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Radical Reactions of Aromatic Polyfluoro-compounds

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The review is devoted to the reactions of aromatic polyfluoro-compounds mainly with alkyl and aryl radicals. Certain features of the behaviour of compounds of this class in radical reactions are examined and the reaction mechanisms are discussed in those cases where they differ significantly from those in the corresponding reactions of non-fluorinated compounds. The bibliography includes 101 references.

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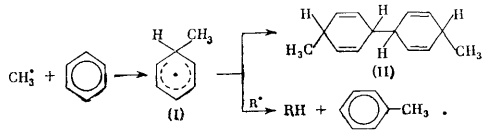
I. INTRODUCTION

Aromatic polyfluoro-compounds have been the object of continuous attention of research workers during the last 10–15 years, after convenient and easy methods for their synthesis were discovered. The data accumulated so far on the chemistry of such compounds permit the conclusion that their reactions with each of the main types of reagents (nucleophiles[1,2], electrophiles[3], and carbenes[4-9]) open general pathways to the synthesis of polyfluoro-compounds of fundamentally new structural types. In this sense, the radical reactions of aromatic polyfluoro-compounds, the study of which has been vigorously developing in recent years, constitute a striking example of the influence of fluorine atoms on the nature of the product formed and on the reactivity of aromatic compounds.

In the present review attention has been concentrated on the reactions of aromatic polyfluoro-compounds with alkyl and aryl radicals. In addition, the reactions with certain other radicals as well as photochemical and thermal reactions involving a free-radical mechanism are discussed.

II. REACTIONS WITH ALKYL RADICALS

In contrast to homolytic arylation reactions of non-fluorinated aromatic compounds, widely described in a number of reviews and monographs[10,11], the radical alkylation reactions have not been surveyed. In order to be able to compare subsequently the available data on the action of alkyl radicals on aromatic polyfluoro-compounds and on their non-fluorinated analogues, it is useful to consider briefly the results of studies of the interaction of non-fluorinated compounds and alkyl radicals. The reactions of aromatic compounds with methyl and trifluoromethyl radicals in both liquid and gaseous phases have been studied in greatest detail. The mechanism adopted, discussed here in relation to the reaction of the methyl radical with aromatic compounds, involves the addition of the radical in the first stage with formation of a σ complex of type I:



(1)

(2)

It is assumed that direct abstraction of hydrogen from the aromatic ring with formation of the phenyl radical does not occur, since biphenyls were not detected in the reaction products[12]. Calculation has also shown that the abstraction of hydrogen from the σ complex (I) [Eqn. (2)] is energetically more favourable than the direct abstraction of hydrogen from the aromatic ring (64 and 100 kcal respectively)[13].

Table 1. The relative rates of methylation and phenylation of compounds of the type C_6H_5X.

Relative rate	X							
	H	F	Cl	Br	CH_3	t-C_4H_9	C_6H_5	OC_6H_5
Methylation (Ref.14)	1	1.51 (2.2)*	2.11 (4.2)	3.87 (3.6)	1.46	0.68	7.47	4.89
Phenylation (Ref.16)	1	1.03	1.06	1.29	1.23	0.64	2.94	—

* The data of Heilman et al.[17] are indicated in brackets.

Comparison of the relative rates of methylation and arylation of benzene and its derivatives (Table 1) shows that $CH_3^{\bullet}$ is more selective than $C_6H_5^{\bullet}$, which may be attributed to the low reactivity of the intermediate σ complex (I) formed. The latter factor results in a significantly different subsequent fate of the σ complexes formed when alkyl or aryl radicals add to aromatic compounds. The σ complexes produced by the addition of alkyl radicals accumulate in the medium and vanish, dimerising in the vapour phase [Eqn. (1)], or react with the radicals of the medium, giving rise to methylbenzenes [Eqn. (2)], [14,15] while the σ complexes produced by the addition of aryl radicals disproportionate preferentially with formation of the corresponding biaryls[10].

In the reactions of aromatic compounds with sources of methyl radicals, the methylation products can be identified, while the formation of dimers of type (II) in most cases merely postulated on the grounds of general considerations[12,14,18]. Only one communication[12] reports the identification by gas–liquid chromatography (GLC) in the mixture of products of the reaction of benzene with $CH_3^{\bullet}$ of 2,2′-, 2,4′-, and 4,4′-dimethylbiphenyls, which might have been formed on dehydrogenation of the corresponding dimers. Other alkyl radicals, such as $C_2H_5^{\bullet}$, iso-$C_3H_7^{\bullet}$, and n-$C_3H_7^{\bullet}$, exhibit a reactivity in relation to aromatic

compounds analogous to that of the methyl radical, which can be inferred from the identical ratios of the isomeric alkyl derivatives obtained in the reaction of C_6H_5Cl with $CH_3^{\cdot}$ and $C_2H_5^{\cdot}$, [19] and from the relative rates of addition of the ethyl[20], isopropyl[21], and n-butyl[22] radicals to aromatic compounds.

The study of the reactions of the trifluoromethyl radical with aromatic compounds showed that, as in the reaction with the methyl radical, the differences between the processes in the gas and liquid phases are insignificant[23] and that the main process is addition to the ring[24,25]. It has been found that $CF_3^{\cdot}$ is more reactive than $CH_3^{\cdot}$, which is in all probability due to its pronounced electrophilic properties (for example the rates of addition of $CH_3^{\cdot}$ and $CF_3^{\cdot}$ to benzene relative to their addition to iso-octane are 0.4 and 7.1 respectively)[26]. The relative rates of addition of $CF_3^{\cdot}$ to substituted benzenes (Table 2) also show that the trifluoromethyl radical is electrophilic.

Table 2. The relative rate constants k_{rel} for the addition of the trifluoromethyl radical to substituted benzenes C_6H_5X.[27]

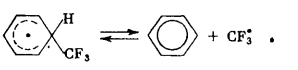
X	H	CH_3	OCH_3	I	Br	Cl	F	CF_3	CCl_3	NO_2	CN
k_{rel}	1	1.43 (1.65)*	1.93 (2.80)	— (1.65)	0.89 (0.77)	— (0.65)	0.35 (0.48)	0.26 (0.30)	0.36** —	— (0.45)	— (0.4)

* The data of Szwarc and coworkers[28] are indicated in brackets.
** Data of Giles and Whittle[29].

The data in Table 2 show that the aromatic ring is activated with respect to the addition of the trifluoromethyl radical by electron donors and deactivated by electron acceptors. The halogens can be arranged in the following sequence in terms of the extent to which they hinder the addition to the compounds C_6H_5Hal: $I > Br > Cl > F$. The deactivating affect of electron-accepting substituents such as CF_3 and CCl_3 proved to be weaker than expected. The influence of other substituents resembles qualitatively the observed influence in the reactions of substituted benzenes with electrophiles and differs from the influence of these substituents in the reactions with methyl and phenyl radicals. However, the much lower dependence, compared with heterolytic reactions, of the rate of the addition reaction on the nature of the substituent in C_6H_5X, noted for all homolytic reactions, persists under these conditions in the reactions of aromatic compounds with the trifluoromethyl radical[11,15,30].

Fundamental differences in the behaviour of other fluorine-containing alkyl radicals in reactions with aromatic compounds have not been observed[31].

An interesting observation was made in a study of the reaction of $CF_3^{\cdot}$ and $C_2F_5^{\cdot}$ with aromatic compounds at different temperatures. When the addition of the trifluoromethyl radical to benzene at 65°C is irreversible in both gaseous and liquid phases, then at 140–150°C [32,33] (and for the perfluoroethyl radical at 110°C)[31] the process becomes reversible:



Proceeding now to the consideration of the reactions of aromatic polyfluorocompounds with alkyl radicals, we may note in the first place the appreciably reduced rate of addition of the trifluoromethyl radical to compounds of the $C_6H_nF_{6-n}$ ($n = 0-6$) series with increase of the number of fluorine atoms (Table 3).

Table 3. The Arrhenius parameters* of the reactions involving the addition of the trifluoromethyl radical to aromatic compounds[27].

