

Doubling of Fluorinated Chains

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When a molecule of $\text{CF}_3\text{CF}_2\text{CF}_2\text{I}$ is treated with zinc in acetic anhydride, a very vigorous reaction takes place at once, resulting in a doubling of the chain length with formation of normal C_6F_{14} in excellent yield. For efficient results, operation at a controlled low temperature is essential, easily accomplished by running the reaction in refluxing methylene chloride. The unused iodide is recovered in the methylene chloride fraction, which can be used in the next run after computation of its composition from its index of refraction.

A molecule of $\text{C}_3\text{F}_7\text{Cl}_4\text{Br}^1$ is doubled to $\text{C}_6\text{F}_6\text{Cl}_8$ with equal facility. Conversely, $\text{CH}_3\text{CF}_2\text{Cl}$ and $\text{CHCl}_2\text{CF}_2\text{CF}_2\text{Cl}$ react in exceedingly poor yield, $\text{CCl}_3\text{CF}_2\text{CCl}_2\text{CCl}_3$ undergoes customary dechlorination to $\text{CCl}_3\text{CF}_2\text{CCl}=\text{CCl}_2$, and propyl or butyl bromide fails to give any detectable octane. These results seem to indicate that the doubling of the chain length might depend on a terminal $-\text{CF}_2\text{X}$ or $-\text{CFCIX}$ group, where X is bromine or iodine, at least for a fast, efficient reaction.

Miller's report² that highly fluorinated organo-zinc derivatives were obtainable in dioxane solution, and his private remarks that they were very sensitive to protonic hydrogen, yet did not seem to condense well with carbonyl compounds prompted a search for a solvent which would not cause reduction and side reactions, as do the conventional alcohols, or delay reaction inconveniently, as does ether. All the experimental results were obtained by my collaborators, as named.

Experimental

A. Synthesis of C_6F_{14} (Robert Brown).— $\text{C}_3\text{F}_7\text{I}$ (40 g. or 0.135 mole), granular zinc (9.3 g. or 0.142 mole), acetic anhydride (28 g. or 0.28 mole) and methylene chloride (67 g. or 50 ml.) were mixed in a 300-ml. flask provided with a sealed stirrer and a water cooled reflux condenser trailed by two Dry Ice traps. Stirring at room temperature caused only a slight cloudiness, but with external heating applied to cause refluxing at 40–45°, a white precipitate began to form; in 24 hours the precipitate was so thick that it interfered with stirring, and the reaction was worked up.

While cooling in an ice-bath, water (20 ml.) was added dropwise. It dissolved the precipitate and caused the formation of three layers. There was no gas evolved; the empty Dry Ice trap showed that $\text{CF}_3\text{CF}=\text{CF}_2$ had not been formed during the zinc attack, nor $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$ during the hydrolysis. The top layer (81 g.) contained acetic acid, water, acetic anhydride and zinc iodide; the middle layer (54 g.) was methylene chloride with about 4% of unused iodide; the bottom layer (17 g.) was the doubled up molecule, C_6F_{14} , quite pure. As 5.5 g. of zinc was recovered, the aggregate weights show a loss of 6.6 g. of material, attributed to mechanical handling and inexperience. There was no indication of a ketonic material which would have resulted from action of the organometallic on the solvent.

The top and middle layers were returned to the flask and neutralized with sodium carbonate. The organic layer was drained from the aqueous layer, and proved to be a clean mixture of methylene chloride with 4% of unused iodide.

The bottom layer was dried on sodium sulfate and distilled; it came over entirely at 57°, the correct boiling point for C_6F_{14} . The refractive index (1.25) was too low to be read on the available instrument; the density was found to be 1.6707 at 25° (lit. 1.6995 at 20°).

(1) A. L. Henne and D. W. Kraus, *THIS JOURNAL*, **73**, 1791 (1951). Also Dorothy W. Kraus, Ph.D. dissertation, The Ohio State University, 1953.

(2) W. T. Miller, Atlantic City Meeting, September, 1952.

The conversion from the iodide was 74%, and as 3.4% of iodide was recovered, the net yield was 77%. A computation based on the amount of zinc consumed shows that an additional 12% might have been formed and lost.

