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Fluorination of trimethylsilylfluoro- and trimethylsilyltetrafluorobenzenes with xenon difluoride

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Abstract

Replacement of hydrogen or trimethylsilyl group by fluorine and the addition of two fluorine atoms to the aromatic ring were found in the reaction of XeF_2 with 1-trimethylsilyl-2,3,4,5- or 2,3,4,6-tetrafluorobenzenes in CH_2Cl_2 under $BF_3 \cdot OEt_2$ catalysis. Only addition of two fluorine atoms took place in the case of 1-trimethylsilyl-2,3,5,6-tetrafluorobenzene. The isomeric trimethylsilylfluorobenzenes underwent fluorodesilylation, fluorodeprotonation and protodesilylation. The assumed reaction pathways include both cation radicals and arylxenon(II) species as reactive intermediates.

Keywords: Trimethylsilylfluorobenzenes; Trimethylsilyltetrafluorobenzenes; Xenon difluoride; Fluorination

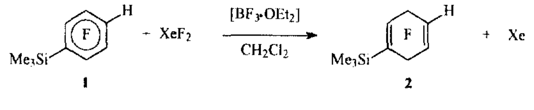
1. Introduction

In 1993, we described the reaction of silyl- and germylpentafluorobenzenes $C_6F_5MX_3$ ($M = Si$, Ge; $X = F$, Cl, Br, Alk) with xenon difluoride in the presence of Lewis acids [1]. When MX_3 was $SiMe_3$, $SiMe_2C_6F_5$ and $SiMe_2F$, the $BF_3 \cdot OEt_2$-catalyzed reactions proceeded smoothly at room temperature to give 1-MX_3-heptafluoro-1,4-cyclohexadienes and traces (1–2%) of hexafluorobenzene. Recently we found that tetrafluorobenzenes C_6HF_4R ($R = F$, Cl, Br, H, CF_3, NO_2) add two fluorine atoms or undergo fluorodeprotonation to yield the corresponding pentafluorobenzene derivatives, C_6F_5R, under the action of XeF_2 in either anhydrous HF or CH_2Cl_2–$BF_3 \cdot OEt_2$ (catalyst) [2]. In continuation of our systematic investigations in that field, the reaction of XeF_2 with partially fluorinated aryltrimethylsilanes has now been studied under the catalysis of Lewis acid.

In general, the introduction of one or more fluorine atoms into a molecule is described 'fluorination' independently of the reaction type. To be more informative these reactions should be named fluorodeprotonation, fluorodesilylation, fluorodecarboxylation, etc. (replacement of hydrogen atom, silyl, carboxy or the other group by fluorine), oxidative fluorination (attachment of fluorine atom(s) with increase of the co-ordination number of the central atom) and fluoridation (nucleophilic substitution of an atom or a functional group by fluoride anion). Fluorine addition (addition of two or four fluorine atoms to the multiple carbon–carbon, carbon–element or element–element bond) and fluorohalogenation, fluoroprotonation, fluoromercuration, etc. (addition of fluorine and halogen, fluorine and mercury, and related processes) are subgroups of oxidative fluorination.

2. Results and discussion

1-Trimethylsilyl-2,3,5,6-tetrafluorobenzene **1** dissolved in CH_2Cl_2 reacted with XeF_2 in the presence of $BF_3 \cdot OEt_2$ to give 1-trimethylsilyl-4-*H*-hexafluoro-1,4-cyclohexadiene **2** in 89% yield. However, the analogous reaction of XeF_2 with 1-trimethylsilyl-2,3,4,6-tetrafluorobenzene **3** led to a variety of products: 1-trimethylsilyl-5-*H*-hexafluoro-1,4-cyclohexadiene **4**, 1-trimethylsilylheptafluoro-1,4-cyclohexadiene **5**, trimethylsilylpentafluorobenzene **6**, pentafluorobenzene **7** and 1-*H*-heptafluoro-1,4-cyclohexadiene **8** together with fluorotrimethylsilane and HF. In a similar manner, compounds **5**, **6**, **7**, **8**, $FSiMe_3$, HF and 1-trimethylsilyl-2-*H*-hexafluoro-1,4-cyclohexadiene **9** were produced from 1-trimethylsilyl-2,3,4,5-tetrafluorobenzene **10** and xenon difluoride under the $BF_3 \cdot OEt_2$ catalysis.



