

## Haloaldehyde Polymers\*

### 28. Synthesis and Polymerization of Fluorochlorobromoacetaldehyde

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#### SUMMARY

Fluorochlorobromoacetaldehyde was synthesized in five steps and in 15% overall yield starting from trifluorochloroethylene. Treatment with sodium methoxide gave 1,2-difluoro-2-chloro-1-methoxyethylene which was brominated and the bromination product hydrolyzed with concentrated sulfuric acid to give methyl fluorochlorobromoacetate. Lithium aluminum hydride reduction and hydrolysis of the reaction product gave fluorochlorobromoacetaldehyde hydrate which was dehydrated to the aldehyde. Polymer grade fluorochlorobromoacetaldehyde was polymerized with sulfuric acid to polyfluorochlorobromoacetaldehyde which was characterized.

#### INTRODUCTION

Perhaloaldehydes and their polymerization was studied by us in the past (1-3). The monomers were prepared in various ways and their polymerization was accomplished by cationic, or more commonly by anionic, polymerization. Most carefully studied was the polymerization of chloral (4,5), but the polymerization of bromal (6) was also accomplished. The thermodynamics of these polymerizations and the determination of the ceiling temperature of the perhaloacetaldehydes are now well established (7).

It was found that at least two chlorine atoms are necessary to provide the bulkiness of the monomer so that polymers prepared from such monomers exist only in the isotactic form (8).

The investigations were the basis for the concept and final realization that optical activity based on macromolecular asymmetry could be achieved; this principle was demonstrated on polychloral (9).

The only one of the nine known perhaloaldehydes that had not been synthesized was fluorochlorobromoacetaldehyde (FCBA). FCBA is also the only perhaloacetaldehyde that can be expected to exist in optically active form due to the fact that the carbon atom of the trihalomethyl group has four different substituents.

It was therefore the objective of this work to prepare FCBA, to characterize this compound and demonstrate its polymerization. Further work is directed toward the optically active FCBA and to achieve its polymerization.

#### EXPERIMENTAL PART

##### Materials

Trifluorochloroethylene (TFCE) (Specialty Chemicals), lithium aluminum hydride, 95% (LAH) (Aldrich Chemical Co.), bromine (Aldrich Chemical Co.), and anhydrous diethylether (Mallinckrodt, Inc.) were used as received.

\* Part 27: O. Vogl, The Chemist, September 1985, p. 16.

Diethylene glycol dimethyl ether (diglyme), 99+% (Gold Label grade), and methanol, 99.9% (Gold Label grade) (Aldrich Chemical Co.) were used as received and stored over 8-12 mesh 3A molecular sieves (Aldrich Chemical Co.).

#### Measurements

Infrared spectra were recorded on a Perkin-Elmer Model 727 or a Shimadzu IR-435 spectrophotometer, as KBr pellets, as a neat film on NaCl plates, or in matched liquid cells.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra were recorded on a JEOL FX90Q multinuclear FT NMR spectrometer. The  $^{13}\text{C}$  NMR spectra were run with complete proton decoupling.

Microanalyses were carried out by the Microlytics Laboratory, South Deerfield. The halogens were determined using three instrumental procedures after Schöniger oxygen flask decompositions of the sample were performed: (1) Ion chromatographic procedures were employed for the determination of the fluoride content. (2) Potentiometry using a bromide ion selective electrode enabled the determination of the bromide content. (3) By determining the "total halide" content through the use of silver coulometry, the chloride content could be determined by subtraction of the bromide content previously determined.

#### Procedures

##### 1. 1,2-Difluoro-2-chloro-1-methoxyethylene (DFCME)

A dry 1000 mL roundbottom flask was equipped with a mechanical stirrer, Dewar condenser, thermometer, and a pressure-equalizing funnel. Under dry nitrogen, the roundbottom flask was charged with 500 mL of diglyme and the funnel with methanol (32.3 mL, 25.6 g, 0.80 mol). Sodium metal (14.1 g, 0.61 mol) was cut under n-hexane, blotted, and added to the diglyme; the temperature was raised to 120°C, and methanol was added dropwise. Hydrogen gas was evolved from the metal surface, and a fine, white precipitate formed. When the sodium had been consumed, the funnel was replaced by an inlet adapter and the excess methanol was distilled off at atmospheric pressure; the temperature rose to 165°C (diglyme b.p. = 162°C).

The system was cooled to room temperature, and gaseous trifluorochloroethylene (b.p. = -27°C) was added over 1.5 hr; the temperature was allowed to rise to 75°C. The pressure was slowly reduced to 25 mm Hg, giving a clear, colorless liquid which after distillation gave DFCME (43.0 g, 0.33 mol, 55% yield) (10).

