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ON SOME NEW TRIFLUOROMETHYL IODINE(III) COMPOUNDS: REACTIONS OF CF_3IF_2 WITH BORON AND SILICON COMPOUNDS AND CF_3ICl_2 WITH SILVER SALTS

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SUMMARY

CF_3IF_2 undergoes fluorine exchange reactions with BX_3 (X = Cl, Br, I, $OCOCF_3$) to form the compounds CF_3IX_2. The reactions of CF_3IF_2 with $(CF_3)_2BN(CH_3)_2$, $(CH_3)_3SiNCO$ and $(CH_3)_3SiN(CH_3)COCF_3$ yield the corresponding new trifluoromethyl iodine (III) nitrogen compounds. A preparative method for the synthesis of CF_3ICl_2 is found by reacting CF_3IF_2 with $(CH_3)_3SiCl$. CF_3ICl_2 reacts with AgX (X = $OCOCF_3$, SCF_3) to yield the corresponding CF_3IX_2 compounds and with $(C_6H_5)_4AsCl$ the novel ion $[CF_3ICl_3]^-$ is detected. Products were identified by n.m.r. spectroscopy.

INTRODUCTION

Since the first synthesis of CF_3IF_2 by Schmeißer and Scharf in 1959 [1] many successful attempts have been made to prepare perfluoroalkyl iodine (III) and iodine (V) compounds by other methods. Two different ways have been developed: (i) oxidation reactions of perfluoroalkyliodides and (ii) fluorine exchange reactions of R_fIF_2 and R_fIF_4. Suitable oxidizers are elemental fluorine [2], halogen fluorides [3,4], ozone [5], compounds with positive chlorine [6-10], peroxo acids [11], and $S_2O_6F_2$ [12]. Fluorine exchange reactions of R_fIF_2 or R_fIF_4 were successful with SiO_2 [5], methylmethoxysilanes [4b], protonic

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acids [13,14], anhydrides [8,15], and with some boron and silicon compounds [13,16]. Finally the fluorination of R_fIO with SF_4 yielded R_fIF_2 [17]. Most of the products prepared by these methods contain either I-F or I-O bonds.

Continuing our investigations on CF_3I (III) derivatives we now describe the reactions of CF_3IF_2 with some boron and silicon compounds, yielding CF_3ICl_2 and I-N compounds, as well as the reactions of CF_3ICl_2 with some silver salts.

RESULTS AND DISCUSSION

Reactions of CF_3IF_2 with boron compounds

While the I(V) compounds CF_3IF_4 and CF_3IOF_2 react with fluoride ion acceptors to eliminate CF_4 and to yield the I(III) salts $[IF_2][AsF_6]$ [4b], $IO[BF_4]$ and $IO[MF_6]$ (M = As, Sb) [18], respectively, we always got decomposition from the corresponding CF_3IF_2 reactions. But when stoichiometric amounts of $B(OTeF_5)_3$ are used instead of BF_3, CF_3IF_2 undergoes a fluorine-pentafluoroorthotellurate exchange [13] according to equation (1)

$$3\ CF_3IF_2 + 2\ B(OTeF_5)_3 \longrightarrow 3\ CF_3I(OTeF_5)_2 + 2\ BF_3. \qquad (1)$$

Using an excess of $B(OTeF_5)_3$ decomposition takes place.

Therefore we were interested in investigating the reactions of CF_3IF_2 with the boron halides BX_3 (X = Cl, Br, I) and with boron tris(trifluoroacetate). In all reactions primarily a fluorine-halogen or a fluorine-trifluoroacetate exchange is observed according to equation (2)

$$3\ CF_3IF_2 + 2\ BX_3 \longrightarrow 3\ CF_3IX_2 + 2\ BF_3 \qquad (2)$$

X = Cl, Br, I, $OCOCF_3$

But only the products CF_3ICl_2 and $CF_3I(OCOCF_3)_2$ are stable in acetonitrile solution. Though ^{19}F-n.m.r. spectroscopic evidence is found for the mixed boron fluoride halides, partially fluorinated iodine derivatives cannot be detected. The reason might be a dismutation equilibrium as previously described [8,15]:

$$2\ CF_3IFX \rightleftharpoons CF_3IF_2 + CF_3IX_2 \qquad (3)$$

Meanwhile it has been shown that fluorine-pentafluorophenyl exchange reactions take place in the systems $B(C_6F_5)_3$/halogen-fluorides or xenon fluorides [19,20]:

$$BrF_5 + B(C_6F_5)_3 \longrightarrow [Br(C_6F_5)_2][BF_4] + C_6F_6 \ldots \qquad (4a)$$

$$C_6F_5IF_2 + B(C_6F_5)_3 \longrightarrow [I(C_6F_5)_2][B(C_6F_5)_{4-x}F_x] \qquad (4b)$$

$$XeF_2 + B(C_6F_5)_3 \longrightarrow [XeC_6F_5][B(C_6F_5)_{4-x}F_x] \qquad (4c)$$

We therefore tried to obtain an unsymmetrically di-substituted perfluoroorgano iodine derivative by reacting $B(C_6F_5)_3$ with CF_3IF_2. From this reaction perfluorotoluene and pentafluorophenyl iodine as well as pentafluorophenyl boronfluorides are detected ^{19}F-n.m.r. spectroscopically as the main products. This can be explained by the following reaction scheme:

$$CF_3IF_2 + B(C_6F_5)_3 \longrightarrow [CF_3IC_6F_5]^+[B((C_6F_5)_{4-x}F_x]^- \qquad (5)$$

$$\downarrow$$

$$C_6F_5CF_3 + "I[B(C_6F_5)_{4-x}F_x]"$$

$$\downarrow$$

$$C_6F_5I + B(C_6F_5)_{3-x}F_x$$

We also tried to obtain bis(trifluoromethyl) substituted iodine derivatives from the reactions of CF_3IF_2 with $CF_3B(N(CH_3)_2)_2$ or $(CF_3)_2BN(CH_3)_2$. With the mono(trifluoromethyl) borane no substitution reaction can be observed, but it seems that the boron compound catalyses a disproportionation reaction of the I(III) compound:

$$2\ CF_3IF_2 \longrightarrow CF_3I + CF_3IF_4 \qquad (6)$$

If the bis(trifluoromethyl) boron compound is used, evidence is found for a fluorine-dimethylamino exchange instead of a fluorine-trifluoromethyl exchange. $(CF_3)_2BF$ is identified by its ^{19}F- and ^{11}B-n.m.r. spectra [21]. New signals in the ^{19}F-n.m.r. spectrum in the region of CF_3I (III) compounds indicate that $CF_3I(N(CH_3)_2)_2$ might have been formed. This compound would be the first example of a trifluoromethyl iodine derivative with an iodine-nitrogen bond:

$$CF_3IF_2 + 2\ (CF_3)_2BN(CH_3)_2 \longrightarrow CF_3I(N(CH_3)_2)_2 + 2\ (CF_3)_2BF \qquad (7)$$

Reactions of CF_3IF_2 with silicon compounds

Trifluoromethyl iodine difluoride undergoes exchange reactions with SiO_2 [5], $SiCl_4$ and $SiBr_4$ [13]. Though CF_3ICl_2 has already been described it was of interest to obtain this compound in a pure form. An alternative reagent for the preparation of CF_3ICl_2 is $(CH_3)_3SiCl$. The advantage of this compound compared to $SiCl_4$ is that only one equivalent chlorine can be exchanged. The resulting $(CH_3)_3SiF$ is a volatile compound that easily can be removed from the reaction mixtures.

If $(CH_3)_3SiCl$ is added to a CF_3IF_2-CH_2Cl_2-suspension at −78 °C a fast reaction occurs yielding CF_3ICl_2 and $(CH_3)_3SiF$ with traces of CF_3I.

$$CF_3IF_2 + 2\ (CH_3)_3SiCl \longrightarrow CF_3ICl_2 + 2\ (CH_3)_3SiF \qquad (8)$$

Trifluoroiodomethane can be formed by a reductive chlorine elimination from CF_3ICl_2.

$$CF_3ICl_2 \underset{\nleftarrow}{\longrightarrow} CF_3I + Cl_2 \qquad (9)$$

This successful attempt encouraged us to check the possibilities of further exchange reactions using trimethylsilicon compounds.

