Journal of Fluorine Chemistry, *41* (1988) 111–162

REVIEW

FLUORINE-CONTAINING CYCLOHEXADIENONES - SYNTHESIS AND PROPERTIES.

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SUMMARY

The Review is devoted to methods of synthesis and chemical properties of polyfluorinated cyclohexadienones - 'proarenes' whose chemistry is the plentiful field of new synthetic ways to fluoroaromatic compounds.

INTRODUCTION

One of the most effective trends in the strategy of synthesis of polyfunctional aromatic compounds is the transformation of the aromatic ring to a highly reactive non-aromatic system, which is afterwards modified to carry out a reverse transformation. A typical example of such system with an inherent potentiality of easy aromatisation is cyclohexadienones. Methods of chemical modification of compounds of this type are closely related with their electron deficient character, and their scope considerably expands if there are electron accepting and nucleophilically mobile substituents, in particular halogen atoms. The presence of the latter is especially important for the fluoroderivatives, as the difficulty of fluorine introduction into organic molecules raises the significance of the approaches based on the transformations of relatively available compounds of this class to the less available ones containing the functional groups that preclude other ways of fluorine introduction.

In our opinion, the fluorine-containing, especially polyfluorinated, cyclohexadienones, owing to their high and varied reactivity, are of great interest from the viewpoint of working out new methods of synthesis of fluoroaromatic compounds. However these potentialities have only been revealed to a small degree. To change this situation, it is necessary to impart a systematic and purposeful character to studies on fluorine-containing cyclohexadienones, which will hopefully be assisted by this review.

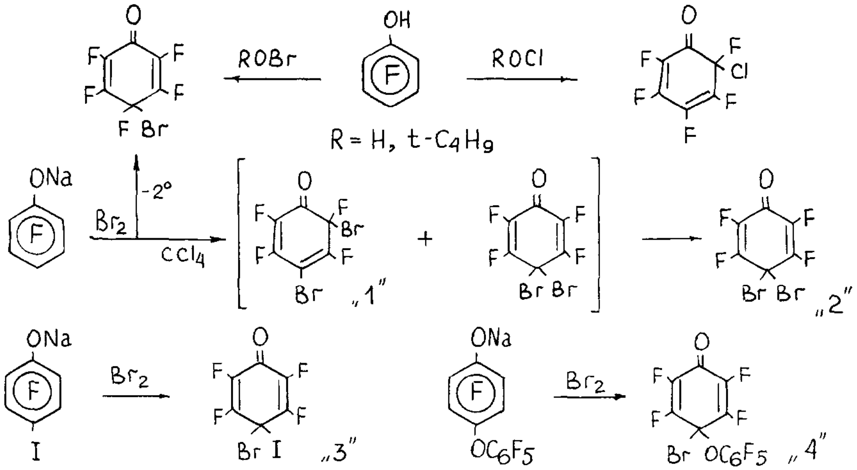
1. METHODS OF SYNTHESIS OF FLUORINE-CONTAINING CYCLOHEXADIENONES.

1.1. Phenol-dienone Rearrangement in the Series of Fluorinated Hydroxyaromatic Compounds.

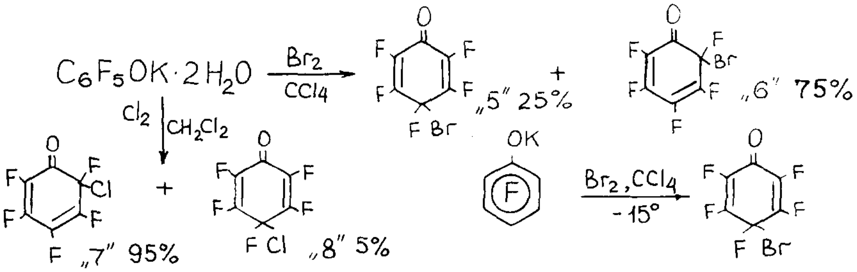
1.1.1. Halogenation of Phenols, Naphthols and Their Alkaline Salts (Including Fluorination).

Polyfluorinated cyclohexadienones containing halogen atoms other than fluorine at a saturated carbon atom, may be synthesized by a general method for the preparation of compounds of this type - halogenation of 2,4,6 - trisubstituted phenols and their salts [1]. Thus treatment of pentafluorophenol and its alkaline salts with tert-butyl hypochlorite leads to polyfluorinated 2,4-cyclohexadien-1-ones, whereas treatment with bromine [2] and tert-butyl hypochlorite - to 2,5-cyclohexadien-1-ones [3]. In the reaction of 2,3,5,6-tetrafluoro-4-bromophenoxides of alkaline metals with bromine in CCl_4, a mixture of 2,4- and 2,5-cyclohexadienones "1" and "2" is formed, and upon its UV irradiation, the 2,4-isomer is quantitatively transformed to the 2,5-isomer [3]. The reaction of bromine with sodium 2,3,5,6-tetrafluoro-4-iodo- or -4-pentafluoro-phenoxyphenoxide gives exclusively 2,5-cyclohexadien-1-ones "3" and "4" respectively [3].

Bromine does not react with pentafluorophenol in CCl_4 at room temperature, nor upon boiling [3], nor (as chlorine) in glacial and aqueous acetic acid, and ether-water mixture at 0 ÷ -10° [4]. With iodine, pentafluorophenol fails to react in CCl_4 even in the presence of iodide ion acceptors [3].

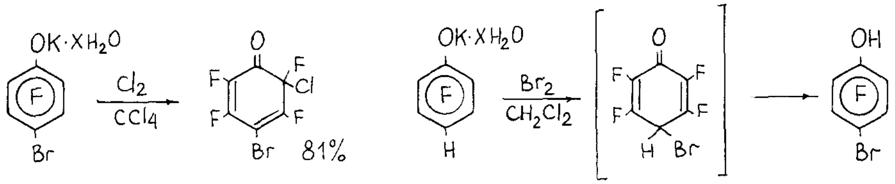


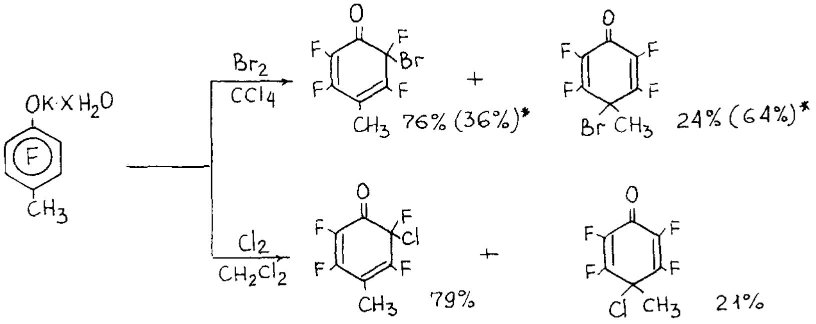
By varying the reagent nature, the alkaline metal cation, the salt hydration degree and the solvent nature, it is possible to selectively change the proportion between 2,4- and 2,5-cyclohexadienones formed in the halogenation reactions of the alkaline salts of polyfluoroaromatic compounds [4]. The reaction of bromine with anhydrous sodium pentafluorophenoxide at -2° [3] or with dihydric sodium pentafluorophenoxide at -15° [4] in CCl_4 yields 2,5-cyclohexadien-1-one "5", which is also formed in the reaction of tert-butyl hypobromite with pentafluorophenol in CCl_4 [3]. In the reaction of bromine with anhydrous potassium pentafluorophenoxide, exlusively ketone "5" is also formed and in the reaction with dihydric potassium pentafluorophenoxide - a mixture of 2,5- and 2,4-dienones "5" and "6" respectively, with the latter predominating [4]. In a similar way, the reaction of chlorine with dihydric potassium pentafluorophenoxide leads to the predominant formation of 2,4-cyclohexadien-1-one "7" (95%) with a small admixture of 2,5-cyclohexadien-1-one "8" (5%).

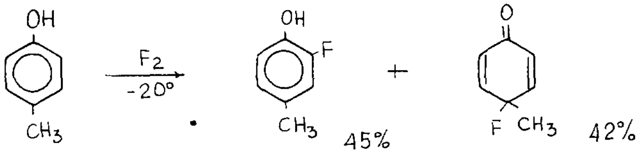


Bromination and chlorination of potassium salts of polyfluorinated phenols in CCl_4 or CH_2Cl_2 is a reasonably general method for the synthesis of polyfluorinated 2,4- and 2,5-cyclohexadien-1-ones [4].

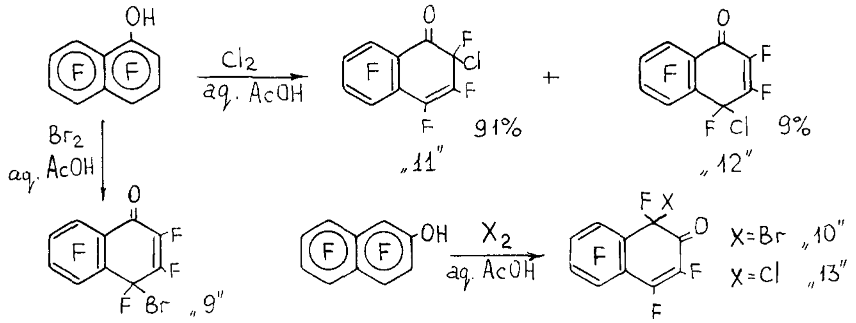
However, fluorine diluted with nitrogen does not react with a suspension of sodium pentafluorophenoxide in carbon tetrachloride at 25° [3]. At the same time, the reaction of fluorine with p-cresol in tetraglyme at -20° leads to the formation of 2,5-cyclohexadienone with fluorine and methyl in the geminal group [5,6]. These reactions are shown in the scheme below:



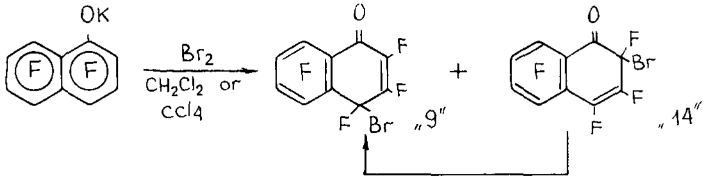


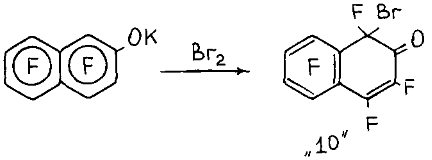


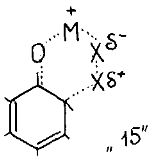
The higher activity of the naphthalene system as compared with the benzene one accounts for the fact that, by contrast with pentafluorophenol, heptafluoro-1- and -2-naphthols smoothly react with halogens. Thus, their reactions with bromine in aqueous acetic acid give 1-oxo-4-bromo-heptafluoro-1,4-dihydronaphthalene "9" and 1-bromo-2-oxo-heptafluoro-1,2-dihydronaphthalene "10" respectively [4]. Treatment of heptafluoro-1-naphthol with chlorine in the same medium leads to a mixture containing 91% of 1-oxo-2-chloro-heptafluoro-1,2-dihydronaphthalene "11" and 9% of 1-oxo-4-chloro-heptafluoro-1,4-dihydronaphthalene "12"; from heptafluoro-2-naphthol, 1-chloro-2-oxo-heptafluoro-1,2-dihydronaphthalene "13" was formed:

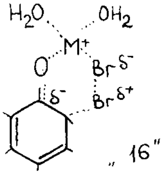


Exclusive formation of paracyclohexadienone "9" in the reaction of bromine with heptafluoro-1-naphthol does not characterise orientation in this reaction because of easy isomerisation of ortho-cyclohexadienone "14" to compound "9". With chlorine, heptafluoro-1-naphthol behaves in a different way than with 2,4-dichloro-1-naphthol whose reaction with chlorine in acetic acid gave the respective para-cyclohexadienone [7]. However, as shown in the same work, the respective ortho-cyclohexadienone is transformed by HCl in the reaction conditions to para-isomer. The ortho-orientation seems to be characteristic for the chlorination of halogenated 1-naphthols in the kinetic control conditions. As shown for cyclohexadienones - the derivatives of 2,3,4-trichloro-1-naphthol, accumulation of halogen atoms inhibits isomerisation of ortho-cyclohexadienones to para-isomers [7].









The possibility to vary the isomeric ratio of cyclohexadienones by varying the solvent nature, the cation and the hydration degree for the heptafluoro-1-naphthol salt is illustrated by the data represented in Tables 1 and 2 [4].

The heptafluoro-2-naphthol potassium salt gives, as expected, only compound "10".

TABLE 1

The Ratio of Cyclohexadienones "9" and "14" Among the Products of the Reaction of Heptafluoro-1-naphthol Potassium Salt with Bromine.

Solvent	Dielectric constant [8]	"9"	"14"
CCl_4	2.23	29	71
CH_2Cl_2*	8.93	32	68
CH_3NO_2	38.57	62	38

* After distillation, a mixture containing 45% of ketone "9" and 55% of ketone "14" was obtained.

TABLE 2

The Ratio of Isomeric Cyclohexadienones Among the Products of Interaction of Heptafluoro-1-naphthol Salts with Chlorine and Bromine in CCl_4.

Salt	Halogen	The product ratio	
		para-CHD	ortho-CHD
$Li.H_2O$	Cl_2	33 "12"	67 "11"
$Li.H_2O$	Br_2	58 "9"	42 "14"
$Na.XH_2O$	Br_2	40 "9"	60 "14"
K	Cl_2	16 "12"	84 "11"
K	Br_2	29 "9"	71 "14"
$K.2H_2O$	Br_2	9 "9"	91 "14"

Formation of cyclohexadienone mixtures in the reactions of the salts of polyfluorinated phenols and naphthols with halogens results from the ambidentate character of anions of the salts (cf.[9]).

There are reasons to believe that in the reactions of polyfluorinated phenol and naphthol salts in the carbon tetrachloride and methylene chloride media there takes place the interaction between molecular halogen and ion pairs or ion aggregates of phenoxide and naphthoxide (cf.[10,11]). The intermediate state of these reactions must be similar in many respects to the intermediate states of the C-alkylation reactions of phenoxides with alkyl halides [12] or fluorinations by perchloryl fluoride [13]. Stabilisation of the leaving anion in the case of poorly solvating solvents results predominantly from the electrostatic interaction with the alkaline metal cation, induced for the ortho-position reactions by the intermediate formation of chelate complexes of type "15" [12]. It is supposed [12] that, generally, the "own" reactivity of the ambidentate anion may not be consistent with the orientation preferable from the viewpoint of chelate complex formation, leading to a competition between these two factors. The reaction of anhydrous potassium pentafluorophenoxide do not seem to produce the 4-coordination required at least for the stability of alkaline metal chelate complexes [14,15,16]. In this case the chelate complexes formation is of no importance, and the reaction pathway is determined by the own tendency of the pentafluorophenoxide anion to the para-position reaction. This tendency may also result from the low steric accessibility of the ortho-position in the anhydrous pentafluorophenoxide ion aggregates. In the case of the dihydric pentafluorophenol potassium salt, the 4-coordinated chelate complex of type "16" is formed, apparently leading to substantial stabilisation of the intermediate state of the reaction in the ortho- position. Similar considerations are applicable to the reactions of heptafluoro-1-naphthol salts with bromine, but here the para-orientation brought about by the 'own' reactivity of the salt anion is possibly not so pronounced as in the case of pentafluorophenoxide. For nitromethane, due to its greater polarity, the role of its reaction with metal cation in stabilisation of the leaving halide anion seems to decrease, the contribution to the general picture of the reactions of 'free' anions or ion pairs with a similar reactivity increasing (cf.[12]).

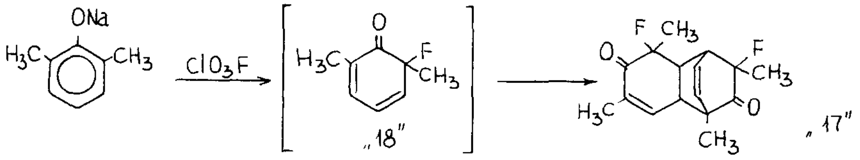
Increased content of 2,5-cyclohexadienone among the products of the reaction of the heptafluoro-1-naphthol salt with bromine on passing from carbon tetrachloride and methylene chloride to nitromethane is obviously called for by a set of these factors.