IR ( $\text{CCl}_4$ ): 1755  $\text{cm}^{-1}$  ( $\nu$  C=C),  $^1\text{H}$  NMR 3H doublet:  $\delta$  in ppm 3.92, 3.91; 3H quartet:  $\delta$  in ppm 3.89, 3.88, 3.88, 3.87 ( $d_6$  acetone, TMS standard).

##### 2. 1,2-Difluoro-2-chloro-1,2-dibromo-1-methoxyethane (DFCDB)

A dry 3-neck, 250 mL roundbottom flask was equipped with a pressure-equalizing funnel, a water condenser, magnetic stirrer, and an inlet adapter which was fitted to a nitrogen-filled balloon. DFCME (14.2 g, 0.11 mol) in carbon tetrachloride (20 mL) was placed in the roundbottom flask and bromine (17.6 g, 0.11 mol) in carbon tetrachloride (50 mL) was added over a 30-min period from a dropping funnel. After the bromine color disappeared, DFCDB was isolated and distilled giving 27.2 g (86% yield), b.p. = 71-73.5°C at 40 mm Hg.

Elemental Analysis: Calculated for  $\text{C}_3\text{H}_3\text{Br}_2\text{ClF}_2\text{O}$ : C, 12.50%; H, 1.05%; Br, 55.43%; Cl, 12.30%; F, 13.18%. Found: C, 12.18%; H, 1.11%; Br, 54.9%; Cl, 14.2%; F, 12.2%.

##### 3. Methyl Fluorochlorobromoacetate (MFCBA)

A dry 3-neck, 25 mL roundbottom flask equipped with a pressure-equalizing funnel, thermometer, magnetic stirrer, and an inlet adapter with a

nitrogen-filled balloon was charged with DFCDB (19.4 g, 0.067 mol) and the flask cooled to 0°C. Sulfuric acid (13.2 g, 0.135 mol) was added with stirring over a 15-min period while the temperature was kept below 5°C. After 3.5 hr stirring at 7 to 10°C, the starting material had disappeared (checked by GC). The mixture was poured onto ice which gave a dark-red oil; the oil was separated, dried over magnesium sulfate, and distilled from solid anhydrous sodium carbonate; it gave nearly colorless MFCBA (8.8 g, 64% yield), b.p. = 75-76.5°C at 98 mm Hg (11).

Elemental Analysis: Calculated for C<sub>3</sub>H<sub>3</sub>BrClFO<sub>2</sub>: 17.54% C, 1.48% H, 38.90% Br, 17.26% Cl, 9.25% F. Found: 17.25% C, 1.44% H, 39.2% Br, 17.1% Cl, 9.1% F.

IR NaCl plate: 1775 cm<sup>-1</sup> (ν C=O), <sup>1</sup>H NMR doublet: δ in ppm: 3.05 (d<sub>e</sub> benzene, TMS standard).

#### 4. Fluorochlorobromoacetaldehyde - 2.5 Hydrate (FCBAH)

A dry 25 mL 3-neck roundbottom flask was equipped with a pressure-equalizing funnel, magnetic stirrer, thermometer, reflux condenser, and an inlet adapter with an argon blanketing; LAH (0.32 g, 7.8 mmol) was suspended in anhydrous diethyl ether (25 mL). MFCBA (5.4 g, 26 mmol) was dissolved in 10 mL of anhydrous diethyl ether. The flask with the LAH solution was cooled to -78°C with a dry ice bath and MFCBA was added dropwise over a 30-min period with the temperature not rising above -72°C. After 30 minutes, the mixture was worked up by pouring it onto ice and water containing 1% sulfuric acid. FCBAH was isolated by extraction with diethyl ether, dried, and distilled. Colorless, viscous FCBAH (4.0 g, 18 mmol, 70% yield) was obtained, b.p. = 62.5-65°C at 120 mm Hg.

Elemental Analysis: Calculated for C<sub>2</sub>HBrClFO•2.5 H<sub>2</sub>O: 10.90% C, 2.75% H, 36.25% Br, 16.08% Cl, 8.62% F. Found: 10.91% C, 2.80% H, 36.6% Br, 17.6% Cl, 8.4% F.

IR NaCl plate: 3400 cm<sup>-1</sup> broad (ν OH). <sup>1</sup>H NMR, doublet: δ in ppm: 5.14, 5.12; OH broad 4.60. O-H/C-H ~ 5/1 (d<sub>e</sub> acetone, TMS standard).

#### 5. Fluorochlorobromoacetaldehyde (FCBA)

A 10 mL roundbottom flask equipped with a magnetic stirrer was charged with FCAEH (6.3 g, 28.5 mmol) and an equal volume of sulfuric acid. The flask was connected to a distillation head and was flushed with argon. Distillation gave FCBA (3.4 g, 19.1 mmol, 67% yield), b.p. = 80°C/760 mm Hg.

