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# Fluorine addition to polychlorinated and polybrominated ethenes and arenes using vanadium pentafluoride

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#### Abstract

Reaction of vanadium pentafluoride with trichloroethene, tetrabromoethene, hexachlorobenzene, and octachloronaphthalene at -20 to 50 °C gave products from fluorine addition, CFCl<sub>2</sub>CFClH, C<sub>2</sub>Br<sub>4</sub>F<sub>2</sub>, C<sub>6</sub>Cl<sub>6</sub>F<sub>6</sub>, and C<sub>10</sub>Cl<sub>8</sub>F<sub>8</sub>, respectively. The fluorine addition to pentachloropyridine and hexabromobenzene was accompanied by the partial replacement of halogen atoms by fluorine and led to products C<sub>5</sub>Cl<sub>4</sub>F<sub>5</sub>N and C<sub>6</sub>Br<sub>4</sub>F<sub>8</sub>, respectively.

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# 1. Introduction

Vanadium pentafluoride is a powerful fluorinating agent which had been used for the fluorine addition to polyfluorinated arenes, alkenes and cycloalkenes (see reviews [1,2]). In general, these reactions has been carried out in chlorofluorocarbons or SO<sub>2</sub>FCl under mild conditions. Reactions of VF<sub>5</sub> with poly- and perchlorinated and perbrominated olefins and arenes have been less investigated. Thus, an addition of fluorine atoms to tetrachloroethene and hexachloro-1,3-butadiene resulted in the formation of 1,2difluorotetrachloroethane and a mixture of two tetrafluorohexachlorobutanes, respectively [3] (Eqs. (1) and (2)).

$$CCl_2 = CCl_2 + 2VF_5 \rightarrow CFCl_2CFCl_2 + 2VF_4$$
(1)

$$CCl_2 = CClCCl = CCl_2 + 4VF_5 \rightarrow CFCl_2CFClCFClCFCl_2$$

$$+ CF_2 ClCCl_2 CFClCFCl_2 + 4VF_4$$
(2)

No replacement of chlorine atom(s) by fluorine(s) took place in either case. Moreover, fluorine addition to halopentafluorobenzenes  $C_6F_5X$  (X: Cl, Br, I) proceeded without C–X bond cleavage and gave halo-undecafluorocyclohexanes  $C_6F_{11}X$  as final products [1]. In contrast, reactions of hexachlorobenzene with elemental fluorine [4–6], chlorine trifluoride [7],  $CoF_3$  [8] or  $SbF_5$  [9] always lead to a mixture of polychloropolyfluorocyclohexenes and/or polychloropolyfluorocyclohexanes which contained less than six chlorine atoms. Similarly, both parallel fluorine addition and F for Cl substitution occurred in reaction of polychloro- and polychlorofluoroalkenes with elemental fluorine, very often accompanied by oligomerisation of olefins [10].

Taking into account these circumstances, we studied the reaction of vanadium pentafluoride with trichloroethene (1), tetrabromoethene (2) and a series of perhalogenated arenes: hexachlorobenzene (3), octachloronaphthalene (4), pentachloropyridine (5) and hexabromobenzene (6).

# 2. Results and discussion

We have found that trichloroethene reacted easily with vanadium pentafluoride at -10 to 10 °C without solvent to give 1,2,2-trichloro-1,2-difluoroethane (7). The formation of significant amounts of 1,1-difluorotrichloroethane or highly fluorinated products were not detected (Eq. (3)).

$$\operatorname{CCl}_{2} = \operatorname{CHCl}_{1} + 2\operatorname{VF5}_{-10 \text{ to } 10 \,^{\circ}\text{C}} \xrightarrow{}_{7} \operatorname{CFCl}_{2} \operatorname{CHClF}_{7} + 2\operatorname{VF4}_{4} \quad (3)$$

