ELSEVIER

Journal of Fluorine Chemistry 77 (1996) 143–146

JOURNAL OF FLUORINE CHEMISTRY

Regiospecific fluorination of the aryl group in C_6F_5I and the preparation of $C_6F_7IF_2$ – the first perfluorovinyl iodine(III) compound

H.J. Frohn *, R. Nielinger

Fachgebiet Anorganische Chemie, Gerhard-Mercator-Universität Duisburg, Lotharstr. 1, D-47048 Duisburg, Germany

Abstract

Pentafluoroiodobenzene was oxidized regiospecificly by IF_5/BF_3 in CH_2Cl_2 to 1-iodo-heptafluoro-1,4-cyclohexadiene. With bromo- and chloro-pentafluorobenzene as substrates, the addition of two fluorine atoms to the aromatic ring proceeded analogously but more slowly. 1-Iodo-heptafluoro-1,4-cyclohexadiene was converted to 1-difluoroiodo-heptafluoro-1,4-cyclohexadiene by low-temperature fluorination. The thermal stability and reactivity of the first example of a perfluorinated vinyl iodine(III) compound are reported.

Keywords: Pentafluoroiodobenzene; 1-Iodoheptafluoro-1,4-cyclohexadiene; 1-Difluoroiodoheptafluoro-1,4-cyclohexadiene; 1-Acetoxy(fluoro)iodo-heptafluoro-1,4-cyclohexadiene; Iodine pentafluoride; Fluorination; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

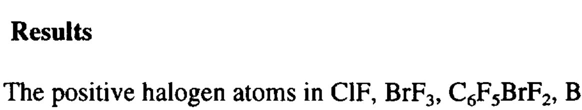
Pentafluorobenzenes, C_6F_5X ($X = Br, Cl, F, H, C_6F_5$), add two fluorine atoms when treated with XeF_2 in CH_2Cl_2 at room temperature in the presence of BF_3 and form 1-X-heptafluoro-1,4-cyclohexadienes [1]. In contrast to other halogenopentafluorobenzenes, pentafluoroiodobenzene cannot be converted to the corresponding diene by this very convenient preparative method. C_6F_5I (**1**) reacts with XeF_2 with oxidative fluorination of the iodine centre. Depending on the stoichiometry and the reaction temperature, pentafluorophenyliodine difluoride, $C_6F_5IF_2$ (**2**), or tetrafluoride, $C_6F_5IF_4$ (**3**), are obtained [2]. Other fluorinating agents such as F_2 [3], ClF_3 [4], ClF, CF_3OCl [5], BrF_3, $C_6F_5BrF_2$, BrF_5 and $C_6F_5BrF_4$ [6] also add fluorine to the iodine centre of **1**.

With VF_5 as fluorinating agent, no fluorine addition at the iodine centre of **1** takes place, but the fluorination of the aromatic ring gives a nearly 1:1 mixture of 1-iodo-heptafluoro-1,4-cyclohexadiene, C_6F_7I (**4**), and 1-iodo-nonafluoro-1-cyclohexene, C_6F_9I (**5**) [7]. In this paper we show that IF_5 (**6**) in the presence of BF_3 is a useful fluorinating agent for **1** when only ring fluorination and diene formation is desired. To our knowledge, no physical or spectrometric data for **4** are given in the literature [7–9]. Hence, we report the physical and spectrometric properties of **4**.

Additionally, we describe the low-temperature fluorination of **4** to 1-difluoroiodoheptafluoro-1,4-cyclohexadiene, $C_6F_7IF_2$ (**7**). Compound **7** is the first IF_3 derivative with a cyclic perfluoroolefin group where I^{III} is bonded in a vinylic position. In addition to its thermal stability, the first examples of the reactivity of **7** are given.

