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METHODS OF SUBSTITUTION OF HYDROGEN ATOMS IN FLUORINATED BENZENES WITH CHLORINE, BROMINE AND IODINE ATOMS

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Abstract: Methods of substitution hydrogen in fluorinated benzenes with chlorine, bromine, and iodine atoms are considered.
Keywords: fluorinated benzenes, chlorination, bromination, iodination.

Nowadays the chemistry of fluorinated benzenes is important area in the chemistry of arenes. It allows to find various solutions for a number of fundamental and applied problems for the different purposes in this field. The intensive development the chemistry of fluorinated aromatic compounds in the last 65 years has made it possible to search for areas of practical using of fluorinated benzenes, for example, in medicine [1-16], agriculture [8, 9, 17, 18], liquid crystals [19-23], semiconductor materials [24-34]. Highly important "building blocks" in the chemistry of fluorinated aromatic compounds are chloro-, bromo-, and iodofluorinated benzenes.

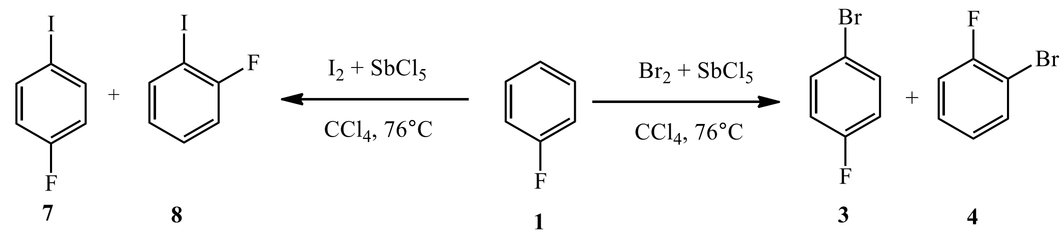
The aim of this work is considering various methods of introducing chlorine, bromine, and iodine atoms into fluorinated benzenes by substitution of hydrogen atom.

1. Chlorination, bromination and iodination of fluorobenzene.

The most well-known method for synthesis of chloro- and bromofluorobenzenes is the interaction of fluorobenzene with chlorine and bromine or other chlorinating and brominating reagents in the presence of Lewis acids. The fluorine atom, like other halogens, has a deactivating effect in electrophilic reactions, but it is also an *ortho*- and *para*-orientant [35]. The introduction of chlorine and bromine atoms in the *para*- and *ortho*-positions of fluorobenzene (**1**) in the reactions under consideration can also be explained by the stabilizing effect on the carbocation center of the resonance effect of the fluorine atom (σ_I = 0.52, σ_R = -0.44 [36]). A comparison of the bromination reactions of benzene (**2**) and fluorobenzene **1** confirms these ideas. Thus, it is known that arene **1** reacts with bromine at room temperature [37]; with high yield (83%). Bromobenzene is obtained by reacting compound **2** with an aqueous HOBr solution at room temperature [38]. At the same time, bromination of fluorobenzene **1** with bromine was carried out in the presence of a catalyst ($FeBr_3$) under heating. A mixture of *para*-bromofluorobenzene (**3**) (98.2%) and ortho-bromofluorobenzene (**4**) (1.8%) with a total yield of ~77% was obtained [39]. Chlorination of arene **1** in the presence of $FeCl_3$ occurred at 0°C and resulted in the formation of a mixture of chloro- (**5**) (84%) and ortho-chlorofluorobenzene (**6**) (16%) with a total yield of 64% [39]. In these reactions, *meta*-substitution occurs by no more than 1% [39]. Optimization of the bromination reaction conditions using Fe, $FeCl_3$, and zeolites as catalysts made it possible to obtain arene **3** with a yield of up to 98% and a purity of >99.8% [40-46]. Heating arene 2 with $FeCl_3$ in the nickel autoclave at 119-124 °C, a mixture of compounds **5** (95%) and **6** (5%) was formed with a total yield of 74%. Increasing the temperature to 145-153°C gave an almost pure compound **5** with a yield of 80% [47]. [

$SbCl_5$ can be used as a catalyst for the selective bromination and iodination reaction [48], while the formation of arene **4** and 1-fluoro-2-iodobenzene (**8**) was observed in small amounts (Scheme 1).

Scheme 1.

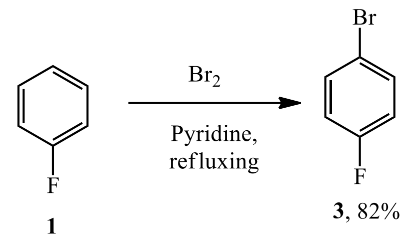


Yield for the mixture of isomers 76% (**7** : **8**, 98 : 2)

Yield for the mixture of isomers 90% (**3** : **4**, 99 : 1)

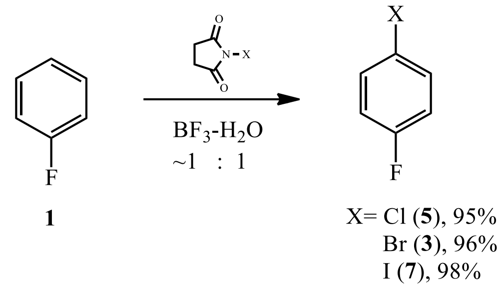
It is worth noting that the selective bromination reaction can be carried out by refluxing arene **1** with Br_2 in pyridine [49] (Scheme 2).

Scheme 2.



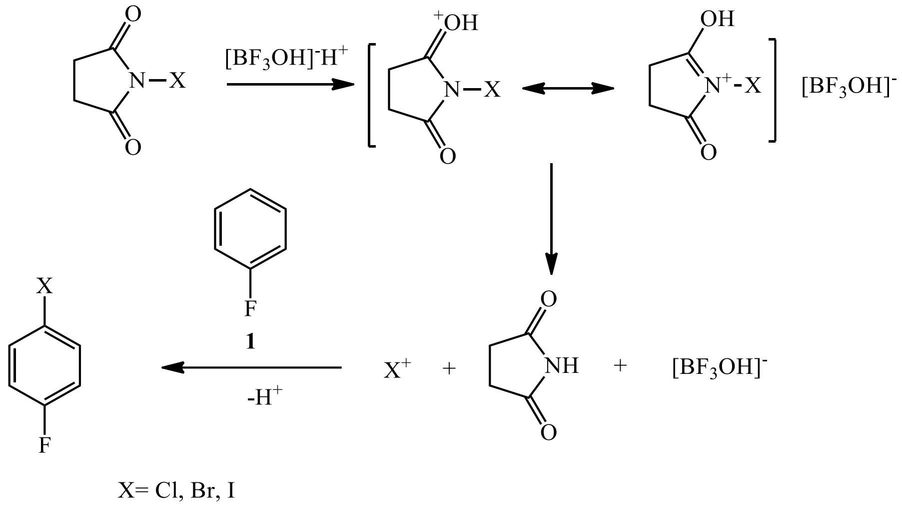
Another approach to introducing a halogen into arene **1** is to use N-halosuccinimides in the presence of BF_3 complex and water taken in ratio of ~1:1 [50] (Scheme 3).

Scheme 3.



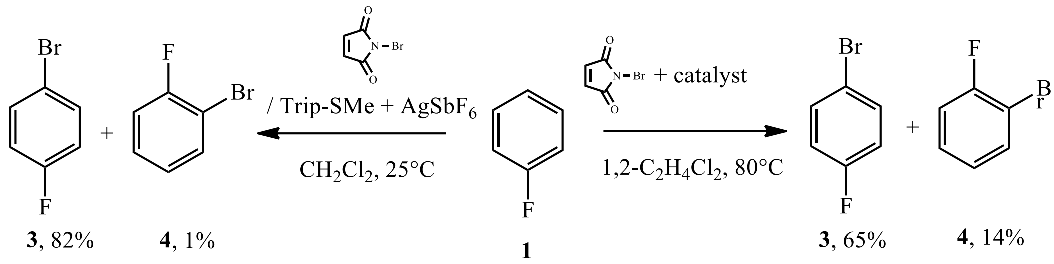
The authors of [50] proposed a mechanism for replacing hydrogen with an atom of chlorine, bromine, and iodine. This mechanism involves the generation of halogen cations from N-halosuccinimides and a complex of BF_3 and water, and the subsequent interaction of halogen cations with arene **1** (Scheme 4).

Scheme 4.



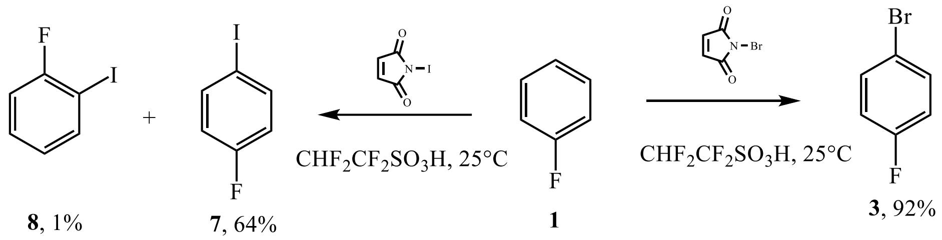
In the case of bromination with N-bromosuccinimide, the possibility of using a gold complex [51], a mixture of 9,10-dihydro-9-(methylthio)-9,10[1',2']-benzoanthracene (Trip-SMe) and $AgSbF_6$ [52] as a catalysts was shown (Scheme 5).