Unlike olefin 1, contact of tetrabromoethene 2 with liquid VF<sub>5</sub> caused a vigourous uncontrolled reaction. Therefore, the fluorination was performed by an addition of VF<sub>5</sub> dissolved in CFCl<sub>3</sub> into a stirred suspension of 2 in CFCl<sub>3</sub> at -25 °C. After 20 min stirring at -10 °C olefin 2 was

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converted in 1,2-difluorotetrabromoethane (8a) and 1,1-difluorotetrabromoethane (8b) (1:1) (ca. 50% conversion) (Eq. (4)).

$$CBr_{2} = CBr_{2} + 2VF_{5} \xrightarrow{CFCl_{3}}_{-25 \text{ to} -10 \,^{\circ}\text{C}} CFBr_{2}CFBr_{2} + CF_{2}BrCBr_{3}$$

$$+ 2VF_{4} \qquad (4)$$

Easy fluorine addition to perchlorinated benzene, naphthalene, pyridine and hexabromobenzene occurred under the action of vanadium pentafluoride, but in every case the reaction proceeded in a peculiar way.

Addition of VF<sub>5</sub> (excess) in CFCl<sub>3</sub> into stirred suspension of hexachlorobenzene **3** in CFCl<sub>3</sub> at 0–20 °C led to dissolution of **3** and precipitation of brown vanadium tetrafluoride. After decantation of the liquid phase and subsequent evaporation of solvent and volatile VF<sub>5</sub> (bp 48 °C), colourless oil was obtained. It solidified within some hours to form a glassy substance (mp 113–117 °C) which could be distilled without decomposition at normal pressure. This substance was also obtained by an addition of **3** to a solution of VF<sub>5</sub> in CF<sub>2</sub>ClCFCl<sub>2</sub> or by the reaction with liquid vanadium pentafluoride under reflux. Taking into account results of fluorine addition to halogenated olefins CCl<sub>2</sub>==CCl<sub>2</sub>, CCl<sub>2</sub>==CClCCl==CCl<sub>2</sub> [3], CCl<sub>2</sub>==CHCl and CBr<sub>2</sub>==CBr<sub>2</sub>, we assumed the formation of hexachlorohexafluorocyclohexanes (**9**) (Eq. (5)).

$$C_{6}Cl_{6} + 6VF_{5} \xrightarrow{CFCl_{3} \text{ or } C_{2}Cl_{3}F_{3}}_{0 \text{ to } 50 \,^{\circ}C} C_{6}Cl_{6}F_{6} + 6VF_{4}$$
(5)

Indeed, analytical data (contents of C, Cl, F) and the molecular mass determination of 9 correspond to C<sub>6</sub>Cl<sub>6</sub>F<sub>6</sub>. Neither the less or the highly fluorinated compounds  $C_6Cl_nF_{12-n}$ ,  $C_6Cl_nF_{10-n}$   $(n \neq 6)$  were detected by GC-MS analysis of 9. Infrared spectrum of 9 does not contain bands at 1600–1750  $\text{cm}^{-1}$  due to the C=C bond of polyhalogenated cyclohexadienes and cyclohexenes. The <sup>19</sup>F NMR spectrum of 9 is too complex for analysis and contains the numerous resonances at -80 to -140 ppm (cf. with spectra of polychloropolyfluorocyclopentanes [11]). The <sup>13</sup>C NMR spectrum of **9** displayed signals between 108 and 120 ppm (CFCl and CF<sub>2</sub> moieties) and the resonance at 90 ppm which was assigned to CCl<sub>2</sub> fragment of polyhalogenated carbon chain [12]. Because GC-MS analysis of 9 showed the presence at least four components with the close retention times, product 9 was assumed to be a mixture of isomers C<sub>6</sub>Cl<sub>6</sub>F<sub>6</sub> with cis- and trans-CFCl-CFCl and CF<sub>2</sub>- $CCl_2$  fragments. Noteworthy, that compounds  $C_6Cl_6F_6$  were previously isolated from the reaction mixtures obtained by the fluorination of **3** with elemental fluorine [4-6], ClF<sub>3</sub> [7], or  $CoF_3$  [8] or prepared by the chlorine addition to  $C_6F_6$ under UV irradiation [13]. In any cases, these products were characterised only by analytical data (C, Cl, F) and melting and/or boiling points [6,7,13].

