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# Aromatic Monocarbonylpolyfluoro-compounds

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The literature data on the methods of synthesis and chemical and photochemical reactions of aromatic polyfluoro-substituted aldehydes and ketones are surveyed and arranged systematically. Attention is concentrated on the most characteristic reactions of these compounds with nucleophiles. The characteristics of the structure and reactivity of monocarbonylpolyfluoro-compounds due to the presence of electron-accepting fluorine atoms in their molecules are considered. Methods are described for the preparation of aromatic *o*-hydroxy- and *o*-amino-substituted polyfluoroketones and certain aspects of their employment in the synthesis of polyfluoro-substituted benzoheterocycles are examined.
The bibliography includes 148 references.

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## I. INTRODUCTION

During the last two decades, there has been an intense development of the chemistry of aromatic polyfluoro-compounds. In recent years a number of reviews devoted to the methods of synthesis[1,2] and individual types of their reactions[3-6] as well as problems of the influence of polyfluorobenzene ring and the reactivity of the functional groups linked to it[7,8] have been published. However, the volume of experimental data has increased so much that its detailed consideration and survey in terms of individual classes of compounds has become necessary. In the present review an attempt is made to do this in relation to aromatic carbonyl polyfluoro-compounds. The review includes data on the methods of synthesis and chemical properties of aromatic polyfluoro-substituted aldehydes and ketones of the type $Ar_FCHO$ and $Ar_FCOR$ containing the C=O group linked directly to the aromatic polyfluoro-ring. Polyfluorobenzoic acids and their derivatives are not considered in this review.

## II. METHODS OF SYNTHESIS OF AROMATIC POLYFLUORO-SUBSTITUTED ALDEHYDES AND KETONES

The classical method of synthesis of aromatic ketones—the Friedel–Crafts acylation[9]—has not been used widely in the chemistry of aromatic polyfluoro-compounds. Only isolated instances of the application of this reaction in the preparation of aromatic polyfluoroketones are known. Thus the possibility of synthesising pentafluorobenzophenones by the reaction of pentafluorobenzoyl chloride with benzene and alkylbenzenes has been demonstrated[10-12]:

$$C_6H_6 + C_6F_5COCl \xrightarrow[90-100^\circ]{AlCl_3} C_6H_5COC_6F_5 \quad (55\%);$$

$$C_6Alk_6 + C_6F_5COCl \xrightarrow[20^\circ]{AlCl_3} C_6Alk_5COC_6F_5 \quad (26-50\%);$$

Alk=Me, or Et .

The acylation reactions of pentafluorobenzene in the presence of aluminiumchloride take place under severe conditions and are complicated by side processes[10], but the synthesis of decafluorobenzophenone and a number of aliphatic aromatic polyfluoroketones by the reaction of pentafluorobenzene with carboxylic acid anhydrides and halides in antimony pentafluoride has been described[13]:

$$C_6F_5H \xrightarrow[SbF_5]{R_FCOX \text{ или } (R_FCO)_2O} C_6F_5COR_F \quad (20-80\%) \qquad R_F=Alk_F, \text{ or } C_6F_5 .$$

Polyfluorobenzophenones have also been obtained by the hydrolysis of the salts of α-fluorodiarylmethyl cations synthesis from partly fluorinated aromatic hydrocarbons and trifluoromethylbenzenes in antimony pentafluoride[14,15]:

$$R^1C_6F_4CF_3 + R^2C_6F_4H \xrightarrow{SbF_5} R^1C_6F_4\overset{+}{C}FC_6F_4R^2 \xrightarrow{H_2O} R^1C_6F_4COC_6F_4R^2 \quad (75-93\%);$$

$R^1$=H, or F; $R^2$=H, F, or Me .

The most widely used method of synthesis of aromatic polyfluoro-substituted aldehydes and ketones is based on organoelemental compounds. Penta- and tetra-fluorobenzaldehydes have been obtained from the corresponding polyfluorophenylmagnesium halides and *N*-methylformanilide in 50–80% yield[16-19]. The attempts to carry out the reaction with ethyl formate or orthoformate resulted in appreciable reduction of the yield of products[16,20]. Pentafluorophenyl-lithium has been used successfully instead of a Grignard reagent[21-23].

Aromatic and aliphatic-aromatic polyfluoroketones are usually obtained by the interaction of polyfluorophenyl derivatives of metal—magnesium, copper, cadmium, and aluminium—with carboxylic acid derivatives[16,17,24-33]. There are extremely few examples of the use of aromatic polyfluoro-substituted carbonyl compounds or their analogues in such reactions[34-36]:

$C_6F_5MgX$ —
- $\xrightarrow{(MeCO)_2O}$ $C_6F_5COMe$ (48%)
- $\xrightarrow{CF_3CO_2Li}$ $C_6F_5COCF_3$ (71%)
- $\xrightarrow{PhCOCl}$ $C_6F_5COPh$ (62%)
- $\xrightarrow{ClCO_2Me}$ $C_6F_5COC_6F_5$ [(33%)] ;

$C_6F_5CN \xrightarrow{RMgX} C_6F_5COR$; R=Me, or Ph (40–60%) ;

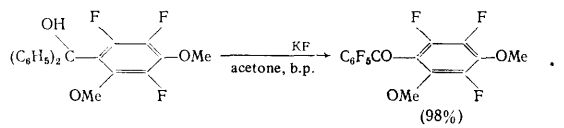
$C_6F_5COCl \xrightarrow{Me_2Cd} C_6F_5COMe$ (56%) .

A preparatively important version of this method is based on the interaction of benzaldehyde or its substituted derivatives with Grignard reagents in combination with the classical reaction involving the oxidation of the secondary alcohols thus produced. The oxidant is usually chromium trioxide in glacial acetic acid[16,37–43]. Polyfluoro-substituted benzo- and aceto-phenones containing various functional groups have been prepared by this method[43–45].

Aliphatic-aromatic polyfluoroketones with ester and other functional groups have been synthesised successfully with the aid of the disodium salt of iron hydrocarbonyl[46]:

$$Na_2Fe(CO)_4 + n\text{-}C_5H_{11}OCO(CH_2)_4CH_2Br + C_6F_5COCl \rightarrow C_6F_5CO(CH_2)_5CO_2C_5H_{11}\text{-}n \ .$$

A specific reaction for the synthesis of aromatic polyfluoroketones involves the cleavage of polyarylfluorocarbinols in an alkaline medium[47–49]. The use of anhydrous potassium fluoride as the base ensures that the process proceeds unambiguously and is preparatively valuable[36,50]:



(98%)

A number of other methods normally employed in the chemistry of non-fluorinated analogues have also been applied successfully in the synthesis of aromatic polyfluoro-substituted carbonyl compounds. Pentafluorobenzaldehyde has been obtained from pentafluorobenzonitrile by reduction with stannous chloride[34] or Raney nickel[35]. The formation of polyfluorobenzophenones by the oxidation of olefins[51] and by the thermolysis of salts of polyfluorobenzoic acids[52–55] or pentafluorobenzoyl chloride in the presence of alkali metal salts[56] has been described.

## III. CHEMICAL PROPERTIES

The substitution of hydrogen atoms in the aromatic ring of the carbonyl compound by fluorine atoms, which are highly electronegative, alters the electronic character of the aromatic ring and the properties of the carbonyl group linked to it. In aromatic polyfluoro-substituted carbonyl compounds the $-I$ effect of the pentafluorophenyl group[57,58] is enhanced by the breakdown of the coplanarity of the molecules, which hinders the conjugation of the carbonyl group with the aromatic ring. The difficulty of the rotation of the $C_6F_5$ groups about the $C_{arom}-C_{C=O}$ bond has been noted for decafluorobenzophenone[59]. The determination of the dipole moments of pentafluorobenzaldehyde and pentafluoroacetophenones in solution and their comparison with the calculated values showed that the formyl and acetyl groups deviate from the plane of the ring (the dihedral angles are 28° and 58° respectively) largly due to the Coulombic repulsion between the oxygen atoms or between the methyl group and fluorine atoms[60]. It is noteworthy that the molecules of the non-fluorinated analogues of these compounds are planar. Direct evidence for the greater electron-accepting influence of the pentafluorophenyl group compared with the phenyl group is provided by the hypsochromic shift (by 20–30 $cm^{-1}$) of the stretching vibration band of the carbonyl group in the infrared spectra of aromatic polyfluoro-substituted aldehydes and ketones[61].

The $-I$ effect of the pentafluorophenyl residue should lead, on the one hand, to an enhancement of the electrophilic properties of the carbon atom of the carbonyl group linked to it and to a facilitation of nucleophilic attack via this carbon atom and, on the other hand, to a decrease of the basicity of the C=O group and a greater difficulty of acid catalysts, which plays an important role in many reactions of carbonyl compounds. Unfortunately there are no quantitative literature data for the relative basicities of aromatic polyfluoro-substituted aldehydes and ketones. It has only been shown that perfluorobenzophenone is appreciably protonated on dissolution in sulphuric or fluorosulphonic acids[62] and forms the corresponding oxycarbonium in in the $SbF_5$–HF–$SO_2ClF$ system[63].

