Reductive addition of polychlorofluoroalkanes to fluorocarbonyl compounds

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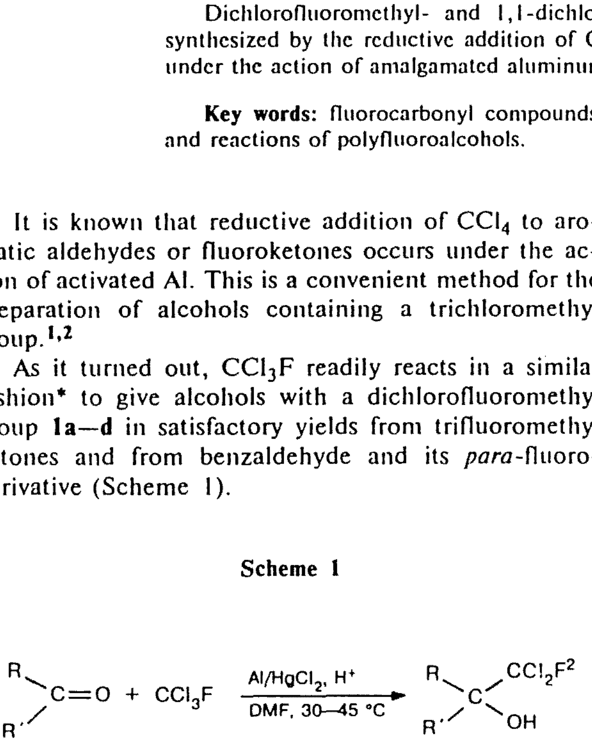
Dichlorofluoromethyl- and 1,1-dichloro-2,2,2-trifluoroethyl-containing alcohols were synthesized by the reductive addition of CCl_3F or CCl_3CF_3 to fluorocarbonyl compounds under the action of amalgamated aluminum.

Key words: fluorocarbonyl compounds, reductive polychlorofluoroalkylation, synthesis and reactions of polyfluoroalcohols.

It is known that reductive addition of CCl_4 to aromatic aldehydes or fluoroketones occurs under the action of activated Al. This is a convenient method for the preparation of alcohols containing a trichloromethyl group.[1,2]

As it turned out, CCl_3F readily reacts in a similar fashion* to give alcohols with a dichlorofluoromethyl group **1a—d** in satisfactory yields from trifluoromethyl ketones and from benzaldehyde and its *para*-fluoroderivative (Scheme 1).

Scheme 1



1a—d

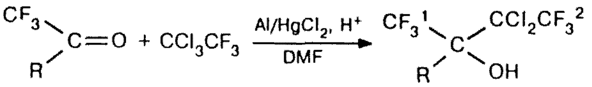
R = R′ = CF_3^1 (**a**); R = CF_3^1, R′ = Ph (**b**);
R = H, R′ = Ph (**c**); R = H, R′ = 4-F-C_6H_4 (**d**);

The similar reaction of CBr_3F and hexafluoroacetone (HFA) afforded $(CF_3^1)_2C(OH)CBr_2F^2$ (alcohol **2**).

It should be noted that CCl_3F in combination with Zn has been previously used for the reductive chlorodifluoromethylation of *N,N*-dimethylformamide on the carbonyl group in its adduct with trialkylchlorosilane.[4] The reductive addition of CCl_3F to non-fluorinated ketones initiated with a Mg—LiCl system has been also described (in this case, the intermediate formation of CCl_2FLi has been assumed).[5]

Trifluoroacetophenone and HFA also enter the reaction with CCl_3CF_3 to afford alcohols (**3a,b**) (Scheme 2).

Scheme 2



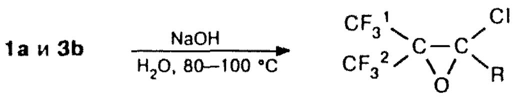
3a,b

R = Ph (**a**), CF_3 (**b**),

At the same time, on the reaction of HFA with CCl_3Me and Al, the reductive dimerization of this fluoroketone mainly takes place, and the corresponding alcohol, $(CF_3)_2C(OH)CCl_2Me$, is formed only as an admixture to perfluoropinacone. We failed to carry out the reaction of freons CF_2Cl_2 and CF_3CH_2Cl with HFA and Al (in this case, only the formation of pinacone from HFA occurred).