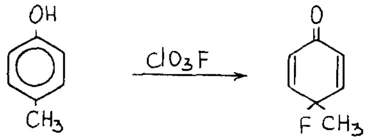
With chlorine, there is a stronger tendency to 2,4-cyclohexadienone formation than with bromine. This may be explained by the smaller polarisability of the chlorine molecule, which is not sensitive to the nature of the solvents in question. Upon chlorination of sodium, potassium, and triethylammonium phenoxides with HOCl and tert-butyl hypochlorite in aqueous medium, the predominant ortho-orientation is also observed, one of the possible reasons for that, according to the authors of [17], being coordination of oxygen of HOCl with the phenoxide ion pair cation, despite the high polarity of the medium.

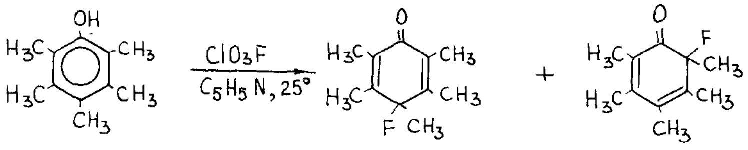
The reaction of perchloryl fluoride with substituted phenols appeared to be a convenient and sufficiently universal method for the synthesis of cyclohexadienones with fluorine at a saturated carbon atom. Para-cresol reacts with perchloryl fluoride in DMF with cooling or at room temperature to give the respective cyclohexadienone [18].

The reaction of 2,6-dimethylphenol with the same reagent in toluene fails to proceed, and in DMF it occurs very slowly to give the 6-fluoro-2,6-dimethyl-2,4-cyclohexadien-1-one dimer "17" in a small yield [13]. Interaction of sodium 2,6-dimethylphenoxide with perchloryl fluoride in hydrocarbons or dioxan [13] also leads to the product of dimerisation of the intermediate cyclohexadienone "18". Formation of the dienone [18] is thought by the authors of [13] to be the result of the electrophilic attack of the ambidentate phenoxide anion by perchloryl fluoride.

Treatment of pentamethylphenol with perchloryl fluoride in pyridine affords a mixture of two dienones 4-fluoro-2,3,4,5,6-pentamethyl-2,5-cyclohexadien-1-one and 6-fluoro-2,3,4,5,6-pentamethyl-2,4-cyclohexadien-1-one, the former being predominant (as shown by PMR, the ratio is 3:1) [19].

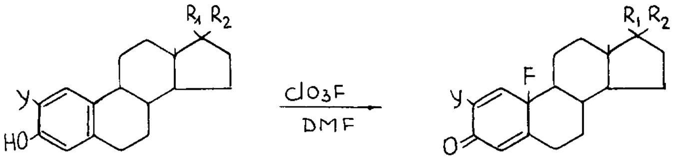


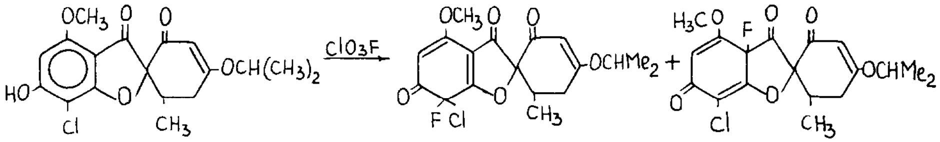




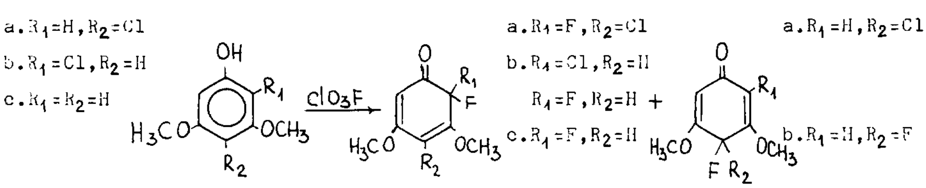
Using estrone steroid phenols as an example, the authors of [20,21] have shown the possibility to obtain in this way 10-fluoro-1,4-estradien-3-ones as a result of angular fluorination of para-position with respect to the phenol function.

The reaction of 4-isopropyl ether of norgriseofulvinic acid with perchloryl fluoride gave a mixture of 2,4- and 2,5-dienones containing fluorine as a geminal substituent [22,23]:





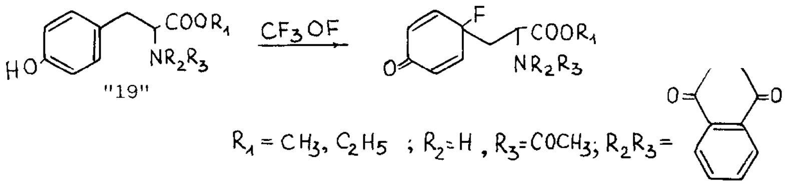
When the starting phenol contains unsubstituted ortho- and para-positions, there may proceed its preliminary fluorination of hydrogen substitution type, with subsequent ipso-fluorination to give cyclohexadienones containing the geminal fluorine atoms. Thus treatment of 3,5-dimethoxyphenol with perchloryl fluoride in pyridine at 20° leads to two isomeric dienones - 6,6-difluoro-3,5-dimethoxy-2,4-cyclohexadien-1-one and 4,4-difluoro-3,5-dimethoxy-2,5-cyclohexadien-1-one [24,25]:



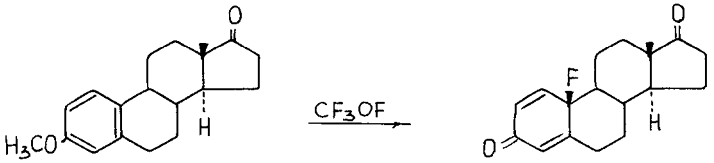
As shown by the paper chromotography analysis of the reaction mixtures, the possible intermediate products in this reaction are 6- and 4-fluorodimethoxyphenols respectively. Interaction of 6-chloro-3,5-dimethoxyphenol with ClO_3F yields a mixture of 6-chloro-6-fluoro-3,5-dimethoxy-2,4-cyclohexadien-1-one and 2,2-difluoro-6-chloro-3,5-dimethoxy-2,5-cyclohexadien-1-one, whereas 4-chloro-3,5-dimethoxyphenol in the same conditions is transformed to a mixture of two dienones, with 4-chloro-4-fluoro-3,5-dimethoxy-2,5-cyclohexadien-1-one predominating.

These examples demonstrate that formation of the -CFX- groups (X=F,Cl), apparently characterised by a high strength of the C-F bond (cf.[26]), is an effective driving force for the reactions of phenols with perchloryl fluoride.

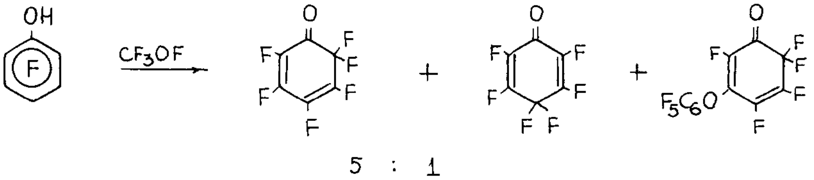
Fluoroxytrifluoromethane reacts with alkylphenols and their ethers in the same way as perchloryl fluoride. [27]. Thus, when CF_3OF reacts with the para-substituted phenol "19", there takes place ipso-fluorination at the para-position with the phenol-dienone rearrangement [27]. From 2,6-dimethylphenol, the 6-fluoro-2,6-dimethyl-2,4-cyclohexadien-1-one dimer "17" is formed; from estrone methyl ether, 10-fluoro-19-norandrosta-1,4-diene-3,17-dione:



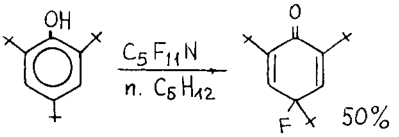
"19"

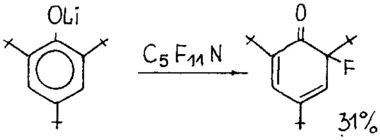


Pentafluorophenol treated with fluoroxytrifluoromethane, gives a mixture of polyfluorinated 2,4- and 2,5-cyclohexadien-1-ones (5:1) [29]:



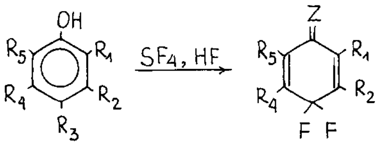
Another reagent for ortho- and para-fluorination of phenols leading to cyclohexadienones is perfluoropiperidine [30]. For example, the fluorine-containing 2,5-cyclohexadien-1-one is formed from 2,4,6-tris(tert.butyl)phenol; and from its lithium salt, 2,4-cyclohexadienone.





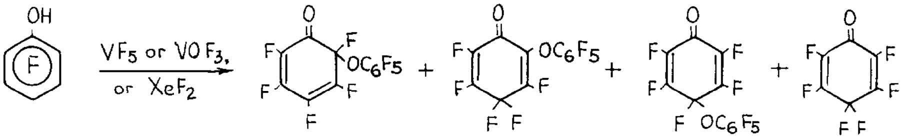
Synthesis of a number of fluorine-containing cyclohexadienones has been claimed [31] by oxidative fluorination of phenols with sulphur tetrafluoride and HF.

In a similar way proceeds oxidation of pentafluorophenol and pentafluoroanisole by vanadium fluorides and xenon difluoride [32], as well as of 2-naphthol, and its ethers, and 5-hydroxybenzo-[C]-phenanthrene by cesium fluoroxysulphate [5].

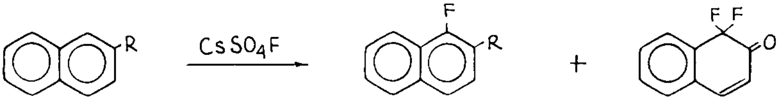


R_1=Cl,Br,F
R_2=H,Cl,F
R_3=H,Cl,F
R_4=Cl,Br,F
R_5=H,Cl,Br,F

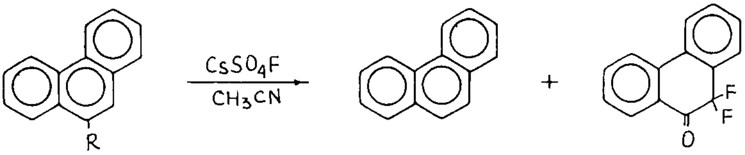
Z=O,F



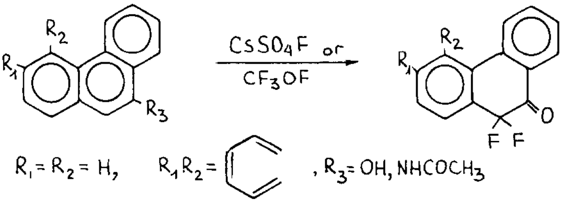
Similar transformations leading to cyclohexadienones take place upon the reactions of CF_3OF and cesium fluoroxysulphate with naphthalene, phenanthrene and benzophenanthrene containing electron-donating substituents [33,34,35]:



R= H, OH, OCH_3, OC_2H_5, OC_3H_7, $NHCOCH_3$

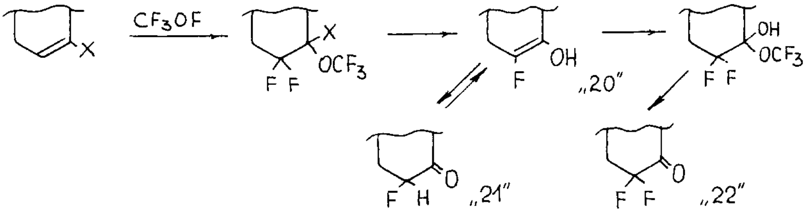


R=H(53%), $NHCOCH_3$(22%)



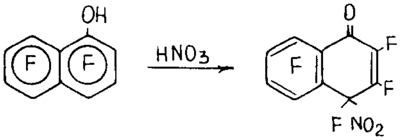
R_1=R_2= H, R_1R_2= , R_3= OH, $NHCOCH_3$

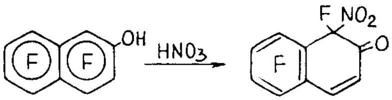
The scheme of oxidation by fluoroxytrifluoromethane suggested by the authors of [34,35] involves addition of fluoroxytrifluoromethane at the double bond. In case of significant steric effects, the reaction is completed by the formation of ketone "21". In the absence of steric effects there occurs addition of CF_3OF at the double bond of fluorophenol "20" and transformation of the addition products to 1,1-difluoroketone "22".



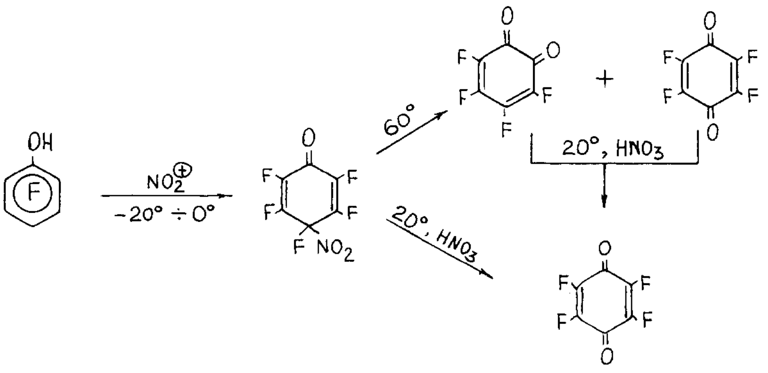
1.1.2. Nitration of Polyfluorinated Phenols and Naphthols.

Heptafluoro-1- and -2-naphthols [36,37] react in mild conditions with concentrated nitric acid giving the respective derivatives of polyfluorinated nitrocyclohexadienones in good yields:



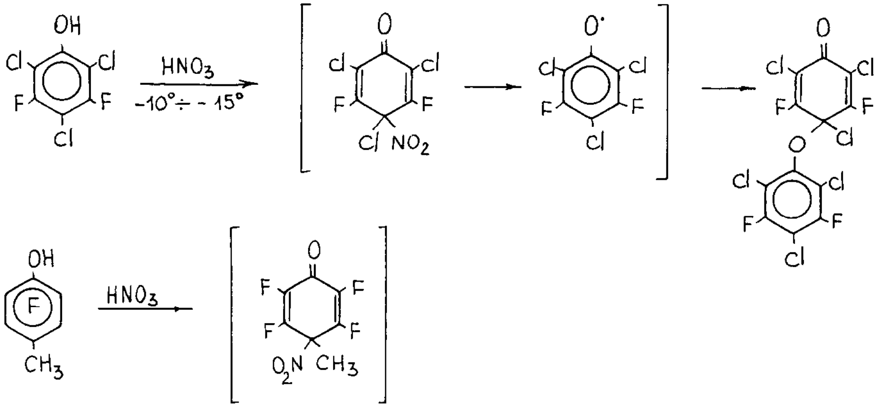


In similar conditions pentafluorophenol is transformed to fluoranil [38], the product of the intermediate nitrocyclohexadienone (quinnitrole), as shown in [39].



The reaction of nitric acid with 2,4,6-trichloro-3,5-difluorophenol fails to yield the respective nitrocyclohexadienone - the suggested primary product of the reaction [40], as it decomposes to form the phenoxy radical which dimerises giving 4-(2,4,6-trichloro-3,5-difluorophenoxy)-2,4,6-trichloro-3,5-difluoro-2,5-cyclohexadien-1-one.

Because of low stability it was impossible to isolate 4-nitro-4-methyltetrafluoro-2,5-cyclohexadien-1-one formed in the reaction of nitric acid with tetrafluoro-para-cresol at -30 -20° and recorded by ^{19}FNMR [41].