Compound	$10^{11} \cdot k_1/k_2^{1/2}$ **	$E_1 - \frac{1}{2}E_2$	$10^8 \cdot A_1/A_2^{1/2}$
o-$C_6H_4(CH_3)_2$	44.9	4.4	29.0
$C_6H_5CH_3$	16.9	4.9	25.0
$C_6H_5CF_3$	3.05	5.8	18.0
C_6H_5Br	10.5	6.7	210
C_6H_6	11.8	5.4	39.0
C_6H_5F	4.14	4.0	1.6
o-$C_6H_4F_2$	2.90	4.7	3.1
m-$C_6H_4F_2$	2.12	4.9	3.06
p-$C_6H_4F_2$	3.10	4.1	1.4
1,2,4-$C_6H_3F_3$	1.40	5.0	2.2
1,3,5-$C_6H_3F_3$	0.782	4.5	0.62
1,2,3,4-$C_6H_2F_4$	1.03	5.8	5.5
1,2,4,5-$C_6H_2F_4$	0.985	4.1	0.42
C_6HF_5	0.679	5.1	1.26
C_6F_6	0.484	5.8	2.8
$C_6F_5CF_3$	0.525	4.6	0.53
p-$C_6F_4(CF_3)_2$	0.143	4.2	0.069
$C_6F_5CH_3$	0.991	3.7	0.24
C_6F_5Br	0.767	5.2	2.0

* The kinetic method is based on the determination of the decrease of the yield of the radical recombination product relative to an internal standard (CO for the generation of the trifluoromethyl radical from hexafluoroacetone) when an aromatic substrate capable of combining with the radical is added to the reaction mixture.
** k_1 is the rate constant for the addition of $CF_3^{\cdot}$ to the aromatic compound and k_2 the rate constant for the dimerisation of trifluoromethyl radicals.

In a theoretical consideration of the addition of radicals to aromatic compounds, it is usual to assume that the changes in the rate constants are caused mainly by the changes in the activation energies for the reactions. The explanation of the deactivation of the aromatic ring by fluorine atoms in terms of electron repulsion effects or the dipolar influence of the medium also presupposes a change in activation energies. However, the data in Table 3 show that the activation energies are actually very close for all substituted benzenes, while the activation entropy (the A factor) depends significantly on the number and nature of substituents.

Evidently the replacement of hydrogen atoms by fluorine in the reaction centre of the aromatic compound can influence both the activation energy and entropy of the radical addition reaction. Szwarc and coworkers[34] quote data showing that the activation entropies for hexafluorobenzene and benzene differ very little, while according to the data of Whittle and coworkers[27] the A factor for aromatic polyfluoro-compounds is lower by a factor of approximately ten than for benzene derivatives without fluorine atoms. The reversibility of the addition of the trifluoromethyl radical to aromatic compounds at high temperatures (150°C for benzene and 180°C for hexafluorobenzene)[34] introduces some uncertainty into both sets of results.

Nevertheless findings such as the similarity of the ratios of the rate constants for the addition of $CF_3^{\cdot}$ to C_6H_6 and C_6F_6, obtained by Szwarc and Whittle in the temperature range 24–80°C ($k_{C_6H_6}/k_{C_6F_6} = 20$), and the observed decrease of the A factor for the addition of the trifluoromethyl radical to a series of other polyfluorobenzenes (Table 3) suggest that the change in activation entropy observed by Whittle and coworkers is greater than the possible experimental error and is therefore more reliable than the data of Szwarc and coworkers. The decrease of the activation entropy for the addition of the trifluoromethyl radical occurring in the presence of substituents at the reaction centre may be a result of a partial restriction of the rotation of the trifluoromethyl group about the C–CF_3 axis in the transition state.

For compounds of the type C_6F_5X with X = H as the standard substituent, the same effects of the substituents are observed in the addition reaction of the trifluoromethyl radical (Table 4) as for the benzene derivatives C_6H_5X (Table 2).

Table 4. The relative rate constants k_{rel} for the addition of the trifluoromethyl radical to compounds of the type C_6F_5X.[27]

X	H	F	Br	Cl	CF_3	CH_3
k_{rel}	1	0.71	1.13	1.12*	0.77	1.46

* The rate constants were calculated from the ratios $k_{C_6H_5Cl}/k_{C_6H_6} = 0.065$ [29] and $k_{C_6F_5H}/k_{C_6H_6} = 0.058$.[27]

Interesting observations have been made on the mode and ease of abstraction of hydrogen from aromatic fluorocompounds by the trifluoromethyl radical[27]. As fluorine atoms accumulate in the $C_6H_nF_{6-n}$ molecule, the abstraction of hydrogen becomes increasingly more difficult, but the addition of $CF_3^{\cdot}$ is hindered at the same time, in agreement with the earlier hypothesis that the abstraction of hydrogen in the reactions of aromatic compounds with alkyl radicals is most likely to occur from σ addition complexes of these radicals rather than directly from the ring. When the benzene ring contains a substituent such as the CH_3 group, hydrogen is abstracted from the latter in $C_6F_5CH_3$ with much more difficulty than in $C_6H_5CH_3$, which can be explained by the greater strength of the C–H bond in pentafluorotoluene.

The abstraction of a bromine atom is observed in the reactions of benzene derivatives such as C_6H_5Br and C_6F_5Br with the trifluoromethyl radical, which can be inferred from the formation of CF_3Br. It is then found that bromine is abstracted from bromopentafluorobenzene approximately six times more readily than from bromobenzene, but the rate constants for these reactions cannot be calculated, since there exist two alternative mechanisms of the abstraction of bromine: (1) directly from the aromatic ring and (2) from the intermediate σ complex in which $CF_3^{\cdot}$ has added to the carbon atom linked to bromine. The observations of Whittle and coworkers[27] tend to support the second mechanism. Firstly, the rate of formation of CF_3Br [and CH_3Br?] from both C_6F_5Br and C_6H_5Br does not change appreciably with temperature and, secondly, the activation energies for the two reactions are less than 2 kcal mole^{-1}, while that for the abstraction of hydrogen is approximately 5 kcal mole^{-1}. Despite the low activation energy, the elimination of bromine from C_6H_5Br proceeds much more slowly than that of hydrogen, probably due to steric factors, which may play a more important role in the abstraction of bromine located in the geminal position with respect to the CF_3 group in the σ complex than in the abstraction of hydrogen from the analogous σ complex. In contrast to the reactions of C_6H_5Br and C_6F_5Br, an appreciable elimination of the chlorine atom was not observed in the reaction of the trifluoromethyl radical with C_6H_5Cl and C_6F_5Cl even at 110–120°C.[29] The calculated activation energy for the elimination of the chlorine atom is approximately 13 kcal mole^{-1}. On the other hand, iodine is abstracted very rapidly from C_6H_5I and C_6F_5I by the trifluoromethyl radical, the rate of abstraction from pentafluoroiodobenzene being approximately four times greater than from iodobenzene.

When $CF_3^{\cdot}$ interacts with pentafluorobenzaldehyde[35], the hydrogen atom is abstracted with formation of trifluoromethane and a pentafluorobenzoyl radical, which recombines with $CF_3^{\cdot}$ to form octafluoroacetophenone:

$$C_6F_5CHO + CF_3^{\cdot} \xrightarrow{h\nu} C_6F_5CO^{\cdot} + CF_3H\ ;$$
$$C_6F_5CO^{\cdot} + CF_3^{\cdot} \rightarrow C_6F_5COCF_3\ .$$

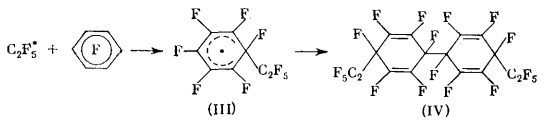
The activation energy for the abstraction of the hydrogen atom from pentafluorobenzaldehyde is higher than for benzaldehyde (8.6 and 4.6 kcal mole^{-1} respectively), but the yield of octafluoroacetophenone is significantly higher than that of acetophenone in the corresponding reaction of benzaldehyde. According to the authors[35], the latter factor may be a result of the low stability of the non-fluorinated benzoyl radical (the dissociation energy of the C_6H_5–CO bond is only 28 kcal mole^{-1}), which readily dissociates with formation of $C_6H_5^{\cdot}$ and CO. On the other hand, it may be that the high yield of octafluoroacetophenone is due to the high reactivity of the pentafluorobenzoyl radical [cf. the reaction of C_6F_5I with $Ni(CO)_4$, see Section V below], which reacts with the trifluoromethyl radical before dissociating with formation of C_6F_5 and CO.

It is of interest to compare the results of the study of the interaction of benzene and hexafluorobenzene with the chlorodifluoromethyl radical generated from 1,3-dichlorotetrafluoroacetone on photolysis[36]. The significant differences between the temperature dependences of the rates of formation of the products of the addition of $CF_2Cl^{\cdot}$ to C_6H_6 and C_6F_6 observed by the authors were interpreted in terms of the different stabilities of the corresponding σ complexes (up to 100°C for $C_6H_6CF_2Cl^{\cdot}$ and up to 250°C for $C_6F_6CF_2Cl^{\cdot}$).