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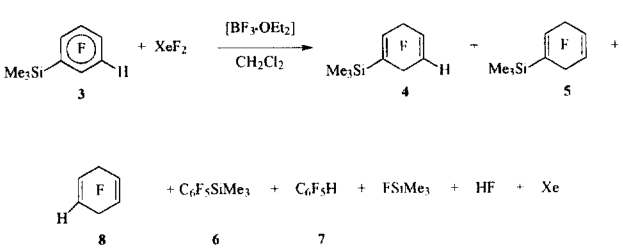
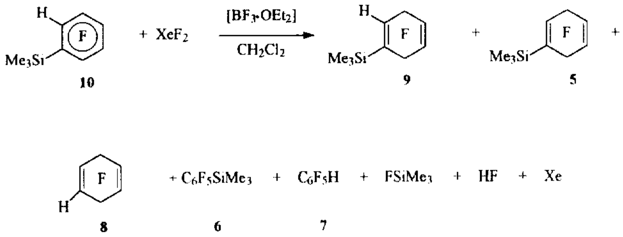
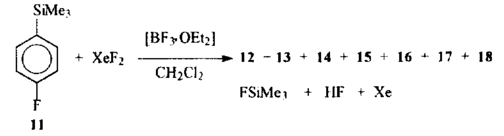


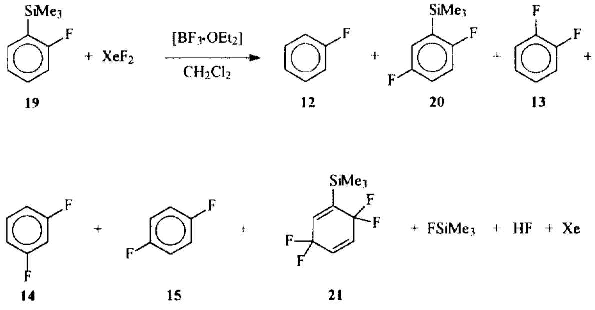


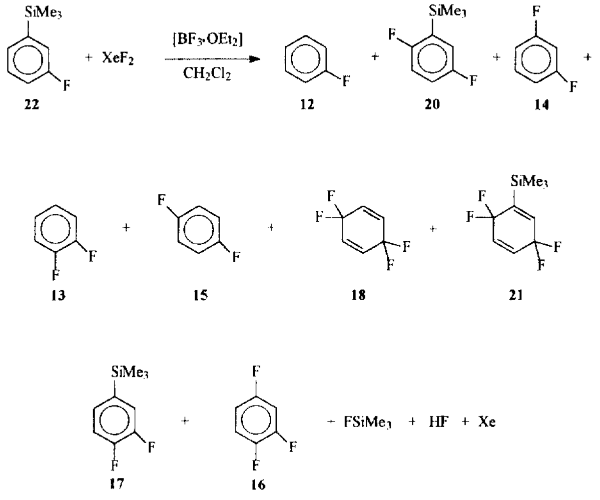
These reactions proceeded easily at room temperature and were complete within 15–20 min. No changes of products were observed during the next 1–2 days in reaction mixtures which contain a slight excess of XeF_2. This demonstrates the stability of silyldienes **2, 4, 5** and **9** towards protodesilylation by HF and fluorodesilylation by XeF_2 and fluorodeprotonation (**2, 4** and **9**) under the reaction conditions (cf. [2]). For this reason, diene **8** must have been produced from pentafluorobenzene which was the product of fluorodesilylation of **3** and **10**.

These results show a close similarity with those obtained earlier with tetrafluorobenzenes C_6HF_4R [2]. The only difference is the partial replacement of the trimethylsilyl group by the fluorine atom in the case of silylbenzenes **3** and **10** while the trimethylsilyl group *para* to hydrogen (silylbenzene **1**) remained unaffected. This demonstrates the influence of the mutual disposition of aromatically bonded fluorine atoms and $SiMe_3$ group on the character of the reaction products. From this viewpoint it was also interesting to investigate the interaction of isomeric trimethylsilylfluorobenzenes with XeF_2 in the presence of Lewis acid. It should be noted that Lothian and Ramsden [3] have reported the reaction of 4-$RC_6H_4SiMe_3$ (R = H, Cl, MeO, *t*-Bu) with excess of XeF_2 in hexafluorobenzene in the absence of Lewis acid. They observed the formation of 4-RC_6H_4F (major), isomers of 4-$RC_6H_3FSiMe_3$ and 4-$RC_6H_3F_2$ (minor) and offered this method for the regiospecific fluorodesilylation of silylbenzenes like the well known regiospecific functionalisation of mono- and di-substituted trimethylsilylbenzenes via desilylation by the action of electrophilic reagents [4].