Therefore we studied the reactions of trimethylsilicon cyanide, isocyanate, isothiocyanate, N-methyl-N-trimethylsilyl trifluoro acetamide (MSTFA) and trimethyltrifluoromethylsilicon with trifluoromethyliodine difluoride in various solvents.

With the cyanide ^{19}F-n.m.r. spectroscopic evidence is found for $CF_3I(CN)_2$.

$$CF_3IF_2 + 2\ (CH_3)_3SiCN \longrightarrow \text{"}CF_3I(CN)_2\text{"} + 2\ (CH_3)_3SiF \qquad (10)$$

With the isothiocyanate decomposition occurs even at -60 °C in solution. If trimethylsilicon isocyanate or MSTFA are used, ligand exchange reactions are observed. Using the isocyanate $CF_3I(NCO)_2$ can be obtained as a white solid that decomposes at approximately 0 °C. $CF_3I(NCO)_2$ is extremely sensitive to moisture and air. With MSTFA the mono- and disubstituted iodine derivatives can be identified by their ^{19}F-n.m.r. spectra. These compounds as well as the above mentioned $CF_3I(N(CH_3)_2)_2$ are the first examples of trifluoromethyliodine derivatives with stable iodine-nitrogen bonds.

$$CF_3IF_2 + 2\ (CH_3)_3SiNCO \longrightarrow CF_3I(NCO)_2 + 2\ (CH_3)_3SiF \qquad (11)$$

$$\begin{aligned} CF_3IF_2 + 2\ (CH_3)_3SiN(CH_3)COCF_3 \longrightarrow\ & CF_3IF(N(CH_3)COCF_3) + \\ & CF_3I(N(CH_3)COCF_3)_2 + \\ & (CH_3)_3SiF \qquad (12) \end{aligned}$$

The mono substituted compound, $CF_3IF(N(CH_3)COCF_3)$, is the first example of a stable ternary trifluoromethyl iodine (III) derivative.

$(CH_3)_3SiCF_3$ does not react with CF_3IF_2 even under vigorous conditions in any solvent. But if CF_3IF_2 is directly suspended in $(CH_3)_3SiCF_3$ a vigorous reaction takes place even at -30 °C. No new products could be identified from the ^{19}F-n.m.r. spectra of the resulting residue in CH_3CN solution.

Reactions of CF_3ICl_2 with silver compounds

The simple preparation of CF_3ICl_2 encouraged us to try whether ligand exchange reactions with silver compounds are possible. CF_3ICl_2 is thought to be as excellent a starting material for exchange reactions with silver compounds as trifluoromethyliodine difluoride is for exchange reactions using boron or silicon compounds. We were successful in synthesizing

$CF_3I(OCOCF_3)_2$ by reacting CF_3ICl_2 with $AgOCOCF_3$ in acetonitrile solution.

$$CF_3ICl_2 + 2\ AgOCOCF_3 \longrightarrow CF_3I(OCOCF_3)_2 + 2\ AgCl \qquad (13)$$

If the nearly insoluble silver cyanide is used instead of silver trifluoroacetate we can detect ^{19}F-n.m.r. spectroscopically after a reaction time of about five days the same signal as in the reaction of $(CH_3)_3SiCN$ with CF_3IF_2. So this resonance can be assigned to $CF_3I(CN)_2$, the first trifluoromethyl iodine compound with more than one iodine carbon bond.

We also tried to obtain trifluoromethyliodine derivatives with iodine sulphur bonds. As an example silver thiocyanate reacts with CF_3ICl_2 even at -60 °C with decomposition. No evidence is found for $CF_3I(SCN)_2$ or $CF_3I(NCS)_2$.