α,α-Dichloroalcohols **1a** and **3b**, like their trichloromethyl analogs,[2] readily undergo dehydrochlorination with aqueous alkali to afford chloroepoxides (**4a,b**) (Scheme 3).

Scheme 3



4a,b

R = F^3 (**a**), CF_3^4 (**b**)

Alcohol **3b** can also be used for the synthesis of chloroolefin (**6**), which has been previously obtained from $Ph_3P=C(CF_3)_2$ by a Wittig reaction[6] (Scheme 4).

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* For a previous communication, see Ref. 3.

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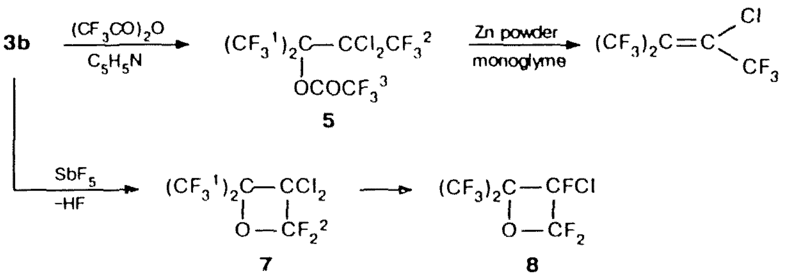
Scheme 4



We found a significant difference in the reactions of dichloroalcohol **3b** and $(CF_3)_2C(OH)CCl_3$ with SbF_5. In the latter case, the exchange of chlorine for fluorine occurs and $(CF_3)_3COH$ is readily formed.[2] Alcohol **3b** undergoes intramolecular dehydrofluorination to afford dichlorooxetane (**7**) followed by the exchange of chlorine for fluorine to form monochlorooxetane (**8**). Intramolecular cyclization of this kind, with the participation of terminal CF_3 groups in the medium of SbF_5, has been recently observed in a series of perfluoroketones, α-diketones, and α-oxides.[7] The structures of oxetanes **7** and **8** are confirmed by the mass spectral data; in particular, the ions that are formed by scission of the four-membered cycle into two halves, $[(CF_3)_2C=CClX]^+$, $[(CF_3)_2C=O]^+$, and $[CF_2=CClX]^+$ (X = Cl, F), are typical of these compounds along with the $[M-F]^+$ and $[M-CF_3]^+$ ions.

Experimental

^{19}F NMR spectra were recorded on a Bruker-200SY instrument (188.3 MHz) in CCl_4 with CF_3COOH as the external standard. Mass spectra (EI, 70 eV) were obtained on a VG-7070E spectrometer.

2-Dichlorofluoromethylhexafluoropropan-2-ol (1a). *A.* $HgCl_2$ (1.4 g) was added to Al chips (2.6 g), preactivated with a 10 % solution of KOH, in abs. DMF (100 mL) in a flow of argon with stirring. After completion of the exothermic reac-

Table 1. Physicochemical characteristics and ^{19}F NMR spectra of compounds **1b—d**, **2—5**, and **7**