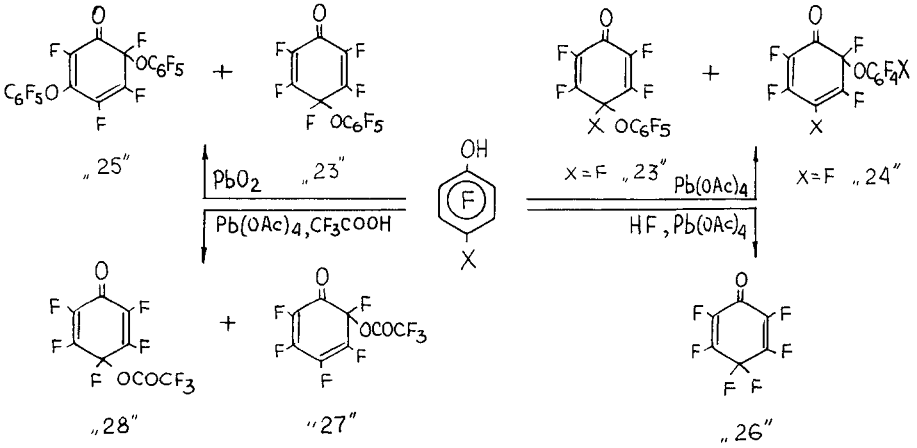


1.1.3. Oxidation of Oxyaromatic Compounds.

Interaction of oxyaromatic compounds, containing no fluorine atoms, with tetravalent lead compounds leads as a rule to substituted cyclohexadienones in a mixture with quinones and diphenyl derivatives [42,43,44]. 4-Fluorophenol is oxidised by lead dioxide forming a complex mixture of products, from which 4-fluoro-6-methyl-6-acetoxy-2,4-cyclohexadien-1-one was isolated [45].

In contrast to this, for polyfluorinated oxyaromatic compounds these reactions are a convenient preparative method for the synthesis of fluorinated cyclohexadienones. Depending on the reaction mechanism - radical or ionic - there may formed respectively either the cyclohexadienones that are the fluorinated aroxy radical dimers or the cyclohexadienones containing a residue of the acid used.

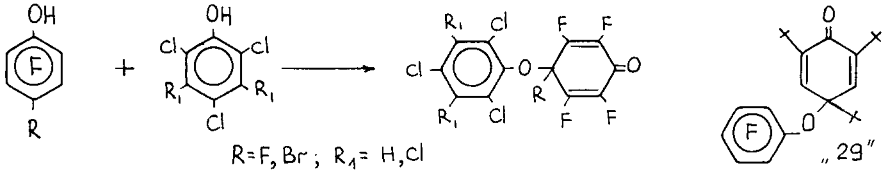
Interaction of pentafluorophenol [46] and 4-X-substituted tetrafluorophenols [47] with lead tetraacetate at room temperature in inert solvents proceeds by the radical mechanism. The main route of the reaction is formation of substituted 2,4-cyclohexadien-1-ones - the dimers of the respective phenoxy radicals. If the phenol contains at position 4 a substituent other than fluorine, this route becomes the single route of the reaction:



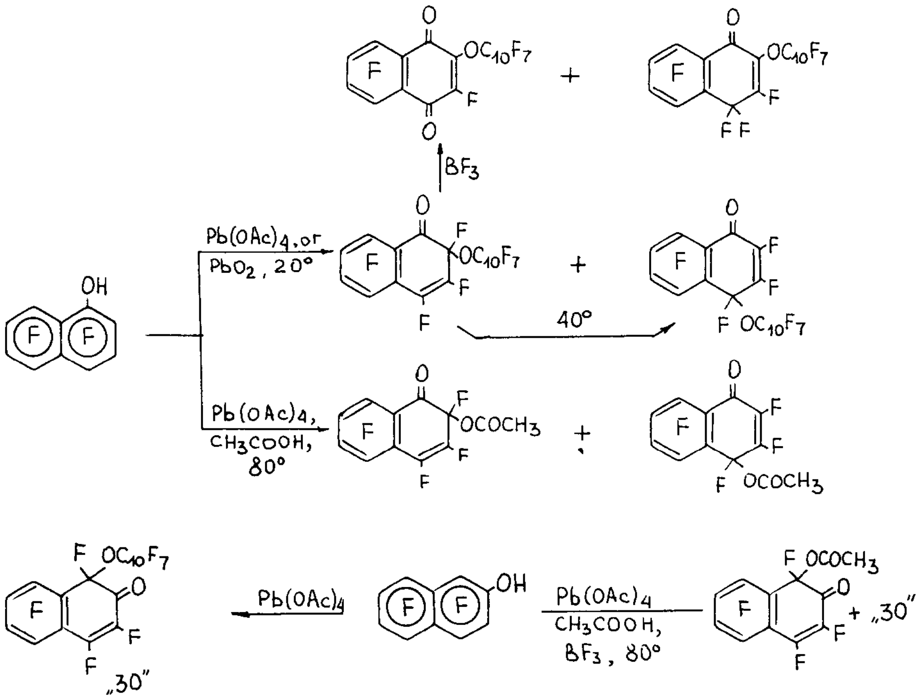
Pentafluorophenol is transformed by lead dioxide, an oxidant most often used to generate phenoxy radicals, to perfluoro-4-phenoxy-2,5-cyclohexadien-1-one "23" [46] and the product of substitution of the pentafluorophenoxy group for the fluorine atom at position 3 of perfluoro-6-phenoxy-2,4-cyclohexadien-1-one "24" - compound "25", which was earlier [48] assigned, without sufficient reason, the structure of perfluoro-2-(4-phenoxyphenoxy)-2,5-cyclohexadien-1-one. If oxidation of perfluorophenol by lead tetraacetate is conducted in anhydrous hydrogen fluoride, the main product is perfluoro-2,5-cyclohexadien-1-one "26" [49]. The absence of the pentafluorophenoxy radical dimers - cyclohexadienones "23" and "24" - among the products of that reaction may indicate the ionic mechanism of oxidation of pentafluorophenol, since, as shown in [50], the dimer "23" is stable in hydrogen fluoride, and its isomer "24" undergoes rearrangement with transition of both the fluorine atom and pentafluorophenoxyl to form respectively perfluoro-2-phenoxy-2,5-cyclohexadien 1-one and dimer "23". When trifluoroacetic acid is used, pentafluorophenol is oxidised by lead tetraacetate to isomeric tetrafluorobenzoquinones [49], whose precursors seem to be 6-trifluoroacetoxy-pentafluoro-2,4-cyclohexadien-1-one "27" and 4-trifluoroacetoxy-pentafluoro-2,5-cyclohexadien-1-one "28", both extremely sensitive to air moisture, which makes their isolation difficult.

Oxidation by lead dioxide of pentafluorophenol or 4-bromotetrafluorophenol together with pentachloro- or 2,4,6-trichlorophenol leads to the products of recombination of two different phenoxy radicals with formation of the cyclohexadienone fragment from the polyfluorinated radical [40,51].

In contrast to this, the simultaneous oxidation of 2,4,6-tris(tert.butyl)phenol and pentafluorophenol yields cyclohexadienone "29", in which the fluorinated part is the aromatic moiety [51].

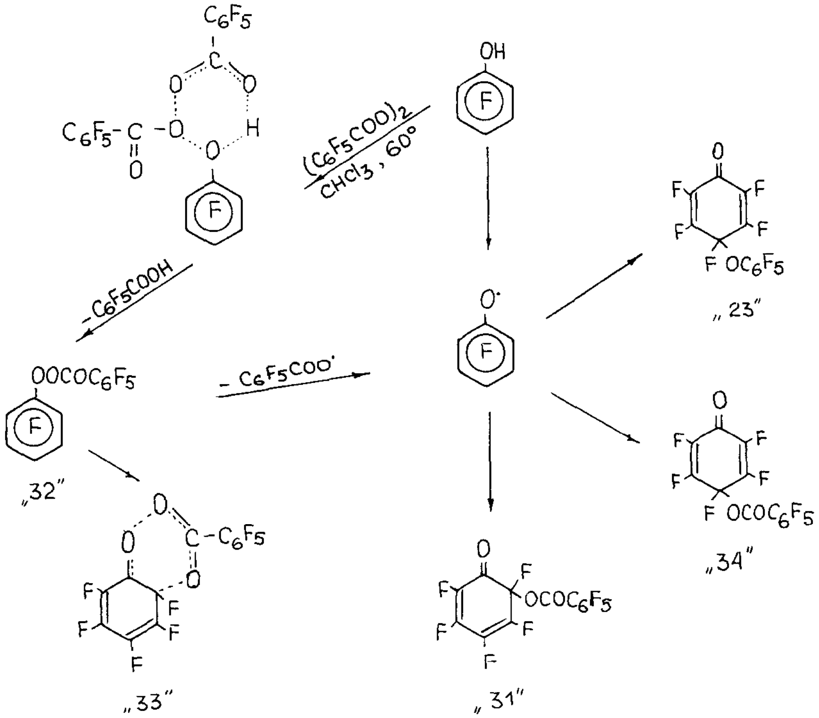


Using the reactions of heptafluoro-1- and -2-naphthols with tetravalent lead compounds as an example, the authors of [52] have shown the possibility to make the oxidation process follow the radical or ionic route by varying the reaction conditions:



The radical route is followed if the reaction is conducted at low temperature or in the inert non-polar solvents; for the ionic route, the increased temperature, polar solvent and acid catalyst (BF_3) are required.

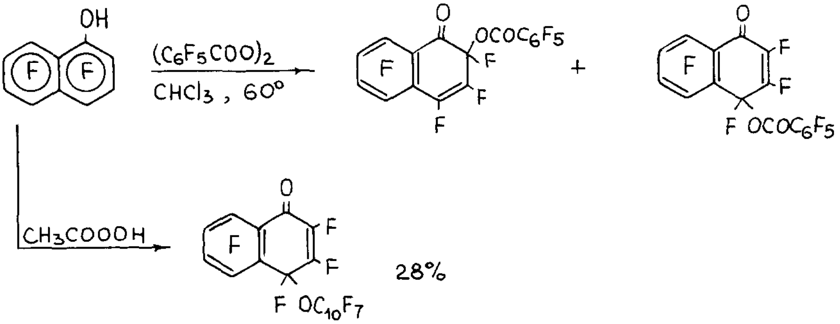
Interaction of pentafluorophenol with pentafluorobenzoyl peroxide leads to the formation of polyfluorinated 2,4- and 2,5-cyclohexadien-1-ones, containing the pentafluorobenzoyloxy group as one of the geminal substituents [53].

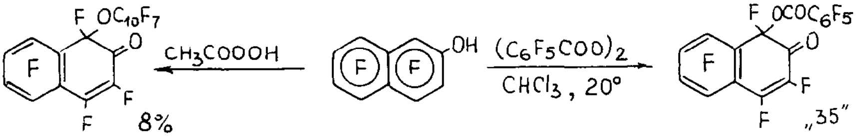


The presence of the pentafluorophenoxy radical dimer "23" among the products of this reaction suggests that the pentafluorobenzoyloxy radical formed as a result of decomposition of pentafluorobenzoyl peroxide removes the hydrogen atom from pentafluorophenol, and further dimerisation of the pentafluorophenoxy radical and its recombination with the pentafluorobenzoyloxy radical leads to the above products. The predominant formation of perfluoro-6-benzoyloxy-2,4-cyclohexadien-1-one "31" is a serious indication to the possible significant contribution of another route – formation of perbenzoate "32", which is further isomerised, apparently by analogy with the Claisen rearrangement, via the intermediate cyclic state "33" to give the main reaction product – perfluoro-6-benzoyloxy-2,4-cyclohexadien-1-one "31".

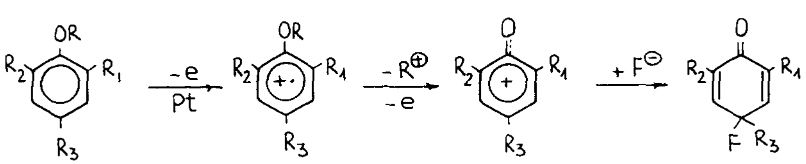
In a similar way, the reaction of pentafluorobenzoyl peroxide with heptafluoro-1-naphthol leads to perfluoro-1-oxo-2-benzoyloxy-1,2-dihydronaphthalene and perfluoro 1-oxo-4-benzoyloxy-1,4-dihydronaphthalene with the former predominating [54], whereas from heptafluoro-2-naphthol, only perfluoro-2-oxo-1 benzoyloxy-1,2-dihydronapthalene "35" is formed [54].

Treatment of heptafluoronaphthols with such an oxidant as acetic peracid yields, in addition to other products, polyfluorinated benzocyclohexadienones (oxodihydronaphthalenes) containing fluorine and the naphthoxy group in the geminal mode [55].





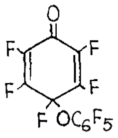
I.L.Knunyants and I.N.Rozhkov have shown the electrochemical oxidation of the ethers of p-fluorophenol or 2,4,6-tris(tert.butylphenol) in the acetonitrile medium in the presence of $Et_4NF.3HF$ to afford 2,5-cyclohexadien-1-ones containing the geminal fluorines, in satisfactory yields [55,57,58]. A mechanism involving the sequential oxidation of phenol to the radical cation, phenoxy cation, and addition of the fluoride ion to the latter, has been suggested:



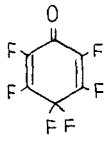
R=H, $R_1=R_2=R_3=C(CH_3)_3$; R=CH_3,C_2H_5, $R_1=R_2=H$, $R_3=F$

The anodic oxidation of unhindered phenols (phenol, p-fluorophenol) in similar conditions does not lead to cyclohexadienones.

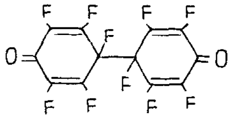
The electrochemical oxidation of pentafluorophenol in the HF medium in the presence of antimony pentafluoride proceeds in a more complex way: apart from perfluoro-2,5-cyclohexadien-1-one "26" (44%), the pentafluorophenoxy radical dimer "23" is formed (56%). In the presence of KF, in addition to these ("26"-56%, "25"-24%), the reaction gives a compound (20%) for which there has unreasonably been suggested the structure "36" of the pentafluorophenoxy radical C-C dimer [59].



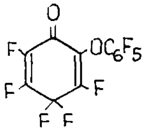
"23"



"26"



"36"

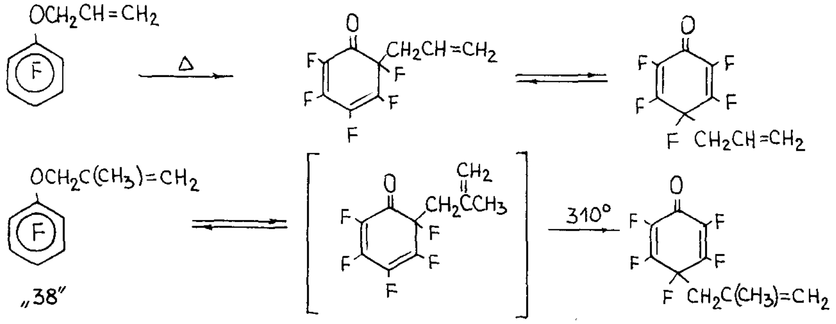


"37"

As shown in [49], the mass-spectrum of this compound given by the authors of [59], corresponds more to the structure of perfluoro-2-phenoxy-2,5-cyclohexadien-1-one "37" - the product of the HF-catalysed isomerisation of the pentafluorophenoxy radical C_2-O dimer "24".

1.1.4. Rearrangements of Ethers of Polyfluorinated Hydroxyaromatic Compounds.

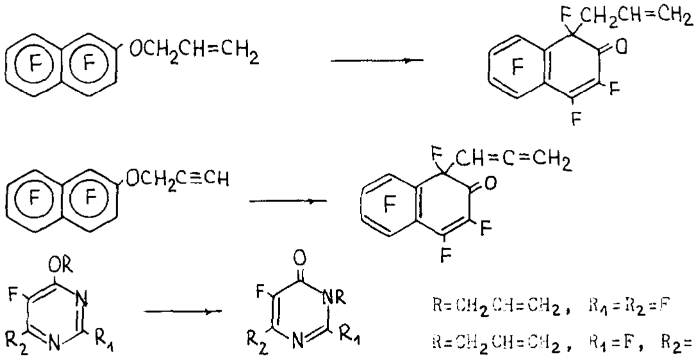
The thermal rearrangement of phenylallyl ethers to isomeric 2-allylphenols is known to proceed via the intermediate formation of cyclohexadienones [1]. For the non-fluorinated compounds, literature reports only one case [60] of formation of the stable cyclohexadienone as a result of the Claisen rearrangement of 1-allyl-2-allylhydroxynaphthalene. In the series of polyfluorinated phenylallyl ethers, formation of cyclohexadienones is a typical result of thermal transformations, as shown in the case of the allyl ether of pentafluorophenol [61,62] and 2-methyl-2-propenyl ether of pentafluorophenol "38" [63]:



„38"

Likewise, from the allyl [64] and propargyl [65] ethers of heptafluoro-2-naphthol boiled in xylene, the Claisen rearrangement products are formed.

