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Rearrangements with Migration of a Fluorine Atom

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The review is devoted to the rearrangement of organic compounds and intermediate species involving the migration of a fluorine atom. The sigmatropic migrations of a fluorine atom are examined from the standpoint of modern theoretical ideas. Special attention has been given in this review to reactions proceeding with migration of a fluorine atom in intermediate species.
The bibliography includes 87 references.

CONTENTS

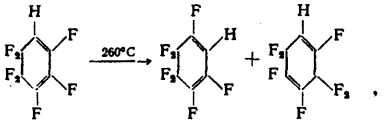
I. Introduction 62
II. Sigmatropic shifts of a fluorine atom in polyfluorinated olefins and cyclo-olefins 62
III. The migrations of a fluorine atom in carbenes, 1,3-biradicals, and radical-ions 64
IV. The migrations of fluorine atoms in radicals 65

I. INTRODUCTION

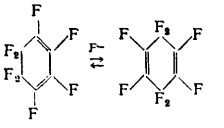
The rearrangements of organic compounds occupy an important place in organic chemistry, serving as a basis of many synthetic methods. In the vast stream of review publications devoted to a wide variety of aspects of rearrangements, much attention has been devoted to rearrangements with migration of halogen atoms in free radicals but there are virtually no reviews on the migration of a fluorine atom.[1] The latter factor is an obstacle to the development of a rigorous theory of reactions of this type, resulting in the propagation of the incorrect view that rearrangements with migration of a fluorine atom are impossible. The work by French investigators devoted to the theoretical study of free-radical rearrangements in which the authors explain the lack of experimental data concerning the 1,2-migration of a fluorine atom by the high barrier of such migration, may serve as an example of this situation.[2] On the other hand, numerous studies indicating the migration of a fluorine atom have been published in the last decade. The aim of the present review is to survey the available literature data on rearrangements with migration of a fluorine atom in a wide variety of situations and to make certain comparisons with the migrations of other halogen atoms, eliminating thereby the contradictions which have arisen between theoretical and experimental studies. The rearrangements in which the fluoride anion participates are not considered in detail in the present review.

II. SIGMATROPIC SHIFTS OF A FLUORINE ATOM IN POLYFLUORINATED OLEFINS AND CYCLO-OLEFINS

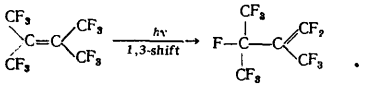
The isomerisation of polyflorinated olefins was first observed by Tatlow[3] in the pyrolysis of octafluorocyclohexa-1,4-diene and 1*H*-heptafluorocyclohexa-1,3-diene in a nickel flow-apparatus:



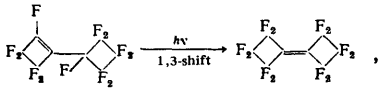
Later, in a study of the isomerisation of two octafluorocyclohexadienes,[4,5] it was shown that the establishment of equilibrium between the two dienes is accelerated by the fluoride anion and it was suggested that isomerisation thermolysis in nickel apparatus[3] also takes place with participation of the fluoride anion:



The photochemical migration of a fluorine atom has been noted in a series of polyflorinated olefins. Thus the photochemical 1,3-shift of a fluorine atom has been resorted to to account for the isomerisation of perfluoro-2,3-dimethylbut-2-ene:[6]



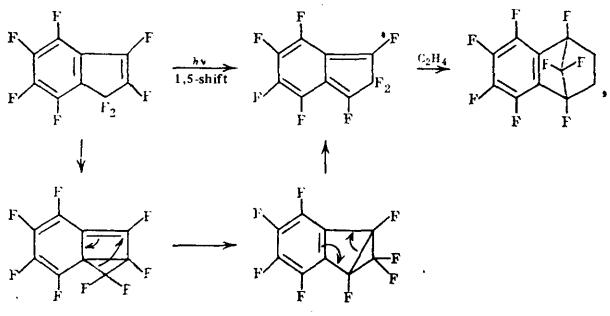
The 1,3-sigmatropic shift of a fluorine atom has been observed in the photolysis of perfluorinated cyclobutene derivatives:[7]



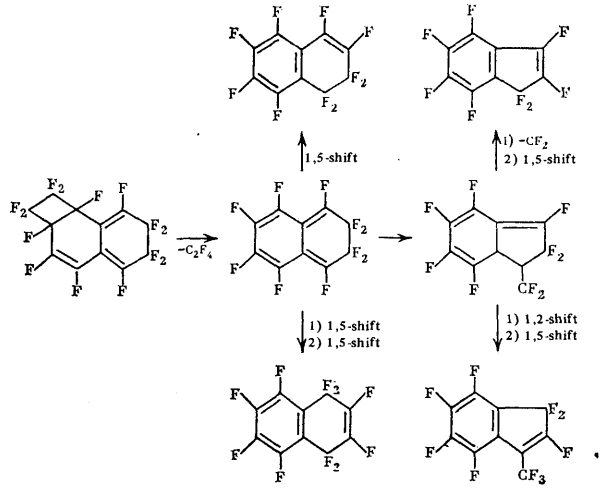
In a series of polycycloalkenes with dienes, the sigmatropic shift of a fluorine atom has been used to explain the isomerisation occurring both in photolysis and in thermolysis:[8-10]

Experimental confirmation of the sigmatropic migration of a fluorine atom in the photolysis of perfluoroindene has been explained—perfluoroisoindene is trapped in the form of an adduct with ethylene.[10] However, there is a possible alternative route to the formation of perfluoroisoindene which does

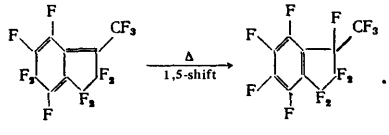
not require the invocation of a sigmatropic shift of a fluorine atom:[11]



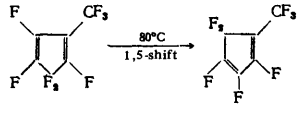
The formation of perfluorinated derivatives of 1,2- and 1,4-dihydronaphthalenes and perfluoroindenes in the thermolysis of perfluorinated bicyclictrienes has been explained by sigmatropic shifts of a fluorine atom:[12]



