Journal of Fluorine Chemistry, *37* (1987) 223–245

Received: March 5, 1987; accepted: July 3, 1987

SYNTHESIS AND CHEMISTRY OF PERFLUORO-2-IODO-2-METHYL-ALKANES

A. PROBST, K. RAAB, K. ULM and K. von WERNER*

Hoechst AG, Werk Gendorf, D-8269 Burgkirchen II (F.R.G.)

SUMMARY

Two novel perfluoro-tert-alkyl iodides $CF_3(CF_2)_{\overline{n+1}}C(CF_3)_2I$ have been obtained from **F**-alkenes $CF_3(CF_2)_n$-$CF=C(CF_3)_2$ (n = 0 and 1) by formal additions of iodine fluoride; these required substantial alterations of known procedures. The **F**-tert-alkyl iodides are the most reactive alkyl halides known so far, and they are also very toxic. The following types of reactions have been studied: (a) Nucleophilic attack of anions at the iodine, leading to **F**-alkenes, (b) elimination of iodine fluoride, caused by metals or metal complexes, (c) pyrolysis, to give very selectively **F**-isobutene and n-perfluoroalkyl iodides, (d) photolysis, and (e) thermally induced insertions into the carbon-iodine bond. Screening results on the inhalation toxicity of the iodides and of some other fluoro-compounds are also reported.

---

* Author to whom correspondence should be addressed.

0022-1139/87/$3.50

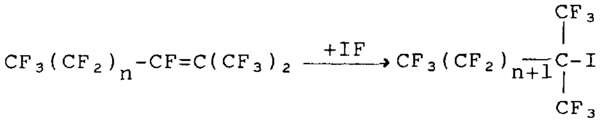
INTRODUCTION

Perfluoro-tert-butyl iodide (**2a**), a white solid that rapidly sublimes even at room temperature, has first been prepared by **Knunyants** and coworkers in 1966 through the reaction of F-isobutene (**1a**) with potassium fluoride and iodine in nitrobenzene at 170°C [1] . The compound **2a** can also be obtained in good yield by the interaction of plasma-generated trifluoromethyl radicals with tetraiodomethane [2] . We have recently disclosed the preparation of F-2-iodo-2-methyl-butane (**2b**) and F-2-iodo-2-methyl-pentane (**2c**) [3] and given a brief description of the chemistry of these higher homologues of F-tert-butyl iodide [4] . In the present work we wish to give a full account of our knowledge on the tertiary iodo-compounds.

RESULTS AND DISCUSSION

Syntheses of F-tert-alkyl iodides

During our attempts to obtain tertiary iodides from the precursors F-2-methyl-2-butene or F-2-methyl-2-pentene, respectively, according to the equation



$$CF_3(CF_2)_n\text{-}CF{=}C(CF_3)_2 \xrightarrow{+IF} CF_3(CF_2)_{n+1}\text{-}\underset{CF_3}{\overset{CF_3}{C}}\text{-}I$$

1b: $n = 0$	**2b:** $n = 0$
1c: $n = 1$	**2c:** $n = 1$

we were repeatedly frustrated by the fact that none of the standard methods gave more than a trace of the desired products. Although the alkenes **1b,c** react readily with caesium fluoride in various solvents, forming carbanions which may be observed by n.m.r. spectroscopy [5] and can even be isolated as stable tris(dimethylamino)sulfonium salts [6] , these carbanions seemingly failed to react with either iodine, iodine bromide or iodine chloride. The method of **Knunyants** [1] proved unsuccessful, as well as reactions of **1b,c** with iodine pentafluoride plus iodine at elevated temperatures, nor did the compound **2c** arise from the treatment of **F**-2-methyl-2-nitroso-pentane with iodine or its interhalogen-compounds.

We finally succeeded in finding two methods which afforded the iodides **2b,c** as stable, distillable liquids in yields between 75 and 95 %:

Method A

Alkenes **1b,c** are transformed with silver(I) fluoride (or a combination of a soluble silver(I) salt and potassium fluoride) in a polar, aprotic solvent, e.g. acetonitrile, into the silver salts of the corresponding carbanions, and these are reacted further with iodine to form **2b,c**. The reactions proceed fast with precipitation of silver iodide under mild conditions. Related reactions of perfluoroalkyl silver compounds have been described before [7,8] .

Method B

The **F**-olefins **1b,c** are reacted at 180-200°C with a mixture of iodine and iodine pentafluoride — in IF-stoichiometry — in the presence of potassium fluoride, so that the molar ratio KF/IF_5 is at least one. Alkenes **1** may be used in excess over the calculated amount of iodine fluoride, since they can be easily separated from the higher boiling products **2** by distillation. **F**-trans-4-methyl-2-pentene, an isomer of **1c**, is inert under the conditions of method B.

A common and very important feature of both methods is the effective removal of iodide ions, in the first case by precipitation with silver ions, and in the second case by oxidation with iodine pentafluoride. We found (c.f. chapter 4.1) that iodide ions rapidly attack the compounds **2**, reverting the reaction under regeneration of the starting alkenes.
It has been reported that **F**-2-iodo-2-methyl-pentane (**2c**)

was formed from the TAS-salt of **F**-2-methyl-pentanide and N-iodosuccinimide at -30°C and could be identified by n.m.r. [6]. Their vain attempts to isolate compound **2c** at 25°C led the authors to the conclusion that it ought to be unstable at this temperature. We believe however, that the product fell victim to a rapid subsequent reaction with succinimide anions while the reaction mixture was being warmed to room temperature.