Scheme 5.



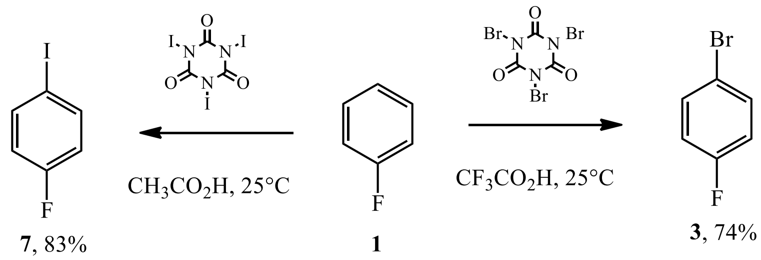
During the bromination reaction in $CHF_2CF_2SO_3H$, the yield of compound **3** was 92% (the ratio of compounds **3** and **4** is not given in this work) [53]. For a similar iodination reaction, a mixture of compounds **7** and **8** was obtained with a total yield of 65% [53] (Scheme 6).

Scheme 6.



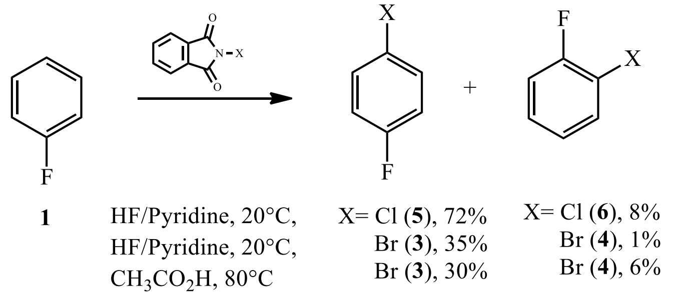
Tribromo- and triiodoisocyanuric acids can be used as a source of bromine and iodine [54, 55] (Scheme 7).

Scheme 7.



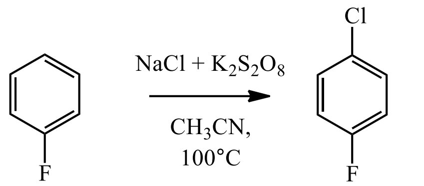
The use of N-halophthalimide as a chlorinating and brominating reagent is complicated by the significant formation of isomers [56] (Scheme 8).

Scheme 8.



Compound **5** can be obtained by heating benzene **1** with NaCl and $K_2S_2O_8$ in MeCN [57] (Scheme 9).

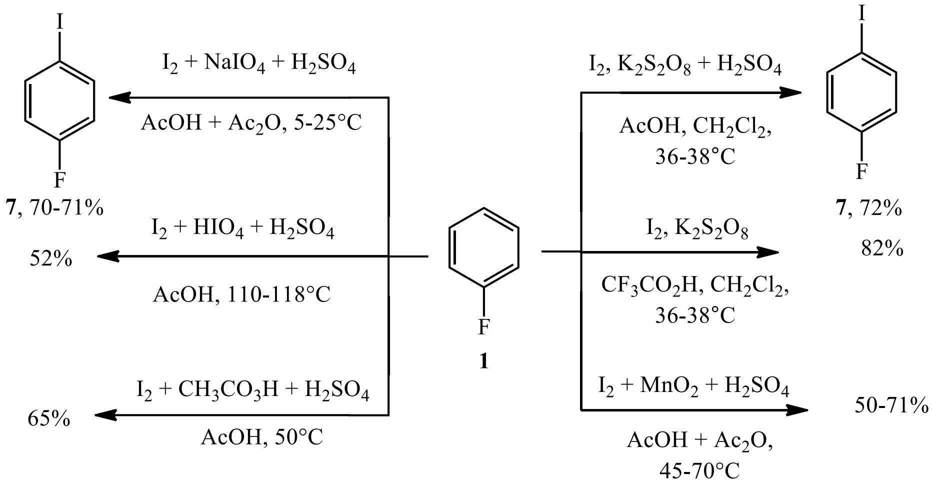
Scheme 9.



1 **5**, ~100%

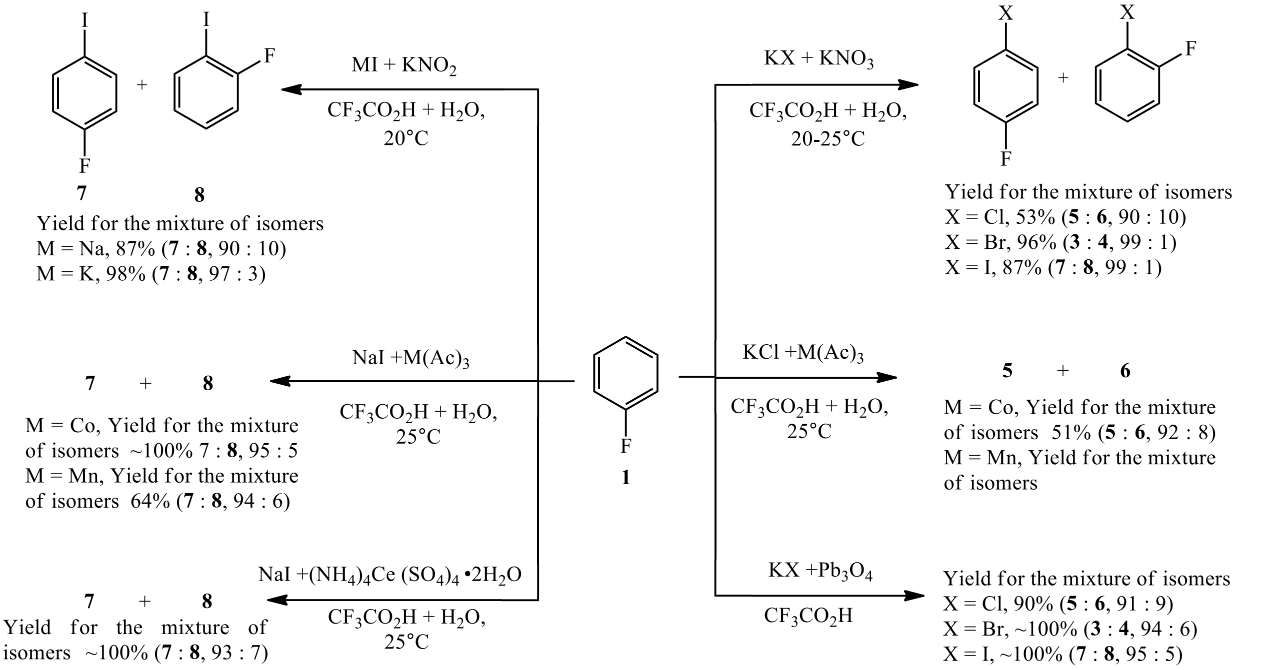
Similarly, heating fluorobenzene **1** with I_2 in an acidic medium and oxidizing agents such as $K_2S_2O_8$ [58], MnO_2 [59, 60], $NaIO_4$ [61, 62], HIO_4 [63, 64], CH_3CO_3H [65] can produce arene **7** (Scheme 10).

Scheme 10.



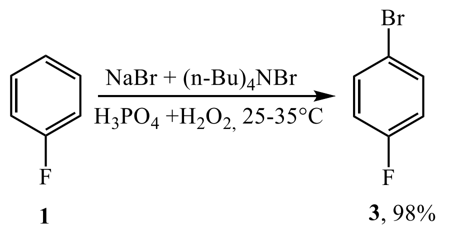
The possibility of chlorination [66], bromination [67] and iodination [68, 69] by the interaction with KCl, KBr, KI or NaI on compound **1** in the presence of $NaNO_3$ or $NaNO_2$ in CF_3CO_2H has been shown (Scheme 11). Co(III), Mn(III) acetates, and ammonium cerium (IV) sulfate can be used as oxidizing agents for the chlorination [70] and iodination [71] reactions of compound **1** (Scheme 11). Pb_3O_4 can also be used as an oxidizer [72] (Scheme 11).

Scheme 11.



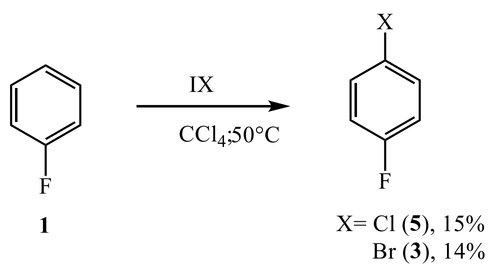
When using H_2O_2 as an oxidizer, arene **3** can be obtained in high yield and purity [73] (Scheme 12).