The only products we could detect from a reaction mixture of $AgSCF_3$ and CF_3ICl_2 are iodine, trifluoroiodomethane, bis-(trifluoromethyl)disulphane and bis(trifluoromethyl)monosulphane. These compounds lead us to the conclusion that $CF_3I(SCF_3)_2$ must have been formed as an intermediate.

$$CF_3ICl_2 + 2\ AgSCF_3 \longrightarrow \text{'}CF_3I(SCF_3)_2\text{'} + 2\ AgCl \qquad (14a)$$

$$\text{'}CF_3I(SCF_3)_2\text{'} \longrightarrow CF_3I + S_2(CF_3)_2 \qquad (14b)$$

$$\text{'}CF_3I(SCF_3)_2\text{'} \longrightarrow CF_3SI + S(CF_3)_2 \qquad (14c)$$

$$2\ CF_3SI \longrightarrow S_2(CF_3)_2 + I_2 \qquad (14d)$$

The unstable intermediate can decompose in two possible ways, firstly a decomposition into trifluoroiodomethane and bis(trifluoromethyl)disulphane according to equation (14b) and secondly a primary decomposition into trifluoromethyliodosulphane and bis(trifluoromethyl)monosulphane (equation (14c)). Trifluoromethyliodosulphane rapidly forms iodine as well as bis(trifluoromethyl)disulphane [22] according to equation (14d).

Acceptor properties of CF_3ICl_2

It is known that CF_3IF_2 forms 1:1 adducts with N-donor-molecules such as acetonitrile, pyridine or quinoline [2a]. A similar behaviour is to be expected from the chloro derivative. Though we have not isolated CF_3ICl_2 solvent adducts a highfield shift of the CF_3-group in the ^{19}F-n.m.r. spectra and dependence on the donor-number of the solvent indicate the formation of adducts.

Therefore it was of interest to study the reactions of CF_3ICl_2 with chlorides.

If $(C_6H_5)_4AsCl$ is added to a suspension of CF_3ICl_2 in CH_2Cl_2 at -78 °C the salt $[(C_6H_5)_4As][I(CF_3)Cl_3]$ is formed.

TABLE

^{19}F-n.m.r. data of CF_3ICl_2 and $[(C_6H_5)_4As][I(CF_3)Cl_3]$ (CH_2Cl_2, -70 °C, CCl_3F ext.)

CF_3ICl_2		$[I(CF_3)Cl_3]^-$	
δ -26.89 ppm		δ -30.56 ppm	
$^1J(^{19}F-^{13}C)$	364.5 Hz	$^1J(^{19}F-^{13}C)$	373.8 Hz
$^1\Delta(^{19}F-^{12/13}C)$	0.1321 ppm	$^1\Delta(^{19}F-^{12/13}C)$	0.1351 ppm

The significant high-field shift and the increase of the spin-spin coupling constant $^1J(^{19}F-^{13}C)$ indicates the formation of the anionic species $[I(CF_3)Cl_3]^-$.

EXPERIMENTAL

All reactions were carried out in a dry nitrogen atmosphere. Condensations were carried out in a glass vacuum line equipped with Young valves. The reaction vessels were commercially available Schlenk-tubes with a volume of approximately 25 ml.

If not mentioned commercially available chemicals were used and purified by normal methods.

The reagents CF_3IF_2 [1]; $B(C_6F_5)_3$ [23]; $CF_3B\ N(CH_3)_2\ _2$ [24]; $(CF_3)_2BNCH_3$ [24]; $(CH_3)_3SiCF_3$ [25]; $AgSCF_3$ [26] used in the reactions were prepared and purified as previously described. The NMR-spectra were recorded with the Bruker spectrometer AM300; ^{19}F: 282.4 MHz; CCl_3F external reference, ^{11}B: 96.3 MHz; $BF_3 \cdot OEt_2$ external reference.

Reactions of CF_3IF_2 with boron compounds

$-BCl_3$

0.36 g CF_3IF_2 (1.5 mmol) were dissolved in 3 ml CH_3CN. 0.1 ml ≙ 0.13 g BCl_3 (1.1 mmol) were condensed onto the frozen solution. The reaction mixture was stirred at -50 °C for 24 hours. ^{19}F-n.m.r. spectra recorded at -43 °C showed the resonances of CF_3ICl_2, BCl_2F, $BClF_2$ and BF_3 [27] among the resonance of CF_3I and low intensity resonances of unassignable compounds.

$-BBr_3$

To a solution of 0.75 g CF_3IF_2 (3.2 mmol) in 5 ml CH_3CN 0.2 ml ≙ 0.53 g BBr_3 (2.1 mmol) were added. The reaction mixture was stirred for several hours at -50 °C. After a few minutes the slightly yellow mixture became bright orange.