Spectroscopic data of F-2-iodo-2-methyl-alkanes

NMR data of the tertiary iodides are listed in Table 1. The ^{13}C-n.m.r. spectra of the compounds R_F-$C(CF_3)_2I$ reveal a small — but significant — deshielding of the tertiary carbon with increasing length of the R_F-group, reflecting the —I-influence of this group. The same explanation could hold for the downfield shift of the trifluoromethyl groups attached to the tertiary carbon, observed in the ^{19}F-n.m.r. spectra, in going from **2a** to **2c**. It is interesting to compare the δ(^{19}F)-values of compound **2c** with the data of the analogous bromo-, chloro- and fluoro-compounds:

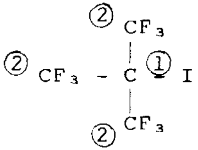
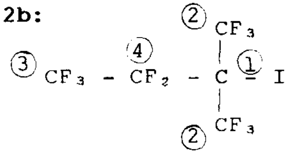
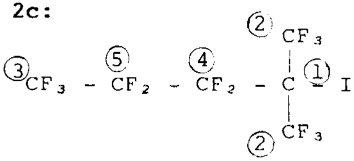
δ(^{19}F) [ppm] of CF_3-CF_2-CF_2-$C(CF_3)_2$-X (vs. external CF_3COOH)

CF_3-	CF_2-	CF_2-	$C(CF_3)_2$-X	X
-2.9	-47.6	-37.6	+5.4	F
-3.2	-45.3	-31.2	+10.3	Cl
-3.2	-44.7	-27.8	+12.7	Br
-3.1	-43.3	-21.6	+16.4	I

The data shows a distinct shift to lower field for the resonances of the groups directly bonded to the tertiary carbon as the atomic weight of X is increased, whereas the ß-CF_2-resonances, although showing the same trend, are much less influenced. A similar dependance of ^{19}F-shifts on the nature of halogens has been shown to exist in a series of F-2-halogeno-2-methyl-propanes [9] .

TABLE 1

NMR Data of **F**-2-Iodo-2-methyl-alkanes

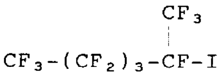
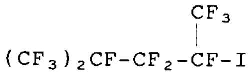
Compound	^{13}C-chemical shifts ($\delta^{13}C$) and (^{13}C,^{19}F)-coupling constants	^{19}F-chemical shifts ($\delta^{19}F$)
2a:  $CF_3-C(CF_3)_2-I$	① 37.09 ppm, decet (30.5 Hz) ② 121.75 ppm, q (290 Hz)	② 14.45 ppm
2b:  $CF_3-CF_2-C(CF_3)_2-I$	① 38.55 ppm, septet (30.5 Hz)of t (25.2 Hz) ② 122.78 ppm, q (286.8 Hz) ③ 118.34 ppm, q (288.4 Hz) of t (35.3 Hz) ④ 113.02 ppm, t (269 Hz) of q (40.4 Hz)	② 16.16 ppm ③ 0.19 ppm ④ - 24.84 ppm
2c:  $CF_3-CF_2-CF_2-C(CF_3)_2-I$	① 38.90 ppm, septet (30.8 Hz)of t (24.6 Hz) ② 122.72 ppm, q (286.5 Hz) ③ 118.61 ppm, q (288.8 Hz) of t (34.1 Hz) ④ 114.68 ppm, t (269.2 Hz) of t (34.0 Hz) ⑤ 109.78 ppm, t (272.8 Hz)of sextets (37.7 Hz)	② 16.36 ppm ③ - 3.06 ppm ④ - 21.55 ppm ⑤ - 43.3 ppm

In $CDCl_3$. ^{13}C-NMR: 50.323 MHz, *vs.* internal TMS. ^{19}F-NMR: 75.393 MHz, *vs.* external CF_3COOH.

In Table 2, a comparison is made between u.v. data of primary, secondary and tertiary **F**-alkyl iodides. It can clearly be seen that there is a close relationship between structure and the position of the absorption maximum. Compound **2c** absorbs at longest wavelength. This compound may also be expected to have the lowest carbon—iodine bond dissociation energy.

TABLE 2

UV Data of Perfluoroalkyl iodides

Compound	λ_{max} (nm)	ε
$CF_3-(CF_2)_5-I$	273.0	278
 $CF_3-(CF_2)_3-\overset{\overset{CF_3}{\vert}}{C}F-I$	282.0	210
 $(CF_3)_2CF-CF_2-\overset{\overset{CF_3}{\vert}}{C}F-I$	281.9	200
2a	287.2	199
2b	292.6	190
2c	294.6	196

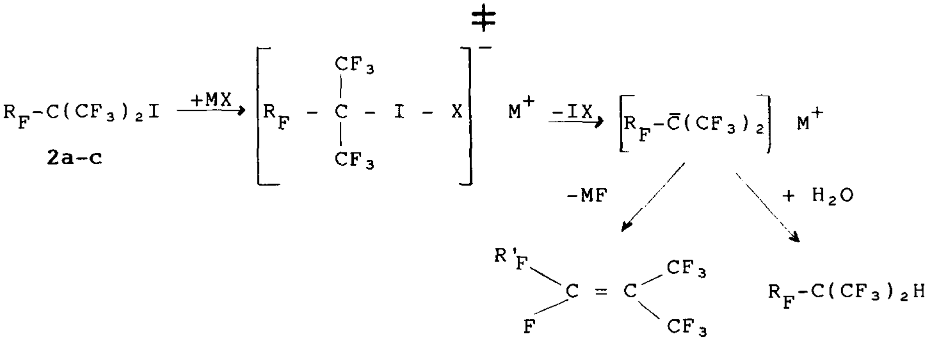
In n-hexane. λ_{max}: absorption maximum. ε:molar extinction.

The chemistry of F-tert-alkyl iodides

The compounds **2b,c** proved to be very stable against strong oxidants: no reaction took place during prolonged refluxing with fuming sulfuric acid, containing 30 % of sulfur trioxide, or concentrated nitric acid, respectively. The iodides also did not react with a 40 %-solution of peroxidoacetic acid in glacial acetic acid. Due to its facile availability from **F**-2-methyl-2-pentene, a well known HFP-dimer, most of the experiments described below have been performed using compound **2c**.