The fact that the elimination of fluorine atoms was not observed in any of the reactions of aromatic polyfluorocompounds with fluorine-containing alkyl radicals may serve as evidence that the main pathway in the reaction of the σ complexes produced by the addition of the radicals to aromatic polyfluoro-compounds involves their dimerisation. We already noted previously that, in the vast majority of the reactions investigated, with both non-fluorinated and fluorinated reagents, dimeric products could not be isolated and the conclusions concerning the mechanism of the reaction of the σ complexes resulting from the addition of alkyl radicals to fluorinated and non-fluorinated aromatic compounds were based on kinetic data. In a study of the reaction of hexafluorobenzene with the perfluoroethyl radical generated from perfluoropropionyl peroxide, the isomeric compounds (IV)—the dimers

of the σ complex produced by the addition of $C_2F_5^{\cdot}$ to C_6F_6 (III)—were recently isolated[37] as the main reaction products:

$$(C_2F_5COO)_2 \xrightarrow{\Delta} 2C_2F_5^{\cdot} + 2CO_2 ;$$



(III) (IV)

The difference in the behaviour of benzene and hexafluorobenzene in their reactions with nitromethane at 550°C is noteworthy[38]. The main product of the reaction of benzene is biphenyl, while the remaining products consist to the extent of 80% of nitrogen compounds (aniline and *N*-methylaniline)[39]; on the other hand, the reaction with C_6F_6 yields mainly pentafluorotoluene and pentafluorophenol, the ratio of which varies with the molar ratio of the reactants (Table 5).

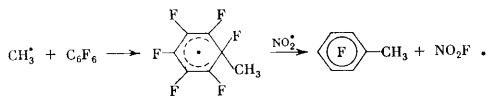
Table 5. The proportions of the products of the reaction of C_6F_6 with CH_3NO_2 (determined as percentages by GLC relative to one mole of C_6F_6).

Reaction product	Nitromethane (no. of moles)		Reaction product	Nitromethane (no. of moles)	
	1	0.1		1	0,1
$C_6F_5CH_3$	37.5	60.0	C_6F_5CHO	6.6	4.6
C_6F_5OH	33.0	3.0	$C_{12}F_{10}$	6.8	2.9
$C_6F_5OCH_3$	5.9	12.7	unknown products	10.2	16.8

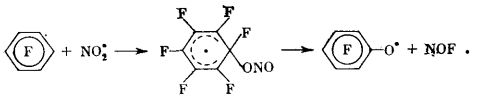
The observed difference between the products of the reactions of nitromethane with benzene and hexafluorobenzene may be attributed to a certain amount of nucleophilic character of the methyl radical, as a result of which its attack on C_6F_6, which is sensitive to nucleophiles[2], becomes the preferred pathway. Possibly the degree of such preference reflects the difference between the bond dissociation energies $D(C_6F_5-CH_3) - D(C_6H_5-CH_3) = 25$ kcal mole^{-1}.[40] The following mechanism is proposed for the formation of the main product of the reaction of CH_3NO_2 with C_6F_6. At a high temperature nitromethane decomposes into two radicals:

$$CH_3NO_2 \rightarrow CH_3^{\cdot} + NO_2^{\cdot} .$$

The methyl radical adds to hexafluorobenzene with formation of a σ complex, from which a fluorine atom is abstracted by the $NO_2^{\cdot}$ radical:



The methyl radical apparently reacts with hexafluorobenzene so fast that there is not sufficient time for the abstraction of a hydrogen atom from nitromethane, as happens in the reaction with benzene. The role of $NO_2^{\cdot}$ in the two reactions is likewise different. The radical abstracts hydrogen from benzene, giving rise to the phenyl radical responsible for the formation of biphenyl in the phenylation of benzene or during dimerisation. Fluorine is apparently abstracted to only an insignificant extent from C_6F_6, since only very small amounts of decafluorobiphenyl are formed. The $NO_2^{\cdot}$ radical is most likely to play the main role in the formation of pentafluorophenol in the reaction with C_6F_6:



The pentafluorophenoxy-radical probably abstracts hydrogen from nitromethane, forming pentafluorophenol.

The alternative mechanism of the formation of pentafluorophenol via pentafluoronitrobenzene or possibly indirectly via pentafluorophenyl nitrite (without the preliminary dissociation of nitromethane as in the formation of phenols from different aromatic nitro-compounds at a high temperature[41]) is probably ruled out owing to the absence of CH_3F from the reaction products.

Pentafluoroanisole may be formed in the reaction of hexafluorobenzene with nitromethane as a result of the attack on C_6F_6 by the methoxy-radical formed in the nitro-nitrite rearrangement or in the recombination–dissociation of nitromethane:

$$CH_3NO_2 \rightarrow CH_3ONO \rightarrow CH_3O^{\cdot} + NO^{\cdot}$$
$$\downarrow$$
$$CH_3^{\cdot} + NO_2^{\cdot} .$$

The preferential elimination of fluorine relative to that of hydrogen in the reactions with the methyl radical generated from nitromethane at high temperatures is clearly seen in the interaction of *p*-difluorobenzene with nitromethane[38]. The main product of this reaction is fluorophenol and the ratio of the yields of the products of the abstraction of fluorine and hydrogen atoms is 33 : 1.

The higher reactivity of hexafluorobenzene relative to benzene was also noted in a study of the reactivity of polyfluorinated unsaturated compounds with respect to the methyl radical generated from acetyl peroxide[43] (Table 6).

Table 6. The affinities of unsaturated compounds and their fluorinated analogues for the methyl radical[42].

Compound	C_6H_6	$CH_2=CH-CH=CH_2$	C_6F_6	$CF_2=CF-CF=CF_2$
k_1/k_2*	0.4[15]	2900[43]	3.1	900

*k_1 is the rate constant for the addition of $CH_3^{\cdot}$ and k_2 the rate constant for the abstraction of hydrogen from the solvent by $CH_3^{\cdot}$.

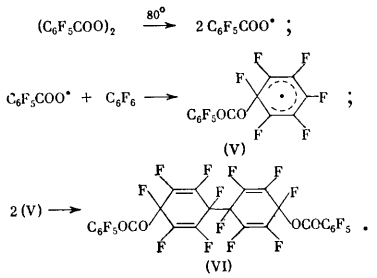
The above reactions of alkyl radicals with aromatic polyfluoro-compounds reveal certain characteristic features of the behaviour of these compounds. In the first place, one should note the higher reactivity of aromatic polyfluoro-compounds with respect to nucleophiles. No less important is the conclusion that the fluorine-containing radical σ-complexes are more stable, which follows from a comparison of the dissociation temperatures of such complexes, formed by the addition of alkyl radicals to benzene and hexafluorobenzene.

III. REACTION WITH ARYL RADICALS

The data described in the previous Section showed that the available information about the reactions of a large set of aromatic polyfluoro-compounds with alkyl radicals

concerns mainly the process kinetics and there are almost no data concerning the synthetic possibilities of the reactions. In the studies on the interaction of aromatic polyfluoro-compounds with aryl radicals, there has been a more successful combination of investigations on these different lines, which make it possible to discover both the quantitative relations governing the behaviour of aromatic polyfluoro-compounds in these reactions as well as interesting synthetic reactions. Mainly aroyl peroxides have been used as the sources of aryl radicals in the reactions investigated, since it was observed that hexafluorobenzene does not react, for example, with the pentafluorophenyl radicals generated from $C_6F_5NHNHNH_2$[44] in the presence of oxidising agents, or from C_6F_5I on photolysis[45], or with a source of $C_6F_5^{\cdot}$ such as $C_6F_5N(NO).COCH_3$, which might have been expected to be effective by analogy with the non-fluorinated compound[46].

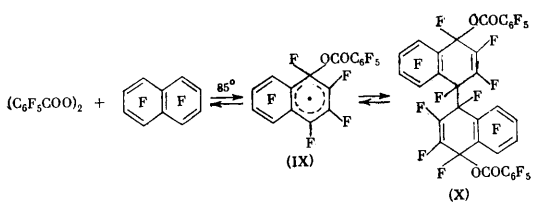
In the decomposition of pentafluorobenzoyl peroxide in hexafluorobenzene at 80°C, 4,4′-di(benzoyloxy)perfluoro-1,1′,4,4′-tetrahydrobiphenyl (VI), resulting from the dimerisation of the σ complex (V) formed by the addition of the pentafluorobenzoyloxy-radical to C_6F_6, is the main reaction product (60%).[47,48]



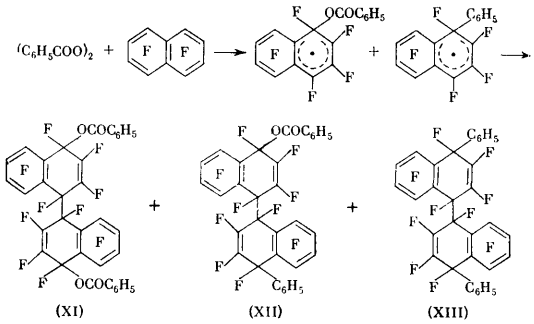
Apart from compound (VI), 3–5% of perfluorophenyl benzoate (VII) and 5–7% of tetrafluorobiphenyl (VIII) are produced. English chemists[49,50] were unable to isolate in a similar reaction any products other than compounds (VII) and (VIII).