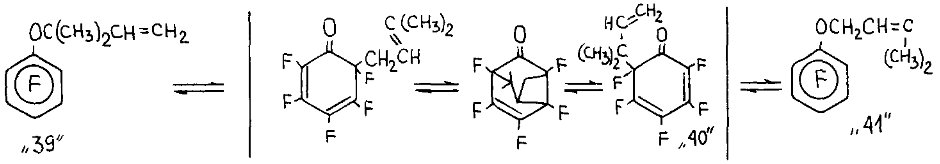
The thermolysis of the allyl ethers of polyfluorinated oxypyridines [65] also gave the products indicating the intermediate formation of the heterocyclic analogues of cyclohexadienones (for details see Section 2.5). In the same conditions the allyl ethers of fluorine-containing pyrimidines were transformed to cyclohexadienone azoanalogues [57].



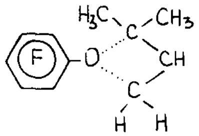
$R=CH_2CH=CH_2$, $R_1=R_2=F$

$R=CH_2CH=CH_2$, $R_1=F$, $R_2=H,OCH_3$

By contrast with ether "38", the 1,1-dimethyl-2-propenyl ether of pentafluorophenol "39" undergoes transformation to the 3,3-dimethyl-2-propenyl ether of pentafluorophenol "40" already at room temperature. This reaction may be represented as a series of the Claisen rearrangement, intramolecular Diels-Alder reaction and splitting of the adduct which is transformed by the reverse Claisen rearrangement to ether "40" [53]:



The fact that the reaction does not give the products corresponding to the cope rearrangement (2,5-dienones) does not preclude other mechanisms of formation of ether "40" from ether "39", for example, the homolytic decomposition and subsequent recombination or any accordant process with the intermediate state of type "42".

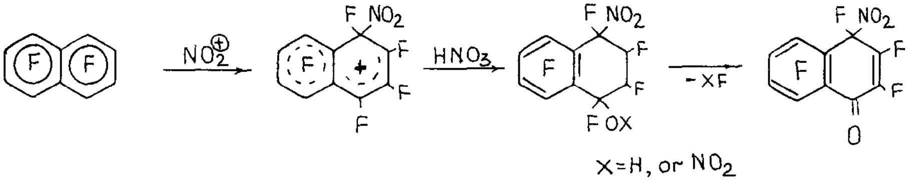


„42"

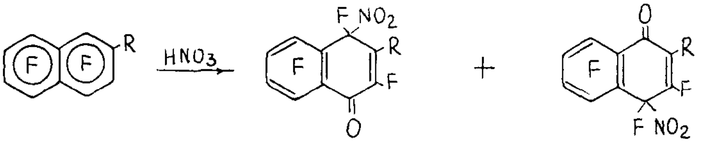
1.2. Electrophilic and Radical ipso-Addition Reactions in the Series of Polyfluoroaromatic Compounds

1.2.1. Reactions with Nitrating Agents

A universal method for the synthesis of polyfluorinated nitrocyclohexadienones is the electrophilic ipso-addition of nitric acid to the multinuclear polyfluoroaromatic compounds first realised in the case of octafluoronaphthalene [35]:

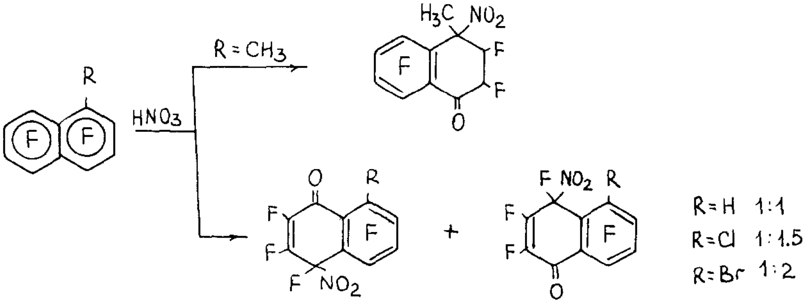


In accordance with the mechanism suggested for this reaction, the structure of the resulting cyclohexadienone is determined by the orientation of the addition of electrophile-nitronium cation, depending on the nature of the aromatic system, the number and position of fluorine atoms and the character of other substituents (in the case of the hydroxy group the reaction proceeds as a phenol-dienone rearrangement, see Section 1.1.2). Thus 2-H- and 2-methylheptafluoronaphthalenes are transformed to the products corresponding to the predominant attack of the substrate at position 4 [68,69].

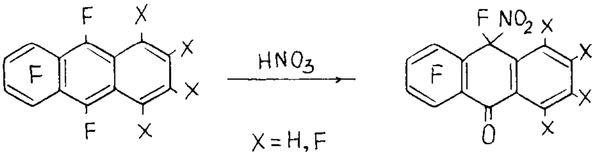


R=H, CH_3 R=CH_3(25%) R=CH_3(75%); R=H(100%)

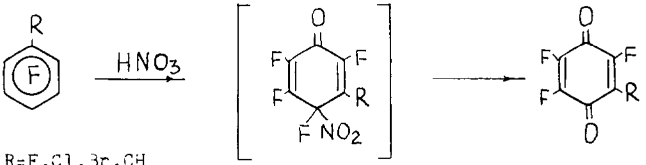
Treatment of 1-X-heptafluoronaphthalenes with HNO_3 may lead, depending on the nature of substituent X, to nitrocyclohexadienones corresponding to the attack by the nitronium cation of either position 1 (X=CH_3) [70] or positions 5 and 8 (X=H,Cl,Br) (in the former case along with small amounts of 1-nitroheptafluoronaphthalene) [71,72]:



The polyfluorinated anthracene derivatives with fluorines at positions 9 and 10, treated with nitric acid, undergo similar transformations corresponding to the attack of just these positions even in the case when one of the side rings is unsubstituted [73]:



Polyfluorinated benzene derivatives except the hydroxy compounds (see Section 1.1.2) react with nitric acid only with heating in view of their relatively low reactivity, which excludes formation of thermally unstable polyfluorinated nitrocyclohexadienones leading to their decomposition products-- quinones [38,68]:



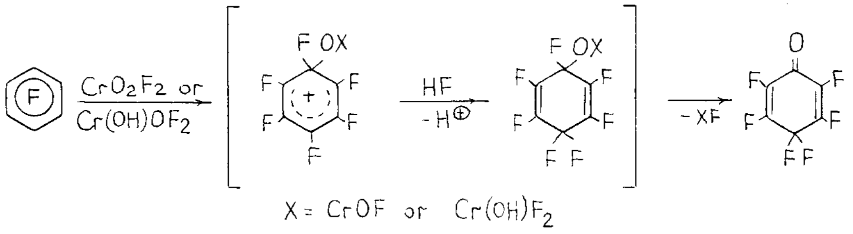
$R=F,Cl,Br,CH_3$

It is interesting that in certain conditions (HNO_3 in oleum) a similar transformation takes place for 1,2,4,5-tetrafluorobenzene, despite the presence of unsubstituted positions and, accordingly, the potentiality of substitution of hydrogen by the nitro group [71] (cf.[75]).

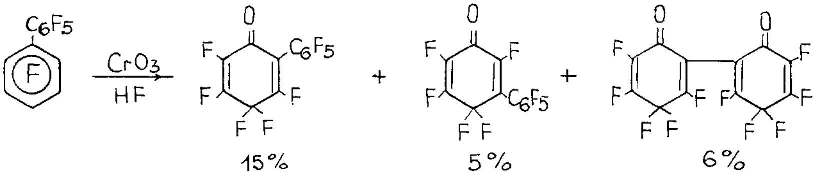
Rationalisation of the data presented in this Section allows to formulate an approach to the synthesis of polyfluorinated cyclohexadienones involving the electrophilic attack of polyfluoroaromatic compounds with subsequent trapping of oxygen-containing nucleophile by the resulting arenonium ion. Development of this approach led to a synthesis of cyclohexadienones by the hydrolysis of stable polyfluorinated arenonium ions generated under the specific conditions of stable polyfluorinated arenonium ions (see Section 1.2.3).

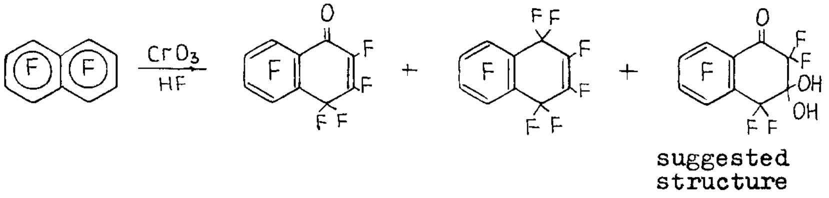
1.2.2. Reaction with CrO_3 in HF

Consideration of the reaction mechanisms described in the preceding Section leads to a conclusion about the possibility of cyclohexadienone formation from polyfluoroaromatic compounds by a route involving the introduction of oxygen to form carbonyl at the first stage, which is achieved by using an oxygen-containing reagent - electrophile or free radical. This was first realised in the case of the reaction of polyfluoroaromatic compounds with CrO_3 in HF [75]. In view of the nature of electrophilic species formed in this system, transformation of hexafluorobenzene to perfluoro-2,5-cyclohexadien-1-one may be represented by the scheme:



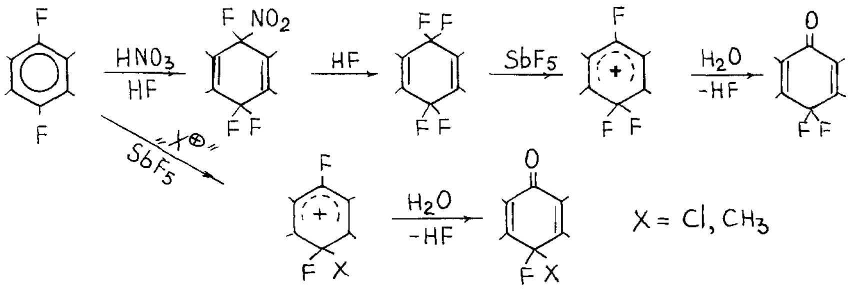
Similar transformations but with formation of product mixtures occur for the perfluorinated biphenyl and naphthalene [76]:



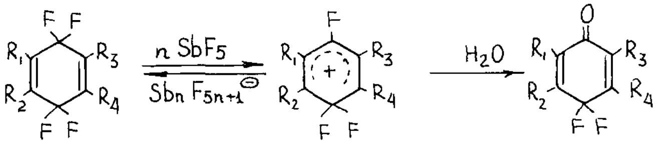


1.2.3. Hydrolysis of Stable Polyfluorinated Arenonium Ions

Using antimony pentafluoride and its SO_2 or SO_2FCl solutions as the system possessing low nucleophilicity and thus providing the increased stability of carbocations allowed to develop methods of generation of stable polyfluorinated arenonium ions [77], whose hydrolysis is quite a general approach to the synthesis of polyfluorinated cyclohexadienones. The substrates are the polyfluorinated aromatic compounds that may be transformed to stable arenonium ions by two routes: either by a sequence involving nitrofluorination, substitution of the nitrogroup by fluorine [78] and the reaction of the polyfluorinated dihydroaromatic compound with SbF_5, or by the direct electrophilic attack in the presence of SbF_5:

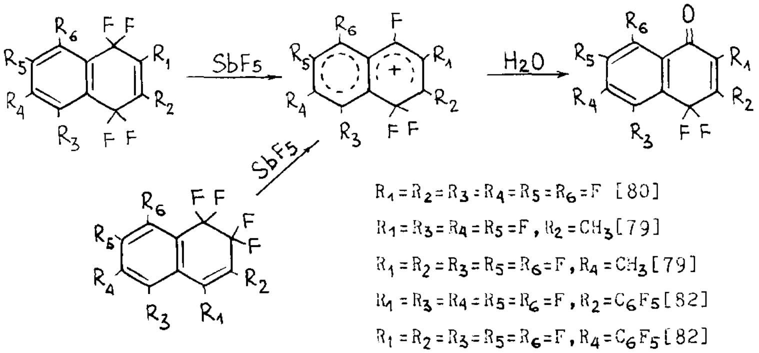


The first route affords cyclohexadienones with two fluorine atoms at the sp$_3$-hybrid carbon atom and substituent other than fluorine in the unsaturated moiety [79,80,81,82,83,84]:



$R_1=R_2=R_3=R_4=F$[80]; $R_1=R_2=R_3=R_4=Cl$[80]

$R_1=R_2=R_3=F$, $R_4=CH_3$[79]; $R_1=R_2=R_3=F$, $R_4=C_6F_5$[82]



$R_1=R_2=R_3=R_4=R_5=R_6=F$ [80]

$R_1=R_3=R_4=R_5=F$, $R_2=CH_3$[79]

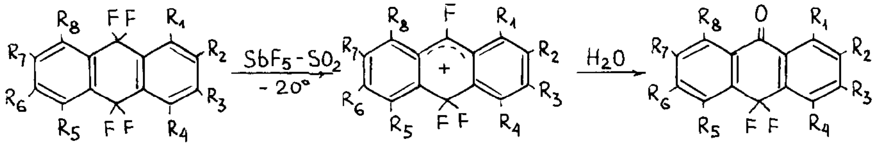
$R_1=R_2=R_3=R_5=R_6=F$, $R_4=CH_3$[79]

$R_1=R_3=R_4=R_5=R_6=F$, $R_2=C_6F_5$[82]

$R_1=R_2=R_3=R_5=R_6=F$, $R_4=C_6F_5$[82]

$R_5=H$, $R_1=R_2=R_4=R_6=F$, $R_3=C_6F_5$[83]

$R_1=R_2=R_4=R_5=R_6=F$, $R_3=C_6F_5$[83]

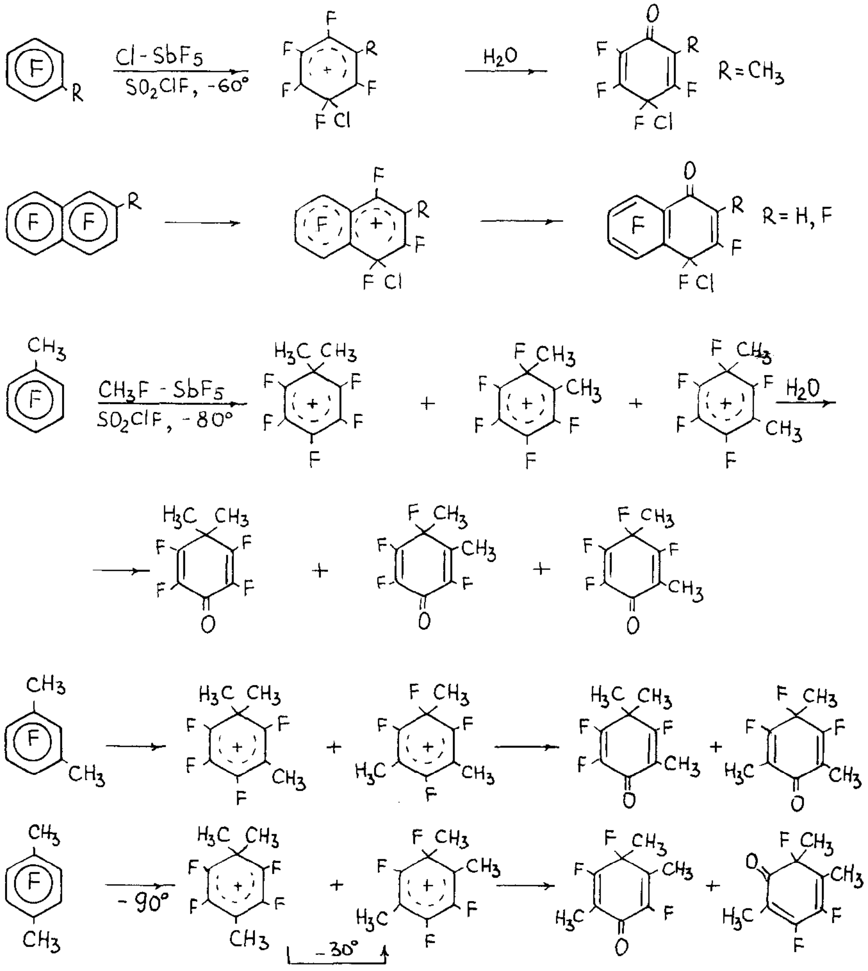


$R_2=R_3=R_4=R_5=R_6=R_7=R_8=H$, $R_1=Cl,Br$

$R_1=R_3=R_4=R_5=R_6=R_7=R_8=H$, $R_2=Cl,Br,F$

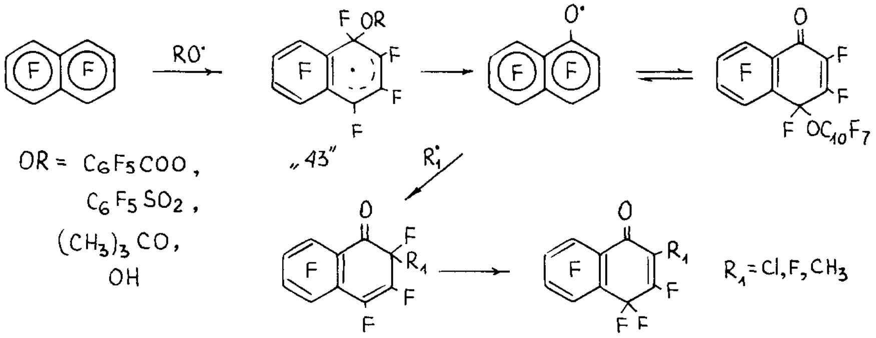
$R_1=R_5=Cl$, $R_2=R_3=R_4=R_6=R_7=R_8=H$; $R_1=R_8=Cl$, $R_2=R_3=R_4=R_5=R_6=R_7=H$
$R_1=R_4=F$, $R_2=R_3=R_5=R_6=R_7=R_8=H$
$R_1=R_2=R_4=F$, $R_3=R_5=R_6=R_7=R_8=H$
$R_1=R_2=R_3=R_4=F$, $R_5=R_6=R_7=R_8=H$ [81,84]