1. Nucleophilic attack of anions at the iodine

Compounds **2a-c** react with a variety of potassium- or sodium salts in polar aprotic solvents at room temperature. Since the tertiary iodides carry a partial positive charge at the iodine atom, it seems very likely that the initial attack of anions X^- leads to a transition state which resembles the type of bonding in the recently discovered iodinanide compounds [10]. Elimination of IX will then lead to **F**-carbanions, which may either loose fluoride to form the alkenes **1a-c**, or, in the presence of moisture, will readily give **F**-2-hydro-2-methyl-alkanes:



R'_F = F: **1a**, CF$_3$: **1b**, C$_2$F$_5$: **1c**

The rate of reaction is dependent on the following factors:

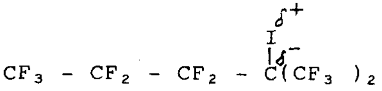
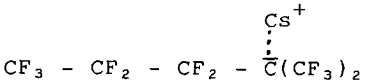
(i) The anion X^-: In acetonitrile, fast reactions of **2c** occur with hydroxide, cyanide and thiocyanate, slower reactions with iodide, sulfite, dithionite, nitrite and carbonate, but no reaction could be observed with fluoride, nitrate and sulfate.

In the cases of hydroxide, cyanide and thiocyanate, subsequent reactions of the alkenes **1a-c** ensued which we did not investigate further.

(ii) Solvent polarity: Generally, reactions in dimethylformamide or dimethylacetamide were much faster than in acetonitrile.

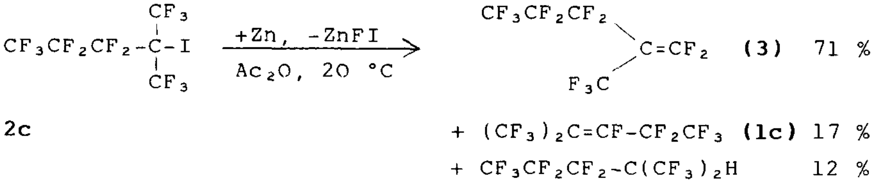
(iii) The iodo-compounds **2**: As was to be anticipated from their ground-state polarization, the iodides showed a decrease of reactivity in the order **2c** $\gg$ **2b** > **2a**. When being reacted with potassium iodide in acetonitrile for one hour at 20°C, under strictly anhydrous conditions, the tertiary iodides gave the following degree of conversion into the corresponding alkenes **1**: **2c**: 26 %, **2b**: 20 %, and **2a**: 5.5 %.

We noticed a surprising similarity between the ^{19}F-shifts of compound **2c**, whose resonances are little solvent-dependent, and the chemical shifts observed for caesium **F**-2-methyl-pentanide in diglyme solution. The fluoro-carbanion seems to form a tight ion-pair with the caesium cation in diglyme, whereas the salt becomes fully dissociated in solvents of higher complexing power, such as tetraglyme or dimethylformamide. We therefore believe that, with regard to charge distribution, **2c** is somewhat comparable to a tight ion-pair.

Compound (^{19}F-shifts in ppm)	Solvent
 $CF_3 - CF_2 - CF_2 - \overset{\overset{\delta^+}{\underset{|\delta^-}{I}}}{C}(CF_3)_2$	
-3.0 -43.3 -21.6 +16.4	chloroform-d
-2.7 -43.2 -21.3 +17.2	dimethylformamide
 $CF_3 - CF_2 - CF_2 - \overset{\overset{Cs^+}{\vdots}}{\bar{C}}(CF_3)_2$	
-2.6 -44.1 -18.0 +20.8	diglyme
$[CF_3 - CF_2 - CF_2 - C(CF_3)_2]^- Cs^+$	
-2.5 -47.6 -14.3 +36.7	tetraglyme
-2.4 -47.7 -14.1 +37.0	dimethylformamide

2. Reactions with metals or metal complexes under elimination of iodine fluoride

It is well known that n-perfluoroalkyl iodides, when being reacted with zinc in acetic anhydride, give high yields of **F**-alkanes due to coupling of the R_F-groups [11]. In contrast, the action of zinc on compound **2c** generates predominantly alkene **3** besides smaller amounts of alkene **1c** and of **F**-2-hydro-2-methyl-pentane. The reaction proceeds obviously under kinetic control, probably via a radical mechanism initiated by a SET-process between zinc and the tertiary iodide.



While this reaction is exothermic, the conversion of **F**-2-bromo-2-methyl-pentane with zinc occurs much slower, but leads to a similar product distribution. In no case could any coupling products (dimers) be detected.

Formation of the alkenes **1c** and **3** is the major side reaction during the pyrolysis of compound **2c** in a stainless-steel vessel, and it even becomes the main reaction in the presence of moisture. We ascribe this influence of water to an activation of the wall metals. We had observed a similar effect before while studying transition metal-catalyzed reactions of n-perfluoroalkyl iodides [12].

It has been reported that oxidative additions of **F**-(n-alkyl) iodides to **Vaska**-type rhodium(I)- and iridium(I)-complexes yield 50-85 % of the expected perfluoroalkyl-metal(III)-complexes [13,14]. However, we did not obtain any perfluoroalkyl-complexes from similar reactions using compound **2c**. The actual course of reaction is the following:

$$\text{trans-M(CO)ClL}_2 + \mathbf{2c} \xrightarrow[\text{r.t.}]{\text{benzene}} \text{M(CO)(Cl)(F)(I)L}_2 + \mathbf{1c} + \mathbf{3} + R_FH$$

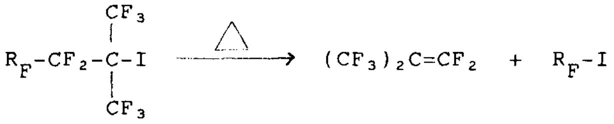
$L = P(C_6H_5)_3$

$$\nu(CO)\text{:Rh: } 2090\ \text{cm}^{-1}$$
$$\text{Ir: } 2070\ \text{cm}^{-1}$$

3. Pyrolysis

Butler and **Snelson** pyrolyzed **F**-tert-butyl iodide at 300°C in a platinum vessel and investigated the products through matrix-i.r.. They found only **F**-isobutene and, presumably, iodine fluoride but no **F**-tert-butyl radicals or **F**-2,2,3,3-tetramethyl-butane, respectively [15] . Measuring the thermal decomposition of the tertiary iodides in a Monel-cell by d.s.c., we obtained the following data: Start of exothermic decomposition: **2a**: 260°C, **2b**: 175°C, and **2c**: 195°C; peak maxima: **2a**: 293°C, **2b**: 205°C, and **2c**: 234°C.