2. Results

The positive halogen atoms in ClF, BrF_3, $C_6F_5BrF_2$, BrF_5 or $C_6F_5BrF_4$ are able to oxidize iodine in **1**, whereas I^V in IF_5 (CH_2Cl_2 or MeCN solutions under reflux or neat at room temperature) is not able to do this. However, under the influence of BF_3, **1** can be oxidized by IF_5 in CH_2Cl_2 solution at room temperature. No oxidation of the iodine centre in **1** takes place; the aromatic ring is oxidized exclusively in a slow reaction and **4** is formed regiospecificly.



1 4

When bromopentafluorobenzene or chloropentafluorobenzene are reacted with IF_5/BF_3 in CH_2Cl_2, instead of **1** the corresponding 1-halogeno-heptafluoro-1,4-cyclohexadienes, C_6BrF_7 (**8**) and C_6ClF_7 (**9**), are obtained. For C_6F_5Br and C_6F_5Cl, the rate of conversion is lower than for **1**.

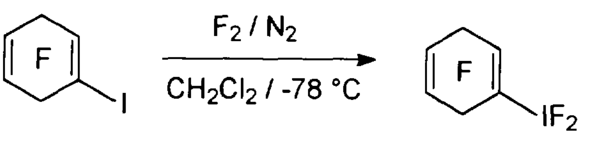
Using Schmeißer's method of low-temperature fluorination [10], diene **4** could be fluorinated with 3% F_2 (diluted

---

* Corresponding author.

0022-1139/96/$15.00 © 1996 Elsevier Science S.A. All rights reserved
PII S0022-1139(96)03399-4

with nitrogen) in CCl_3F solution at −78 °C. 1-Difluoroiodoheptafluoro-1,4-cyclohexadiene (**7**) was isolated in high yield (93%).



4 **7**

Attempts to fluorinate **7** with XeF_2 in CH_2Cl_2 up to 50 °C, in order to obtain 1-tetrafluoroiodoheptafluoro-1,4-cyclohexadiene, were not successful. Compound **7** was not stable in basic solvents like MeCN. One of the fluorine atoms bonded to iodine could be substituted by a trifluoroacetoxy group. Attempts to also substitute the second fluorine atom ended in decomposition. Compound **7** acted as a fluorinating agent towards phosphanes.

3. Discussion

The problem of converting perfluoroaromatic iodo compounds into fluorinated iodocyclohexadienes consists in the suppression of the easy addition of fluorine to the iodine centre. Thus difluorine, as well as strong or non-Lewis acidic fluorination agents (ClF, CF_3OCl, BrF_3, $RBrF_2$, BrF_5, $RBrF_4$), preferably oxidize the iodine centre, whereas strong Lewis acids and weak fluorination agents (VF_5 [7], SbF_5 [11]) add two or four fluorine atoms preferably to the aromatic ring.

IF_5 does not possess strongly distinct Lewis acidity as a result of its pseudo-octahedral valence shell, but fluoridotropic properties are still known. Thus it reacts with fluoride ions to give $[(IF_5)_nF]^-$, $n = 1–3$ [12], and with strong Lewis acids like SbF_5 with $[IF_4]^+$ formation [13]. IF_5 belongs to the group of weaker oxidizers within the halogen fluorides. Its oxidation ability is best characterized by the oxidation of polarized chlorine or chloride ion to elemental chlorine. Neither in MeCN or CH_2Cl_2 solution nor neat is IF_5 capable of attacking C_6F_5I, but in the presence of the Lewis acid BF_3 diene **4** is formed exclusively. ^{19}F NMR spectroscopic monitoring shows that during the reaction the multiplet structure of IF_5 is destroyed, e.g. the four equatorial fluorine atoms which exhibit a doublet structure in CH_2Cl_2 solution collapse to a broad singlet but do not shift. At the end of reactions with excess IF_5, the multiplet structure becomes observable again.