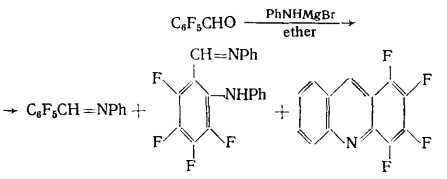
The presence of the polyfluoroaryl residue in the molecule of the aromatic polyfluoro-substituted carbonyl compound not only transforms the properties of the carbonyl group but is also responsible for the possibility of nucleophilic substitution in the fluorine atoms. The carbonyl group has an activating influence on this process. Overall, aromatic polyfluoro-substituted aldehydes and ketones are polyfunctional compounds, the characteristics and chemical properties of which are determined by the mutual influence of the carbonyl and polyfluorophenyl groups linked directly.

### 1. Reactions with *N*-Nucleophiles

The interaction of aromatic aldehydes and ketones with nitrogen bases, which is the most important and most thoroughly investigated type of their reactions, usually leads to the formation of derivatives of the carbonyl group. The reactions of aromatic polyfluoro-substituted carbonyl compounds with *N*-nucleophiles are less unambiguous. Depending on the structure of the reactants under the reaction conditions, they can involve both the carbonyl group, with formation of the corresponding nitrogen-derivatives, or the haloform decomposition of the initial compound, or the substitution of fluorine atoms.

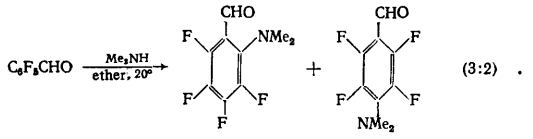
Aromatic polyfluoroaldehydes react with hydrazine, semicarbazide, thiosemicarbazide, and 2,4-dinitrophenylhydrazine, forming the corresponding derivatives of the carbonyl group under the usual conditions[18–20,34,64,65]. When pentafluorobenzaldehyde was allowed to react with *O*,*N*-bis(trifluoroacetyl)-hydroxylamine—a new reagent for the carbonyl group—pentafluorobenzonitrile was obtained in 76% yield[66].

Pentafluorobenzaldehyde exhibits a high reactivity in relation to primary aliphatic and aromatic amines via its carbonyl group. It reacts with ethylamine in water without the elimination of fluoride ions, forming *N*-(pentafluorobenzylidene)-ethylamine[64]. Its react with aniline and the very weakly basic pentafluoroaniline ($pK_a = -0.28$) [67] leads to the formation of the corresponding Schiff bases[16,17,68]. The interaction with the more nucleophilic bromomagnesylaniline results in the formation not only of the anil of pentafluorobenzaldehyde but also of products of its further reactions[68]:

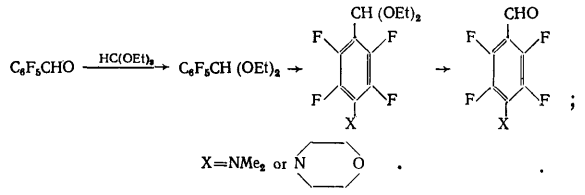



Pentafluorobenzaldehyde reacts with dimethylamine in ethereal solution at room temperature, the process involving the substitution of a fluorine atom by the dimethylamino-group[64]. The preferential *ortho*-directing effect observed in

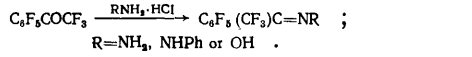
this reaction is in all probability caused by the specific interaction of the reagent with the formyl group:



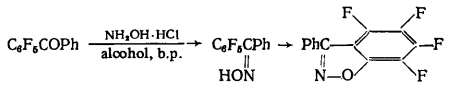
*p*-Aminotetrafluorobenzaldehydes can be obtained by an indirect method via the diethyl acetal of pentafluorobenzaldehyde[69]:



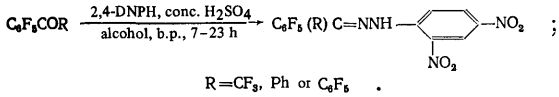
2,3,4,5,6-Pentafluoroacetophenone† exhibits a reactivity towards substituted hydrazines which resemble that of the non-fluorinated analogue[34,70]. Octafluoroacetophenone, containing the highly electronegative trifluoromethyl group, reacts vigorously with free hydrazine[71]. However, in contrast to aliphatic polyfluoroketones[72,73], it does not then form a stable geminal addition product, but undergoes the haloform decomposition with elimination of the relatively stable pentafluorophenyl anion[8]. Reactions with the less nucleophilic phenylhydrazine and hydroxylamine take place on heating and lead to appreciable elimination of fluoride ions and formation of complex mixtures. Derivatives of the carbonyl group have been obtained on refluxing octafluoroacetophenone with the hydrochlorides of the corresponding bases in an aqueous alcoholic medium[71,74]:



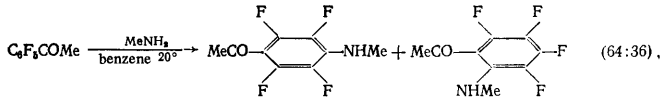
The oximes of 2,3,4,5,6-pentafluoro- and decafluoro-deoxybenzoins[75] as well as the oxime of pentafluorobenzophenone have been obtained similarly. The latter is unstable and undergoes spontaneous cyclisation to an oxazole derivative[16,74]:



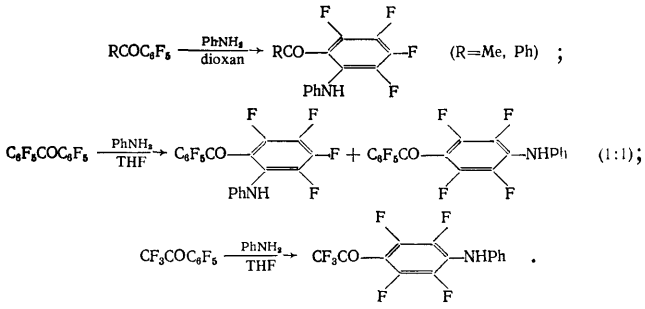
Polyfluorobenzophenones react with hydrazine and phenylhydrazine with substitution of a fluorine atom by the RNHNH group and do not change on prolonged refluxing with their hydrochlorides in an aqueous alcoholic solution[39,71]. The lack of interaction with free bases via the carbonyl group can be accounted for by the influence of a number of factors, the most important of which is apparently the steric effect of the *ortho*-fluorine atoms, which hinder the approach of the nucleophile to the central carbon atom[16,71,76]. The reduced reactivity of aromatic polyfluoroketones under the conditions of acid catalysis, caused by their low basicity, is also manifested under very severe conditions, compared with the non-fluorinated analogues, in the synthesis of 2,4-dinitrophenylhydrazones[39,71]:



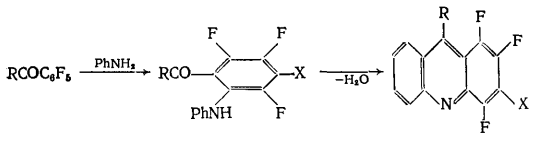
Aromatic polyfluoroketones react with ammonia and aliphatic amines with substitution of one or several fluorine atoms by the corresponding amino-groups, exhibiting at the same time a higher reactivity than hexafluorobenzene[48,77-79]. A preferential *para*-directing effect is shown in a polar medium, while the reaction is a non-polar solvent can lead to an increased content of the *ortho*-isomer in the product[77]:



The interaction of polyfluoro-substituted aceto- and benzophenones with aromatic amines in aromatic solvents proceeds only via the substitution of fluorine by the arylamino-group. The isomeric composition of the reaction product depends on the structure of the initial ketones and on the polarity of the medium[80-82]:



When the reaction of aromatic polyfluoroketones with aniline is carried out without a solvent in the presence of an excess of aniline, somewhat different results are obtained. The main reaction products are in this case polyfluoroacridines, the formation of which can be represented schematically in the following manner[80]:



The unusual conditions of the intramolecular cyclisation of *o*-anilinoketones, which usually occurs in acid media, are striking[83]. Presumably in this instance the $PhNH_3^+$ ions, formed as a result of the nucleophilic substitution of fluorine, play the role of the acid catalyst. Accordingly, the addition of potassium carbonate to the reaction mixture prevents the formation of acridines[80,81].

† Henceforth the positions of the fluorine atoms in 2,3,4,5,6-pentafluoroacetophenone and 2,3,4,5,6-pentafluorobenzophenone will not be indicated in this review.

# 2,4-DNPH = 2,4-dinitrophenylhydrazine [2,4-$(NO_2)_2C_6H_3$.$NHNH_2$].

The study of the interaction of aromatic polyfluoroketones with aniline showed that nucleophilic addition to the carbonyl group, leading to the formation of anils, takes place to an appreciable extent only for octafluoroacetophenone[80]. A method of synthesising anils from other ketones of this series has been recently discovered[84]. It consists in the interaction of the ketone with aniline in benzene or chlorobenzene in the presence of anhydrous aluminium chloride. The role of the latter evidently reduces to the activation of the carbonyl group with respect to nucleophilic attack as a result of complex formation via the oxygen atom:

$$C_6F_5COR \xrightarrow[C_6H_6 \text{ or } C_6H_5Cl]{PhNH_2,\ AlCl_3} C_6F_5C(R)=NPh\ ;\quad R=Me,\ Ph,\ \text{or}\ C_6F_5\ .$$

## 2. Reactions with *O*-Nucleophiles

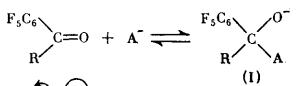
Aliphatic perfluoro-substituted aldehydes and ketones, in which the electrophilic properties of the carbonyl group are greatly enhanced as a result of the strong electron-accepting influence of the perfluoroalkyl groups, react extremely readily with compounds of the type ROH (R = H or alkyl), forming geminal addition products[72,73,85].

