Journal "Fluorine Notes", Volume # 3(46), May - June 2006

PRESENT-DAY CONDITION OF FLUOROAROMATIC COMPOUNDS PRODUCTION TECHNOLOGY

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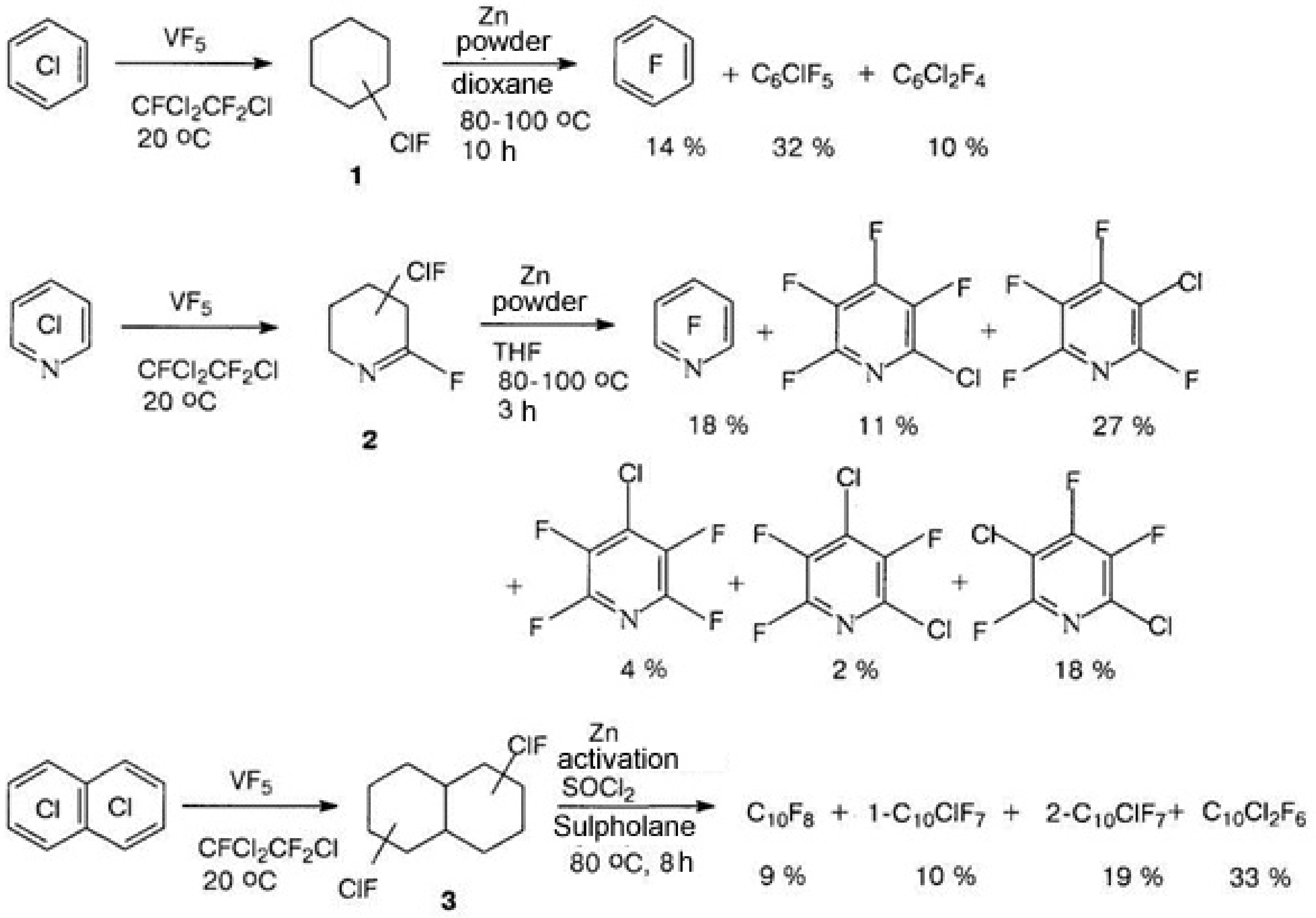
Here we describe effectiveness of interphase transfer catalysts use to obtain polyfluoroarom compounds by potassium fluoride influence on polychlorbenzenes. Such catalysts hexaethylguanidine chloride, tetra-(diethylamino)- phosphonium bromide are involved stabilization of intermediate s-complex. Catalytic participation of polyethers (tetraethylenegly dimethyl ether, 18-crown-6) in fluorodechlorinating process doesn't go beyond increasin "active" fluoride-ion concentration. Here we consider the opportunities of mechanic and chen 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 synthes fluoroaromatic compounds out of commercial chladones (freons) and polyfluorolefines.

Contents

3. Using Processes of Polyhaloidbenzenes Fluorination and of Fluorination Products Dehalogenat as an Obtaining Method of Hexafluorobenzene and Other Aromatic Compounds

Polyfluoroaromatic compounds obtaining method was worked out, a process of halogens removal in alkanes had formed its base. For example, initially fluorine containing cycloalkane $C_6BrCl_6F_5$ is obtained o hexachlorobenzene under the influence of BrF_3-SbF_5this cycloalkane is turned into hexafluorobenzene [76] u the influence of zinc powder in ethyl alcohol. In the work [77] hexachlorohexafluorocyclohexane **1** is obtained quantitive yield by fluorinating of hexafluorobenzene VF_5 in chlorofluorocarbons ($CFCl_3$, $CFCl_2CF_2Cl$) at 20-5 Analogously tetrachlorpentafluoro-1-azacyclohexenes **2** and octachlorooctafluorobicyclo[4.4.0]-decenes-1(were obtained out of pentachloropyridine and octachloronaphtalene respectively. Dechlorination of t compounds using zinc in different status (zinc activated complex $NiCl_2$*$6H_2O$*2,2'-dipyridil; treated with S powder; zinc-copper pair) results in forming of mixture containing hexafluorobenzene, chloropentafluoroben and dichlorotetrafluorobenzene [78].

Both solvent origin and zinc condition [78] influence the yield of dechlorination products. It should be noted, other reagents are effective for this process as well.



For example, at tris(diethylamino)phosphine $P(NEt_2)_3$ influencing onto **1** and **3** compounds the mixture fluorobenzenes and naphthalene with different number of fluorine atoms were obtained[78].