As has already been mentioned in paragraph 2., pyrolysis in stainless-steel was hampered by massive wall effects. However, we noticed that the main reaction was a rather unexpected fragmentation, provided carefully dried iodides were used:



$$R_F\text{-}CF_2\text{-}C(CF_3)_2\text{-}I \xrightarrow{\Delta} (CF_3)_2C{=}CF_2 + R_F\text{-}I$$

R_F: **2b**: CF_3, **2c**: C_2F_5

A pyrolysis of compound **2c** in a thick-walled quartz ampoule at 250°C showed that perfluoroisobutene and **F**-ethyl iodide were formed in a molar ratio of 1:1 and with a selectivity of 97 %. In addition, we found small amounts of **F**-2-methyl-pentane (1.5 %) and of iodine. Very fast decomposition occurred when vapours of compounds **2b** or **2c** were brought into contact with the hot surface of an uncooled high-pressure mercury lamp. In each case, the selectivity for **F**-isobutene and **F**-alkyl iodide amounted to over 95 %.

Space-filling models of compounds **2b** and **2c** (see Fig. 1) can only be assembled with difficulties. In contrast to the less crowded compound **2a**, models of **2b,c** break apart if rotation of the trifluoromethyl groups at the tertiary carbon is attempted. Another striking feature of these models is the close distance between the iodine and the γ-carbon.

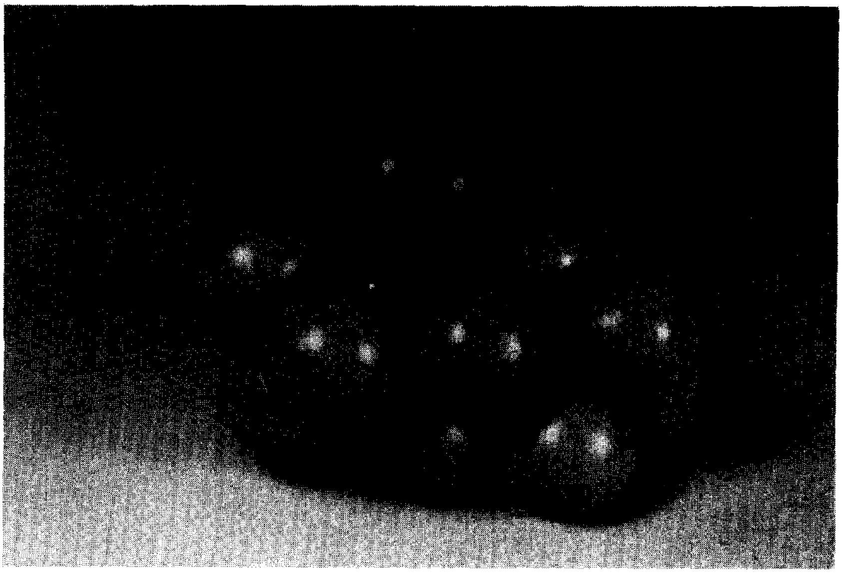
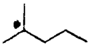


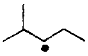
Fig. 1. Molecular model of compound **2c**.

It seems reasonable to assume that the first step in the pyrolysis of **2b,c** consists in the fission of the carbon-iodine bond, under formation of a tertiary radical. The collapse of this radical into **F**-isobutene and an **F**-alkyl radical, which recombines with iodine, would then give the observed products. Since the photolysis experiments described in paragraph 4. show that the cleavage of the CI-bond is an almost completely reversible process, and recombinations of **F**-alkyl radicals with iodine proceed very fast in general [25,27], the homolytic cleavage of the CC-bond appears to be rate-determining.

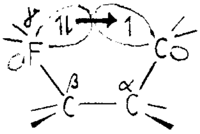
It is tempting to believe that the high over-all selectivity might be in some way related to the proximity of iodine and γ-carbon, encountered in the ground-state of compounds **2b,c.**

Recent e.s.r.-work has led to the surprising discovery that the tertiary radical **A**, which should act as a transient intermediate in the pyrolysis of **2c**, appears to be less stable than its secondary isomer **B** [16] .

A =


B =


The astounding persistence of some perfluorinated radicals, for example of **Scherer's** radical (**F**-2,4-dimethyl-3-isopropyl-3-pentyl) [17], has been largely attributed to steric reasons. We have demonstrated previously by means of ^{13}C- and ^{17}O-n.m.r. studies that, in saturated sp^3-systems, the shielding of a certain nucleus is governed by the number of fluorines in γ-position to this nucleus [18,19] . It is to be expected that γ-fluorines will also increase the electron density in the partly filled orbital at a radical center:



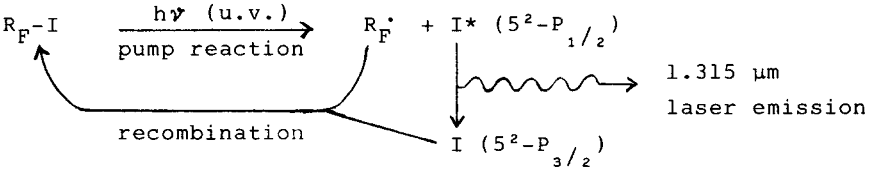
It seems worth checking by MO-calculations whether such an electronic effect would result in a net stabilization of perfluorinated radicals. If this were the case, radical B (9 γ-F) should be more stable than radical **A** (2 γ-F), although only some of the γ-fluorines will be able to interact with the radical center owing to conformational restrictions. A theoretical study on the influence of fluorines in different positions on perfluorinated radicals will be performed by others who are better equipped for calculatory work.