As far as the influence of BF_3 is concerned, we assume that this weak Lewis acid polarizes IF_5 and strengthens the oxidation ability of IF_5. A second aspect may result from a weak donor–acceptor interaction of BF_3 with the iodine atom in **1** which leads to the inhibition of this potential reaction centre toward fluorination with the electrophilic polarized IF_5. A similar reactivity was observed in the case of the isoelectronic cation $[C_6F_5Xe]^+$ which could be fluorinated by XeF_2 in AHF to 1-Xe(+)-heptafluoro-1,4-cyclohexadiene [14]. In both cases the electrophilic fluorinating agents generated from IF_5 or XeF_2 and the Lewis acids BF_3 or HF caused the regiospecific 1,4-addition of two fluorine atoms to the aromatic ring.

It should be mentioned that the addition of diiodine accelerates the fluorination of **1** with IF_5/BF_3. As well as the nature of the iodine-containing byproduct which results from IF_5, the mechanistic aspects of this fluorination reaction require further investigation.

^{19}F NMR spectral comparison of the F-2 (−104.4; −119.0; −128.6 ppm) and F-6,6 (−95.6; −101.4; −105.6 ppm) shift values in the C_6F_7Hal series (Hal = I, Br, Cl) shows a good linear correlation of these values with Pauling's *EN* values. However, Hal = F (F-2: −158; F-6,6: −114 ppm [15]) deviates significantly from the linear correlation. Consequently, in the case of Hal = I, Br and Cl, F-2 and F-6,6 are mainly influenced by inductive interaction and not by orbital overlap of the halogens into the olefinic π-electron system [9]. In the mass spectrum (EI mode), the molecular cation appears with high intensity whilst its fragmentation to the arenium cation radicals $C_6F_5I^{+\cdot}$ and $C_6F_6^{+\cdot}$ showed a differentiated picture. The latter was formed with high intensity whereas the iodine-centred cation radical $C_6F_5I^{+\cdot}$ was only found in traces.

A lot is known about the thermal stability and reactivity of perfluoroaromatic [2,16] and perfluoroaliphatic [17] derivatives of IF_3 and IF_5 from the literature. To our knowledge, however, compounds with perfluorovinylic fragments bonded to the iodine difluoride or tetrafluoride fragment are still unknown. Non-fluorinated species of this type are known but are less stable than the corresponding aromatic derivatives [17]. Hence, we decided to investigate the fluorination of **4** to **7** and to 1-tetrafluoroiodo-1,4-heptafluorocyclohexadiene. Compound **4** can be converted in nearly quantitative yield to **7** by low-temperature fluorination with nitrogen-diluted fluorine. Compound **7** is a colourless solid at room temperature and melts at 103 °C (DTA: endothermic without decomposition) and is still stable above 150 °C. In the EI MS (70 eV), the molecular cation radical appears at a lower intensity than the iodonium cation $[C_6F_7IF]^+$. The C_6F_7I cation radical possesses the highest intensity by far. Furthermore, the IF_2^+ cation appeared with a low and the cation radical $IF^{+\cdot}$ with a high intensity. The ^{19}F NMR spectrum of a CH_2Cl_2 solution of **7** showed the following resonances: δ −95.65 (F-2); −98.00 (F-6,6); −110.95 (F-3,3); −149.88 (F-5); −156.01 (F-4); −158.36 (-IF_2) ppm. The IF_2 group appeared at room temperature as a singlet (hwt = 16 Hz) with a similar shift value and also with a singlet structure as in **2**.