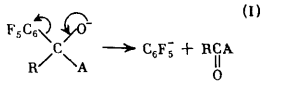
Decafluorobenzophenone, which is an aromatic perfluoroketone, does not form a hydrate[16]. In contrast to its non-fluorinated analogue, pentafluorobenzaldehyde reacts with methanol in the absence of acid to form a hemiacetal. Its acetals have been obtained only after prolonged refluxing with alcohols in the presence of concentrated hydrochloric acids[64]. The use of orthoformic ester instead of alcohol made it possible to obtain a high yield of the diethyl acetal of pentafluorobenzaldehyde[69].

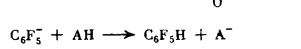
In contrast to its non-fluorinated analogue, pentafluorobenzaldehyde exhibits a very high tendency towards the haloform decomposition; under the conditions of the Cannizzaro reaction, it is cleaved with formation of pentafluorobenzene and formic acid[16,86]. 4-X-tetrafluorobenzaldehydes[64] as well as aromatic polyfluoroketones[16,38,45,71] undergo a similar reaction in an alkaline medium. Among the latter, the highest reactivity is shown by decafluorobenzophenone, which decomposes at room temperature under the influence of 10% KOH:[71]

$$C_6F_5COC_6F_5 \xrightarrow[H_2O,\ 20^\circ]{KOH} C_6F_5H + C_6F_5CO_2H\ .$$

The mechanism of the cleavage of aromatic polyfluoro-substituted carbonyl compounds is in all probability analogous to that proposed earlier for the decomposition of non-enolising ketones in an alkaline medium[87]:


(1)


(2)


(3)

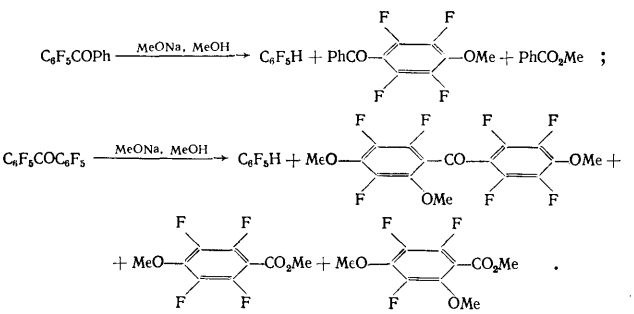
The increased tendency of aromatic polyfluoroketones to undergo cleavage compared with their non-fluorinated analogues can be explained by the more marked electrophilic properties of the carbon atom of the carbonyl group and also by the possibility of the elimination of the stable pentafluorophenyl anion. The relative ease of decomposition of decafluorobenzophenone is evidently caused by the favourable energy change in stage (2) in consequence of the steric strain in the intermediate anion (I) and also the electron shift, indicated in the above scheme by arrows, under the influence of the two electron-accepting pentafluorophenyl groups.

The mode of the cleavage reaction is determined by the relative stability of the carbanions, which are potential leaving groups. A detailed analysis of the products of the cleavage of aliphatic-aromatic polyfluoroketones, carried out by Coe et al.[38] (see Table), confirmed this view. The relative stability of the anions corresponding to the hydrocarbons formed decreases in the sequence [8,88] $CCl_3^- > C_6F_5^- > CF_3^- > C_6H_5^-$.

The haloform decomposition of aliphatic-aromatic fluoroketones (4 *N* KOH, refluxing for 4 h).[38]

| Initial ketone | Reaction product | |
|---|---|---|
| | hydrocarbon | acid |
| $C_6F_5COMe$ | $C_6F_5H$ | $MeCO_2H$ |
| $C_6F_5COCH_2Br$ | $C_6F_5H$ | $BrCH_2CO_2H$ |
| $C_6F_5COCHCl_2$ | $C_6F_5H$ | $Cl_2CHCO_2H$ |
| $C_6F_5COCF_3$ | $C_6F_5H$ | $CF_3CO_2H$ |
| $C_6F_5COCCl_3$ | $CHCl_3$ | $C_6F_5CO_2H$ |
| $C_6H_5COCF_3$ | $CHF_3$ | $C_6H_5CO_2H$ |

The haloform decomposition reaction is extremely characteristic of aromatic polyfluoro-substituted carbonyl compounds and proceeds in the presence of not only aqueous alkali but also of other charged nucleophiles. It is possible that this process is in fact the cause of the low yield of 4-methoxytetrafluorobenzaldehyde, obtained by the reaction of pentafluorobenzaldehyde with sodium methoxide in methanol[64]. In contrast to their non-fluorinated analogue, which is stable under the conditions of prolonged refluxing with sodium methoxide in methanol, penta- and deca-fluorobenzophenones undergoe reactions of two kinds in this medium at room temperature; nucleophilic substitution of fluorine atoms by methoxy-groups and cleavage with elimination of the pentafluorophenyl residue and the formation of methyl esters of benzoic and pentafluorobenzoic acids[38,89]:



In order to reduce the extent of the second process and to increase the yield of methoxy-ketones, one must prevent the presence of an excess of sodium methoxide in the reaction mixture[62].

## 3. Reactions with Sulphur Compounds

Pentafluorobenzaldehyde forms a bisulphite compound on being shaken with a saturated solution of sodium bisulphite[16]. Its equimolar mixture with thiophenol in acetone gives rise to a crystalline hemithioacetal partly dissociated into the initial components on dissolution in carbon tetrachloride or acetone[64].

On the other hand, according to other data[90], pentafluorobenzaldehyde does not react appreciably, like its non-fluorinated analogue, with propane-1-thiol in methylene chloride solution in the absence of acid; the addition of the latter leads to the formation of the thioacetal. The diethyl thioacetal has been obtained from pentafluorobenzaldehyde by reaction with ethanethiol in the presence of concentrated hydrochloric acid[64] or with phenyldi(ethylthio)borane[91].

$$C_6F_5CHO + PhB(SEt)_2 \rightarrow 1/3\,(PhBO)_3 + \underset{(45\%)}{C_6F_5CH(SEt)_2} \quad .$$

Several examples of the nucleophilic substitution of fluorine in pentafluorobenzaldehyde by sulphur-containing residues are known[64]. 4-Mercaptotetrafluorobenzaldehyde has been obtained in 61% yield by the reaction of pentafluorobenzaldehyde with sodium hydrogen sulphide in dimethylformamide (DMF) at 0 °C. The reaction with sodium thiophenoxide in DMF proceeds with evolution of heat and the substitution of all five fluorine atoms by PhS groups; in methanol the main reaction product is 4-phenylthiotetrafluorobenzaldehyde (yield 68%).[64]

The interaction of aromatic polyfluoro-sbustituted aldehydes and ketones with sulphur tetrafluoride leads to the substitution of the carbonyl oxygen atom by two fluorine atoms. The reaction conditions depend on the structure of the initial carbonyl compound and the introduction into its molecule of electron-accepting groups leads to a decrease of reactivity. The reaction with perfluoroketones requires either a high temperature or the presence of acid catalysts. This reaction can serve as a method for the preparation of polyfluorinated hydrocarbons containing fluorine atoms in both the aromatic ring and in the side chain, which are otherwise difficult to obtained:

$$C_6F_5COR \xrightarrow{SF_4} C_6F_5CF_2R \quad ;$$

R=H, 140—170°, yield 51%[92] or 100°, HF, 80%[93]; R=Me, 115°, 79%[93];

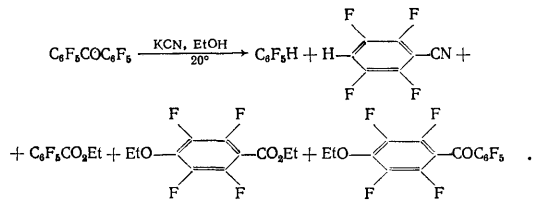
R=$CF_3$, 170°, HF, 85%[93]; R=$Alk_F$, 180°, $AlF_3$, 90%[91,94];

R=Ph, 180°, 40%[95]; R=$C_6F_5$, 235°, 88%[95].

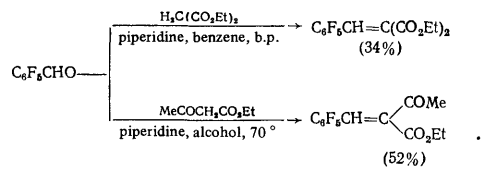
## 4. Reactions with *C*-Nucleophiles

(a) *Reactions with pseudoacids.* In contrast to its non-fluorinated analogue, pentafluorobenzaldehyde does not undergo the benzoin condensation with potassium cyanide in aqueous alcoholic solution[86]. Its cyanohydrin has been obtained in a low yield by the reaction of the bisulphite derivative with NaCN in aqueous solution[20].

