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PRESENT-DAY CONDITION OF FLUOROAROMATIC COMPOUNDS PRODUCTION TECHNOLOGY

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Here we describe effectiveness of interphase transfer catalysts use to obtain polyfluoroarom compounds by potassium fluoride influence on polychlorbenzenes. Such catalysts hexaethylguanidine chloride, tetra-(diethylamino)- phosphonium bromide are involved stabilization of intermediate s-complex. Catalytic participation of polyethers (tetraethyleneglyc dimethyl ether, 18-crown-6) in fluorodechlorinating process doesn't go beyond increasing "active" fluoride-ion concentration. Here we consider the opportunities of mechanic and chem technology application to synthesize fluoroaromatic compounds by substituting chlorine for fluo in the solid phase of chloroaromatic compounds and fluorides of alkali, alkali-landed metals composite mixtures based on them. We also discuss the question regarding synthesi fluoroaromatic compounds out of commercial chladones (freons) and polyfluorolefines.

Contents

Introduction

The success of contemporary scientific and technical revolution using of its achievements in practice inseparably tied together and are to a great extent caused by the progress reached in the fields of new chem compounds synthesis and commercial production methods working out. All that can be explained by the fact the variety of structural, physical, and chemical characteristics of organic compounds and materials base them is much larger than of traditional non-organic products and metals. Fluororganic compounds at attention of many organic chemists and specialists of other fields of science because of their unique proper that determined the perspectives of their use to solve a number of chemistry principal theoretical issues industrial and medical goals. Being a new filed of organic chemistry, created solely by human's mind and ha

the chemistry of fluororganic compounds even by the present time has played an important role for the pro of several branches of industry, it also has produced new, unknown in the nature materials and compou possessing a number of specific properties. Mainly this refers to polyfluorinated organic molec Accumulating of fluorine atoms in carbon skeleton of molecule leads to formation of new properties. At that introduction of other elements atoms does not largely allow to reach them. It provides an opportunity to cr new fluorine materials. Poly-fluorinated compounds of aliphatic row found a most wide application, while fluoroaromatic derivatives are being used to a smaller extent in practice. It was considered, polyfluoroaromatic derivatives didn't have any practical value and were out of interest. However, time pr this statement incorrect. Thus, polyfluorobenzoic acids are widely used to create synthetic antibi (fluoroquinolones), pentafluorobrombenzene is used to synthesize tris(pentafluorophenyl)boron used as catalyst to create highly effective catalysts for polymerization of ethylene and propylene and to obtain st xenon compounds of the C-Xe bond. Octafluorotoluene is used as semi-product for synthesis of fluororub used for aviation and for synthesis of oxygen carriers ("blue blood") etc. This mainly is related to our relat narrow knowledge of them and lack of perfection in their obtaining methods. Only in recent years, the fie their practical application and of fluorine materials based on them began to develop intensively.

Poly-fluoroaromatic compounds are known for a rather long period of time as a class of aromatic compou In a contemporary development of polyfluoroaromatic compounds chemistry we can separate out two tendencies. First is related to search for synthesis methods of poly-fluoroaromatic derivatives and to studyin their reactivity. Here we have to mark the working out of a simple and most convenient obtaining metho hexafluorobenzene, which was carried out in the USSR by N.N. Vorozhtsov and G.G. Yakobson. The meth an exchange of chlorine atoms inside polychloroarenes for fluorine atoms under the influence of potas fluoride [1-3]. It had become a base for expanding a complex of researching regarding studying of fluoroaromatic compounds chemical characteristics and it had opened practically unlimited opportuniti create new materials based on them [1]. Second tendency is related to increased interest for hetero-org compounds posessing pentafluorophenyl ring.

