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REVIEW

SOME PECULIARITIES OF RADICAL REACTIONS OF POLYFLUOROAROMATIC COMPOUNDS

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SUMMARY

This paper reviews the reactions of main polyfluoroaromatic compounds with free radicals of widely varying polarity and steric requirements. These works had been carried out during a number of years at the Laboratory of Haloid Compounds of the Novosibirsk Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences. The results of these studies were partially published in the author's review in the Russian Chemistry Reviews Journal in 1977. The same review considered the data on the radical reactions of polyfluoroaromatic compounds, available in literature at that time [1].

1.INTRODUCTION

Radical reactions represent one of the principal types of interaction in organic chemistry, though only a little more than 50 years have passed since participation of free radicals in

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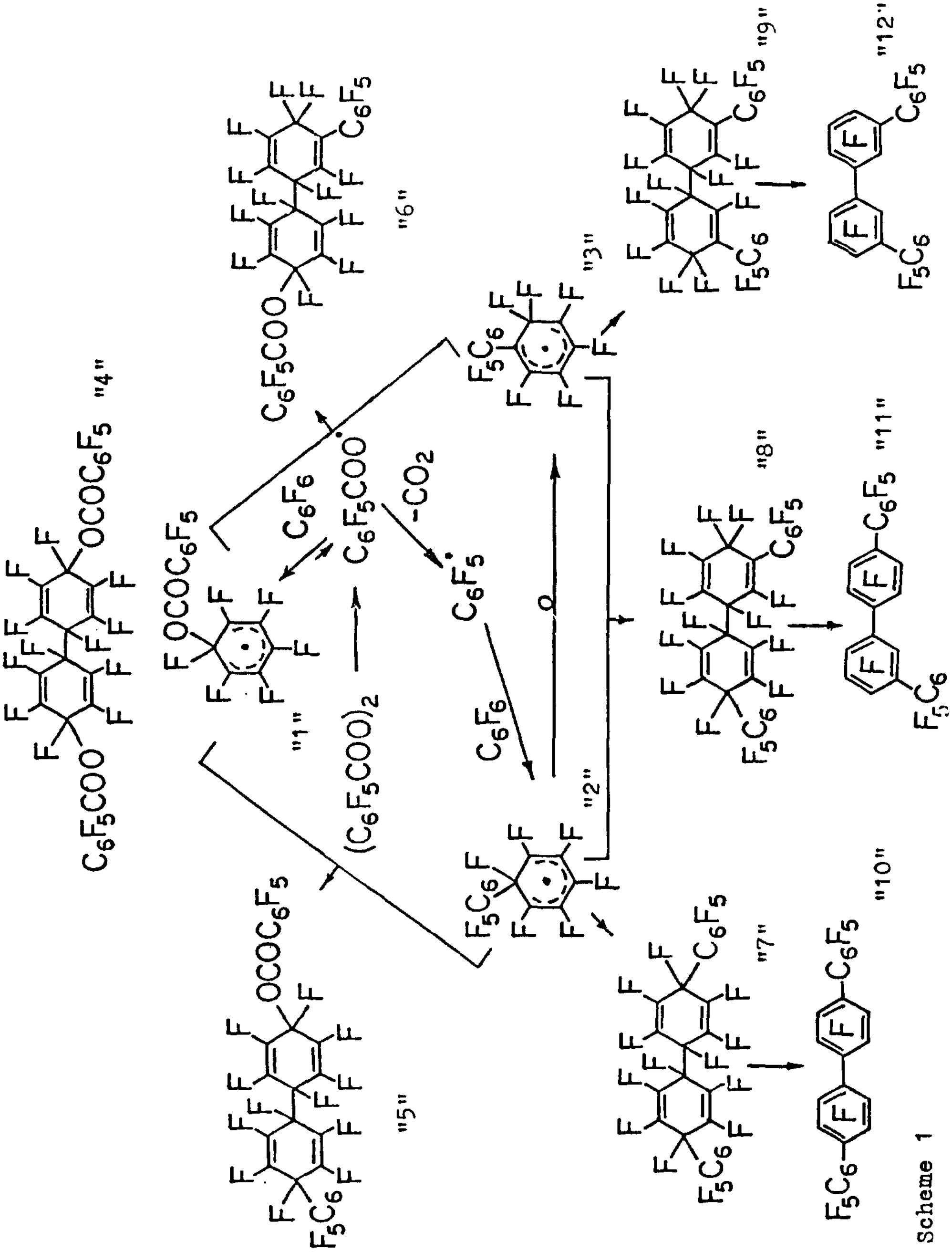
chemical transformations was proved. The continuous expansion of literature on the radical reactions of organic compounds indicates constant growth of interest in such processes, arising from the fact that the free-radical mechanism may be realised for a variety of reactions with different synthetic results.

For the mechanistic studies of radical reactions in the aromatic series, polyfluoroaromatic compounds are an essentially new subject which allows one to investigate some effects on the reaction mechanism that were absent in the previously studied models. This refers first of all to the possibility of radical attack on the aromatic ring position occupied by the fluorine atom, and, consequently, the effect of fluorine as an ipso-substituent on the rate and orientation of the attack, and as a geminal substituent in the intermediate radical σ-complexes on the route of their transformation. Second, this refers to the total effect of fluorine atoms in positions of the aromatic substrate (or the unsaturated part of intermediate) other than the attacked position, on the above-mentioned reaction characteristics.

The data presented in this review have been obtained as a result of the systematic studies of radical reactions of perfluorinated aromatic hydrocarbons: hexafluorobenzene, octafluorotoluene, decafluorobiphenyl, and octafluoronaphthalene.

2.REACTIONS OF POLYFLUORINATED COMPOUNDS OF THE BENZENE SERIES

The thermal decomposition of pentafluorobenzoyl peroxide [2] in hexafluorobenzene at 80° [3] leads to the predominant formation(70%) of the dimer of the pentafluorobenzoyloxy radical - hexafluorobenzene addition σ-complex and at 200°, to the dimer of the pentafluorophenyl radical - hexafluorobenzene addition σ-complex [4]. The structure of the latter ("9"), proved by the spectral data and confirmed by the results of its defluorination which gave m,m′ -perfluoroquaterphenyl "12" in a quantitative yield, indicates that the initially formed pentafluorophenyl radical - hexafluorobenzene addition σ-complex "2" undergoes a rearrangement "2"$\longrightarrow$"3" as a result of fluorine migration from the geminal to adjacent position. Such a type of free radical

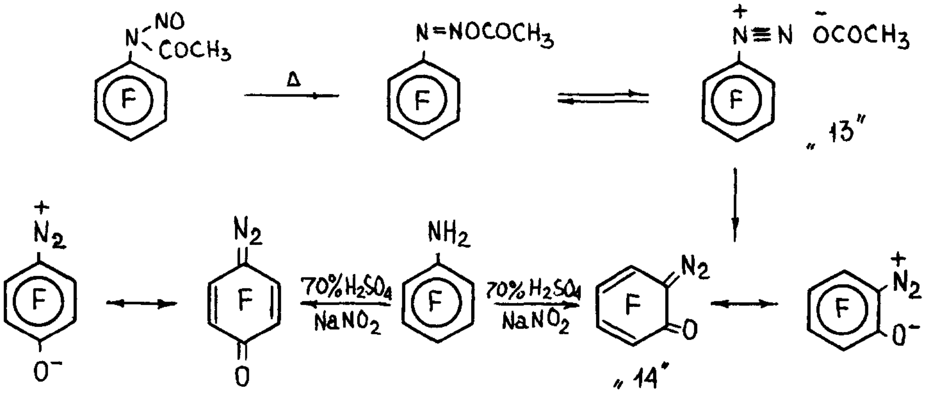

C_6F_5COO … $OCOC_6F_5$ "4"
F OCOC$_6$F$_5$
"1"
$(C_6F_5COO)_2$
C_6F_6
$C_6F_5COO^\bullet$
$-CO_2$
$C_6F_5^\bullet$
C_6F_6
Q
C_6F_5COO … C_6F_5 "6"
F_5C_6 "3"
F_5C_6 "2"
$OCOC_6F_5$ … F_5C_6 "5"
"7"
"8"
"9"
"10"
"11"
"12"
F_5C_6
C_6F_5

Scheme 1

rearrangement was previously unknown and is the most important distinction of the radical reactions of hexafluorobenzene. In the 80-200^{0} temperature range (Table 1), one can obtain all possible products ("4","5","6","7","8",and "9") of recombination of the three radical σ-complexes "1","2",and "3" generated in the reaction of hexafluorobenzene with pentafluorobenzoyl peroxide [5] (Scheme 1).

With pentafluorophenylhydrazine or pentafluorophenylazotriphenylmethane as the pentafluorophenyl radical source [6], the reaction also gives the dimers of both rearranged and unrearranged pentafluorophenyl radical - hexafluorobenzene addition σ-complexes ("7","8",and "9").

An attempt has been made to use pentafluoro-N-nitrosoacetanilide as a precursor of pentafluorophenyl radicals [7]. The utility of its non-fluorinated analogue in the studies of radical reactions of aromatic compounds is well known. It appeared however that upon the thermolysis in hexafluorobenzene, pentafluoro-N-nitrosoacetanilide is transformed to tetrafluoro-ortho-benzoquinone diazide "14", due to the high nucleophilic mobility of the fluorine atom in pentafluorobenzene diazoacetate "13", the primary product of the thermolysis, which is confirmed by a similar reaction route in diazotisation of pentafluoroaniline :



The reaction of hexafluorobenzene with benzoyl peroxide [8] affords, depending on the reaction conditions, 6 to 50% of the products of the dimers of the phenyl radical - hexafluorobenzene addition σ-complexes, whose defluorination products structure

TABLE 1

Decomposition of Pentafluorobenzoyl Peroxide in Hexafluorobenzene

T °C	Concentration of peroxide mol	Yields of the reaction products, mol/mol of the peroxide x 10						Rearrangement degree **
		"4"	"5"	"6"	"7"*	"8"*	"9"*	
80	0.025	71.74	5.84	6.64	0.45	0.45	0.63	1.17
100	0.1	56.20	19.95	6.26	3.23	1.59	0.57	0.34
	0.025	29.12	12.00	23.20	2.61	9.18	10.88	2.08
	0.005	16.10	10.10	47.40	0.56	5.06	11.88	4.72
200	0.025	-	-	-	-	-	92.45	92.45

* From the GLC data of the defluorination products of a mixture of dimers "7","8" and "9".