Reaction of octachloronaphthalene **4** with VF<sub>5</sub> in  $C_2Cl_3F_3$  gave the product of composition  $C_{10}Cl_8F_8$  (**10**) (Eq. (6)). The absence of bands at 1600–1750 cm<sup>-1</sup> in the IR spectrum

indicated the absence of the -CX=CY- (X, Y: F, Cl) moieties in molecule (cf. with IR spectra of perfluorinated bicyclo[4.4.0]-1(2), -2 and -3-decene isomers [14]). Based on the IR spectrum, analytical data and molecular mass determination, product **10** was identified as octachloroocta-fluorobicyclo[4.4.0]-1(6)-decene (a mixture of isomers with *cis*- and *trans*-CFCl–CFCl and, probably, CF<sub>2</sub>–CCl<sub>2</sub> fragments). For comparison, the fluorination of octafluoronaphthalene with VF<sub>5</sub> led to perfluorobicyclo[4.4.0]-1(6)-decene and the residual C=C bond remained intact toward the fluorine addition just at 250 °C [15].

$$C_{10}Cl_8 + 8VF_5 \xrightarrow[45-50]{C_2Cl_3F_3}{C_{10}Cl_8F_8} + 8VF_4$$
(6)

While the fluorine addition to perhaloethenes 1, 2 and perchloroarenes 3 and 4 gave compounds with the same numbers of chlorine atoms as their precursors, the reaction of pentachloropyridine 5 with vanadium pentafluoride in  $C_2Cl_3F_3$  gave in the less chlorinated tetrachloropentafluoro-1-azacyclohexenes  $C_5Cl_4F_5N$  (11) (Eq. (7)). The <sup>19</sup>F NMR spectrum of 11 is very complex, although the resonances at -38 to -60 ppm indicate the presence of N=CF, CFCl-N=C and CF<sub>2</sub>-N=C moieties [16]. This is not contradict to results deduced from the IR spectrum where bands at 1746 cm<sup>-1</sup> (N=CF) and 1677 cm<sup>-1</sup> (N=CCl) are presented. Evidently, the IR spectrum of product  $C_5Cl_4F_5N$  obtained by the photochemical chlorination of pentafluoropyridine contains the band at 1734 cm<sup>-1</sup> (N=CF) [17].

$$C_{5}Cl_{5}N + 5VF_{5} \xrightarrow[45-50]{C_{2}Cl_{3}F_{3}}{\xrightarrow{C_{2}Cl_{3}F_{3}}{C_{5}Cl_{4}F_{5}N}} + 5VF_{4} + \frac{1}{2}Cl_{2}$$
(7)

An addition of six fluorine atoms as well as replacement of two bromine atoms by fluorine atoms, took place in reaction of hexabromobenzene 6 with vanadium pentafluoride (excess) which gave tetrabromooctafluorocyclohexanes (12) (Eq. (8)).

$$C_{6}Br_{6} + 8VF_{5} \xrightarrow[50\,^{\circ}C]{} C_{6}Br_{4}F_{8} + 8VF_{4} + Br_{2}$$
(8)

In contrast to perhalogenated arenes 3, 4, 5 and 6, compounds 9–12 are readily soluble in CFCl<sub>3</sub>, CF<sub>2</sub>ClCFCl<sub>2</sub> and in common organic solvents (pentane, hexane, benzene, acetone, ethanol, ether, diglyme, THF, dioxane, MeCN and DMF), partially chlorinated hydrocarbons (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CH<sub>2</sub>ClCH<sub>2</sub>Cl) and perhalocarbons (CCl<sub>4</sub>, CF<sub>2</sub>-BrCF<sub>2</sub>Br, C<sub>6</sub>F<sub>6</sub>, C<sub>6</sub>F<sub>5</sub>Cl).