^{19}F-n.m.r. spectra recorded at -43 °C indicate that primarily CF_3I has been formed. Evidence is found for a couple of boron bromide fluorides [27]. (A singlet at -23.41 ppm might be assigned to CF_3IBr_2.)

$-BI_3$

0.47 g CF_3IF_2 (2.0 mmol) were dissolved in 5 ml CH_3CN at -50 °C. Solid BI_3 (0.49 g (1.4 mmol)) was added to the mixture. After a while a black solid precipitated ($I_n^+BF_4$(?)). ^{19}F-n.m.r. spectra recorded from the yellow suspension at -71.5 °C only showed the resonance of CF_3I and two broad signals at +7 ppm and -22 ppm. (The signal at -22 ppm might be assigned to CF_3I_3.)

$-B(OCOCF_3)_3$

To a solution of 0.80 g CF_3IF_2 (3.4 mmol) in 8 ml CH_3CN 0.80 g

$B(OCOCF_3)_3$ (2.3 mmol) were added. The solution was stirred at -40 °C for about 24 hours. The main products formed were $CF_3I(OCOCF_3)_2$ and CF_3I among a couple of fluorine-containing boron compounds.

$-B(C_6F_5)_3$

0.30 g CF_3IF_2 (1.3 mmol) were dissolved in 5 ml CH_3CN at -35 °C. 0.50 g $B(C_6F_5)_3$ (1.0 mmol) were added to the solution. The reaction mixture was stirred for 4 hours at -35 °C and additionally for 2 hours at room temperature. The products we could detect ^{19}F-n.m.r. spectroscopically were $C_6F_5CF_3$, C_6F_5I, BF_3, and unreacted $B(C_6F_5)_3$ among traces of CF_3I.

$-CF_3B[N(CH_3)_2]_2$

A: 0.15 g CF_3IF_2 (0.64 mmol) were suspended in 3 ml CH_2Cl_2. 0.22 g $CF_3B\ N(CH_3)_2\ _2$ (1.30 mmol) dissolved in 1 ml CH_2Cl_2 were added to the reaction mixture at -78 °C. The nearly colourless solution turned green; after 5 minutes the green colour disappeared to leave a yellow solution. ^{19}F-n.m.r. spectra recorded after 1.5 hours at -63 °C showed the resonances of the starting materials, CF_3I, traces of CF_3IF_4 and IF_5 as well as of some boron fluorides.

B: 0.25 g CF_3IF_2 (1.06 mmol) were dissolved in 3 ml DMF at -50 °C. 0.34 g $CF_3B[N(CH_3)_2]_2$ (2.03 mmol) dissolved in 1 ml CH_3CN were added to the frozen DMF solution (-196 °C). The reaction mixture was warmed to -40 °C for about 5 minutes and then again cooled to -78 °C. At -40 °C a green colour appears but after cooling the solution became yellow. In the ^{19}F-n.m.r. spectrum recorded at -63 °C after a reaction time of 1.5 hours similar resonances as described above could be detected.

$-(CF_3)_2BN(CH_3)_2$

The reactions were carried out in the same manner as described above. A: 0.36 g CF_3IF_2 (1.53 mmol) and 0.28 g $(CF_3)_2BN(CH_3)_2$ (1.45 mmol) were used in the CH_2Cl_2 batch; B: 0.26 g CF_3IF_2 (1.11 mmol) and 0.20 g $(CF_3)_2BN(CH_3)_2$ (1.04 mmol) in the DMF/CH_3CN batch.

Colour effects were not observed.
The ^{19}F-n.m.r. and ^{11}B-n.m.r. spectra of the reaction mixtures gave evidence for the formation of $CF_3I[N(CH_3)_2]_2$ and CF_3BF_2 and $(CF_3)_2BF$ adducts.

