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Synthesis of 1,2,3,4-tetrachlorohexafluorobutane

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The condensation of 1-iodo-1,2,2-trifluoro-1,2-dichloroethane induced by granulated Zn in the presence of catalytic amounts of AcOEt without a solvent results in 1,2,3,4-tetra-chlorohexafluorobutane in high yield.

Key words: 1,2-dichloro-1,2,2-trifluoro-1-iodoethane, 1,2,3,4-tetrachlorohexafluorobutane, hexafluorobutadiene, granulated zinc, Wurtz condensation.

Most of simple methods of synthesis of fluorinated alkenes are based on dehalogenation of vicinal polyfluorodihaloalkanes. A multipurpose coolant, 1,2,3,4-tetrachlorohexafluorobutane (1), is used as the starting compound in the synthesis of an industrial monomer, hexafluorobutadiene (2). This is formed in high yield in the reaction of compound 1 with Zn dust in boiling EtOH.^{1,2} 1,2,3,4-Tetrachlorohexafluorobutane (1) is usually prepared by coupling of two 1,2-dichloro-1,2,2-trifluoro-1iodoethane (3) molecules (the Wurtz-type condensation). This condensation is performed in the presence of metallic mercury under UV radiation³ or with zinc in dioxane,³ in CH₂Cl₂-AcOEt,⁴ or CH₂Cl₂-Ac₂O^{5,6} as solvent systems; however, the yield of compound 1 is usually low due to the side processes, in particular, elimination of ICl to give chlorotrifluoroethylene (4).^{3,4,7} According to published data, 5,6 the yield of compound 1 reaches 50-70%; however, a complicated procedure for purification of the target product is required.

In the present work, we studied the condensation of 1,2-dichloro-1,2,2-trifluoro-1-iodoethane (3) with the aim of optimizing the production process of 1,2,3,4-tetrachlorohexafluorobutane (1). A 4 : 1 mixture of iodides 3 and 5 (Scheme 1), whose composition and structure had been studied in detail,⁸ was used as the starting compounds.

Iodides do not react with Zn without solvents at 20 °C. However, treatment of the mixture of iodides 3 + 5 with activated Zn dust in a CH₂Cl₂—AcOEt (1 : 1) solvent mixture induces vigorous deiodochlorination of iodide 3 even at 0 °C to give chlorotrifluoroethylene (4), iodide 5 remaining intact under these conditions. The order or the rate of mixing the reactants have no influence on the reaction outcome, in particular, no condensation takes Scheme 1 $\begin{array}{c}
i \\
CF_2 = CFCI \xrightarrow{ICl} CF_2CI - CFICI + CF_2I - CFCI_2 \rightarrow 4 \\
4 \\
3 \\
5 \\
\xrightarrow{ii} (CF_2CI - CFCI -)_2 + (CFCI_2 - CF_2 -)_2 + 1 \\
6 \\
\downarrow \\
CF_2 = CF - CF = CF_2 \\
7 \\
CF_2 = CF - CF = CF_2
\end{array}$

Reagents and conditions: *i*. Activated Zn dust, CH₂Cl₂—AcOEt; *ii*. Zn grains, AcOEt (catalyst).

place, olefin **4** being the only product. We found that iodide **3** is easily condensed on treatment with granulated Zn at 20 °C without a solvent in the presence of catalytic amounts of AcOEt; no side elimination of ICl giving ole-fin **4** takes place.

CLC and GLC/MS analyses showed that the condensation results in complete conversion of iodide 3, while iodide 5 is converted to a relatively small extent (by 15–20%). Apparently, under these conditions, the CFCl–I bond dissociates much more easily than CF_2 –I. As a result, tetrachlorohexafluorobutanes 1, 6, and 7 are formed in 96 : 2 : 2 ratio. A simple workup of the reaction mixture (dilution with water to remove ZnI₂, separation and drying of the organic layer) affords a mixture consisting of 1,2,3,4-tetrachlorohexafluorobutane (1), non-

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consumed iodide 5, small amounts of tetrachlorohexafluorobutanes 6 and 7, and AcOEt. Compound 1 containing $\leq 4\%$ of compounds 6 and 7 as impurities can be isolated by fractional distillation; however, we used the crude mixture for the synthesis of hexafluorobutadiene.

GC/MS analysis of compound **1** on a capillary column at 30 °C revealed the presence of two diastereomers in approximately equal amounts, the mass spectra of both diastereomers being identical. The ¹⁹F NMR spectrum shows splitting of signals due to chirality.

Dechlorination of 1,2,3,4-tetrachlorohexafluorobutane (1) with Zn dust in PrⁱOH at 80 °C furnishes chromatographically pure hexafluorobutadiene (2) in quantitative yield. Hexafluorobutadiene is successfully used as a cross-linking reagent in the synthesis of thermally and chemically stable and frost-resistant polymers based on perfluoroalkylene oxides containing peroxide groups according to a known procedure.⁹

Thus, we demonstrated that 1,2-dichloro-1,2,2-trifluoro-1-iodoethane is quantitatively condensed on treatment with granulated zinc at 20 °C without a solvent in the presence of catalytic amounts of ethyl acetate.