When **7** is dissolved in the basic solvent MeCN, rapid decomposition also takes place at low temperature. This is different to the behaviour of **2** which is stable in MeCN solution, although the parent molecule IF_3 has been described as being unstable in the presence of bases [18]. Attempts to oxidize **7** with XeF_2 in CH_2Cl_2 failed below 50 °C. Also nucleophilic fluorine–aryl substitution reactions at the IF_2 group in **7** which can readily occur with **2** were not successful. The fluorine–trifluoroacetoxy substitution reaction investigated by Schmeißer and Naumann [19] for perfluoroalkyliodine difluorides cannot be simply transferred to **7**. We were able to show that $C_6F_7I(F)O_2CCF_3$ is formed in CH_2Cl_2 solution, but that the product became unstable and decomposed rapidly when the second fluorine atom was substituted. Compound **7** itself possesses fluorination abilities which could be demonstrated by the conversion of the phosphane $(p\text{-}FC_6H_4)_3P$ to the difluorophosphorane $(p\text{-}FC_6H_4)_3PF_2$.

4. Experimental details

All experiments were performed in FEP–PTFE tube reactors or inliners under a dry Ar atmosphere. IF_5 was prepared from the elements and distilled over NaF. BF_3 (BASF) was pretreated over NaF at −78 °C and handled in a stainless steel vacuum line with appropriate gas reservoirs. ^{19}F NMR measurements were performed in FEP inliners using Varian EM 360 L (56.45 MHz) and Bruker WP 80 SY spectrometers (75.39 MHz). Shift values are referred to CCl_3F using C_6F_6 as internal or SR standard [$\delta(C_6F_6) = -162.9$ ppm]. ^{13}C NMR spectra were measured with a Bruker WM 300 spectrometer at 75.47 MHz with TMS as SR standard, IR spectra with a Nicolet 20 DXB (extended version: CsI beam splitter) instrument and MS (EI, 20 or 70 eV) with a Varian MAT 311 A spectrometer. Fragments are reported without charge.

*4.1. Fluorination of **1** under normal pressure (FEP tube reactor fitted with stopper)*

Boron trifluoride, BF_3 (2 mmol), was bubbled through 500 μl of a CH_2Cl_2 solution (0 °C) consisting of 305 mg (1.38 mmol) of IF_5 and 1014 mg (3.45 mmol) of C_6F_5I over a period of 10 min. The solution became dark brown. After 72 h at room temperature (r.t.) only traces of **4** had been formed. Again the same quantity of BF_3 was bubbled through the solution, but this time at −78 °C. After a total reaction time of 168 h at r.t., 5% of **1** had been converted to **4**. BF_3 (2.7 mmol) was then fed through the solution over 20 min at −78 °C and after allowing a total reaction time of 213 h at r.t., it was shown that all the IF_5 has been consumed (^{19}F NMR). Even at this stage 54% of **1** was still present, the other part having been oxidized to **4**. Small amounts of CH_2ClF were also detected. For the separation and purification of the products, see later.

*4.2. Fluorination of **1** under normal pressure in the presence of I_2 (FEP tube reactor fitted with stopper)*

To a suspension consisting of 7.73 g (30.45 mmol) of I_2 in 25 ml of CH_2Cl_2, 26.05 g (88.62 mmol) of C_6F_5I and a solution consisting of 13.61 g (61.33 mmol) of IF_5 in 5 ml of CH_2Cl_2 were added. Then 62 mmol of BF_3 were bubbled through the suspension at −78 °C over a period of 25 min with stirring. After 24 h at r.t. and in the absence of light, a second amount of BF_3 was introduced at −78 °C. This led to 40% of **1** being converted to **4**. After storage for 21 d at r.t. without intermediate rate control, 100% of **1** was fluorinated to **4**. The yield of **4** after separation and distillation was 27.86 g (83.93 mmol, 94.7%).