^{19}F-n.m.r. data (-30 °C; CCl_3F ext.; DMF: CH_3CN = 3:1)

δ -36.99 ppm, s $CF_3I[N(CH_3)_2]_2$
δ -67.94 ppm, s, $^2J(^{19}F-^{11}B)$ 34 Hz $(C\underline{F}_3)_2BF\cdot D$
δ -204.77 ppm, s, $^1J(^{19}F-^{11}B)$ 51 Hz $(CF_3)_2B\underline{F}\cdot D$
δ -66.32 ppm, s, $^2J(^{19}F-^{11}B)$ 37 Hz $C\underline{F}_3BF_2\cdot D$
δ -171.62 ppm, s, $^1J(^{19}F-^{11}B)$ 50 Hz $CF_3B\underline{F}_2\cdot D$ [21]

^{11}B-n.m.r. data (20 °C; $BF_3\cdot OEt_2$ ext.; CH_2Cl_2)

δ -1.6 ppm $CF_3BF_2\cdot D$
δ -3.9 ppm $(CF_3)_2BF\cdot D$

Reactions of CF_3IF_2 with silicon compounds

-$(CH_3)_3SiCl$

3.0 g CF_3IF_2 (12.8 mmol) were suspended in 20 ml CH_2Cl_2 at -78 °C. 3.8 ml $(CH_3)_3SiCl$ (30.0 mmol) were added dropwise to the colourless suspension. The primarily colourless solution became yellow and a white solid precipitated.
CF_3ICl_2 can be isolated either by low-temperature filtration or by removing all volatile compounds from the white residue by vacuum distillation at -25 °C. CF_3ICl_2 can be isolated in 76-90 % yield as a white solid. By-products formed were CF_3I, elemental chlorine and trimethylsilicon fluoride.

-$(CH_3)_3SiCN$

A: 1.0 g CF_3IF_2 (4.28 mmol) were suspended in 5 ml CH_2Cl_2 at -78 °C. 0.5 ml $\hat{=}$ 0.41 g $(CH_3)_3SiCN$ (4.15 mmol) were added. The reaction mixture was stirred for about 12 hours at -78 °C. To complete the exchange excess $(CH_3)_3SiCN$ (0.5 ml) was added.

^{19}F-n.m.r. spectra recorded after 24 hours at -71 °C show the resonances of CF_3IF_2, $(CH_3)_3SiF$, CF_3IF_4, CF_3I, traces of CF_3CN and a singlet at -21.88 ppm, $^1J(^{19}F-^{13}C)$ 360.8 Hz, $\Delta\delta$ 0.1389 ppm that was assigned to $CF_3I(CN)_2$.

B: If CH_3CN was used as a solvent and the reaction was carried out at -25 °C, decomposition occurred. CF_3I, CF_3CN and $(CH_3)_3SiF$ could be detected ^{19}F-n.m.r. spectroscopically.

–$(CH_3)_3SiNCO$

A: 1.2 g CF_3IF_2 (5.13 mmol) suspended in 6 ml CH_2Cl_2 were stirred at -78 °C after adding 0.6 ml $\hat{=}$ 510.6 mg $(CH_3)_3SiNCO$ (4.43 mmol). 12 hours later 0.6 ml $(CH_3)_3SiNCO$ were added to complete the exchange reaction. The reaction mixture was warmed up to -30 °C and additionally stirred for 24 hours. $CF_3I(NCO)_2$ could be isolated after distilling off all volatile compounds as a white to pale-orange solid, that explosively decomposes when warmed up to room temperature.

B: 0.53 g CF_3IF_2 (2.27 mmol) were dissolved in 4 ml CH_3CN at -25 °C. 0.6 ml $\hat{=}$ 0.52 g $(CH_3)_3SiNCO$ (4.50 mmol) were added to the reaction mixture. After a reaction time of about 48 hours at -25 °C $(CH_3)_3SiF$ and CH_3CN were distilled off at -20 °C. The remaining white to yellow solid was dissolved in $CDCl_3$. The ^{19}F-n.m.r. spectrum gives a singlet at -26.27 ppm, $^1J(^{19}F-^{13}C)$ 366.2 Hz; $\Delta\delta$ 0.1369 ppm. CF_3I as well as traces of CF_3IF_2 and CF_3IF_4 can also be detected in the n.m.r. spectrum.