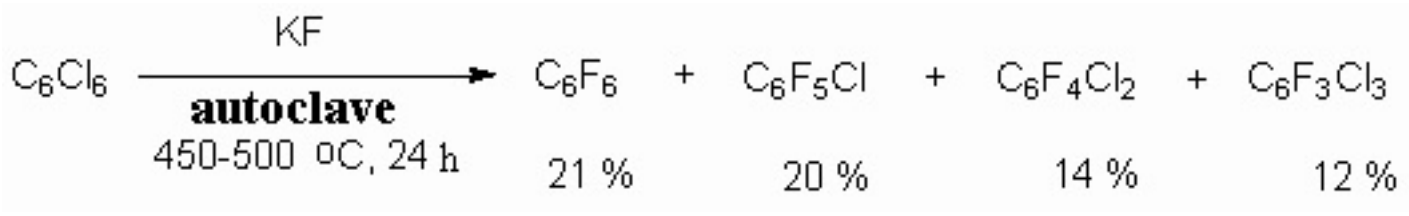
If an obtaining technology of polyfluorinated benzene derivatives has nevertheless been created, we can' so about low-fluorinated derivatives. Due to the limited number of obtaining methods of partly fluorin benzene derivatives the problem of working out approaches for synthesis of low-fluorinated benzene deriva is increasing. Such approach is justified by the fact, that many drugs, biologically active compounds, die contain one or two fluorine atoms. One of approaches to obtain them is use of poly-fluoraromatic compoun raw materials. That's why it is not surprising, that many works are devoted to their transformation into fluorinated.

Low- fluorinated benzenes are obtained using different methods, among which we can notice fluorin either by elemental fluorine in trifluoromethansulpho-acid [4], or in sulphuric acid [5], or by fluorine car according to Schiemann reaction in anhydrous hydrogen fluoride [6]. The analysis of these methods has carried out rather in details in monography [6] and here we do not review it.

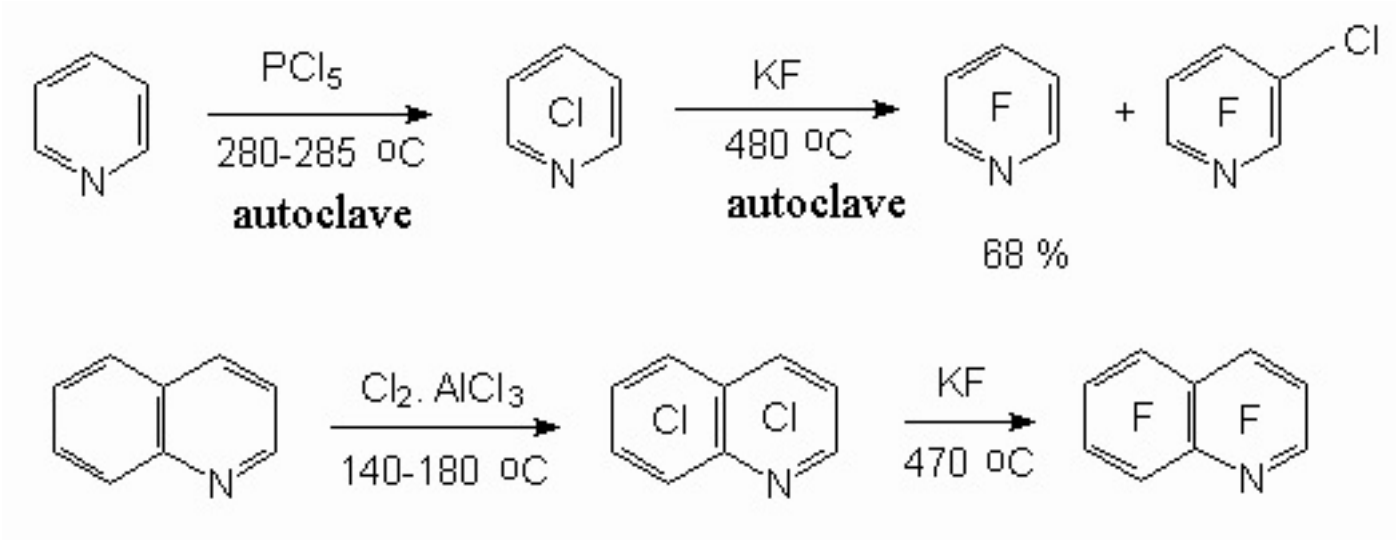
A simplified and more economical method of fluorobenzene manufacturing has been worked out. It is b on fluorination of benzene using anhydrous hydrogen fluoride and oxygen in the presence of CuF_2 catalyst [The process is carried out in tube nickel reactor in two stages. At first stage the copper oxide is being fluorin under the influence of anhydrous hydrogen fluoride till CuF_2 at 400 ^oC. At the second stage the flow of ben (2 cm^3/min) and nitrogen (20 cm^3/min) are being run through catalyst at 450-550 ^oC to produce fluoroben and to reduce CuF_2 up to metal copper. The selectivity of formation of fluorobenzene exceeds 95 %, conversion of benzene is 30% at 550 ^oC. The conversion of benzene is decreasing in time due to reducing C to metal, which covers the particles of catalyst.