4. Photolysis

The photodissociation and recombination of **F**-alkyl iodides or bromides has been the subject of several experimental investigations [20-22], and a three-dimensional theory has been used to calculate the photodissociation spectrum of trifluoromethyl iodide [23].

When iodide **2c** (deoxygenated vapour) was irradiated at 20-60°C for 12 hours in a quartz reactor, using either a low-pressure or a high-pressure mercury lamp, some etching of the quartz occured and a small amount of iodine was formed. We recovered ca. 97 % of the starting material, besides 1.5-2.0 % of **F**-2-methylpentane. **F**-tert-butyl iodide gives very similar results [24].

In the last decade there has been a great deal of interest in atomic iodine lasers based on perfluoroalkyl iodides [25], in particular in high energy lasers which can even be used for fusion experiments [26]. The basic mode of operation of such a photodissociation laser is shown below:



Competing reaction: $2\ R_F\text{-}I \longrightarrow R_F\text{-}R_F + I_2$

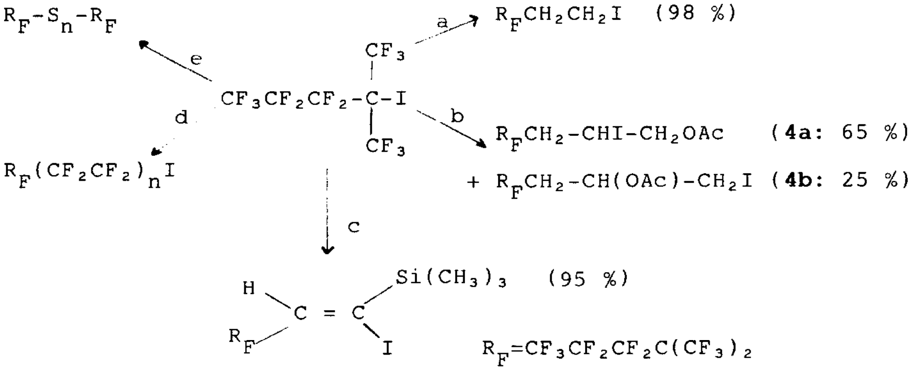
Due to this side reaction, primary and secondary iodides are slowly converted to **F**-alkanes and iodine. The molecular iodine reduces the energy output further, since it deactivates the excited iodine atoms very fast in radiationless collisions. In contrast, **F**-tert-butyl iodide shows a greatly reduced tendency to form R_F-dimers and is thus a more stable lasing medium [27].

Compound **2c** seemed a promising candidate in particular for solar-pumped lasers on behalf of its long-wavelength u.v. absorption. **2c** was investigated in a closed-cycle pulsed laser system pumped by xenon flashlamps. The experimental procedure has been described in ref. [28]. As gas filling 28 mbar **2c** and 100 mbar sulfur hexafluoride was used. The lasing properties of **2c** are nearly identical with those of compound **2a**, which had been tested before in the same system. The decrease of laser energy during the first thirty shots was about six times smaller for **2a,c** than for **F**-isopropyl iodide.

None of the photolysis experiments with iodide **2c** gave the corresponding R_F-dimer. We believe that this dimer is unstable, at least at room temperature, in consequence of steric repulsion between the tertiary centers.

5. Thermally induced insertions into the carbon–iodine bond

Some radical-type additions of compound **2c** to CC-unsaturated substrates are shown in the next scheme. Simple heating of the reagents gave much better results than the use of radical initiators Except for the reaction with sulfur, analogous reactions of primary **F**-alkyl iodides require markedly higher temperatures to achieve similar rates. This finding is no surprise, considering the greater thermal stability (<u>i.e.</u>, stronger CI-bond) of the primary iodides.



[a] 15 bar C_2H_4, 140°C, 2h. [b] $CH_2=CH-CH_2OAc$, 130°C, 15 h: **4b** is formed from **4a** by thermal rearrangement. [c] $HC\equiv C-Si(CH_3)_3$, 150°C, 15 h. [d] Molar ratio C_2F_4/**2c** = 2.0, 150°C, 5h: 72 % conversion to n = 1-6. [e] S_8, 180°C, 12 h: 55 % conversion to n = 1-3 (mainly n = 2).

Toxicity studies

Predictions on the toxicity of organo-fluorine compounds, based on structural elements, can be rather unreliable even for closely related substances. In order to secure safe working with new chemicals, we have set up a test, using albino mice, which allows to determine the magnitude of acute inhalation toxicity of volatile fluorine compounds [29]. Data of most of the compounds mentioned in the present paper are listed in Table 3. The lowest dosage that could be adjusted with sufficient accuracy was 30 ppm with our experimental equipment. Thus, in the case of some highly toxic compounds, the exact LC 50-values may be in fact considerably lower than the upper-limit values given in the table.

TABLE 3

Inhalation Toxicity Data of **F**-alkyl halides and of **F**-hexenes.

Compound	1h-LC 50 (ppm)	Compound	1h-LC 50 (ppm)
n-$C_6F_{13}I$	>13.500*	$C_3F_7(CF_3)_2CBr$	<100
$(CF_3)_2CFI$	1.000-2.000 (900*)	$C_3F_7(CF_3)_2CCl$	500-1.000
$(CF_3)_2CF\text{-}CFI\text{-}CF_3$	250-500	$C_3F_7(CF_3)_2CH$	100-250
$(CF_3)_3CI$ (**2a**)	30-100	trans- $(CF_3)_2CF\text{-}CF{=}CF\text{-}CF_3$	2.500-5.000
$C_2F_5(CF_3)_2CI$ (**2b**)	<50	$(CF_3)_2C{=}CF\text{-}C_2F_5$ (**1c**)	100-250
$C_3F_7(CF_3)_2CI$ (**2c**)	<50 (<25*)	$(C_3F_7)(CF_3)C{=}CF_2$ (3)	<35

Unmarked values: Pre-screening with NRMI-mice.