The second route opens up wider possibilities, as the direct electrophilic attack of polyfluoroaromatic compounds results in the generation of arenonium ions containing substituents other than fluorine at the sp^3-hybrid carbon atom, which may be isomerised to form ions of the same type but containing those substituents in the unsaturated moiety. Hydrolysis of both ions leads to polyfluorinated cyclohexadienones with similar structural characteristics [85,86,87]:



1.2.4. Reactions of Polyfluoroaromatic Compounds with Oxygen-containing Radicals

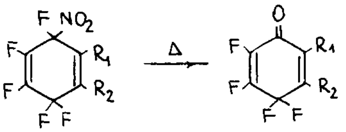
Polyfluoroaromatic compounds may be transformed to cyclohexadienones as a result of the addition of oxygen-containing radicals. Thus the reactions of octafluoronaphthalene with pentafluorobenzoyl [88] and tert.butyl peroxides, and with pentafluorobenzenesulphonyl halide in the presence of copper and its salts [89] lead to the derivatives of fluorine-containing oxodihydronaphthalenes. The basic transformation of the scheme suggested for these reactions is decomposition of the radical-attack intermediate - cyclohexadienyl radical of type "43" - to the heptafluoronaphthoxyl radical, whose recombination with the free radicals available in the system leads to fluorine-containing cyclohexadienones:



1.3. Transformations of the Derivatives of Dihydroaromatic Compounds

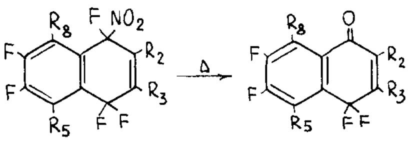
1.3.1. Thermal Transformation of Nitrocompounds

A general method for the synthesis of polyfluorinated cyclohexadienones is the thermolysis of cyclohexadienones containing the fluorine atom and the nitrogroup as the geminal substituents [68,90]:

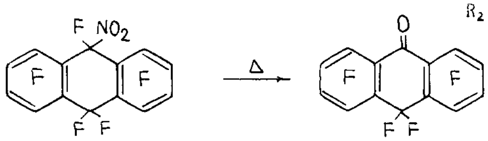


R_1=F, R_2=H,CH_3Cl,Br,F
R_1=Cl, R_2=F
R_1=Br, R_2=F

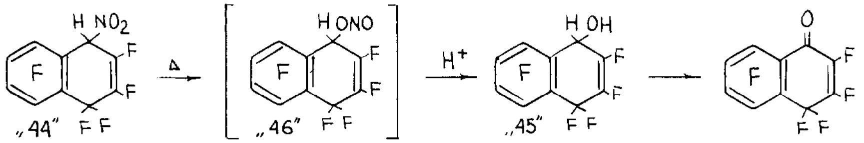
The thermal transformations of polyfluorinated-1-nitro-1,4-dihydronaphthalenes and 9-nitro-9,10-dihydroanthracenes proceed in a similar way leading to benz- and dibenzcyclohexadienones (oxo-dihydronaphthalenes and -anthracenes) [68,70,72,73,91]:



$R_2=R_3=R_5=R_8=F$ [91]
$R_3=CH_3$, $R_2=R_5=R_8=F$ [68]
$R_2=R_3=R_5=F$, $R_8=Cl$ [72]
$R_8=CH_3$ [70]
$R_2=R_3=R_8=F$, $R_5=Cl$ [72],
$R_5=CH_3$ [70]



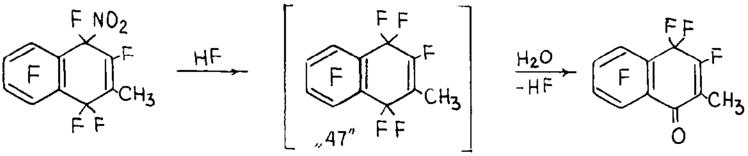
The scheme suggested for these reactions is similar to that for the thermal transformations of nitrocyclohexadienones [41] and involves isomerisation of the starting nitrocompounds to nitrites [71]:



Evidence in favour of this scheme was obtained in the studies on the thermolysis of 1-H-1-nitro-2,3,4,4,5,6,7,7-octafluoro-1,4-dihydronaphthalene "44" containing no fluorine geminal to the nitrogroup. The thermolysis gave alcohol "45" formed most likely in the hydrolysis of the primary product of rearrangement of nitrite "46". Formation of the nitrite in the thermolysis of compound "44" is confirmed by the IR spectrum of the primary product mixture [71].

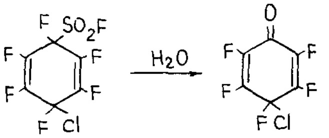
1.3.2. Hydrolysis

Partial hydrolysis of polyfluorinated dihydroaromatic compounds containing fluorines at the sp^3-hybride carbon atoms leads to polyfluorinated cyclohexadienones and seems to involve at the elementary stage the hydrolysis of polyfluorinated arenonium ions formed as a result of acid-catalysed heterolysis of the C–F bond of the substrate (the hydrolysis is described in Section 1.2.3). 3-Methyl-1-nitrooctafluoro-1,4-dihydronaphthalene treated with HF yields 1-oxo-2-methylheptafluoro-1,4-dihydronaphthalene, apparently as a result of the hydrolysis of the intermediate 2-methylnonafluoro-1,4-dihydronaphthalene "47" [68]:

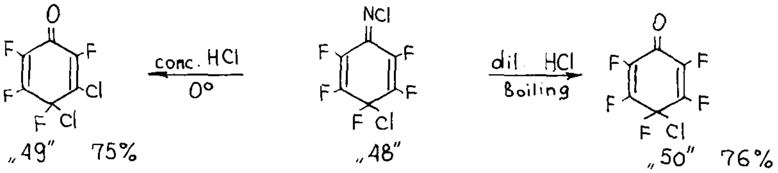


Hydrogen fluoride may be "moist" partially because of nitrous acid formed in the process. The structure of the resulting cyclohexadienone is consistent with the transformations of dihydronaphthalene "47" as a result of the reactions with SbF_5 and H_2O (see Section 1.2.3). Comparison of the transformations represented in the three preceding schemes shows nitrofluorination of polyfluorinated compounds leading to the polyfluorinated nitrodihydroaromatic compounds [68,70,71,72] to be a universal route to cyclohexadienones affording various isomers depending on the further transformations of the nitrofluorination product.

The hydrolysis of 4-chloro-pentafluoro-2,5-cyclohexadiene fluorosulfate formed in the addition of $ClOSO_2F$ to hexafluorobenzene [92] gave 4-chloro-pentafluoro-2,5-cyclohexadien-1-one in a good yield [93]:



A starting compound for the synthesis of fluorinated cyclohexadienones may be polyfluorinated N-chlorimine "48". Treatment of this compound with conc. HCl at 0° or with diluted HCl at boiling leads to good yields of 3,4-dichloro-2,4,5-tetrafluoro-2,5-cyclohexadien-1-one "49" and 4-chloro-2,3,4,5,6-pentafluoro-2,5-cyclohexadien-1-one "50" respectively [94]:



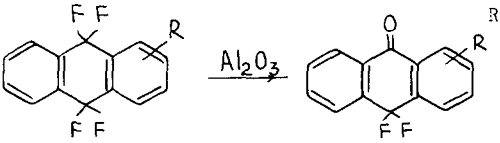
„49" 75%

„48"

„50" 76%

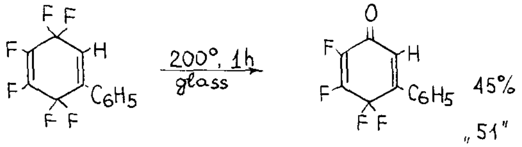
Likewise, compound "48" treated with CF_3SO_3F, HSO_3F and HSO_3Cl is transformed to dienone "50" [95].

A convenient method for partial hydrolysis of polyfluorinated 9,10-dihydroanthracenes is the prolonged keeping of these compounds, applied in a thin layer to acid (pH 3-4) aluminium oxide, in air [96]:



R=H, 1-F, 1-Cl, 1-Br,
2-F, 2-Cl, 2-Br,
1,8-Cl_2, 1,4-F_2 1,2,4-F_3

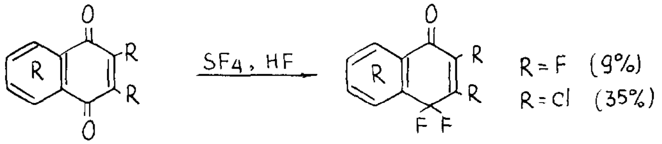
Heating of 1,1,2,3,4,4-hexafluoro-5-phenyl-2,5-cyclohexadiene in a glass tube at 200° affords polyfluorinated cyclohexadienone "51" [97]:

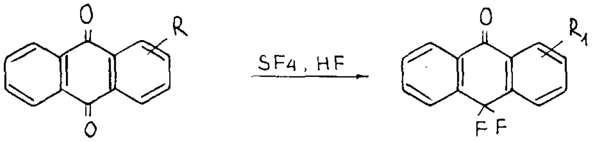


In both latter cases, a source of oxygen for the reaction product may be the substrate or the reactor's wall material. To initiate the reaction, traces of moisture and acid are supposedly sufficient, as the reaction is promoted by hydrogen fluoride formed in the process.

1.3.3. Reactions of Quinones with Sulphur Tetrafluoride

Cyclohexadienones are formed in the reactions of sulphur tetrafluoride with polyfluorinated naphtho- [98] and anthraquinones [96,99]:





R=H, R_1=H(10%); R=1-F, R_1=1-F(44%); 4-F(4%)

R=2-F, R_1=2-F(13%),3-F(17%); R=1-Cl,R_1=1-Cl(30%),4-Cl(22%)

R=2-Cl, R_1=2-Cl(7%),3-Cl(7%); R=1-Br,R_1=1-Br(15%),4-Br(5%)

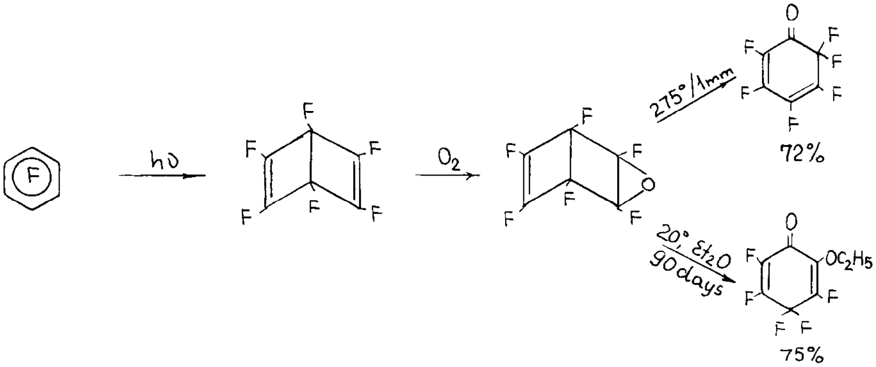
R=2-Br, R_1=2-Br(11%),3-Br(12%);R=R_1=1,8-Cl_2(10%);R=R_1=8-F(5%)

R=R_1=1,2,3,4-F_4(13%); R=1,4-$(OH)_2$, R_1=1,4-F_2(5%)

Upon heating with SF_4 in the presence of HF, halo- and hydroxyanthraquinones give the respective 9,9-difluoroanthrones-10, in which case for 1-chloro-, 2-chloro- and 2-bromanthraquinones, formation of the products of substitution of chlorine and bromine by fluorine has been observed, and in the case of 1,4-dioxyanthraquinone the fluorine atoms are substituted for both hydroxy groups. The predominant formation of 1-substituted 9,9-difluoroanthrones-10 from halogenanthraquinones seems to be the consequence of activation of the carbonyl group of the starting quinone by the adjacent halogen atom. The 2-substituted anthraquinones do not show any such difference in the activity of two carbonyl groups [96].

1.3.4. Transformations of the Dewar Hexafluorobenzene

An interesting precursor for the synthesis of polyfluorinated cyclohexadienones is the Dewar hexafluorobenzene oxide obtained by the UV irradiation of a gaseous mixture of hexafluorobenzene, nitrogen and oxygen. The thermolysis of this epoxide leads to hexafluoro-2,4-cyclohexadien-1-one, and prolonged keeping of it in diethyl ether to 2-ethoxy-3,4,4,5,6-pentafluoro-2,5-cyclohexadien-1-one [100]:



This approach illustrated by the above examples seems to be quite general in view of the possibility to involve a wide variety of polyfluoroaromatic compounds into such photochemical transformations to obtain various modifications of the Dewar benzene derivatives and further on fluorinated cyclohexadienones.

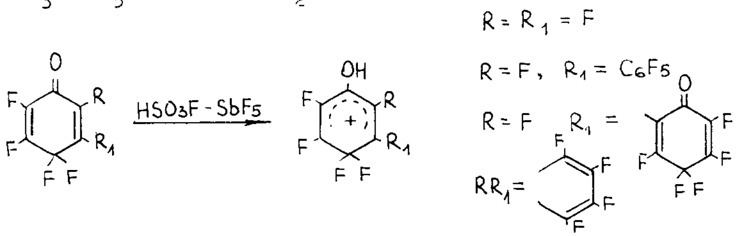
2. CHEMICAL PROPERTIES OF FLUORINE-CONTAINING CYCLOHEXADIENONES.

2.1. Protonation of Polyfluorinated Cyclohexadienones

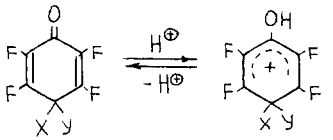
Since the acid-catalysed transformations [1] play an important role in the chemical properties of cyclohexadienones, investigation of their interaction with protic acids is essential for the development of the chemistry of such compounds. These studies are also stimulated by the fact that the conjugated acids of cyclohexadienones are the hydroxyarenonium ions modelling the intermediates of the reactions of aromatic compounds with electrophiles [101]. Protonation of polyfluoroaromatic cyclohexadienones was studied from this point of view [71].

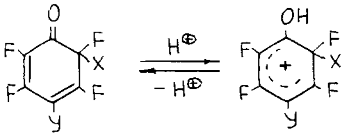
An essential level of protonation of polyfluorinated cyclohexadienones is only achieved by using superacids, indicating a decreased basicity of these compounds due to the effect of fluorine atoms as compared to cyclohexadienones with other substituents [101]. This may be attributed above all to the effect of fluorine atoms located in the non-resonance positions of the hydroxyarenonium ions formed in the process [77].