## 3. Experimental

<sup>19</sup>F NMR spectra were measured on a BRUKER WP 200 SY spectrometer at 188.28 MHz in CDCl<sub>3</sub>. The chemical shifts are referenced to CCl<sub>3</sub>F with  $C_6F_6$  as secondary reference (-162.9 ppm). IR spectra were recorded on a BRUKER Vector 22 spectrometer. GC-MS analyses were performed on HEWLETT-PACKARD G1800A and HEW-LETT-PACKARD GS6890 instruments.

Hexachlorobenzene, trichloroethene, hexabromobenzene, CFCl<sub>3</sub> and CF<sub>2</sub>ClCFCl<sub>2</sub> were commercial products. Octachloronaphthalene (94%) and pentachloropyridine (94%) were prepared in Novosibirsk Institute of Organic Chemistry. Tetrabromoethene was purified by crystallisation from ethanol. Vanadium pentafluoride (Siberian Chemical Enterprise, Russia) was prepared by fluorination of vanadium with elemental fluorine at 300–350 °C and distilled over NaF before use. All manipulations with VF<sub>5</sub> were performed in a Pyrex equipment under atmosphere of dry argon.

Vanadium tetrafluoride formed in above reactions was fine brown powder (Anal. Calcd. for VF<sub>4</sub>: F, 59.9. Found: F, 59.2). It dissolved rapidly in water yielding an acidic solution with the characteristic rich blue colour of vanadium(IV) [18].

# 3.1. Fluorination of trichloroethene (1)

Trichloroethene (8.2 g, 0.062 mol) was added dropwise to vanadium pentafluoride (32 g, 0.22 mol) at -10 to  $10 \,^{\circ}$ C under stirring. The reaction mixture was kept at  $0-5 \,^{\circ}$ C for 30 min and all volatile product were distilled into receiver filled with ice water. The organic layer was separated, washed with water and dried with MgSO<sub>4</sub>. The colourless liquid obtained (5.2 g) contained 80% of trichlorodifluoroethane 7 (<sup>19</sup>F NMR) beside unknown components (content of each did not exceed 2–5%).

#### 3.2. Fluorination of tetrabromoethene (2)

Solution of VF<sub>5</sub> (38 g, 0.26 mol) in CFCl<sub>3</sub> (50 ml) was added to cold (-25 °C) stirred suspension of tetrabromoethene (34.4 g, 0.10 mol) in CFCl<sub>3</sub> (100 ml) within 20 min. After additional 20 min stirring at -10 °C, the reaction mixture was poured onto ice cooled with liquid nitrogen. Red organic phase was separated and aqueous one was extracted with CFCl<sub>3</sub> (30 ml). Combined extract was washed with aqueous K<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, with water and dried with CaCl<sub>2</sub>. Solvent was distilled off to give a liquid (34.4 g) which contained C<sub>2</sub>Br<sub>4</sub> (52%) and C<sub>2</sub>Br<sub>4</sub>F<sub>2</sub> (43%) (GLC). The <sup>19</sup>F NMR spectrum displayed two single resonances at -55.8 ppm (olefin **8a**) and -64.7 ppm (olefin **8b**) of equal intensity. GC-MS analysis showed the presence of two isomers C<sub>2</sub>Br<sub>4</sub>F<sub>2</sub> [ $M^+$  378 (<sup>79</sup>Br)] with the different fragmentation routes beside olefin **2**.