In contrast to hexafluoroacetone, which forms stable cyanohydrin salts on interaction with sodium or potassium cyanides in tetrahydrofuran[96], aromatic polyfluoroketones remain unchanged on being refluxed with KCN in this solvent. In alcohol the reaction proceeds in several ways, the main one involving the haloform decomposition of the initial ketone and also of the product of the substitution of the *p*-fluorine atom of the carbonyl group can be in this instance either the cyanide ion or the $EtO^-$ ion. The presence of the latter in the reaction mixture is indicated by the formation of the corresponding nucleophilic substitution products. Among aromatic polyfluoroketones, the most reactive is decafluorobenzophenone, which forms a complex mixture of products on reaction with KCN in alcohol at room temperature[44]:



Polyfluorobenzaldehydes undergo aldol condensation with compounds containing active methyl or ethylene groups, exhibiting the usual reactivity or a reactivity which is somewhat reduced compared with its non-fluorinated analogues. Pentafluorobenzaldehyde reacts with malonic and acetoacetic esters in the pesence of piperidine under more severe conditions than does benzaldehyde, forming the corresponding α,β-unsaturated carbonyl compounds[97]:



2,3,4,5-Tetrafluorocinnamic acid has been obtained by the reaction of 2,3,4,5-tetrafluorobenzaldehyde with malonic acid (in pyridine, in the presence of piperidine)[19]. On the other hand, the initial condensation product (the hydroxy-acid) was obtained under similar conditions from pentafluorobenzaldehyde and then converted into 2,3,4,5,6-pentafluorocinnamic acid by heating with concentrated $H_2SO_4$.[16]

Pentafluorobenzaldehyde could not be made to undergo the Claisen–Schmidt reaction with acetone and acetaldehyde in the presence of aqueous alkali[97]. In alcoholic solutions of alkalis the reaction with acetone leads to a low yield of 2,3,4,5,6-pentafluorobenzylideneacetone and its *p*-alkoxy-derivative[98]:

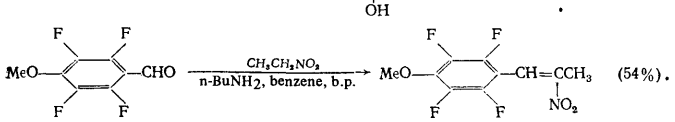
$$C_6F_5CHO \xrightarrow[HO^-,\,ROH]{(CH_3)_2CO} \underset{(6—13\%)}{C_6F_5CH{=}CHCOCH_3} + \underset{(26\%)}{n\text{-}ROC_6F_4CH{=}CHCOCH_3} \quad .$$

The condensation of pentafluorobenzaldehyde with acetaldehyde was achieved only in an anhydrous medium in the presence of piperidine and the formation of the aldol (II) was detected[97]:

$$C_6F_5CHO \xrightarrow[\text{piperidine, }35°]{CH_3CHO} \underset{OH\ (II)}{C_6F_5CHCH_2CHO} \xrightarrow{I_2} C_6F_5CH{=}CHCHO \quad (47\%) \, .$$

The increased stability of the aldol addition products, obtained from pentafluorobenzaldehyde, is in all probability due to the electron-accepting influence of the pentafluorophenyl group, which hinders dehydration by increasing the amount of double bond character of the C=O linkage and strengthening it[16,97]. The formation of nitroalcohols instead of nitro-olefins from pentafluorobenzaldehyde and nitroalkanes when the reaction is carried out in aqueous alcoholic alkali at 0 °C can be explained similarly[34,99,100]. More severe reaction conditions are essential for the synthesis of nitro-olefins[23]:

$$C_6F_5CHO \xrightarrow[MeOH—H_2O,\ 0°]{CH_3NO_2,\ NaOH} \underset{OH}{C_6F_5CHCH_2NO_2} \quad (78\%) \quad ;$$



Pentafluorobenzaldehyde has been successfully made to undergo the Perkin reaction[16]:

$$C_6F_5CHO \xrightarrow[130^\circ]{(CH_3CO)_2O,\ CH_3CO_2K} C_6F_5CH{=}CHCO_2H \quad (36\%)\ .$$

The interaction with 2,3,4,5,6-pentafluorophenylacetic acid gives rise to decafluoro-α-phenylcinnamic acid with an admixture of 3-pentafluorophenyl-5,6,7,8-tetrafluorocoumarin, which is apparently a product of the subsequent reaction of the latter[101]:

$$C_6F_5CHO + C_6F_5CH_2CO_2H \xrightarrow[Et_3N,\ b.p.]{(CH_3CO)_2O} C_6F_5CH{=}C(C_6F_5)CO_2H + \underset{(2\%)}{\text{coumarin}}\ .$$

(64%)

The condensation of polyfluorobenzaldehydes with thiocyanogen[18] and hippuric acid[102–104] has been described. A complex mixture of products has been obtained from pentafluorobenzaldehyde and 2,3,4,5,6-pentafluorophenylacetonitrile in dimethoxyethane in the presence of KF.[105]

The reaction of pentafluorobenzaldehyde with acetophenone in aqueous alcoholic alkali leads to the formation of 2,3,4,5,6-pentafluorobenzylideneacetophenone[27,97]. Pentafluoroacetophenone can serve as the methylene component; the concentration of alkali should not exceed 1.5% to avoid the subsequent haloform decomposition of decafluorobenzylideneacetophenone into pentafluorobenzene and pentafluorocinnamic acid:

$$C_6F_5CHO + CH_3COAr \xrightarrow[\text{aq. alcohol}]{NaOH} C_6F_5CH{=}CHCOAr\ ;$$
$$Ar = Ph \text{ or } C_6F_5\ .$$

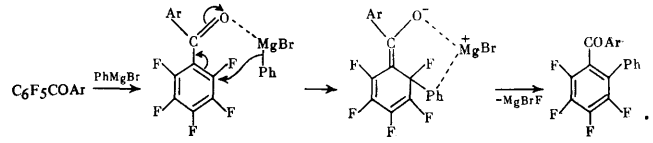
The condensation of pentafluoroacetophenone with aromatic aldehydes can proceed in the presence of a strong protic acid, but in this case it is accompanied by the interaction of the resulting benzylideneacetophenones with the initial ketone, which leads to the formation of pentafluorophenylpyrylium salts[106].

The use of pentafluoroacetophenone as the methylene component in condensation reactions with aromatic and aliphatic acid esters has been described[28,107,108].

On the basis of general ideas concerning the mechanisms of the reactions of carbonyl compounds with C–H acids[109], presumably the enolic form of pentafluoroacetophenone, which can be formed under the influence of both a base and an acid§, can serve as an intermediate in the reactions of this compound described above regardless of the medium. The ambident behaviour of the aromatic fluorine atom of the enolate pentafluoroacetophenone anion, obtained by the reaction of sodium hydride in polar aprotic solvents, has been demonstrated[111] in a nucleophilic substitution reaction:

$$C_6F_5COCH_3 + C_6F_5CF_3 \xrightarrow[\text{diglyme}]{NaH} p\text{-}CF_3C_6F_4CH_2COC_6F_5 + p\text{-}CF_3C_6F_4OC{=}CH_2\ .$$
$$\qquad\qquad\qquad

ketone and a PhMgBr molecule[116], which is promoted when weakly polar ethyl ether is used as the solvent:



(III)

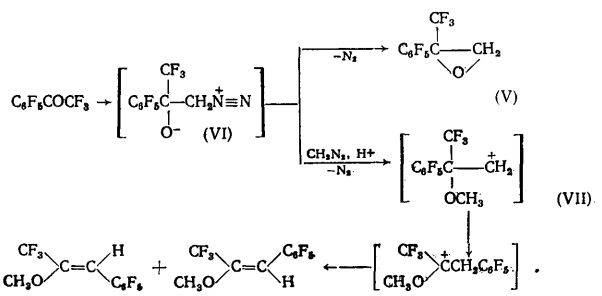
Methylmagnesium iodide, whose reactions via the carbonyl group are less sensitive to steric hindrance[118], reacts with polyfluorobenzophenones and also with octafluoroacetophenone mainly via the carbonyl group with formation of tertiary alcohols[117,119]. On the other hand, the reaction of pentafluoroacetophenone with methylmagnesium iodide is complicated by the aldol condensation. The diol (IV) isolated is a product of the interaction of the intermediate aldol with the reagent:

$$C_6F_5COMe \xrightarrow[\text{ether, } 20^\circ]{MeMgI} \underset{\substack{|\\OH}}{C_6F_5CMe_2} + \underset{\substack{|\\OH}}{C_6F_5(Me)}\underset{\substack{|\\OH}}{CCH_2}\underset{\substack{|\\OH}}{C(Me)}C_6F_5$$

(32%) (IV)

The interaction of aromatic polyfluoro-substituted carbonyl compounds with organolithium compounds has been little investigated. It has only been shown that aromatic polyfluoroketones react with pentafluorophenyl-lithium via the carbonyl group with formation of tertiary alcohols[120,122]. Presumably their interaction with other organolithium compounds is complicated by the reaction involving the substitution of fluorine atoms.