Practically complete protonation of perfluoro-2,5-cyclohexadien-1-one and perfluoro-1-oxo-1,4-dihydronaphthalene is achieved when these ketones are dissolved in the HSO_3F-SbF_5 mixture (the content of the latter component is 15 to 20% by weight), or upon their reactions with 2.6mol of an equimolar HSO_3F-SbF_5 mixture in SO_2 [102].



Protonation of polyfluorinated cyclohexadienones containing chlorine and bromine at a saturated carbon atom, as well as methyl group, gave hydroxyarenonium ions modelling the intermediates of the electrophilic reactions of aromatic compounds [103,104]:



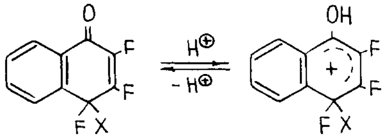


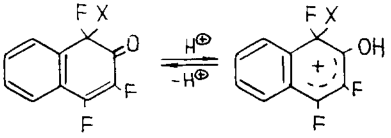
X=F, Y=Cl,Br

X=CH_3, Y=Cl,Br

X=Cl, Y=F,Br,CH_3

X=Br, Y=F,CH_3

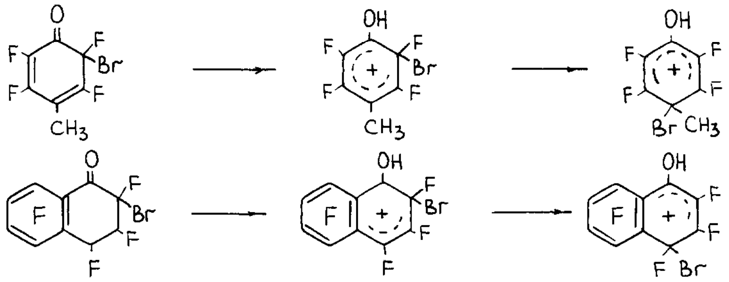




X=Cl,Br

X=Cl,Br

In the case of cyclohexadienones containing the bromine atom at the sp^3-hybrid carbon atom, the intermolecular migration of the former may generate the hydroxyarenonium ion that is more stable than the ion corresponding to protonation of the starting cyclohexadienone [103].



The 1-hydroxy-2-chloroheptafluoro-2-naphthalenonium ion formed in the protonation of 1-oxo-2-chloroheptafluoro-1,2-dihydronaphthalene also undergoes isomerisation [55], but with migration of fluorine, a lighter halogen than in the previous case. The reaction supposedly follows the "quasiintramolecular" mechanism similar to the one considered in Section 2.4.3. [105].

2.2. Nucleophilic Substitution at the Double Bonds of Polyfluorinated Cyclohexadienones

The reactions of nucleophilic reagents with cyclohexadienones containing halogen only at a saturated carbon atom generally lead to the reduction of the latter to phenols or substitution of halogen to form the respective substituted cyclohexadienones [1,2].

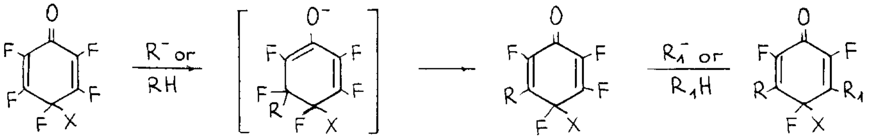
In contrast to this, polyfluorinated cyclohexadienones readily react with nucleophilic reagents with substitution of one or two fluorine atoms at the double bonds, which is a consequence of both the high activity of compounds with the fluorinated double bond in the nucleophilic reactions in general and a further activation of the double bond by its conjugation with the carbonyl group [108]. This is also characteristic of polyfluorinated benzoquinones.

Under the influence of the carbonyl group in 2,5-cyclohexadien-1-ones, the fluorine atoms at positions 3 and 5 are substituted most rapidly. This reaction route involves the intermediate states stabilised, unlike the substitution at positions 2 and 6, by the effect of the carbonyl group on charge delocalisation.

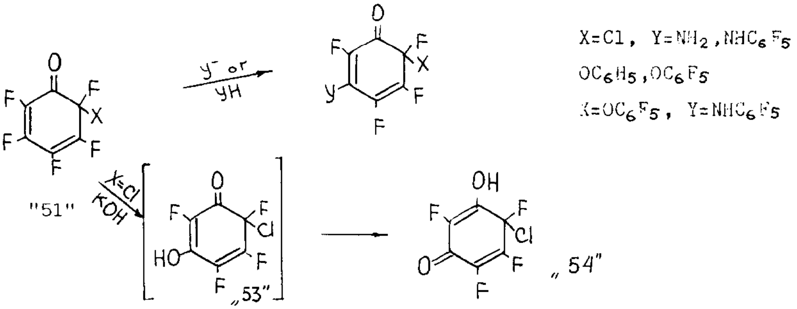
In polyfluorinated 2,4-cyclohexadien-1-ones the carbonyl effect is such that position 3 is more active than position 5, which is consistent with the ^{19}F NMR spectral data for these compounds [109]. A similar conclusion was made in the MO studies of charge distribution in polyhalogenated 2,4-cyclohexadien-1-ones [110].

Perfluoro-2,5-cyclohexadien-1-one (X=F) was transformed to 3-morpholinopentafluoro-2,5-cyclohexadien-1-one and 3,5-diaminotetrafluoro-2,5-

cyclohexadien-1-one [111], and perfluoro-4-phenoxy-2,5-cyclohexadien-1-one ($X=OC_6F_5$) was converted to the products of substitution of both fluorine atoms at positions 3 and 5 by groups NH_2, $N(CH_3)_2$, NHC_6H_5 and OC_6F_5, as well as to the mixed 3-aminomonosubstituted product [112].

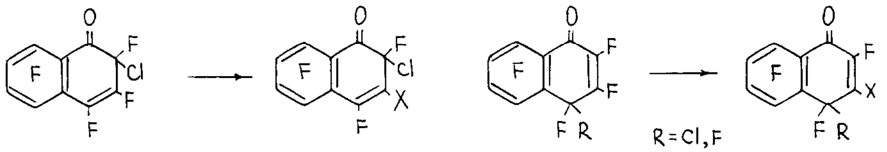


Sodium pentafluoro- and pentachlorophenoxides are not active enough to substitute the fluorine atom in 4-X-pentafluoro-2,5-cyclohexadien-1-ones ($X=Cl$, OC_6Cl_5) and 4,4-dibromotetrafluoro-2,5-cyclohexadien-1-one in boiling CCl_4 [51]. In contrast to this, 6-chloro-perfluoro-2,4-cyclohexadien-1-one reacts in carbon tetrachloride not only with ammonia but also with pentafluoroaniline, sodium phenoxide and pentafluorophenoxide, forming in all these cases 3-substituted tetrafluoro-2,4-cyclohexadien-1-ones [111]. Pentafluoroaniline reacts in a similar way with perfluoro-6-phenoxy-2,4-cyclohexadien-1-one [112].

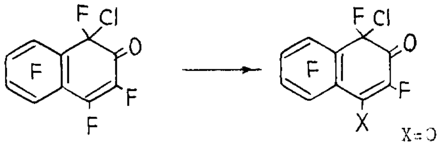


Dienone "52" reacts with an equimolar quantity of aqueous potassium hydroxide with substitution of fluorine at position 3 by the hydroxy group [111]. However extraction with heptane or carbon tetrachloride leads to the extracts containing not the 2,4-cyclohexadien-1-one "53" expected as the reaction product but its tautomer - 3-hydroxy-4-chloro-2,5-cyclohexadien-1-one "54".

Upon the reactions of nucleophilic reagents (methanol, ammonia, aniline, and piperidine) with 1-chloro-2-oxo- and 1-oxo-2-chloroheptafluoro-1,2-dihydronaphthalenes, as well as 1-oxo-4-X-heptafluoro-1,4-dihydronaphthalenes ($X=F,Cl$), there takes place substitution of fluorine atoms of the cyclohexadienone fragments: F4 - in the former case, and F3 -in the two latter cases [111]. The preferable substitution in the cyclohexadienone fragment may be explained by the fact that, due to the carbonyl effect on charge delocalisation, the aromaticity of the benzene ring in the intermediate states is not broken, unlike substitution in the benzene ring.



X=OH, OCH_3, OC_6H_5, OC_6F_5,
NH_2, NHC_6H_5

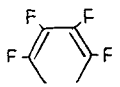


X=OCH_3, NH_2, NHC_6H_5, NC_5H_{10}

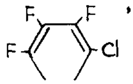
2.3. Reduction of Fluorinated Cyclohexadienones to Phenols

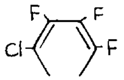
The fluorinated cyclohexadienones containing halogen atoms at a saturated carbon atom have one common feature - the ability to be converted to phenols in the reduction reactions (cf.[1]). The reducing agents for these reactions are zinc in combination with acetic or hydrochloric acids, sodium iodide, and sodium hydrosulphite. When the saturated carbon atom has fluorine and a heavier halogen atom (chlorine or bromine), the reduction proceeds with elimination of the latter.

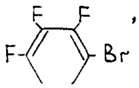
$R_1=R_2=R_3=R_4=F$; X=OC_6F_5, Y=F [2,48]

R_1R_2=  , $R_3=R_4=F$; X=F, Y=NO_2 [37]

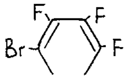
$R_1=R_2=R_3=R_4=X=Y=F$ [76]

R_1R_2=  , $R_3=R_4=X=Y=F$ [72]

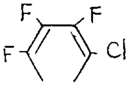
R_1R_2=  , $R_3=R_4=X=Y=F$ [72]

R_1R_2 =


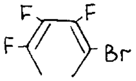
, $R_3=R_4=X=Y=F$, debromination [72]

R_1R_2 =


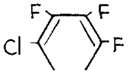
, $R_3=R_4=X=Y=F$, debromination [72]

R_1R_2 =


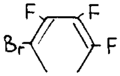
, $R_3=R_4=X=F$, $Y=NO_2$ [72]

R_1R_2 =


, $R_3=R_4=X=F$, $Y=NO_2$, debromination [72]

R_1R_2 =


, $R_3=R_4=X=F$, $Y=NO_2$ [72]

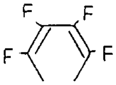
R_1R_2 =


, $R_3=R_4=X=F$, $Y=NO_2$, debromination [72]

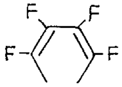
$R_1=R_2=R_3=R_4=X=F$, $Y=Br$ [3,4], debromination

$R_1=R_2=R_3=R_4=F$, $X=Br$, $Y=I$ [3], deiodination

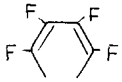
$R_1=R_2=R_3=X=y=F$, $R_4=CH_3$ [68]

R_1R_2 =


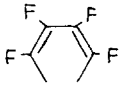
, $R_3=CH_3$, $R_4=X=F$, $Y=NO_2$
$R_3=X=F$, $R_4=CH_3$, $Y=NO_2$ mixture 3:1 [69]

R_1R_2 =


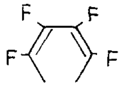
, $R_3=X=Y=F$, $R_4=CH_3$ [68]

R_1R_2 =


, $R_4=X=Y=F$, $R_3=CH_3$ [68]

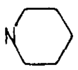
R_1R_2 =


, $R_3=H$, $R_4=X=F$, $Y=NO_2$ [69]

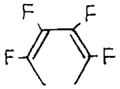
R_1R_2 =


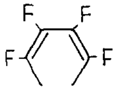
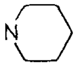
, $R_3=Cl$, $R_4=X=Y=F$ [113]

$R_1=R_2=R_4=X=Y=F$, $R_3=Cl$ [113]

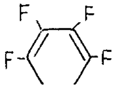
$R_1=R_2=R_3=X=Y=F$, $R_4=$  [111]

$R_1=R_2=R_3=X=F$, $R_4=OH$, $Y=Cl$ [111]

$R_1R_2=$  , $R_3=X=Y=F$, $R_4=OH, OCH_3, OC_6F_5, NH_2$ [111]

$R_1R_2=$  , $R_3=X=F$, $Y=Cl$, $R_4=$  [111]

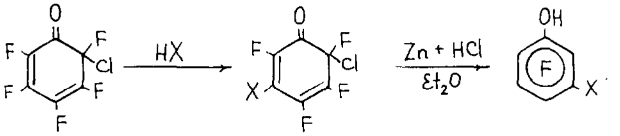
$R_1=R_3=R_4=X=F$, $R_2=Y=Cl$ [113]

$R_3R_4=$  , $R_1=X=F$, $Y=Cl$, $R_2=OCH_3$ [111]

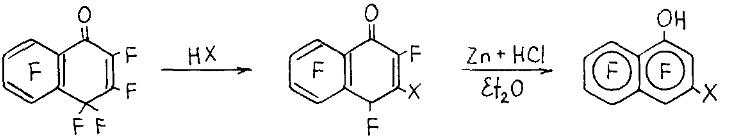
$R_1=R_3=R_4=X=F$, $R_2=Y=OC_6F_5$ [46]

$R_1=R_3=R_4=X=F$, $Y=Cl$, $R_2=NH_2$, NHC_6F_5, OC_6F_5, OC_6H_5 [111]

These transformations are useful in structure determination of cyclohexadienones. As a method for the synthesis of polyfluorinated phenols they are most advantageous when used in combination with the reactions of nucleophilic substitution at a double bond of cyclohexadienone (see Section 2.2), as illustrated by the following examples:



$X=OH$, OC_6H_5
OC_6F_5, NH_2
NHC_6F_5



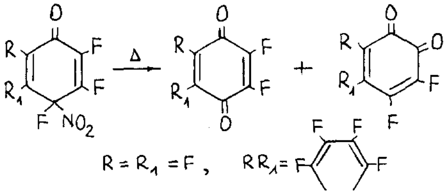
$x=OH$, OCH_3, OC_6F_5, NH_2

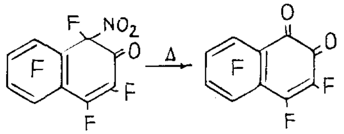
In view of the fact that the most convenient syntheses of cyclohexadienones are based on the use of polyfluorinated hydroxyaromatic compounds as the starting compounds (see Section 1.1), a sequence of above reactions presents a general approach to the synthesis of substituted phenols, which involves temporary modification of a starting phenol by its transformation to cyclohexadienone to facilitate the nucleophilic substitution of fluorine.

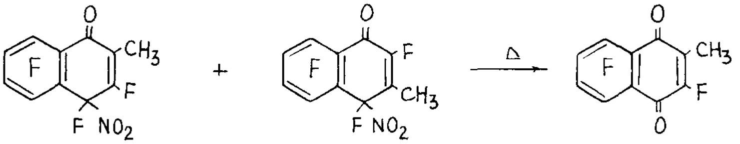
2.4. Transformations of Polyfluorinated Cyclohexadienones Involving a Saturated Carbon Atom

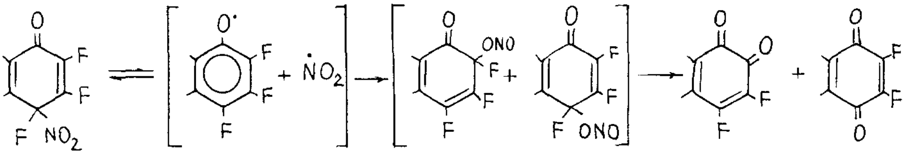
2.4.1. Thermolysis and Substitution at a Saturated Carbon Atom

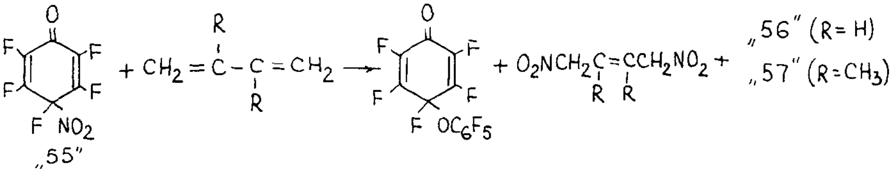
Like other cyclohexadienones and, generally, the compounds containing the geminal halogen and nitro group, the polyfluorinated nitrocyclohexadienones undergo upon heating the reactions involving the transformation of the $-CFNO_2$-group to the carbonyl group with elimination of nitrosyl fluoride. A typical feature of these transformations is a possible formation, apart from the polyfluorinated quinone corresponding in structure to the starting cyclohexadienone, of its isomer corresponding to conversion of the para-quinoid structure to the ortho-quinoid one [36,39,41,68].