Scheme 12.



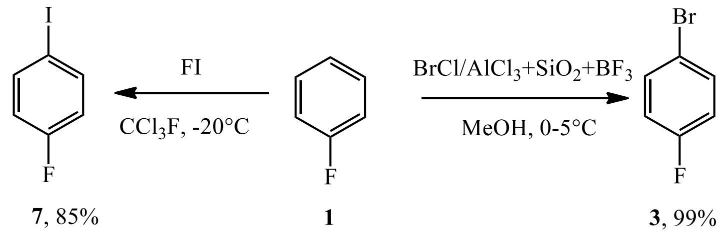
The chlorination and bromination reactions under the action of ICl and IBr has been described, however, the yields of compounds **3** (96.1% isomer content in the mixture) and **5** (91.2% isomer content in the mixture) were not high [39] (Scheme 13).

Scheme 13.



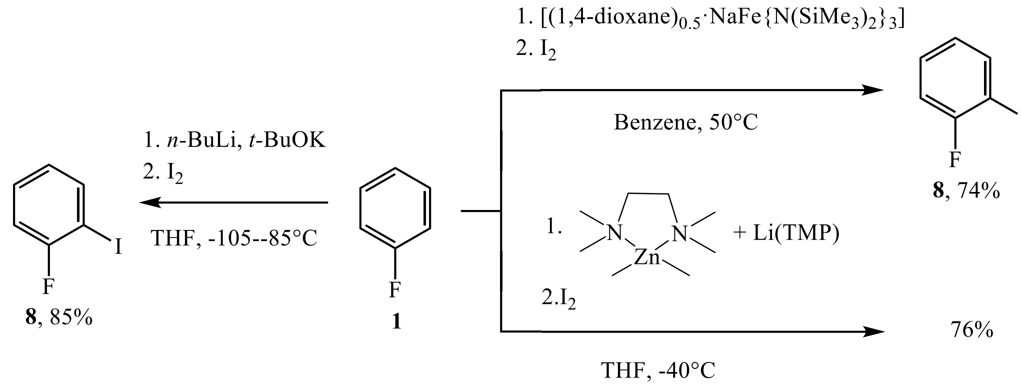
Using BrCl [74] and FI [75], was allowed to carry out the reaction of bromination and iodination of fluorobenzene **1** with good yields (Scheme 14).

Scheme 14.



Benzene **8** can be obtained via organometallic compounds with good yields [76-78] (Scheme 15).

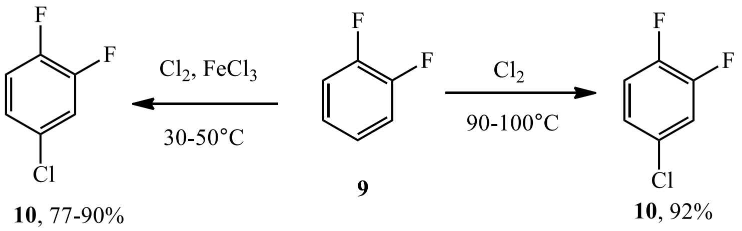
Scheme 15.



2. Introduction of chlorine, bromine and iodine atoms into difluorobenzenes.

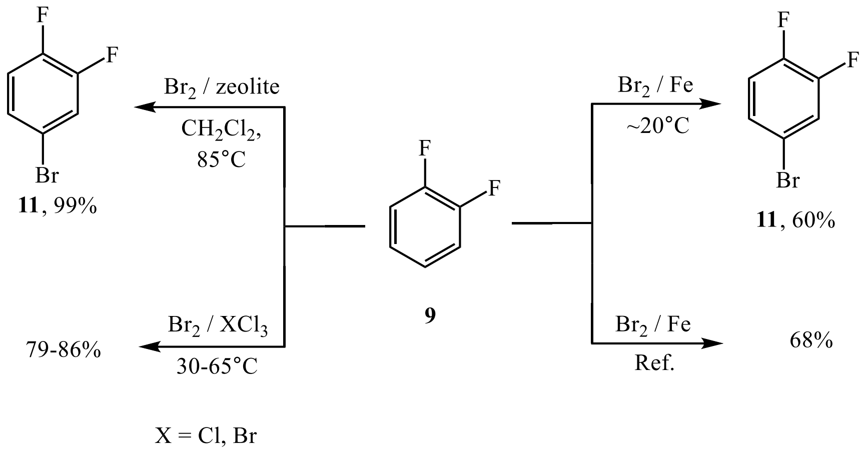
The interaction 1,2-Difluorobenzene (**9**) with chlorine [79] in the presence of $FeCl_3$ [80, 81] lead to yields 1-chloro-3,4-difluorobenzene (**10**) (Scheme 16).

Scheme 16.



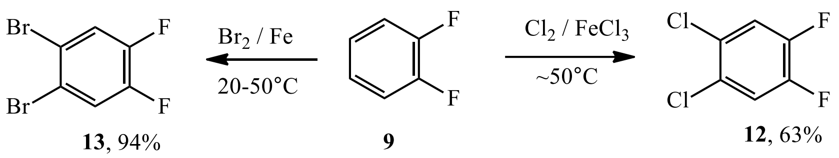
When benzene **9** reacts with bromine in the presence of iron [82, 83], zeolite [46] or XCl_3 (X = Al, Fe) [81, 84], 1-bromo-3,4-difluorobenzene (**11**) is formed (Scheme 17).

Scheme 17.



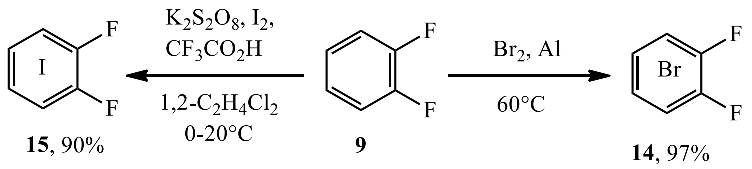
Similarly, dichloro- and dibromo derivatives **12** and **13** can be obtained from benzene **9** for a long heating [85] (Scheme 18).

Scheme 18.



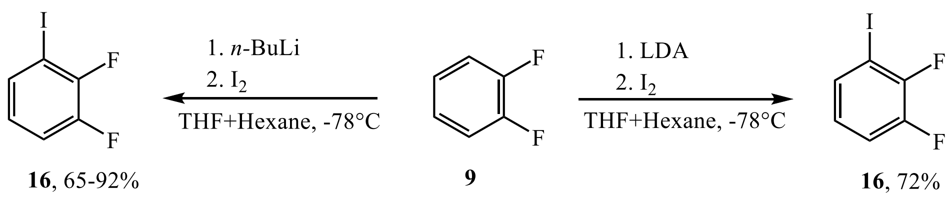
The possibility of obtaining 1,2,3,4-tetrabromo- and 1,2,3,4-tetraiododifluorobenzenes (**14** and **15**) from benzene **9**, was shown [86, 87] (Scheme 19).

Scheme 19.



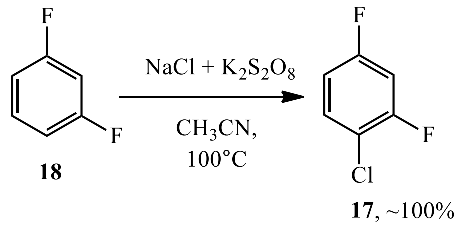
The possibility of selective iodination of benzene **9** to 1,2-difluoro-3-iodobenzene (**16**) [88-90] is also interesting (Scheme 20).

Scheme 20.



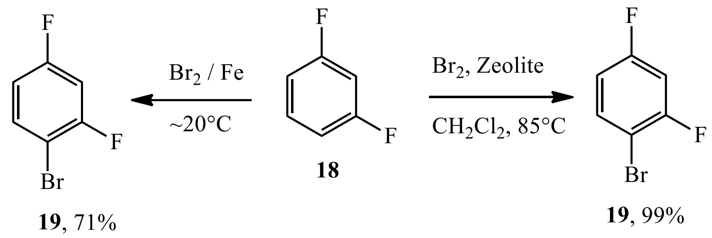
1-Chloro-2,4-difluorobenzene (**17**) can be obtained by heating 1,3-difluorobenzene (**18**) with NaCl and $K_2S_2O_8$ in MeCN [57] (Scheme 21).

Scheme 21.



