

2,2,2-TRIFLUORODICHLOROETHYLZINC CHLORIDE AND SOME OF ITS REACTIONS

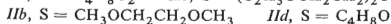
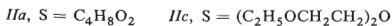
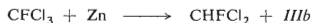
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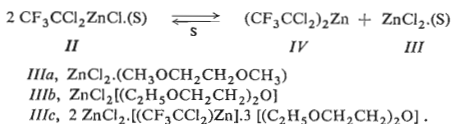
2,2,2-Trifluorodichloroethylzinc chloride (*II*) was prepared on reaction of 1,1,1-trifluorotrichloroethane with zinc in ethers. Fluorotrichloromethane gave fluorodichloromethane under analogous conditions. It was shown that in ethereal solution substance *II* exists in equilibrium with di-(2,2,2-trifluorodichloroethyl)zinc (*IV*). Under the effect of dilute sulfuric acid and acetic anhydride the organometallic derivative *II* decomposes to 1,1,1-trifluorodichloroethane (*V*).

In a previous study¹ we investigated the effect of zinc on 1,1,1-trifluorotrichloroethane (*I*) in protic solvents, leading to the reduction of the trichloromethyl group. This paper deals with the reaction of fluoroalkane *I* with zinc in ethers, during which the organozinc compound *II* is formed, and with some reaction of this organometallic derivative. Recently a communication² appeared in patent literature on the preparation of compound *II*. Some conclusions of the patent publication², *i.e.* those discussing the structure of the substances in solutions, are made doubtful by our own results. When haloethane *I* is heated with zinc in ethers, such as dioxane, 1,2-dimethoxyethane, diethylene glycol diethyl ether, or tetrahydrofuran, organozinc compound *II* is formed, crystallizing with one molecule of the solvent (Table I). In pure state only derivative *IIa* could be isolated. Under similar conditions fluorotrichloromethane in diethylene glycol diethyl ether under pressure gave a product of reduction, *i.e.* fluorodichloromethane and the organozinc salt *IIIb*.



When purifying the organozinc compounds *IIb* and *IIc* by precipitation of their ethereal solution with *n*-hexane, we isolated addition compounds of zinc chloride with corresponding ether (*IIIa*, *IIIb*), as well as the addition compound *IIIc* in the form

of crystalline, hygroscopic substances. Attempts at isolation of similar compounds with dioxane or tetrahydrofuran were unsuccessful. The precipitation of salts *IIIa*–*IIIc* from the solutions of organometallic derivatives *Ib* and *Ic* must be accompanied by the formation of an equivalent amount of dialkylzinc *IV*; hence, it may be assumed that equilibrium³ is taking place in the solution of the organometallic derivative:



The reaction of derivative *IIa* with bromine and its thermal decomposition was carried out² earlier. In our case the reaction of *IId* with bromine gave 1,1,1-trifluorodichlorobromoethane in a 66% preparative yield. On pyrolysis of organo derivative *Ib* we obtained 1,1-difluorodichloroethylene in 83% yield. Hydrolysis of compound *IIa* with dilute sulfuric acid afforded 1,1,1-trifluorodichloroethane (*V*). On heating of derivative *IIa* with difluorochloroacetyl chloride in dioxane at 30–40°C the expected ketone was not formed, in contrast to the reaction of perfluoroalkylzinc iodides with perhalogenated acyl halides⁴. When alkylzinc chloride *IIa* was reacted in the presence of acetic anhydride hydro derivative *V* was formed. The result of the reaction shows that acetic anhydride acts on organo derivative *IIa* as a C-acid. Perfluoroalkylzinc iodides decompose⁴ in a similar manner. The second product is the

TABLE I
Reaction of 1,1,1-Trifluorotrchloroethane (*I*) with Zinc

<i>I</i> , g (mol)	Zn, g (mol)	Time, min °C	Product	Yield, %
15.3 (0.0816) ^a	5.31 (0.0812)	14 80–90	<i>IIa</i>	55.1
25.0 (0.133) ^b	8.7 (0.131)	18 75–78	<i>IIb</i>	45.8
25.0 (0.133) ^c	8.7 (0.133)	1 80–100	<i>IIc</i>	65.7
50.1 (0.267) ^d	17.4 (0.266)	1 60–67	<i>IId</i>	68.7

^a In dioxane; ^b in 1,2-dimethoxyethane; ^c in diethylene glycol diethyl ether; ^d in tetrahydrofuran.

intermediate *VI* which on reaction with bromine in the cold and darkness and subsequent ethanolysis afforded ethyl bromoacetate (*VII*).

EXPERIMENTAL

The melting points are not corrected. The IR spectra were measured on a Zeiss UR 10, gas chromatography was carried out on a Chrom 2 apparatus (Laboratory apparatus, Prague; FID).

