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REACTIONS OF TERTIARY PERFLUOROALKYL HALIDES WITH HALIDE ANIONS

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SUMMARY

The reactivities of the F-tert.-alkyl halides $(CF_3CF_2CF_2(CF_3)_2CX$ (1a-c: X = I, Br, Cl) towards the corresponding lithium halides LiY (2a-c: Y = I, Br, Cl), in acetonitrile, reflect the electron acceptor properties of compounds 1 and the donator strength of the anions Y^-. The tertiary carbanion F-2-methylpentanide acts as the key intermediate in the formation of the main products (F-2-methyl-2-pentene, F-2-methyl-1-pentene and F-2-hydro-2-methylpentane), and also of the halide substitution products obtained from 1a. No support for the participation of any perfluoroalkyl radical could be found.

INTRODUCTION

Two classes of alkyl halides are notoriously resistant to displacement of halide under S_N2 conditions: (i) Compounds for which the nucleophilic backside attack is precluded by steric hindrance (e.g. 1-substituted bridgehead compounds) and (ii) perfluoroalkyl halides [1]. Several authors used the single-electron transfer (SET) concept to explain the reactions of F-alkyl halides with nucleophiles. However, there are only a few well-documented examples of SET-initiated reactions of primary and secondary F-alkyl iodides with simple anions, and in these cases a $S_{RN}1$ mechanism involving $R_F^{\bullet}$-radicals is likely to operate [2,3]. In the case of secondary iodides, some results were indicative of the simultaneous formation of F-carbanions and F-radicals.

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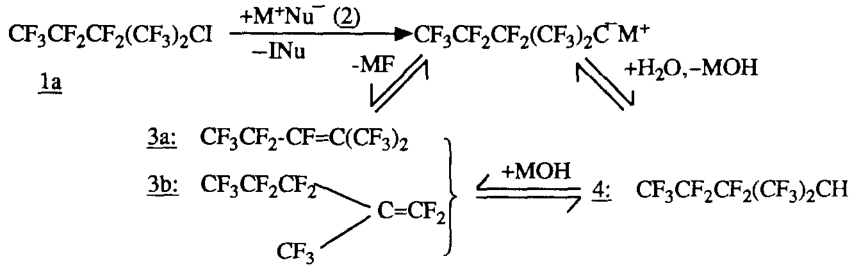
As we have reported [4], tertiary F-alkyl iodides (in the presence of polar, aprotic solvents) react with various anions, including iodide. Fluoride failed to react, and bromide and chloride were not tested in our earlier study. The main course of the reactions, as deduced from the final products, is illustrated in the following scheme for F-2-iodo-2-methylpentane:



M = alkali metal, Nu^- = I^-, SCN^-, OH^-, N_3^-, NO_2^-, CN^-, 1/2 SO_3^{2-}, 1/2 $S_2O_4^{2-}$

Scheme 1.

The same products resulted also from the interaction of 1a with electron donors, i.e. metals (zinc) or complexes of low-valent transition metals ($(Ph_3P)_2M(CO)Cl$ (M=Rh, Ir) or $(Ph_3P)_2NiBr_2$). Interestingly, Igumnov and Pletnev succeeded to obtain the SCN-analogue of 1a in high yield from 1a and dithiocyanato-mercury (II) [5]. We believe that the gist of this synthesis is the precipitation of insoluble HgI_2; thus iodide ions are prevented to re-attack the product.

We report now the results of a detailed study of reactions between F-2-halogeno-2-methylpentanes and lithium halides in which the following educts were used:

R_F-X (R_F = $CF_3CF_2CF_2(CF_3)_2C$) 1a-d

Li^+Y^- 2a-d

	X
1a	I
b	Br
c	Cl
d	F

	Y^-
2a	I^-
b	Br^-
c	Cl^-
d	F^-

Acetonitrile was chosen as solvent because of its good solubilizing properties for ionic species and its chemical stability in redox processes that accounts for its widespread use in electrochemistry.

RESULTS AND DISCUSSION

The experimental results of equimolar reactions are given in Table 1. The data shows that the reactivity of the tertiary halides decreases in the order of 1a > 1b > 1c and the reactivity of the lithium halides in the order of 2a > 2b > 2c. The F-alkyl iodide 1a is clearly the most reactive compound. It reacts with iodide, bromide and chloride anions (but not with fluoride), whereas 1b reacts with iodide and bromide and 1c with iodide only. Attempts at a reaction of 1b with lithium chloride in a more polar solvent (dimethylformamide) and a less polar solvent (1,2-dichloroethane) remained unsuccessful. Another approach to stimulate this reaction, namely irradiation with UV-light (253.7 nm), did not work either.

The perfluorinated compound 1d failed to react with lithium iodide, both in acetonitrile and in DMF, even at high temperature. 1d, too, is not attacked by the strong nucleophile potassium thiophenolate in hot DMF [6]. Hence, it seems plausible to assume that nucleophilic attack will take place only at higher substituted tertiary carbons, which are present for instance in F-decaline or F-methylcyclohexane.