The principal characteristics of this reaction are the virtual absence of the products of homolytic substitution and the preferential involvement of pentafluorobenzoyloxy-radicals in the reaction. We may recall that non-fluorinated reagents give rise mainly to biphenyls under these conditions. Compounds (VII) and (VIII), which are formed in insignificant amounts, can be regarded either as a result of the reaction of the radicals generated from pentafluorobenzoyl peroxide (for example the dimerisation of $C_6F_5^{\cdot}$ or the recombination of $C_6F_5^{\cdot}$ and $C_6F_5COO^{\cdot}$) or as products of the reaction of these radicals with hexafluorobenzene.

The interaction of octafluoronaphthalene (OFN) with pentafluorobenzoyl peroxide leads to results analogous to those obtained in the reaction with hexafluorobenzene. The main product at 85°C (in acetonitrile) is the dimer (X) of the σ complex resulting from the addition of the pentafluorobenzoyloxy-radical to the 1-position of OFN (IX):[51]

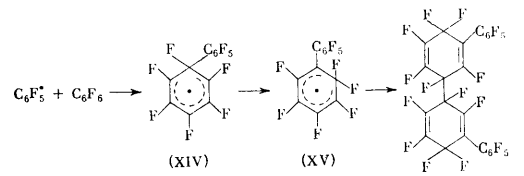


The reaction of OFN with the non-fluorinated benzoyl peroxide under the same conditions[51] probably yields a mixture of the dimers (XI), (XII), and (XIII):



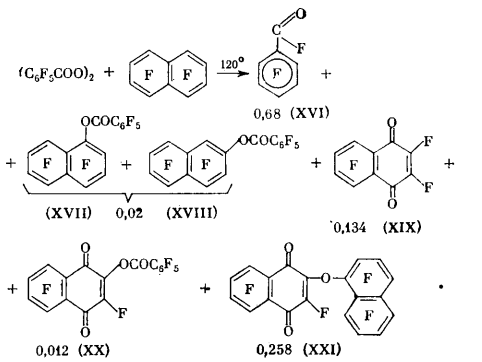
The involvement of both benzoyloxy- and phenyl radicals in this reaction, in contrast to the reactions with pentafluorobenzoyl peroxide, indicates a significant influence of the introduction of the fluorine atoms into the peroxide molecule on the nature of its decomposition (this problem will be discussed below).

The exclusive involvement of the pentafluorophenyl radical in the reaction of C_6F_6 with $(C_6F_5COO)_2$ is observed only at high temperatures. Thus a mixture of isomeric dimers of the σ complex formed by the addition of the pentafluorophenyl radical to hexafluorobenzene is produced at 200°C.[48] The structure of these dimers, confirmed by their spectroscopic characteristics and their defluorination to perfluoro-*m*,*m*′-quaterphenyl, shows that the reaction probably involves the dimerisation of the σ complex (XV), formed as a result of the migration of the fluorine atom in the initial σ complex of type (XIV):

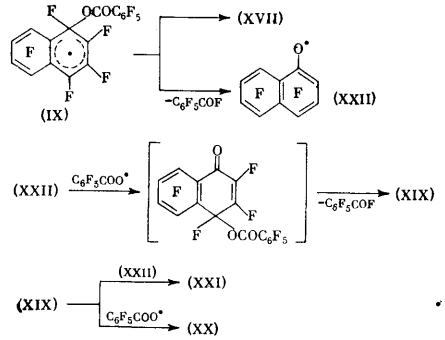


The driving force of the migration of the fluorine atom in the σ complex (XIV) is probably the considerable increase of the stability of the rearranged σ complex (XV) as a result of the possibility of the involvement of the pentafluorobenzene ring in the delocalisation of the unpaired electron.

It is of interest that an increase of temperature in the reaction of pentafluorobenzoyl peroxide with OFN does not lead to the formation of products with participation of the pentafluorophenyl radical. At 120°C this reaction already proceeds via a completely unusual pathway[65], resulting in the formation of a mixture of products in which 2-(1′-naphthoxy)perfluoro-1,4-naphthoquinone (XXI) predominates:



The formation of the naphthoquinone derivatives (XIX), (XX), and (XXI), which has no analogies in the familiar reactions of aroyl peroxides with naphthalene and its derivatives, is attributed to the following reactions:



The radical σ complex (IX) can, on the one hand, lose a fluorine atom and be converted into typical homolytic substitution products–perfluorobenzoyloxynaphthalenes, and, on the other hand, it can split off pentafluorobenzoyl fluoride (XVI) to give a new radical, i.e. the heptafluoronaphthoxy-radical (XXII), which is responsible for the subsequent reactions leading to the formation of compounds (XIX), (XX), and (XXI). This pathway to the stabilisation of the σ complex (IX) is probably due to the presence of the fluorine atom and the benzoyloxy-group in the geminal unit, which is confirmed by the formation of compounds (XIX) and (XXI) when OFN reacts with benzoyl peroxide at 85 °C in the absence of an inert solvent[53]. Hexafluoronaphthoquinone derivatives are formed in this reaction together with homolytic substitution products and the products of the reaction of benzoyl peroxide without the involvement of a fluorinated substrate (Table 7).

Table 7. The results of the interaction of benzoyl peroxide with octafluoronaphthalene (the yields are expressed in moles per mole of peroxide; peroxide : OFN = 1 : 4; 30 h).

Compound	Reaction temperature	
	85°	110°
1-Benzoyloxyheptafluoronaphthalene	0.045	0.019
2-Benzoyloxyheptafluoronaphthalene	0.037	0.012
1-Phenylheptafluoronaphthalene	0.104	0.287
2-Phenylheptafluoronaphthalene	0.031	0.120
3,5,6,7,8-Pentafluoro-2-(heptafluoro-1'-naphthoxy)-1,4-naphthoquinone (XXI)	0.056	0.019
Hexafluoro-1,4-naphthoquinone	0.022	0.018
Benzoyl fluoride	0.515	–
Biphenyl	0.051	0.094
Phenyl benzoate	0.566	0.048

The data in Table 7 show that a change in reaction temperature has only an insignificant effect on the qualitative composition of the reaction products, but does influence appreciably their quantitative proportions. With increase of temperature, the yield of phenylheptafluoronaphthalenes increases, as has been observed in the reaction of naphthalene with benzoyl peroxide[54]. The proportions of the isomers remain almost unchanged as the temperature is altered and indicate the greatest sensitivity of the α-position in the OFN molecule to radical attack, in agreement with the calculated radical localisation energy of OFN.

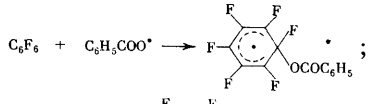
It is very remarkable that the reaction of OFN with $(C_6H_5COO)_2$ involves the homolytic substitution of a fluorine atom, which constitutes at the same time the preferred process. This may imply that the absence of products of the homolytic substitution of fluorine atoms in reactions of OFN and C_6F_6 with $(C_6F_5COO)_2$ is not solely due to the great strength of the C–F bond in the initial aromatic polyfluoro-compounds [$D(C_6F_5–F)$ = 140 kcal;[55] $D(C_6H_5–H)$ = 102 kcal [56]], but is also associated with the nature of the radical.

For example hexafluorobenzene reacts with $(C_6H_5.COO)_2$ [57–61] and some of its substituted derivatives[62] to form homolytic substitution products. High yields (60–80%) of the corresponding pentafluorobiphenyls were obtained in the reactions with benzoyl peroxide itself and its 3-methyl derivative but, after the introduction of electron-accepting substituents (3-chloro-, 3-bromo-, and 4-nitro-) into the peroxide molecule, the yields of the arylation products are appreciably reduced, particularly in the case of the nitroderivative of the peroxide. Williams and coworkers[62] used this mode of reaction as a basis for the conclusion that the mechanism of the arylation of aromatic polyfluoro-compounds is similar to the familiar mechanism of the arylation of non-fluorinated aromatic compounds and involves the formation of biaryls either via the disproportionation of the corresponding σ complexes or via the elimination of a fluorine atom from the latter by any radical present in the mixture.

