

FLUOPINATION OF POLYFLUOROAROMATIC COMPOUNDS WITH VANADIUM
PENTAFLUORIDE

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SUMMARY

Fluorination of polyfluoro-derivatives of benzene and diphenyl with vanadium pentafluoride at -25 to -10 °C afforded fluorinated cyclohexadienes and cyclohexenes. Octafluoronaphthalene was converted under these conditions to perfluoro-1,4-dihydronaphthalene, perfluorotetralin, perfluoro-1,4,5,8-tetrahydronaphthalene and perfluoro-1,2,3,4,5,8-hexahydronaphthalene.

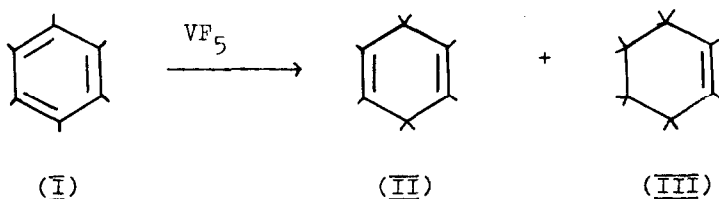
INTRODUCTION

The controlled homogeneous fluorination of polyfluoroaromatic compounds has been illustrated in the literature by their reactions with xenon difluoride [1,2], bromine trifluoride [3,4] and the salts of fluoroxenonium [5] and fluorochalogenonium [6] cations.

As a continuation of the studies on the effect of electrophilic fluoro-oxidants on polyfluoroaromatic compounds, we investigated the reactions of these compounds with vanadium pentafluoride. It should be noted that the chemical properties of VF_5 have not as yet been fully investigated.

RESULTS AND DISCUSSION

The reaction of hexafluorobenzene I with two equivalents of vanadium pentafluoride in SO_2FCl at -25 to -10 °C gave perfluoro-1,4-cyclohexadiene, II, and perfluorocyclohexene, III, as shown by the GLC and ^{19}F NMR data. Perfluoro-1,3-cyclohexadiene and perfluorocyclohexane have not been detected (see the Table)*.

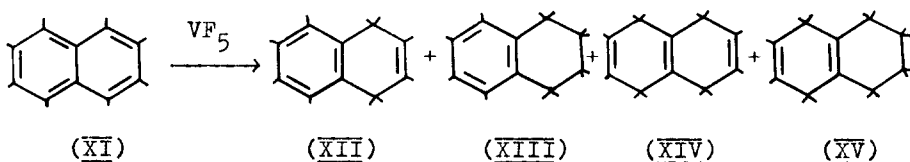
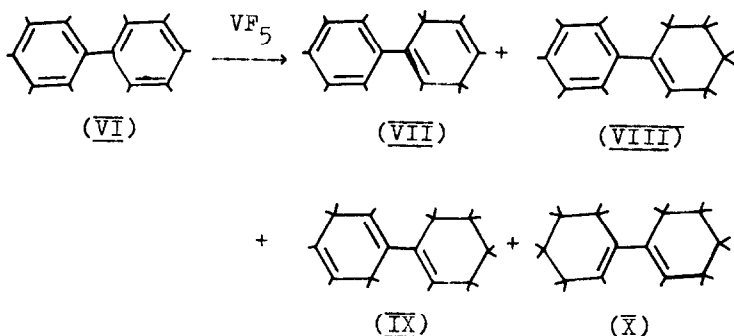


Octafluorotoluene (IV) reacted with vanadium pentafluoride (1:2) giving perfluoro-1-methyl-1,4-cyclohexadiene, V, and perfluoro-1-methylcyclohexene (conversion of the fluorotoluene IV, 51%, yields of products 55 and 8% respectively). With the proportion of VF_5 increased up to 1:4, the conversion of the fluorotoluene IV appeared to be 96%, but the major product was still the diene V (68% yield) (see Table).

Interaction of vanadium pentafluoride with decafluorodiphenyl VI led to the formation of a multicomponent mixture containing the products of addition of 2 to 8 fluorine atoms. With an 8-fold mole excess of VF_5 , the reaction gave perfluoro-1-phenyl-1,4-cyclohexadiene VII, perfluoro-1-phenylcyclohexene VIII, perfluoro-3,3',4,5,6,6'-hexahydrodiphenyl IX and perfluoro-3,3',4,4',5,5',6,6'-octahydrodiphenyl X, the two latter compounds being the major products of the reaction (yields 36 and 20% respectively).