Values denoted by an asterisk: More elaborate tests with Wistar-rats.

The toxicity of perfluoroalkyl iodides is clearly related to their structure, decreasing in the order of tertiary > secondary > primary. The tertiary iodides can be expected to react with nucleophiles under physiological conditions, forming again toxic products, such as **F**-2-hydro-2-methyl-pentane. Even the bromo-analogue of compound **2c** is very toxic. It has been reported earlier that the toxicity of **F**-alkenes may be correlated with their susceptibility to nucleophilic attack [30]. This explanation is supported by our data obtained for three **F**-hexenes. **F**-2-methyl-1-pentene, possessing a **F**-isobutene-like structure, shows by far the highest toxicity among these hexenes.

EXPERIMENTAL

The n.m.r. spectra have been recorded with a Bruker AC 200 spectrometer (^{13}C: 50.323 MHz, ^{1}H: 200.13 MHz, vs. internal TMS) and a Bruker WP 80 SY spectrometer (^{19}F: 75.393 MHz, vs. external CF_3COOH). The u.v. spectra have been measured using a Lambda 5 UV/VIS spectrophotometer. Volatile products were analysed by low-temperature n.m.r. at -35°C and by g.l.c., respectively. The starting materials have been prepared by standard procedures: **1a** [31], **1b** [32], **1c** by CsF-catalyzed isomerization in diglyme of **F**-4-methyl-2-pentene [33], **2a** [1].

WARNING: Due to the high toxicity of several compounds (c.f. toxicity chapter), the chemistry described in this work requires great alertness. All experiments have to be performed in a well-vented fume cupboard, using protective gloves.

F-2-iodo-2-methyl-butane (2b: n.c.)

Method A

In a 250 ml four-necked flask, equipped with stirrer, thermometer and a dry ice condenser, whose top outlet was connected to a tube filled with blue gel, potassium fluoride (11.6 g, 0.2 mole) was dried in vacuo at 200°C. After cooling to r.t. under argon, anhydrous acetonitrile (100 mL) and silver(I) trifluoroacetate (22.1 g, 0.1 mole) were filled in, and the flask was sealed with a rubber septum. The contents of the flask were cooled to 10°C,

and **F**-2-methyl-2-butene (25.0 g, 0.1 mole) was injected with a cooled syringe. The mixture was stirred for 1 h at r.t., then for 30 min. at 30 °C. On cooling to 20 °C, iodine (25.4 g, 0.1 mole) was added and stirring was continued for 1 h at r.t. and then for 3 h under reflux. From the cooled solution, the solids (potassium fluoride, potassium trifluoroacetate and silver(I) iodide) were removed by filtration on a frit, using a slightly increased pressure of nitrogen, and washed with some acetonitrile. The filtrate was diluted with icewater, and the organic phase was separated, washed with cold water and dried with a small amount of magnesium sulfate. Distillation through a slot-tube column afforded 31.4 g of **2b** (79.3 %, b.p. 89-90 °C) as a pale violet liquid.
Analysis: found: C 15.0 %, F: 52,7 %, I 32,2 %, calcd.: C 15.17 %, F 52.78 %, I 32,05 %.

Method B

Potassium fluoride (5.8 g, 0.1 mole) was placed in a 250-mL stainless-steel autoclave and dried in vacuo at 200 °C for 1 h. After cooling to r.t., iodine pentafluoride (11.1 g, 0.05 mole) and iodine (25.4 g, 0.1 mole) were introduced into the autoclave under dry argon. The vessel was cooled to -70 °C, evacuated and compound **1b** (62.5 g, 0.25 mole) was condensed in. The autoclave was heated, with shaking, to 185 °C within 2 h and shaken for 12 h at this temperature. After cooling to r.t., the autoclave was let down in a fume hood and the liquid contents were poured into an ice-cold aqueous 10 %-solution of sodium hydroxide (100 mL) with stirring. The organic phase was worked up as described under **A** to give 72.3 g of **2b** (73 %); its purity was 99.5 % from g.l.c..

F-2-iodo-2-methyl-pentane (**2c**: n.c.)

Similar procedures as described for the preparation of compound **2b** have been employed.

Method A

To a solution containing the fluorocarbanion formed from silver(I) fluoride (12.7 g, 0.1 mole) and **F**-2-methyl-2-pentene (30.0 g, 0.1 mole) in anhydrous acetonitrile (100 mL) under exclusion of light, iodine (25.4 g, 0.1 mole) was added. The mixture was stirred at r.t. for 1 h and then under reflux for 2.5 h. Workup was done as described before. Fractional distillation could be

dispensed with, since the washed and dried crude product consisted of pure **2c**, according to ^{19}F-n.m.r.. The yield was 41.9 g (94 %). Silver(I) iodide (23.1 g, 98.5 %) was recovered by washing with water the filter residue and drying.
Analysis: found: C 16.1 %, F 54.9 %, I 28,6 %, calcd.: C 16.16 %, F 55.39 %, I 28.46 %.

Method B

A mixture consisting of anhydrous potassium fluoride (5.8 g, 0.1 mole), iodine pentafluoride (11.1 g, 0.05 mole), iodine (25.4 g, 0.1 mole) and of alkene **1c** (120 g, 0.4 mole) was heated at 190 °C for 15 h in an autoclave, with shaking. Subsequent treatment of the liquid parts with aqueous sodium hydroxide and water, drying over molecular sieve, and fractionating distillation afforded 99.7 g of **2c** (89.4 %, b.p. 115 °C). At 22 °C, the density is 2.14 g/mL and the vapour pressure is 28 mbar.

If caesium fluoride was used instead of potassium fluoride, comparable yields were obtained. Independent experiments with caesium hexafluoroiodate proved that this salt is not involved in the formation of **2c**.