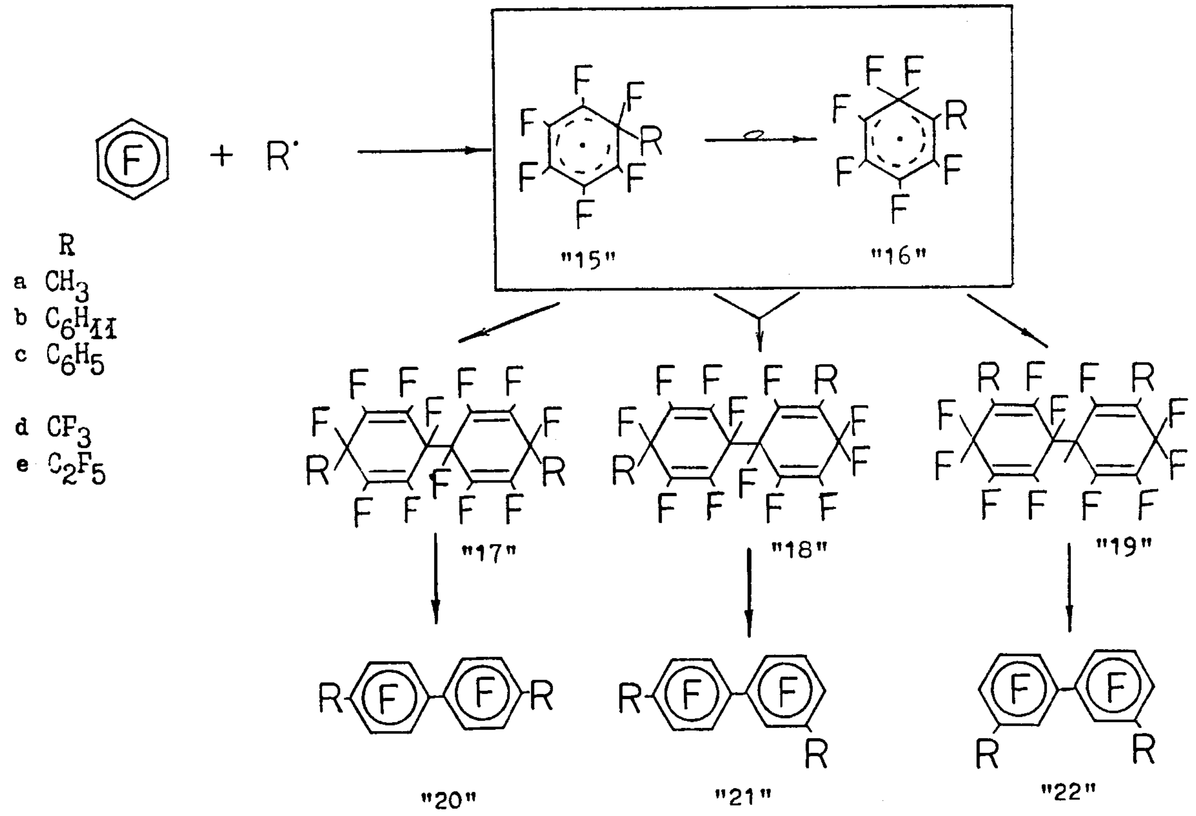
** Calculated from the proportion $\frac{\text{"9"}+1/2\text{"8"}}{\text{"7"}+1/2\text{"8"}}$

("20c" and "21c") indicates the occurrence of a rearrangement with fluorine migration in the initially formed σ-complex "15c" (Table 2).

TABLE 2
Reaction of Benzoyl Peroxide with Hexafluorobenzene

Concentration of peroxide	T °C	Time h	Yield %		Ratio of 20c:21c
			$C_6H_5C_6F_5$	$C_{24}H_{10}F_{12}$	
0.0125	60	200	17	50	49:39
0.025	80	72	43.5	25	22:42
0.025	80	100	62.5	6	8:55

Investigation of the reactions of hexafluorobenzene with alkyl radicals differing in polarity and steric requirements (methyl [9] and cyclohexyl [10] radicals generated from tert-butyl peroxide in the absence of a solvent (140°) in the former case, and in cyclohexane (140°) in the latter case) has shown formation in high yields of the mixtures of dimerisation and recombination products of both rearranged ("16a,b") and unrearranged ("15a,b") σ-complexes of addition of these radicals to hexafluorobenzene ("17a,b", "18a,b","19a,b"). The structures of these products have been confirmed by the results of their defluorination which gave the respective derivatives of polyfluorobiphenyl ("20a,b","21a,b","22a,b") (Scheme 2). In the reaction of hexafluorobenzene with the methyl radical generated from acetyl peroxide [11], the recombination products of the rearranged methyl radical - hexafluorobenzene addition σ-complexes are obtained in an insignificant amount (42% of "17a", 5% of "18a", 1% of "19a"). This obviously results from the fact that the reaction of hexafluorobenzene with acetyl peroxide proceeds at a lower temperature (80°), which leads to a lower rearrangement rate; another reason is the higher decomposition rate of acetyl peroxide as compared with tert-butyl peroxide, leading to the higher concentration of σ-complexes in the solution, their decreased lifetime, and, consequently, the decreased rearrangement rate.



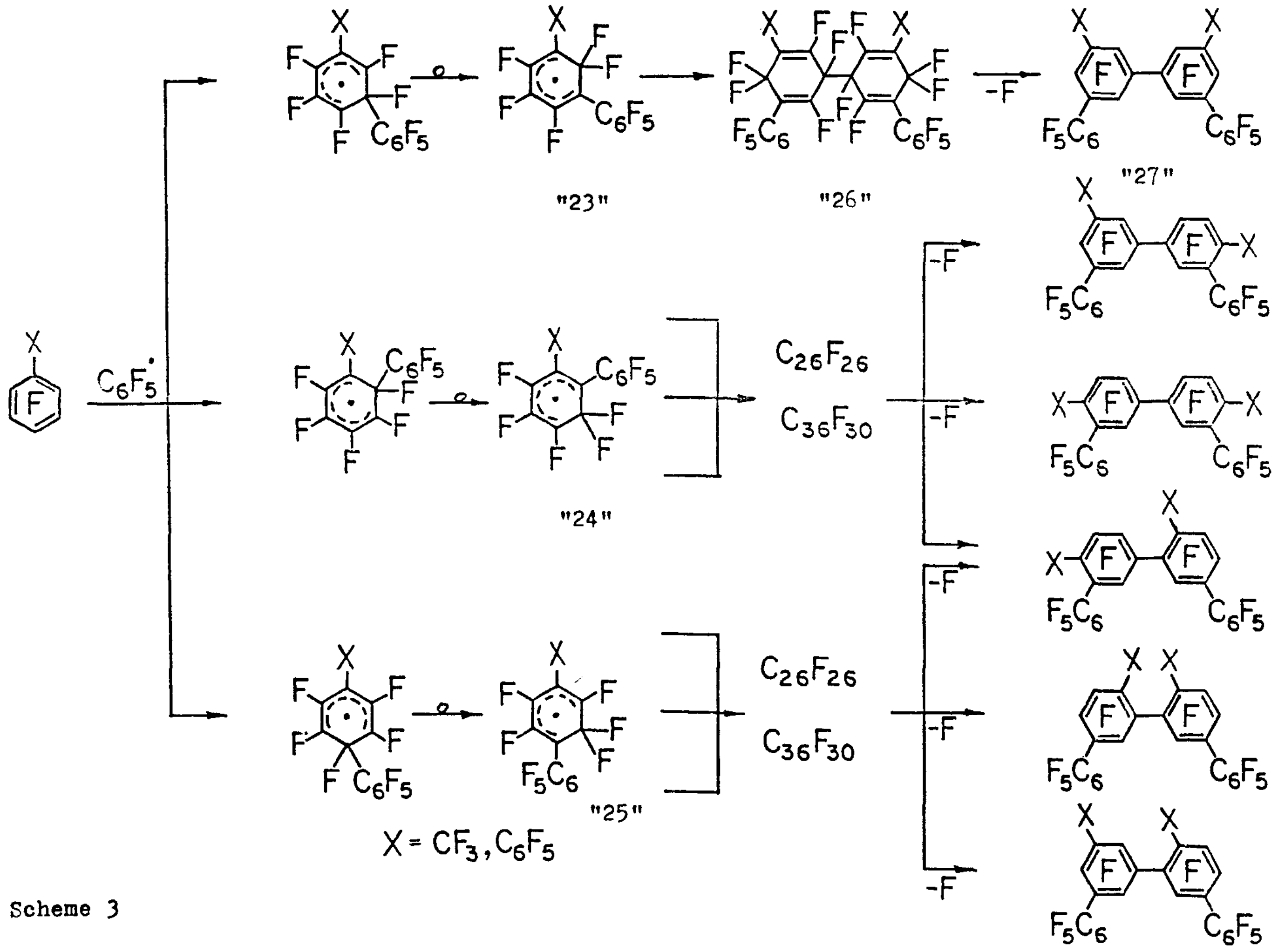
Scheme 2

With perfluoroalkyl radicals ($CF_3^{\cdot}$ and $C_2F_5^{\cdot}$) [9,11,12], as well as the pentafluorobenzoyloxyl radical, hexafluorobenzene forms only the dimers of unrearranged radicals - hexafluorobenzene addition σ-complexes - compounds "17d" and "17e".

Substitution of one fluorine atom in the hexafluorobenzene molecule by the groups strongly differing in their steric requirements and ability to take part in the unpaired electron density delocalisation (trifluoromethyl and pentafluorophenyl groups) affords a picture characterising the effect of these factors on the direction of radical attack and the regularities of reactions in the polyfluoroaromatic series found with reference to hexafluorobenzene, in particular, on the ability of σ-complex radicals to undergo dimerisation and the possibility of their rearrangement with fluorine migration.

The reactions of octafluorotoluene [13] and decafluorobiphenyl [14] with pentafluorobenzoyl peroxide, as opposed to a similar reaction of hexafluorobenzene, proceed, even in mild conditions (80^{o}), with formation of the dimers of pentafluorophenyl radical - substrate addition σ-complexes in high yields. The major role in formation of all the reaction products here is played by the rearranged $C_6F_5^{\cdot}$ -octafluorotoluene and -decafluorobiphenyl meta-addition σ-complexes "23a,b". There are also insignificant attacks at the ortho- and para-positions of these substrates, and the resulting σ-complexes undergo rearrangement with fluorine migration, as judged from the structure of the defluorination products of isomeric dimer mixtures (Scheme 3). Along with the dimers, both reactions give small amounts of the homolytic substitution products - perfluoromethylbiphenyls in the reaction of octafluorotoluene and perfluoroterphenyls in the reaction of decafluorobiphenyl (Tables 3 and 4).