(c) *Reactions with diazomethane.* Acetophenone reacts with diazomethane at an appreciable rate only in the presence of an acid catalyst[123]. Pentafluoroacetophenone also remains unchanged when the reaction is carried out in ether at room temperature without added catalyst[124]. Like aliphatic polyfluoroketones[125], octafluoroacetophenone reacts readily with diazomethane in an ethereal solution at 0 °C, being wholly converted into a mixture of substances whose main component is 1-pentafluorophenyl-1-trifluoromethylepoxyethane (V).[124] Furthermore, the geometrical isomers of 1-methoxy-2-pentafluorophenyl-1-trifluoromethylethylene have been isolated from the mixture. They are not products of the conversion of the epoxide (V), since it has been established that the latter is resistant to the action of diazomethane at room temperature. Their formation can be represented by the following scheme, which includes stages where the intermediate species (VI) is methylated with subsequent rearrangement of the carbonium ion (VII) via the migration of the $C_6F_5$ group to a neighbouring electron-unsaturated carbon atom:



(V) (VI) (VII)

The possibility of such migration has been confirmed in relation to the acid-catalysed conversion of decafluorodiphenylacetaldehyde into decafluorodeoxybenzoin[33].

## 5. Reactions with Phosphorus Compounds

Like other aromatic aldehydes containing electron-accepting substituents[126], pentafluorobenzaldehyde readily reacts with tris(dimethylamino)phosphine to give a mixture of diastereoisomeric oxides of decafluorostilbene[33]:

$$2C_6F_5CHO + (Me_2N)_3P \rightarrow C_6F_5CH\text{—}CHC_6F_5 + (Me_2N)_3P{=}O$$

(O)

Triphenylphosphine imine causes the haloform decomposition of octafluoroacetophenone in ether at room temperature[71]:

$$C_6F_5(CF_3)C{=}O \xrightarrow[\text{ether, } 20^\circ]{Ph_3P{=}NH} C_6F_5H + CF_3CON{=}PPh_3$$

A similar reaction has been observed[127] in an attempt to explain the imine of nitroperfluoroacetone. The interaction of octafluoroacetophenone and also 4-anilineheptafluoroacetophenone with triphenylphosphine *N*-phenylimine, which is less nucleophilic than $Ph_3{=}NH$, led to the formation of their anils[71]:

$$Ar_F(CF_3)C{=}O \xrightarrow[\text{ether}]{Ph_3P{=}NPh} Ar_F(CF_3)C{=}NPh \quad (58\text{—}83\%)$$

$Ar_F = C_6F_5$ or *p*-$PhNHC_6F_4$.

Pentafluoroacetophenone and pentafluorobenzophenone do not react with triphenylphosphine *N*-phenylimine on refluxing in ether. Decafluorobenzophenone reacts with the latter compound to form a very complex mixture of products from which *p*-anilinononafluorobenzophenone was isolated[71] in a low yield. The ability of triphenylphosphine *N*-phenylimine to substitute fluorine via a nucleophilic mechanism had been pointed out earlier[128].

Pentafluorobenzaldehyde reacts with pentafluorophenyl- and pentafluorobenzoylmethylenetriphenylphosphoranes, the corresponding products of the reaction via the carbonyl group being formed[129,130]:

$$C_6F_5CHO \xrightarrow{RCH{=}PPh_3} C_6F_5CH{=}CHR \quad (32\text{—}50\%)$$

$R = C_6F_5$ or $C_6F_5CO$.

The attempt to carry out the Wittig reaction between aromatic polyfluoroketones and methylenetriphenylphosphorane led to their haloform decomposition[71]. Phosphorus pentachloride reacts with pentafluorobenzaldehyde and octafluoroacetophenone to form the corresponding dichloro-derivatives:

$$C_6F_5(R)C{=}O \xrightarrow[100^\circ]{PCl_5} C_6F_5(R)CCl_2$$

R=H, yield 100%[16];

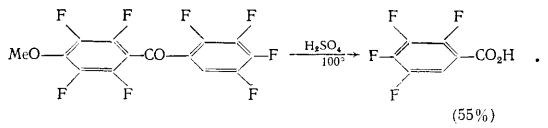
$R = CF_3$, yield 87%[38].

The resistance of decafluorobenzophenone to the action of $PCl_5$ under severe conditions has been noted[131].

## 6. Oxidation Reactions

Only a few examples of the oxidation of polyfluorobenzaldehydes to the corresponding acids are known. Pentafluorobenzaldehyde is oxidised smoothly to pentafluorobenzoic acid in oxygen at 110 °C.[16] The oxidation can be carried out under the influence of potassium or sodium dichromate in sulphuric acid at 100 °C. This method is convenient and can be used in the preparative synthesis of polyfluorobenzoic acid[132] and also for the oxidation of other polyfluorobenzaldehydes[19,69] or their diacetals[69]. It has been shown[45] that *p*-methoxy-2,2',3,3',4,5,5',6-octafluorobenzophenone undergoes oxidative cleavage with formation of 2,3,4,5-tetrafluorobenzoic

acid on heating with concentrated sulphuric acid at 100 °C:



(55%)

### 7. Reduction Reactions

The reduction reactions of aromatic polyfluoro-substituted carbonyl compounds take place under the usual conditions, but are in many instances complicated by the side processes.

Polyfluorobenzaldehydes are reduced to the corresponding alcohols by refluxing with Raney nickel in alcohol[64] and with lithium tetrahydroaluminate in ether at 20 °C.[16,22] Decafluorodiphenylmethanol has been obtained in a low yield by the reaction of decafluorobenzophenone with $LiAlH_4$.[131] When this method of reduction is used for aromatic polyfluoro-substituted carbonyl compounds, one should bear in mind that the reaction may be accompanied by the substitution of the *o*-fluorine atom by hydrogen[42].

The reduction of decafluorobenzophenone with hydriodic acid in the presence of red phosphorus at 170–200 °C yielded bis(pentafluorophenyl)methane[131]. At the instant of evolution (Zn + acetic acid) hydrogen reduces this ketone to decafluorodiphenylmethanol, while pentafluorobenzophenone is reduced to the corresponding pinacol[40]. The reduction of pentafluorobenzaldehyde by metallic zinc in the presence of hydrochloric acid in alcohol did not lead to the formation of the expected decafluorohydrobenzoin, the corresponding acetal of the initial aldehyde being produced instead[86]:

$$3C_6F_5CHO \xrightarrow[\text{alcohol}]{Zn+HCl} C_6F_5CH\langle^{OCHC_6H_5}_{OCHC_6F_5} \quad (78\%)$$

The photochemical reduction of aromatic ketones is a convenient preparative method for the synthesis of pinacols. The ability of carbonyl compounds to undergo photochemical reduction depends mainly on the nature of the lowest triplet state and its energy. A high efficiency of the intercombination transition is characteristic of decafluorobenzophenone as well as its non-fluorinated analogue and the $n,\pi^*$-triplet state has the lowest energy[133]. Its energy in polar and non-polar media is close to that of the corresponding excited state of benzophenone.

The initial stages of the photochemical reduction of decafluorobenzophenone, involving the abstraction of a hydrogen atom from the medium and the formation of a ketyl radical, are analogous to the reactions of benzophenone, but they are much faster owing to the higher polarisation of the charge in the triplet state caused by the inductive effect of the fluorine atoms. The EPR spectrum of the radical obtained by the ultraviolet irradiation of decafluorobenzophenone in alcohol at 80 °C in the cuvette of the EPR spectrometer has been described[134] and agrees fully with the calculated spectrum. The addition of sodium methoxide to the irradiated solution enabled the authors[135] to observe the EPR spectrum of the corresponding radical-anion. Unsuccessful attempts to obtain the latter had been reported earlier[136,137].

The ketyl radicals generated by irradiating decafluorobenzophenone in cyclohexane undergo recombination and radical–radical aromatic substitution reactions to give a tertiary alcohol and cyclohexylnonafluorobenzophenones[133]:

$$(C_6F_5)_2C{=}O \xrightarrow{h\nu} (C_6F_5)_2\dot{C}{-}\dot{O} \xrightarrow{RH} (C_6F_5)_2\dot{C}{-}OH \rightarrow C_6H_{11}\overset{OH}{\overset{|}{C}}(C_6H_5)_2 +$$
$$+ C_6F_5COC_6F_4C_6H_{11}\text{-}n + C_6F_5COC_6F_4C_6H_{11}\text{-}o \quad .$$

In contrast to its non-fluorinated analogue, decafluorobenzophenone does not give rise to perfluoropinacol (VIII) on irradiation in a hydrocarbon medium or in isopropyl alcohol even in the presence of reducing agents[40,133,138–140]. Evidently the dimerisation of ketyl radicals is difficult owing to the repulsion of the $C_{ortho}$–F bond dipoles and also owing to the shift of the unpaired electron density to the ring as a result of the electron-accepting influence of the fluorine atoms.

The pinacol (VIII) has been obtained by the photolysis of a solution of decafluorobenzophenone in perfluoromethylcyclohexane containing isopropyl alcohol[141]. It is unstable and decomposes in alcohols with formation of decafluorobenzophenone and decafluorodiphenylmethanol; in ether and hydrocarbons this process is much slower. The pinacols (IX) and (X), obtained by the photochemical reduction of octafluoroacetophenone[142] and pentafluorobenzophenone[40], are stable compounds:

$$C_6F_5COR \xrightarrow{h\nu} C_6H_5(R)\,C(OH){-}C(OH)(R)\,C_6F_5 \quad ;$$

(VIII), R=$C_6F_5$ (в $C_7F_{14}$); (IX), R=Ph in n-hexane–isopropyl alcohol mixture, (X), R=$CF_3$ in isopropyl alcohol.