<sup>1</sup>H doublet: δ in ppm: 9.35, 9.30  $\overset{\text{O}}{\parallel}\text{HC}-\text{CX}_3$  (d<sub>e</sub> acetone, TMS standard).

<sup>13</sup>C doublet: δ in ppm: 181.57, 180.33  $\overset{\text{O}}{\parallel}\text{HC}-\text{CX}_3$  (d<sub>e</sub> acetone, TMS standard);

doublet: δ in ppm: 110.10, 96.07  $\overset{\text{O}}{\parallel}\text{HC}-\text{CX}_3$ . <sup>19</sup>F singlet: δ in ppm: -77.48

$\overset{\text{Br}}{\text{X}}\overset{\text{O}}{\parallel}\text{C}-\text{CH}$  (d<sub>e</sub> acetone, CFCl<sub>3</sub> standard).

#### 6. Poly(fluorochlorobromoacetaldehyde) (PFCBA)

To a dry, septum-capped test tube, using a syringe, FCBA (1.31 g, 7.51 mmol) was added, followed by sulfuric acid (0.0037 g, 0.038 mmol, 0.51 mol%). Within 30 min the solution had gelled completely. After one day, the product had become a white plug, which was ground and stirred for 2 hr in ethanol. The polymer was isolated by filtration and washed with acetone; it gave a white powder of PFCBA which was dried at 0.25 mm Hg for one day: 0.77 g, 60% yield.

Elemental Analysis: Calculated for  $(C_2HBrClFO)_n$ : 13.70% C, 0.58% H, 45.56% Br, 20.21% Cl, 10.83% F. Found: 13.51% C, 0.61% H, 45.3% Br, 20.1% Cl, 10.3% F.

### RESULTS AND DISCUSSION

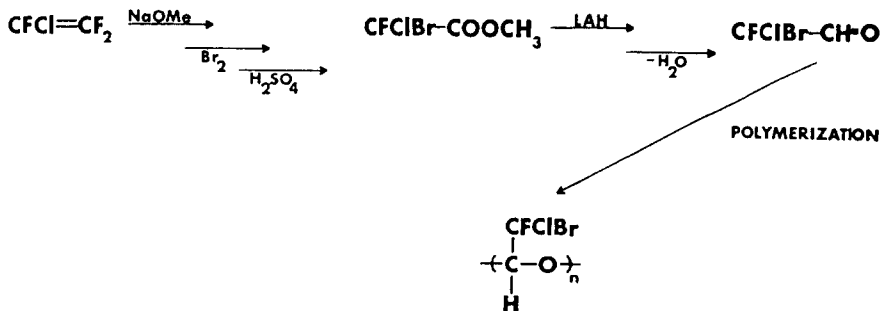
FCBAA was synthesized in a series of five steps in an overall yield of 15%. With sulfuric acid as the initiator, it formed a solid polymer with polyacetal structure. For the synthesis of FCBAA, TFCE was used as the starting material. The first few steps followed established procedures, although significant modifications were made to optimize the individual reactions (Equation).

In the first step of the synthesis, TFCE was treated with sodium methoxide. The reaction gave not only DFCME but also the saturated compound 1,1,2-trifluoro-2-chloro-1-methoxyethane.

We prepared sodium methoxide in anhydrous diglyme; into the fine sodium methoxide suspension TFCE was added dropwise; in an exothermic reaction, DFCME was formed and isolated in 55% yield (based on sodium metal). The reaction product was actually a mixture of the cis and trans isomers which could be shown by NMR spectroscopy.

DFCME was brominated with elemental bromine in carbon tetrachloride and gave DFCDBME in almost 90% yield (12). DFCDBME was hydrolyzed in concentrated sulfuric acid to MFCBA in a yield of about 65%. This hydrolysis had to be carried out carefully, otherwise further hydrolysis occurred. MFCBA was the key compound in our synthesis sequence and was carefully characterized by elemental analysis of all the elements, NMR and IR spectroscopy. In our future work, this compound will be hydrolyzed to the acid for the separation of the enantiomers. Partial reduction of MFCBA with LAH at  $-78^\circ\text{C}$  in diethyl ether gave the hydrate of FCBAA. The exact identification of the hydrate proved to be a problem because the hydrate, distilled at constant temperature, gave a single peak in GC, but was not the expected hydrate,  $CFC_1BrCH(OH)_2$ . Quantitative determination of the hydroxyl protons of the hydrate by integration indicated a 5:1 ratio in respect to the acetal proton. Recalculation of the elemental analysis made it clear that FCBAA had been obtained as the 2.5 hydrate.  $[CFC_1BrCH(OH)_2 \cdot 1.5 H_2O]$ . Hydrates of aldehydes, especially perhaloaldehyde and perhaloketones, do not always form 1:1 hydrates. Chloral gives a 1:1 hydrate, hexafluoroacetone a 1.5 hydrate, and formaldehyde gives an oligomeric "hydrate."