Experimental

¹³C and ¹⁹F NMR spectra were recorded on a Bruker AC-200 P spectrometer for CDCl₃ solutions; the chemical shifts are given in the δ scale relative to Me₄Si and CFCl₃. Mass spectra were run on a VG-7070 E GC/MS instrument (EI, 70 eV) with a capillary column (SE-54, 50 m × 0.2 mm, He as the carrier gas), the thermostat temperature was raised at a rate of 10 °C min⁻¹. The reaction was monitored on a Chrom-5B gas liquid chromatograph (SE-30 columns for liquids and PORAPAK Q columns for gases, 2.5 m × 2.0 mm). The starting mixture of iodides **3** + **5** (4 : 1) was prepared by a known procedure.³

Chlorotrifluoroethylene (4). Freshly distilled CH₂Cl₂, AcOEt, and Zn dust (activated by brief treatment with 10% aqueous HCl, repeated washing with distilled H₂O to a neutral pH, and drying for 10 h at 200 °C in vacuo (10 Torr)) were used in the reaction. The reaction was carried out a four-necked flask equipped with a stirrer, a thermometer, a device for the addition of Zn dust, and a reflux condenser with a trap cooled to -70 °C. Zinc dust (6.5 g, 0.1 mol) was added in portions at 0 °C over a period of 1 h to a vigorously stirred solution of iodides 3+5(22.5 g, 0.08 mol) in 36 mL of a CH₂Cl₂-AcOEt mixture (1:1). After addition of every portion, violent foaming and gas evolution were observed. The reaction mixture was stirred for 1 h at 20 °C and filtered to remove Zn salts. The filtrate was analyzed by GLC/MS, which showed the presence of CH₂Cl₂, AcOEt, and iodide 5. The contents of the trap represented chromatographically pure chlorotrifluoroethylene (4). Yield 7.0 g (93%, relative to iodide 3).

1,2,3,4-Tetrachlorohexafluorobutane (1). Granulated Zn (7.15 g, 0.11 mol) (grain size 3–5 mm) was added with stirring over a period of 1 h at 20 °C to a mixture of iodides 3 + 5 (55.8 g, 0.2 mol) in 2 mL of anhydrous AcOEt. The reaction mixture was stirred for 40 h at 20 °C and diluted with 50 mL of water. The organic layer was separated, washed with water (2×10 mL), and dried with MgSO₄ to give 35.0 g of as mixture of 1,2,3,4-tetrachlorohexafluorobutane (1), iodide 5, two butane isomers 6 and 7, and AcOEt in 70: 26: 1: 1: 2 ratio (GC/MS analysis). Fractional distillation (column, h = 30 cm) gave 24.6 g of a mixture of compounds 1, 6, and 7. The total content of compounds 6 and 7 was not higher than 4%, the yield of the target product **1** was 97% (relative to **3**), b.p. 134–135 °C, n_D^{20} 1.3855 (cf. Ref. 3: b.p. 134–134.5 °C, n_D^{23} 1.382). ¹³C NMR, δ : 106.6 $(dm, 2 CF, J_{C,F} = 279.2 Hz); 124.3 (dt, 2 CF_2, {}^{1}J_{C,F} = 303.4 Hz)$ $^{2}J_{C,F} = 32.5$ Hz). ¹⁹F NMR, δ : -120.6 (br.s, 2 CF, meso-form); -120.9 (m, 2 CF, d,l-form); -61.5 (m, 2 CF₂). MS, m/z (I_{rel} (%)): 267 [M - Cl]⁺ (0.1), 217 [M - CF₂Cl]⁺ (1.2), 198 $[M - CF_2Cl - F]^+$ (0.9), 182 $[M - CF_2Cl - Cl]^+$ (7.4), 163 $[M - CF_2Cl - Cl - F]^+$ (2.4), 151 $[C_2F_3Cl_2]^+$ (23.6), 147 $[C_{3}F_{4}Cl]^{+}$ (11.1), 135 $[C_{2}F_{4}Cl]^{+}$ (14.6), 116 $[C_{2}F_{3}Cl]^{+}$ (9.1), 101 $[CFCl_2]^+$ (10.5), 93 $[C_3F_3]^+$ (3.7), 85 $[CF_2Cl]^+$ (100), 69 $[CF_3]^+$ (11.4) (cf. Ref. 7).

Hexafluorobutadiene (2) was prepared by analogy with a known procedure² by the reaction of 1,2,3,4-tetrachlorohexafluorobutane (1) with Zn dust in $Pr^{i}OH$ for 2 h at 80 °C. The syntheses were carried out with both purified compound 1 containing $\leq 4\%$ of butanes 6 and 7 and a crude mixture of compounds 1, 5, 6, 7, and AcOEt in 70 : 26 : 1 : 1 : 2 ratio. The chromatographic yield of hexafluorobutadiene (2) was 93–98% relative to hexafluorotetrachlorobutane 1, b.p. 5–6 °C (*cf.* Ref. 2: b.p. 5.8 °C).

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