The possibility of the formation of radicals of the ketyl type on joint irradiation of aromatic polyfluoroketones and bis(triethylgermyl)mercury in benzene solution has been demonstrated[143]:

$$C_6F_5COR \xrightarrow[\text{benzene}]{h\nu,(Et_3Ge)_2Hg} C_6F_5(R)\,\dot{C}{-}OGeEt_3 \quad R=C_6F_5,\ Ph,\ \text{or}\ CF_3 \quad .$$

The study of the photolysis of pentafluorobenzaldehyde in the vapour phase showed that, like benzaldehyde, it undergoes decarbonylation with formation of pentafluorobenzene and carbon monoxide via intramolecular elimination [reaction (4)] and radical decomposition [reaction (5)] reactions. The involvement of both singlet and triplet excited states has been postulated[144]:

$$C_6F_5CHO \rightarrow C_6F_5H + CO \quad ; \qquad (4)$$

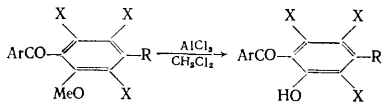
$$C_6F_5CHO \rightarrow \dot{C}_6F_5 + \dot{C}HO \quad . \qquad (5)$$

## IV. AROMATIC *o*-HYDROXY- AND *o*-AMINO-SUBSTITUTED POLYFLUOROKETONES

Intramolecular reactions involving the nucleophilic substitution of fluorine, which made it possible to obtain polyfluorobenzoheterocycles of various kinds, play an important role in the chemistry of aromatic and heterocyclic polyfluoro-compounds[145]. The use for this purpose of *o*-hydroxy- and *o*-hydro-substituted polyfluorobenzophenones, the methods of preparation and cyclisation reactions which will be examined in this section, has been described.

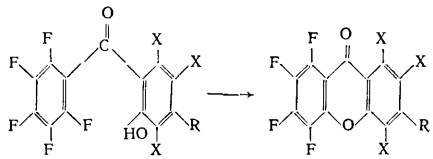
The synthesis of 2-hydroxypolyfluorobenzophenones by the nucleophilic substitution of a fluorine atom by the hydroxy-group or by the methoxy-group with subsequent demethylation is hindered by the haloform cleavage of aromatic polyfluoroketones. Thus the yield of 2,4-dimethoxy-3,5,6-trifluorobenzophenone in the reaction of pentafluorobenzophenone with sodium methoxide in methanol is extremely low[36]. The method based on the interaction of pentafluorophenylmagnesium bromide with *o*-methoxy-substituted carbonyl compounds is preparatively the most convenient. The demethylation of *o*-methoxybenzophenones is readily achieved under the influence of anhydrous aluminium chloride in methylene

chloride[36]:



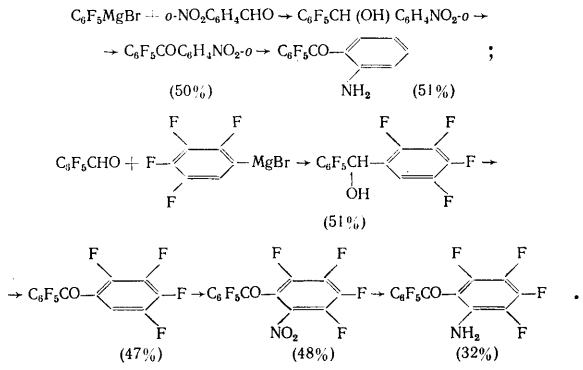
Ar=Ph or $C_6F_5$, X=H or F; R=H, MeO, or OH .

The presence of an intramolecular hydrogen bond, whose strength is comparable to that in non-fluorinated analogues, has been established in 2-hydroxypolyfluorobenzophenones by infrared and ultraviolet spectroscopy and $^1H$ NMR.[49] They readily undergo the intramolecular nucleophilic substitution of fluorine, giving rise to polyfluoroxanthones. The much milder, compared with 2-halogeno-2-hydroxybenzophenones[146], conditions in the cyclisation reaction, which partly occurs on simple dissolution in aqueous alkali or in polar solvents such as DMF, are due to the high nucleophilic mobility of the fluorine atoms in aromatic polyfluoroketones. Polyfluoroxanthones have been obtained in high yields on refluxing 2-hydroxypolyfluorobenzophenones with anhydrous KF in acetone or under the influence of ignited potassium carbonate in DMF at room temperature[36]:

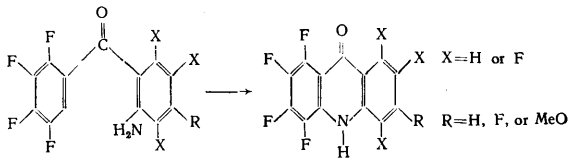


X=H or F; R=H, OH, or MeO .

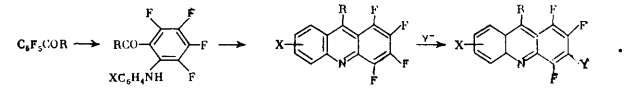
The reactions of aromatic polyfluoroketones with aqueous ammonia and aliphatic amines in organic solvents leads to the preferential substitution of the *p*-fluorine atom[48,77] and cannot therefore be used as a method for the synthesis of *o*-aminoketones. They were synthesised by the reduction of the corresponding nitro-compounds, which were obtained in their turn from aromatic carbonyl compounds and polyfluorophenylmagnesium bromides in accordance with the schemes presented below[41,43,45]:



2-Aminopolyfluorobenzophenones have been converted into polyfluoroacridones by electrolytic oxidation or by heating with KF in anhydrous DMF:[41,45]:



The above methods for the synthesis of polyfluoroacridine derivatives can be of no preparative value in view of the large number of their stages and their limited applicability. A more promising approach has been demonstrated in other studies[80,81,147,148]. It includes as the first stage the nucleophilic substitution of the *o*-fluorine atom in aromatic polyfluoro-substituted carbonyl compounds by an arylamino-group and makes it possible to obtain a large set of polyfluoroacridines from readily available aromatic polyfluoro-compounds:



Thus the chemical properties of aromatic polyfluoro-substituted aldehydes and ketones are to a large extent different from those of their non-fluorinated analogues. The presence in their molecules of several electron-accepting fluorine atoms not only alters their reactivity in relation to nucleophiles but also greatly complicates the reactions owing to the ease of the haloform decomposition with ejection of the relatively stable polyfluorophenyl anion, and also because of the possibility of the nucleophilic substitution of one or several fluorine atoms. This wide variety of chemical reactions of aromatic polyfluoro-substituted carbonyl compounds and their relative availability are responsible for the continued interest in these compounds by investigators and lead to wide possibilities for synthesis.

## REFERENCES


1. N.N.Vorzhtsov, Jr., Zhur.Vses.Khim.Obshch.im. Mendeleeva, **15**, 52 (1970).
2. G.G.Yakobson and V.M.Vlasov, Synthesis, 652 (1976).
3. L.S.Kobrina, Fluorine Chem.Rev., **7**, 1 (1974).
4. V.E.Platonov and G.G.Yakobson, Synthesis, 374 (1976).
5. R.Bolton and G.H.Williams, "Advances in Free-Radical Chemistry" (Edited by G.H.Williams), Elek Science, London, 1975, Vol.5, p.1.
6. L.S.Kobrina, Uspekhi Khim., **46**, 660 (1977) [Russ. Chem.Rev., No.4 (1977)].
7. V.M.Vlasov and G.G.Yakobson, Uspekhi Khim., **43**, 1642 (1974) [Russ.Chem.Rev., No.9 (1974)].
8. R.Filler, Fluorine Chem.Rev., **8**, 1 (1978).
9. P.H.Gore, "Friedel-Crafts and Related Reactions", (Edited by G.A.Olah), Interscience Publ., New York–London–Sydney, 1964, Vol.3, Part 1, p.1.
10. S.A.Anichkina, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Zhur.Obshch.Khim., **38**, 2493 (1968).
11. V.A.Koptyug, B.I.Mokrousov, and A.N.Rezvukhin, Zhur.Org.Khim., **4**, 662 (1968).
12. G.A.Olah and S.Kobayashi, J.Amer.Chem.Soc., **93**, 6964 (1971).
13. G.G.Furin and G.G.Yakobson, Izv.Sibir.Otd.Akad. Nauk SSSR, Ser.Khim.Nauk, No.2, Issue 1, 78 (1974).
14. Yu.Pozdnyakovich and V.D.Steingarts, J.Fluorine Chem., **4**, 317 (1974).
15. G.G.Furin, L.N.Shchegoleva, and G.G.Yakobson, Zhur.Org.Khim., **11**, 1290 (1975).
16. A.K.Barbour, M.W.Buxton, P.L.Coe, R.Stephens, and J.C.Tatlow, J.Chem.Soc., 808 (1961).
17. N.N.Vorozhtsov, Jr., V.A.Barkhash, N.G.Ivanova, S.A.Anichkina, and O.I.Andreevskaya, Dokl.Akad. Nauk SSSR, **159**, 125 (1964).
18. M.D.Castle, R.G.Plevey, and J.C.Tatlow, J.Chem.Soc. (C), 1225 (1968).
19. L.J.Belf, M.W.Buxton, and J.F.Tilney-Basset, Tetrahedron, **23**, 4719 (1967).