Chemicals used: 1,1,1-Trifluorotrichloroethane was prepared according to the literature¹. Difluorochloroacetyl chloride was obtained on acid hydrolysis¹ of 1,1-difluorotetrachloroethane.

2,2,2-Trifluorodichloroethylzinc Chloride (*Ila*–*Ild*)

Zinc powder was added gradually to a mixture of haloethane *I* and anhydrous ether (50 ml) under stirring at 80–100°C. When the reaction was over the liquid was filtered under pressure at 40–50°C and the remaining zinc was extracted with hot ether and the combined filtrates were dried. After evaporation *in vacuo* substance *Ila* was obtained in the form of white, hygroscopic needles. For $C_6H_8Cl_3F_3O_2Zn$ (340.9) calculated: 31.21% Cl, 16.72% F, 19.18% Zn; found: 30.87% Cl, 16.91% F, 19.28% Zn. Substance *Ila* could not be isolated in pure form but only as a mixture with the salts of the type of compound *IIla*. Organometallic derivatives *Ilb* and *Ild* were used for the reactions in unpurified form. *Isolation of salts IIIa–IIIc:* A solution of compound *Ila* (3.0 g; 8.8 mmol) in dioxane (50 ml) was diluted with n-hexane (15 ml) at 50°C. After cooling to 20°C the salt *IIIa* crystallised out (0.75 g; 3.3 mmol) in the form of hygroscopic needles. For $C_4H_{10}Cl_2O_2Zn$ (226.4) calculated: 31.31% Cl, 28.82% Zn; found: 31.22% Cl, 28.68% Zn. The salt *IIIb* was obtained on cooling the solution of derivative *Ilc* in diethylene glycol diethyl ether to 20°C. For $C_8H_{18}Cl_2O_3Zn$ (294.8) calculated: 23.76% Cl, 21.90% Zn; found: 23.60% Cl, 21.76% Zn. After dilution of the mother liquor with n-hexane (one half of the volume of the solution) the addition compound *IIIc* crystallized out. For $C_{28}H_{54}Cl_8F_6O_9Zn_3$ (1128.5) calculated: 25.14% Cl, 10.14% F, 17.38% Zn; 24.47% Cl, 10.11% F, 17.51% Zn.

Reaction of Fluorotrichloromethane with Zinc

A mixture of zinc dust (26.1 g; 0.397 mol), fluorotrichloromethane (55 g; 0.402 mol), and diethylene glycol diethyl ether (100 ml) was shaken in a glass ampule at 70°C for 6 h. On distillation off the mixture 38.3 g of volatile products were collected which contained fluorodichloromethane (9.53 g; 23.1%) and the starting substance (28.8 g; 52.5%) (gas chromatography: silicone elastomer E 301, 30°C; poly(ethylene glycol) 400, 30°C, hydrogen). After filtration under pressure of the residue at 50°C the addition compound *IIIb* crystallized out on cooling.

Hydrolysis of Derivative *Ila*

Substance *Ila* (12.1 g; 35.5 mmol) was mixed with 5% H_2SO_4 (50 ml) and heated at 50°C under stirring for 2 h. Rectification of the mixture afforded 3.87 g (71.5%) of hydro derivative *V* boiling within a 26–28°C. temperature range (literature⁵: b.p. 27.1°C; for IR spectrum⁶, purity 98% (gas chromatography: poly(propylene sebacate), 70°C, nitrogen).

Reaction of Organometallic Derivative *Ila* with Acetic Anhydride

Substance *Ila* (9.0 g; 26.4 mmol) was heated with acetic anhydride (5.21 g; 51 mmol) under stirring at 60–80°C for 3 h. In the condensing container, cooled with dry ice, hydro derivative *V*

(1.51 g) condensed; a second fraction of this substance was obtained on rectification (0.96 g). Total yield 2.47 g (61.1%). Bromine was added to the reaction mixture (4.30 g; 26.8 mmol) and this was stirred at 20–25°C in darkness for 4 hours. It was then diluted with Freon 113 (20 ml), washed with a sodium hydrogen sulfide solution, sodium hydrogen carbonate solution, and water, and then dried over magnesium sulfate. During rectification hydro derivative V (25–35°C) was collected first, followed by a fraction boiling at 45–80°C which contained a mixture of Freon 113, ethyl acetate, and 1,1,1-trifluorodichlorobromoethane (0.51 g; 8.3%). Distillation of the residue (1.6 g) gave 0.98 g (20%) of ethyl bromoacetate (VII), b.p. 54–62°C/18 Torr (lit.⁷ gives b.p. 57–58°C/15 Torr), purity 89% (gas chromatography: silicone elastomer E 301, 100°C; poly(propylene sebacate), 150°C, hydrogen).

Elemental analyses were carried out in the analytical department (head Dr L. Helešic) and the IR spectra were measured in the spectral department (head Dr P. Adámek) of the Central Laboratories of this Institute.

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