These results suggest that the relative stability of isomeric σ-complexes formed by the pentafluorophenyl radical addition to substituted polyfluoroaromatic compounds does not depend on the ability of substituent to participate in the unpaired electron density delocalisation in the initially formed radical σ-complexes.That is,the influence of fluorine atoms in the



Scheme 3

TABLE 3

Reaction of Pentafluorobenzoyl Peroxide with Decafluorobiphenyl

T °C	Concentration of the peroxide, M	Yields of the dimers*	Yields of perfluoroterphenyls	Ratio of perfluoro terphenyls o:m:p **	$\frac{o+p}{m}$
80	0.25	0.60	0.11	1.0:4.6:2.1	0.68
200	0.25	0.59	0.26	1.0:1.7:1.2	1.3

TABLE 4

Reaction of Pentafluorobenzoyl Peroxide with Octafluorotoluene[***]

T °C	Concentration of the peroxide, M	Yields of the dimers*	Yields of perfluoromethylbiphenyls	Ratio of perfluoro methylbiphenyls o:m:p **	$\frac{o+p}{m}$
80	0.1	0.57	0.05	1.00:15.20:0.97	0.13
200	0.1	0.51	0.12	1.00:1.25:0.97	1.57

* From the isolated products in mol/mol of the peroxide

** Yields and isomer ratio of perfluoroterphenyls and perfluoro methylbiphenyls have been calculated from the GLC data

*** The reaction also gives 0.26mol perfluoro-tris(phenyl)-tris(methyl)octahydroquaterphenyl ($C_{45}F_{44}$) at 80°, and 0.13mol - at 200°

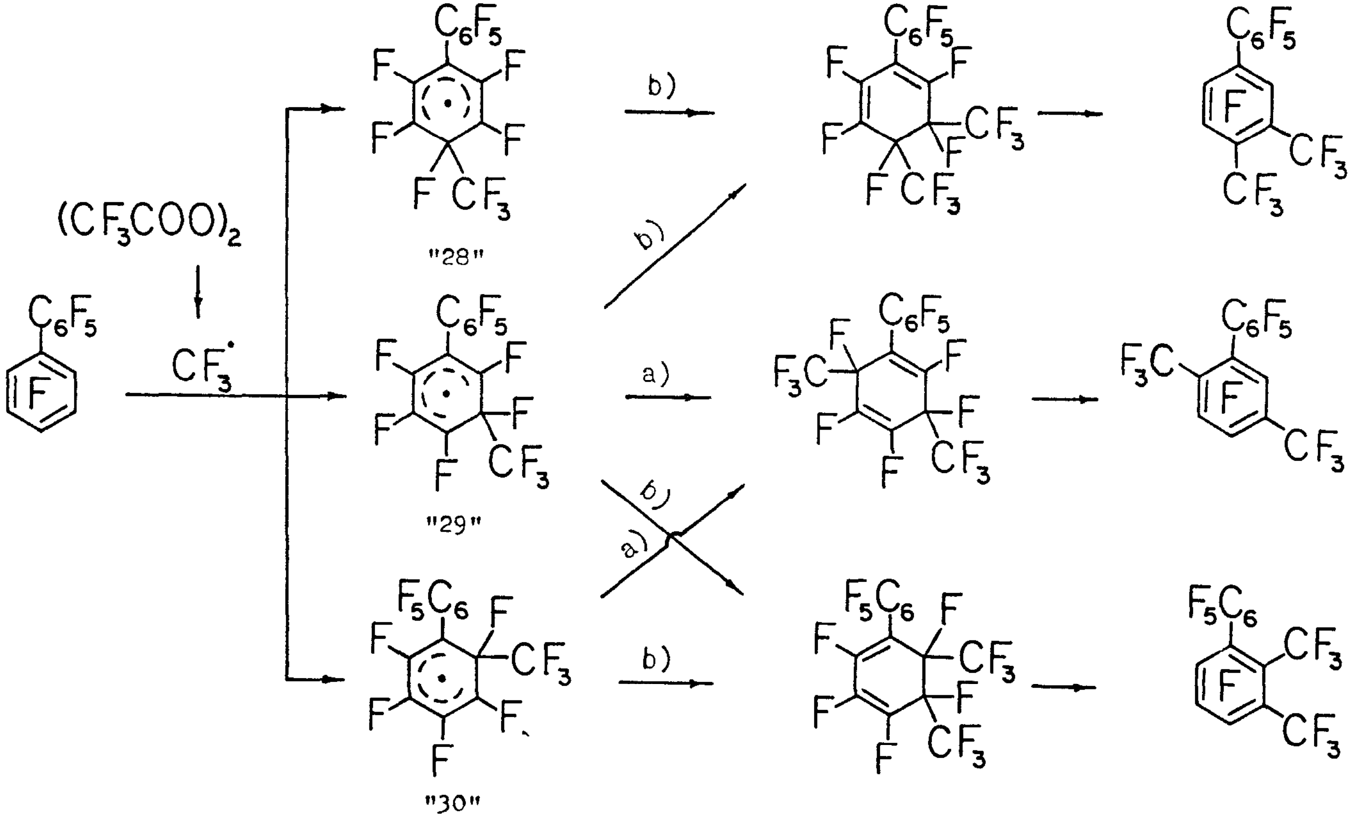
unsaturated moiety of cyclohexadienyl radicals on the stability of these species exceeds that of such substituents as the trifluoromethyl and pentafluorophenyl groups. In the latter case this may be due to the non-coplanarity of the phenyl and cyclohexadienyl fragments.

In the reaction of decafluorobiphenyl with the trifluoromethyl radical [15], the resulting σ-complexes "28","29","30" do not undergo the rearrangement with fluorine migration, and their stabilisation is achieved not only by dimerisation, but also by recombination with the starting trifluoromethyl radical, forming the polyfluorinated derivatives of cyclohexadienes. The major role in formation of all the reaction products, likewise the reaction with the pentafluorophenyl radical, is played by the $CF_3^{\bullet}$ -decafluorobiphenyl meta-addition σ-complex (Scheme 4).

The above-considered reactions of polyfluoroaromatic compounds of the benzene series allow comparisons of the behaviour of these compounds in radical reactions relative to their non-fluorinated analogues. In the reactions of polyfluoroaromatic compounds there is no disproportionation specific to the radical reactions of non-fluorinated aromatic compounds, and the homolytic substitution typical for the latter compounds, is insignificant. The main route of transformation of radical σ-complexes initially formed in these reactions is their dimerisation. In this case, all σ-complexes, except those formed in the reactions with perfluoroalkyl and pentafluorobenzoyloxy radicals, undergo the earlier unknown rearrangement with fluorine migration from the geminal to adjacent position (Scheme 2)

3.REACTIONS OF OCTAFLUORONAPHTHALENE

The reaction of octafluoronaphthalene (OFN) with pentafluorobenzoyl peroxide in acetonitrile (80°) [16] proceeds with predominant formation of the dimer of pentafluorobenzoyloxy radical - OFN-1 addition σ-complex. Formation of this dimer seems to be a reversible process, as its thermolysis at 120° gives OFN and a mixture of compounds obtained in the reaction of pentafluorobenzoyl peroxide with OFN at 120° in the absence of inert solvent [17]. The main components of the mixture are:



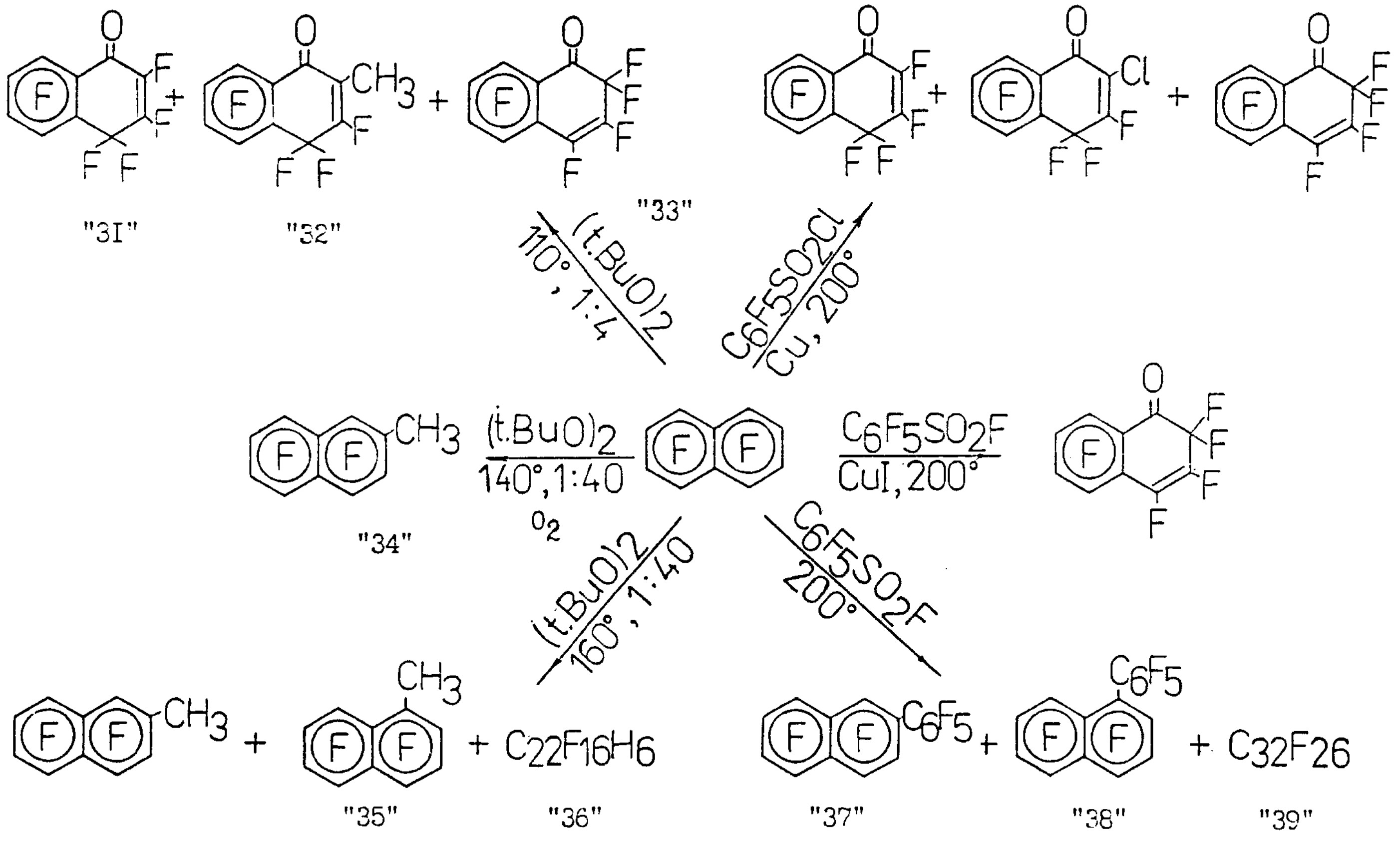
Scheme 4

pentafluorobenzoyl fluoride, hexafluoronaphthoquinone-1,4, perfluoro-1-oxo-2(naphthoxy-1′)dihydronaphthalene-1,4, and perfluoro-1-oxo-2(benzoyloxy)dihydronaphthalene-1,4, which are the precursors of perfluorinated naphthoxy- and benzoyloxy-naphthoquinones. As a result of homolytic substitution in octafluoronaphthalene, small amounts of 1- and 2-perfluoronaphthylbenzoates are formed (1.5%), but no products indicating participation of the pentafluorophenyl radical in this reaction have been detected.