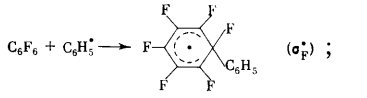
However, a detailed study of the kinetics and products of the reaction of hexafluorobenzene with benzoyl peroxide led to the abandonment of disproportionation as a pathway to the formation of biaryls and a new mechanism was postulated for this reaction, based on the involvement of benzoic acid as a defluorinating agent. The mechanism, which also includes stages common to the reactions of non-fluorinated compounds, is given below[59–61] (the compounds which were islated from the products of this reaction are underlined):

$$(C_6H_5COO)_2 \rightarrow 2C_6H_5COO^{\cdot} \quad ; \qquad (3)$$

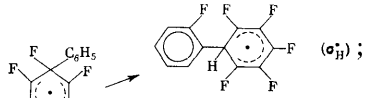
$$C_6H_5COO^{\cdot} \rightarrow C_6H_5^{\cdot} + CO_2 \quad ; \qquad (4)$$



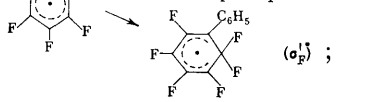
(5)



(6)



(7)



(8)

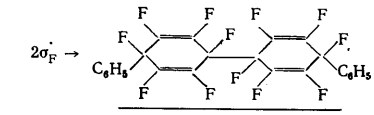
$$\sigma_H^{\cdot} + (C_6H_5COO)_2 \rightarrow \underline{o\text{-}FC_6H_4C_6F_5} + \underline{C_6H_5COOH} + C_6H_5COO^{\cdot} \quad ; \qquad (9)$$

(XXIII)

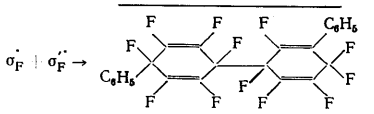
$$\sigma_F^{\cdot}(\sigma_F'') + (C_6H_5COO)_2 \rightarrow \sigma_F - OCOC_6H_5 + C_6H_5COO^{\cdot} \quad ; \qquad (10)$$

$$\sigma_F^{\cdot}(\sigma_F'') + C_6H_5COOH \rightarrow \underline{C_6H_5C_6F_5} + HF + C_6H_5COO^{\cdot} \quad ; \qquad (11)$$

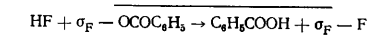
$$C_6H_5^{\cdot} + C_6H_5COOH \rightarrow C_6H_6 + C_6H_5COO^{\cdot} \quad ; \qquad (12)$$



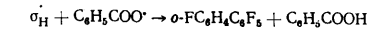
(13)



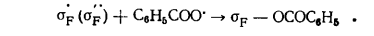
(14)



(15)



(16)



(17)

The first stages in this mechanism [stages (3) and (4)] are well known and require no explanation. Like the subsequent addition of the radicals to the substrate [Eqns. (5) and (6)], they are analogous to the stages of the interaction of aroyl peroxides with other aromatic systems. The stage involving the rearrangement of the initially formed σ complex ($\sigma_{\dot{F}}$) with migration of the fluorine atom to the unsubstituted cyclic compound [Eqn. (7)] and the subsequent reaction with benzoyl peroxide [Eqn. (9)] of the rearranged σ complex ($\sigma_{\dot{H}}$) explain in the simplest manner the formation in this reaction of small amounts of 2,2',3,4,5,6-hexafluorobiphenyl (XXIII) and benzoic acid. The formation of compound (XXIII) was also observed in the high-temperature (600°C) reaction of hexafluorobenzene with nitrobenzene (mass-spectrometric data)[41,63], for which a radical mechanism has been proposed.

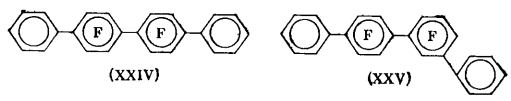
Stages (9) and (10) reflect the contribution of the induced decomposition of benzoyl peroxide to the reaction, which follows also from the analysis of the kinetic parameters of the reaction[61]. The rearrangement [Eqn. (8)] of the σ complex ($\sigma_{\dot{F}}$) with migration of the fluorine atom to a neighbouring position (a 1,2-shift), competing with the rearrangement [Eqn. (7)] to a σ complex ($\sigma_{\dot{H}}$) probably takes place to a greater extent, as can be seen from the yields of the products of dimerisation with participation of the rearranged σ complex ($\sigma''_{\dot{F}}$).[59]

Defluorination of the σ complex ($\sigma_{\dot{F}}$) with participation of benzoic acid [Eqn. (11)] is one of the main stages of the reaction. It leads to the formation of pentafluorobiphenyl and is a pathway to the regeneration of the benzoyloxy-radical and a source of HF. The absence of benzoic acid, an effective defluorinating agent, is probably the reason for the low yields of pentafluorobiphenyl in the reactions of hexafluorobenzene with other sources of phenyl radicals, such as phenylazotriphenylmethane[64] and $C_6H_5N=NOC_5H_{11}$.[65] The important role of benzoic acid is demonstrated by the increase of the yield of pentafluorobiphenyl when the decomposition of phenylazotriphenylmethane is carried out in hexafluorobenzene in the presence of benzoic acid[64].

The proposed mechanism for the interaction of hexafluorobenzene with benzoyl peroxide includes several pathways to the generation of benzoic acid. Apart from stage (9) mentioned above, reaction (15) and to a lesser extent reaction (16) merit attention. The required amounts of esters may be formed in subsequent reactions of the σ complex produced by the addition of the benzoyloxy-radical to hexafluorobenzene [Eqn. (5)] or via reactions (10) and (17). Since pentafluorophenyl benzoate, the formation of which may be expected when the substrate undergoes aroyloxylation initiated by reaction (5), is absent from the reaction products, all the esters are probably formed in radical–radical reactions. The most significant contribution apparently comes under these conditions from the ester $\sigma_F-OCOC_6H_5$, the formation of which includes the recombination of two radicals present at high steady-state concentrations.

It is of interest that the combination of stages (10), (11), and (15) ultimately leads to the formation of pentafluorobiphenyl and heptafluorodihydrobiphenyls†, i.e. to the products which can be formed also by the disproportionation of the σ complex ($\sigma_{\dot{F}}$).

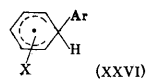
The abandonment of disproportionation as one of the stages of the process was dictated by the following considerations. The disproportionation is a single-stage reaction and requires that the radical–radical combination processes resulting in dimers should not take place preferentially. However, since dimerisation and disproportionation are kinetically equivalent, the rate being equal to $k[\sigma_{\dot{F}}]^2$, the process with the lower activation energy, namely dimerisation, is the most probable, ruling out the elimination of a fluorine atom. The contribution of the dimerisation processes [Eqns. (13) and (14)] varies as a function of the reaction conditions and the yields of the dimers vary from 3 to 50%.[59] The formation on defluorination of the mixture of dimers of compounds (XXIV) and (XXV) (octafluoroquaterphenyls) confirms the rearrangement of the σ complex ($\sigma_{\dot{F}}$) formed initially to the σ complex ($\sigma'_{\dot{F}}$) with 1,2-migration of the fluorine atom[59]:



(XXIV) (XXV)

The results of the interaction of benzoyl fluoride with substituted aromatic polyfluoro-compounds are presented in Table 8, which includes for comparison also data for certain non-fluorinated compounds.

The transition state in the arylation of simple benzene derivatives (C_6H_5X) is generally believed to have a structure intermediate between that of the ground state and that of a σ complex of type (XXVI):



(XXVI)

It is assumed that the unpaired electron is delocalised over the entire ring, including the substituent. Such delocalisation with participation of the substituent determines to a large extent the observed mode of substitution in homolytic arylation. In aromatic polyfluoro-systems (C_6F_5X), there is a choice between two structures in which the substituent involved in delocalisation is X or F, which may lead to differences in the isomeric composition of the arylation products C_6F_5X and C_6H_5X.