Fluorination of octafluoronaphthalene XI with vanadium pentafluoride (1:2) at -25 to -10 °C gave perfluoro-1,4-dihydronaphthalene XII, perfluorotetralin XIII, perfluoro-1,4,5,8-terahydronaphthalene XIV and perfluoro-1,2,3,4,5,8-hexahydronaphthalene XV, conversion of the starting naphthalene XI being 35%.

* Here and further on all unspecified bonds are to fluorine.

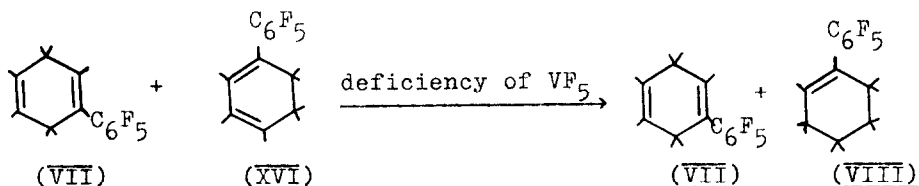


With a large excess of VF_5 (1:8), conversion of octafluoro-naphthalene reached 100%, the major products being again compounds XII - XV in essentially the same yields.

Thus, the results of the reactions of aromatic perfluorinated hydrocarbons with vanadium pentafluoride reveal the high fluorinating ability of this fluoride, which allows synthesis of a variety of perfluorinated unsaturated cyclic compounds without the use of elemental fluorine or a special apparatus for gas-phase fluorination. The chemical activity of VF_5 in these reactions is considerably higher than that of antimony pentafluoride (cf. [7]) and is comparable to that of fluoro-oxidants of the type $\text{XF}_n^+ \cdot \text{MF}_m^-$ ($X = \text{Cl}, \text{Br}, \text{Xe}$) [5,6]. At the same time, we have previously shown [5,6] regiospecificity of addition of two fluorine atoms of the latter to the molecule of a polyfluoroaromatic compound. Though fluorinations of aromatic perfluorocarbons with VF_5 also give the products of 1,4-addition of two fluorine atoms, the intermediate formation of cyclohexadiene derivatives with conjugated double carbon-carbon bonds

should not be excluded, since such cyclohexadienes may be converted by VF_5 to cyclohexene derivatives.* To verify this, we carried out a competing reaction of perfluoro-1-phenyl-1,3-cyclohexadiene XVI and perfluoro-1-phenyl-1,4-cyclohexadiene VII with vanadium pentafluoride.

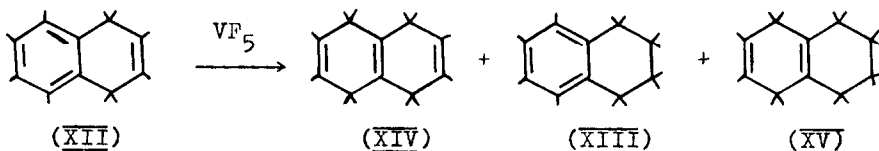
Under the conditions of the competing fluorination, practically all the perfluoro-1-phenylcyclohexene is formed from the conjugated 1,3-isomer XVI:



We believe therefore that the pathway of the reaction of perfluorinated derivatives of cyclohexadiene with VF_5 does not exclude the possibility of intermediate formation of conjugated cyclic 1,3-dienes in fluorinations of aromatic perfluorocarbons by VF_5 .

This peculiarity of the reaction of vanadium pentafluoride with perfluoroaromatic compounds seems to have close connection with the question of the order of formation of the reaction products.

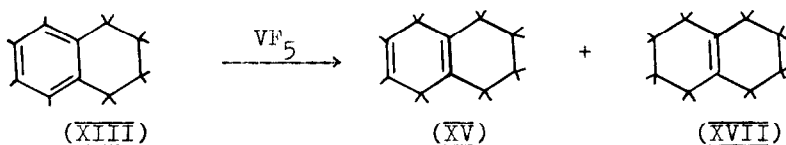
The reaction of perfluoro-1,4-dihydronaphthalene with VF_5 gave perfluorotetralin XIII, along with perfluorinated tetrahydronaphthalene XIV and hexahydronaphthalene XV.