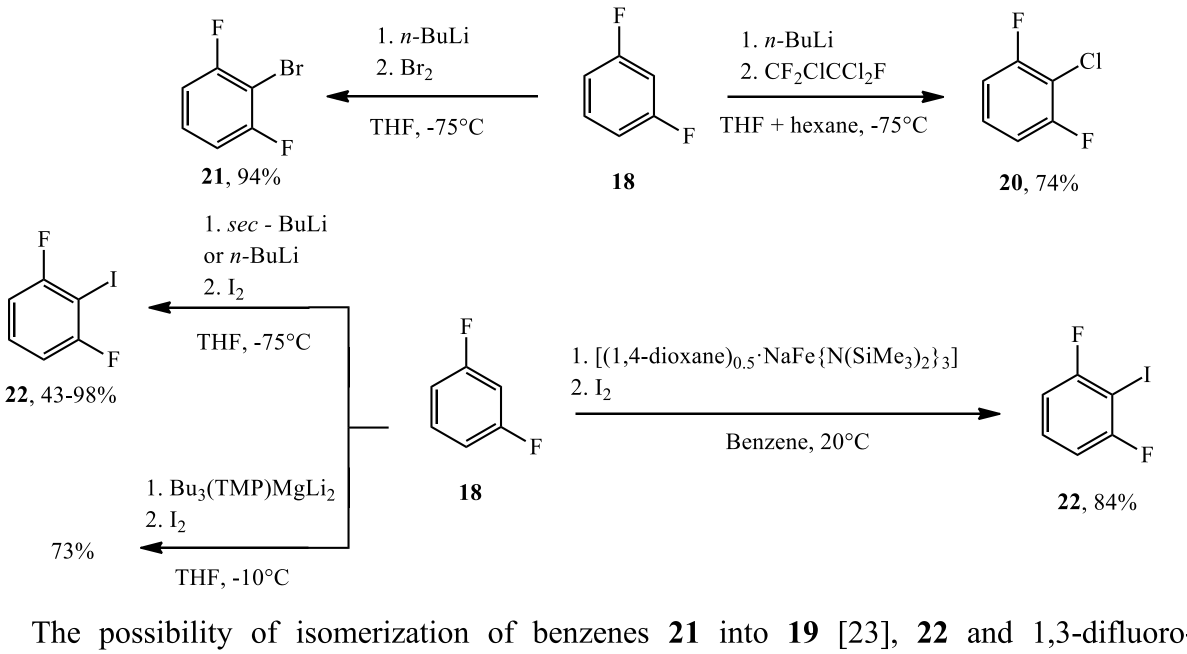
Arene **18** can be easily brominated to 1-bromo-2,4-difluorobenzene (**19**) with good yield [46, 91] (Scheme 22).

Scheme 22.



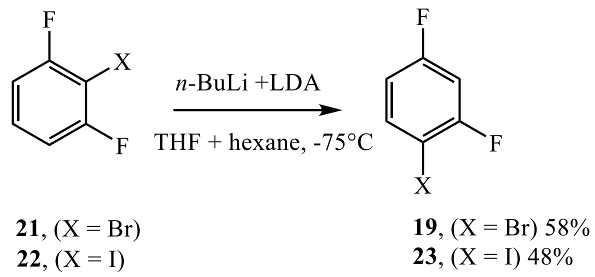
1-Chloro-2,6-difluorobenzene (**20**), 1-bromo-2,6-difluorobenzene (**21**), and 1,3-difluoro-2-iodobenzene (**22**) can be obtained from compound **18** and *n*-BuLi (*sec*-BuLi) with subsequent treatment with 1,1,2-trifluoro-1,2,2-trichloroethylene [92], bromine [93] or iodine [94-99] (Scheme 36). Benzene **22** can also be obtained using other organometallic compounds [77, 100] (Scheme 23).

Scheme 23.



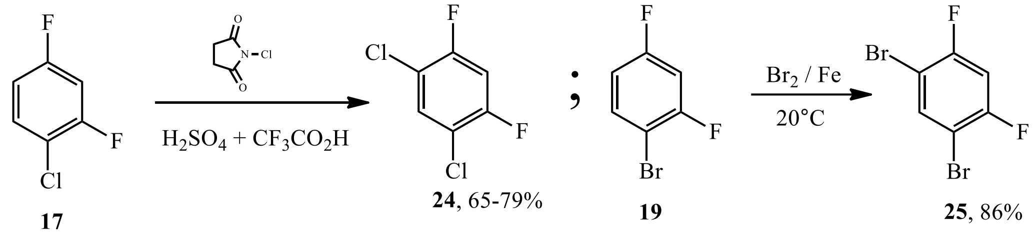
The possibility of isomerization of benzenes **21** into **19** [23], **22** and 1,3-difluoro-4-iodobenzene (**23**) [94] is also interesting (Scheme 24).

Scheme 24.



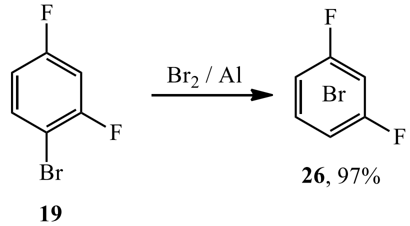
It is worth noting that the interaction of compound **17** with *N*-chlorosuccinimide leads to 1,3-dichloro-2,4-difluorobenzene (**24**) [101, 102], and benzene **19** with bromine to 1,3-dibromo-2,4-difluorobenzene (**25**) [101, 103] Scheme 25).

Scheme 25.



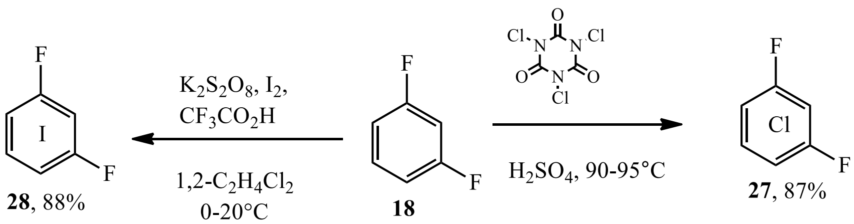
The possibility of exhaustive bromination of 1,2,3,5-tetrabromo-4,6-difluorobenzene (**26**) also has been shown for benzene **19** [104] (Scheme 26).

Scheme 26.



Exhaustive chlorination and iodination of arene **18** was carried out using trichloroisocyanuric acid [105] or $K_2S_2O_8$ +I_2 [91] (Scheme 27).

Scheme 27.



Reaction of 1,4-difluorobenzene (**29**) with SO_2Cl_2 [106] in the presence of $AlCl_3$ and I_2 yields 1,4-difluoro-5-chlorobenzene (**30**), and with Br_2 and Fe [107, 108] or Br_2 with the addition of zeolites [44, 46] yields 1-bromo 2,4-difluorobenzene (**31**) (Scheme 28).

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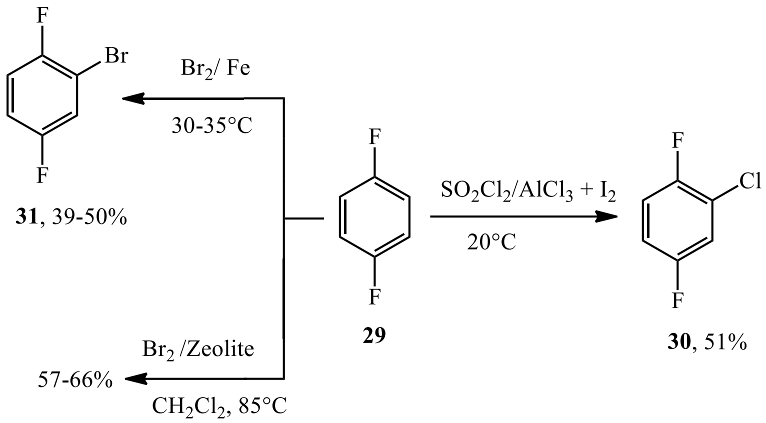
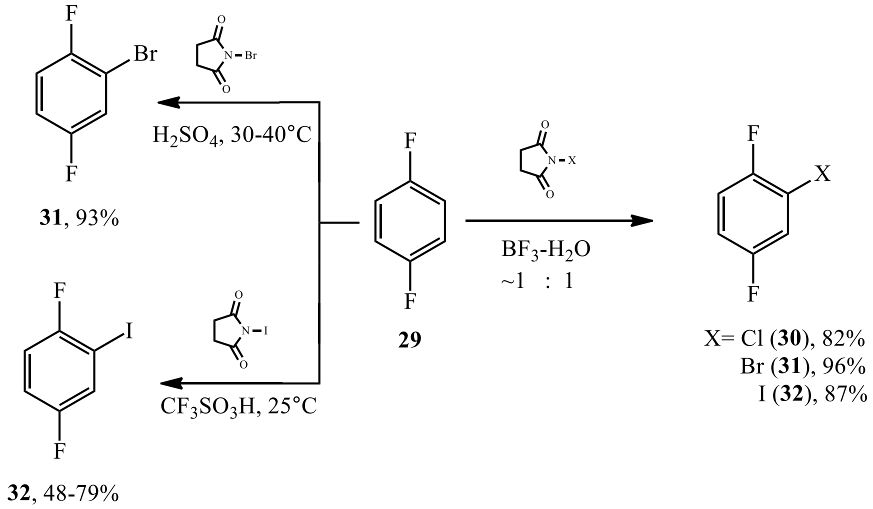
Scheme 28.