Table 1

^{13}C NMR data for **4** (CH_2Cl_2, 25 °C): coupling constants in Hz

	F-2	F-3,3	F-4	F-5	F-6,6
C-1	25.6	1.9	5.4	5.4	33.2
C-2	277.6	24.5	6.4	3.0	9.1
C-3	23.0	242.4	28.5	7.1	3.0
C-4	7.8	25.1	278.1	11.0	7.9
C-5	1.9	7.1	10.2	282.9	27.6
C-6	10.9	2.3	7.6	22.6	236.1

*4.3. Fluorination of **1** under 43 bar pressure (FEP inliner in a stainless steel reactor)*

IF_5 (381 mg, 1.72 mmol) and 835 mg (2.84 mmol) of C_6F_5I were dissolved in 400 μl of CH_2Cl_2 in a FEP inliner inside the stainless steel reactor. Into this solution was condensed 1.7 mmol of BF_3 at −196 °C. The stainless steel reactor was warmed up to r.t. when the pressure inside increased to 43 bar. After 120 h at r.t., BF_3 was separated and ^{19}F NMR analysis of the reaction mixture showed that all the IF_5 had been consumed and that 82% of **1** had reacted to **4**. In addition, traces of CH_2ClF, CH_2F_2 and C_6F_5Cl were also found.

*4.4. Separation and purification of **4***

The cold reaction mixture was poured on to a mixture of ice, $CaCO_3$ and KOH (10%) with vigorous stirring. The CH_2Cl_2 phase was separated and the aqueous phase extracted three times with the same amount of CH_2Cl_2. The combined CH_2Cl_2 phases were washed with dilute H_2SO_4 and treated with $NaHSO_3$ solution at a pH of 2 until the iodine colour had disappeared. After washing with water (until neutral) and drying over $NaSO_4$, CH_2Cl_2 was distilled off and the residue fractionated using a 30 cm Vigreux column (b.p. 126.5–127 °C); $d^{20} = 2.169$ g cm^{-3}; m.p. −35.0 °C.

Compound **4**: ^{19}F NMR (CH_2Cl_2, 35 °C) δ: −95.59 (F-6,6); −104.36 (F-2); −111.84 (F-3,3); −149.65 (F-5); −157.87 (F-4) ppm. [^3J(F-2, F-3) = 24.3 Hz, ^4J(F-2, F-4) ~ 0 Hz, ^4J(F-2, F-6) = 10.2 Hz, ^5J(F-2, F-5) = 2.7 Hz, ^3J(F-3, F-4) = 19.6 Hz, ^4J(F-3, F-5) = 10.6 Hz, ^5J(F-3, F-6) = 4.6 Hz, ^3J(F-4, F-5) = 4.5 Hz, ^4J(F-4, F-6) = 10.3 Hz, ^3J(F-5, F-6) = 23.1 Hz]. ^{13}C NMR (CH_2Cl_2, 25 °C) δ: 78.33 (C-1); 106.76 (C-3); 109.59 (C-6); 138.52 (C-4); 139.48 (C-5); 155.44 (C-2) ppm[1]. MS (20 eV) m/z (rel.

---

[1] The ^{13}C NMR coupling constants for compound **4** are listed separately in Table 1.

int./%, fragment): 332 (81, $M^{+\cdot}$); 313 (3, C_6F_6I); 294 (2, C_6F_5I) 282 (2, C_5F_5I); 263 (5, C_5F_4I); 205 (73, C_6F_7); 186 (59, C_6F_6); 167 (7, C_6F_5); 155 (100, C_5F_5); 136 (16, C_5F_4); 131 (5, C_3F_5); 127 (24, I); 124 (4, C_4F_4); 117 (79, C_5F_3); 105 (13, C_4F_3); 98 (13, C_5F_2); 93 (49, C_3F_3); 86 (14, C_4F_2); 79 (8, C_5F); 74 (15, C_3F_2); 69 (60, CF_3); 55 (C_3F). IR (KBr, ν/cm^{-1}): 1772 (s); 1735 (s); 1374 (m); 1347 (w); 1306 (vs); 1227 (vs); 1068 (vs); 1055 (vs); 960 (vs); 795 (s); 774 (s); 638 (w); 596 (m); 463 (m).