20. E.Nield, R.Stephens, and J.C.Tatlow, J.Chem.Soc., 166 (1959).
21. P.L.Coe, R.Stephens, and J.C.Tatlow, J.Chem.Soc., 3227 (1962).
22. R.Filler and E.W.Choe, J.Amer.Chem.Soc., **91**, 1862 (1969).
23. W.L.White and R.Filler, J.Chem.Soc.(C), 2062 (1971).
24. A.E.Jukes and H.Gilman, J.Organomet.Chem., **17**, 145 (1969).
25. A.F.Webb and H.Gilman, J.Organomet.Chem., **20**, 281 (1969).
26. A.E.Jukes, S.S.Dua, and H.Gilman, J.Organomet. Chem., **21**, 241 (1970).
27. R.Filler, V.D.Beaucaire, and H.H.Kang, J.Org.Chem., **40**, 935 (1975).
28. R.Filler, J.S.Rao, A.Biezais, F.N.Miller, and V.D.Beaucaire, J.Org.Chem., **35**, 930 (1970).
29. M.Schmeisser and M.Weidenbruch, Chem.Ber., **100**, 2306 (1967).
30. R.D.Chambers and J.A.Cunningham, J.Chem.Soc.(C), 2185 (1967).
31. P.L.Coe and A.Whittingham, J.Chem.Soc., Perkins Trans.I, 917 (1974).
32. R.D.Chambers and D.J.Spring, J.Chem.Soc.(C), 2394 (1968).
33. R.Filler and Y.S.Rao, J.Org.Chem., **39**, 3421 (1974).
34. N.B.Chapman, K.Clarke, R.M.Pinder, and S.N.Sawhney, J.Chem.Soc.(C), 293 (1967).
35. J.M.Birchall, R.N.Haszeldine, and M.E.Jones, J.Chem. Soc.(C), 1343 (1971).
36. E.G.Lubenets, T.N.Gerasimova, and E.P.Fokin, Zhur. Org.Khim., **7**, 805 (1971).
37. G.E.Ditchfield and A.E.Pedler, J.Fluorine Chem., **10**, 447 (1977).
38. P.L.Coe, R.G.Plevey, and J.C.Tatlow, J.Chem.Soc. (C), 597 (1966).
39. T.N.Gerasimova, T.N.Vasilevskaya, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Izv.Akad.Nauk SSSR, Ser Khim., 450 (1967).
40. R.Filler and H.H.Kang, J.Org.Chem., **40**, 1173 (1975).
41. C.M.Jenkins, A.E.Pedler, and J.C.Tatlow, Tetrahedron, **27**, 2557 (1971).
42. T.N.Gerasimova, N.V.Semikolenova, and E.P.Fokin, Zhur.Org.Khim., **14**, 100 (1978).
43. P.L.Coe, A.E.Jukes, and J.C.Tatlow, J.Chem.Soc.(C), 2020 (1966).
44. T.N.Vasilevskaya, A.G.Badashkeeva, T.N.Gerasimova, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Zhur.Org. Khim., **6**, 126 (1970).
45. D.M.Owen, A.E.Pedler, and J.C.Tatlow, J.Chem.Soc., Perkin Trans.I, 1380 (1975).
46. J.P.Collman and N.W.Hoffman, J.Amer.Chem.Soc., **95**, 2689 (1973).
47. S.A.Anichkina, G.S.Khramtsova, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Zhur.Obshch.Khim., **39**, 1766 (1969).
48. T.N.Gerasimova, E.G.Lokshina, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Zhur.Obshch.Khim., **37**, 1300 (1967).
49. E.G.Lubenets, Candidate's Thesis, Institute of General Chemistry, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1971.
50. T.N.Gerasimova, E.G.Lubenets, and V.A.Barkhash, Zhur.Org.Khim., **8**, 430 (1972).
51. V.V.Brovko, V.M.Vlasov, L.I.Kann, T.D.Petrova, V.A.Sokolenko, and G.G.Yakobson, Zhur.Org.Khim., **11**, 1042 (1975).
52. P.Sartori and M.Weidenbruch, Angew.Chem., **77**, 1076 (1965).
53. P.Sartori and M.Weidenbruch, Chem.Ber., **100**, 3016 (1967).
54. M.Schmeisser, P.Sartori, and M.Weidenbruch, German P.1 242 208 (1965); Chem.Abs., **67**, 73 364 (1967).
55. V.N.Odinokov, G.G.Yakobson, and N.N.Vorozhtsov, Jr., Zhur.Obshch.Khim., **37**, 176 (1967).
56. G.G.Yakobson, V.E.Platonov, and L.I.Kann, USSR P.413 772 (1972); Byul.Izobret., No.52, 167 (1975).
57. W.A.Sheppard, J.Amer.Chem.Soc., **92**, 5419 (1970).
58. W.A.Sheppard and C.M.Sharts, "Organic Fluorine Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1972, p.381.
59. D.B.Farmer and S.Walker, Trans.Faraday Soc., **63**, 966 (1967).
60. M.J.Aroney, G.Cleaver, R.K.Pierens, and R.J.W.Le Fèvre, J.Chem.Soc., Perkin Trans.II, 1854 (1976).
61. I.K.Korobeinicheva, A.K.Petrov, and V.A.Koptyug, "Atlas Spektrov Aromaticheskikh i Geterotsiklicheskikh Soedinenii" (Atlas of the Spectra of Aromatic and Heterocyclic Compounds), Izd.Nauka, Novosibirsk, 1967, No.1.
62. R.D.Chambers and D.J.Spring, Tetrahedron, **25**, 565 (1969).
63. G.A.Olah and J.K.Mo, J.Org.Chem., **38**, 2682 (1973).
64. E.V.Aroskar, P.J.N.Brown, R.G.Plevey, and R.Stephens, J.Chem.Soc.(C), 1569 (1968).
65. N.P.Buu-Hoi and G.Saint-Ruf, Bull.Soc.chim.France, 661 (1968).
66. L.J.Belf, M.W.Buxton, and G.Fuller, J.Chem.Soc., 3373 (1965).
67. V.P.Petrov and V.A.Koptyug, Reakts.Sposobn.Org. Soed., **3**, No.1 (7), 135 (1966).
68. T.N.Gerasimova, N.V.Semikolenova, and E.P.Fokin, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser.Khim.Nauk, No.4, Issue 2, 142 (1977).
69. V.I.Vysochin, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Zhur.Obshch.Khim., **39**, 1607 (1969).
70. A.T.Prudchenko and V.A.Barkhash, Zhur.Org.Khim., **6**, 727 (1970).
71. T.N.Vasilevskaya, Candidate's Thesis, Institute of General Chemistry, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1971.
72. N.P.Gambaryan, E.M.Rokhlin, Yu.V.Zeifman, Chen Cheng-Yun, and I.L.Knunyants, Angew.Chem., **78**, 1008 (1966).
73. C.G.Krespan and W.J.Middleton, Fluorine Chem.Revs., **1**, 145 (1967).
74. G.S.Shchegoleva, Candidate's Thesis, Institute of General Chemistry, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1971.
75. G.S.Shchegoleva and V.A.Barkhash, Izv.Sibir.Otd. Akad.Nauk SSSR, Ser.Khim.Nauk, No.14, Issue 6, 123 (1971).
76. R.Filler and A.E.Fiebig, Chem.Comm., 606 (1968).
77. L.S.Kobrina, G.G.Furin, and G.G.Yakobson, Zhur. Org.Khim., **6**, 512 (1970).
78. P.P.Rodionov and S.M.Shein, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser.Khim.Nauk, No.7, Issue 3, 86 (1971).
79. S.M.Shein and P.P.Rodionov, Kinetika i Kataliz, **14**, 1128 (1973).
80. T.N.Vasilevskaya, I.I.Baturina, M.I.Kollegova, T.N.Gerasimova, and V.A.Barkhash, Zhur.Org.Khim., **7**, 1230 (1971).
81. T.N.Gerasimova, L.L.Gelumbovskaya, I.I.Baturina, and E.P.Fokin, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser.Khim. Nauk, No.4, Issue 2, 88 (1973).
82. O.P.Sheremet, P.P.Rodionov, and S.M.Shein, Izv. Sibir.Otd.Akad.Nauk SSSR, Ser.Khim., No.14, Issue 6, 71 (1975).