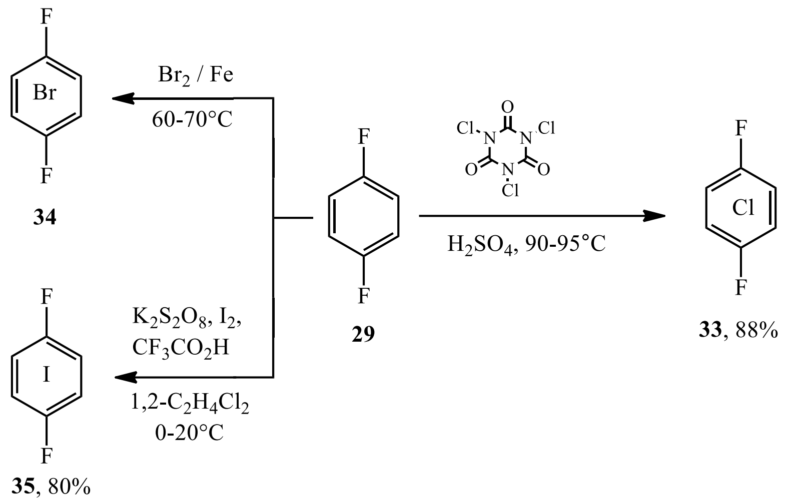
Chlorination [54], bromination [54, 109] and iodination [54, 110, 111] of compound **29** can also be performed using *N*-halosuccinimides (Scheme 29).

Scheme 29.



For arene **29**, chlorination [105], bromination [112] (yield not given), and iodination [87] to tetrachloro-, tetrabromo- and tetraiododifluorobenzenes are possible (Scheme 30).

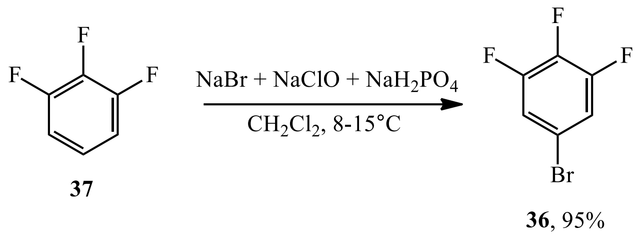
Scheme 30.



3. Chlorination, bromination and iodination of trifluorobenzenes.

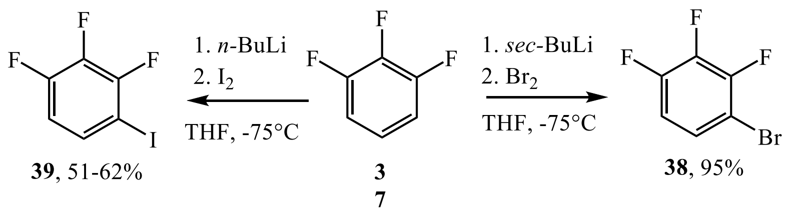
1-Bromo-3,4,5-tetrafluorobenzene (**36**) can be obtained by reacting 1,2,3-trifluorobenzene (**37**) with NaBr in the presence of NaClO and NaH_2PO_4 with high yield [113] (Scheme 31).

Scheme 31.



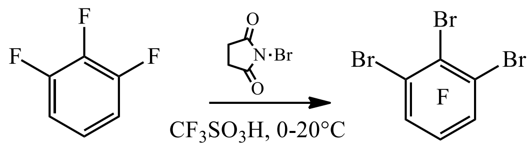
Bromination [114] and iodination [115, 116] in the position 4 of benzene **37** can proceed selectively through an organolithium derivative with good yields (Scheme 32).

Scheme 32.



For benzene **37**, the possibility of exhaustive bromination to 1,2,3-tribromo-4,5,6-trifluorobenzene (**40**) was shown [21] (Scheme 33).

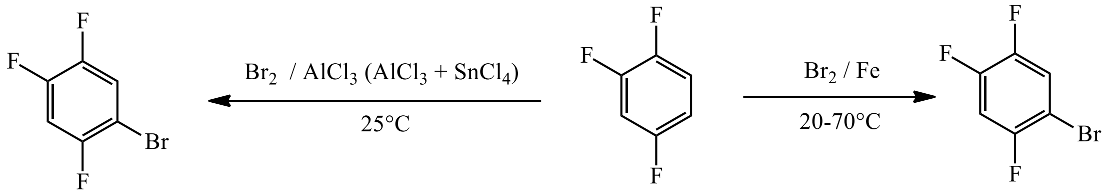
Scheme 33.



37 **40**, 27%

The bromination of 1,2,4-trifluorobenzene (**41**) Br_2 to 1-bromo-2,4,5-trifluorobenzene (**42**) with the addition of [117-122], $SnCl_4$ [123], $AlCl_3$ + $SnCl_4$ [124] as catalysts was described (Scheme 34).

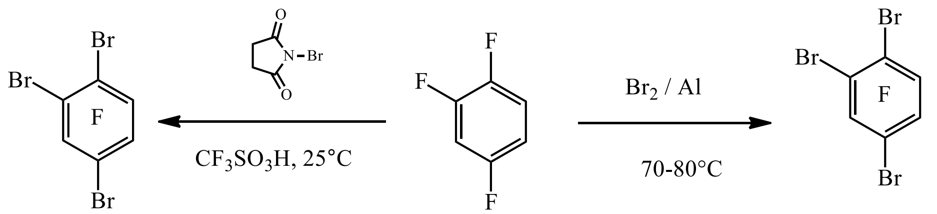
Scheme 34.



42, 95-99% **41** **42**, 64-94%

The exhaustive bromination of benzene **41** by the action of Br_2 in the presence of Al [125] was shown (Scheme 65). Arene **43** also can be obtained by the interaction benzene **41** with *N*-bromosuccinimide [21] (Scheme 35).

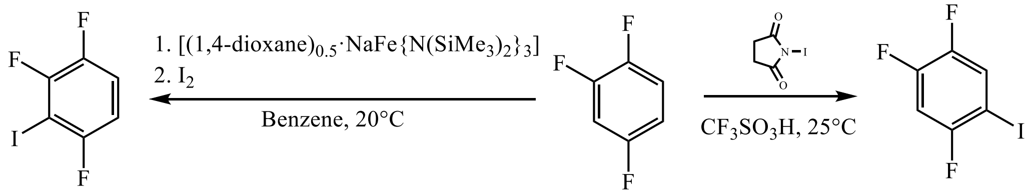
Scheme 35.



43, 49% **41** **43**, 75%

The possibility of selective iodination at the third [77] or fifth position [111] of the aromatic ring has been shown for benzene **41** (Scheme 36).

Scheme 36.

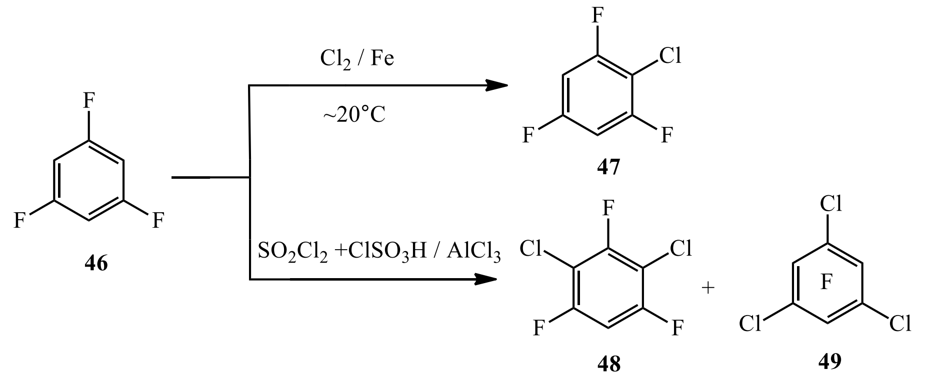


44, 80% **41** **45**, 80%

It was shown when 1,3,5-trifluorobenzene (**46**) Cl_2 is chlorinated in the presence of Fe at the room temperature, 1,3,5-trifluoro-4-chlorobenzene (**47**) is formed as the main product [126]. When the mixture of SO_2Cl_2 and $ClSO_3H$ acts on compound **46** in the presence of $AlCl_3$, mainly 1,3,5-

trifluoro-2,4-dichlorobenzene (**48**) and a small amount of 1,3,5-trifluoro-2,4,6-trichlorobenzene (**49**) are formed (Scheme 37).

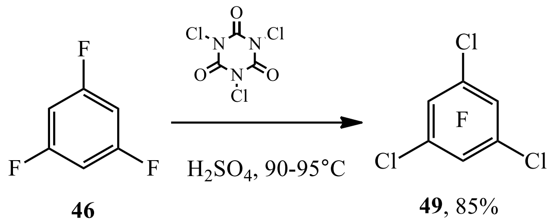
Scheme 37.