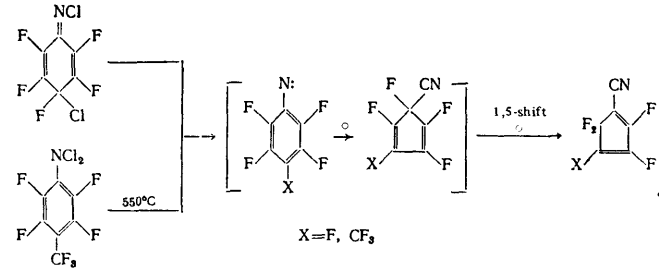
In the literature there are several further examples of thermal isomerisations involving a 1,5-sigmatropic shift of a fluorine atom. Thus, in the thermolysis of perfluoro-7-methylbicyclo[4.3.0]nona-1,4,6-triene, the migration of a fluorine atom leads to perfluoromethylindan:[13]



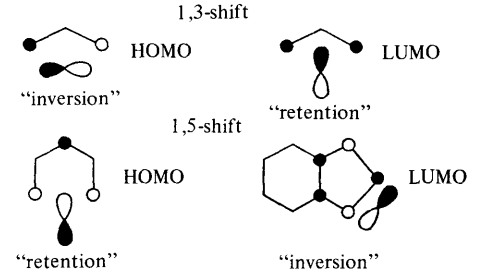
The sigmatropic migration of a fluorine atom has been observed in the thermolysis of perfluoro-2-methylcyclopentadiene:[14]



The 1,5-sigmatropic shift of a fluorine atom has also been invoked to account for the formation of polyfluorinated derivatives of cyclopentadiene in the thermolysis of the epoxy-derivatives of Dewar hexafluorobenzenes[15] and in the thermal isomerisation of perfluorinated arylnitrenes:[16,17]

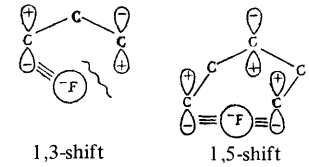


The great practical importance of isomerisations involving a sigmatropic shift of a fluorine atom in the chemistry of polyfluorinated olefins and cyclo-olefins led to attempts at a systematic and theoretical treatment of these processes. The sigmatropic shift of a fluorine atom has been discussed[5] from the standpoint of the theory of frontier orbitals. The frontier orbital approximation shows that, as for the migration of alkyl groups, the 1,3- and 1,5-shifts are allowed for a fluorine atom. The migration can be represented as the displacement of a fluorine atom in allyl or pentadienyl radicals:



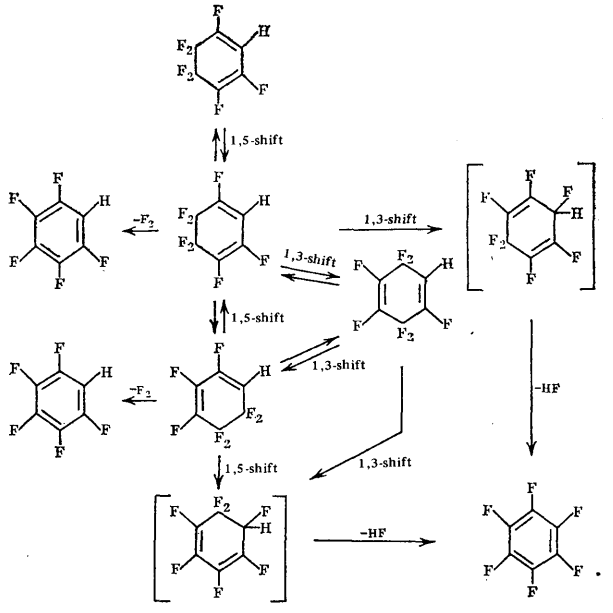
Two lobes of the atomic *p* orbital of the fluorine atom participate in the thermal 1,3-shift and the orbitals of the fluorine atom undergo "inversion" in the migration process. In the photochemical 1,3-rearrangement, occurring in the excited state, the configuration of the orbitals is retained. The rules are reversed for the 1,5-shift: for thermal reactions, the configuration of the orbitals is retained while for photochemical processes "inversion" should be observed.

It is believed[18] that the description of the migration of a fluorine atom within the framework of the sigmatropic shift can be complicated by the involvement of the unshared electron pairs of the fluorine atom. An approximate picture of this effect is secured by considering the migration of fluorine in the form of an anion, having spherical symmetry, in the allyl or pentadienyl cation. In this treatment, only the 1,5-shift is allowed from the standpoint of orbital interaction.

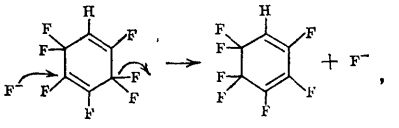


Indeed the pyrolysis of polyfluorocyclohexadienes shows that the 1,5-shift of a fluorine atom is preferred to the 1,3-shift.[18] However, these data cannot indicate the "prohibition" of the 1,3-shift of a fluorine atom. Analysis of the results presented at the beginning of this Section also demonstrates that the thermal 1,5-shifts[12-17] and the photochemical 1,3-shifts of a fluorine atom proceed more readily,[6,7] i.e. those processes in which the configuration of the orbitals of the fluorine atom should be "retained". A

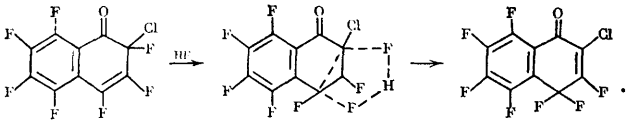
study of the interconversion of heptafluorocyclohexadienes led to the conclusion[5] that the fluorine atom migration processes occurring with "retention" of the configuration of the orbitals of the fluorine atom are preferable to those requiring the "inversion" of such configurations, although the extent of such preference is not high.



The results of the study by Burdon et al.[18] also show that the interpretation of the observed isomerisation invoking sigmatropic shifts of a fluorine atom should be approached with caution, since the 1,3- and also probably the 1,5-migration of a fluorine atom is catalysed by the fluoride anion:



Thus the results of the thermolysis of hepta- and octafluorocyclohexadienes in new Pyrex and quartz tubes differ appreciably from the results obtained in old tubes where more than 20 pyrolyses have been carried out. In pyrolyses in old tubes and also in pyrolyses in the presence of sodium fluoride, the 1,3-migration of a fluorine atom and the aromatisation of the initial dienes begin to proceed to an appreciable extent. Furthermore, fairly numerous examples of the HF-catalysed 1,3-migration of a fluorine atom are known in the literature.[19,20] Such an example is provided by the isomerisation of polyfluorinated cyclic dienones:



III. THE MIGRATION OF A FLUORINE ATOM IN CARBENES, 1,3-BIRADICALS, AND RADICAL-IONS

Numerous instances of the 1,2-shift of a fluorine atom in carbenes are known.[21,22] The observed series based on the capacity for migration[23] shows that hydrogen, chlorine, and the perfluoroalkyl group migrate more readily than the fluorine atom:[21,24] $Cl > H > C_2F_5 > F$.