The present method can also be used to synthesize other benzene low fluorine derivatives, for exa fluorotoluenes, difluorobenzenes [9], pyridine [8].

Key works regarding working out obtaining method of totally fluorinated hexafluorobenzene [1,2] octafluoronaphtalene [3] by anhydrous potassium fluoride influencing hexafluorobenzene octafluoronaphtalene in circulating autoclave at 450-500 ^oC were carried out under the direction of of VorozhtsovandG.G. Yakobson in Russia.

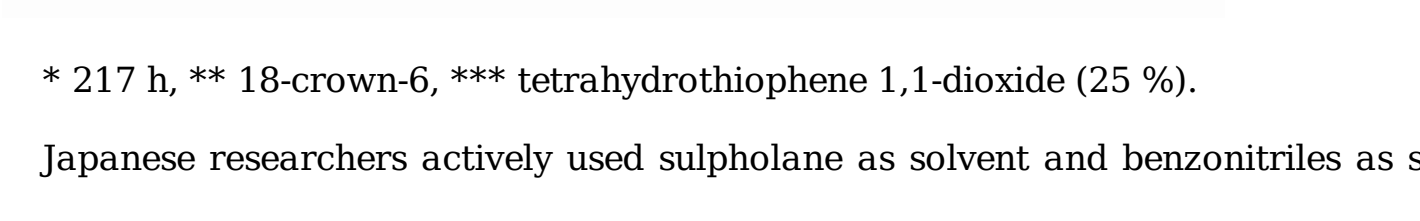


Method was used for heterocyclic compounds, for example pyridine [10-12] and quinoline derivatives [13].



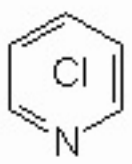
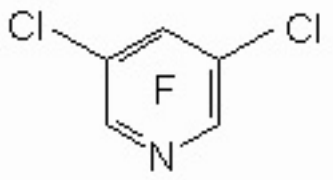
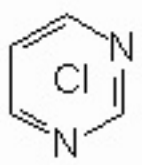
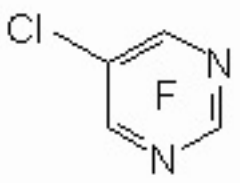
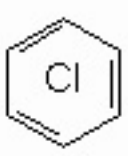
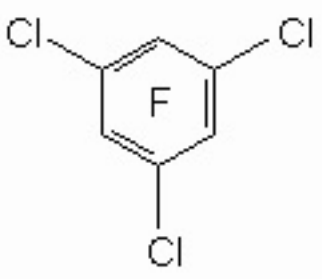
The problem of poly-fluoroaromatic compounds is described in books [14-17] and reviews [18,19].

The reaction can be carried out also in a liquid phase way in solvents like dimethylformamide and sulpho at air pressure. Thus, carrying out a process in sulpholane at 230-240 ^{o}C produced the same mixture of proc as while using a "dry" method. However, hexafluorobenzene was obtained with the yield equal only to 0 while the yield of octafluoronaphtaline was about 52% [21]. The disadvantages of reaction's carrying o solvent are its high cost, and also the need to either regenerate it or to eliminate it after carrying ou synthesis.