Mechanistic considerations

It is well known that perfluoroalkyl halides form 1:1 adducts with polar donor molecules [7]. The geometric and electronic structures of the tertiary halides of type 1a-c have been calculated [8], and their reduction potentials have also been measured [9]. As a result of all these informations, it is very likely that compounds 1 will also form adducts with anionic donors, for instance halide anions. This leads to a prearrangement of the reactands which should facilitate their reaction. In the following schemes 2-4, we will discuss three possible reaction mechanisms, using the available experimental evidence.

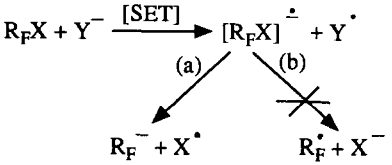
TABLE 1

Reactions of F-2-halogeno-2-methylpentanes with lithium halides in acetonitrile [a]

Exp.-No.	Educts		Conditions		Product distribution (mol-%) [b]						
	R_FX	LiY	temp.(°C)	time (h)	1a	1b	1c	1d	3a	3b	4
1	1a	2a	0	0.33	39	-	-	-	42,5	17	1,5
2	1a	2b	0	0.25	25	22	-	-	32	13	8
3	1a	2b	0	0.5	-	39	-	-	35.5	16	9.5
4	1a	2c	0	0.25	44	-	3.5	-	30	13	9.5
5	1a	2c	0	0.75	15	-	2.5	-	45	23	14.5
6	1a	2d	50	5	100	-	-	-	-	-	
7	1b	2a	0	0.5	-	86	-	-	10,5	3.5	trace
8	1b	2a	25	5	-	54	-	-	27	19	trace
9	1b	2b	25	1	-	88	-	-	9	3	trace
10	1b	2b	25	5	-	67	-	-	22	9	2
11	1b	2b	50	1	-	79.5	-	-	11	6.5	3
12	1b	2c	70	5	-	100	-	-	-	-	-
13	1c	2a	25	2	-	-	62.5	-	26.5	11	-
14	1c	2b	25	5	-	-	100	-	-	-	-
15	1c	2c	70	5	-	-	100	-	-	-	-
16	1d	2a	130	7	-	-	-	100	-	-	-

[a] For details, see ' Experimental '. [b] Determined by ^{19}F NMR .

1. The single-electron transfer, non-chain mechanism

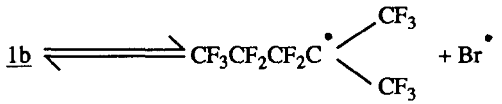


$R_F = CF_3CF_2CF_2(CF_3)_2C$; X, Y = I, Br, Cl

Scheme 2.

AM 1 calculations, performed by Rozhkov and co-workers [10], gave two important results: (i) The tertiary F-alkyl halide anion radicals $R_FX^{\dot{-}}$ may indeed be formed as the primary products from the initial SET process, and (ii), the decomposition according to route (a), giving the F-alkyl carbanion, is strongly favored over route (b). While the radicals $R_FX^{\dot{-}}$ are probably only transient intermediates with extremely short life times around room temperature, $R_F^{\bullet}$ radicals should be observable by means of ESR. In fact, the F-2-methylpentyl radical has been obtained from 1b and a mercury carboranyl compound and its ESR spectrum could be measured at 120 °C [11].

However, no perfluoro radical could be observed when reactions of 1b with 2a or 2b were performed in the cell of an ESR spectrometer, at a detection threshold of *ca*. 10^{-7} mol/l. Interestingly, the ESR spectrum of the F-2-methylpentyl radical could easily be created in the same instrument by irradiation of neat 1b with a xenon arc lamp, due to the fast equilibrium:



$$\underline{1b} \rightleftharpoons CF_3CF_2CF_2C^{\bullet}(CF_3)_2 + Br^{\bullet}$$

The observed spectrum was confirmed by computer simulation and the fine structure agreed well with the data given in ref. [11].

The perfluoro radical would be certainly reactive enough to abstract deuterium from CD_3CN. Therefore, we performed the reactions of 1a with 2a and 2b also in this solvent. However, we found only the hydrogen derivative 4, which is formed from the tertiary C_6-carbanion and traces of water, as shown in Scheme 1.

With regard to the factors influencing the stability of tertiary carbanions [12, 13], the lithium salt of F-2-methylpentanide can be expected to loose fluoride very rapidly in acetonitrile, under formation of the alkenes 3a and 3b. When the carbanion is generated under mild conditions (low temperature), as in the reactions of 1a, it may exist long enough to allow its known reactions with halogenes (chlorine, bromine [14], iodine [4]) or interhalogenes (e.g. iodine chloride [15]) to occur. These reactions account for the formal displacement of anions. In the case of 1a and 2a, this, of course, would be an identity reaction.