Reaction of compound 2c with zinc

A 150 mL-flask, equipped with a dropping funnel, thermometer and a stirring bar, was charged with zinc-powder (6.54 g, 0.1 mole) and dried at 150 °C in vacuo. The flask was slowly cooled to r.t. by introducing a slow stream of dry argon, and acetic anhydride (100 mL) was filled in. The iodide **2c** (44.6 g, 0.1 mole) was then added dropwise with stirring in the course of 35 min.; a temperature of 15-20 °C was maintained by external cooling. The mixture was stirred for 3 h at r.t., then it was poured into ice-cold diluted hydrochloric acid. The lower phase was separated, washed with ice-cold water and dried over molecular sieve. Distillation at normal pressure gave 23.2 g of condensate (b.p. 48-60 °C), leaving very little residue. According to g.l.c., the volatiles consisted of 3 components, the molar distribution of which was determined by ^{19}F-n.m.r: 71.4 % of **3**, 16.7 % of **1c** and

11.9 % of $C_3F_7C(CF_3)_2H$. The data were confirmed by the integrals of some particularly characteristic peaks in the ^{13}C-n.m.r. spectrum (inverse-gated): Olefinic carbons of **3** (162.2 ppm, t, $^1J(CF)$= 309.5 Hz; 86.0 ppm, m) and of **1c** (158.7 ppm, dt, $^1J(CF)$= 293.9 Hz, $^2J(CF)$= 32.7 Hz; 78.8 ppm, m), tertiary carbon of $C_3F_7C(CF_3)_2H$ (52.6 ppm, m).

Compound **3** (359-72-8) could easily be separated from **F**-2-hydro-2-methyl-pentane (30320-28-6), b.p. 60 °C, but could only be enriched to a mixture containing 10 % of **1c** (1584-03-8), b.p. 50-52 °C.

^{19}F-n.m.r. of **3** (δ, ppm): 21.7 (CF_3), 18.9-19.3 ($=CF_2$), -2.0 (CF_3), -30.6 (CF_2), and -48.2 (CF_2).

Pyrolysis of iodide **2c**

Compound **2c** (3.0 g) was placed in a 20-mL thick-walled quartz Carius-ampoule and degassed at -70 °C in vacuo. The ampoule was sealed by fusing, immersed in a heating bath and was kept for 4 h at 250 °C. After successive cooling to 20 °C and then to -190 °C, the tube was opened under dry argon, and its volatile contents were condensed into a -70 °C-trap. A little iodine and some white dust remained in the Carius tube.

A portion of the contents of the trap was transferred to a n.m.r.-tube containing -40 °C-$CDCl_3$, and ^{19}F- and ^{13}C-spectra were recorded at -35 °C. The ^{19}F-n.m.r. showed the resonances of **1a** (complex $[A_3B]_2$-pattern: 18.8 ppm (2 CF_3), 15.1 ppm (CF_2)) and of C_2F_5I (12.8 ppm (CF_2), -6.9 ppm (CF_3)), in a molar ratio of 1:1, plus some minor signals due to $C_3F_7C(CF_3)_2F$ at 5.2, -3.0, -37.6, -47.0 and -108 ppm. ^{13}C-n.m.r.: **1a** (159.2 ppm, t; 120.0 ppm, q; 85.0 ppm, m), CF_3CF_2I (116.4 ppm, qt; 88.0 ppm, tq). The gas-phase i.r.-spectrum revealed $\nu(C=C)$ of **1a** at 1750 cm^{-1} as a strong band. Analysis on a g.l.c.-column, which had been standardized for the quantitative determination of **F**-isobutene and **F**-ethyl iodide, gave further evidence of the 1:1-ratio of these two products.

Products from insertion reactions of 2c (see chapter 5.)

(R_F= $CF_3CF_2CF_2C(CF_3)_2$; n.m.r.: δ-values in ppm, couplings in Hz, in $CDCl_3$-solutions)

$R_FCH_2CH_2I$ (b.p. 51-52 °C/17 mbar)

n.m.r.:

^1H: 3.38 (t, CH_2), 2.80 (t, CH_2I).

^{19}F: 14.5 ($2CF_3$), -2.1 (CF_3), -28.9 (CF_2), -44,8 (CF_2).

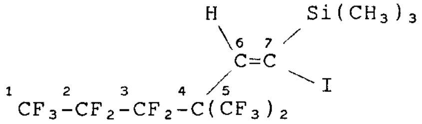
^{13}C: 130.6-103.3 (CF-signals), 62.1 (tert-C, m), 33.2 (CH_2, $^1J(CH)$= 136.5), -7.2 (CH_2I, $^1J(CH)$= 151.7).

$R_F\text{-}\overset{3}{C}H_2\text{-}\overset{5}{C}HI\text{-}\overset{2}{C}H_2\text{-}O\text{-}\overset{1}{C}O\text{-}\overset{4}{C}H_3$ **(4a)**

^{13}C-n.m.r.: (1): 170.9, (2): 70.7, (3): 37.0, (4): 21.2, (5): 15.4.

$R_F\text{-}\overset{3}{C}H_2\text{-}\overset{2}{C}H(O\text{-}\overset{1}{C}O\text{-}\overset{4}{C}H_3)\text{-}\overset{5}{C}H_2I$ **(4b)**

^{13}C-n.m.r.: (1): 170.4, (2): 67.4, (3): 34.4, (4): 20.9, (5): 9.1.



n.m.r.:

^1H: 7.34 (1H), 0.75 ($3CH_3$). The Z-configuration of this product was proved by ^1H-NOE-difference-spectra: irradiation of the $^1H(Si(CH_3)_3)$-resonance under observation of the =C-^1H-resonance.

^{19}F: 18.5 ($2CF_3$), -2.4 (CF_3), -28.1 (CF_2), -45.1 (CF_2).