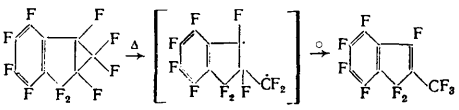
$$CF_3CH: \rightarrow CF_2{=}CHF ,$$
$$C_2F_5{-}CF_2CH: \rightarrow CF_2{=}CH{-}C_2F_5 .$$

In connection with the study of the vinylidene–acetylene rearrangement, much attention has been devoted recently to the possibility of the formation of difluoroacetylene in the isomerisation of difluorovinylidene:

$$CF_2{=}C: \rightarrow CF{\equiv}CF .$$

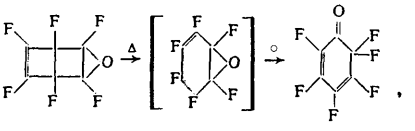
The corresponding calculations by various quantum-chemical methods have been described in a number of publications[25–26] and demonstrated the presence of a fairly high energy barrier (~36 kcal mol^{-1}) to the migration of a fluorine atom in this process, while a hydrogen atom migrates almost without a barrier in an analogous reaction.[26] The presence of a high barrier to the 1,2-migration of a fluorine atom has been attributed by Pople[26] to the antiaromatic character of the cyclic 4π-electron transition state. The high energy barrier to the 1,2-shift of a fluorine atom in this reaction is probably the reason why it has not so far been possible to effect experimentally the rearrangement of difluorovinylidene to difluoroacetylene.[28]

The 1,2-migration of a fluorine atom has been observed in the thermal isomerisation of perfluorocyclopropane derivatives with ring opening:[12,29]



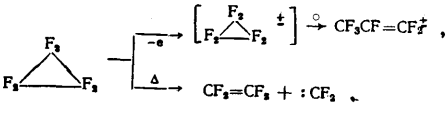
Perfluoromethylindene may be formed in the thermolysis of perfluorinated tricyclic cyclopropane derivatives both as a result of isomerisation wth the opening of the cyclopropane ring and subsequent 1,2-migration of a fluorine atom in the intermediate 1,3-biradical and synchronously.[29]

Perfluorocyclohexa-2,4-dien-1-one is formed similarly in the thermolysis of the epoxy-derivative of Dewar hexafluorobenzene,[15] which probably proceeds via the formation of the epoxy-derivative of hexafluorobenzene:



In contrast to the thermal reactions of perfluorocyclopropane derivatives quoted above, it has been suggested that cyclohexadienone is formed from the epoxy-derivative of Dewar hexafluorobenzene as a result of the migration of a fluorine atom in the zwitter-ion.[15]

A rearrangement with migration of a fluorine atom has been observed in the photoionisation of perfluorocyclopropane:[30]

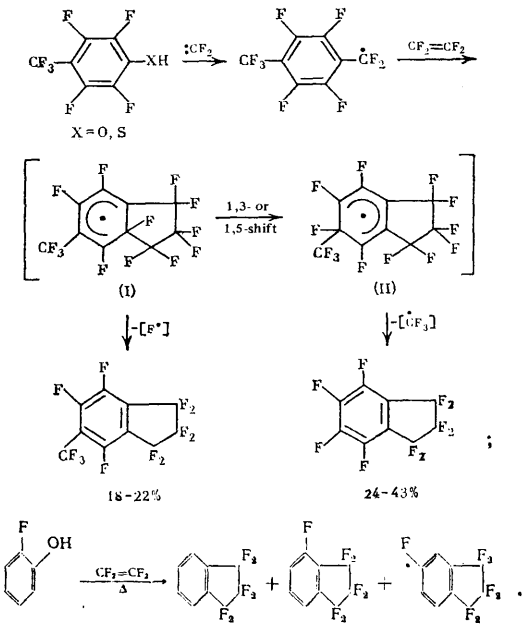


It is noteworthy that the thermolysis of perfluorocyclopropane does not lead to the formation of perfluoropropene but is accompanied by decomposition to tetrafluoroethylene with elimination of difluorocarbene.[31]

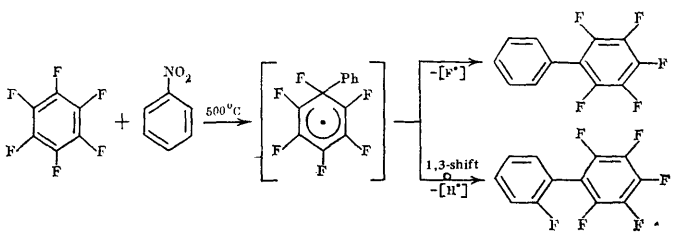
IV. THE MIGRATIONS OF FLUORINE ATOMS IN RADICALS

1. The 1,3- and 1,5-Shifts in Cyclohexadienyl Radicals

In order to account for the preferential formation of perfluoroindan in the copyrolysis of perfluoro-*p*-cresol and perfluoro-*p*-thiocresol with tetrafluoroethylene,[32] a mechanism has been proposed according to which a 1,3- or 1,5-sigmatropic shift of a fluorine atom takes place in the corresponding σ-complexes (I) with formation of the isomeric σ-complex (II). The stabilisation of the σ-complex (II) with abstraction of the trifluoromethyl radical leads to perfluoroindan. An analogous mechanism has been proposed also to explain the formation of 1,1,2,2,3,3,5-heptafluoroindan together with hexafluoroindan and 1,1,2,2,3,3,4-heptafluoroindan in the copyrolysis of *o*-fluorophenol with tetrafluoroethylene in proportions of 1 : 2.5 : 2.2 respectively:[33]

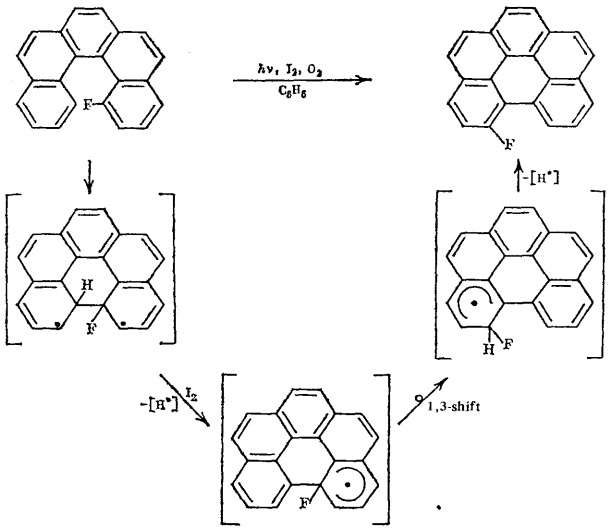


It has been suggested that the migration of a fluorine atom occurs also in the high-temperature reaction of nitrobenzene with hexafluorobenzene[34] in which 2,2',3,4,5,6-hexafluorobiphenyl was detected mass-spectrometrically:

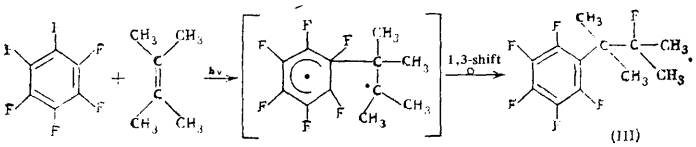


The formation of the same product has been detected in the reaction of benzoyl peroxide with hexafluorobenzene.[35]

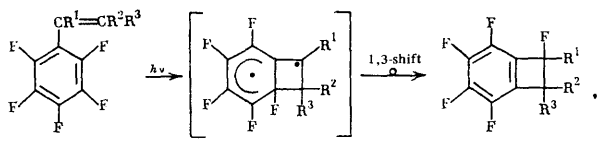
A similar migration of a fluorine atom has been proposed recently to account for the mechanism of the photocyclisation of 1-fluoro[5]helicene:[36]



The photolysis of hexafluorobenzene in the presence of 2,3-dimethylbut-2-ene leads mainly to the product (III), whose formation is apparently associated with the 1,3-migration of a fluorine atom from the ring to the side chain in the intermediate biradical:[37]

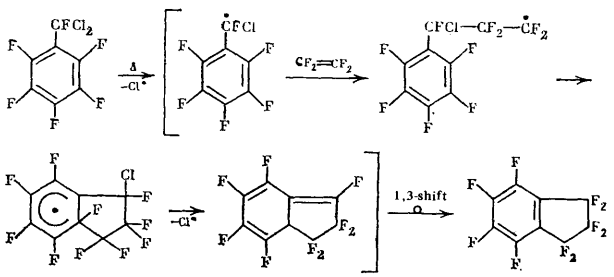


The migration of a fluorine atom has also been observed in the photocyclisation of polyfluorinated alkenylbenzenes in the gas phase,[38] leading to the formation of fluorine-containing benzocyclobutenes:



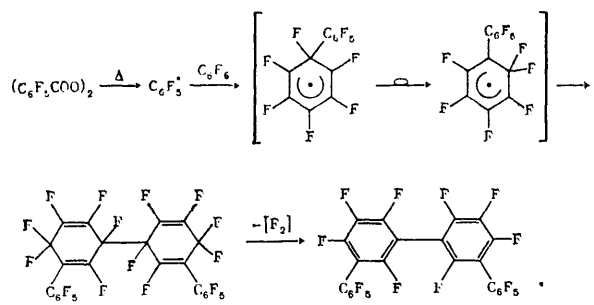
The migration of a fluorine atom can occur as a 1,3-sigmatropic shift concerted with the cyclisation process or following the latter, although the authors do not rule out the possibility of a repeated 1,5-shift of a fluorine atom.

Similar cyclisation with migration of a fluorine atom to the side chain has been observed also in the copyrolysis of pentafluoro(trichloromethyl)benzene with chlorotrifluoroethylene[39] and of αα-dichlorohexafluorotoluene with tetrafluoroethylene:[40]

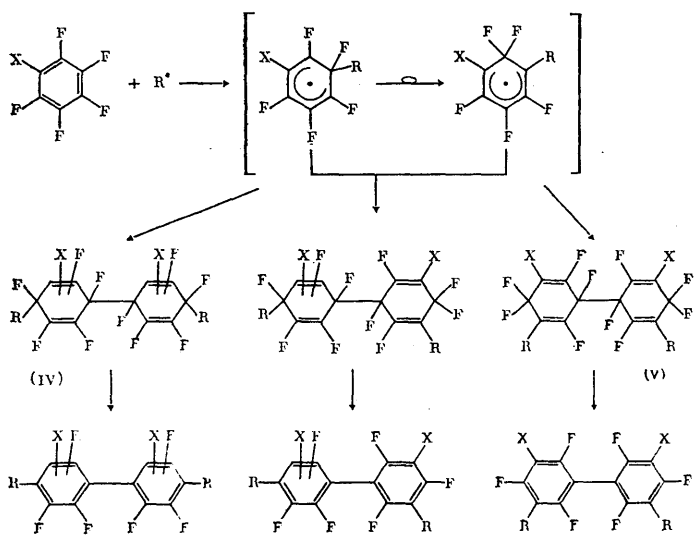


2. The 1,2-Migration of a Fluorine Atom in Cyclohexadienyl Radicals

Ten years ago the 1,2-migration of a fluorine atom in radicals was still regarded as impossible.[41] During the intervening period, a series of studies providing experimental evidence that such migration is achievable under certain conditions have been published. The 1,2-migration of a fluorine atom in cyclohexadienyl raidcals, formed in the radical reactions of aromatic polyfluoro-compounds, has been studied in greatest detail. The rearrangement of cyclohexadienyl radicals with migration of a fluorine atom was first observed in a study of the interaction of hexafluorobenzene with pentafluorobenzoyl peroxide at 200 °C.[42] The defluorination of the mixture of products of this reaction having the composition $C_{24}F_{22}$ led to the formation of perfluoro-*mm'*-quaterphenyl in a quantitative yield, which provided grounds for the assumption that its precursor is perfluoro-3,3'-diphenyl-1,1',4,4'-tetrahydroquaterphenyl—the dimer of the σ-complex resulting from the addition of the pentafluorophenyl radical to hexafluorobenzene. Evidently, this dimer cannot be obtained by the dimerisation of the primary σ-complex but is the product of the dimerisation of the secondary σ-complex formed on rearrangement with migration of a fluorine atom from the geminal site in the cyclohexadienyl radical to a neighbouring position:

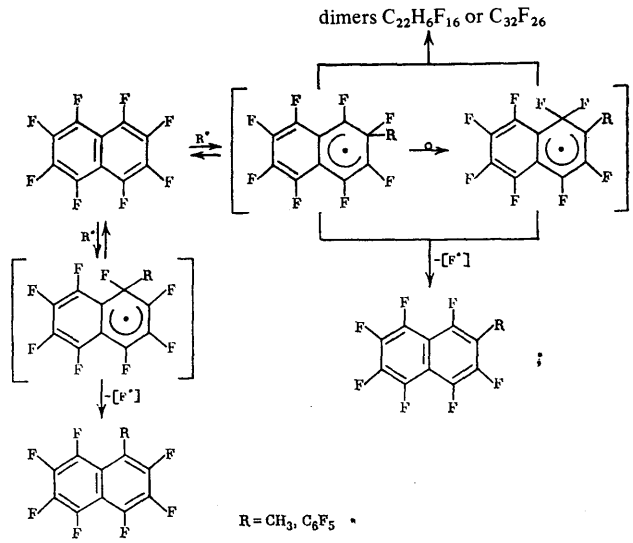


An analogous rearrangement takes place in the cyclohexadienyl radical formed in the reaction of hexafluorobenzene with phenyl,[43] methyl,[44] and cyclohexyl[45] radicals and also in the reactions of octafluorotoluene[46] and decafluorobiphenyl[47] with the pentafluorophenyl radical:



X: F F F F C_6F_5 CF_3
R: CH_3 C_6H_{11} C_6H_5 C_6F_5 C_6F_5 C_6F_5

In the cyclohexadienyl radicals formed by the addition of perfluoroalkyl radicals[44,48,49] or the pentafluorobenzoyloxy-radical[42,50] to aromatic polyfluoro-compounds, a rearrangement with migration of a fluorine atom does not take place. The general character of the rearrangement of polyfluorinated cyclohexadienyl radicals with 1,2-migration of a fluorine atom has been confirmed by the results of the reaction of octafluoronaphthalene with the methyl and pentafluorophenyl radicals:[51]



A characteristic feature of these reactions is a relatively high yield of 2-substituted octafluoronaphthalene derivatives, which can be attributed to the reversible addition of the methyl and pentafluorophenyl radicals to the aromatic ring and the consequent possibility of the interconversions of the isomeric σ-complexes. The irreversible removal from the equilibrium of the σ-complexes formed when these radicals are added to the 2-position in octafluoronaphthalene, as a result of a rearrangement with migration of a fluorine atom from the geminal site in the cyclohexadienyl radical to the 1-position, ensures the accumulation of more stable σ-complexes, whose defluorination actually affords 2-substituted heptafluoronaphthalenes.

A kinetic scheme for the interaction of aromatic polyfluoro-compounds with radicals has been analysed for the reaction of hexafluorobenzene with the cyclohexyl radical.[45] It follows from this analysis that the rearrangement is a unimolecular process, since the ratio of the yields of the products (IV)/(V) (see the scheme above) is a linear function of the concentration of the cyclohexyl radical R', which depends on the initial concentration c_0 of the source of this radical:

$$(IV)/(V) = K[R^{\cdot}] = f(c_{0\ \text{peroxide}}).$$

The analogous analysis performed on the assumption of a bimolecular rearrangement gives rise to the ratio (IV)/(V) which is independent of the radical concentration. The experimental data show that in reality the product ratio (IV)/(V) varies with the concentration of di-t-butyl peroxide.

The dependence of the degree of rearrangement on the reaction temperature and the concentration of the source of the radical has been established for the interaction of hexafluorobenzene with the phenyl, pentafluorophenyl, and cyclohexyl radicals.[44] An increase in the reaction temperature increases the degree of the rearrangement. With an increase in the concentration of the source of the radical,

the lifetime of the radical σ-complexes diminishes as a result of the increase in their concentration in solution and there is a consequent decrease in the degree of rearrangement.

Assessment of the role of factors associated with the structure of the geminal site in polyfluorinated cyclohexadienyl radicals in a rearrangement with migration of a fluorine atom has shown that the possible contribution by the steric hindrance in the geminal site of the σ-complexes is extremely insignificant. The influence of the concentration of the source of the radical on the degree of rearrangement is the same for the σ-complexes formed by the addition to hexafluorobenzene of both the methyl and cyclohexyl radicals, which have similar polarities, but differs appreciably as regards its steric requirements[44] (See Table).

Estimation of the contribution of steric effects to the driving forces of the rearrangement.[44]

Concentration of di-t-butyl peroxide, M	Degree of rearrangement	
	$CH_3^{\cdot}$	cyclo-$C_6H_{11}^{\cdot}$
0.77	0.29	0.27
0.42	0.50	0.32
0.38	0.58	0.47
0.33	0.85	0.58
0.19	1.12	0.68

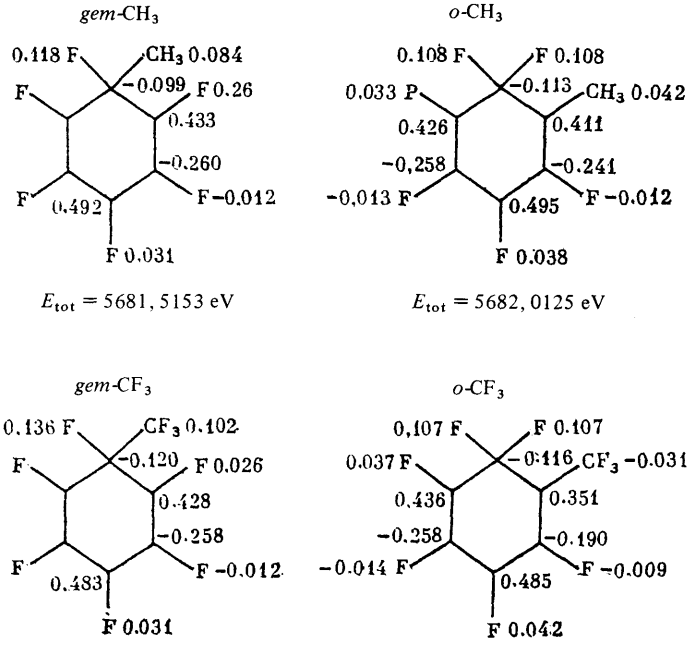
In order to estimate the influence of the nature of the substituents at the geminal site on the stability of the radical σ-complex, the total energies E_{tot} and the distribution of the spin densities in the rearranged and non-rearranged σ-complexes of the methyl and trifluoromethyl radicals with hexafluorbenzene were calculated.[44] The calculations were performed by the unrestricted Hartree–Fock method in terms of the INDO approximation with the standard parametrisation of Pople and Segal.[52] The bond lengths and angles optimal for fluorinated cyclohexadienyl radicals, obtained[53] by INDO calculations with the same parametrisation, were used.