B. Synthesis of $\text{C}_6\text{F}_6\text{Cl}_8$ (Dorothy Kraus).— $\text{C}_3\text{F}_7\text{Cl}_4\text{Br}$ (205 g. or 0.65 mole), obtained by addition of CCl_3Br to $\text{CF}_2=\text{CFCl}$, see ref. 1, granulated zinc (42 g.), a volume of acetic anhydride equal to that of $\text{C}_3\text{F}_7\text{Cl}_4\text{Br}$ and another volume of methylene chloride were placed together and stirred under reflux. The reaction started spontaneously and was held under control at 40–45° by external cooling; this shows that much more anhydride and methylene chloride should have been used, as in A. White salt came out progressively and the mixture remained clean and only light yellow, but when the solid accumulated, control of the temperature became inadequate, and the mixture was quenched before deterioration set in appreciably.

The working up recovered 31 g. (0.1 mole) of starting material, and 60 g. of a solid, m.p. 39–39.5°, which contained 24.1% F and 59.6% Cl (analysis by Mary Renoll); the correct values for $\text{C}_6\text{F}_6\text{Cl}_8$ are 24.2% F and 60.4% Cl. As the solid represents 0.13 mole, a 40% conversion was obtained or a 55% yield when the recovered material is taken into count.

C. Synthesis of $\text{CCl}_3\text{CF}_2\text{CCl}=\text{CCl}_2$ (Mary Renoll).—Crude $\text{CCl}_3\text{CF}_2\text{C}_2\text{Cl}_5$ (32 g. or 0.09 mole) was dissolved in chloroform (30 ml.) and dripped into a flask containing mossy zinc (5.85 g. or 0.09 mole) covered with acetic anhydride (75 ml.). The reaction started promptly and raised the temperature to 45–50°, where it was kept by control of the rate of addition and stirring. Addition took an hour, after which the mixture was stirred at 45–50° for another 40 minutes. The mixture remained clean, pale yellow and the salt which came down was not gummy; this is in marked contrast with the amount of resinification, decomposition and difficulty in handling which occur with other solvents.³ After pouring into ice-water and adding 50 ml. of chloroform, the two layer mixture was kept overnight at 4° for good decantation, and recovery of 2.4 g. of zinc. This indicated that 58% of the zinc had been used. From the bottom layer, distillation separated chloroform, 12 g. of the olefin $\text{C}_4\text{F}_2\text{Cl}_6$ and 12 g. of the original paraffin $\text{C}_6\text{F}_6\text{Cl}_8$. There was no still residue. The conversion to the olefin was 45%, or after deducing recovered material, a 76% yield. There was no doubling up.

This dechlorination is to be contrasted with the difficulties reported by Newby,³ whose maximum yields were 30% in ethanol and 10–15% in dioxane, with resinification of the balance of his material. The observed properties, b.p. 85–86° at 10 mm., d_4 1.7842 and n_D 1.5052 at 20°, MR 49.69 and AR_F 1.24 agree well with Newby's who found: m.p. –6.0 to –6.8°, b.p. 212° at 745 mm., d_4 1.7803 and n_D 1.5029 at 25°, MR 49.64 and AR_F 0.97. The last figure is miscalculated and should be 1.2, in good agreement.

D. Attempted Synthesis of *n*-Octane (John Gordon).—Butyl bromide (28 g. or 0.2 mole), granular zinc (13.1 g. or 0.2 mole), acetic anhydride (27.6 g. or 0.3 mole) with an equal volume of Skellysolve F (b.p. 35–60°) were stirred at 65° for 4 days. After that period, 12.2 g. of zinc was recovered unused, showing that practically no reaction had occurred. The working up recovered 3 g. of material b.p. 65–100° (a mixture of solvent and bromide), then 15 g. of butyl bromide, and there was less than 1 g. of a black residue. There was no indication of octane, and about 40% of the starting material was lost by decomposition.

(3) Thomas Newby, Master's Thesis, Ohio State University, 1944, also A. L. Henne and Thos. Newby, *THIS JOURNAL*, **70**, 130 (1948).

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Ionization Constant of Fluorinated Acids. II

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The fact that butyric acid is a little more highly ionized than its lower homolog ($K_A \times 10^{-6}$ being 1.51 and 1.34, respectively) is sometimes explained¹

(1) J. F. Dippy, *J. Chem. Soc.*, 1122 (1938).