The ratio of compounds **48** and **49** is not given [126].

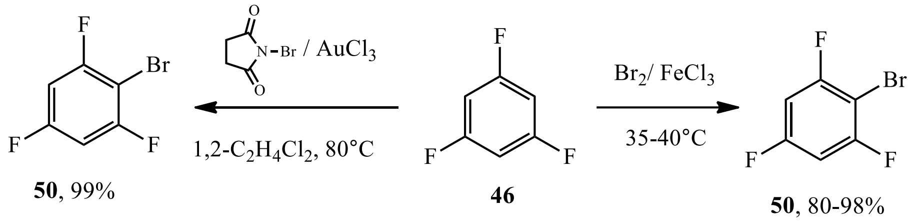
Arene **49** can be obtained by chlorination of benzene **46** with trichloroisocyanuric acid [105] (Scheme 38).

Scheme 38.



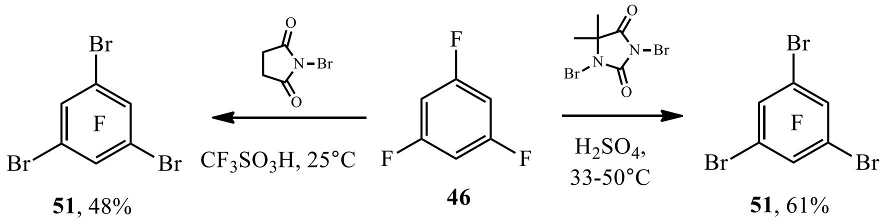
Bromination of arene **46** to 1-bromo-2,4,6-trifluorobenzene (**50**) can be carried out using Br_2 in the presence of $FeCl_3$ [127-130], or *N*-bromosuccinimide [131] (Scheme 39).

Scheme 39.



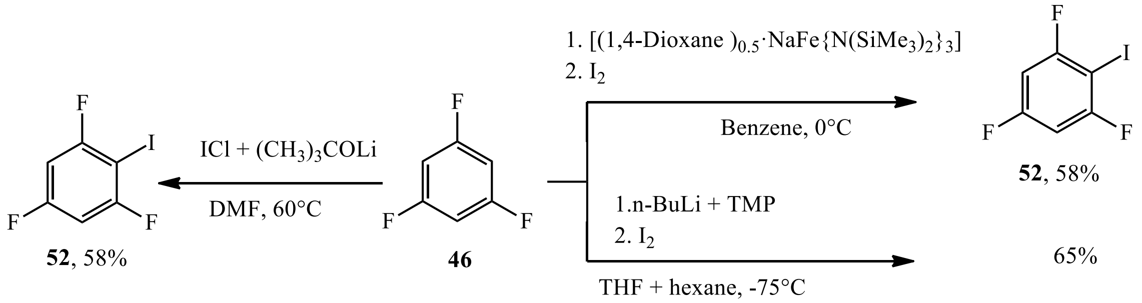
1,3,5-Tribromo-2,4,6-trifluorobenzene (**51**) can be obtained by heating benzene **46** with 1,3-dibromo-5,5-dimethylhydantoin [132] or *N*-bromosuccinimide [21] (Scheme 40).

Scheme 40.



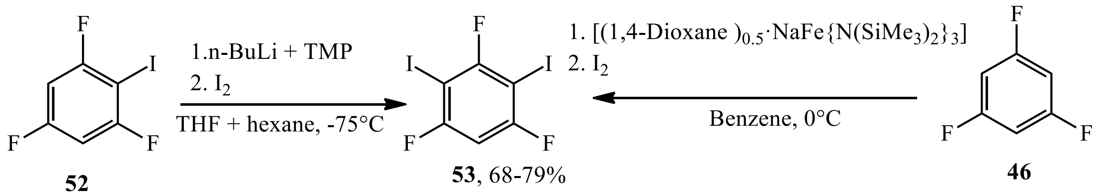
Iodination of benzene **46** using organometallic compounds leads to 1,3,5-trifluoro-2-iodobenzene (**52**) [77, 115, 133, 134] (Scheme 41).

Scheme 41.



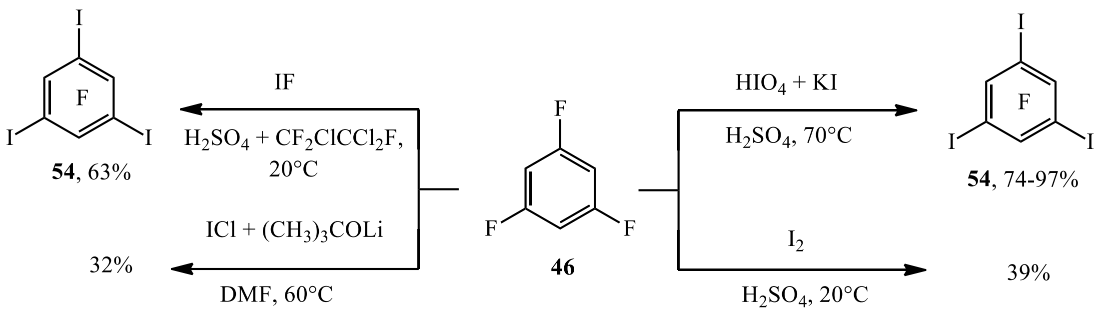
1,3-Diiodo-2,4,6-trifluorobenzene (**53**) was synthesized from compounds **46** [134] and **52** [77] (Scheme 42).

Scheme 42.



1,3,5-Triiodo-2,4,6-trifluorobenzene (**54**) was obtained by heating arene **46** in concentrated H_2SO_4 with HIO_4 and KI [135-141, by reaction benzene **46** with I_2 or IF in concentrated H_2SO_4 [142], or by heating with ICl and $(CH_3)_3COLi$ in DMF [115, 133] (Scheme 43).

Scheme 43.

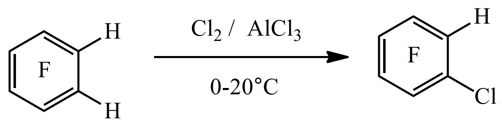


4. Chlorination, bromination and iodination of tetrafluorobenzenes.

Increasing the number of fluorine atoms in the benzene ring to four leads to the fact that reactions of replacing a hydrogen atom with a halogen usally occur under rather harsh conditions.

Chlorination of 1,2,3,4-tetrafluorobenzene (**55**) with Cl_2 in the presence of $AlCl_3$ leads to a monochlorine derivative [143] (Scheme 44).

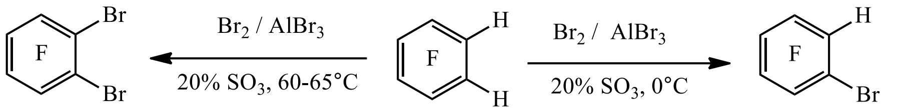
Scheme 44.



55 **56**, 62-67%

1-Bromo-2,3,4,5-tetrafluorobenzene (**57**) was synthesized from benzene **55** and Br_2 in 20% oleum in the presence of $AlBr_3$ at 0°C [144, 145], and 1,2 dibromotetrafluorobenzene (**58**) was synthesized upon heating [146] (Scheme 45).

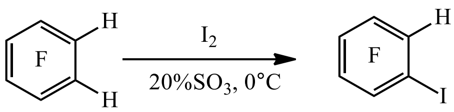
Scheme 45.



58, 38% **55** **57**, 25-49%

1,2,3,4-Tetrafluoro-5-iodobenzene (**59**) can be obtained from benzene **55** and I_2 in 20% oleum [144] (Scheme 46).

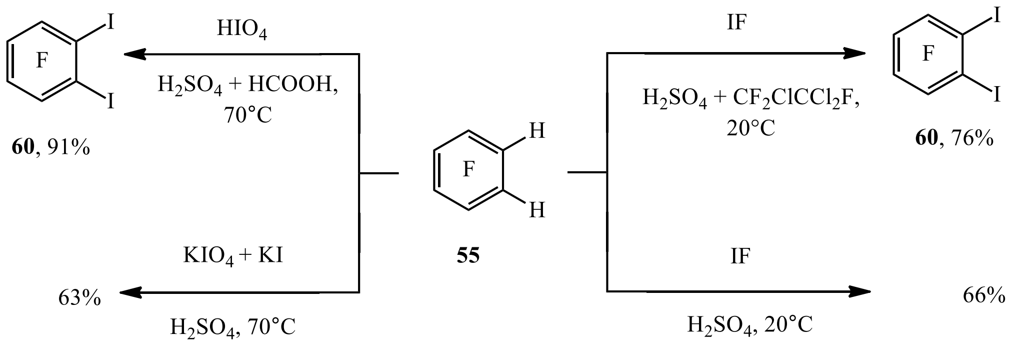
Scheme 46.