4.5. Low-temperature fluorination of 4 with F_2

Into a cold (−78 °C), stirred solution containing 3.469 g (10.45 mmol) of **4** in 40 ml of CCl_3F was discharged a precooled gas mixture (3% F_2/N_2, ≤ 18 mmol F_2) over 35 h. During such discharge, compound **7** precipitated as colourless solid. After separation and washing with cold CCl_3F, **7** was dried in vacuum. Yield 3.579 g (9.67 mmol, 93%). To achieve further purification, **7** was recrystallized from CH_2Cl_2. Yield 2.846 g (7.69 mmol, 74%); m.p. 103.0 °C (DTA): 106.5 °C endothermic maximum); neutralization equivalent; 180.45 (calc. 184.98) g mol$^{-1}{}_{OH^-}$.

Compound **7**: ^{19}F NMR (CH_2Cl_2, 35 °C) δ: −95.65 (F-2); −98.00 (F-6,6); −110.95 (F-3,3); −149.88 (F-5); −156.01 (F-4); −158.36 (s, IF_2) ppm. ^{13}C NMR (CH_2Cl_2, 25 °C) δ: 153.7 (C-2, $^1J_{C,F}=297$ Hz); 138.2 (C-5, $^1J_{C,F}=278$ Hz); 136.9 (C-4, $^1J_{C,F}=280$ Hz); 109.0 (C-6, $^1J_{C,F}=254.4$ Hz); 105.2 (C-3, $^1J_{C,F}=246$ Hz) ppm. MS (70 eV) m/z (rel. int./%, fragment): 370 (2, $M^{+\cdot}$); 351 (16, C_6F_7IF); 332 (100, C_6F_7I); 313 (4, C_6F_6I); 301 (2, C_5F_6I); 294 (2, C_6F_5I); 282 (3, C_5F_5I); 263 (5, C_5F_2I); 224 (30, C_6F_8); 205 (69, C_6F_7); 193 (4, C_5F_7); 186 (47, C_6F_6); 174 (11, C_5F_6); 167 (5, C_6F_5); 165 (2, IF_2); 162 (2, C_4F_6); 155 (87, C_5F_5); 146 (50, IF); 143 (4, C_4F_5); 136 (12, C_5F_4); 131 (7, C_3F_5); 127 (15, I); 124 (8, C_4F_4); 117 (46, C_5F_3); 112 (2, C_3F_4); 105 (8, C_4F_3); 98 (6, C_5F_2); 93 (28, C_3F_3); 86 (6, C_4F_2); 79 (4, C_5F); 74 (7, C_3F_2); 69 (32, CF_3); 55 (3, C_3F); IR (KBr, ν/cm^{-1}): 1833 (vw); 1773 (s); 1751 (s); 1700 (s); 1471 (vs, b); 1356 (vs); 1308 (s); 1263 (vs); 1229 (vs); 1214 (sh); 1176 (s); 1140 (s); 1099 (s); 1085 (sh); 1077 (s); 990 (sh); 948 (vs); 880 (sh); 801 (s); 785 (vs); 777 (s); 710 (w); 661 (w); 653 (w); 640 (w); 628 (w); 609 (m); 594 (m); 541 (m); 526 (s); 512 (s); 475 (s, b); 464 (s); 417 (w).

4.6. Fluorine–trifluoroacetoxy substitution on 7 (under stoichiometric reaction conditions)

To a solution consisting of 50 mg (135 μmol) of **7** in 300 μl of CH_2Cl_2 at −10 °C, <28.4 mg (135 μmol) of $[CF_3C(O)]_2O$ were added with stirring. The ^{19}F NMR spectrum at −10 °C showed, beside small quantities of **7**, equimolar amounts of $CF_3C(O)F$ [δ: −74.5 (CF_3); 16.4 (C(O)F) ppm] and $C_6F_7I(F)OC(O)CF_3$ [δ: −93.4 (F-2); −98.2 (F-6,6); −111.2 (F-3,3); −137.7 (IF); −149.5 (F-5); −155.5 (F-4) ppm]. Addition of a further equivalent of $[CF_3C(O)]_2O$ or warming up to r.t. caused decomposition of the iodo compound.