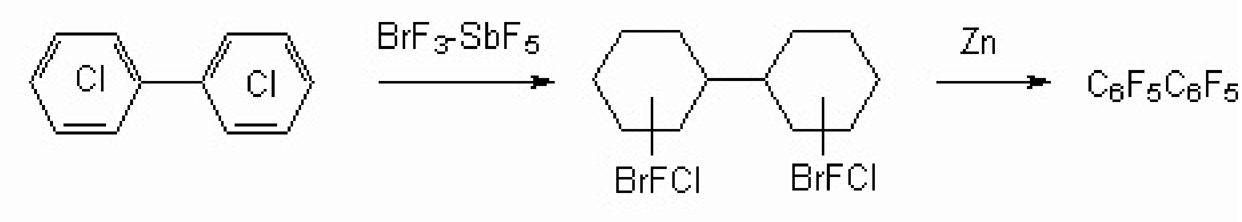
$$\mathbf{1} \xrightarrow[\text{HMPA, } 20\ ^{o}\text{C, 1 h}]{P(NEt_2)_3} C_6F_6 + C_6ClF_5 + C_6Cl_2F_4 + C_6HF_5$$

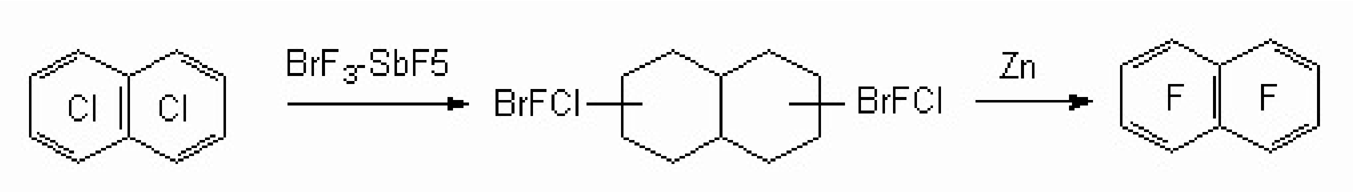
18 % 32 % 14 % 7 %

$$\mathbf{3} \xrightarrow[CH_2Cl_2\text{, } 20\ ^{o}\text{C, 1h}]{P(NEt_2)_3} C_{10}F_8 + C_{10}ClF_7 + C_{10}Cl_2F_6 + C_{10}Cl_3F_5$$

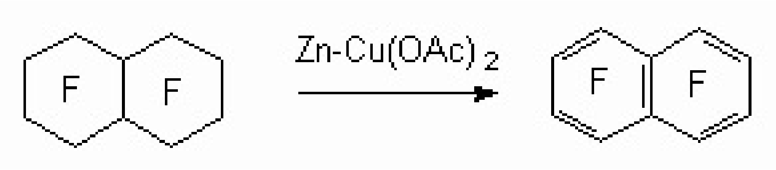
16 % 42 % 24 % 15 %

The method is rather effective and it was used to obtain other polyfluoroaromatic compou decafluorobiphenyl [79,80], octafluoronaphtalene and others.

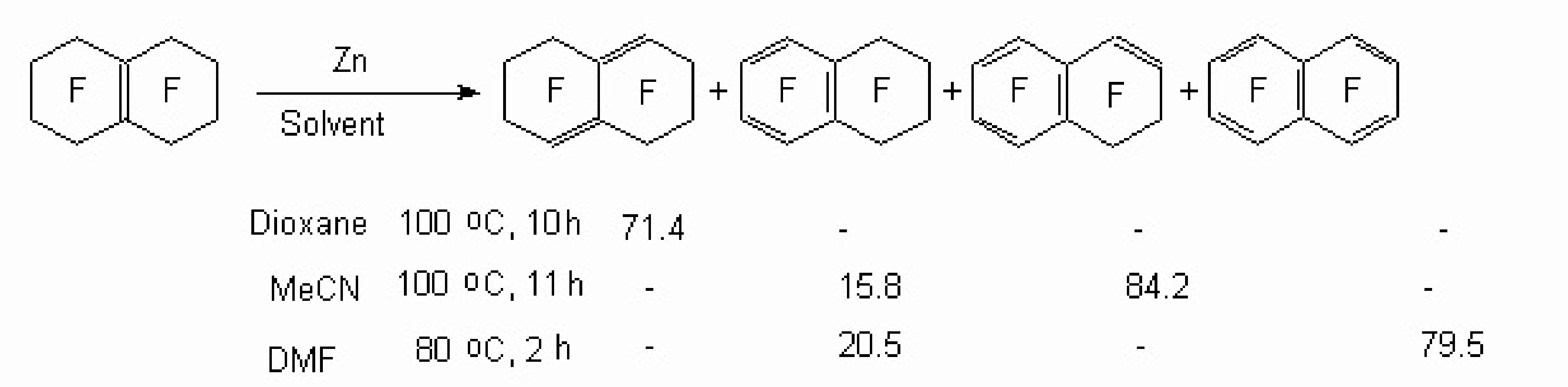




Zinc-copper pair can act as dechlorinating agent in dimethylformamide (DMF) or dimethylacetamide. octafluoronaphtalene of good yield [81] and hexafluorobenzene were obtained.

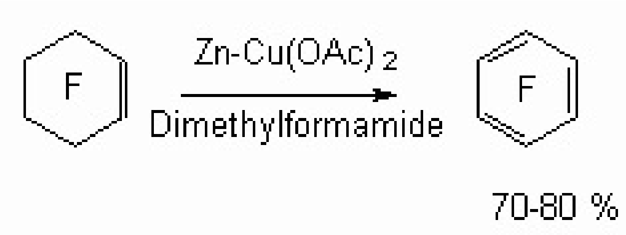


It should be noted, that zinc as itself is not effective, here we need a solvent [82]. It is shown using an exa of hexadecafluorobicyclo[4.4.0]dec-1(6)-ene.