2. The halophilic S_N2_X reaction

Although the SET mechanism of scheme 2 looks plausible at first sight, it suffers from a severe flaw. When the reduction potentials of 1 a-c and the oxidation potentials of the halide anions are taken into account, it becomes evident that almost all of the reactions between these partners have to run uphill against considerable overpotentials (e.g.: 0.88 V for 1a, Cl^-; 0.79 V for 1b, Br^-; 1.32 V for 1c, I^-, based on the data from [9]). A way out of this dilemma is offerred by the S_N2 reaction at the halogene of 1a-c, as we have proposed already [4].

$$C_3F_7(CF_3)_2C\text{-}X + Y^- \longrightarrow [C_3F_7(CF_3)_2C\cdots X\cdots Y]^{-\ddagger}$$

$$\downarrow$$

$$C_3F_7(CF_3)_2C^- + XY$$

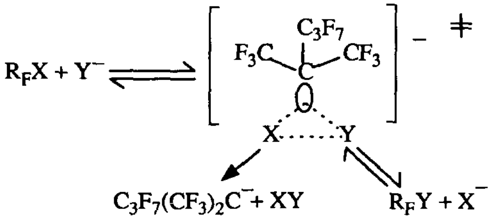
X, Y = I, Br, Cl

Scheme 3.

Recently, Grady and Dittmer investigated the reactions of F-iodobenzene and F-bromobenzene with sulfur-containing nucleophiles [16]. On the base of their experimental findings, the authors tended to favor the halophilic S_N2 reaction in comparison with the alternatives $S_{RN}1$ or S_NAryl.

3. A three-center mechanism

It seems possible that the approaching halide ion interacts mainly with the σ*-orbital of the CX-bond of 1, only lengthening this bond without any discrete electron transfer. This type of interaction may lead to a 3-center transition state, which could enable the formation of new bonds in a nearly concerted manner.



(R_F, X, Y as defined in schemes 2 and 3)

Scheme 4.

Such a mechanism can be regarded as a compromise between the extremes of SET and S_N2_X reactions.

EXPERIMENTAL

The tertiary halides 1a-d were prepared by literature procedures [4, 14] and purified to more than 99 % by distillation through a slot tube column. The salts 2a-d were purchased from Riedel de Haen. Acetonitrile (from Merck) was dried by distillation over P_4O_{10}, and the constant boiling main fraction was stored over molecular sieve (3Å) under dry argon.

^{19}F-NMR spectra were recorded on a Bruker WP 80 SY spectrometer at 75.393 MHz, ^{13}C NMR spectra on a Bruker AC 200 spectrometer at 50.323 MHz. The analysis by NMR of the reaction mixtures was based on the known ^{19}F and ^{13}C NMR spectra of all educts and products.

Caution: Because of the high inhalation toxicity of several starting materials and products (in particular compounds 1a, 1b and 3b), all experiments had to be performed in a well ventilated fumes hood. Workers wore long, thin rubber gloves during all manipulations. The analyzed reaction mixtures and analytic samples were detoxified by adding them to a large excess of a stirred solution of KOH in methanol.

Reactions of 1a-c with the lithium halides 2a-c

All reactions were run under dry argon. When the reaction was performed at room temperature or below, 2.1 mmol of the lithium halide and a PTFE-coated stirring bar were introduced into a 25 ml flask and the salt was dried for 5 h at 150 °C and 0.5 mbar with stirring. After cooling to room temperature, 10 ml of anhydrous acetonitrile (saturated with argon) was added, the mixture was cooled to the required temperature, and 2.0 mmol of the F-alkyl halide was added. The flask was stopperred and stirring was continued for the period indicated in Table 1. Directly at the end of the experiment, a 1 ml-sample of the solution was mixed with the same amount of -10 °C $CDCl_3$ in a pre-cooled NMR tube, and the ^{19}F-NMR spectrum was recorded at -10 °C. In some cases, it was necessary to add Freon 113 to ensure complete miscibility. The correctness of the assignments was proved in several cases by means of GLC and ^{13}C NMR. Some ^{13}C signals are particularly characteristic, for instance the resonance of the tertiary carbon of 4, a septet of triplets at 52.0 ppm ($^2JCCF_3 = 30.3$ Hz, $^2JCCF_2 = 22.8$ Hz).

For reactions at 50 °C, an additional cooler was used, topped with a bubbler, filled with silicone oil, whose outlet was connected to a blue-gel drying tube. Reactions at even higher temperatures were performed in a small rocking autoclave (stainless steel), equipped with an electrical heating jacket.

Reaction of 1a with bis-(triphenylphosphine)-dibromo-nickel

A solution of 148.8 mg $(Ph_3P)_2NiBr_2$ (0.2 mmol) in acetonitrile (10 ml) was cooled to -10 °C under argon and 416.8 µl 1a (0.2 mmol) was added from a micro-syringe with stirring. The color changed almost immediately from green to dark brown. After a reaction of 15 min at -10 °C, a sample of the solution was diluted with -10 °C $CDCl_3$, and the products were determined by ^{19}F NMR: 42 % 3a, 20 % 3b and 38 % 4. The same products were obtained from 1a and bis-(tributylphosphine)-dibromo-nickel.

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