This possibly indicates that fluorinations of the aromatic ring and of the cyclohexadienyl fragment proceed in parallel. Currently it is difficult to compare the relative rates of these

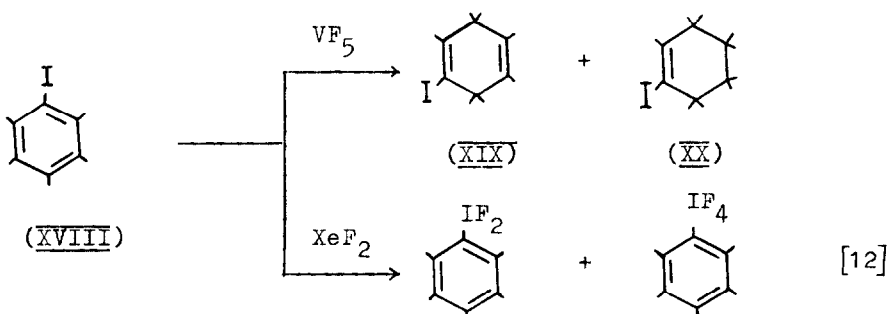
* The regiospecificity in fluorinations of polyfluoroaromatic compounds by halogen fluorides was reported in [3,4].

processes, since tetralin XIII is fluorinated by VF_5 giving hexahydronaphthalene XV and perfluoro-1,2,3,4,5,6,7,8-octahydronaphthalene XVII. The GLC and ^{19}F NMR data show no formation of perfluorodecalin.



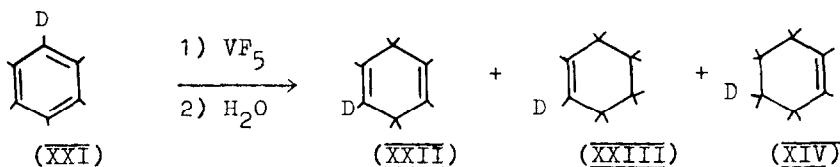
The mechanism of fluorination of polyfluoroaromatic compounds by vanadium pentafluoride is not clear yet. However, a free radical mechanism as in the reactions with fluorine or XeF_2 (in the gas phase, without a catalyst) seems unlikely. This is indicated, first, by the high V-F bond energy $E_{\text{V-F}}$ (VF_5) equal to $477 \text{ kJ}\cdot\text{mol}^{-1}$ [8] as compared to the F-F and Xe-F bond energies $E_{\text{F-F}}$ (F_2) and $E_{\text{Xe-F}}$ (XeF_2) equal to 155 [9] and 134 [10] $\text{kJ}\cdot\text{mol}^{-1}$ respectively, and second, by the absence in the reaction mixture of oligomers generally present when C_6F_6 is treated with fluorine [11].

This is in agreement with the formation of 1-iodoheptafluoro-1,4-cyclohexadiene XIX and 1-iodononafluorocyclohexene XX from VF_5 and iodopentafluorobenzene, whereas fluorination of the latter in the gas phase by XeF_2 gave polyvalent iodine derivatives [12].



In the reaction of partially fluorinated aromatic compounds with vanadium pentafluoride, the C-H bond is not involved. Thus in the reaction of deuteriopentafluorobenzene XXI with VF_5 and subsequent hydrolysis of the reaction mixture, there is no

substitution of deuterium by protium in the starting compound XXI or the reaction products 1-D-heptafluoro-1,4-cyclohexadiene XXII, 1-D-nonafluorocyclohexene XXIII and 4-D-nonafluorocyclohexene XXIV.



For the sake of comparison, hydrolysis of vanadium aromatic compounds of the type $(\text{C}_6\text{F}_5)_n\text{VCl}_{4-n}$ leads to the formation of pentafluorobenzene [13].

EXPERIMENTAL

Conditions for recording the ^{19}F NMR and IR spectra, the GLC analysis and isolation of compounds by the preparative GLC are reported in [6]. The IR and ^{19}F NMR spectra of compounds obtained coincide with those of the previously reported products.

Vanadium pentafluoride was synthesised by treatment of vanadium with fluorine in a flow nickel reactor. Before use, VF_5 was distilled over NaF in an apparatus of nickel and stainless steel.

Reactions of aromatic perfluorocarbons with VF_5

An aromatic fluorocarbon and 40-50 ml of SO_2FCl were placed in a polychlorotrifluoroethylene reactor provided with a Teflon stirrer and a thermocouple in a Teflon well. The mixture was cooled to -25°C and VF_5 was added in portions, with stirring, while the temperature was kept down at -10°C . Immediately after that, a light brown precipitate of VF_4 was formed. The reaction mixture was stirred for 20-25 min., then poured onto ice, the organic layer was separated, washed with water and dried over MgSO_4 .