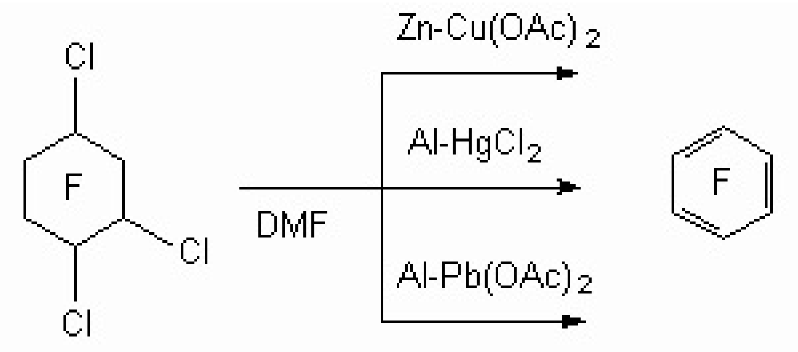


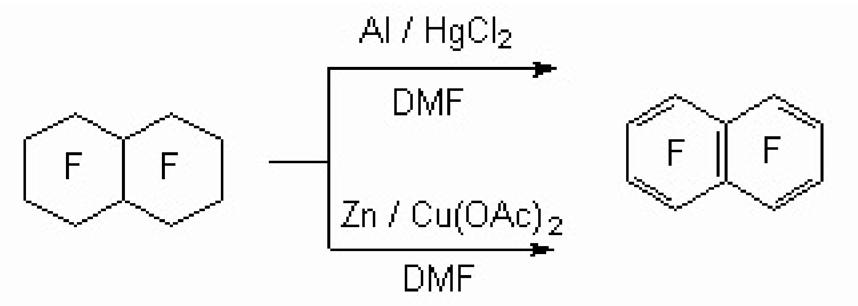
Dioxane	100 oC, 10h	71.4	-	-	-
MeCN	100 oC, 11 h	-	15.8	84.2	-
DMF	80 oC, 2 h	-	20.5	-	79.5

The aromatization process of perfluorocyclohexene is going analogously.

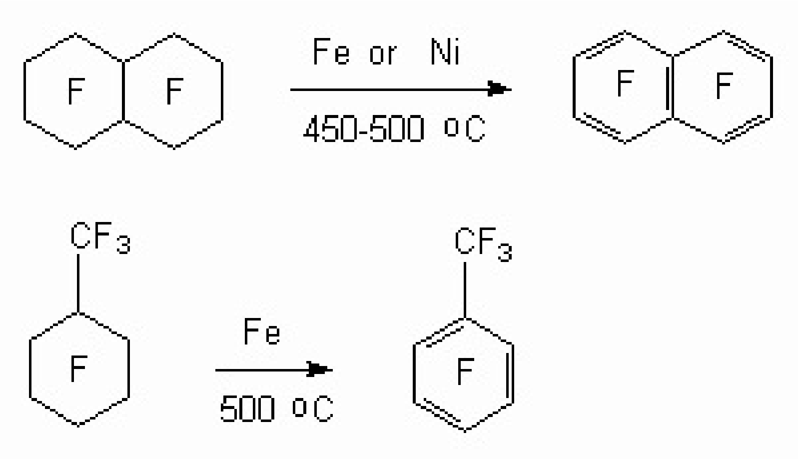


Poly-chlorofluorocycloalkanes are being dehalogenated using M/M^{2+} metals system, where M = Zn, Al; and = Cu^{2+}, Hg^{2+}, Sn^{2+}, Pb^{2+} . The yield of hexafluorobenzene and octafluoronaphtalene amounts to 70 - 80 %.

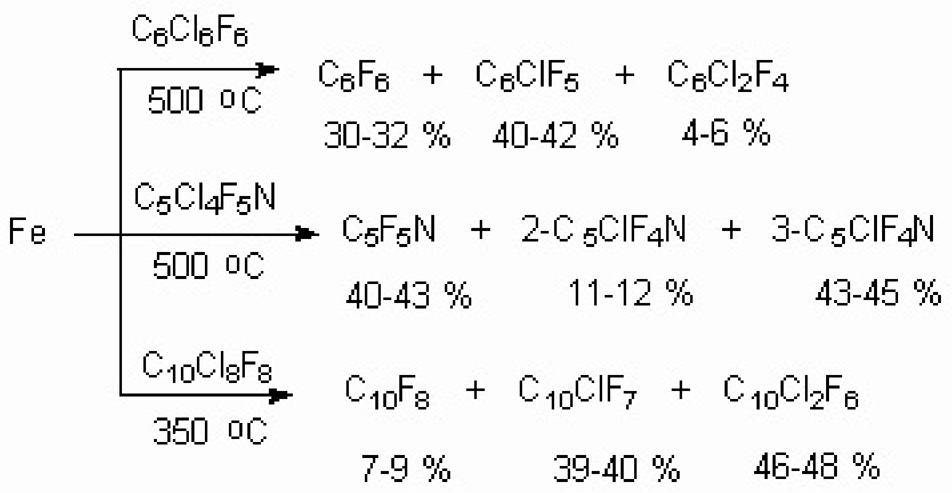




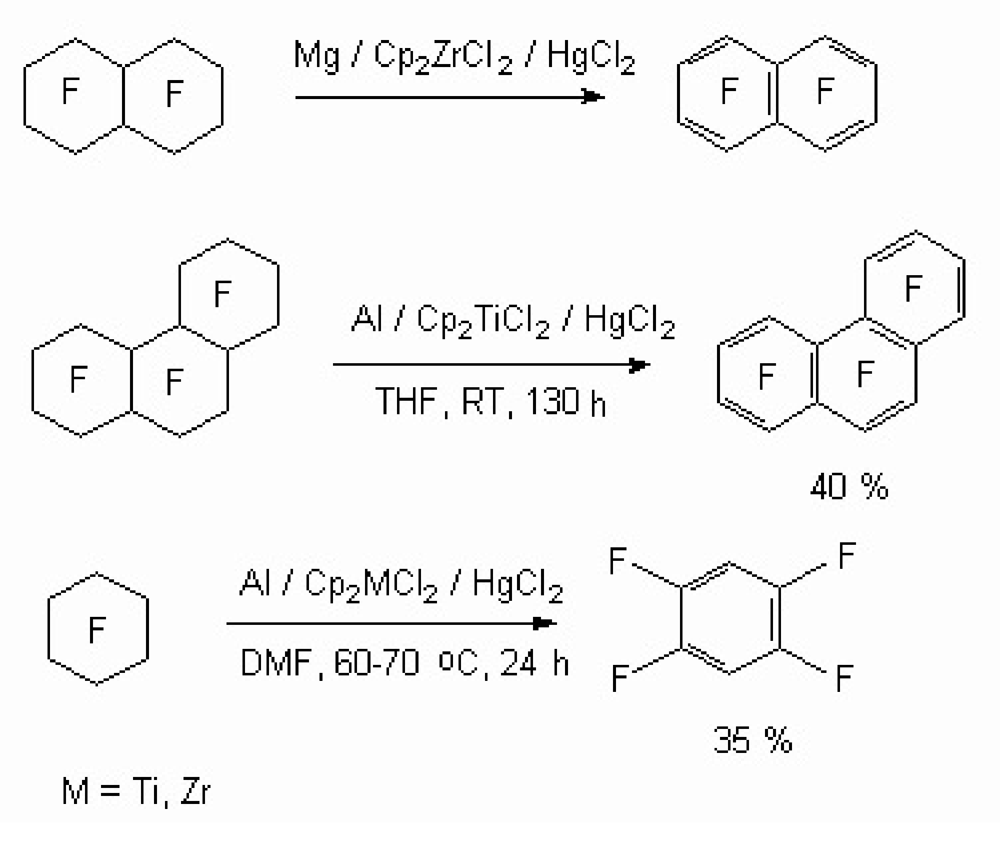
One of the approaches to synthesis of polyfluoroaromatic compounds is a transforming of saturated perfluorocarbones under the influence of nickel, iron at 400-600^{o}C [83,84]. This approach had been develop 60-s. However, because of low yield of target products and unavailability of original substrates it had not fou wide spread occurrence and commercial application. At the same time it showed a fundamental opportun implementation of such approach to synthesis of poly-fluoroaromatic and poly-fluoroheterocyclic compounds.