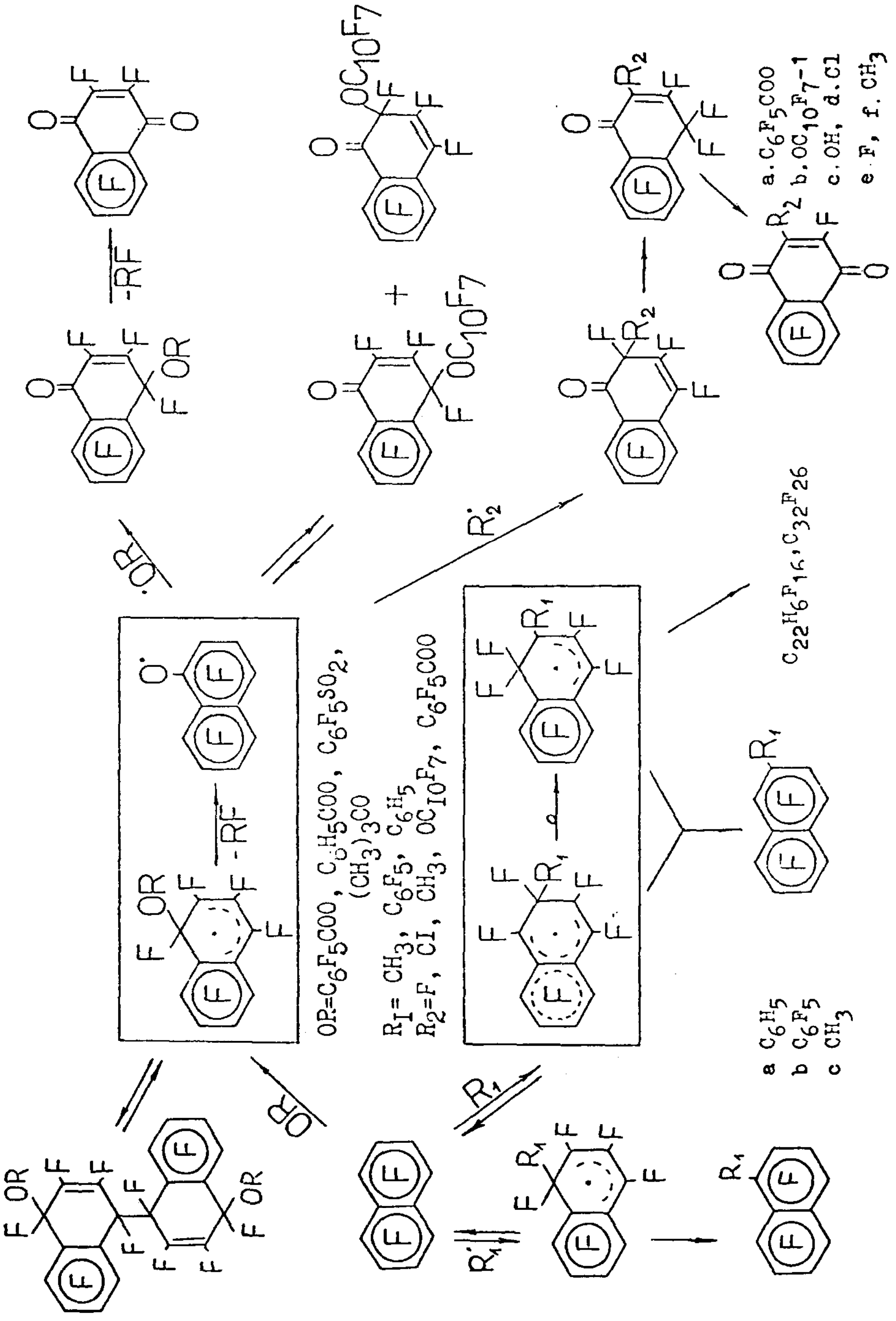
Formation of oxygen-containing compounds in the reactions of OFN with pentafluorobenzoyl peroxide has no analogy among the known reactions of non fluorinated compounds and seems to be due to generation of the heptafluoronaphthoxy radical by elimination of pentafluorobenzoyl fluoride from the pentafluorobenzoyloxy radical - OFN-1 addition σ-complex. The possible routes of transformation of the heptafluoronaphthoxy radical are shown in Scheme 6.

The reaction of OFN with benzoyl peroxide in acetonitrile [16] gives the dimers of benzoyloxy radical - OFN addition σ-complexes, whereas at higher temperatures and in the absence of a solvent, the main products are 1- and 2-phenylheptafluoronaphthalenes [18]. The presence of hexafluoronaphthoquinone-1,4 and perfluoro-2(naphthoxy-1′)naphthoquinone-1,4 among the products of the latter reaction indicates that here again the heptafluoro-1-naphthoxy radical is generated (Table 5).

The reaction of octafluoronaphthalene with pentafluorobenzene sulphonylhalides (Scheme 5) follows two routes [19].
In the absence of copper salts, pentafluorobenzene sulphonyl chloride does not react with OFN even at 200°, and decomposition of pentafluorobenzene sulphonylfluoride in OFN at 160° leads (Table 6) to the formation of perfluoro-2-phenylnaphthalene "37" and a mixture of the dimers "39" of the pentafluorophenyl radical-octafluoronaphthalene addition σ-complexes ($C_{32}F_{26}$). The ^{19}F NMR data suggest formation of recombination products both of the rearranged and unrearranged $C_6F_5^{\cdot}$-OFN 2-addition σ-complexes.
In the presence of copper salts, both pentafluorobenzene sulphonylhalides react with OFN, forming the perfluorinated derivatives of 1-oxo-dihydronaphthalenes "31" and "33".


"3I"
"32"
"33"
(t.BuO)2
110°, 1:4
C6F5SO2Cl
Cu, 200°
"34"
(t.BuO)2
140°,1:40
O2
C6F5SO2F
CuI, 200°
(t.BuO)2
160°, 1:40
C6F5SO2F
200°
C22F16H6
C32F26
"35"
"36"
"37"
"38"
"39"

Scheme 5


·OR
-RF
R2·
R1
R1'
OR=C6F5COO, C6H5COO, C6F5SO2, (CH3)3CO
R1= CH3, C6F5, C6H5
R2=F, Cl, CH3, OC10F7, C6F5COO
a C6H5
b C6F5
c CH3
a. C6F5COO
b. OC10F7-1
c. OH, d. Cl
e. F, f. CH3
C22H6F16, C32F26
OC10F7

Scheme 6

TABLE 5

Variation of the Product Ratio in the Reaction of Octafluoronaphthalene with Benzoyl Peroxide (%) with Temperature *

Compound name	Reaction temperature	
	85°	110°
1-Phenylheptafluoronaphthalene	9.9	30.7
2-Phenylheptafluoronaphthalene	3.0	12.9
1-Benzoyloxyheptafluoronaphthalene	4.9	2.3
2-Benzoyloxyheptafluoronaphthalene	4.0	1.5
Perfluoro-2-(naphthoxy-1)naphthoquinone-1,4	8.8	3.2
Hexafluoronaphthoquinone-1,4	1.7	1.6
Benzoyl fluoride	18.6	-
Biphenyl	2.3	4.7
Phenyl ether of benzoic acid	32.6	3.0
The rest to 100% are unidentified compounds		

* Concentration of peroxides is 0.25M; 0.2mol of octafluoro naphthalene per 1 mol of benzoyl peroxide reacts at 85°, and 0.6mol - at 110°.

The same oxygen-containing products are also formed in the reaction of OFN with di-tert-butyl peroxide at a low temperature (110°). At a higher reaction temperature (140°) and in the presence of air, only 2-methylheptafluoronaphthalene "34" is formed in a high yield, and in the inert gas - a mixture of the dimer products ($C_{22}H_6F_{16}$) "36" and 2-methylheptafluoronaphthalene (Scheme 5, Table 7).

Thus, the interaction of OFN with the alkyl and aryl radicals proceeds both with the homolytic substitution of fluorine atoms in the 1- and 2-position, and dimerisation of the radical-OFN-2 addition σ-complexes (Scheme 6). In the latter case, as well as in the reactions of polyfluorinated benzene compounds, there seems to occur a rearrangement with fluorine migration from the geminal to adjacent position of radical - OFN addition σ-complexes. The reactions of OFN with oxygen-

TABLE 6

Reaction of Pentafluorobenzene Sulphonylfluoride with Octafluoronaphthalene

T °C	Concentration of $C_6F_5SO_2F$	Yields in % from the changed octafluoronaphthalene		
		"38"	"37"	"39"
160	1	-	11	16
160	0.1	-	14	34
160	0.05	-	10	34
200	0.05	2	19	6

TABLE 7

Decomposition of Di-tert-butyl Peroxide in Octafluoronaphthalene

T °C	Concentration of the peroxide (mol)	Yields in % from the changed octafluoronaphthalene					
		"35"	"34"	"33"	"31"	"32"	"36"
110	0.25	-	-	12	8	60	-
110	0.025	-	21	-	-	26	36
140	0.25	-	13	-	-	-	24
140	0.05	-	31	-	-	-	58
140	0.025	-	15	-	-	-	34
140	0.025	-	82	-	-	-	-
160	0.05	4	18	-	-	-	36
160	0.025	5	36	-	-	-	54

containing radicals may proceed either via the dimerisation of the $C_6F_5COO^\cdot$ - or $C_6H_5COO^\cdot$ - OFN -1 addition σ-complexes, or via the earlier unknown route involving stabilisation of the σ-complexes by elimination of a fragment from the geminal position to generate the heptafluoro-1-naphthoxy radical, whose transformations with participation of medium radicals determine formation of polyfluorinated derivatives of naphthoquinone and oxodihydronaphthalene (Scheme 6).

By varying the free radical source, it is possible to provide the conditions required for the reaction of octafluoronaphthalene with the radicals to follow one of the routes represented in Scheme 6.

4.FLUORINE EFFECT ON THE REACTIVITY OF AROMATIC COMPOUNDS AND RADICAL POLARITY

The fluorine effect on the electrophilicity of radicals is in good agreement with the known dependence of radical polarity on the electronic nature of radical substituents. Thus Kurz and Pellegrini [20] showed that introduction of electron accepting substituents into the benzoyloxyl radicals increases their electrophilicity. Based on these data, and on the fact that the effect of pentafluorophenyl group is similar to that of the 2,4-dinitrophenyl group [21], one could expect the electrophilicity of pentafluorobenzoyloxy radical to be much higher than that of the non-fluorinated analogue.

The increased electrophilicity of the pentafluorobenzoyloxy radical shows itself in the high degree of 1-substitution in the reaction of pentafluorobenzoyl peroxide with naphthalene [22]. The ratio of 1- and 2-naphthylpentafluorobenzoates for that reaction is 10:1, whereas for the reaction of naphthalene with non-fluorinated benzoyl peroxide, the ratio of 1- and 2-naphthylbenzoates is 2.7:1 [23].