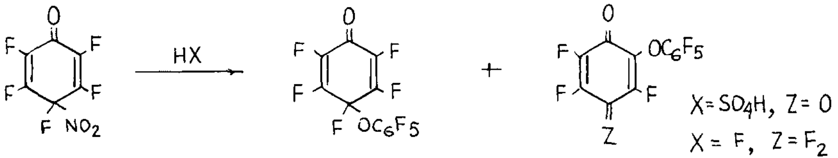

"55"

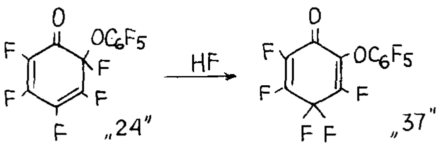
"56" (R= H)

"57" (R=CH₃)

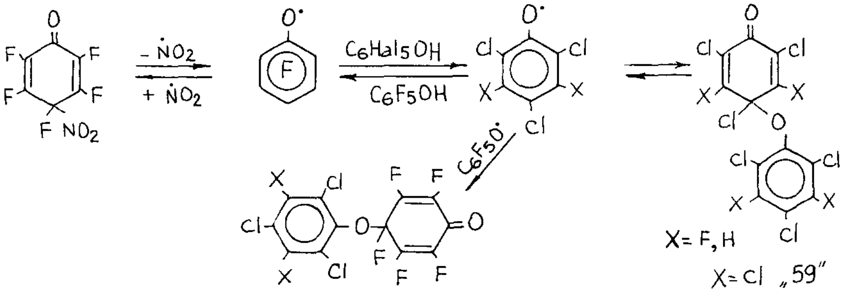
Realisation of the above rearrangement suggests the homolytic character of the C-N bond cleavage at the initial stage of these transformations with subsequent recombination of the polyfluorinated aroxyl radical and nitrogen dioxide to form isomeric quinol nitrites [41].

Formation of nitrosyl fluoride as one of the reaction products has been proved experimentally [41]. The nature of the first stage was confirmed by decomposition of quinnitrole "55" in the presence of butadiene and 2,3-dimethylbutadiene as radical traps. In both cases, formation of the pentafluorophenoxyl radical dimer "23" was recorded, and in the case of 2,3-dimethylbutadiene - the product of 1,4-addition of nitrogen dioxide to the diene. Besides, in both cases the reactions gave compounds formally corresponding to 1,2-addition of two pentafluorophenoxyl radicals to the diene, adducts "56" and "57" respectively (the structures of these adducts suggested in [41] are unreasonably given in [114] as proved). However compounds "56" and "57" seem more likely to be the Diels-Alder adducts formed as a result of the reactions of butadiene and isoprene as dienophiles with the isomer of compound "23" - the pentafluorophenoxyl radical dimer "24" reacting as a diene. Formation of the mixture of cyclohexadienones "23" and "24" as a result of dimerisation of the pentafluorophenoxyl radical was shown in [46] to be the result of oxidation of pentafluorophenol by lead tetraacetate. In accordance with these ideas, decomposition of quinnitrole "55" in sulphuric acid and hydrogen fluoride leads to dimer "23" and pentafluorophenoxytrifluoro-1,4-benzoquinone "58" or 2-pentafluorophenoxypentafluoro-2,5-cyclohexadien-1-one "37" respectively, and the latter was suggested to result from the isomerisation of the initially formed dimer "24" promoted by HF [50]. The occurence of this transformation has been shown in [49].



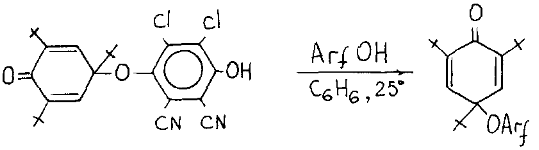


In the light of these ideas, formation of 4-pentahalogenophenoxypentafluoro-2,5-cyclohexadien-1-ones in the reactions of quinnitrole "55" with pentahalogenophenols or perchloro-4-phenoxy-2,5-cyclohexadien-1-one "59" may be represented by the following sequence [40]:



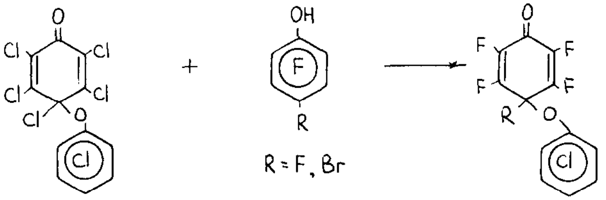
Formation of only "mixed" ethers in the reactions of this type involving chlorinated phenols seems to be due to the higher stability of the chlorinated phenoxyl radicals as compared to the pentafluorophenoxyl radical, which allows them to be considered as stable radicals in this system. This implies that in the reaction of quinnitrole with polychlorophenols the reaction mixture always contains the chlorinated phenoxyl radical in a much higher concentration than that of the pentafluorophenoxyl radical, due to which the predominant reaction is recombination of the polychlorophenoxyl and pentafluorophenoxyl radicals [40].

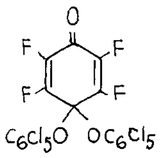
Interaction of phenoxycyclohexadienones with polyfluorinated phenols at room temperature leads to new cyclohexadienones containing fluorine atoms in the aromatic moiety [51].



$Ar_f = C_6F_5$, C_6HF_4,
C_6BrF_4, C_6IF_4,
$C_6F_5OC_6F_5$,
$C_6F_5OC_6F_4OC_6F_5$

By the contrast with this, the reactions of perchloro-4-phenoxy-2,5-cyclohexadien-1-one and fluorinated phenols lead to the fluorinated cyclohexadienones containing fluorine atoms in the dienone moiety [51]:



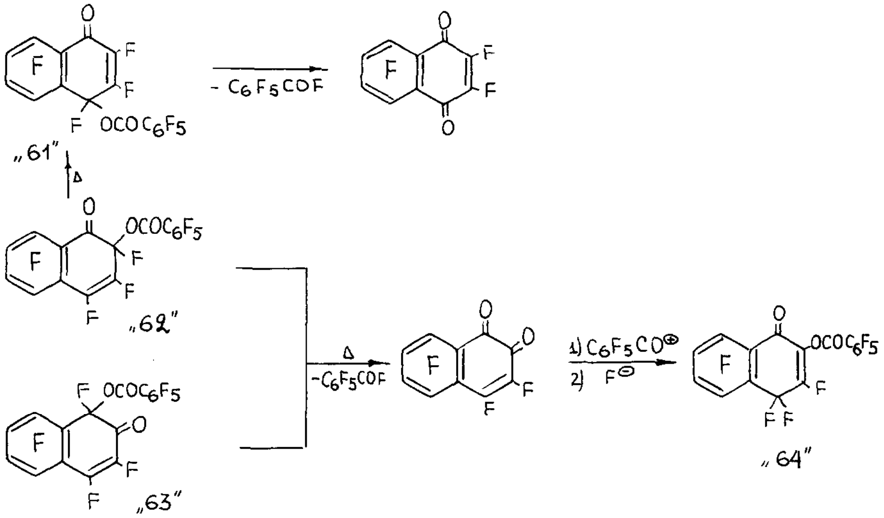


„60”

In the case when a fluorinated phenol has bromine in the para-position to the hydroxy group, the reaction proceeds with substitution of bromine to give dienone "60" containing the geminal pentafluorophenoxyl groups.

The available data suggest the interaction of cyclohexadienones capable of the homolytic decomposition with phenols to be a model reaction for the studies of recombination tendencies of phenoxyl radicals.

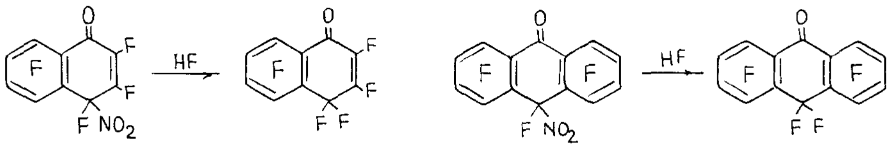
Perfluorinated oxodihydronaphthalenes containing the geminal fluorine and pentafluorobenzoyloxy groups are more stable upon heating than quinnitrols. Thus, they remain unchanged upon heating to 160°, and at 150° compound "61" is converted to a mixture of pentafluorobenzoyl fluoride and hexafluoro-1,4-naphthoquinone. Compound "62" gives, in addition to these products, hexafluoro-1,2-naphthoquinone and dienone "64" formed by fluorine migration [54]. The latter compound is also formed in the thermolysis of compound "63" together with hexafluoro-1,2-naphthoquinone and pentafluorobenzoyl fluoride.



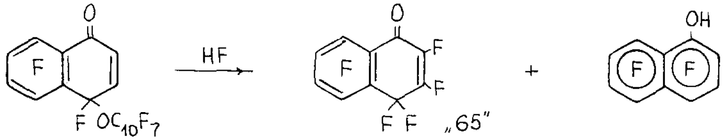
Formation of compound "64" from both 1-oxo- and 2-oxo-1,2-dihydronaphthalenes ("62" and "63") may result from the acylation of the intermediate hexafluoro-1,2-naphthoquinone by the acylium cation generated from pentafluorobenzoyl fluoride under the influence of HF traces, with subsequent stabilisation of the resulting naphthalenonium ion by addition of the fluorine anion [54]. This supposition has been justified by producing compound "64" from hexafluoro-1,2-naphthoquinone and C_6F_5COF in the presence of the catalytic amounts of anhydrous HF upon heating [54].

2.4.2. Reactions of Fluorinated Cyclohexadienones with Hydrogen Fluoride

Cyclohexadienones containing the geminal fluorine and nitro group easily exchange the latter for fluorine when treated with hydrogen fluoride [73,91]:

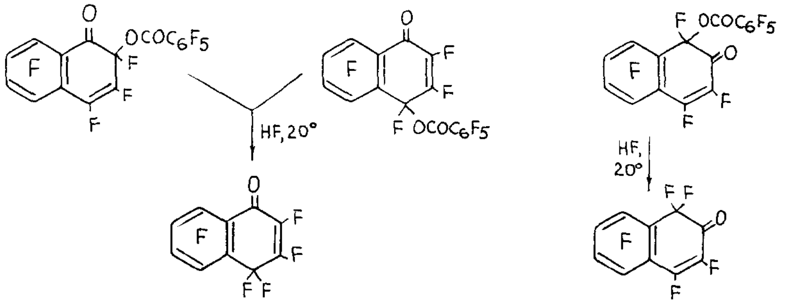


It seems obvious that the high mobility of the nitro group in these cases arises from its allyl-benzyl position. Such mobility is also characteristic of the polyfluorinated aryloxy and acyloxy groups. Thus interaction of perfluoro- 1-oxo-4(naphthoxy-1')-1,4-dihydronaphthalene with anhydrous HF at 20° leads to formation of perfluoro-1-oxo-1,4-dihydronaphthalene "65" together with heptafluoro-1-naphthol [50]:



„65"

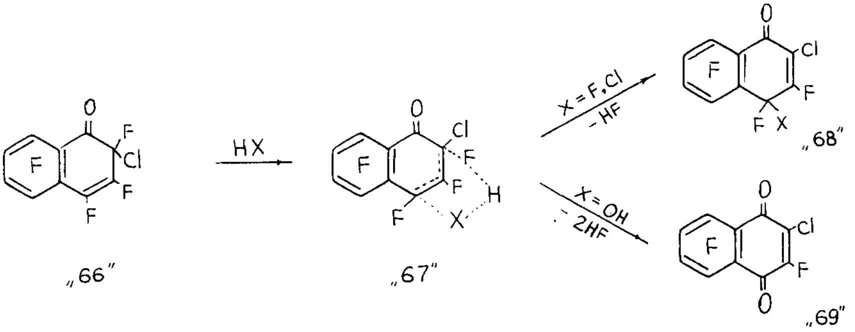
In a similar way the fluorine atom is substituted for the pentafluorobenzoyloxy group in the polyfluorinated derivatives of oxodihydronaphthalene [54], which in the case of perfluoro-1-oxo-2-benzoyloxy-1,2-dihydronaphthalene is accompanied by the rearrangement to the 1,4-dihydronaphthalene derivative:



2.4.3. Rearrangements

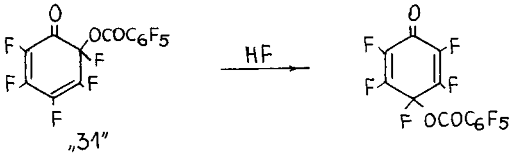
The transformations of 2,4-cyclohexadienones containing the geminal fluorine, chlorine or bromine, to 2,5-isomers seem to be specifically the result of the presence of hydrogen fluoride in the medium. Its action is dual:

on the one hand, there may proceed protonation of the starting dienone at oxygen to generate the hydroxyarenonium ion, in which halogen atoms other than fluorine are expected to have a higher migrating mobility (cf.[101]). By this mechanism, apparently, proceeds isomerisation of polyfluorinated cyclohexadienones induced by the bromine migration [3]. In the cases when the fluorine atom is more mobile [52,113], the reaction seems to follow the mechanism suggested in [105] and involving formation of the cyclic intermediate state of type "67":

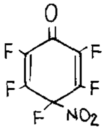


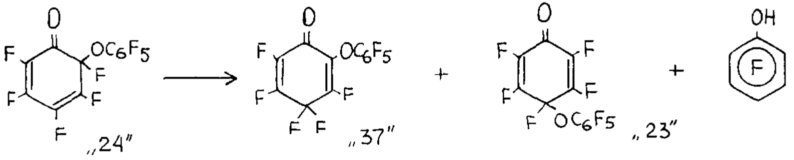
In the reaction of dienone "66" with chlorosulphonic acid, formation of analogous intermediate states involving hydrogen chloride may lead to dienone "68", of those involving water - to quinone "69". Removal from the sp^3-hybrid of the fluorine rather than chlorine atom seems to result from the greater stability of the H-Hal bond for fluorine as compared to chlorine [108].