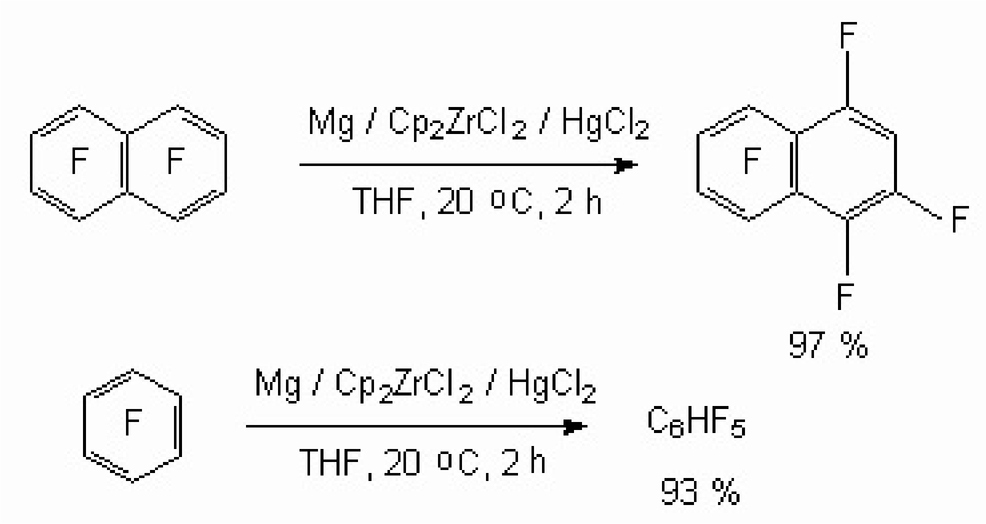
Dechlorinating by iron powder at 500 ^{o}C was carried out for chlorine containing cyclic alkenes, at that as a there is being formed a mixture of products [78].



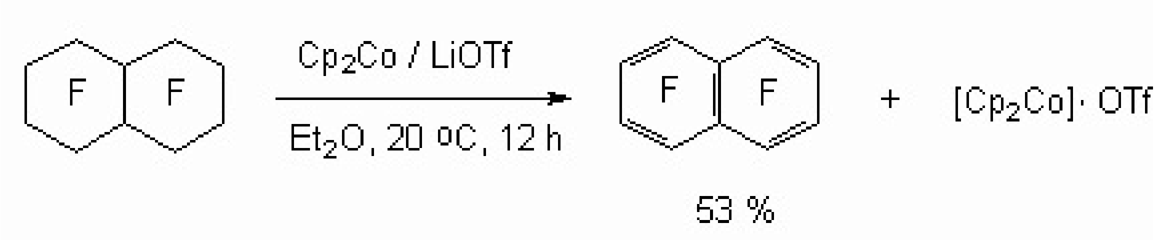
Along with development of direct fluorinating methods of aromatic compounds and cyclic carbons a materials base had appeared for realization of defluorination and dechlorination of compounds of such type. use not only metals of variable valency as reagents for this process in the presence of catalysts but also a radicals of some organic compounds [85]. Thus, Mg, Al metals in the presence of Cp_2MCl_2 (M = Ti, Zr)-I system, acting as catalyst, carry out defluorinating of perfluorinated cyclic compounds at room tempera forming polyfluoroaromatic compounds [85].



It should be noted, that in case of perfluorocyclohexane C-F bond hydrogenolysis must occu hexafluorobenzene, forming during this process under the influence of reagents. Indeed it was shown[86], present system of titanocene and zirconocene complexes catalyses reduction process of polyfluoroaror compounds under the influence of magnesium in the tetrahydrofurane solution. Thus, heptafluoronaphtalene pentafluorobenzene are formed out of octafluoronaphtalene and hexafluorobenzene respectively.