The results of the calculation (see Figure), show that, when the methyl radical adds to hexafluorobenzene, the rearranged σ-complexes are more stable than the non-rearranged complexes by 11.6 kcal mol^{-1}, whereas in the case where hexafluorobenzene is attacked by the trifluoromethyl radical, the reverse situation obtains—the non-rearranged σ-complexes are found to be more stable (by 3.8 kcal mol^{-1}).

The ratio of the unpaired electron densities in various positions in the unsaturated part of the non-rearranged σ-complexes of the methyl and trifluoromethyl radicals with hexafluorobenzene are virtually the same, whereas for the geminal sites appreciable differences are observed on passing from the non-rearranged σ-complexes to the rearranged complexes: when the methyl radical adds on, a greater fraction of the spin density is found to be concentrated on the fluorine atoms of the difluoromethylene group at the geminal site, whereas in the case where the trifluoromethyl radical is added the fraction of spin density on the fluorine atoms of the geminal site is smaller than in the non-rearranged σ-complex.

Thus the results of the calculations show that the rearrangement may be caused by the energy gain on formation of the geminal unit with two fluorine atoms. The increase in the C–F bond strength as the geminal fluorine atoms accumulate has been described in the literature[54] and there exist data indicating the higher stability of the polyfluorinated arenium ions having two fluorine atoms in the geminal unit compared with isomers containing in the geminal unit substituents other than fluorine atoms.[55]

Although the difluoromethylene group is saturated, nevertheless it exhibits an electron deficient character.[56] For example, perfluoroalkanes form complexes with electron-donating solvents.[57] In the analysis of the electronic effect of the difluoromethylene group, Liebman used these data to justify treating it as an analogue of the carbonyl group.[58]



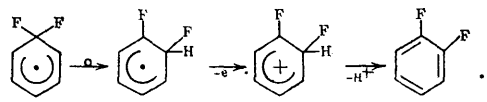
Distribution of spin density and total energies of polyfluorinated cyclohexadienyl radicals.[44]

If this approach is applied to the analysis of the stability of radical σ-complexes, then in the case where the geminal unit contains two fluorine atoms, the σ-complex can be regarded as a substituted phenoxy-radical after the replacement of the difluoromethylene group by the carbonyl group. The relatively high stability of different substituted phenoxy-radicals has long been known.[59]

In those cases where the geminal unit contains a fluorine atom and a substituent with a high electronegativity (perfluoroalkyl and pentafluorobenzoyloxy-groups), the electron-accepting properties of the unit produced remain extremely powerful. There exist literature data demonstrating the capacity of the trifluoromethyl group for conjugation with the radical centre.[60] On the other hand, the replacement of a fluorine atom in the difluoromethylene unit of a polyfluorinated radical σ-complex by an electron-donating substituent (the methyl or cyclohexyl group) should apparently lead to a sharp weakening of the electron-accepting properties of the saturated unit. These differences do in fact determine to some extent the possibility of the rearrangement of fluorinated radical σ-complexes with migration of a fluorine atom from the geminal unit to a neighbouring position.

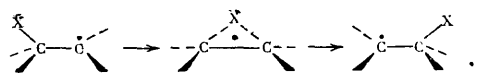
Burdon and Parsons[61] invoked the 1,2-shift of a fluorine atom in radical σ-complexes to explain the formation of fairly large amounts of aromatic polyfluoro-compounds in the reaction of benzene with $CsTlF_4$. Their calculation of the energy

of the cyclohexadienyl radicals by the CNDO/2 method showed that the stage involving the 1,2-migration of the fluorine atom is exothermic.

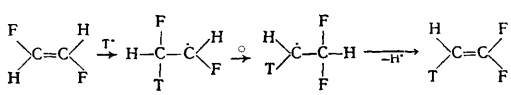


The authors believe that this is a key stage in the fluorination of aromatic compounds despite the fact that, in their view, it is prohibited from the standpoint of orbital symmetry rules. However, such prohibition tends to be regarded as absolute. The driving force of the rearrangement can apparently have a purely thermodynamic nature associated with the fact that the radical formed as a result of the rearrangement is much more stable than the initial radical.

In 1981 French workers published a theoretical study[2] of free-radical migration. They carried out a calculation by the STO-3G RHF method for a series of 1,2-rearrangements of β-substituted ethyl radicals. The difference between the energies of the β-substituted ethyl radical and the symmetrical bridge structure, adopted as the transition state in the process, was adopted as the energy barrier to the reaction:

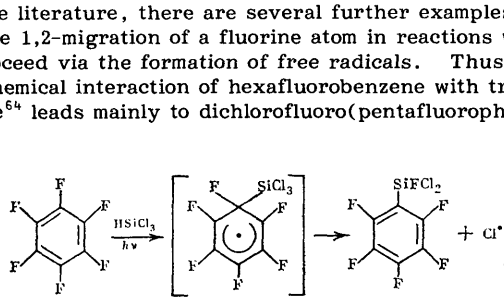


The calculation for the 1,2-shift of a fluorine atom, like that for the 1,2-shift of a hydrogen atom and groups such as OH, NH_2, and CH_3 yielded a very high barrier to the reaction (E = 107 kcal mol^{-1}, H = 88 kcal mol^{-1}). The authors believe that the activation energies for these rearrangements are much higher than the activation energies for processes such as recombination, transfer, etc. and that this is the reason why these rearrangements have not been detected experimentally. The authors were probably unaware of either the results of studies on the radical reactions of aromatic polyfluoro-compounds,[42-51] discussed above, or of a study[62] of the 1,2-shift of a fluorine atom in the 1,2-difluoroethyl radical obtained as a result of the addition of tritium to *trans*- and *cis*-1,2-difluoroethylenes:



It is also noteworthy that the method employed by Fossey and Nedelec[2] yields barriers to the rearrangements which are much too high. A calculation has been recently carried out for the 1,2-migrations in free radicals by the MNDO SCF-MO method.[63] The barriers to the rearrangement calculated in the above study are much lower than in the previous investigation[2] and agree with experimental data for rearrangements known in the literature. Unfortunately, the authors[63] did not carry out a calculation for the 1,2-migration of a fluorine atom.

In the literature, there are several further examples involving the 1,2-migration of a fluorine atom in reactions which can proceed via the formation of free radicals. Thus the photochemical interaction of hexafluorobenzene with trichlorosilane[64] leads mainly to dichlorofluoro(pentafluorophenyl)-silane:



It has been suggested that the formation of this product is associated with a rearrangement in the initial σ-complex of the trichlorosilyl radical with hexafluorobenzene. It was later shown that such rearrangement is a common reaction in the series of organosilicon compounds:[23]

$$ClCH_2CF_2SiCl_3 \xrightarrow{\Delta} ClCH_2CFClSiFCl_2 \xrightarrow{\circ} ClCH_2CCl_2SiF_2Cl\ .$$

The photochemical exchange of hydrogen and fluorine atoms is observed in the photolysis of isomeric difluoroethylenes:[65]

$$CFH{=}CFH \underset{}{\overset{h\nu}{\rightleftarrows}} CF_2{=}CH_2\ .$$

The mechanism of such exchange has not so far been investigated.