## 3.3. Fluorination of hexachlorobenzene (3)

1. A 1 l, three-necked round-bottom Pyrex flask equipped with mechanic stirrer, thermometer and reflux condenser was charged with vanadium pentafluoride (650 g, 4.5 mol) and 1,1,2-trichlorotrifluoroethane (300 ml). Hexachlorobenzene (142 g, 0.5 mol) was added in small portions so the temperature was kept below 25–30 °C. The mixture was stirred at this temperature for 1.5 h and volatile substances ( $C_2Cl_3F_3$  and  $VF_5$ ) were distilled-off. Residue was extracted with 1,1,2-trichlorotrifluoroethane  $(2 \times 250 \text{ ml})$  and combined extracts were evaporated. Initially formed colourless oil was solidified within some hours to yield glassy product **9** (152 g, 76%). Yield of VF<sub>4</sub> was 384 g (3.0 mol).

- 2. Hexachlorobenzene (6 g, 0.021 mol) was added to refluxed (bp 48 °C) vanadium pentafluoride (36 g, 0.24 mol) under stirring. The reaction mixture was kept at 50 °C (bath) for 1.5 h, cooled below 30 °C and reflux condenser was replaced with distillation head. Excess of VF<sub>5</sub> (14 g) was distilled-off and residue was extracted with 1,1,2-trichlorotrifluoroethane (2 × 40 ml). After evaporation of C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub> from the combined extracts, initially formed, a colourless oil was solidified within 3 h to yield glassy product **9** (6.2 g, 74%). Yield of VF<sub>4</sub> was 21 g.
- Solution of VF<sub>5</sub> (277 g, 1.9 mol) in CFCl<sub>3</sub> (180 ml) was added dropwise into stirred suspension of hexachlor-obenzene (55 g, 0.19 mol) in CFCl<sub>3</sub> (400 ml) at 0–20 °C. The reaction mixture was stirred at 20–24 °C for 3 h and cooled to 0–4 °C. Vanadium tetrafluoride was filtered-off and washed with CFCl<sub>3</sub> (20 ml). Solvent (bp 24 °C) and excess of VF<sub>5</sub> (91 g, 83%) were evaporated to give 9 (62 g, 81%). Yield of VF<sub>4</sub> was 148 g.

*Hexachlorohexafluorocyclohexanes* (**9**): mp 113– 117 °C (lit. mp 94–96 °C [6], 101–102 °C [13]), bp 241 °C (lit. bp 137 °C at 30 mmHg [7], 248 °C [13]). Anal. Calcd. for C<sub>6</sub>Cl<sub>6</sub>F<sub>6</sub>: M 399; C, 18.0; Cl, 53.3; F, 28.6. Found: M 399; 402 (in CHCl<sub>3</sub>); C, 18.0; Cl, 53.0; F, 29.2. IR (CCl<sub>4</sub>): v 1229, 1197, 1178, 1147, 1128, 1100, 1074, 1044, 977, 959, 905, 890, 841, 826, 803, 792, 768, 749, 730, 712, 619 cm<sup>-1</sup>.

## 3.4. Fluorination of octachloronaphthalene (4)

- 1. Octachloronaphthalene (10 g, 0.025 mol) was added in portions to a stirred solution of vanadium pentafluoride (39 g, 0.27 mol) in CF<sub>2</sub>ClCFCl<sub>2</sub> (40 ml) at the temperature below 40–45 °C. Suspension was refluxed for 3 h, the mother liquor was decanted and residue was extracted with CF<sub>2</sub>ClCFCl<sub>2</sub> ( $3 \times 20$  ml). After the evaporation of solvent and excess of VF<sub>5</sub>, product **10** (colourless oil; 11g, 85%) was obtained. Yield of VF<sub>4</sub> was 28 g.
- 2. Octachloronaphthalene (8 g, 0.02 mol) was fluorinated with VF<sub>5</sub> (32 g, 0.22 mol) in CF<sub>2</sub>ClCFCl<sub>2</sub> (40 ml) as above. After cooling to 20 °C, excess of VF<sub>5</sub> was quenched by addition of trichloroethene (3 ml) and formed vanadium tetrafluoride (28 g) was filtered-off. Filtrate was evaporated to give product **10** (10 g, 92%).