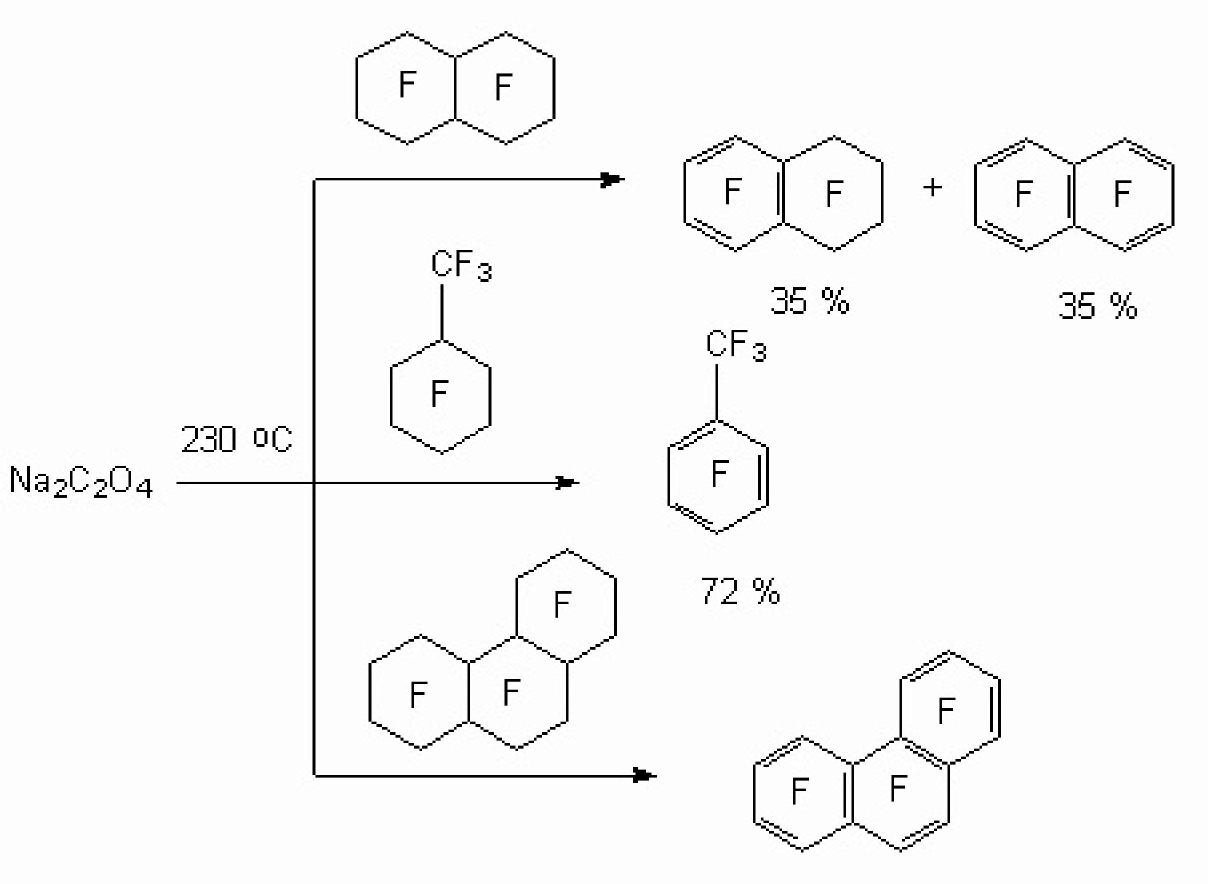


It was shown [87], that acting of stochiometric quantities of cobaltocene in the presence of LiO_3SCF_3 a
influence on perfluorodecalin results in forming of octafluoronaphtalene.

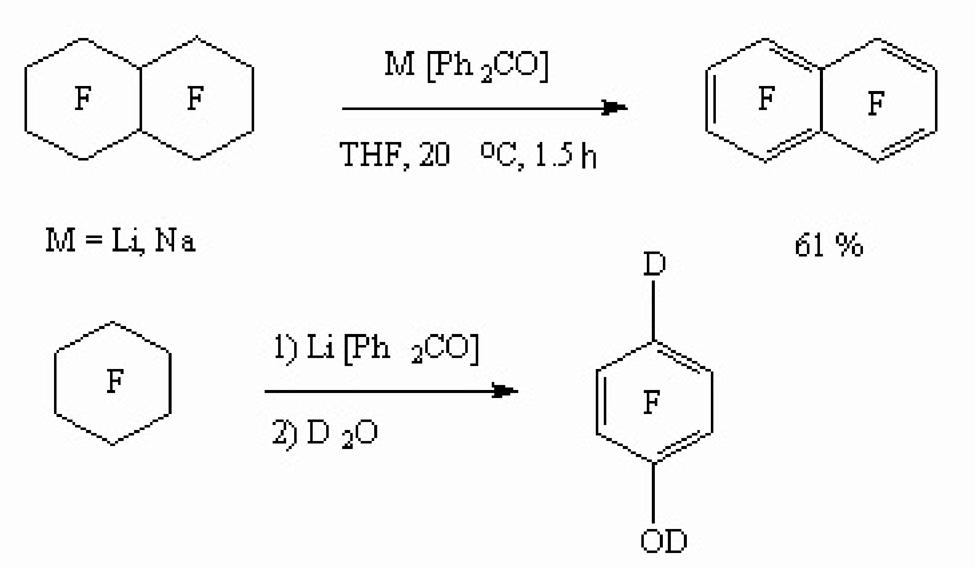


[(η^{5}C5H5)2TiF2] or [(η^{5}C5H5)2ZrCl2] systems act the same way / catalyst, Al / HgCl2, THF, 20^{o}C, 130 h (yield 4
[85].

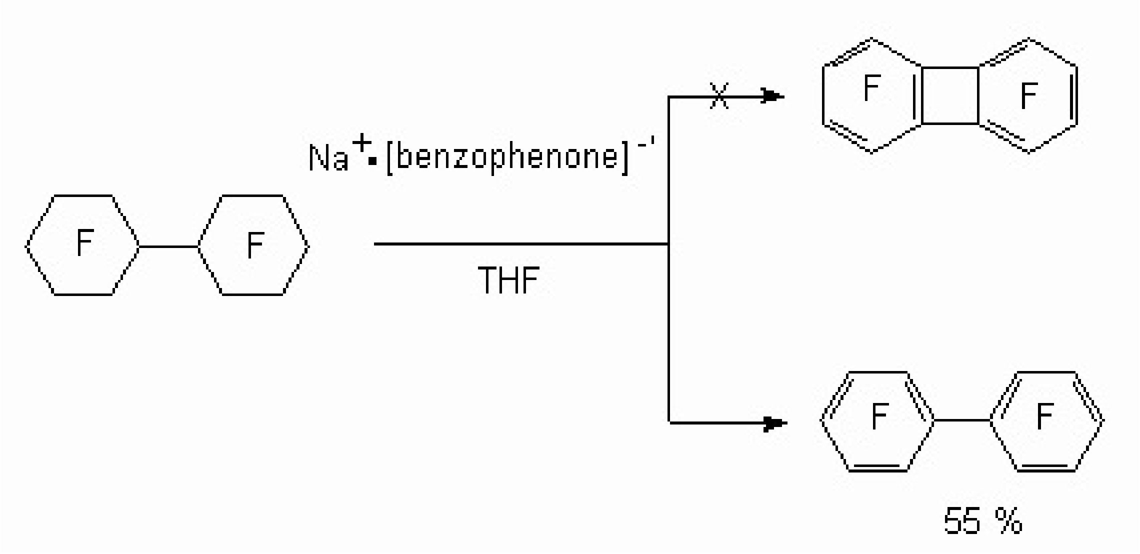
Thermal method was also used for these purposes. Thus, influencing of sodium oxalate onto perfluorodeca
perfluoromethylcyclohexane at heating up to 230^{o}C octafluoronaphtalene and octafluorotoluene were obta
respectively [88-91].