83. R.M.Acheson, "Acridines", Interscience Publ., New York, 1956, p.39.
84. T.V.Fomenko, T.N.Gerasimova, and E.P.Fokin, Zhur. Vses.Khim.Obshch.im.Mendeleeva, **24**, 92 (1979).
85. H.P.Braendlin and E.T.McBee, "Advances in Fluorine Chemistry" (Translated into Russian), Izd.Khimiya, Leningrad, 1970, Vols.3–4, p.231.
86. N.N.Vorozhtsov, Jr., V.A.Barkhash, and L.M.Bova, Izv.Akad.Nauk SSSR, Ser.Khim., 362 (1966).
87. D.G.Davies, M.Derenberg, and P.Hodge, J.Chem.Soc. (C), 455 (1971).
88. K.J.Klabunde and D.J.Burton, J.Amer.Chem.Soc., **94**, 5985 (1973).
89. E.G.Lubenets, T.N.Gerasimova, V.V.Furov, and V.A.Barkhash, Zhur.Org.Khim., **6**, 365 (1970).
90. L.Field and B.J.Sweetman, J.Org.Chem., **34**, 1799 (1969).
91. R.H.Cragg and J.P.N.Husband, Inorg.Nuclear Chem. Letters, **6**, 773 (1970).
92. R.H.Mobbs, J.Fluorine Chem., **1**, 361 (1972).
93. B.G.Oksenenko, V.A.Sokolenko, V.M.Vlasov, and G.G.Yakobson, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser. Khim.Nauk, No.2, Issue 1, 102 (1970).
94. J.C.Tatlow and P.L.Coe, B.P.1 102 693 (1964); Chem. Abs., **69**, 43 602 (1968).
95. E.P.Fokin, T.N.Gerasimova, T.N.Vasilevskaya, I.I.Baturina, and K.I.Matoshina, Izv.Sibir.Otd.Akad. Nauk SSSR, Ser.Khim.Nauk, No.9, Issue 4, 135 (1971).
96. T.Mill, J.O.Rodin, R.M.Silverstein, and C.Woolf, J. Org.Chem., **29**, 3715 (1964).
97. N.G.Ivanova, V.A.Barkhash, and N.N.Vorozhtsov, Zhur.Obshch.Khim., **39**, 1347 (1969).
98. B.Unterhalt and U.Pindur, Arch.Pharm., **306**, 589 (1973); Chem.Abs., **79**, 136 717 (1973).
99. V.P.Petrov, V.A.Barkhash, G.S.Shchegoleva, T.D.Petrova, T.P.Savchenko, and G.G.Yakobson, Dokl.Akad.Nauk SSSR, **178**, 864 (1968).
100. V.V.Petrov and V.A.Barkhash, Zhur.Obshch.Khim., **39**, 1615 (1969).
101. V.P.Molosnova, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Zhur.Obshch.Khim., **39**, 1774 (1969).
102. G.V.Shishkin and V.P.Mamaev, Zhur.Obshch.Khim., **36**, 660 (1966).
103. A.T.Prudchenko, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser. Khim.Nauk, No.14, Issue 6, 95 (1970).
104. R.Filler, N.R.Ayyagar, W.Gustowski, and H.H.Kang, J.Org.Chem., **34**, 534 (1969).
105. V.M.Vlasov and G.G.Yakobson, Zhur.Obshch.Khim., **39**, 2071 (1969).
106. V.M.Vlasov, Izv.Sibir.Otd.Nauk SSSR, Ser.Khim.Nauk, No.4, Issue 2, 96 (1971).
107. J.F.Engel and C.C.Chappelow, J.Chem.Eng.Data, **16**, 381 (1971).
108. C.C.Chappelow and J.F.Engel, US.P.3 742 062 (1970); Chem.Abs., **79**, 78 395 (1973).
109. J.W.Baker, "Electronic Theories of Organic Chemistry: An Introductory Treatment" (Translated into Russian), Izd.Mir, Moscow, 1977, p.327.
110. V.M.Vlasov and G.G.Yakobson, Izv.Akad.Nauk SSSR, Ser.Khim., 893 (1969).
111. O.V.Zakharova, V.M.Vlasov, and G.G.Yakobson, Izv. Akad.Nauk SSSR, Ser.Khim., 1670 (1974).
112. V.A.Barkhash, O.I.Andreevskaya, and N.N.Vorozhtsov, Jr., Dokl.Akad.Nauk SSSR, **166**, 1343 (1966).
113. O.I.Andreevskaya, V.A.Barkhash, I.K.Korobeinicheva, E.D.Krivousova, V.A.Sokolenko, G.G.Yakobson, and L.M.Yan'kova, Zhur.Org.Khim., **6**, 711 (1970).
114. S.C.Cohen and A.G.Massey, "Advances in Fluorine Chemistry" (Edited by J.C.Tatlow, R.D.Peacock, and H.H.Hyman), London, 1970, Vol.6, p.83.
115. W.F.Beckert, "The IIIrd International Symposium on Fluorine Chemistry, Abstracts of Papers, Munich, 1965", p.200.
116. T.N.Gerasimova, I.I.Baturina, T.V.Fomenko, V.S.Chertok, V.F.Kollegov, and E.P.Fokin, Zhur.Org. Khim., **10**, 2166 (1974).
117. G.N.Gerasimova, T.V.Fomenko, and E.P.Fokin, Zhur. Org.Khim., **13**, 1562 (1977).
118. G.N.Gerasimova, T.V.Fomenko, and E.P.Fokin, Izv. Sibir.Otd.Akad.Nauk SSSR, Ser.Khim.Nauk, No.12, Issue 5, 100 (1975).
119. S.A.Pozdnyakovich, Candidate's Thesis, Institute of General Chemistry, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1971.
120. N.N.Vorozhtsov, Jr., V.A.Barkhash, T.N.Gerasimova, E.G.Lokshina, and N.G.Ivanova, Zhur.Obshch.Khim., **37**, 1293 (1967).
121. T.N.Gerasimova, A.G.Badashkeeva, E.G.Lubenets, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Zhur.Org. Khim., **5**, 2199 (1969).
122. R.Filler, Chen-Shen Wang, M.A.McKinney, and F.N.Miller, J.Amer.Chem.Soc., **89**, 1026 (1967).
123. H.O.House, E.J.Grubbs, and W.F.Gannon, J.Amer. Chem.Soc., **82**, 4099 (1960).
124. T.N.Vasilevskaya, T.N.Gerasimova, L.A.Kazbaeva, and V.A.Barkhash, Zhur.Org.Khim., **6**, 1645 (1970).
125. H.E.Simmons and D.W.Wiley, J.Amer.Chem.Soc., **82**, 2288 (1960).
126. V.Mark, J.Amer.Chem.Soc., **85**, 1884 (1963).
127. Yu.V.Zeifman, N.P.Gambaryan, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 450 (1965).
128. N.P.Gambaryan, E.M.Rokhlin, Yu.V.Zeifman, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 749 (1965).
129. V.P.Molosnova, V.I.Vysochin, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Izv.Akad.Nauk SSSR, Ser.Khim., 146 (1969).
130. V.M.Vlasov, Zhur.Vses.Khim.Obshch.im.Mendeleeva, **15**, 476 (1970).
131. N.N.Vorozhtsov, Jr., V.A.Barkhash, and S.A.Anichkina, Dokl.Akad.Nauk SSSR, **166**, 598 (1966).
132. V.M.Vlasov, G.F.Grebenshchikova, A.Ya.L'vova, and G.G.Yakobson, "Sintesy Ftororganicheskikh Soeninenii" (Syntheses of Organofluorine Compounds), Izd.Khimiya, Moscow, 1973, p.168.
133. J.Dedinas and T.H.Regan, J.Phys.Chem., **76**, 3926 (1972).
134. F.P.Sargent and M.G.Bailey, Canad.J.Chem., **76**, 3926 (1972).
135. F.P.Sargent and M.G.Bailey, Canad.J.Chem., **49**, 2350 (1971).
136. J.F.Brown and W.G.Williams, Trans.Faraday Soc., **64**, 298 (1968).
137. S.V.Kulkarni and C.Trapp, J.Amer.Chem.Soc., **92**, 4809 (1970).
138. N.Filipescu, J.P.Pinion, and E.L.Minn, Chem.Comm., 1413 (1970).
139. P.Margaretha, J.Gloor, and K.Schaffner, Chem.Comm., 565 (1974).
140. G.Gauglitz and U.Kolle, J.Photochem., **4**, 309 (1975).
141. J.Dedinas, J.Amer.Chem.Soc., **95**, 7172 (1973).
142. J.S.Chang, J.T.Price, A.J.Tomlinson, and C.J.Willis, Canad.J.Chem., **50**, 512 (1972).
143. D.V.Gendin, O.Ya.Kruglaya, T.I.Vakul'skaya, L.P.Petukhov, and N.S.Vyazankin, Zhur.Obshch.Khim., **47**, 1427 (1977).

144. J.R.Majer, S.-A.M.A.Naman, and J.C.Robb, Trans. Faraday Soc., **65**, 1846 (1969).
145. G.G.Yakobson, T.D.Petrova, and L.S.Kobrina, Fluorine Chem.Rev., **7**, 115 (1974).
146. M.Kulka, J.Amer.Chem.Soc., **76**, 5469 (1954).
147. T.N.Gerasimova, N.V.Semikolenkova, N.A.Orlova, T.V.Fomenko, and E.P.Fokin, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser.Khim.Nauk, No.14, Issue 6, 54 (1975).
148. N.A.Orlova, L.L.Dmitrieva, T.N.Gerasimova, and E.P.Fokin, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser.Khim. Nauk, No.7, Issue 3, 109 (1976).

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