Compound	Yield (%) (method)	B.p./°C (p/Torr)	n_D^{20}	Found/Calculated (%) C	H	F	Molecular formula	δ ^{19}F (J/Hz)
1b	60.5 (**B**)	75—76 (2)	1.4790	38.04 38.99	2.16 2.17	26.82 27.44	$C_6H_6Cl_2F_4O$	−6.29 (d, F^1); −13.81 (q, F^2, J = 12)
1c	39 (**B**)	92—95 (3)	1.5322	46.56 45.93	3.16 3.35	8.87 9.10	$C_8H_7Cl_2FO$	−13.9 (d, J_{F-H} = 7.5)
1d	61.7 (**B**)	85—87 (2)	1.5125	42.44 42.21	2.72 2.64	17.10 16.76	$C_8H_6Cl_2F_2O$	−12.5 (d, F^2); 34.0 (s, F^1, J_{F-H} = 7.5)
2	30 (**A**)	47—49 (2)	1.3010	13.65 13.41	0.27 0.28	38.52 37.15	$C_4HBr_2F_7O$	−13.06 (hept, F^2); −7.25 (d, F^1, J = 12)
3a	57.5 (**B**)	83—85 (2)	1.4630	36.49 36.70	1.82 1.83	35.08 34.86	$C_{10}H_6Cl_2F_6O$	−7.52 (q, F^1); −5.85 (q, F^2, J = 5)
3b	79 (**A**)	122—123	1.3485	18.72 18.81	0.39 0.31	53.61 53.51	$C_5HCl_2F_9O$	−7.0 (q, F^1); −3.0 (hept, F^2, J = 7.5)
4a	35.4 (**C**)	35—36	<1.3	20.38 20.65		57.07 57.20	C_4ClF_7O	−7.1 (m, F^1,F^2); 11.4 (m, F^3);
4b	33 (**C**)	58	<1.3	21.17 21.24		58.73 60.53	C_5ClF_9O	−10.8 (qq, F^1); −9.7 (q, F^2); −5.5 (q, F^3; J_{F1-F2} = 11, J_{F1-F3} = 14)
5	86	129—130	1.3320	20.24 20.24		54.65 54.94	$C_7Cl_2F_{12}O_2$	−12.2 (q, F^1); −2.86 (hept, F^2); −0.93 (s, F^3; J_{F1-F2} = 6)
7	26	86—87	1.3280	20.18 20.07		51.09 50.84	$C_5Cl_2F_8O$	−7.26 (s, F^2); −4.78 (s, F^1)

tion, CCl_3F (22 g) was added at 0—5 °C. Then HFA (16 g) was passed through the mixture for 0.5 h at ≤30 °C. After the exothermic reaction was completed, the mixture was stirred for 2 h at 45—50 °C and poured into dilute HCl, the organic layer was extracted with ether, the ether was distilled off, and the residue was distilled *in vacuo* (20 Torr) over conc. H_2SO_4. Repeated distillation afforded 13.2 g (51 %) of alcohol **1a**, b.p. 103—105 °C. Its ^{19}F NMR spectrum was identical to that described previously.[8]

3,3-Dichloro-2-phenylhexafluorobutan-2-ol (3a). ***B.*** A solution of trifluoroacetophenone (5 g) in CCl_3CF_3 (12 g) was added dropwise with stirring to a mixture of Al (1.4 g) and $HgCl_2$ (0.7 g) in abs. DMF (55 mL). After the exothermic reaction was completed, the mixture was stirred for 3 h at 40—50 °C and poured into dilute HCl. The oil that formed was extracted with ether, dried with $MgSO_4$, and the residue was distilled to afford alcohol **3a**.

1-Chloro-1,3,3,3-tetrafluoro-2-trifluoromethyl-1,2-epoxypropane (4a). *C.* A solution of NaOH (3 g) and alcohol **1a** (9.9 g) in H_2O (15 mL) was boiled with a Dean—Stark trap, and the organic layer from the trap was distilled over conc. H_2SO_4 to afford oxirane **4a**.

3,3-Dichloro-2-trifluoroacetoxy-2-trifluoromethylhexafluorobutane (5). Pyridine (14 mL) was added dropwise with cooling by ice water to a mixture of alcohol **3b** (44 g) and trifluoroacetic anhydride (32 g). The mixture was kept for 0.5 h at 20—30 °C. Crude trifluoroacetate **5** was then distilled *in vacuo* (10 Torr), shaken with conc. H_2SO_4, and distilled again.

The yields, physicochemical characteristics, and ^{19}F NMR spectral data of compounds **1b—d**, **2—5** are given in Table 1.