The proportions of the isomeric biphenyls in the reactions of benzoyl peroxide with chloro- and bromo-pentafluorobenzenes are analogous to those observed in the

† The heptafluorodihydrobiphenyls were not isolated, but it was postulated that they are converted into pentafluorobiphenyl during the treatment of the reaction products, since it has been shown that the distillation of the mixture of products under severe conditions (300°/760 mmHg instead of 100°/15 mmHg) results in an increase of the yield of pentafluorobiphenyl almost by a factor of 1.5 and to the same decrease of the yield of an unidentified tarry residue[66].

non-fluorinated series, which may be a result of the similar efficiencies of chlorine, bromine, and fluorine atoms in the delocalisation of the unpaired electron in the corresponding σ complexes. The isomeric composition of the pentafluorobenzene phenylation products shows that substitution in the 1- and 3-positions takes place most readily, which apparently corresponds to a greater ease of formation of the corresponding σ complexes which are stabilised by the involvement of three fluorine atoms in the resonance, in contrast to σ complexes formed when the 2- and 4-positions are attacked. The greater ease of substitution of hydrogen compared with fluorine is probably also determined by the difference between the mechanisms of the aromatisation of the corresponding σ complexes[68]. For the same reasons as in the case of C_6F_5H, the 3-position is the most reactive in $C_6F_5CF_3$. The additional decrease of the reactivity of the 2-position is attributed to steric factors and the relatively greater reactivity of the 3-position relative to the 4-position is thought to be due to the presence of three fluorine atoms involved in the stabilisation of the σ complexes formed in the former case and of two such atoms in the latter[68].

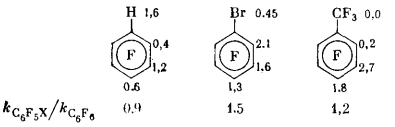
Table 8. The ratio of the isomers formed in the phenylation of aromatic compounds at 80°C (determined as percentages by GLC).

Compound	Isomeric composition of phenylation products		
	2-	3-	4-
C_6F_5Cl[66]	44.1	35.0	20.9
C_6H_5Cl[67]	50.1	31.6	18.3
C_6F_5Br *[66,68]	43.6 (45.0)	39.0 (36.0)	17.4 (14.0)
C_6H_5Br[69]	49.3	33.3	17.4
$C_6F_5CF_3$[68]	5.0	71.0	24.0
C_6F_5H **[68]	15.0	45.0	11.0
C_5F_5N[66]	47.7	22.1	30.3
C_5H_5N[70]	54.0	32.0	14.0

* The data of Bolton et al.[68], according to which approximately 5% of the product resulting from the substitution of the bromine atom is also formed, are indicated in brackets.

** The formation of 29% of the product of the substitution of a hydrogen atom was also noted.

The partial rate factors for attack in different positions in C_6F_5X, determined by comparing the composition of the reaction products and the relative rate constants obtained from competition experiments with equimolar amounts of C_6F_6 and C_6F_5X, are indicated below[68]:

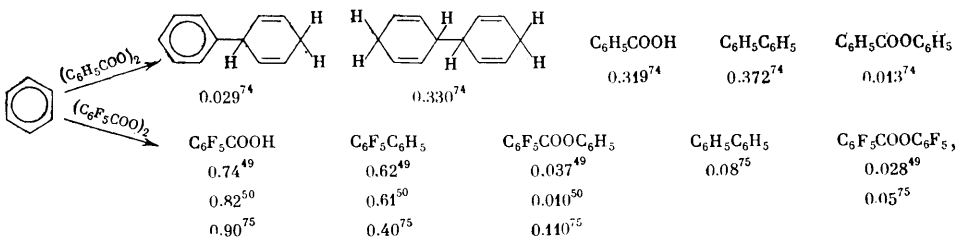


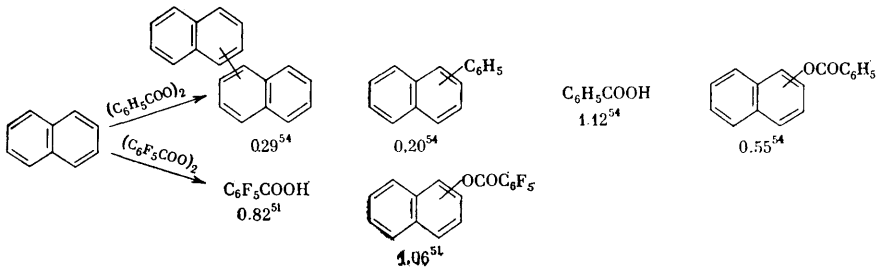
The relative rates of arylation of aromatic polyfluoro-compounds shown here differ from those obtained previously from the competing reactions of each substrate with benzene (for example $k_{C_6F_5Br}/k_{C_6F_6} = 1.0$).[11] This discrepancy is probably determined by the fact that, when benzene is used as the standard, the atoms substituted and the mechanisms of their substitution are different, and in addition there is a possibility of the formation of complexes by the mixture components[71]. For this reason, the results obtained from the competing reactions with C_6F_6 are more reliable[68].

It has already been stated that the high reactivity of the *meta*-position in all the compounds C_6F_5X can be explained by the formation of a σ complex having three fluorine atoms capable of involvement in delocalisation. However, attack on the hexafluorobenzene itself also involves the formation of a σ complex with three stabilising fluorine atoms and yet the partial rate factors for attack in the *meta*-position are greater than unity for all the substrates. Such anomalous activation of the *meta*-position is believed to be a result of the formation of complexes of different stabilities by the precursor of the phenyl radical and the aromatic polyfluoro-substrate[68].

The greater ease of substitution of a hydrogen atom compared with a fluorine atom has been demonstrated for the reactions of C_6F_5H with the phenyl radical[68]. Similar results were obtained for certain other substituted aromatic polyfluoro-compounds containing fluorine and hydrogen atoms in the molecule simultaneously. For example, the interaction of 1,2,4,5-tetrafluorobenzene[72] and 2,3,4,5,6-pentafluorobiphenyl[73] with the pentafluorophenyl radical, generated from C_6F_5I on photolysis or thermal decomposition, leads to the formation in high yields only of products resulting from the substitution of hydrogen atoms: 2,2′,3,3′,4,5,5′,6,6′-nonafluorobiphenyl and three isomeric decafluoroterphenyls (14% of the *o*-isomer, 49.7% of the *m*-isomer, and 36.3% of the *p*-isomer) respectively.

In order to estimate the influence of fluorine atoms on the reactivity of aromatic polyfluoro-compounds in radical reactions, it is necessary to compare the above data for the interaction of hexafluorobenzene and octafluoronaphthalene with benzoyl and pentafluorobenzoyl peroxides with the results of the corresponding reactions of benzene and naphthalene presented in the scheme below (the yields are quoted in mole per mole of the peroxide):





The known increase of the yield of benzoyloxylation products relative to the yield of phenylation products in the case of highly reactive substrates[76] and of the formation of products of the reaction of the peroxide without the involvement of the aromatic substrate when the reactivity of the latter is low[77] may be adopted as a basis for a qualitative comparison. Analysis of all the results presented from this standpoint justifies the assumption that the reactivities of hexafluorobenzene and octafluoronaphthalene in reactions with aroyl peroxides are greatly reduced compared with those of non-fluorinated substrates. Thus, benzoyloxation products are absent in the reaction of hexafluorobenzene with benzoyl peroxide (they are formed in the corresponding reaction of benzene) and considerable amounts of biphenyl are produced. The formation of the products of the conversion of benzoyl peroxide itself (biphenyl and phenyl benzoate) is also observed in the reaction of OFN, although the relative contributions of the benzoyloxylation and phenylation processes remain the same as in the reaction of benzoyl peroxide with naphthalene.

The decrease of the reactivity of aromatic polyfluoro-compounds is characterised quantitatively by the ratio of the rates of phenylation of benzene and hexafluorobenzene found from the competing reactions of the latter with benzoyl peroxide: $k_{C_6F_6}/k_{C_6H_6} = 0.44$.[68] The reduced reactivity of aromatic polyfluoro-compounds may be caused by the influence of the fluorine atoms both in the stage involving the addition of the radical with formation of the σ complex and in the stage where the σ complex is stabilised by the elimination of a fluorine atom. The series based on the relative reactivities of aromatic compounds with respect to electrophilic benzoyloxy-radicals ($C_6H_5OCH_3 > C_6H_5CH_3 > C_6H_6 > C_6H_5Cl > C_6H_5NO_2$)[79,80] shows that electron-accepting substituents in the substrate hinder benzoyloxylation. On the other hand, regardless of the electronic nature, all the substituents facilitate phenylation, as shown by the following series of relative rates of phenylation of benzoyl peroxide[30]: C_6H_6 (1); C_6H_5F (1.03); C_6H_5Cl (1.06); $C_6H_5NO_2$ (2.94); 1,3,5-$C_6H_3Cl_3$ (3.68). Comparison of these two series shows that the influence of fluorine atoms in the substrate on the first stage—the addition of the radical with formation of a σ complex—should be of the opposite types for the phenyl and benzoyloxy-radicals. However, experimental results show that the reactivity of aromatic polyfluoro-compounds is reduced both relative to the electrophilic benzoyloxy-radical and relative to the neutral phenyl radical. The latter fact may be due to the steric shielding of the reaction centre by the *ortho*-fluorine atoms, which prevent attack by phenyl radicals. An example of the influence of steric shielding of the reaction centres by the *ortho*-fluorine atoms on the reactivity is provided by the reduced reactivity of pentafluorobenzaldehyde relative to benzaldehyde in nucleophilic reactions involving the carbonyl group[81].