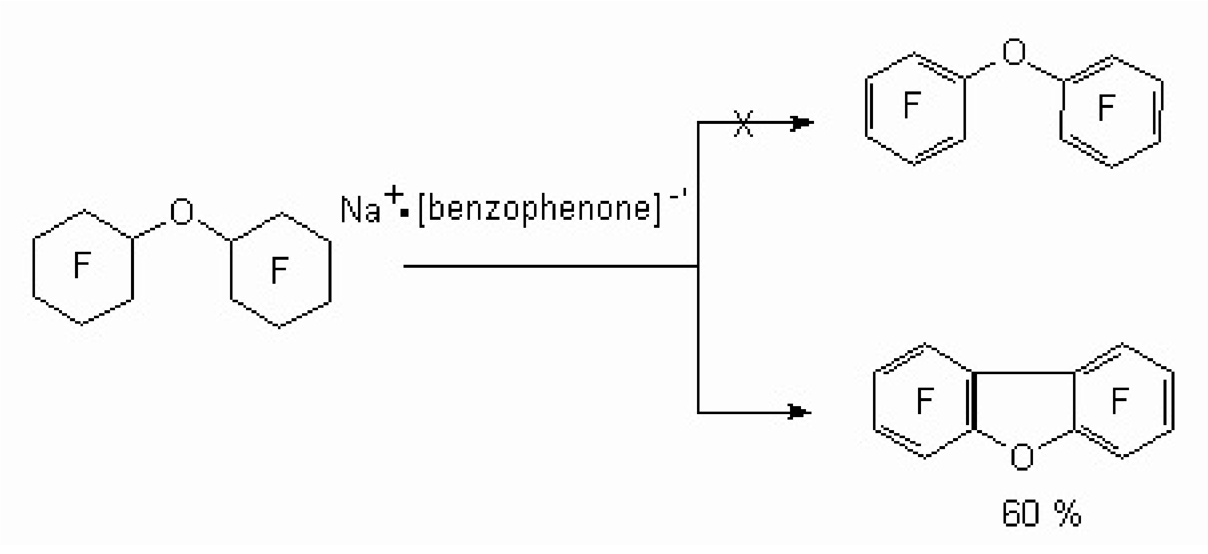
Perfluorocarbons high selective reduction process is implemented using an example of benzophenonee a
radical influencing perfluorodecalin and perfluorocyclohexane in terahydrofuran [89-91].



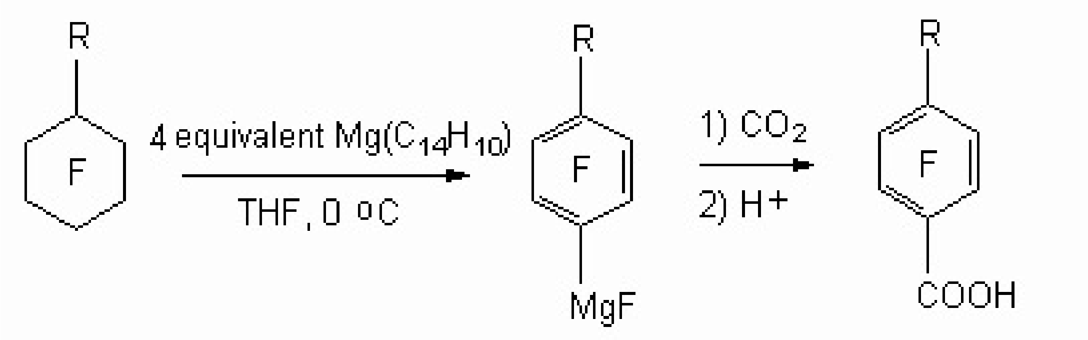
In case of perfluorocyclohexane there is a formation of low yield of terafluorophenols. At the same time
benzophenone anion-radical influencing perfluoro(bicyclohexyl) reduction defluorination goes at high selectiv
low temperature forming decafluorodiphenyl but not octafluorodibenzobutane [92].



At the same time the reductive defluorination of perfluorobicyclohexyl ester is followed not by formir
perfluorodiphenyl ester, but by forming of perfluorodibenzofuran [92].



Perfluorocyclohexane and perfluoromethylcyclohexanen were exposed of reductive defluorination at actic
antracene mono-anion $MgC_{14}H_{10}$ in tetrahydrofuran at -41 ^{o}C producing corresponding Grignard reactive. Fu
they reacted with carbon dioxide producing pentafluorobenzoic and 4-trifluoromethyl-2,3,5,6-tetrafluorobe
acids correspondingly [93].

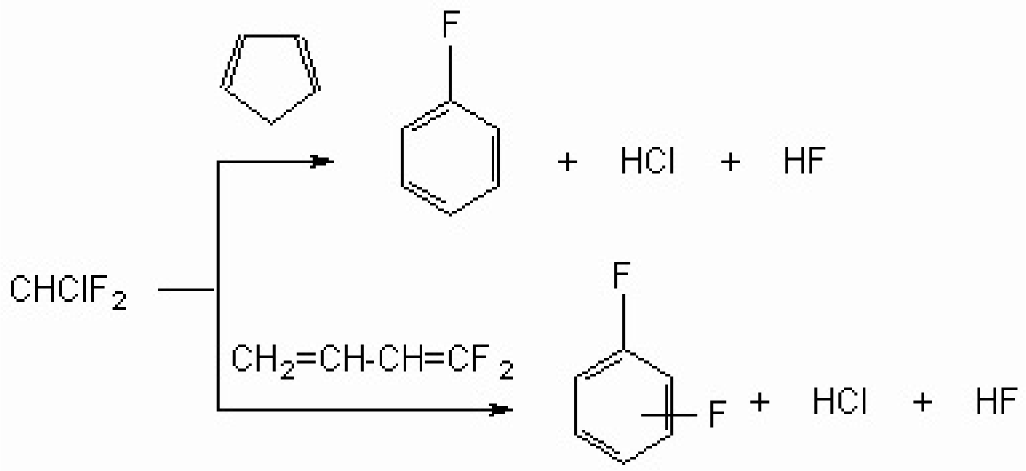


R = F (14 %), CF_3 (5.7 %)