3. Comparison of the 1,2-Migration of a Fluorine Atom with the 1,2-Migration of Other Halogen Atoms

In contrast to the 1,2-migration of a fluorine atom, the 1,2-migration of other halogen atoms, in particular chlorine and bromine, in radicals is well known. Thus the 1,2-migration of a chlorine atom in alkyl radicals is very common:[1,66,67]

$$XCCl_2\dot{C}YCH_2Z \xrightarrow{\circ} X\dot{C}ClCClYCH_2Z\ ,$$
$$X{=}H,\ F,\ Cl,\ CH_3\quad Y{=}H,\ Cl,\ Br,\ CH_3\quad Z{=}Br,\ CCl_3,\ SR\ .$$

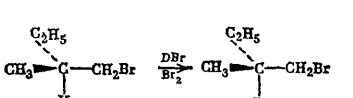
The data accumulated permitted the claim that this migration takes place intermolecularly and theoretical calculations[2,65] have shown that the 1,2-migration of a chlorine atom proceeds via a bridged transition state with a relatively low energy barrier (26.4 kcal mol^{-1}).[65] A series based on the relative stabilities of the radicals has been constructed,[6,7] its left-hand side coinciding with the familiar series based on the relative stabilities of hydrocarbon radicals (primary < secondary < tertiary):

$$RCH_2 < R_2CH < R_3C < RCHCl < R_2CCl < RCCl_2\ ,$$

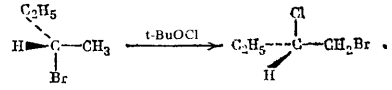
It is noteworthy that in the case of possible competition between the 1,2-shifts of a chlorine or a fluorine atom, the shift of a chlorine atom always takes place:[68,69]

$$CH_2{=}CH{-}CCl_2F + \dot{C}Cl_3 \rightarrow CCl_3CH_2\dot{C}HCCl_2F \xrightarrow{\circ}$$
$$\rightarrow CCl_3CH_2CHCl\dot{C}ClF \xrightarrow{t\text{-}BuNO} CCl_3CH_2CHClCClF{-}N(O\cdot){-}Bu\text{-}t.$$

The 1,2-migration of a bromine atom in alkyl radicals occurs at even higher rates than the migration of chlorine. Analysis of literature data[70] has led to the conclusion that the rates of these rearrangements can reach values >10^8 s^{-1} for chlorine and >10^{10} s^{-1} for bromine. The 1,2-migration of a bromine atom is not as common a process as the 1,2-migration of a chlorine atom probably because the β-bromoradicals can decompose fairly readily with formation of unsaturated compounds. The problem of "bridged" radicals is very closely related to the problem of the mechanism of the 1,2-migrations of bromine and chlorine atoms. It has been shown that in radical reactions of bromoalkanes the bromine atom is involved in anchimeric cooperation with the abstraction of a β-hydrogen atom.[1,70] This is manifested, for example, in radical reactions of optically active bromoalkanes. Thus the deuterium exchange reaction involving (+)-(*S*)-1-bromo-2-methylbutane proceeds with full retention of optical activity:[70]

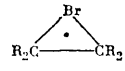


Asymmetry can be fully retained also in processes accompanied by the 1,2-migration of a bromine atom, for example, in the chlorination of (+)-(*S*)-2-bromobutane:[70,71]



Like the bromine atom, the chlorine atom is also involved in anchimeric assistance in the abstraction of a β-hydrogen atom, although to a lesser extent than bromine. Thus the racemisation of the intermediate chloroalkyl radical takes place to an appreciable extent in the bromination of (+)-(*S*)-1-chloro-2-methylbutane.[70] Similar anchimeric assistance has not been detected for the fluorine atom. The radical fluorination of (+)-(*S*)-1-fluoro-2-methylbutane leads to complete racemisation.[70]

These results can be explained by the formation in the intermediate β-bromo- and β-chloro-radicals of a bridged structure in which the rotation about the C_α–C_β bond is to a large extent hindered and the stabilisation of such a radical leads to the retention of asymmetry in the reaction products.



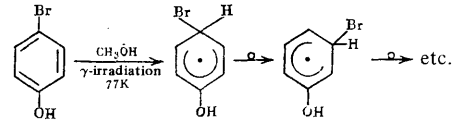
Analysis of the EPR spectra of β-chloroethyl radicals showed that the chlorine atom is in the eclipsed conformation with respect to the *p* orbital of the radical centre. Hence, it has been suggested that the radical has an asymmetric bridged structure.[72,73] In the β-fluoroethyl radical, the angle between the *p* orbital and the C–F bond is 50°.[72,74] These data agree with calculations by the MNDO method.[75] The different structures of the β-chloroethyl and β-fluoroethyl radicals are caused, according to the authors, by a combination of steric and electronic factors.[72,75]

Hudson[76] estimated from the standpoint of the perturbation theory the stabilisation of radicals as a result of bridge formation for β-halogenethyl radicals:

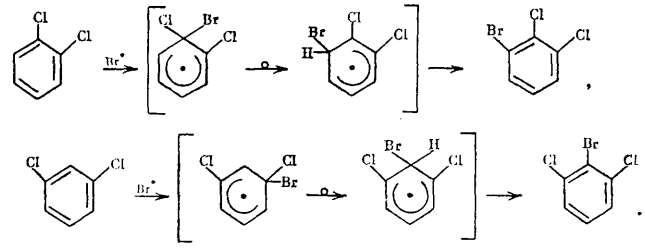
$-\Delta E$ (kcal mol^{-1}): I (7.54) Br (2.97) Cl (0.22) F (— 1.30) O (—0.72) .

These data show that bridge formation is unfavourable for fluorine and oxygen atoms. According to the author, this is caused mainly by the large difference between the energies of the interacting orbitals, which diminishes on passing from fluorine to bromine and iodine. The ease of the 1,2-migration of a halogen atom varies in the same direction. Thus it is apparently possible to distinguish three energy factors influencing the ease and direction of the 1,2-migration of a halogen atom: (1) the degree of interaction of the *p* orbital of the radical centre with the halogen atom; (2) the dissociation energy of the C–Hal bond in the β-halogenoethyl radical, which decreases from fluorine to bromine (46.3 kcal mol^{-1} for fluorine, 22.0 kcal mol^{-1} for chlorine, and 7.9 kcal mol^{-1} for bromine[2]); (3) the relative stabilities of the radicals formed.