We have found that the reaction of trimethylsilylfluorobenzenes with XeF_2 under acidic catalysis proceeds in a more complex way. Trimethylsilyl-4-fluorobenzene **11** reacted with a slight excess of xenon difluoride and a catalytic amount of $BF_3 \cdot OEt_2$ in CH_2Cl_2 to give fluorobenzene **12**, 1,2-difluorobenzene **13**, 1,3-difluorobenzene **14**, 1,4-difluorobenzene **15**, 1,2,4-trifluorobenzene **16**, 1-trimethylsilyl-3,4-difluorobenzene **17** and 3,3,6,6-tetrafluoro-1,4-cyclohexadiene **18**. Similar reactions took place with the other isomeric trimethylsilylfluorobenzenes. Treatment of 1-trimethylsilyl-2-fluorobenzene **19** with xenon difluoride in the presence of $BF_3 \cdot OEt_2$ gave fluorobenzene **12**, difluorobenzenes **13–15**, 1-trimethylsilyl-2,5-difluorobenzene **20** and 1-trimethylsilyl-3,3,6,6-tetrafluoro-1,4-cyclohexadiene **21**. Compounds **12–18, 20** were obtained by the reaction of XeF_2 with 1-trimethylsilyl-3-fluorobenzene **22**. In all cases fluorotrimethylsilane, HF and traces of CH_2FCl were detected among the reaction products while the initial amount of xenon difluoride was totally consumed. The reactions of **11**, **19** and **22** were accompanied by the formation of tar as for the fluorination of mono-substituted benzenes C_6H_5R [5] but the formation of fluorinated biphenyls was not found by ^{19}F NMR spectrometry or GC-MS.







Obviously, for silylbenzenes $C_6FH_4SiMe_3$ no regioselectivity was found for the fluorodesilylation reactions. The complex composition of the reaction mixtures arises from further interactions of the primary aromatic products with

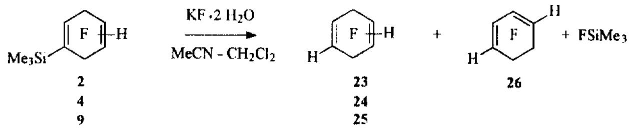
Table 1
The ^1H and ^{19}F NMR spectra of polyfluorinated silylcyclohexadienes

Compound	δ (H) ppm	δ (F) ppm					Coupling constants, Hz
		F-2	F-3	F-4	F-5	F-6	
2	5.92, 0.36	−112.4	−101.0	–	−122.5	−97.8	(2, 3) 23, (2, 4) 8, (2, 6) 11, (3, 4) 5, (3, 5)11, (3, 6) 5, (4, 5) 10, (4, 6) 2.5, (5, 6) 22
4	6.06, 0.35	−117.1	−117.1	−131.4	–	−83.4	(4, 5) 10.5, (5, 6) 5
9	6.36, 0.30	–	−103.1	−157.0	−153.5	−97.8	(2, 3) 4.7, (2, 4) 7.5, (3, 4) 19.4, (3, 5) 11.2, (3, 6) 6.2, (4, 5) 6.3, (4, 6) 12.1, (5, 6) 21.5
21	6.3–6.5, 0.30	–	−95.6	–	–	−90.1	

XeF_2, from dehydrofluorination of fluorocyclohexadienes and from the protodesilylation by evolved HF. Therefore xenon difluoride cannot be used for preparative-scale synthesis of difluorobenzenes from $C_6FH_4SiMe_3$ under acidic catalysis.