4. Fluorine Aromatic Compounds Synthesis Using Commercial Chladones and Polyfluorolefines

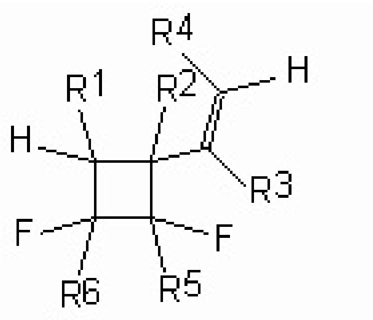
The alternative strategy of fluoroaromatic synthesis lies in synthetic production of assigned fluorobenzen structures with using reactive fluorine containing fragments (fluorosynthones). The application opportunitie this methods for synthesis of mono-, di-, tri- and polyfluorosubstituted arenas are based on applicatic commercial chladones (freons) and poly-fluoroolefines as feedstock or fluorine containing structure blocks [94 $CHCl_3$, $CHClF_2$, $CHCl_2F$, $CClF_3$, $CF_2=CF_2$, $CF_3CF=CF_2$, CF_2CFCl, $CF_2=CFC_4F_9$, $CF_3CF=CFC_3F_7$etc. are used as such [18]. This approach opens large synthetic perspectives for introducing fluorine into aromatic nucleus. It is bas gas-phase generating and cyclic addition of fluorocarbenes and poly-fluorolefines to unsaturated hydrocar followed by thermal isomerization of fluorine containing cyclopropanes and cyclobutanes. Butadiene and its m derivatives, cyclopentadiene etc are used as such compounds.

Obtaining method of fluorine aromatic compounds using gas-phase reaction of difluorocarbene and co dienes was implemented in the form of universal mono- and difluorobenzenes obtaining technology. The techn lies in gas-phase copyrolysis of difluorochlomethane (chladone 22) and cyclopentadiene (fluorobenzene obta [96-99]) either by butadiene -1,3 (obtaining of difluorobenzenes [97-100]). The process is carried out in system on a continuous mode with water vapour, water-ammonia mixtures [95] or at alkaline packing [87], li isolating halogen hydrogens, what increases selectivity of synthesis and lowers the resinification [18].



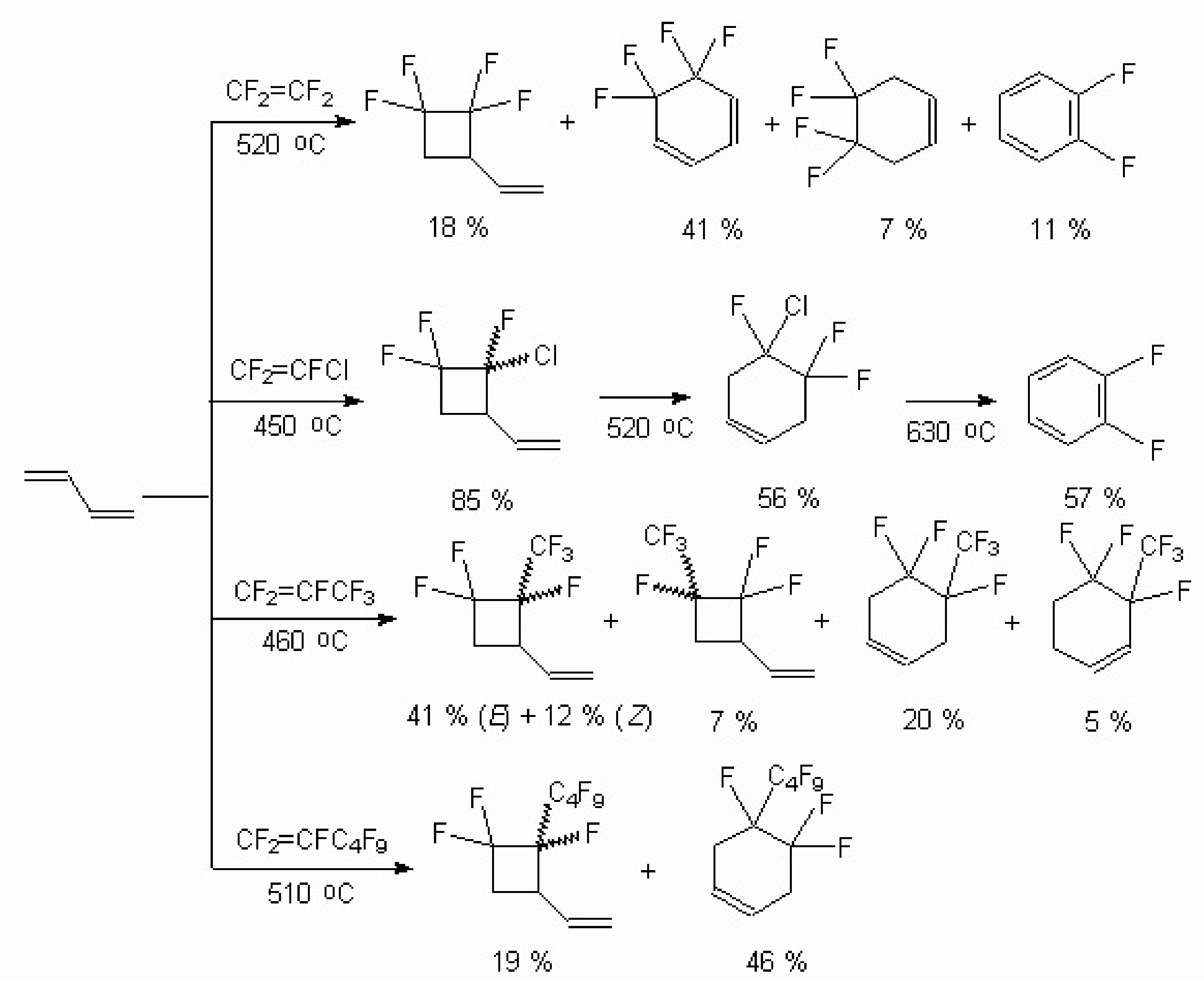
Carbenes method was successfully used to synthesize the fluorine containing bicyclic aromatic compound fluoronaphthalene (yield is 68-80 %), starting from indan and $CHClF_2$ at 600-670^oC [101], 2,3-difluoronaphth (yield is 16-65 %), starting from styrene and $CHClF_2$ at 650 ^oC [102,103].

Obtaining method of 1,2-difluorobenzene, 3,4-difluorotoluol, 2,3- difluorotoluol and 1-fluo trifluoromethylbenzene is based on pyrolysis of substituted derivatives of vinylcyclobutane of the type listed at 600-800 ^oC in the presence of water vapour [104]. Thus, 2,3-difluoro-2,3-dichlorocylobutane produces o difluorobenzene after water steaming and ammonia treatment, and 1-vinyl-2,3-difluorocyclobutane transforms 1,2-difluorobenzene with the yield of 61.5 % (conversion of starting one is 80 %) [104].