FCBA was obtained in 70% yield. It was dehydrated with sulfuric acid and gave the free FCBAA, b.p.  $80^\circ\text{C}$ , which was characterized by its  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectrum (Figure 1), and the IR spectrum (Figure 2).



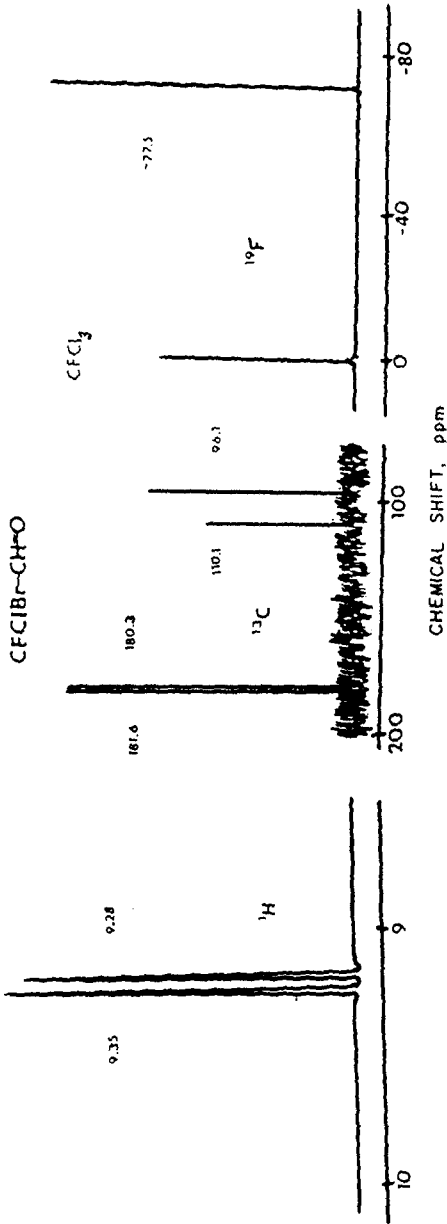


Figure 1: <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F Spectra of Fluorochlorobromoacetaldehyde

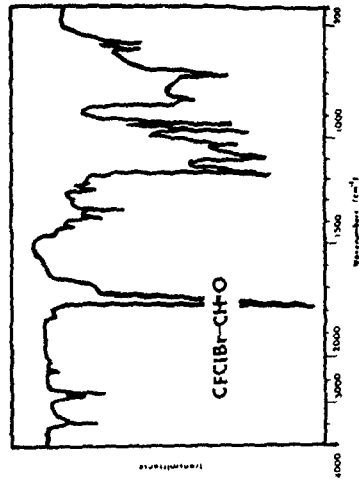


Figure 2: IR Spectrum (Solution) of Fluorochlorobromoacetaldehyde

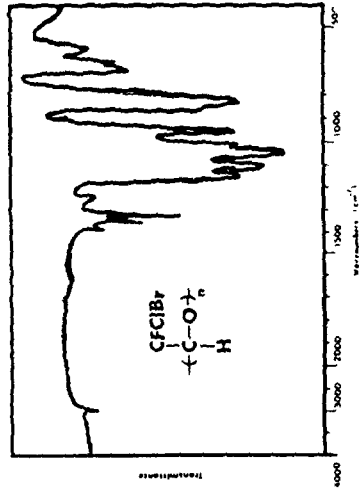


Figure 3: IR Spectrum (KBr Pellet) of Polyfluorochlorobromoacetaldehyde

Anhydrous FCBA prepared in this manner was treated with sulfuric acid and gave in about 60% yield a solid which was identified as poly-FCBA by its elemental analysis. The IR spectrum (Figure 3) showed it to be a poly-acetal. As in the case of other perhaloaldehyde polymers, poly-FCBA is insoluble in common solvents; in our preliminary experiments, we have not detected any "soluble fractions," which might indicate an "atactic" portion of the polymer. The polymer appears to be crystalline and, if analogies with other perhaloaldehyde polymers are permissible, seems to be isotactic.

In conclusion, in our continued, systematic work on perhaloacetaldehydes and their polymerization, we have synthesized the tenth and last of the perhaloacetaldehydes (containing fluorine, chlorine, and bromine substituents) and have polymerized it. Work on the preparation of the optically active form of this aldehyde and its polymerization is in progress.

#### ACKNOWLEDGMENTS

This work was supported by a fellowship from the Pittsburgh Plate Glass Company and in part by a grant from the National Science Foundation. We would like to thank Elizabeth Cary for her assistance in preparing this manuscript and Marco Wismer for valuable suggestions.

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