Despite the secondary processes, the primary reaction of trimethylsilylfluorobenzenes with XeF_2 in acidic media is a process of electrophilic fluorination (both fluorodeprotonation and fluorodesilylation). This result can be compared with other electrophilic reactions of trimethylsilylfluorobenzenes, for instance with HNO_3–Ac_2O [6]. In both cases the substitution of the hydrogen atom and of the $SiMe_3$ group by the formal electrophile E^+ (E = F or NO_2) took place, and the directing effect of the aromatically bonded fluorine atom exceeded that of the trimethylsilyl group. This qualitative similarity can arise from a common reaction pathway: the addition of the electrophilic species to the aromatic ring followed by deprotonation or desilylation of the cationic σ-complex. When the electrophile was $[NO_2]^+ [OAc]^-$ or related species [6], trimethylsilylfluoronitrobenzene and fluoronitrobenzene were formed. When the electrophile is $[FXe^{\delta+}\text{-}F\ldots\cdot\ldots BF_3^{\delta-}]$, the corresponding arylxenon(II) species may be formed. This assumption does not contradict the recently reported synthesis of arylxenon(II) salts by electrophilic replacement of hydrogen with xenon [7,8]. The intermediate arylxenon(II) salts $[RC_6H_4Xe]^+$ are unstable in dichloromethane above −60°C and their decomposition gives aryl fluorides RC_6H_4F (R = F, CF_3) and xenon [9]. Trimethylsilyltetrafluorobenzenes are less nucleophilic than trimethylsilylfluorobenzenes. Their interaction with XeF_2 under acidic catalysis proceeds similarly to that of tetrafluorobenzenes C_6HF_4R [2] via one-electron oxidation rather than the direct addition of the $[FXe]^+$ cation to the polyfluoroaromatic ring. However, the one-electron oxidation process cannot be excluded completely for trimethylsilylfluorobenzenes as both pathways are possible.

The analysis of the reaction products was performed by the ^1H, ^{19}F NMR spectrometry and by GC-MS. Fluorinated benzenes **6**, **7**, **12–16** were proved by addition of the individual substances into the reaction mixtures, while the known cyclohexadienes **8** [10,11], **5** [1], **23–25** [2], **18** [12], **26** [10–13], and silanes **17** [14] and **20** [15] were identified by their ^1H and ^{19}F NMR spectra. It is noteworthy that the δ (F) values of F-4 and F-5 in the ^{19}F NMR spectra of 1-*H*-heptafluoro-1,4-cyclohexadiene **8** which was given in Ref. [11] must be interchanged. The compounds **2**, **4**, **9** and **21** were characterised spectroscopically (Table 1) and dienes **2**, **4** and **9** were proved additionally by their protodesilylation to the corresponding cyclohexadiene derivatives using KF · 2 H_2O in MeCN–CH_2Cl_2 solution.



3. Experimental

NMR spectra were measured on Bruker WP 200 SY or AC 200 spectrometers (^1H at 200 MHz and ^{19}F at 188.28 MHz) using the internal references TMS or C_6F_6. The chemical shifts δ (F) are referred to $CFCl_3$ using δ (C_6F_6) = −162.9 ppm. All reactions were performed in FEP inliners. Yields of products were determined by ^{19}F NMR spectrometry using $PhCF_3$ as a quantitative internal reference.

Trimethylsilylfluorobenzenes **11**, **19** and **22** were prepared from the corresponding Grignard reagents and $ClSiMe_3$ [16]. Trimethylsilyltetrafluorobenzenes **1** [17] and **10** [18] were obtained by published methods.

3.1. 1-Trimethylsilyl-2,3,4,6-tetrafluorobenzene 3

1-Bromo-2,3,4,6-tetrafluorobenzene (3.0 g, 13.0 mmol) and $ClSiMe_3$ (1.8 g, 16.6 mmol) were dissolved in CH_2Cl_2 (6 ml) and $P(NEt_2)_3$ (3.8 g, 15.4 mmol) was added with a syringe over 5 min at 5–10°C under stirring. After 2 h the ^{19}F NMR spectrum showed total consumption of aryl bromide and formation of silylbenzene **3**, 1,2,4,6-tetrafluorobenzene and 1,3-bis(trimethylsilyl)tetrafluorobenzene [19, 20]. The reaction mixture was washed with conc. HCl, water and dried with $CaCl_2$. The solvent was distilled-off, and silylbenzene **3** was isolated by distillation in 48% yield (1.4 g), b.p. 168–170°C (lit. 65–66°C at 19 Torr [21]). ^1H NMR (CH_2Cl_2), δ: 6.69 (1H), 0.41 (9H) ppm. ^{19}F NMR

(CH_2Cl_2), δ: −100.4 (F-6), −120.3 (F-2), −130.1 (F-4), −166.5 (F-3) ppm (cf. Ref. [21]).