A similar increase of the ratio of 1- and 2-naphthylbenzoates was found in the decomposition of ortho-nitrobenzoyl peroxide in naphthalene (4.3:1), whereas in the decomposition of para-nitrobenzoyl peroxide in naphthalene, the ratio of 1- and 2-naphthylnitrobenzoates remains the same as in the reaction of Unsubstituted benzoyl peroxide [24]. Such difference in orientation of o- and p-nitrobenzoyloxy radicals in their reactions with naphthalene is also attributable to the greater electrophilicity of the o-nitrobenzoyloxy radical as compared with the p-substituted one, due to a difference between the effects of para- and ortho-nitro groups, as the polarity of aryl radicals is known to be most greatly affected by the substituents ortho to the reaction centre [25]. The greater electrophilicity of the pentafluorobenzoyloxy radical as compared to the non-fluorinated radical leads to its higher reactivity in the reaction with unsubstituted aromatic compounds. Thus the reaction of pentafluorobenzoyl peroxide with benzene [2] leads to large amounts of phenyl pentafluorobenzoate and the high-molecular product of several substitutions of hydrogen by the pentafluorobenzoyloxy radical, and the reaction with naphthalene gives predominantly naphthyl pentafluorobenzoates [22].The electrophilic pentafluorobenzoyloxy radicals more readily promote hydrogen removal, e.g. from cyclohexanone [26] and pentafluorophenol [27]. In the light of these results, the predominant participation of electrophilic pentafluorobenzoyloxy radicals in the reactions with such substrates as hexafluorobenzene and octafluoronaphthalene seems to be an inconsistency. Thus, as shown by Kurz, the p-nitrobenzoyloxy radical, which is more electrophilic than the benzoyloxy one, reacts with chlorobenzene much more slowly than with benzene: the relative p-nitrobenzoyloxylation rate of these substrates is 0.28 [20].

The fluorine atoms seem to considerably enhance the stability of pentafluorobenzoyloxy radicals, which is indicated by facile decomposition of pentafluorobenzoyl peroxide as compared with the non-fluorinated benzoyl peroxide. Its decomposition rate constants both in benzene and hexafluorobenzene are higher than for benzoyl peroxide [28] (Table 8). The reason for the high stability of pentafluorobenzoyloxy radicals may be the more efficient delocalisation of the unpaired electron density involving the polyfluorinated aromatic ring. The high stability of pentafluorobenzoyloxy radical obviously entails the high stationary concentration of the radicals upon decomposition of pentafluorobenzoyl peroxide in hexafluoro-

TABLE 8

Kinetic Parameters of the Decomposition of Benzoyl and Pentafluorobenzoyl Peroxides in Benzene and Hexafluorobenzene

Peroxide	Substrate	mol/l of peroxide	T, °C	$\tau/2$ min	$k \cdot 10$ min^{-2}	Error	lg k	E kcal/mol	lg A
$(C_6H_5COO)_2$	C_6H_6	0.02413	80	350	2.5	∓0.3		30.4∓1.5	16.3∓0.8
		0.2377	80	256	2.9	∓0.1	-2.53417		
		0.2437	90		10.6	∓0.4	-1.97510		
		0.2447	100		29.7	∓2.0	-1.52695		
	C_6F_6	0.02447	80	514	1.3	∓0.1		33.6∓1.6	18.0∓0.9
		0.2417	80	420	1.5	∓0.1	-2.81531		
		0.2446	90		6.4	∓0.6	-2.19607		
		0.2471	100		19.9	∓2.0	-1.70115		
$(C_6F_5COO)_2$	C_6H_6	0.02437	80	71	8.9	∓1.0		29.1∓0.1	16.0∓0.1
		0.2429	80	90	8.6	∓1.0	-2.06454		
		0.2458	90		27.2	∓1.5	-1.56591		
		0.2438	100		79.7	∓8.0	-1.09843		
	C_6F_6	0.02485	80	264	2.5	∓0.1		31.3∓0.6	16.7∓0.5
		0.2433	80	280	2.5	∓0.2	-2.60241		
		0.2519	90		8.2	∓0.5	-2.08783		
		0.2443	100		27.2	∓1.5	-1.56575		

benzene and octafluoronaphthalene, which leads in mild conditions to the predominant formation of the products of the reaction of pentafluorobenzoyloxy radicals.

The pentafluorophenyl radical also seems to possess electrophilic character, which is vividly demonstrated by its interaction with substituted benzenes [29,30]. Thus the relative pentafluorophenylation rate of chlorobenzene whose ring is deactivated to electrophilic attack, is lower than its relative phenylation rate (relative to benzene; 0.72 and 1.06 respectively). But the ratio of the substitution in the less deactivated ortho- and para-positions to meta-substitution is higher for pentafluorophenylation than for phenylation: o-+ p- /m- = 3.9 and 2.9 respectively. In the reaction of pentafluorophenyl radicals with nitrobenzene, the electrophilic character of the radical shows itself in a significant increase of meta-substitution: for $C_6H_5^{\bullet}$, o-+p- /m- = 9.2; for $C_6F_5^{\bullet}$, = 0.87. With 1,2,4,5-tetrafluorobenzene, the pentafluorophenyl radical generated from pentafluoroiodobenzene by photolysis or thermal decomposition, gives 2,2',3,3',4,5,5',6,6'-nonafluorobiphenyl in a good yield. The reaction proceeds at the highest electron density position, also indicating the electrophilic character of the pentafluorophenyl radical [31].

The electrophilic character of the pentafluorophenyl radical accounts for the high yield of diphenyls in the reactions of pentafluorobenzoyl peroxide and other precursors of the pentafluorophenyl radical with benzene and its derivatives [29,30,32,33]. At the same time, the absence of the pentafluorobenzene product in these reactions, possibly indicating the difficulty of hydrogen elimination by the pentafluorophenyl radical, suggests that the reactivity of the pentafluorophenyl radical in the reaction with benzene derivatives is lower than that of radicals with similar electrophilicity, possibly due to fluorine screening of the reaction centre. The relative pentafluorophenylation and phenylation rates of benzene (0.15), obtained from the competing decomposition reaction of benzoyl and pentafluorobenzoyl peroxides in benzene, support this supposition to some extent [9].

As to the fluorine effect on the polarity of alkyl radicals, the increased electrophilicity of the trifluoromethyl radical as compared with the methyl radical is vividly demonstrated by the relative rates of addition of these radicals to benzene (0.4 and 7.1 respectively) [34]. The relative rates of $CF_3^{\bullet}$ addition to substituted benzenes [35] also indicate the electrophilic character of this radical (Table 9). As seen from Table 9, the aromatic ring is activated in the addition reaction of the trifluoromethyl radical by the electron donors and deactivated by the acceptors. The rate constant of $CF_3^{\bullet}$ addition to fluorinated aromatic compounds was noted to markedly decrease with increase of the number of fluorine atoms in such compounds [35] (Table 10). In the theoretical treatment of radical addition to aromatic compounds, rate constant variations are commonly considered to be brought about by variations in the activation energies of the reactions. The explanation of fluorine deactivation of the aromatic ring in terms of the electronic repulsion effects or the medium dipole effect is also prompted by the activation energy variations. However the data of Table 10 show that this may be a simplification: the activation energies of all the substituted benzenes are very close, whereas the activation entropies (the A-factor) substantially depend on the number and character of substituents.

The substitution of hydrogen by fluorine at the reaction centre of aromatic compounds presumably affects both the activation energy and entropy of radical addition. A decrease in the activation entropy of $CF_3^{\bullet}$ addition, which is observed if there are substituents at the reaction centre, may result from the partial restriction of rotation of the trifluoromethyl group around the C——CF_3 bond in the transition state.

High electrophilicity has also been reported for the perfluoroethyl radical [38].

The use of qualitative criteria for the relative reactivity estimations of various substrates, worked out in the case of radical reactions in the non-fluorinated series, and of the competing-reactions method allows us to draw a conclusion about the decreased reactivity of polyfluoroaromatic compounds in the reactions with electrophilic pentafluorobenzoyloxy, pentafluoro-

TABLE 9

Relative Rates of $CF_3^{\cdot}$ Addition to Substituted Benzenes C_6H_5X [35]

Substituent	H	CH_3	OCH_3	I	Br	Cl	F
Relative rate	1	1.43 (1.65)	1.93 (2.80)	- (1.65)	.89 (0.77)	- (0.65)	0.35 (0.48)

Substituent	CN	CF_3	CCl_3	NO_2	C_6F_6
Relative rate	- (0.42)	0.26 (0.30)	0.36[37] -	- (0.42)	0.04 -

In parentheses are the data of [36]

TABLE 10

Arrhenius Parameters of $CF_3^{\cdot}$ Addition [35]

Compound	$k_1/k_2^{1/2}\cdot 10^{11}$ $cm^{3/2}\cdot mol^{-1/2}\cdot sec^{-1/2}$	$E_1-1/2E_2$ kcal/mol	$A_1/A_2^{1/2}\cdot 10^8$
C_6H_6	11.8	5.4	39.0
C_6H_5F	4.14	4.0	1.6
$m\text{-}C_6H_4F_2$	2.12	4.9	3.06
$1,3,5\text{-}C_6H_3F_3$	0.782	4.5	0.62
$1,2,3,4\text{-}C_6H_2F_4$	1.03	5.8	5.5
C_6HF_5	0.679	5.1	1.26
C_6F_6	0.484	5.8	2.8

k_1, rate constant of $CF_3^{\cdot}$ addition to aromatic compounds

k_2, rate constant of $CF_3^{\cdot}$ dimerisation phenyl and perfluoroalkyl radicals, and in the reactions with the neutral phenyl radical. As a rule, low reactivity of a substrate leads to formation of the products of transformation of radical reagents without participation of the aromatic substrate. In the reactions of hexafluorobenzene [8] and octafluoronaphthalene [18] with benzoyl peroxide, appreciable amounts of biphenyl and phenyl benzoate are formed, the reaction of octafluorotoluene with pentafluorobenzoyl peroxide [13] gives decafluorobiphenyl and perfluorophenyl benzoate, and the reactions of hexafluorobenzene and decafluorobiphenyl with perfluoroalkyl radicals give the low-boiling recombination products of these radicals [11,12,15]. The reactions of hexafluorobenzene with benzoyl peroxide give no products formed with participation of benzoyloxy radicals, which is also a criterion of the low reactivity of substrates in the radical reactions of aromatic compounds with benzoyl peroxides. Using the latter criterion for the reactions of octafluorotoluene and decafluorobiphenyl with pentafluorobenzoyl peroxide shows the reactivity of these substrates to be much lower than that of hexafluorobenzene, as no one of these reactions gives the products containing pentafluorobenzoyloxy groups. The latter circumstance may be explained if we admit the decarboxylation rate of pentafluorobenzoyloxy radical to be higher than the rate of addition of this radical to the above polyfluoroaromatic compounds,which leads to predominance of decarboxylation.