55 **59**, 65%

The iodination of benzene **55** to 1,2-diiodo-2,3,4,5-tetrafluorobenzene (**60**) can be carried out by the interaction of the latter with IF [142], HIO_4 [147] and KIO_4 + KI [148] (Scheme 47).

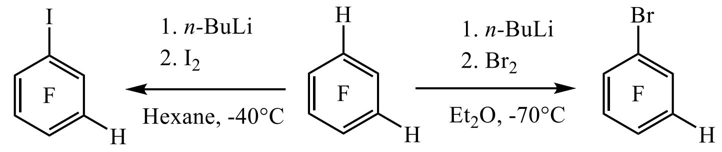
Scheme 47.



60, 91% **60**, 76% **55**

1-bromo-2,3,4,6-tetrafluorobenzene (**61**) and 1,3,5,6-tetrafluoro-2-iodobenzene (**62**) can be synthesized via organolithium derivative of 1,2,3,5-tetrafluorobenzene (**63**) [149, 150] (Scheme 48).

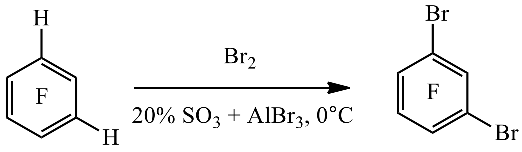
Scheme 48.



62, 49% **63** **61**, 61%

Benzene **63** under the action of bromine in 20% oleum in the presence of $AlBr_3$ at 0°C gives 1,3-dibromotetrafluorobenzene (**64**) [144] (Scheme 49).

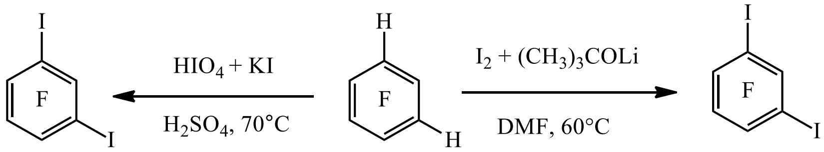
Scheme 49.



63 **64**, 68%

The iodination of compound **63** to 1,3-diiodo-2,4,5,6-tetrafluorobenzene (**65**) can be carried out by heating with iodine in the presence of $(CH_3)_3COLi$ in DMF [133], or by heating with mixture of HIO_4 and KI in H_2SO_4 [151, 152] (Scheme 50).

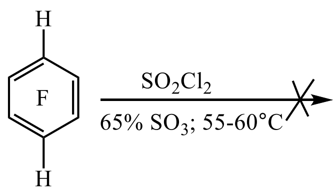
Scheme 50.



65, 61% **63** **65**, 95%

In studying the reactions of chlorination, bromination, and iodination of 1,2,4,5-tetrafluorobenzene (**66**), it was found that only bromination and iodination of this compound could be achieved. Thus, in work [153], an unsuccessful attempt was made to chlorinate benzene **66** using SO_2Cl_2 in 65% oleum upon heating (Scheme 51).

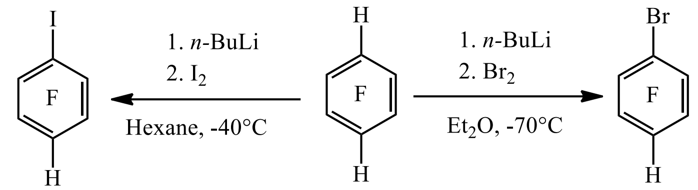
Scheme 51.



66

1-Bromo-2,3,5,6-tetrafluorobenzene (**67**) and 1-iodio-2,3,5,6-tetrafluorobenzene (**68**) can be obtained via organolithium derivative from benzene **66** [149, 150] (Scheme 52).

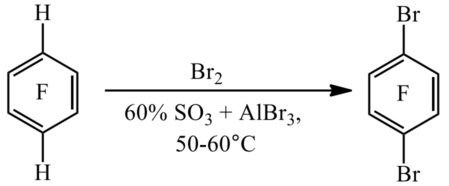
Scheme 52.



68, 73% **66** **67**, 74%

When bromine acts on tetrafluorobenzene **66** in 60% oleum in the presence of $AlBr_3$, 1,4 dibromotetrafluorobenzene (**69**) is formed upon heating [154] (Scheme 53).

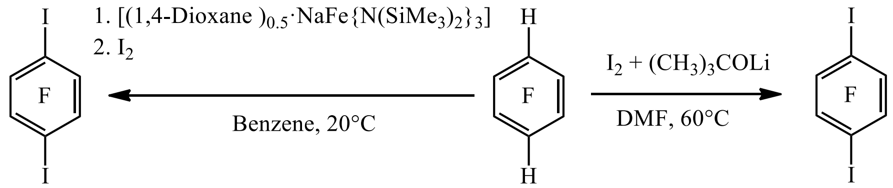
Scheme 53.



66 **69**, 78%

1,4-Diiodotetrafluorobenzene (**70**) can be obtained from arene **66** via organometallic compounds [77, 115] (Scheme 54).

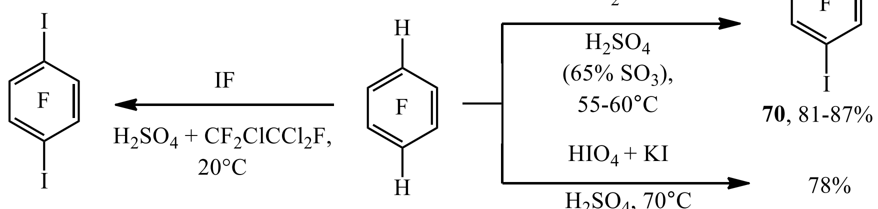
Scheme 54.



70, 88% **66** **70**, 95%

Another approach to the synthesis of arene **70** may involve the interaction of benzene **66** with I_2, fuming H_2SO_4 [155] or oleum [153], in concentrated H_2SO_4 with HIO_4 and KI [140], or with IF in concentrated H_2SO_4 [142] (Scheme 55).

Scheme 55.