The influence of fluorine atoms in aromatic substrates on the stage involving the stabilisation of radical σ-complexes reflects the formation of dimerisation products of these complexes in the reactions of hexafluorobenzene and octafluoronaphthalene with benzoyl and pentafluorobenzoyl peroxides. This influence may be associated with the difference between the C–H and C–F bond dissociation energies[55,56], with the increased stability of the fluorinated radical σ complexes, and also with the greater stability of the fluorinated dimers.

As already mentioned, one of the characteristics of the reactions of aromatic polyfluoro-compounds with aroyl peroxides is that, in the reactions of both hexafluorobenzene and octafluoronaphthalene with pentafluorobenzoyl peroxide under mild conditions (80–85°C), products involving the participation of the pentafluorobenzoyloxy-radical are formed preferentially. This may be caused by the influence of fluorine atoms on the reactivity of the radicals, which is manifested by an enhancement of their electrophilic properties.

Kurz and Pellegrini[80] showed that the benzoyloxy-radical is electrophilic and that the introduction of electron-accepting substituents into the peroxide molecule enhances the electrophilic properties of the benzoyloxy-radicals formed on its decomposition. The enhancement of the electrophilic properties of the pentafluorobenzoyloxy-radical can be explained satisfactorily by the overall inductive electron-withdrawing effect of the pentafluorophenyl group, resembling the effect of the 2,4-dinitrophenyl residue[82]. The enhanced electrophilic properties of the pentafluorobenzoyloxy-radical are reflected in a higher degree of α-substitution in the reaction of naphthalene with pentafluorobenzoyl peroxide: the ratio of the α- and β-naphthyl pentafluorobenzoates in this reaction is 10:1,[51] while in the reaction of naphthalene with benzoyl peroxide it is 2.7:1[54] (the α-position in naphthalene is known to be most reactive in electrophilic reactions). The more marked electrophilic properties of the pentafluorobenzoyloxy-radical compared with the benzoyloxy-radical apparently lead to its increased reactivity in reactions with aromatic substrates. On the other hand, the high steady-state concentration of pentafluorobenzoyloxy-radicals, which can also indirectly reflect the influence of fluorine atoms on the reactivity of fluorinated radicals, may play a significant role in the preferential formation of benzoyloxylation products.

Kinetic data for the decomposition of benzoyl and pentafluorobenzoyl peroxides in benzene and hexafluorobenzene (Table 9)[83] show that pentafluorobenzoylperoxide is less resistant to unimolecular thermal decomposition than is benzoyl peroxide, since the rate constant for its decomposition in both benzene and hexafluorobenzene is greater than for the non-fluorinated peroxide. The reduced stability of the fluorinated peroxide may be associated, for example, with the appearance of an additional Coulombic repulsion between the *ortho*-fluorine

atoms in the benzene ring of the peroxide. The possibility of such a field effect has been used by Blomquist and Buselli[84] to account for the higher rate of decomposition of *ortho*-substituted symmetrical peroxides compared with their *meta*- and *para*-analogues. On the other hand, the ease of decomposition of pentafluorobenzoyl peroxide may be a result of the increased stability of the pentafluorobenzoyloxy-radical, which is confirmed by the kinetics of the decomposition of benzoyl and pentafluorobenzoyl peroxides in the absence of solvents[78]. The rate constant for the formation of CO_2 in the decomposition of benzoyl peroxide is greater than in the decomposition of pentafluorobenzoyl peroxide (36.5×10^{-2} and 10.1×10^{-2} min^{-1} respectively), i.e. pentafluorobenzoyloxy-radicals are more resistant to decarboxylation. The higher stability of pentafluorobenzoyloxy-radicals may be caused by the more effective delocalisation of the unpaired electron with participation of the benzene ring. All these factors taken together may promote a higher steady-state concentration of pentafluorobenzoyloxy-radicals.

Table 9. Kinetic parameters of the benzoyl and pentafluorobenzoyl peroxide decomposition reactions in benzene and hexafluorobenzene (80°C; initial peroxide concentration between 0.024 and 0.24 M).[83]

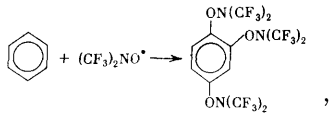
Peroxide	$(C_6H_5COO)_2$		$(C_6F_5COO)_2$	
Substrate	C_6H_6	C_6F_6	C_6H_6	C_6F_6
10^3k, min^{-1}	2.9	1.5	8.6	2.5
E, kcal $mole^{-1}$	30	34	29	31
$\lg A$	16	18	16	17

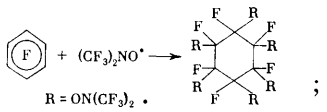
Evidently the pentafluorophenyl radical is also electrophilic, which is clearly illustrated by data for its interaction with substituted benzenes[65,85]. Thus the relative rate of the pentafluorophenylation of chlorobenzene is lower than that of its phenylation (0.72 and 1.06 respectively). However, the ratio of the degree of substitution in the *ortho*- and *para*-positions to the dgree of substitution in the *meta*-position is greater for pentafluorophenylation than for phenylation: $(o-+p-)/m- = 3.9$ and 2.9 respectively. In the reaction of the pentafluorophenyl radical with nitrobenzene, the electrophilic nature of the radical is manifested by an appreciable increase of the degree of substitution in the *meta*-position: $(o-+p-)/m- = 9.2$ ($C_6H_5^{\cdot}$) and $(o-+p-)/m- = 0.87$ ($C_6F_5^{\cdot}$). On reaction with 1,2,4,5-tetrafluorobenzene, the pentafluorophenyl radical generated from pentafluoroiodobenzene on photolysis of thermal decomposition gives a high yield of 2,2',3,3',4,5,5',6,6'-nonafluorobiphenyl, reacting at the site of the maximum electron density, which also indicates the electrophilic nature of the pentafluorophenyl radical[72].

The electrophilic properties of the pentafluorophenyl radical explain the high yield of biphenyls in the corresponding reactions of pentafluorobenzoyl peroxide and other sources of the pentafluorophenyl radical with benzene[75] and its derivatives[45,65,85,86]. On the other hand, the absence of pentafluorobenzene in these reactions and the fairly severe conditions under which the pentafluorophenyl radical reacts with hexafluorobenzene suggest a reduced reactivity of this radical, which may be attributed to the shielding of the radical reaction centre by the *ortho*-fluorine atoms.

IV. OTHER REACTIONS

Hexafluorobenzene reacts with the bis(trifluoromethyl)-nitroxy-radical, combining with two, four, or six $(CF_3)_2NO$ residues, depending on the reaction conditions[87]. Under analogous conditions, the reaction of $(CF_3)_2NO^{\cdot}$ with benzene leads to the formation of the 1,2,4-trisubstituted product only[88]:

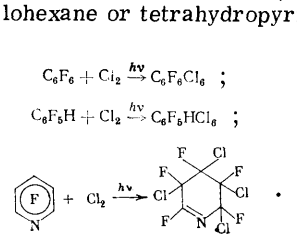




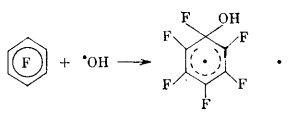
Addition takes place exclusively in the reactions of this radical with other aromatic polyfluoro-compounds. Thus the number of $(CF_3)_2NO$ groups with which the fluoro-compound combines is four for pentafluoropyridine[89], two, four, or six for chloropentafluorobenzene, four for octafluorotoluene, two, four, or six for pentafluorobenzoic acid, four or six for pentafluorobenzaldehyde, two or six for pentafluorophenol, and two, four, or six for pentafluoroaniline[90].

When perfluorodiphenylacetylene reacts with hexafluorodimethylnitrogen oxide, it is possible to identify only decafluorobibenzoyl (in 25% yield), but the unidentified reaction products include compounds containing the $(CF_3)_2NO$ group[91].