The decreased reactivity of polyfluoroaromatic compounds is characterised by the relative phenylation rate of benzene and hexafluorobenzene, found from the competing reaction of these compounds with benzoyl peroxide : $K_{C_6F_6}/K_{C_6H_6} = 0.44$ [1]. The increased reactivity of polyfluoroaromatic compounds in the reactions with the nucleophilic methyl and cyclohexyl radicals is in agreement with the known data on the increased relative rate of CH_3 addition to hexafluorobenzene and benzene (3.1 and 0.4 respectively)[39].

The fluorine effect on the reactivity of polyfluoroaromatic compounds in radical reactions is consistent with the polarity and orbital control concept, which is demonstrated by the frontier molecular orbitals estimation of the relative reactivities of these compounds as compared to the non-fluorinated analogues. An approach used in [40,41] characterises the interaction of half-occupied molecular orbital (s) with the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals in the radical-unsaturated substrate system in terms of delocalisation energy in the transition state of the corresponding type of frontier orbital interaction. To characterise the donating-accepting ability of radicals in the reactions with unsaturated substrates, a magnitude was used, which was termed 'philicity' (polarity) of radicals, and which is also specified by the frontier orbital energies of the reagents. Being the function of the electron structure of both reagents, the radical polarity characterises a concrete radical-substrate system and is therefore a relative but not absolute value. Hence interpretation of polarity in terms of frontier orbital interactions in the radical-substrate system suggests that a radical may show different polarity towards different substrates. Tables 11 and 12 represent the radical polarity values, as well as the relative reactivities of polyfluoroaromatic compounds with different radicals. A good agreement between the calculated values of the reactivities of polyfluoroaromatic compounds relative to benzene and hexafluorobenzene in the radical reactions with the experimental data, and a clear-cut tendency of the reactivity dependence on radical polarity shows the utility of such approach [40,41] in characterising the radical reactions of polyfluoroaromatic compounds (with increase of radical electrophilicity, the values $K_{C_6F_6}/K_{C_6H_6}$, $K_{C_6F_5CF_3}/K_{C_6F_6}$, and $K_{C_{12}F_{10}}/K_{C_6F_6}$ decrease).

5.ROUTES OF TRANSFORMATIONS OF THE FLUORINATED RADICAL σ-COMPLEXES

The results of the reactions of polyfluoroaromatic compounds with radical reagents allow us to judge about the main routes of transformations of radical σ-complexes and the dependence of favourableness of a route on the structure characteristics of σ-complexes. Scheme 7 represents the possible routes of transformations of polyfluorinated radical

TABLE 11

Polarity of Radicals in the Reactions with Polyfluoroaromatic Compounds

Compound*	$CH_3^{\bullet}$	$C_6H_5^{\bullet}$	$CF_3^{\bullet}$	$C_6F_5^{\bullet}$
C_6H_6	-0.0272(a)	-0.0858(e)	-0.2358(e)	-0.4993(e)
C_6F_6	0.0844(n)	0.0180(a)	-0.1041(e)	-0.2451(e)
$C_6F_5CF_3$	0.1251(n)	-0.0520(n)	-0.0686(e)	-0.3413(e)
$C_{12}F_{10}$	0.1002(n)	0.0208(a)	-0.1254(e)	-0.3074(e)

(a) - the radical is ambiphilic, (n) - nucleophilic,

(e) - electrophilic

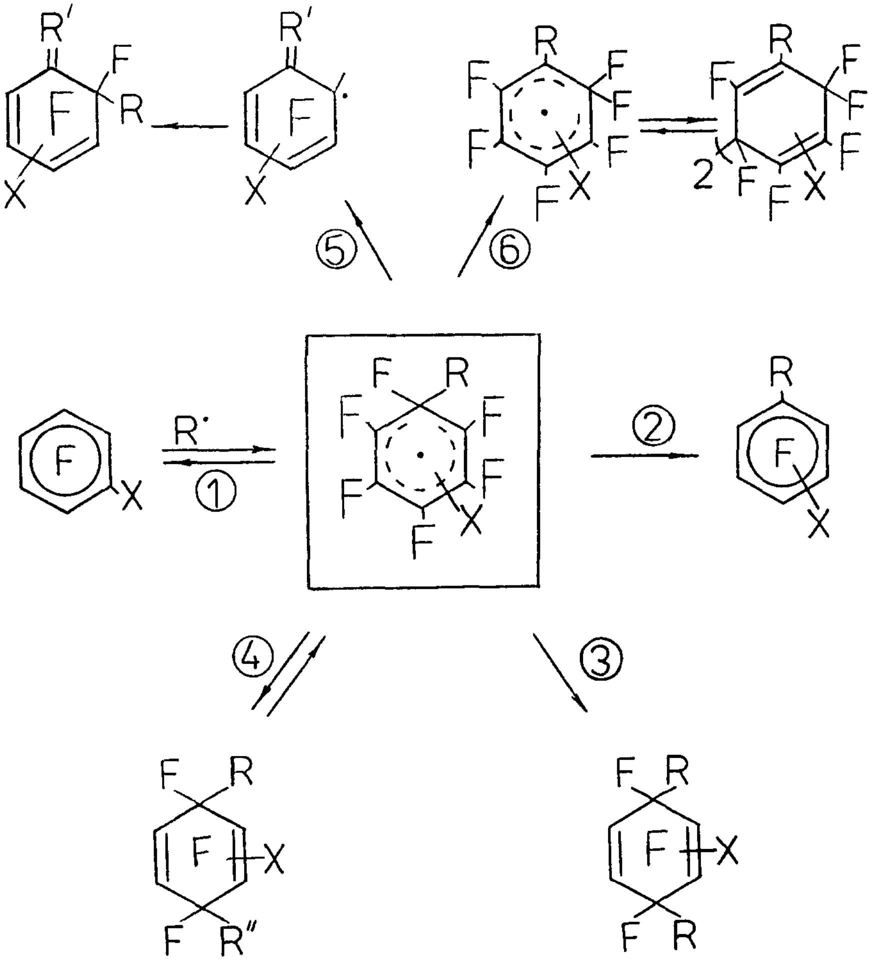
* C_6H_6 - EI 9.24 eV [42], ES 1.15 eV [43]
C_6F_6 - EI 10.2 eV [44], ES 0.52 eV [45]

TABLE 12

Relative Reactivities of Polyfluoroaromatic Compounds in Radical Reactions

Relative rate	Radical						
	$CH_3^{\bullet}$		$C_6H_5^{\bullet}$		$CF_3^{\bullet}$		$C_6F_5^{\bullet}$
	calc.	exp.	calc.	exp.	calc.	exp.	calcul.
$K_{C_6F_6}/K_{C_6H_6}$ (80°)	1.7	7.8 [39] 65°	0.7	0.44 [1]	0.4	0.39* [35]	0.1
$K_{C_6F_5CF_3}/K_{C_6F_6}$ (80°)	2.6	1.4 [46] 65°			0.5	0.8 [46] 50°	0.3
$K_{C_{12}F_{10}}/K_{C_6F_6}$ (80°)	2.0				1.0		0.7

* The result for gas [35]


R'
F
R
F
X
R'
F
X
R
F
F
F
F
F
X
F
R
F
F
F
F
2
F
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F
F
F
F
F
X
②
R
F
X
④
③
F
R
F
X
F
R''
F
R
F
X
F
R

Scheme 7

σ-complexes:

1)reversible addition of radical R to polyfluoroaromatic compounds with regeneration of the substrate;

2)defluorination of σ-complexes with formation of the homolytic substitution products;

3)recombination with the starting and other radicals;

4)dimerisation;

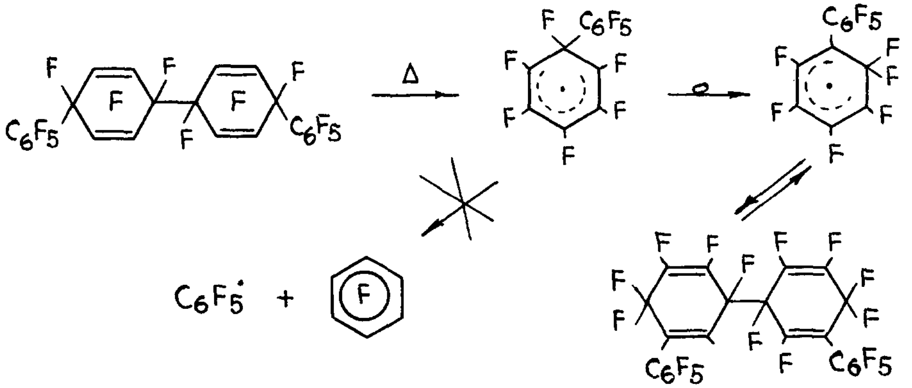
5)elimination of a geminal fragment with generation of a new radical;

6)rearrangement with fluorine 1,2-migration from the geminal group and formation of the dimers of the rearranged σ-complexes.

The question of reversibility of radical addition to polyfluoroaromatic compounds is very important, as many conclusions about orientation in these reactions are based on the suggested irreversibility of the stage of radical addition to polyfluorinated aromatic compounds. The analysis of literature data shows that addition of the methyl radical[47]to benzene and cyclohexyl radical[48,49]to dihalobenzenes is irreversible over a wide temperature range. Experimental support of irreversibility of cyclohexyl radical addition to hexafluorobenzene is provided by the thermolysis results for the dimers of the σ-complexes formed by the addition of these radicals to hexafluorobenzene at 200°. These data show no hexafluorobenzene in these reactions, which should be necessarily formed in the thermolysis in the case of irreversible radical addition.

Addition of the trifluoromethyl radical to hexafluorobenzene becomes reversible only at temperatures above 180° [50]. The perfluoroethyl radical supposedly dissociates from the σ-complex at a lower temperature, by analogy with reversibility of formation of trifluoromethyl- and perfluoroethyl-benzene addition σ-complexes at different temperatures: 150° [51,52] and 110° [37] respectively. However, for hexafluorobenzene, the temperatures are much lower.

As for the addition of aryl radicals to aromatic compounds, there is considerable disagreement in the literature about its reversibility (see, e.g., [53,54,55,56]), which necessitated obtaining a strict chemical evidence of irreversibility of these reactions. Such evidence was obtained in the studies on stabilities of the dimers of б-complexes of pentafluorophenyl radicals addition to perfluoroaromatic compounds of the benzene series. Prolonged heating of these dimers at 200° does not lead to their transformation, whereas raising the thermolysis temperature to 220-250° gives the defluorination products of the б-complexes, with no substrate regenerated in the process. For the dimers of the rearranged б-complexes of pentafluorophenyl radical addition to polyfluoroaromatic compounds, these results may not be considered unequivocal, as the total irreversibility of the process seems to be due to the irreversibility of the rearrangement. However, thermolysis of the dimer of unrearranged pentafluorophenyl radical-hexafluorobenzene addition б-complex, leading to formation of only the rearranged dimer without regeneration of hexafluorobenzene, unambiguously indicates irreversibility of the pentafluorophenyl radical addition to hexafluorobenzene.