^{13}C: (1): 117.8, $^1J(CF)$= 288.6, $^2J(CF)$= 33.1, (2) and (3): ~115.0, $^1J(CF)$= 270, $^2J(CF)$= 33, (4): 63.6, $J(CCF_3)$= 26.9, $J(CCF_2)$= 22.8, (5): 121.5, $^1J(CF)$= 291.7, (6): 128.6, $^1J(CH)$= 165.5, (7): 122.2, $^2J(CH)$= 9.3.

^{29}Si (vs. TMS): 11.3, $^1J(^{29}Si^{13}C(CH_3))$= 54.7, $^2J(^{29}Si^{13}C(=C))$= 57.0; isotopic effect $^{12}C/^{13}C$= -0.0093 ppm.

$R_FCF_2CF_2I$ (b.p. ~140 °C)

^{19}F-n.m.r.: 25.7 (CF_2I), 19.5 ($2CF_3$), -2.3 (CF_3), -11.5 (CF_2), -23.0 (CF_2), -42.8 (CF_2).

u.v.: λ_{max}= 279.6 nm.

R_F-SS-R_F

^{19}F-n.m.r.: 17.8 ($4CF_3$), -2.7 ($2CF_3$), -26.3 ($2CF_2$), -44.2 ($2CF_2$).

ACKNOWLEDGEMENTS

We thank E. Emslander, W. Gasafi-Martin, H. Katzenberger and J. Schatz for experimental assistance.
The expert laser experiments of Dr. K. J. Witte (MPI für Quantenoptik, Garching) are gratefully appreciated.
We also thank Professor B. Wrackmeyer (Universität Bayreuth) for some sophisticated NMR-work and interesting discussions.

REFERENCES

1 E.P. Mochalina, B.L. Dyatkin, I.V. Galakhov and I.L. Knunyants, Dokl. Akad. Nauk SSSR 169,1346 (1966).

2 R.A. Jacob, L.L. Gerchman, T.J. Juhlke and R.J. Lagow, J.C.S, Chem. Commun. 128 (1979).

3 A. Probst, K. Raab and K. v. Werner (Hoechst AG), German patent application P 36 00 108.2 (1986).

4 K. v. Werner and K. Raab, Abstracts of the International Symposium on Fluorine Chemistry in Paris, p. 77 (1986).

5 A.E. Bayliff, M.R. Bryce, R.D. Chambers and R.S. Matthews, J.C.S., Chem. Commun. 1018 (1985).

6 B.E. Smart, W.J. Middleton and W.B. Farnham, J. Am. Chem. Soc. 108,4905 (1986).

7 W.T. Miller, Jr., and R.J. Burnard, J. Am. Chem. Soc. 90, 7367 (1968).

8 B.L. Dyatkin, B.I. Martynov, L.G. Martynova, N.G. Kizim, S.R. Sterlin, Z.A. Stumbrevichute and L.A. Fedorov, J. Organometall. Chem. 57,423 (1973).

9 R. Eujen and R. Mellies, J. Fluorine Chem. 22,263 (1983).

10 W.B. Farnham and J.C. Calabrese, J. Am. Chem. Soc. 108,2249 (1986).

11 A.L. Henne, J. Am. Chem. Soc. 75,5750 (1953).

12 K. v. Werner, J. Fluorine Chem. 28,229 (1985).

13 H.C. Clark and K.J. Reimer, Can. J. Chem. 54,2077 (1976).

14 J.P. Collmann and C.T. Sears, Jr., Inorg. Chem. 7,27 (1968).

15 R. Butler and A. Snelson, J. Fluorine Chem. 15,345 (1980).

16 K.V. Scherer, Jr., R.E. Fernandez and P.B. Henderson, Abstracts of the International Symposium on Fluorine Chemistry in Paris, p. 1 (1986).

17 K.V. Scherer, Jr., T. Ono, K. Yamanouchi, R. Fernandez and P. Henderson, J. Am. Chem. Soc. 107,718 (1985).

18 K. v. Werner and B. Wrackmeyer, J. Fluorine Chem. 19,163 (1981).

19 K. v. Werner and B. Wrackmeyer, J. Fluorine Chem. 31,183 (1986).

20 D. Krajnovich, L.J. Butler and Y.T. Lee, J. Chem. Phys. 81,3031 (1984).

21 V.N. Bagratashvili, V.N. Burimov, M.V. Kuz'min, V.S. Letokhov and A.P. Sviridov, Laser Chem. 1,133 (1983).

22 A.M. Pravilov, I.I. Sidorov and V.A. Skorokhodov, Kinet. Katal. 26,1044 (1985).

23 D.C. Clary, J. Chem. Phys. 84,4288 (1986).

24 K.V. Scherer, Jr. , private communication.

25 L.A. Schlie and R.D. Rathge, J. Quantum Electron. QE-20,1187 (1984).

26 K.T. Witte, G. Brederlow, K. Eidmann, R. Volk, E. Fill,

J. Hohla and R. Broadmann. 'Photodissociation lasers for controlled thermonuclear fusion', Springer Series Opt. Sci., vol. 9,142 (1978).

27 J.H. Lee, J.W. Wilson, T. Enderson, D.H. Humes, W.R. Weaver and R.M. Tabibi, Opt. Commun. 53,367 (1985).

28 W. Fuss and K. Hohla, Opt. Commun. 18,427 (1976).

29 K. Ulm, J. Fluorine Chem. 21,69 (1982); Abstracts of the International Symposium on Fluorine Chemistry in Paris, p. 252 (1986).

30 E.W. Cook and J.S. Pierce, Nature 242,337 (1973).

31 J.A. Young and T.M. Reed, J. Org. Chem., 32,1682 (1967).

32 G.L. Fleming, R.N. Haszeldine and A.E. Tipping, J. Chem. Soc. Perkin I, 574 (1973); R.N. Haszeldine, I.-ud-D. Mir and A.E. Tipping, ibid. 565 (1979).

33 S.P. v. Halasz, F. Kluge and T. Martini, Chem. Ber. 106,2950 (1973).