3.2. Reactions of xenon difluoride with trimethylsilyltetrafluorobenzenes

3.2.1. 1-Trimethylsilyl-2,3,5,6-tetrafluorobenzene 1

Xenon difluoride (100 mg, 0.59 mmol) was added in portions to the solution of silylbenzene **1** (101 mg, 0.45 mmol) and $BF_3 \cdot OEt_2$ (ca. 15 mg) in dichloromethane (0.2 ml) at 0°C. After each addition the reaction mixture was warmed to room temperature until gas evolution was ceased. The ^1H and ^{19}F NMR spectra showed the presence of silyldiene **2** (yield 89%), traces of CH_2FCl and $BF_3 \cdot OEt_2$. That solution was washed with water, diluted with MeCN (0.3 ml) and treated with excess of $KF \cdot 2\,H_2O$. After 24 h, the organic phase was separated from the solid residue and analysed by ^1H and ^{19}F NMR spectrometry. Hexafluorocyclohexadienes **23** and **26** were obtained in 62 and 18% yields, respectively, together with $FSiMe_3$ and $(Me_3Si)_2O$.

3.2.2. 1-Trimethylsilyl-2,3,4,6-tetrafluorobenzene 3

Similarly, silyldienes **4** (55%), **5** (10%), diene **8** (4%), silane **6** (4%) and pentafluorobenzene **7** (15%) were obtained from silylbenzene **3** (162 mg, 0.73 mmol), $BF_3 \cdot OEt_2$ and XeF_2 (156 mg, 0.92 mmol) in dichloromethane (0.2 ml) together with HF and $FSiMe_3$ (^1H, ^{19}F NMR). Treatment of the reaction mixture with $KF \cdot 2\,H_2O$ (excess) and MeCN overnight led to the conversion of silanes **4**, **5** and **6** into the known compounds **24**, **8** and **7**.

3.2.3. 1-Trimethylsilyl-2,3,4,5-tetrafluorobenzene 10

In a similar way, silylbenzene **10** (82 mg, 0.37 mmol), XeF_2 (84 mg, 0.49 mmol), $BF_3 \cdot OEt_2$ (ca. 20 mg) in CH_2Cl_2 (0.2 ml) gave compounds **9** (57%), **8** (5%), **5** (19%), **6** (2%) and **7** (2%) besides HF and $FSiMe_3$. Washing with water following treatment with excess of $KF \cdot 2\,H_2O$ in CH_2Cl_2–MeCN overnight led to the conversion of **9**, **5** and **6** into dienes **25**, **8** and pentafluorobenzene, respectively (^1H, ^{19}F NMR).

3.3. Reactions of xenon difluoride with trimethylsilylfluorobenzenes

3.3.1. 1-Trimethylsilyl-2-fluorobenzene 19

Reaction of silylbenzene **19** (110 mg, 0.65 mmol) with XeF_2 (115 mg, 0.68 mmol) in CH_2Cl_2 (0.2 ml) in the presence of $BF_3 \cdot OEt_2$ was performed as above and was complete within 10–15 min. Silylbenzene **20** (30%), fluorobenzene **12** (16%), difluorobenzenes **13** (3%), **14** (4%), **15** (5%) and diene **21** (5%) plus $FSiMe_3$, HF and traces of CH_2FCl were identified by ^1H and ^{19}F NMR spectrometry.

3.3.2. 1-Trimethylsilyl-3-fluorobenzene 22

Compounds **12** (6%), **13** (4%), **14** (10%), **15** (16%), **16** (3%), **18** (3%), **20** (17%) and **21** (4%) were obtained from silylbenzene **22** (125 mg, 0.74 mmol) and XeF_2 (154 mg, 0.91 mmol) in CH_2Cl_2 (0.2 ml) in the presence of $BF_3 \cdot OEt_2$. Additionally traces of silylbenzene **17** plus fluorotrimethylsilane, HF and CH_2FCl were detected (^1H, ^{19}F NMR).

3.3.3. 1-Trimethylsilyl-4-fluorobenzene 11

Silylbenzene **11** (80 mg, 0.47 mmol) was treated with XeF_2 (105 mg, 0.62 mmol) in CH_2Cl_2 (0.2 ml) in the presence of ca. 15 mg of $BF_3 \cdot OEt_2$ and formed compounds **12** (13%), **13** (3%), **14** (4%), **15** (34%), **16** (4%), **17** (3%) and **18** (5%) together with HF and $FSiMe_3$ (^1H, ^{19}F NMR).

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