TABLE
 Reactions of polyfluoroaromatic compounds with vanadium pentafluoride

Compound, mmols	VF ₅ mmols	Substrate conversion, %	Product yields, % *	Ref.
Hexafluorobenzene <u>I</u> , 33.3	66.4	70	C ₆ F ₈ <u>II</u> , 61; C ₆ F ₁₀ <u>III</u> , 13	14
Octafluorotoluene <u>IV</u> , 27.5	63.0	51	C ₆ F ₇ CF ₃ <u>V</u> , 55; C ₆ F ₉ CF ₃ , 8	15, 16
Octafluorotoluene <u>IV</u> , 25.0	100.0	96	C ₆ F ₇ CF ₃ <u>V</u> , 68; C ₆ F ₉ CF ₃ **, 16	15, 16
Decafluorodiphenyl <u>VI</u> , 13.2	109.6	95	C ₆ F ₇ C ₆ F ₅ <u>VII</u> , 3; C ₆ F ₉ C ₆ F ₅ <u>VIII</u> , 15; C ₆ F ₉ C ₆ F ₇ <u>IX</u> , 36; C ₆ F ₉ C ₆ F ₉ <u>X</u> , 20	17, 18 16, 19
Octafluoronaphthalene <u>XI</u> , 22.1	44.5	35	C ₁₀ F ₁₀ <u>XII</u> , 43; C ₁₀ F ₁₂ <u>XIII</u> , 4; C ₁₀ F ₁₂ <u>XIV</u> , 6; C ₁₀ F ₁₄ <u>XV</u> , 4	20, 21 19
Octafluoronaphthalene <u>XI</u> , 40.4	315.1	100	C ₁₀ F ₁₀ <u>XII</u> , 46; C ₁₀ F ₁₂ <u>XIII</u> , 9; C ₁₀ F ₁₂ <u>XIV</u> , 10; C ₁₀ F ₁₄ <u>XV</u> , 6	20, 21 19
Perfluoro-1,4-dihydro- naphthalene <u>XII</u> , 16.1	75.3	98	C ₁₀ F ₁₂ <u>XIV</u> , 9; C ₁₀ F ₁₂ <u>XIII</u> , 31; C ₁₀ F ₁₄ <u>XV</u> , 29	19, 20
Perfluorotetralin <u>XIII</u> , 14.9	68.5	54	C ₁₀ F ₁₄ <u>XV</u> , 36; C ₁₀ F ₁₆ <u>XVII</u> , 21	19
Iodopentafluorobenzene <u>XVIII</u> , 55.1	219.9	77	C ₆ F ₇ I <u>XIX</u> , 49; C ₆ F ₉ I <u>XX</u> , 44	16, 22
Deuteriopentafluorobenzene <u>XXI</u> , 4.7	19.9	84	C ₆ DF ₇ <u>XXII</u> , 39; C ₆ DF ₉ <u>XXIII</u> , 27; C ₆ DF ₉ <u>XXIV</u> , 25	16, 23 24

* The GLC data; ** Perfluoro-1-methylcyclohexene.

Reaction of a mixture of compounds XVI and VII with VF_5

In a similar way, mixing a solution of 0.6 g of perfluoro-1-phenylcyclohexadienes containing 42% of compound XVI and 49% of compound VII, in 11 ml of SO_2FCl , and a solution of 0.2 g of VF_5 in 2 ml of SO_2FCl gave 0.6 g of the product containing 5% of the solvent, 48% of compound VII, 7% of compound XVI and 30% of phenylcyclohexene VIII (the GLC data).*

Reactions of compounds XVIII and XXI with VF_5

The polyfluoroaromatic compound and an equal volume of fluorotrichloromethane were placed in the reactor described above. The solution was cooled to $-30^\circ C$ and a solution of VF_5 in an equal volume of the same solvent was added, with stirring, while the temperature was kept within the range of -25 to $-30^\circ C$. The reaction mixture was then placed on ice, the organic layer was washed with water and dried with $CaCl_2$.

Charges of the reagents and product yields are given in the Table.

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* The content of each of the minor components was $\leq 1\%$.

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