The picking out of solvent system allows to increase greatly the yield of perfluorinated derivatives of aror compound. The information on interaction between potassium fluoride and chlorine derivatives in the pres of crown-ether or sulpholane in perfluoroperhydrophenanthrene (b.p. is 215 ^{o}C) (table 1) can be an exar [22,23].

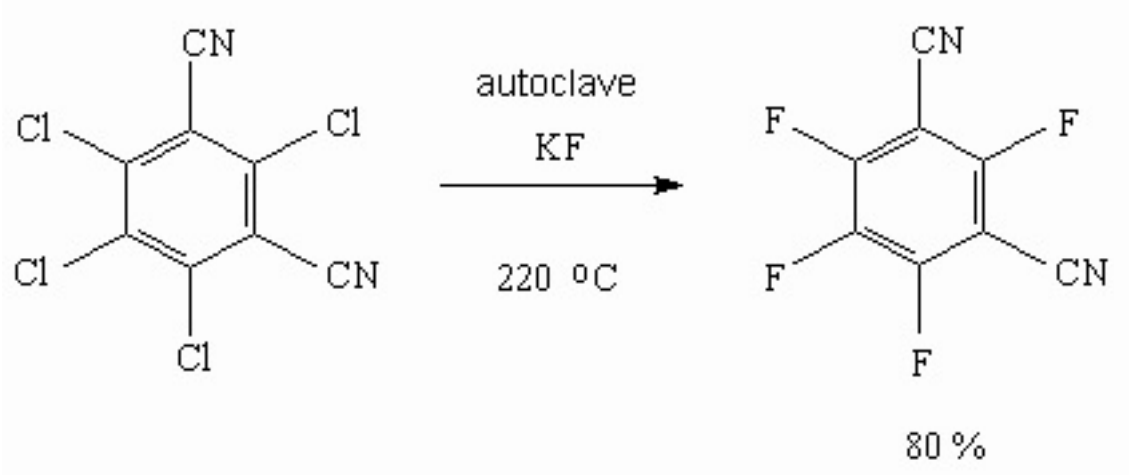
Table 1.*Fluorination of organochlorine derivatives by KF in perfluoroperhydrophenanthrene solution (^{o}C, 15 h) [21]*

Substrate	Reaction product	Yield, % **	Yield, % ***
		84	59
		91	71
		60 *	83

* 217 h, ** 18-crown-6, *** tetrahydrothiophene 1,1-dioxide (25 %).

Japanese researchers actively used sulpholane as solvent and benzonitriles as starting substrates, which

undergone chlorination in advance. Thus, while dry potassium fluoride in the form of powder was influer pentachlorbenzonitrile in sulpholane or benzonitrile at 300-315 ^{o}C for 18 hours we can ol pentafluorobenzonitrile with the yield higher than 85% [23]. The influence of potassium fluoride tetrachlorophthalonitrile [24] or tetrachlorisophthalonitrile [25] at 220 ^{o}C produces correspor terafluoroderivatives.



2,6-Difluorobenzonitrile is obtained by potassium fluoride influencing 2,6-dichlorobenzonitrile dimethylsulphoxide (190 ^{o}C, 3 h) with the yield of 69 % [25].

The main reason of low yield and need to work at high temperatures is caused by low solubility of potas and cesium fluorides in polar aprotic solvents like sulpholane, N-methylpyrrolidone, dimethylformamide. T why Halex methodology works well only in case of activated benzene derivatives and is hardly suitabl temperature unstable substrates. Besides that, the isolating of target product is often hard to be carried ou that ecologically unsafe solvents don't transform at all and lead to unnecessary waste.