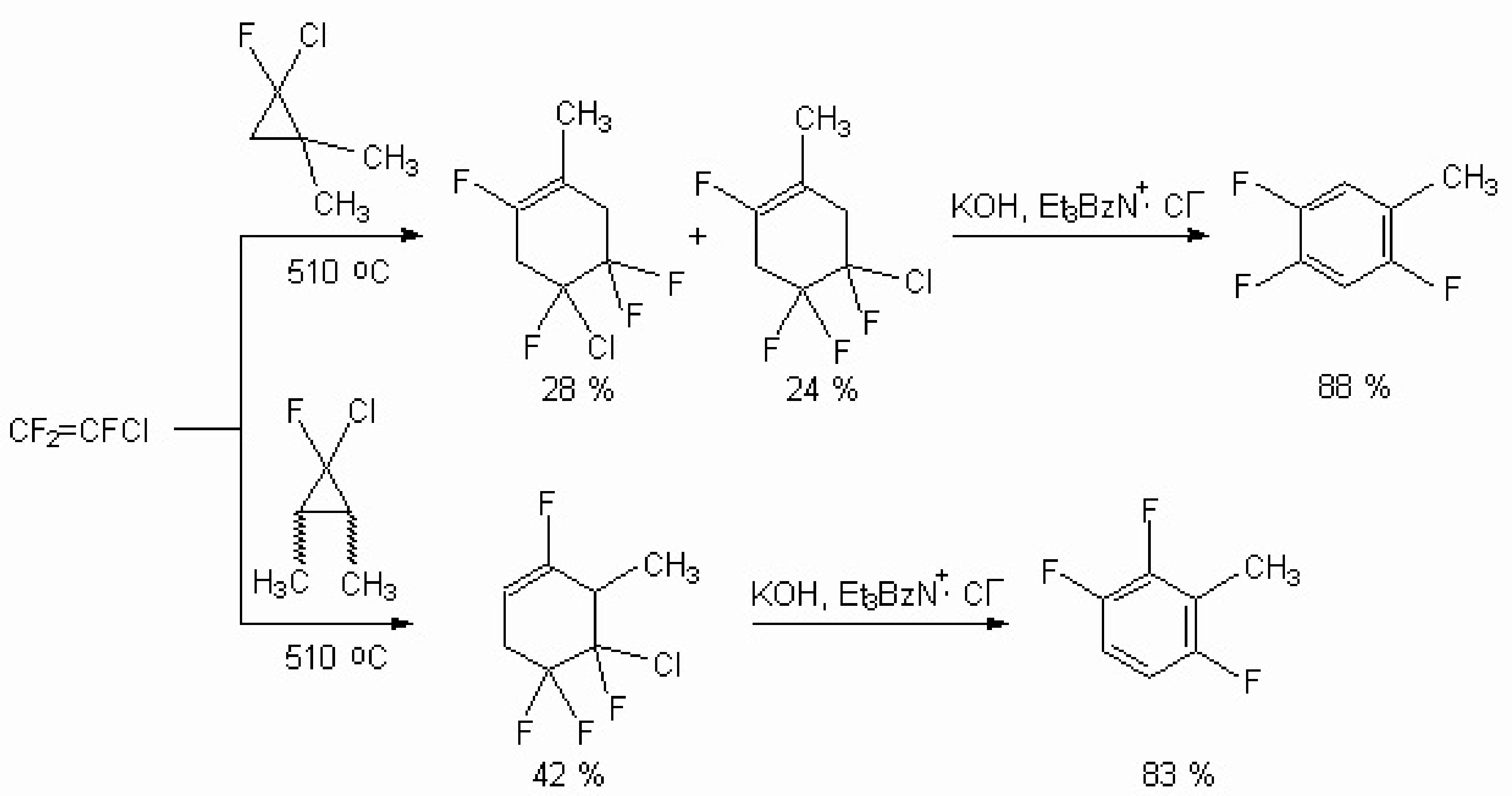


R1 - R4 = H, Me;
R5 = F, Cl, CF_3;
R6 = F, Cl

Fluorolefines can thermally add 1,3-dienes in a mode of [4+2] and [2+2]- cycloaddition [105]. Fluori cyclohexene and vinylbutane adducts formed during that processes can be transformed into partly fluori aromatic compounds either directly by the following dehydrohalogenation or through the preliminary sta vinylcyclobutane-cyclohexene rearrangement [106,107]. This approach was used for working out the obta method of partly fluorinated benzene derivatives using available fluorolefines. It lies in constructing fluoroben like structures by fluorolefines thermal cyclic addition of 1,3-diens and further aromatization of forming fluorin carboxylic adducts. Thus, interaction of tetrafluoroethylene and 1,3-butadiene in a flow reactor results eith forming of 1-vinyl-2,2,3,3-tetrafluorocyclobutane (temperature was 450-470 ^{o}C, contacting period 4-6 seconds) the yield within 78-85% or in forming of fluorocyclohexane (temperature 490-520^{o}C) [106]. The reaction h common nature and trifluorochloroethylene, hexafluoropropylene, perfluoropropylene, perfluorohex perfluorohex-2en are introduced into it.



Not only derivatives of 1,3-butadiene (2-methyl-1,3-butadiene, piperylene, 2,3-dimethyl-1,3-butad haloisoprene derivatives) but also hem-fluorochlorocyclopropane are introduced into the reaction [106] example, the interactrion of trifluorochloroethylene and 1,1-dimethyl-2-fluoro-2-chlorocyclopropane resul forming of isomeric methyltetrafluorocyclohexenes as main products, which not being separated are transfo into 2,4,5-trifluorotolyol by alkali dehydrohalogenation under the conditions of inter-phase catalysis [106].



Thus, new methods of fluoroaromatic compounds synthesis using the reactions of thermal transformati poly-fluoroolefines allows to offer alternative to traditional methods of solving a problem of obtaining fluorinatinated benzene derivatives not only for preparative purposes but also for commercial production.

Conclusion

The aims of present review are analyzing of new file of information regarding reactivity of fluoroaro compounds, which was accumulated during the last decade, describing of fluorine atoms introduction's benzene ring influence on properties of some benzene derivatives, also describing of development of new met of fluorine containing aromatic compounds synthesis, latest achievements of this class of compounds. Her also targeted on presenting the information on practical using of fluorinated aromatic compounds. In our opi it can forward a wider attracting of poly-fluorinated organic compounds to solve a number of crucial questio theoretical organic chemistry and also to purposefully synthesize compounds, possessing useful properties.

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