4.7. Fluorinating ability of 7: fluorination of phosphane

Compound **7** (125 mg, 338 μmol) in 600 μl of CH_2Cl_2 was added to a solution of 107 mg (338 μmol) of $(p\text{-}FC_6H_4)_3P$ dissolved in 300 μl of CH_2Cl_2. $(p\text{-}FC_6H_4)_3PF_2$ was formed quantitatively [^{19}F NMR δ: −39.6 (d, PF_2, $^1J_{FP}=667.4$ Hz); −108.6 (p-F) ppm].

Acknowledgements

The authors gratefully acknowledge financial support from the Fonds der Chemischen Industrie and Solvay Fluor und Derivate GmbH for the contribution of chemicals.

References

[1] S. Stavber and M. Zupan, *J. Org. Chem.*, *46* (1981) 300.

[2] I.I. Maletina, V.V. Orda, N.N. Aleinikov, B.L. Korsunskii and L.M. Yagupol'skii, *Zh. Org. Khim.*, *12* (1976) 1371.

[3] M. Schmeißer, K. Dahmen and P. Sartori, *Chem. Ber.*, *103* (1970) 307.

[4] J.A. Berry, G. Oates and J.M. Winfield, *J. Chem. Soc., Dalton Trans.*, (1974) 509.

[5] H.J. Frohn and J. Helber, *J. Fluorine Chem.*, *16* (1980) 568.

[6] H.J. Frohn, unpublished results.

[7] V.V. Bardin, A.A. Avramenko, G.G. Furin, G.G. Yakobson, V.A. Krasilnikov, P.P. Tushin and A.I. Karelin, *J. Fluorine Chem.*, *28* (1985) 37.

[8] J. Riera and R. Stephens, *Tetrahedron*, *22* (1966) 2555.

[9] S.F. Campbell, A.G. Hudson, E.F. Mooney, A.E. Pedler, R. Stephens and K.N. Wood, *Spectrochim. Acta, Ser. A*, *23* (1967) 2119.

[10] M. Schmeißer and E. Scharf, *Angew. Chem.*, *71* (1959) 524.

[11] V.V. Bardin, G.G. Furin and G.G. Yakobson, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, (1978) 142.

[12] (a) A.R. Mahjoub, A. Hoser, J. Fuchs and K. Seppelt, *Angew. Chem.*, *101* (1989) 1528; (b) A.R. Mahjoub and K. Seppelt, *Angew. Chem.*, *103* (1991) 309; (c) A.R. Mahjoub and K. Seppelt, *Eur. J. Solid State Inorg. Chem.*, 29 (1992) 635.

[13] K. Christe and W. Sawodny, *Inorg. Chem.*, *12* (1973) 2879.

[14] H.J. Frohn and V.V. Bardin, *J. Chem. Soc., Chem. Commun.*, (1993) 1072.

[15] S. Berger, S. Braun and H.O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen*, G. Thieme Verlag, Stuttgart, 1994.

[16] H.J. Frohn and S. Görg, *Z. Anorg. Allg. Chem.*, *621* (1995), 1251.

[17] A. Varvoglis, *The Organic Chemistry of Polycoordinated Iodine*, Verlag Chemie, Weinheim, 1992.

[18] (a) M. Schmeißer, W. Ludovici, D. Naumann, P. Sartori and E. Scharf, *Chem. Ber.*, *101* (1968) 4214; (b) E. Lehmann, D. Naumann and M. Schmeißer, *J. Fluorine Chem.*, *7* (1976) 33.

[19] (a) M. Schmeißer, D. Naumann and R. Scheele, *J. Fluorine Chem.*, *1* (1971) 369.
(b) D. Naumann and J. Baumanns, *J. Fluorine Chem.*, *8* (1976) 177.