A successful carrying out of chloroaromatic compounds fluorodechlorinating using potassium flu depends on several factors. Among them the most important things are the state of potassium fluoride cr structure and substrate own reactivity. Potassium fluoride was tested using example of chlorine exchang fluorine in benzene ring, containing NO_2 group. It was prepared by different methods: obtained by temperature drying and spraying of aqueous KF solution (fine-dispersed powder) [26], dispersed onto ne CaF_2 [27], re-crystallized out of methyl alcohol [28], drying and freezing [29]. In all of the cases we have a increasing of KF specific surface due to decreasing of crystal sizes, that in its turn result in noticeable gro reactivity in reactions of nucleophilic substitution of aromatically bonded chlorine for fluorine. At tha solvent can play the main part.

The authors of work [30] carefully studied the influence of potassium fluoride quality on chlorine exchang fluorine in hexachlorobenzene, going without solvent and at high temperature. They used inert underc potassium fluoride and barium fluoride. In table 2 you can see the results of the research. When using drie spraying potassium fluoride the summary yield of fluorination products doesn't exceed 6%, while the applica of potassium fluoride, put over calcium fluoride in comparable conditions exceeds the yield of fluorina products: tetrachlorodifluorobenzene was obtained with the yield of 46%. In case of using potassium fluorid on barium fluoride we get almost the same results.

Table 2. *Interaction of Potassium Fluoride and Hexachlorobenzene (230^{o}C, 42.5 h)*

Reagents, mole			T, ^{o}C	Time, h	Products, %					
C_6Cl_6	KF	catalyst.			C_6F_5Cl	$C_6F_4Cl_2$	$C_6F_3Cl_3$	$C_6F_2Cl_4$	C_6FCl_5	C_6Cl_6
2,37	19,66	-	230	42,5	-	-	-	1	5	94
2,37	17,7	CaF_2	230	39	-	5,5	21	46	21	6,5
2,37	17,7	BaF_2	230	39	-	9,5	39,5	50	1	-
1,75	11	CaF_2 , *	220	18	24,8	45	30	-	-	-
2,37	19,66	*	220	24	13,5	37	45	4	-	-
$C_6F_4Cl_2$:1	1	*	150	4,5	23,1	77				
$C_6F_4Cl_2$:1	1	CaF_2 , *	150	4,5	24	76				

* tetrakis(diethylamino)phosphonium bromide

In spite of the successful putting of this process into production, the development of poly-fluoroaror compounds chemistry was suppressed by the imperfection of poly-chlorobenzenes potassium fluoride fluorina technology (Halex process), and by the its high inputs. Due to these circumstances, the researches regar search for new and upgrading the known obtaining method of hexafluorobenzene itself continued and in re

years the same researches regarding obtaining of octafluoronaphtalene also have begun. Here we mark several main directions:

1. The upgrading of hexafluorobenzene obtaining method based on finding catalysts of inter-phase tran preparation of potassium fluoride with highly developed surface and application of high-boiling aprotic solve

2. The application of physical effects to speed up the exchange process of chlorine for fluorine and to l the reaction temperature.

3. Using of fluorinating processes of poly-haloidbenzenes using elemental fluorine and other reagents follo by further dehalogenation under the metal's influence.

4. Fluoroaromatic compounds synthesis out of commercial chladones and polyfluorolefines.

5. Using fundamentally new solvents or systems of ionic liquids type.

Seeing a main task and subject of chemistry as studying of compounds' transformations during chem processes we'll make an attempt to concentrate our general attention on synthesis of key compounds of fluoraromatic row that is hexafluorobenzene and octafluoronaphtalene, and on discussing method intensification of a known process and on development of new approaches. Simultaneously we have paid attention to a most important obtaining method of not only low-fluorinated benzenes, but also of polyfluorin ones, based on Halex-process. Obtaining of low-fluorinated aromatic compounds by fluorinating of are containing chlorine atom in positions, activated for example by NO_2 group, is rather perspective in term creating pilot scale productions of a number of functional low-fluorinated arenas. Both parts are united common approach based on the exchange process of chlorine for fluorine under the alkali metals' influence.