When chlorine is allowed to act on hexafluorobenzene[92], pentafluorobenzene[93], or pentafluoropyridine[89] under irradiation, it combines with the substrate, forming the corresponding cyclohexane or tetrahydropyridine derivatives:

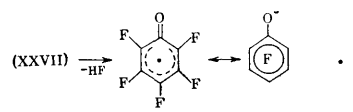


The interaction of fluorinated benzenes (1,2,3,4-$C_6H_2F_4$, C_6F_5H, and C_6F_6) with e_{aq}^- and $^{\cdot}OH$ in aqueous solutions under pulse radiolysis and γ-irradiation[94] leads in the former case to the generation of the pentafluorophenyl radical and other fluorinated radicals with almost quantitative elimination of the fluoride anion: $C_6F_6 + e_{aq}^- \rightarrow C_6F_5^{\cdot} + F^-$, and in the latter case results in the addition of $^{\cdot}OH$ with formation of the σ complex (XXVII):

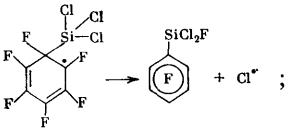


(XXVII)

The σ complex (XXVII) is unstable, since a fluorine atom and the OH group are attached to the same carbon atom, but can be stabilised by the elimination of HF and the formation of a new radical:



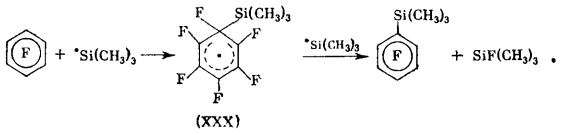
A photochemical interaction of the type of substitution takes place between hexafluorobenzene and trichlorosilane[95]. The reaction results in the formation of dichlorofluoro(pentafluorophenyl)silane (XXIX) as the main product together with *o*-, *m*-, and *p*-disubstituted compounds. It is suggested that the formation of compound (XXIX) is associated with a rearrangement in the σ complex (XXVIII) formed initially followed by the stabilisation of the new σ complex as a result of the elimination of a chlorine atom which initiates the reaction:



(XXVIII) (XXIX)

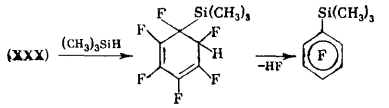
$$Cl^{\cdot} + SiHCl_3 \rightarrow HCl + {}^{\cdot}SiCl_3 .$$

The photochemical reaction between hexafluorobenzene and trimethylsilane proceeds in a somewhat different manner, yielding preferentially pentafluorophenyltrimethylsilane, which indicates the stabilisation of the σ complex (XXX), [analogous to the σ complex (XXVIII)] as a result of the abstraction of a fluorine atom by a second trimethylsilyl radical[95]:



(XXX)

Nor can one exclude the possibility that pentafluorophenyltrimethylsilane is formed in the dehydrofluorination of the adduct (XXXI):



(XXXI)

Irradiation of a solution of C_6F_6 in cyclohexane[96] leads to a fairly complex mixture of products in which it is possible to identify cyclohexylpentafluorobenzene, pentafluorobenzene, decafluorobiphenyl, and a compound with the overall formula $C_{18}H_{22}F_4$, which is most probably dicyclohexyltetrafluorobenzene. The nature of the products shows that a free-radical process takes place in all probability. It is evident that the initial dissociation of hexafluorobenzene into a fluorine atom and a pentafluorophenyl radical is unlikely not only because C_6F_6 is resistant to irradiation in the absence of hydrocarbons but also owing to the high C–F bond energy in C_6F_6.[55] The process probably proceeds via the following mechanism:

$$C_6F_6 \xrightarrow{h\nu} C_6F_6^{*}; \quad C_6F_6^{*} + HR \rightarrow C_6F_6^{\cdot} + HF + R^{\cdot} \rightarrow C_6F_5R;$$

$$2C_6F_5^{\cdot} \rightarrow C_{12}F_{10} \xrightarrow[RH]{h\nu} \text{high-molecular weight products;}$$

$$C_6F_5^{\cdot} + C_6F_6 \rightarrow C_{12}F_{11}^{\cdot} \rightarrow C_{12}F_{10}; \; C_6F_5^{\cdot} + RH \rightarrow C_6F_5H + R^{\cdot}; \; 2R^{\cdot} \rightarrow R_2.$$

A mechanism involving the formation of the pentafluorophenyl radical is postulated for the reaction of C_6F_5I with $Ni(CO)_4$,[97] the main products of which are decafluorobiphenyl, decafluorobenzophenone, and pentafluorobenzene when it is carried out in dimethylformamide. The pentafluorophenyl radical may be formed as a result of the direct reaction of pentafluoroiodobenzene with nickel tetracarbonyl {in the decomposition of the complex $[C_6F_5Ni^{I}(CO)_n]$} or as the product derived from the pentafluorobenzoyl radical formed initially. The following reaction mechanism is most probable:

$$C_6F_5I + Ni(CO)_4 \rightarrow [C_6F_5CONi(I)(CO)_n] + (3-n)\,CO;$$

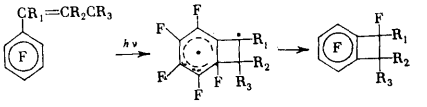
(XXXII)

$$(XXXII) \xrightarrow{-[NiI(CO)_{n+1}]^{\cdot}} C_6F_5^{\cdot}; \; C_6F_5^{\cdot} + RH \rightarrow C_6F_5H + R^{\cdot}; \; 2C_6F_5^{\cdot} \rightarrow C_6F_5C_6F_5;$$

$$C_6F_5^{\cdot} + CO \rightleftarrows C_6F_5CO^{\cdot}; \; C_6F_5CO^{\cdot} + C_6F_5^{\cdot} \rightarrow C_6F_5COC_6F_5.$$

The absence of decafluorobibenzoyl from the reaction products [bibenzoyl is the sole product of the reaction of C_6H_5I with $Ni(CO)_4$] [98] demonstrates a high reactivity of $C_6F_5CO^{\cdot}$, which is present at a low concentration and reacts with the medium before dimerisation. In the analogous reaction with $Ni(CO)_4$, bromopentafluorobenzene is less reactive and hexafluorobenzene is recovered unchanged from the reaction mixture.

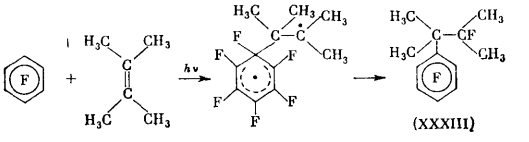
In a study of the gas-phase photolysis of polyfluorinated alkenylbenzenes, they were found to be converted into fluorine-containing benzocyclobutenes with migration of a fluorine atom from the aromatic ring to the side chain. The proposed mechanism of the photochemical rearrangement involves the intermediate formation of biradicals[99]:



(a) $R_1=R_2=R_3=F$; (b) $R_1=R_2=R_3=H$; (c) $R_1=F$, $R_2=R_3=H$; (d) $R_1=CH_3$, $R_2=R_3=H$; (e) $R_1=R_2=H$, $R_3=CH_3$.

The migration of the fluorine atom may occur as a sigmatropic, 2,3-shift concerted with the cyclisation process or following the latter, although the authors[99] do not rule out the possibility of repeated sigmatropic 1,5-shifts of the fluorine atom.

The photolysis of hexafluorobenzene in the presence of 2,3-dimethylbut-2-ene yields mainly compound (XXXIII), the formation of which is probably associated with the migration of a fluorine atom from the ring to the side chain in the intermediate biradical[100]:

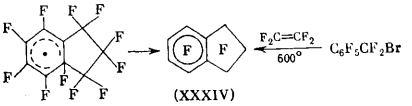


(XXXIII)

The reaction of a number of substituted aromatic polyfluoro-compounds with tetrafluoroethylene at a high temperature, giving rise mainly to the formation of perfluoroindan (XXXIV), which has been described recently[101] is of interest. The mechanism proposed by the authors includes the intermediate formation of the perfluorobenzyl radical (the way in which it is generated in this reaction is still obscure):

$$C_6F_5X \xrightarrow[600-700^{\circ}]{CF_2=CF_2} C_6F_5CF_2^{\cdot} \xrightarrow{CF_2=CF_2} C_6F_5CF_2CF_2CF_2^{\cdot} \rightarrow$$

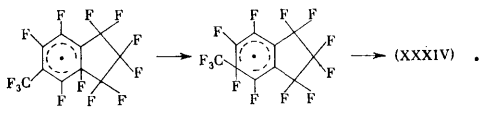
X = OH, SH, OCH_3, NH_2



(XXXIV)

Compound (XXXIV) is the main product also in the reaction of perfluoro-*p*-cresol and perfluoro-*p*-thiocresol with tetrafluoroethylene, which the authors attribute to the isomerisation of the intermediate σ complex (XXXV) to the σ complex (XXXVI) via a sigmatropic 1,3-shift of a fluorine

atom with subsequent elimination of the CF_3 group from the σ complex formed:



The possibility of the involvement of the perfluorobenzyl radical in these reactions has been confirmed by the formation of compound (XXXIV) (again in 80% yield) during the joint pyrolysis of tetrafluoroethylene with perfluorobenzyl bromide, which is a source of $C_6F_5CF_2^{\cdot}$.[101]

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