Several examples of the migration of bromine and chlorine atoms in cyclohexadienyl radicals are also known. Thus the γ-irradiation of methanol solutions of bromobenzene and *p*-bromophenol at 77 K generates cyclohexadienyl radicals with bromine atoms in the geminal unit.[77] Analysis of the EPR spectra of these radicals shows that the bromine atom "rotates" around the ring via a rapid 1,2-shift (the lifetime in this state is $<10^{-7}$ s):

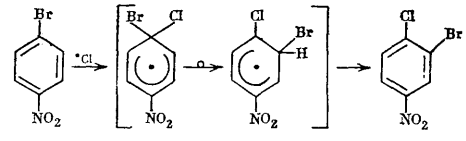


In his analysis of the work of Belgian chemists[79] on the photobromination of dihalogenobenzenes, Traynham[78] drew attention to the fact that 1,2,3-trihalogenobenzenes constitute an appreciable proportion of all the isomeric trihalogenobenzenes formed. He suggested that radical unco-σ-complexes are formed and that the halogen undergoes 1,2-migration in these σ-complexes:



The Belgian scientists, who did not agree with this interpretation of their results, carried out a thorough investigation of the isomeric composition of the products of the photobromination of *o*- and *m*-dihalogenbenzenes.[80] They showed that the reaction products contain only 3-bromo-1,2-dichlorobenzene (reaction of *o*-dichlorobenzene) and 2-bromo-1,3-dichlorobenzene (reaction of *m*-dichlorobenzene). However, the formation of these products fits within Traynham's scheme, while the absence of other isomeric 1,2,3-trihalogenobenzenes can be accounted for by the different capacities for migration of chlorine and bromine atoms (Br > Cl).

Yet another process in which the 1,2-migration of the halogen in cyclohexadienyl radicals has been demonstrated is the free-radical chlorination of *p*-halogenonitrobenzenes:[81,82]



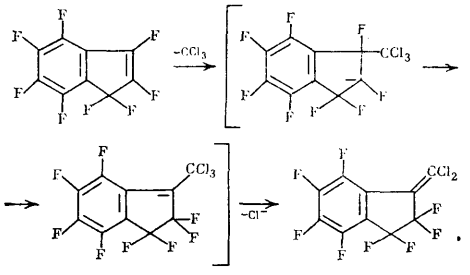
The structure of the rearranged product of this reaction also indicates the greater ease of the 1,2-migration of a bromine atom compared with a chlorine atom.

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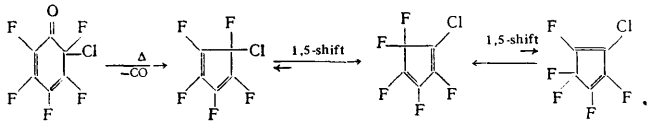
Thus analysis of the literature data shows that, whereas the migrations of a fluorine atom in neutral compounds are fairly common reactions and are consistent with modern theoretical views, the shifts of a fluorine atom in the intermediate species proceed via a fairly high energy barrier and require further theoretical consideration.

Most data available for the migration of a fluorine atom in intermediate species concern migrations in free radicals and, in particular, the 1,2-shift of a fluorine atom in cyclohexadienyl radicals. However, hitherto it is impossible to distinguish all the factors influencing the direction and energetics of the process. Presumably the energy of the 1,2-migration of a fluorine atom in radicals is intermediate between those of the 1,2-migrations in cations and anions. Although there is no experimental proof in the literature of the occurrence of the 1,2-shift of a fluorine atom in cations, Burdon and Parsons[61] believe that the 1,2-shift of a fluorine

atom in arenium ions is possible. Calculation by the CNDO/2 method of the relative energies of the isomeric arenium ions has shown that the stage involving the 1,2-shift of a fluorine atom is exothermic, but such a rearrangement should take place via a high energy barrier. It is believed that[61] it is achievable in the temperature range 200–500 °C. As regards the 1,2-shift of a fluorine atom in anions, the latter can apparently take place via a lower energy barrier than in the case of radicals and cations. Admittedly, in the latter case the interpretation of experimental data is hindered by the ease of abstraction of a fluoride ion from the anions. Nevertheless, for certain isomerisations proceeding with participation of anions, it is possible to postulate an intramolecular mechanism. For example, the formation of 1-dichloromethyleneperfluoroindan on interaction of perfluoroindene with sodium trichloroacetate can be represented as the result of isomerisation with formal 1,2-migration of a fluorine atom in the intermediate anion, although one cannot rule out pathways via the consecutive abstraction and addition of the fluoride anion:[83]



During the preparation of the manuscript for publication, several studies concerning the migration of a fluorine atom appeared in the literature. Thus the thermal 1,5-shift of a fluorine atom has been invoked[84] to account for the isomeric composition of the chloropentafluorocyclohexadienes formed on thermolysis of chloropentafluorocyclohexadienone:



Mal'tsev et al.[85] studied the isomerisation of bis(trifluoromethyl)carbene to perfluoropropene. The initial carbene was detected by IR spectroscopy in an argon matrix at 12–40 K:

$$(CF_3)_2C: \xrightarrow[\text{1,2-shift}]{} CF_3CF{=}CF_2 .$$

A study of the 1,2-migration of a fluorine atom in the 1,1,2-trifluoroethyl radical has been published recently.[86] The authors used the method proposed previously,[62] which consists in the addition of tritium atoms to fluorinated olefins:

$$CF_2{=}CHF \xrightarrow{T^{\cdot}} \dot{C}F_2{-}CHFT \xrightarrow{\circ} CF_3{-}CHT \xrightarrow[-[F^{\cdot}]]{} CF_2{=}CHT .$$

Kotaka and Sato[86] explained by the 1,2-migration of a fluorine atom in the 1,1,2-trifluoroethyl radical the results of an earlier study[87] in which the formation of $CF_3CH_2CH_2CF_3$ was observed when a hydrogen atom was added to trifluoroethylene. Scott and Jennings[87] discussed the results of a calculation by the INDO method of the activation energies for the 1,2-migration of fluorine and hydrogen atoms in the radicals $\dot{C}F_2$–CHFT and $\dot{C}$FH–CFHT and suggested that in the excited radicals the 1,2-migration of a fluorine atom and not a hydrogen atom is energetically more favourable.

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