–$(CH_3)_3SiNCS$

0.81 g CF_3IF_2 (3.46 mmol) were dissolved in 5 ml CH_3CN at -25 °C. 0.95 ml $\hat{=}$ 0.88 g $(CH_3)_3SiNCS$ (6.70 mmol) were added to the colourless solution. At once the reaction mixture turned brown. ^{19}F-n.m.r. spectra only indicated the generation of CF_3I and $(CH_3)_3SiF$ with a couple of compounds that could not be assigned. No ^{19}F-n.m.r. spectroscopic evidence for iodine (III) derivatives was found.

Further reactions carried out at -60 °C in CH_3CN/DMF-mixtures or CH_2Cl_2 led to comparable results.

-$(CH_3)_3SiN(CH_3)(COCF_3)$ (MSTFA)

A: 0.23 g CF_3IF_2 (1.00 mmol) were suspended in 5 ml CH_2Cl_2 at -78 °C. 67 mg ≙ 63 µl $(CH_3)_3SiN(CH_3)(COCF_3)$ (0.34 mmol) dissolved in 0.6 ml DMF and 0.3 ml CH_3CN were added. 201 mg ≙ 188 µl MSTFA (1.01 mmol) were added after a reaction time of about 4 hours. The mixture was stirred for additional 6 hours at -45 °C. A slight clouding occurred. ^{19}F-n.m.r. spectra recorded at -71 °C showed the signals of CF_3I; CF_3IF_2; $CF_3IF(N(CH_3)COCF_3)$; $CF_3I(N(CH_3)COCF_3)_2$; and $(CH_3)_3SiF$ with a couple of signals between -66 ppm and -71 ppm. The CF_3-resonance of $CF_3IF(N(CH_3)COCF_3)$ is split into a doublet at -31.19 ppm, $^3J(^{19}F-^{19}F)$ 3.1 Hz; $^1J(^{19}F-^{13}C)$ 364.7 Hz; $\Delta\delta$ 0.1351 ppm. The resonance of the IF fragment as well as the $COCF_3$-group could not be unambiguously assigned. $CF_3I(N(CH_3)COCF_3)_2$ was detected as two singlets at -31.44 ppm, $^1J(^{19}F-^{13}C)$ 361.6 Hz, $\Delta\delta$ 0.1351 ppm for the CF_3 group and -70.07 ppm for the $COCF_3$ group. If a ^{19}F-n.m.r. spectrum was recorded at room temperature the resonances of $CF_3IF(N(CH_3)COCF_3)$ and CF_3IF_2 disappeared. The only CF_3I-compounds we could detect were CF_3I, as the main product, and $CF_3I(N(CH_3)COCF_3)_2$ at -32.4 ppm and -71.1 ppm.

B: 0.25 g CF_3IF_2 (1.07 mmol) were dissolved in 6 ml DMF and 2 ml CH_3CN at -78 °C. 67 mg ≙ 63 µl $(CH_3)_3SiN(CH_3)COCF_3$ (0.34 mmol) dissolved in 0.6 ml DMF and 0.3 ml CH_3CN were added. After a reaction time of 4 hours additionally 201 mg ≙ 188 µl MSTFA were added. The reaction mixture was stirred for 6 hours at -45 °C. A comparison of the ^{19}F-n.m.r. spectra of A and B indicated a slower exchange. Even at room temperature no complete exchange could be observed. ^{19}F-n.m.r. spectra recorded after an additional reaction time of 12 hours at room temperature showed the resonances of CF_3IF_2.

-$(CH_3)_3SiCF_3$

The reactions of CF_3IF_2 with $(CH_3)_3SiCF_3$ were carried out in several manners. All reactions had in common that the stoichiometry of $(CH_3)_3SiCF_3$ to CF_3IF_2 always was about 2:1. Since no successful exchange was observed only the solvents and the reaction temperatures are listed: none (-78 °C and -30 °C); acetonitrile (-30 °C); pyridine (-25 °C and room temperature); tetrahydrofurane (-78 °C and -25 °C); glyme (-25 °C); dichloromethane (-78 °C); trimethylamine (-78 °C); dimethylformamide (-50 °C), diethylether (-78 °C and -25 °C), and butanoicacid-3-oxoethylester (-25 °C).