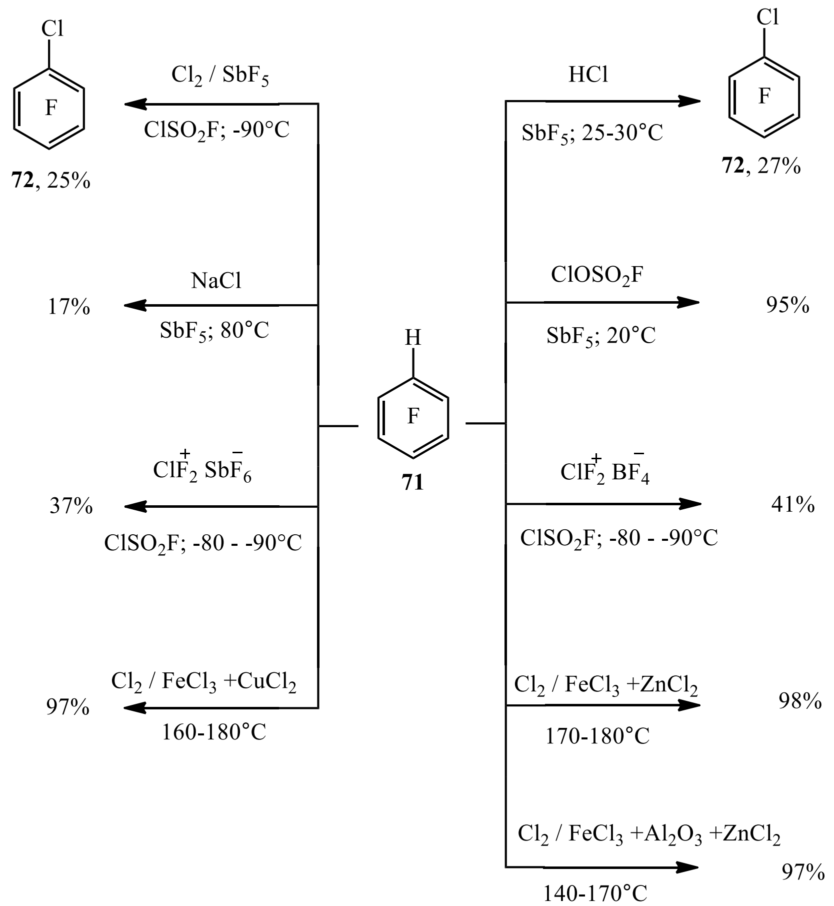
70, 81-87%

70, 68% **66**

5. Synthesis of chloropentafluorobenzene, bromopentafluorobenzene and iodopentafluorobenzene from pentafluorobenzene.

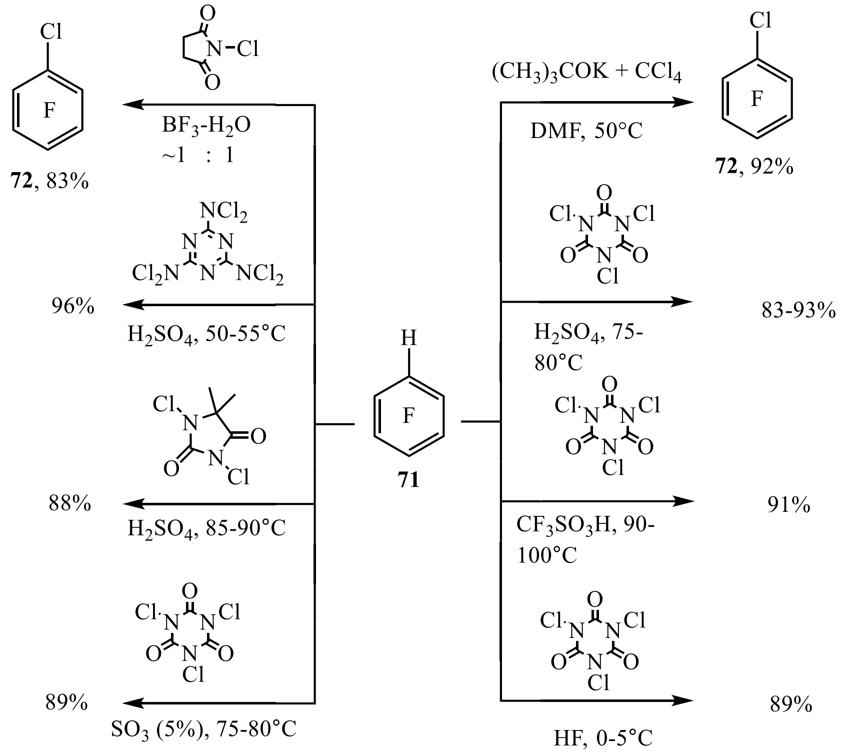
The substitution of a hydrogen atom for chlorine in pentafluorobenzene (**71**) by the action of Cl_2 in the presence of SbF_5 in $ClSO_2F$ [156] has been demonstrated (Scheme 55). HCl or NaCl [157], as well as $ClOSO_2F$ [158] can be used as chlorine sources (Scheme 55). The hydrogen atom was also replaced by chlorine in compound **71** by the action of difluorochloronium cation salts in the presence of SbF_5 or BF_3 in $ClSO_2F$, resulting in the production of pentafluorochlorobenzene (**72**) [159] (Scheme 56). However, these reactions are complicated by the formation of polyfluorinated cyclohexadiene derivatives [159]. The chlorination reaction of arene **71** can be catalyzed by $FeCl_3$ [160] (Scheme 56).

Scheme 56.



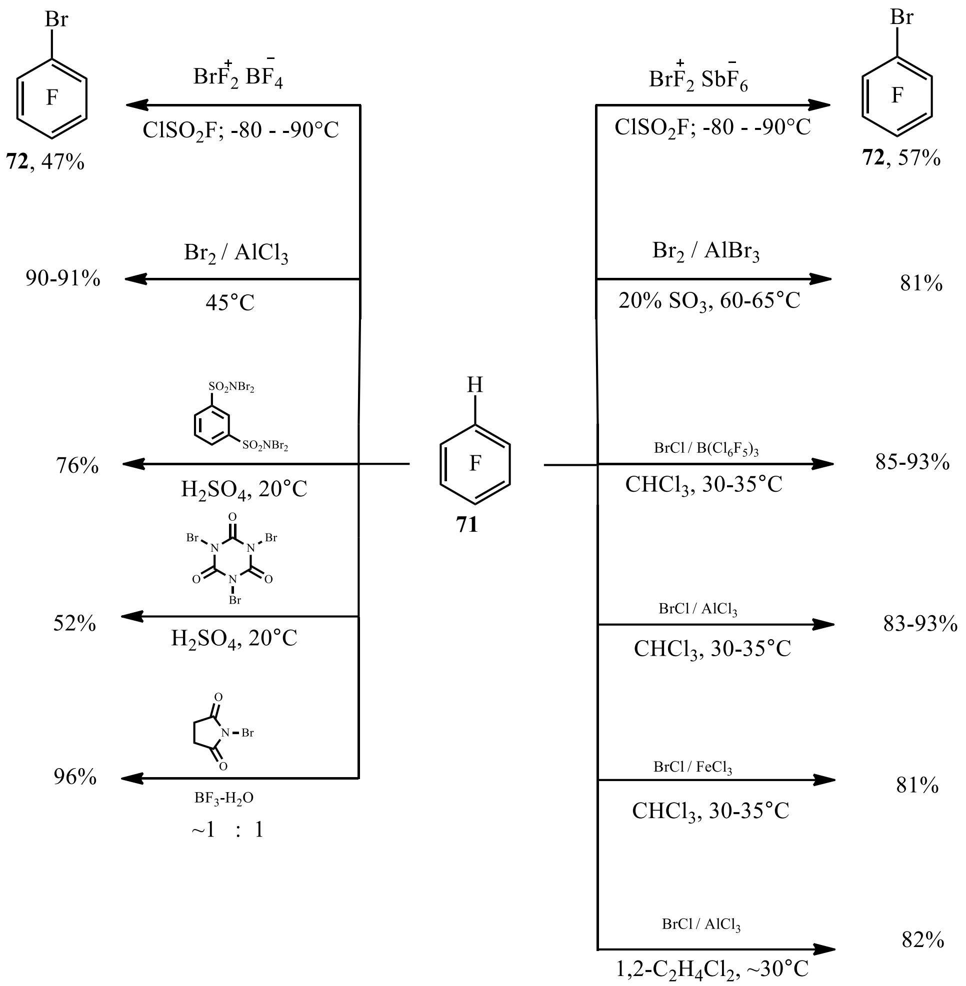
Chlorination of arene **71** can also be carried out using *N*-chlorosuccinimide **[50]**], CCl_4 [161], trichloroisocyanuric acid [105], hexachloromelamine [105], 1,3-dichloro-5,5-dimethylhydantoin [105] (Scheme 57).

Scheme 57.



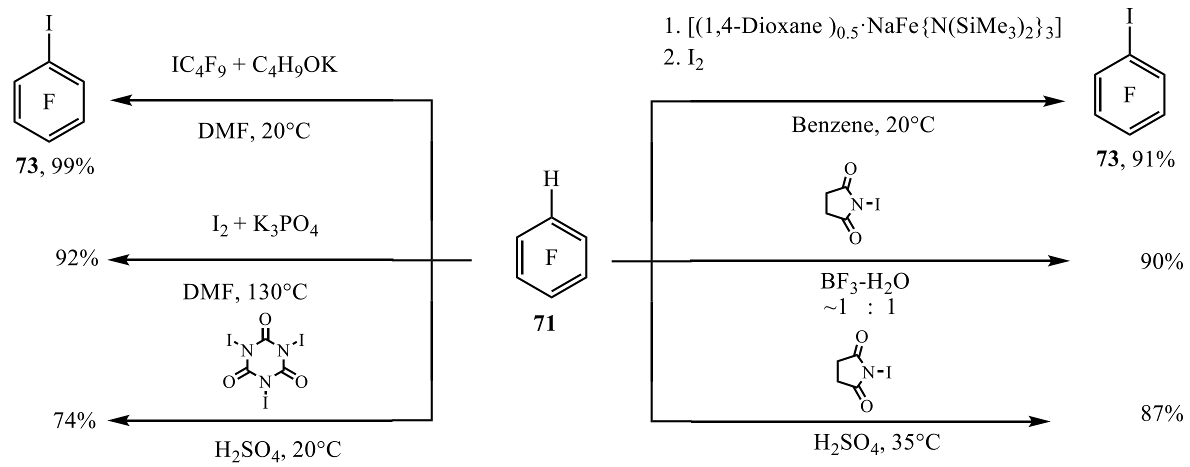
Similarly to the chlorination reaction in the presence of SbF_5 or BF_3 in $ClSO_2F$, shown in Scheme 57, the hydrogen atom was replaced by bromine in compound **71** [159] (Scheme 58). Brompentafluorobenzene (**72**) can be obtained by the action of bromine in 20% oleum in the presence of $AlBr_3$ [162] or bromine in the presence of $AlCl_3$ [163, 164] (Scheme 58). BrCl [165], *N,N,N',N'*-tetrabromobenzene-1,3-disulfonamide [166], tribromisocyanuric acid [167], or N-bromosuccinimide [50] can be used as bromine sources (Scheme 58).

Scheme 58.



The iodination of arene **71** can be carried out using IC_4F_9 [168], complex of [(1,4 dioxane)0.5NaFe{N(SiMe$_3$)$_2$}$_3$] and I_2 [77], *N*-iodosuccinimide [50, 169], I_2 and K_3PO_4 [115, 133], 1,3,5-triiodo-1,3,5-triazine-2,4,6-trione [167] (Scheme 59).

Scheme 59.



Acknowledgements

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