As for the addition of the pentafluorobenzoyloxy radical to aromatic compounds, besides the strict proof of its reversibility available in the literature [57, 58], experimental evidence has been obtained in support of reversibility of addition of this radical to hexafluorobenzene and octafluoronaphthalene. Thus thermolysis of the dimers of pentafluorobenzoyloxy radical-hexafluorobenzene addition б-complexes [4] and those with octafluoronaphthalene [16] gives the substrate-containing mixtures (60% of hexafluorobenzene and 40% of octafluoronaphthalene respectively). For other oxygen-containing radicals such as pentafluorophenyl sulphonyl and tert-butoxyl, no intermediates containing these radicals can be isolated. Due to this, and to the fact of isolation of RF from the σ-complex even in mild conditions, the stage of addition of these radicals to polyfluoroaromatic compounds may be regarded as irreversible.

Defluorination of σ-complexes to form the homolytic substitution products depends essentially on the radical character and in most reactions occurs to an insignificant extent. Thus in the reactions with perfluoroalkyl radicals [11,12], no homolytic substitution products are formed at all, and with the alkyl radicals containing no fluorine, e.g., hexafluorobenzene gives the respective alkyl derivatives only in certain conditions: in the presence of agents promoting defluorination of σ-complexes. Pentafluorotoluene may be obtained in a *ca*. 15% yield in the reaction of hexafluorobenzene with acetyl peroxide, at a high concentration of the methyl radical precursor [11], and cyclohexylpentafluorobenzene in a 20% yield in the reaction of hexafluorobenzene with di-tert-butyl peroxide in cyclohexane, in presence of air [10]. If the methyl magnesium iodide-diethyl ether-silver/copper halide system is used as a radical precursor [59], the principal route of the reactions with polyfluoroaromatic compounds is the homolytic substitution of fluorine atoms. The reactions give not only the methyl-substituted derivatives but also the products of the reaction of the secondary ethoxyethyl radical which seems to be generated by the methyl radical attack at the diethyl ether:

$$CH_3MgI \xrightarrow{MX} MCH_3 \xrightarrow{ArF} ArCH_3 + CH_3CH(Ar)OCH_2CH_3$$

MX = AgCl, CuI; Ar = C_6F_5, C_6F_4Y, $C_{10}F_7$; Y = CF_3, C_6F_5.

As opposed to hexafluorobenzene, interaction of octafluoronaphthalene with the methyl radical generated from di-tert-butyl peroxide leads to the formation of 2-methylheptafluoronaphthalene in a high yield (72% at 140° and 65% at 160°) [19], which may be attributed to the increased stability of the respective methyl radical-octafluoronaphthalene addition σ-complexes, resulting from participation of the condensed ring in the unpaired electron density delocalisation. This enhances the lifetime of σ-complexes and the possibility of their defluorination by their reaction with the radical of the medium.

In the reactions with pentafluorobenzoyloxy and pentafluorophenyl radicals, the respective products of homolytic substitution in polyfluorinated aromatic compounds are formed in very low yields: 1-1.5% of pentafluorobenzoyloxy-substituted derivatives in the reactions of hexafluorobenzene and octafluoronaphthalene, 2.5-5.5% of pentafluorophenyl-substituted derivatives in the reactions of octafluorotoluene and decafluorobiphenyl at 80°, and 6-13% at 200° [13,14].

The yields of the products of homolytic fluorine substitution by the phenyl and benzoyloxy radicals are somewhat higher : with hexafluorobenzene, about 33% of pentafluorobiphenyl is formed [8], with octafluoronaphthalene - 13% of phenylheptafluoronaphthalene isomers [18] at 85°, and 43% at 110°. In general, for most radical reactions of polyfluoroaromatic compounds, raising the reaction temperature, as would be expected, affects both the yield and the isomer ratio of the homolytic substitution products. For example, the reactions of octafluoronaphthalene with pentafluorobenzene sulphonylfluoride proceeding at high temperatures (200°) lead to the formation of perfluoro-2-phenylnaphthalene in a *ca.* 54% yield [19]. Increased yield of these products may be explained by the greater ease of defluorination of σ-complexes with increased temperature. The defluorination seems to occur by interaction with radicals present in the mixture, with reagents, such as copper or silver halides, or with reactor walls. The latter interaction is indicated by the formation of silicon tetrafluoride identified in the reactions of octafluoronaphthalene with aroyl peroxide [17,18].

The isomer ratio of polyfluorinated aryl-substituted derivatives obtained in the decomposition of pentafluorobenzoyl peroxide in octafluorotoluene and decafluorobiphenyl at 200° reflects the decreased selectivity of the pentafluorophenyl radical in more rigid conditions (Table 3 and 4).

The problems of isomer ratio of the arylation products of polyfluoroaromatic compounds were discussed in our previous review [1] and the references cited in it. In particular, it was noted that for pentafluorochloro- and pentafluorobromobenzenes, the biphenyl isomer ratio in the phenylation reaction is similar to that for the non-fluorinated analogues (o->m->p-), whereas for pentafluorobenzene and octafluorotoluene, the predominant tendency is substitution of the fluorine meta to the substituent (H,CF_3). The predominant arylation at meta-position to the substituent has also been noted for the reactions of decafluorobiphenyl and octafluorotoluene with pentafluorobenzoyl peroxide [13,14].

The ratio of perfluoroterphenyl and perfluoromethylbiphenyl isomers (m->p->o-) apparently reflects the reactivity ratio of the respective positions of decafluorobiphenyl and octafluorotoluene, because, as already mentioned, in radical σ-complexes there is neither isomerisation with phenyl migration, nor fragmentation with phenyl radical formation. Table 13 summarises the perfluoromethylbiphenyl and perfluoroterphenyl isomer ratios for the arylation reactions of biphenyl, decafluorobiphenyl, and octafluorotoluene, which demonstrate variation of the meta-substitution degree depending on the presence of fluorine atoms in a substrate and radical.

Table 13

Arylation of Biphenyl, Decafluorobiphenyl, and Octafluorotoluene

Substrate	Radical precursor	T °C	Isomer ratio			$\frac{o- + p-}{m-}$
			o-	p-	m-	
$C_{12}H_{10}$	$(C_6H_5COO)_2$ [60]	80	48	29	23	3.6
	C_6F_5I [61]	80	24	39	37	1.7
$C_{12}F_{10}$	$(C_6F_5COO)_2$ [14]	80	13	27	60	0.7
$C_6F_5CF_3$	$(C_6H_5COO)_2$ [62]	80	5	24	71	0.4
	$(C_6F_5COO)_2$ [13]	80				0.13

Thus introduction of fluorine atoms into the radical raises the meta-substitution degree in biphenyl by factor of about two. The meta-substitution degree increases to a still greater extent when both the substrate and the radical contain fluorine atoms, as exemplified by the reactions of octafluorotoluene.

The reactions of octafluorotoluene and decafluorobiphenyl with nucleophilic radicals, such as the methyl radical, shows that the orientation may vary. Thus with the CH_3MgI-diethyl ether-silver/copper halide system as a source of the methyl radical, octafluorotoluene gives a mixture of methyl-substituted derivatives in the ratio of o-:m-:p- = 37:24:42, in about 40% yield considering the changed octafluorotoluene. Along with the methyl derivatives, the reaction yields the products of homolytic substitution of fluorine by the diethyl ether residue. The mixture of isomers produced in the reaction contains the small amount of ortho-derivative, the main product being the para-isomer (yield of the mixture of ethoxyethyl-substituted derivatives is 53%, the ratio of o-:m-:p- = 8:18:74). Decafluorobiphenyl reacts in similar conditions with predominant formation of a mixture of ethoxyethyl-substituted derivatives, with the para-isomer predominating (yield of the mixture of isomers is 91% considering the changed decafluorobiphenyl, the isomer ratio being o-:m-:p- = 2:16:82).

It seems interesting to discuss the problems of orientation in the radical reactions of octafluoronaphthalene leading to the homolytic substitution products. As stated above, the phenyl and benzoyloxy radicals substitute the 1- and 2-fluorine atoms in octafluoronaphthalene with 1-phenylheptafluoronaphthalene formed in predominance to the 2-isomer (3:1), and 1-/2-benzoyloxyheptafluoronaphthalenes formed in about equal proportion [18], though the 1-substitution degree in octafluoronaphthalene would seem to be higher for the electrophilic benzoyloxy radical than for the neutral phenyl radical. This may be explained by the suggested comparableness of the rates of defluorination of benzoyloxy radicals - octafluoronaphthalene addition σ-complexes and stabilisation of these σ-complexes by the release of benzoyl fluoride and generation of heptafluoronaphthoxy radical participating in formation of the reaction products containing the oxo group. Indeed, if the yields of these products and 1-benzoyloxyheptafluoronaphthalene are summed up, the ratio of the attack of benzoyloxy radical at the 1- and 2-position of octafluoronaphthalene turns out to be 4:1.

The preferred attack of electrophilic radicals at the 1-position of octafluoronaphthalene is supported by **its** reactions with oxygen-containing radicals: pentafluorobenzoyloxy, pentafluorobenzenesulphonyl and tert-butoxy ones.

The exclusive formation of 2-substituted methylheptafluoronaphthalene and perfluorophenylnaphthalene in the reactions with methyl and pentafluorophenyl radicals seems unexpected at first sight. If for the methyl radical the preferred 2-orientation may be attributed to its nucleophilic character, for the electrophilic pentafluorophenyl radical such selectivity may not be explained by the electronic factors. The exclusive formation of 2-isomer in the reactions of octafluoronaphthalene with methyl and pentafluorophenyl radicals generated from di-tert-butyl peroxide and pentafluorobenzene sulphonylfluoride respectively is likely to be due to the fact that these reactions proceed at such temperatures (140-200^{o}) when the addition of the radicals to octafluoronaphthalene becomes reversible. In this case, the σ-complexes of addition of these radicals at the 2-position of OFN may be irreversibly withdrawn from the reaction as a result of the rearrangement with fluorine migration from the 2- to 1-position to form more stable σ-complexes, owing to which the equilibrium is shifted to the right (Scheme 6). At the elevated temperature the defluorination rate of σ-complexes increases, and the end products contain a small amount of 1-isomer (Table 6 and 7).

The results of the reaction of octafluoronaphthalene with the methyl radical generated from methylmagnesium iodide in diethyl ether at low temperature (25-30^{o}) confirm this supposition. The ratio of 1- and 2-methylheptafluoronaphthalenes formed in this reaction is 9:1. As with other reactions of polyfluoroaromatic compounds with this methyl radical source, the reaction of octafluoronaphthalene is accompanied by the formation of ethoxyethyl-substituted derivatives, the 1- to 2-isomer proportion being about equal, which may be due to steric effects. Depending on the proportion between octafluoronaphthalene and CH_3MgI, the reaction may preferably give the methyl-substituted derivatives (yield 79%, the substrate to reagent ratio 1:10), or the ethoxyethyl derivatives (yield 63%, the substrate to reagent ratio 1:2). Yields are from the changed octafluoronaphthalene.