*Octachlorooctafluorobicyclo*[4.4.0]-1(6)-decenes (**10**): bp 150–160 °C (2 mmHg). Anal. Calcd. for  $C_{10}F_8Cl_8$ : M 556; C, 21.6; Cl, 51.0; F, 27.3. Found: M 559, 560 (in CHCl<sub>3</sub>); C, 21.6; Cl, 51.1; F, 26.6. IR (CCl<sub>4</sub>): v 1224, 1187, 1140, 1026, 976, 944, 864, 804, 781, 746, 712, 621, 600 cm<sup>-1</sup>.

## 3.5. Fluorination of pentachloropyridine (5)

- 1. Pentachloropyridine (10 g, 0.025 mol) was added in portions into stirred solution of VF<sub>5</sub> (39 g, 0.27 mol) in CF<sub>2</sub>ClCFCl<sub>2</sub> (40 ml) and kept at 45–50 °C for 4 h. Solution was decanted at 20–25 °C and precipitate was washed with CF<sub>2</sub>ClCFCl<sub>2</sub> (3 × 40 ml) to give vanadium tetrafluoride (33 g). Combined extract was evaporated and product **11** (colourless oil; 11 g, 85%) was obtained.
- 2. Reaction of pyridine **5** (25 g, 0.01 mol) with VF<sub>5</sub> (89 g, 0.61 mol) in CF<sub>2</sub>ClCFCl<sub>2</sub> (80 ml) was performed in similar way. After cooling to 18–20 °C, excess of VF<sub>5</sub> was reacted with trichloroethene (5 ml) to give insoluble vanadium tetrafluoride. The reaction mixture was filtered, cake was washed with CF<sub>2</sub>ClCFCl<sub>2</sub> (2 × 35 ml) and combined extract was evaporated to give product **11** (23 g, 74%). Vanadium tetrafluoride was isolated in 90% yield (70 g).

*Tetrachloropentafluoro-1-aza-cyclohexenes* (**11**): bp 50–95 °C (12 mmHg) (lit. 60 °C (8 mmHg) [17]);  $d_4^{20}$  2.0. Anal. Calcd. for C<sub>5</sub>Cl<sub>4</sub>F<sub>5</sub>N: C, 19.3; Cl, 45.6; F, 30.6; N, 4.51. Found: C, 19.3; Cl, 45.7; F, 30.7; N, 4.59. IR (CCl<sub>4</sub>):  $\nu$  1746, 1677, 1320, 1275, 1260, 1180, 1120, 1065, 965, 950 cm<sup>-1</sup>.

#### 3.6. Fluorination of hexabromobenzene (6)

Hexabromobenzene (5.5 g, 0.01 mol) was added in portions to the stirred refluxed vanadium pentafluoride (30 g, 0.20 mol). The reaction mixture was refluxed for 1.5 h, cooled to 25 °C and suspended in dichloromethane (25 ml). Suspension was poured onto ice, brown organic phase was separated and aqueous one was extracted with CH<sub>2</sub>Cl<sub>2</sub> (25 ml). Combined extract was washed in sequence with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> and water and dried with CaCl<sub>2</sub>. After evaporation of solvent, the colourless oil was solidified within some days to give soft solid **12** (1.6 g, 29%). *Tetrabromooctafluorocyclohexanes* (**12**): Anal. Calcd. for  $C_6Br_4F_8$ : M 544; C, 13.3; Br, 58.8; F, 28.0. Found: M 553, 556 (in CHCl<sub>3</sub>); C, 13.3; Br, 58.0; F, 28.5. IR (KBr): *v* 1230, 1205, 1185, 1165, 1125, 1110, 1040, 970, 955, 915, 895, 865, 830, 790, 770, 690, 600 cm<sup>-1</sup>.

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