Reactions of CF_3ICl_2 with silver salts

CF_3ICl_2 was prepared as described above.

- $AgOCOCF_3$

1.05 g CF_3ICl_2 (3.94 mmol) were dissolved in 5 ml CH_3CN at -40 °C. A solution of 1.70 g $AgOCOCF_3$ (7.70 mmol) in 3 ml CH_3CN (-40 °C) was added. As soon as the solutions were mixed a yellowish-white solid precipitated (AgCl). The ^{19}F-n.m.r. spectra of the solution recorded after 2 hours showed the resonances of $CF_3I(OCOCF_3)_2$ (δ -26.10 ppm, $^1J(^{19}F-^{13}C)$ 360.1 Hz; $\Delta\delta$0.1369 ppm for the CF_3I-group and δ -73.03 ppm for the $OCOCF_3$-group), CF_3I and CF_3Cl.

AgCl was separated by low-temperature filtration. The solvent, CF_3I and CF_3Cl were removed from the solution by vacuum condensation at -15 °C. The remaining residue could be identified ^{19}F-n.m.r. spectroscopically as $CF_3I(OCOCF_3)_2$. 0.94 g $CF_3I(OCOCF_3)_2$ (2.23 mmol) could be obtained in 56 % yield.

-AgCN

Solid AgCN (0.27 g ≙ 2.00 mmol) was added to a suspension of 0.28 g CF_3ICl_2 (1.05 mmol) in 3 ml CH_2Cl_2 at -30 °C. After a reaction time of about 5 days $CF_3I(CN)_2$ could be detected ^{19}F-n.m.r. spectroscopically (δ -22.62 ppm, $^1J(^{19}F-^{13}C)$ 367.8 Hz; $\Delta\delta$ 0.1411 ppm).

-AgSCN

0.63 g CF_3ICl_2 (2.35 mmol) were suspended in 5 ml CH_2Cl_2 at -78 °C. 0.83 g solid AgSCN (5.00 mmol) were added. The yellow suspension decolourised. No spectroscopic evidence was found for trifluoromethyliodine (III) derivatives.

$\underline{-AgSCF_3}$

A: 0.55 g CF_3ICl_2 (2.06 mmol) were dissolved in a DMF/CH_3CN mixture at -78 °C (3 ml DMF/1 ml CH_3CN). 0.84 g $AgSCF_3$ (4.00 mmol) were added. The initially purple solution became yellow and a solid precipitated. The ^{19}F-n.m.r. spectrum of the reaction mixture recorded after 18 hours at a temperature of -71 °C showed the resonances of CF_3I and CF_3ICl_2. Two resonances at δ -34.51 ppm and δ -44.40 ppm (integration: 1:2.2) might be assigned to $CF_3I(SCF_3)_2$. The resonance at δ -44.40 ppm; $^1J(^{19}F-^{13}C)$ 315.9 Hz; $\Delta\delta$ 0.1351 ppm could be assigned to $S_2(CF_3)_2$.

B: 0.60 g CF_3ICl_2 (2.25 mmol) were suspended in 4 ml CH_2Cl_2 at -78 °C. 0.90 g $AgSCF_3$ (4.29 mmol) were added. The slight yellow solution became colourless and later light purple. Later a decolouration occurred. A ^{19}F-n.m.r. spectrum recorded at -71 °C showed the resonances of CF_3I (δ -5.50 ppm), CF_3ICl_2 (δ -26.62 ppm), $S(CF_3)_2$ (δ -45.61 ppm) and $S_2(CF_3)_2$ (δ -48.50 ppm). The assignment of the sulphane resonances was made using the splitting of the ^{13}C-satellites.

The acceptor properties of CF_3ICl_2

0.3 g CF_3IF_2 (1.3 mmol) were suspended in 4 ml CH_2Cl_2 at -78 °C. 0.4 ml $(CH_3)_3SiCl$ (3.16 mmol) were added dropwise. After the exchange was complete 0.42 g $(C_6H_5)_4AsCl$ (1.01 mmol) were added. The suspended CF_3ICl_2 dissolved but after a few minutes a yellow solid precipitated. The solid could be isolated by filtration. The ^{19}F-n.m.r. data are listed in the results section.

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