Recombination of radical σ-complexes with starting radicals forming the polyfluorinated cyclohexadiene derivatives is observed in the reaction of decafluorobiphenyl with the trifluoromethyl radical [15]. Analysis of the reason for such route of stabilisation of σ-complexes, which makes the principal contribution to the general scheme of this reaction, suggests that an essential role is played by the increased life-time of a solvent cage due to the high viscosity of decafluorobiphenyl.

On the one hand, this leads to a substantial recombination degree of primary radicals in a cage: comparison of decomposition of trifluoroacetyl peroxide in hexafluorobenzene and decafluorobiphenyl shows that in the latter case, the yield of the products of interaction of the trifluoromethyl radical with the substrate is half that in the former case (yields for the reaction with C_6F_6 and $C_{12}F_{10}$ are 60 and 30% respectively). Literature also contains the data on a similar effect of substrate viscosity on the reaction route. Thus, in decaline, radical recombination in a cage reaches 80% of the general quantity of changed alkyl radicals, whereas in low-viscous pentane, only 15% of radicals recombinate in a cage [63].

On the other hand, the greater life-time of a cage, along with the high reactivity of trifluoromethyl radicals, leads to the reaction of one of the trifluoromethyl radicals of the primary radical pair with the σ-complex produced in the reaction of another trifluoromethyl radical with cage-forming decafluorobiphenyl. Hence there occurs recombination of the secondary radical pair leading to polyfluorosubstituted cyclohexadienes. Participation of the cage-forming molecules of the solvent in formation of the secondary radical pair, the so-called cage-wall effect, has earlier been reported in the works by Ward [64].

Dimerisation of σ-complexes is the main route of their stabilisation forming the dimeric products. It should be mentioned that by dimers we mean the recombination products of both two similar and different σ-complexes. It would be reasonable to attribute the favourableness of this route of stabilisation of radical σ-complexes to the presence of the fluorine atom in a geminal group, whose removal should be energetically difficult due to the high stability of the C-F bond. Kinetically, dimerisation is equivalent to disproportionation which determines formation in the non-fluorinated series of biaryl derivatives (the rate = $k \cdot [\sigma]^2$). In the fluorinated series, the most favourable of the two processes will be the one with the lower activation energy - *i.e.* the dimerisation, which rules out fluorine elimination.

The total yields of recombination and dimerisation products of different σ-complexes in all the reactions are rather high, in some cases reaching 85-90%. Yields of the dimers are practically independent of the reaction temperature and concentration of the radical reagent, except for the cases when these factors produce a significant effect on the competing reactions withdrawing the radicals from the reaction. Thus in the decomposition of perfluoropropionyl peroxide in hexafluorobenzene [12], the elevated reaction temperature leads to about a two-fold decrease of the yield of the dimers, and a 25-fold increase in concentration of the peroxide (the peroxide to hexafluorobenzene mole ratio is 1:40 and 1:1.5 respectively) decreases the yield of the dimers by a factor of 10. In the reaction of hexafluorobenzene with acetyl peroxide [11], a similar increase in concentration of the peroxide leads to practically no dimers among the reaction products. A 4-fold increase in the concentration of di-tert-butyl peroxide upon its decomposition in hexafluorobenzene brings about a nearly 3-fold decrease of the yield of the dimers. In all these cases increased reaction temperature and peroxide concentration leads to pronounced recombination of radicals in solvent cages, as indicated by the formation of significant quantities of low-boiling products. Besides, in the reaction of di-tert-butyl peroxide, increased competing reaction of the tert-butoxy radical is possible, which eliminates hydrogen from the starting peroxide. The high activity of this radical in the hydrogen elimination reactions is well-known [65].

The low yield of dimers in the decomposition of trifluoroacetyl peroxide in decafluorobiphenyl may be attributed to the high reactivity of trifluoromethyl radicals which undergo essential recombination in a cage. For other, less reactive radicals, there is no dependence, as already mentioned, of the yields of the dimers on the reaction temperature or radical reagent concentration.

All the schemes suggested for the reactions of polyfluoroaromatic compounds with radical reagents are based on the assumption about the stability of dimers in the radical reaction conditions. The main evidence of dimer stability is their thermal behaviour: prolonged heating in inert solvent at the reaction temperature does not lead to mutual transformations of the dimers or formation of any other products in the reaction mixtures. Formation of dimers in the reaction conditions seems to be reversible, as mentioned above, only in the case of addition of pentafluorobenzoyloxy radicals to polyfluoroaromatic compounds. Decomposition of all other dimers to σ-complexes occurs, as a rule, at temperatures exceeding by far the reaction temperature.

Mass spectra of all the dimer products contain no peaks corresponding to molecular ion, or they are of low-intensity. The most intense peak is the one corresponding to the ion with M/e=1/2M. In most cases, the dimer products seem to have the structures with double bonds in the 1,4-position of the cyclohexadienyl fragment.

In the IR spectra of the dimers with substituents other than fluorine at the C_4 and $C_{4'}$ carbon atoms (compounds "4","5","7", and "23a,b,c,d,e"), the absorption band of the isolated fluorinated double bond -CF=CF- lies at 1720-1740cm^{-1}. In the IR spectrum of perfluorotetrahydrobiphenyl-1,1′ [66], the -CF=CF- absorption band lies at 1730cm^{-1}.

For compounds with the fluorine atom at one double bond or fluorines at two double bonds of different cyclohexadienyl rings substituted by any alkyl, perfluoroalkyl, or aryl substituents (compounds "6","8","9","18a","19a", and "26a"), the IR spectrum contains two bands at 1710-1725 and 1740-1770cm^{-1}, both bands being of medium or low intensity, except for compounds with the methyl group. Likewise, substitution of fluorine at one or two double bonds of perfluorocyclohexadiene-1,4 (the -CF=CF- absorption is at 1739 cm^{-1} [67])by other substituents leads to two absorption bands of the fluorinated double bond in the IR spectrum. For example, in the IR spectrum of perfluoro-1-phenylcyclohexadiene-1,4, the fluorinated double bond absorbs at 1730 and 1780cm^{-1} [68], and for perfluoro-1,5-bisphenylcyclohexadiene-1,4 - at 1720 and 1750cm^{-1} [69]. For perfluorocyclohexadiene-1,3 and its substituted derivatives, the situation is reversed: when fluorine of one of the double bonds is substituted by other substituents, the IR spectrum contains only one band (1740cm^{-1}); this is observed both for perfluoro-1-phenylcyclohexadiene-1,3 [68] and perfluoro-1,2-dihydronaphthalene [70].

Accumulation of substituents other than fluorine at the fluorinated double bonds leads to a substantial decrease of the intensity of the bands; thus for compound "26b", only a weak band at 1740cm^{-1} is observed.

The IR spectrum of the dimer of the pentafluorobenzoyloxy radical-octafluoronaphthalene addition σ-complex contains an intensive and slightly broadened band at 1765cm^{-1}. The broadening seems to be the result of vibrations of the carbonyl group of the pentafluorobenzoyloxy fragment in the same region (1760-1780cm^{-1}). Hence, in the dihydronaphthalene fragments, the double bonds are also likely to be in 2,3-position, as in perfluoro-1,4-dihydronaphthalene the band of the fluorinated double bond vibration is at 1770cm^{-1}, and in the 1,2-isomer - at 1740cm^{-1} [70].

When the para-position of the σ-complex (relative to the geminal group) is occupied by a substituent other than fluorine (C_6F_5,CF_3), or when in the 4,4′-recombination of two σ-complexes there arises considerable steric strain, there occurs the 2,2′- or 2,4′-recombination. The 2,2′- and 2,4′-recombination products have not been isolated individually, but upon the defluorination of the dimer mixtures, the polyfluorinated diphenyl derivatives were identified, whose structure indicates that such recombination does occur (Scheme 3).

Elimination of the RF fragment from the geminal group of σ-complex to generate a new radical takes place in the reaction of octafluoronaphthalene with oxygen radical precursors. The heptafluoronaphthoxy radical formed in the fragmentation of the initial radical σ-complexes participates in the formation of all oxo-derivatives and naphthoquinones in the radical reactions of octafluoronaphthalene, as confirmed by the results of the reaction of octafluoronaphthalene and heptafluoronaphthols-1 and -2 with hydrogen peroxide, the hydroxy radical precursor [71]. With the simplest of oxygen radicals-hydroxyl, hexafluorobenzene also forms a σ-complex, which undergoes fragmentation with generation of aroxy radical [72]. Hexafluorobenzene in this reaction is transformed to pentafluorophenol, which in its turn react with an excess of hydrogen peroxide with cleavage of the aromatic ring to form difluoromaleic acid, and with the lack of the peroxide it gives perfluorotetraphenoxybenzoquinone-1,4 in a high yield.

Rearrangement of σ-complexes with the earlier unknown 1,2-fluorine migration from the saturated carbon atom to the adjacent radical centre is one of the most important routes of radical σ-complex stabilisation. Fluorine migrates by the 1,2-shift, as indicated by the structure of the dimers of the rearranged pentafluorophenyl radical - octafluorotoluene and - decafluorobiphenyl addition σ-complexes (compound "26a,b"), and the recombination product of the rearranged, unrearranged phenyl radical - hexafluorobenzene addition σ-complex (compound "18c"), and the structure of the defluorination products of isomeric dimer mixtures. Dependence of the rearrangement degree on the reaction temperature, reagent concentration, and the factors related to the structure of the geminal group of radical σ-complex is discussed in detail in review [73]. The principal moving force of the rearrangement seems to be the energy gain resulting from the formation of the geminal group with two fluorine atoms. In the case when the geminal group of the initially formed σ-complexes contain the fluorine atom and a highly electronegative substituent (e.g., perfluoroalkyl or pentafluorobenzoyloxy groups), there is no energy gain and no rearrangement.

6. CONCLUSION

To sum up, the most important features in the behaviour of polyfluorinated aromatic compounds in radical reactions are as follows:

- The predominant dimerisation of radical σ-complexes is to form tetrahydrobiaryls in the absence of defluorinating agents, whose role may be played by both the reagents and some intermediate products.
- The decreased reactivity of polyfluoroaromatic compounds towards electrophilic radicals and increased reactivity towards nucleophilic ones as compared with the non-fluorinated analogues.
- The predominant meta-orientation in the reactions of compounds of the general formula C_6F_5X ($X=CF_3$, C_6F_5) with electrophilic radicals (CF_3, C_6F_5), and para-orientation in the case of nucleophilic ones (CH_3, $CH(CH_3)OC_2H_5$).
- For octafluoronaphthalene - the preferable attack at the 1-position in the reactions with oxygen and alkyl radicals at low temperatures, and the predominant formation of the products of an attack at the 2-position by the alkyl and aryl radicals at high temperatures.
- An earlier unknown rearrangement of free radicals with fluorine 1,2-migration for the polyfluorinated cyclohexadienyl radicals - the short-living intermediates of radical reactions (σ-complexes).
- A new type of stabilisation of radical σ-complexes - by their fragmentation to the respective aroxyl radicals, is specific to the reactions of polyfluoroaromatic compounds with oxygen radicals.

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