation, as it forms, there may not be a fluorine species of the required type in the vicinity and so some sort of movement will have to occur within the HVMF lattice to bring one to the surface. (Almost all the available fluorine, e.g. one per CoF_3, can be used in a fluorination, so the reaction is not a removal of a surface layer only—there has to be a way of getting at the fluorines in the interior of a CoF_3 particle.) It is our thesis that the time required to bring a fluorine to the surface is different for the different fluorinating agents: if this process is slow, radicals of type XII or cations of type XIII would have longer lifetimes and hence a greater opportunity to undergo the type of migrations discussed in this paper. This appears to be the situation with the benzenes and pyridines and $CsCoF_4$ and $CsTlF_4$. The ions or radicals (e.g. XIX) from polynuclear aromatics—naphthalene, anthracene, phenanthrene—would be more stable, relative to their aromatics, or their quenched products, than the benzenium species (e.g. XII) because of greater delocalization, and so would be longer-lived even in an environment where fluorines were more freely available; once again there would be time for F (and H) migrations to occur and we suggest that this is what happens over $CsCoF_4$ and $KCoF_4$, but not over CoF_3 where the F atom or ion flux is still too great and quenching of the ions occurs faster than migration.

Exactly what type of atom movements occur within the HVMF lattices is a matter for speculation. In CoF_3, it is reasonable to suppose that once the surface CoF_3 has been converted into, formally, CoF_2, the small Co^{2+} ions would migrate through the fluoride lattice into vacancies in the interior and so leave an effective layer of CoF_3 on the surface again; this could be very fast. With $KCoF_4$, $CsCoF_4$ etc., it is more difficult to suggest what might be happening. These compounds have layered structures (two-dimensional layers having the empirical formula CoF_4^-, with the potassium or caesium ions placed between them): the obvious mechanism now for getting fluorine to the surface of a particle involves, at some point, F atom or ion movement between the layers, across the gap occupied by the K or Cs ions. This would be slower for $CsCoF_4$ than for $KCoF_4$ because the gap is larger (the c spacing[5] is 12.49 Å in $CsCoF_4$ and 11.55 Å in the isostructural $KCoF_4$), and hence there would be more time for the 1,2-migrations of fluorine to occur with $CsCoF_4$ than with $KCoF_4$, as is observed.

The migration mechanism discussed in this paper is not restricted to fluorination. 1,2-Migrations of nitro-groups[40] and alkyl groups (the dienone-phenol rearrangement) have been reported in cyclohexadienyl cations; indeed migrations of deuterium, phenyl, and bromine have been reported[41] in a Ce^{4+} oxidation reaction where the proposed mechanism involved cation-radicals similarly to our fluorination mechanism. 1,2-Migration of Cl and Br in a benzenium radical was mentioned earlier.[26] It seems to us possible that 1,2-migrations are more general than has hitherto been suggested and that high *ortho*-substitution in an aromatic reaction might always indicate some intervention by such a mechanism. For example, anodic acetoyxlation and cyanation[42] sometimes give abnormally high *ortho*-reaction, as do a number of free-radical aromatic substitutions.[43]

We wish to emphasise that we are *not* abandoning the favoured mechanism of our first paper[1] (e.g. Scheme 1) in favour of the migration sequences discussed here. We suggest that for a given substrate both sequences can occur, the predominant one being determined by the availability of fluorine at the surface of the HVMF and the stability of the benzenium or similar radicals or cations. The two routes divide at species of the type XII—*either* oxidation and then quenching with fluoride ion *or* 1,2-migration of fluorine (or the equivalent with cations like XIII)—and since similar species occur several times along either route, neither is forced to be the sole pathway until quite late in a fluorination; furthermore the stabilities of particular types of radicals or cations might well change with the degree of fluorination and so it is possible that a fluorination might even change from being predominantly of the 1,2-migration type to the "favoured scenario" type or *vice-versa* during a fluorination.

Calculations

These have been carried out on the University of Birmingham ICL 1906A computor using the well-known CNDO/2 method. The geometries for the benzenes, naphthalenes, anthracenes, and ions and radicals derived from them, were as in Part I.[1] For the pyridines and pyridinium ions and radicals, the bond lengths (Å) were: all C–F = 1.33; all C–H = 1.08; $N_1–C_2 = 1.34$; $C_2–C_3 = 1.395$; $C_3–C_4 = 1.394$. The bond angles were: $N_1–C_2–C_3 = 123.9°$; $C_2–C_3–C_4 = 118.5°$; $C_3–C_4–C_5 = 118.4°$; $C_6–N_1–C_2 = 116.8°$. The exocyclic C–F (or C–H) bonds were placed so that they made equal angles with the two vicinal C–C (or C–N) ring bonds. The angle between the C–X bonds (X = H or F) at the tetrahedral position (CX_2) in the pyridinium ions and radicals was taken as 109.5° in all cases.

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