3-Chloro-2-trifluoromethylhexafluorobut-2-ene (6). A solution of trifluoroacetate **5** (49 g) in monoglyme (10 mL) was added dropwise with stirring to a suspension of Zn powder (13 g) preactivated with $HgCl_2$ (1.8 g) in monoglyme (110 mL). The temperature was kept at 50—60 °C. After 1 h, the mixture was poured into water, and the organic layer that formed was distilled over conc. H_2SO_4 to afford 23 g (73 %) of olefin **6**, b.p. 57—58 °C, identical to that described previously[6] (^{19}F NMR).

Reaction of alcohol 3b with SbF_5. A mixture of SbF_5 (20 g) and **3b** (7 g) was stirred for 15 h at ~20 °C and then poured onto ice. The organic layer that formed was distilled over conc. H_2SO_4 to afford 4.5 g of a mixture containing (^{19}F NMR) oxetane **7** (57 %) and alcohol **3b** (43 %). The mixture was washed with a 20 % NaOH solution and distilled again over conc. H_2SO_4 to afford 1.8 g (26 %) of 3,3-dichloro-4,4-difluoro-2,2-bis(trifluoromethyl)oxetane (**7**). MS, *m/z* (I_{rel} (%)) (for the ions containing Cl, *m/z* and *I* for the ^{35}Cl isotope are given): 279 $[M-F]^+$ (1.2), 232 $[M-COF]^+$ (27.6), 229 $[M-CF_3]^+$ (2.2), 197 $[M-COF_2-Cl]^+$ (15.6), 166 $[C_3F_6O]^+$ (0.4), 147 $[C_3F_5O]^+$ (20.4), 132 $[C_2F_2Cl_2]^+$ (26.3), 109 $[C_3F_2Cl]^+$ (9.4), 97 $[C_2F_3O]^+$ (25.2), 82 $[CCl_2]^+$ (4.8), 69 $[CF_3]^+$ (100).

A mixture of SbF_5 (25 g) and **3b** (7.8 g) was stirred for 1 h at 80 °C, and following the usual work-up was distilled as usual over conc. H_2SO_4 to afford 5 g (58 %) of 3-chloro-3,4,4-trifluoro-2,2-bis(trifluoromethyl)oxetane (**8**), b.p. 55—57 °C. Its ^{19}F NMR spectrum was identical to that described previously.[9] MS, *m/z* (I_{rel} (%)): 263 $[M-F]^+$ (7.7), 216 $[M-COF_2]^+$ (13.2), 213 $[M-CF_3]^+$ (2.1), 181 $[M-COF_2-Cl]^+$ (43.6), 166 $[C_3F_6O]^+$ (1.7), 147 $[C_3F_5O]^+$ (14), 116 $[C_2F_3Cl]^+$ (29.9), 97 $[C_2F_3O]^+$ (17.2), 69 $[CF_3]^+$ (100).

References

1. H. Tanaka, Sh. Yamashita, M. Yamanoue, and S. Torii, *J. Org. Chem.*, 1989, **54**, 444.
2. Yu. V. Zeifman, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 464 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 370 (Engl. Transl.)].
3. Yu. V. Zeifman, S. A. Postovoi, and L. S. German, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2159 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1915 (Engl. Transl.)].
4. R. W. Lang, *Helv. Chim. Acta*, 1988, **71**, 369.
5. Chang-Ming Nu and Ming-Hu Tu, *J. Fluor. Chem.*, 1994, **67**, 10.
6. A. Yu. Volkonskii, E. I. Mysov, and E. M. Rokhlin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 1356 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 1246 (Engl. Transl.)].
7. S. D. Chepik, V. F. Cherstkov, E. I. Mysov, A. F. Aerov, M. V. Galakhov, S. R. Sterlin, and L. S. German, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2611 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 2285 (Engl. Transl.)].
8. R. E. Dear, *Synthesis*, 1970, 561.
9. V. A. Petrov, F. Davidson, and B. E. Smart, *J. Org. Chem.*, 1995, **60**, 3419.

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