In many cases the transformations of polyfluorinated 2,4- and 2,5-cyclohexadienones in the reactions with HF also proceed via rearrangements. Thus dienone "31" treated with HF undergoes isomerisation to the corresponding 2,5-dienone. The isomerisation supposedly proceeds via migration of the pentafluorobenzoyloxy group, in the arenonium ion formed in the protonation of the starting dienone [53]:

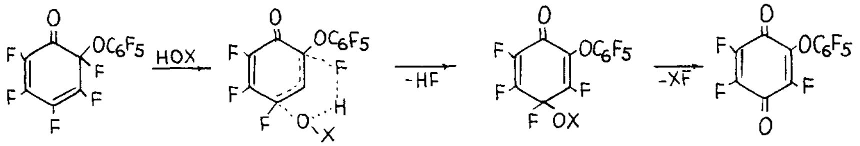


Perfluoro 4-phenoxy-2,5-cyclohexadien-1-one "23" remains unchanged in the reaction with HF at 20° [49], whereas perfluoro-6-phenoxy-2,4-cyclohexadien-1-one is isomerised with migration of both the fluorine atom and the pentafluorophenoxy group. These two processes seem to follow different mechanisms:

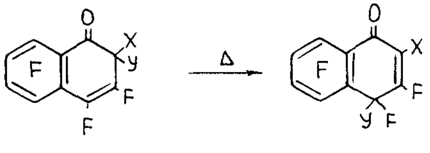

"55"


"24" "37" "23"

The transformation of dienone "24" to compound "37" is a 1,3-allyl rearrangement catalysed by HF, and the transformation to dienone "23" proceeds most likely by migration of the pentafluorophenoxy group in the arenonium ion formed in the protonation of dienone "24" [49]. The same products - compounds "23" and "37" - are formed in the reaction of 4-nitro-perfluoro-2,5-cyclohexadien-1-one "55" [50], possibly as a result of the homolytic dissociation of the C-N bond in quinnitrole "55" with generation of the pentafluorophenoxyl radical (see Section 2.4.1). Dimerisation of the latter gives compound "23" and ortho-dienone "24", which, as shown above, isomerises in these conditions to compound "37". The acid-catalysed transformations of this type are general enough. As shown in Section 2.4.1, quinnitrole "55" undergoes similar transformations in other strong acids (sulphuric, fluorosulphonic) [50], but the reaction also gives the polyfluoro 1,4 benzoquinone derivative possibly formed by the following route:



Similar transformations take place in the series of polyfluorinated 1-oxo-1,2-dihydronaphthalenes (benzocyclohexadienones):



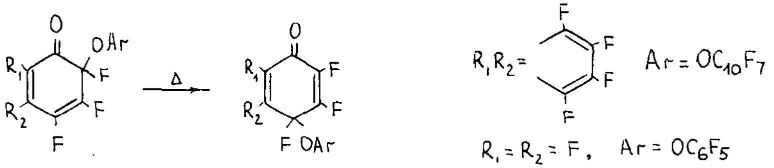
X=Cl, Y=F

X=F, Y=$OC_{10}F_7$

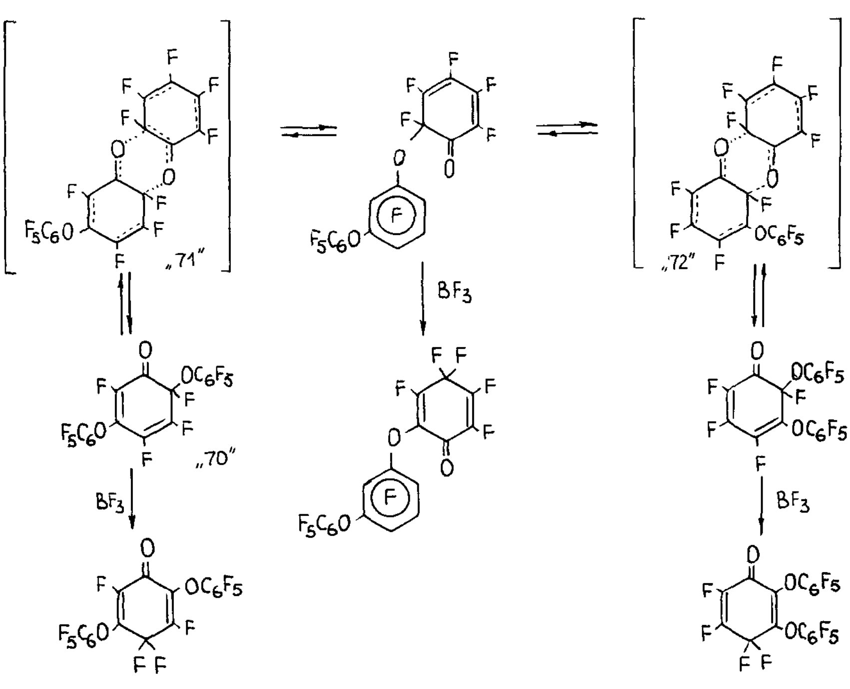
X=$OC_{10}F_7$, Y=F

X=F, Y=Br

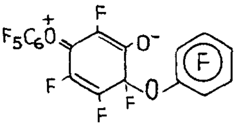
By contrast with the above acid-catalysed reactions, thermal isomerisations of 2,4-cyclohexadienones and 1-oxo-1,2-dihydronaphthalenes having the geminal fluorine and perfluoroaroxyl group (the pentafluorophenoxyl and heptafluoronaphthoxyl radical dimers) to 2,5-dienones and 1-oxo-1,4-dihydronaphthalenes respectively apparently proceed by the dissociation to the corresponding aroxyl radicals [52,115].



A new type of thermal rearrangement of cyclohexadienones was found for perfluoro-3,6-bis(phenoxy)-2,4-cyclohexadien-1-one "70" [116]. In this case the geminal substituent migrates with preservation of the structure of 2,4-cyclohexadien-1-one, obviously via the intermediate states of types "71" and "72". This process is similar to the Claisen rearrangement of phenylallyl ethers [4,117,118], the difference being that instead of the double bond of the allyl fragment there is the π-system of the cyclohexadienone ring:



Ease of the rearrangement of compound "70" is possibly explained by some charge separation, which may be represented by the following structure:

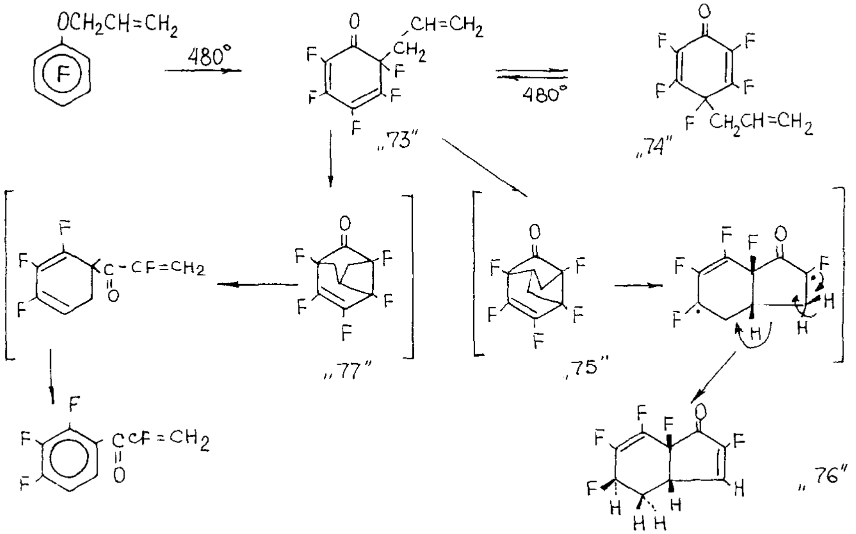


A similar substituent effect was observed for the Claisen rearrangement of meta-substituted phenylallyl ethers. The rate of rearrangement of such ethers correlates with σ_p^+ rather than σ_m^-, indicating a direct conjugation of substituent with the reaction centre [119,120].

The three equilibrating 2,4-cyclohexydien-1-ones formed in the reaction, isomerise in the presence of boron trifluoride to more stable 2,5-cyclohexadien-1-ones.

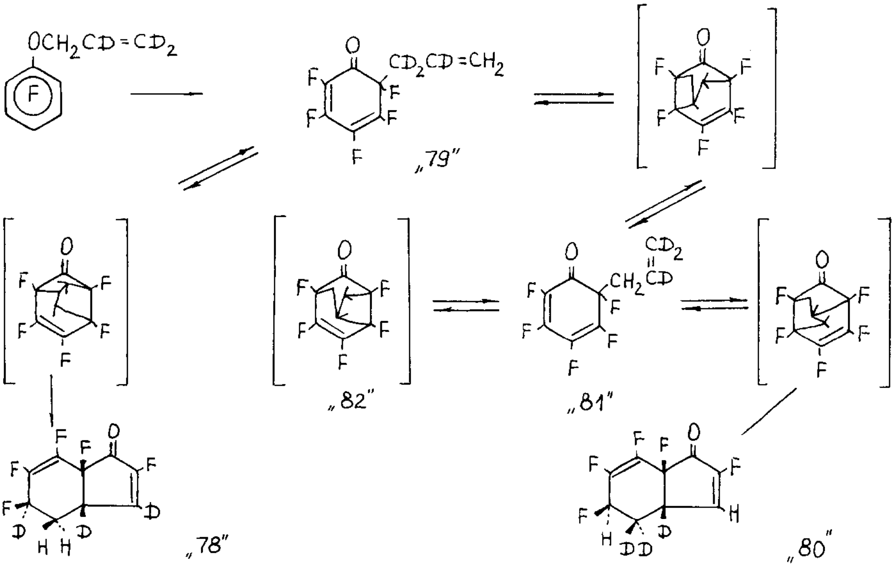
2.5. Cycloaddition Reactions

If the thermolysis of fluorinated phenylallyl ethers leading as a result of the Claisen-Cope rearrangement to cyclohexadienones "73" and "74" [61] (see Section 1.1.4)is conducted in more vigorous conditions,then the intramolecular Diels-Alder reaction of the above cyclohexadienones and subsequent rearrangement of adduct "75" yield 2,5β,6,7,7α,β - pentafluoro - 3α,β,4,5,7α- - tetrahydroinden-1-one "76" [62].

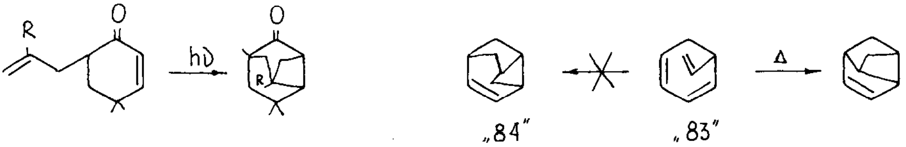


Conducting the reaction at 440° enables trapping of 2,3,4-trifluorophenyl-1-fluorovinylketone, apparently indicating the formation of another possible intramolecular Diels-Alder adduct "77" from compound "73" [63,121]. This is in agreement with the results obtained in the pyrolysis of pentafluorophenyl(2,3,3-$^2H_3$)-prop-2-enyl ether "77" leading not only to (3,3α,β,5α $^2H_3$)2,5,6,7,7α,β-pentafluoro-3α,4,5,7β tetrahydroinden-1-one "78" corresponding to the intermediate formation of 2-[(1,1,2 $^2H_3$)prop-2-enyl]-3,5 cyclohexadienone "79", but also to (3α,β,4,4, $^2H_3$)-2,5β,6,7,7α,β-pentafluoro-

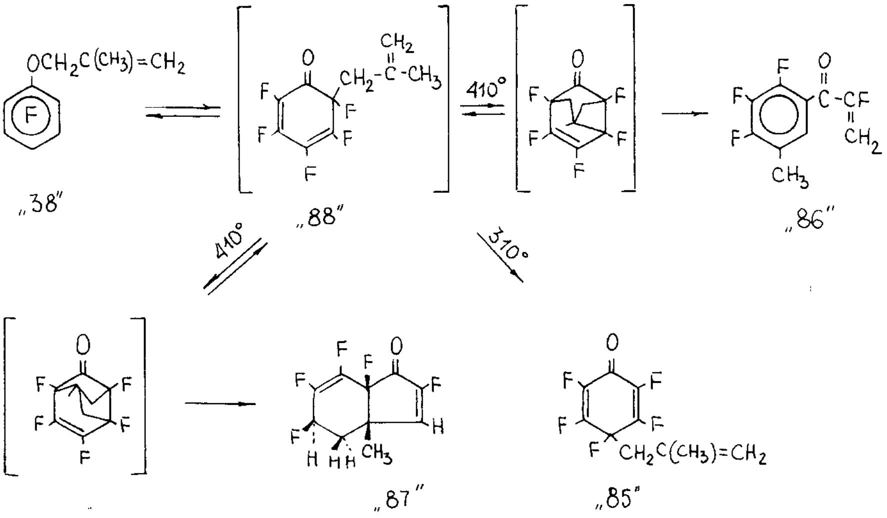
3α,4,5,7α-tetrahydroinden-1-one "80". The latter seems to be formed from 2-[(2,3,3-$^{2}H_{3}$)prop-2-enyl]-3,5-cyclohexadienone "81". In its turn, its formation indicates the intermediate formation of an adduct similar in structure to compound "82" [62,121].



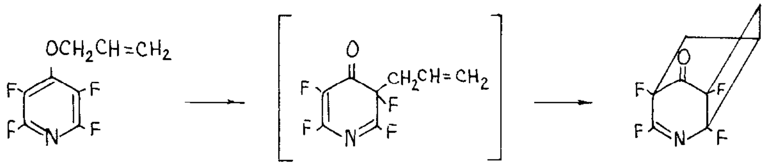
These transformations are interesting because the adduct of type "82" is a rare example of compound having the (3,3,1,0)tricyclononane frame. There are two known examples of this type of compounds containing no fluorine, for which the intramolecular cyclisation similar to the transformations of "83" → "84" fails to proceed, as opposed to the fluorinated compounds. The reason for such difference seems to be the stabilising effect of the aliphatic C–F bond, as well as a high reactivity of the tetrafluoro-1,3-diene systems with hydrocarbon dienophiles [122].

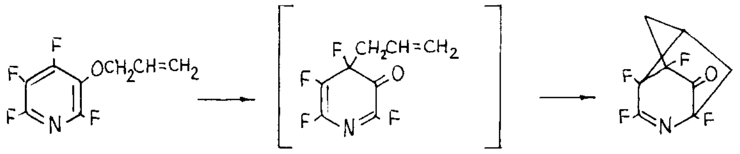


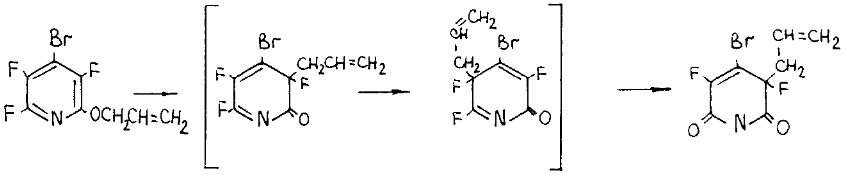
The gas-phase pyrolysis of pentafluorophenyl-2-methylprop-2-enyl ether "58" gives a mixture of 1-fluorovinyl-2,3,4-trifluoro-5-methylvinylketone "86" and 2,5β,6,7,7α,β-pentafluoro-3α,β-methyl 3α,β,4,5,7α-tetrahydroinden-1-one "87" [63], indicating the intermediate formation of two intramolecular Diels-Alder adducts from dienone "88", as in the case of the thermolysis of pentafluorophenylallyl ether:

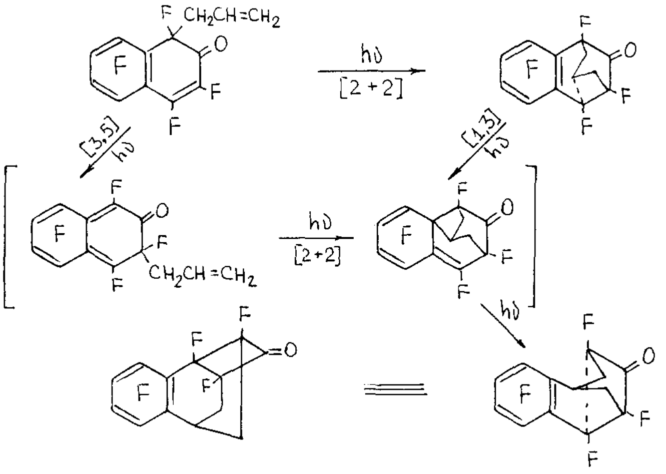


The similar ethers of isomeric polyfluorohydroxypyridines [56] behave upon thermolysis like the fluorinated phenylallyl ethers, as well as 1,2,4,5,6,7,8-heptafluoro-1-(prop-2-enyl)naphthalen-2-one upon photolysis [64]:



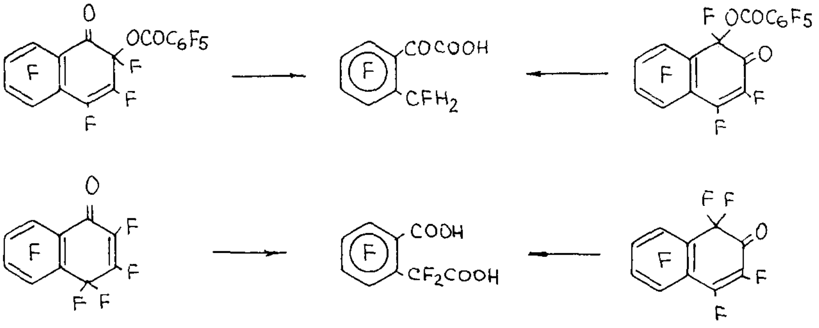






2.6. The Oxidative Ring Cleavage

The reaction of acetic peracid with the polyfluorinated substituted 1- and 2-oxo-1,2-dihydronaphthalenes and 1-oxo-1,4 dihydronaphthalenes leads to the cleavage of the cyclohexadienone cycle and formation of the substituted polyfluoroaromatic carboxylic acids [55]:



Various potentialities for further modification of substituents and nucleophilic substitution of fluorine in the products of this reaction provide access to the unavailable polyfluorobenzene derivatives of a definite structural type.

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