Haloaldehyde polymers: 44. Synthesis and polymerization of racemic fluorochlorobromoacetaldehyde*†

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Methyl fluorochlorobromoacetate was reduced either with lithium aluminium hydride or, better, with diisobutyl aluminium hydride. Work-up in the presence of water gave a mixture of the hydrate and methyl hemiacetal of fluorochlorobromoacetaldehyde. The mixture was dehydrated with phosphorus pentoxide/sulphuric acid to fluorochlorobromoacetaldehyde, which was characterized. Purified fluorochlorobromoacetaldehyde was polymerized to poly(fluorochlorobromoacetaldehyde) with anionic and cationic initiators. The insoluble, presumably isotactic, polymer was characterized by spectroscopic means and by thermal analysis.

(Keywords: synthesis; fluorochlorobromoacetaldehyde; hydride reduction; haloaldehyde polymers; characterization)

INTRODUCTION

Fluorochlorobromoacetaldehyde (FCBA) is the last of the ten perhaloaldehydes (excluding those with an iodine substituent) which had not been synthesized until recently[1]. The other perhaloacetaldehydes have either been known previously (fluoral, chloral, or bromal) or have been synthesized in recent years[2–12]. FCBA is unique among the perhaloacetaldehydes because its trihalomethyl group is chiral and FCBA can exist in optically active form.

Highly purified perhaloacetaldehydes have been polymerized to polyacetals with anionic or cationic initiators. Most poly(perhaloacetaldehydes) exist as isotactic polymers. When the bulkiness of the trihalomethyl group of the trihaloacetaldehydes is large (at least two chlorine atoms in the trihalo group), the polymers exist exclusively in their isotactic structure. In some cases, soluble oligomers (degree of polymerization, $DP \simeq 8$–12) were isolated[5,8,13] when the polymers were made from monomers with smaller groups.

Detailed studies of the polymerization behaviour of perhaloacetaldehydes showed that the ceiling temperature of polymerization (T_c) is related to the bulkiness and electronegativity of the trihalomethyl group. Fluoral has a T_c of $+85°C$, whereas bromal has a T_c of $-75°C$; other trihaloacetaldehydes have T_c values between these temperatures. When the polymers were made from monomers with small trihalomethyl groups, a high degree of stereospecificity was observed, which is the consequence of severe steric hindrance imposed by the bulky trihalomethyl group on the polyacetal backbone, as evidenced in polychloral[14–20].

Polymerization of chloral with chiral initiators has resulted in the formation of optically active polychoral[21–26]. The optical activity of polychloral is based on macromolecular asymmetry (helicity). A number of reviews have recently been published on this subject[2,27–29].

It was the objective of this work to synthesize and characterize FCBA by i.r. and by ^1H, ^{13}C and ^{19}F n.m.r. spectroscopy. Highly purified (polymerization-grade) FCBA was expected to undergo polymerization with anionic initiators. We expected the polymer to be primarily isotactic, but we had also hoped that the racemic FCBA with chiral initiators might give optically active PFCBA.

EXPERIMENTAL

Materials

Lithium tertiary butoxide was sublimed at 150°C/0.1 mmHg and was handled under a nitrogen atmosphere.

Methylcyclohexane (the polymerization solvent) was distilled from sodium/benzophenone at atmospheric pressure under argon. A centre cut (b.p. = 101°C) was stored in a dry Schlenk tube.

Triphenylphosphine was recrystallized from diethyl ether and dried at 25°C/0.1 mmHg.

Aldrich anhydrous-grade solvents were found to be adequate for all reactions except for polymerizations.

All chemicals were used as received.

Measurements

Infra-red spectra were recorded on a Perkin–Elmer model 1320 or on a Shimadzu IR-435 spectrophotometer. Solid samples were measured as KBr pellets; liquid samples were measured in 4% w/v carbon tetrachloride solutions using matched KBr liquid cells. Peak assignments were made to the nearest 5 cm^{-1}.

^1H n.m.r. spectra were recorded on a JEOL JNM-FX90Q multinuclear *FT* n.m.r. spectrometer and on a Varian EM 390 n.m.r. spectrometer.

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* Part 43 of this series: Ute, K., Nishimura, T., Hatada, K., Xi, F. and Vogl, O. *Makromol. Chem.* 1991, **192**, 35. Part 45 of this series: Doyle, T. R. and Vogl, O. *Polymer* 1991, **32**, 751

† This paper is dedicated to Professor Burghard Philipp on the occasion of his 65th birthday

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^{13}C n.m.r. spectra were recorded on a JEOL JNM-FX90Q multinuclear *FT* n.m.r. spectrometer with complete proton decoupling.

^{19}F n.m.r. spectra were recorded on a JEOL JNM-FX90Q multinuclear *FT* n.m.r. spectrometer, on a Bruker WP 200 spectrometer, or on a Varian EM 390 n.m.r. spectrometer.

Melting points were determined on a MEL-TEMP capillary melting-point apparatus and are uncorrected.

The decomposition temperature of PFCBA was determined on a Perkin–Elmer DSC-F differential scanning calorimeter. The instrument was calibrated against an indium standard.

Gas chromatograms were obtained on a Varian Associates model 920 gas chromatograph.

The purity of FCBA (water content) was determined by g.c. using 36% w/w diisodecyl phthalate coated on Chromosorb W (100/120 mesh) as a stationary phase and was reported in area per cents. A typical procedure involved injecting 10 μl of sample into the g.c. apparatus. This method for the detection of impurities was estimated to be sensitive to 10 ppm.

Microanalyses were carried out by the Microlytics Laboratory, South Deerfield, MA. The halogens were determined using three instrumental procedures after Schoeniger oxygen flask decompositions of the sample were performed.

PREPARATIONS

Methyl fluorochlorobromoacetate (MFCBA) was synthesized in a three-step procedure from chlorotrifluoroethylene in an overall yield of 40% as described in our previous communication[1].

Lithium aluminium hydride (LAH) reduction of MFCBA

A typical LAH reduction of MFCBA proceeded as follows. A dry 250 ml three-necked round-bottomed flask was equipped with a magnetic stirrer, pressure addition funnel, thermometer and flow control adaptor, which was connected by a 'T' joint to an argon cylinder. The argon flow was monitored by a bubbler. The round-bottomed flask was charged with anhydrous diethyl ether (130 ml), MFCBA (27 g, 0.13 mol) and cooled in a dry ice/acetone bath. Into the septum-capped addition funnel was placed LAH, 1.0 M in diethyl ether (39 ml, 39.2 mmol), with a dry syringe. The LAH solution was added to the MFCBA solution over a 1.5 h period; during the addition the reaction temperature was not allowed to exceed −70°C. Upon completion of the LAH addition, the solution was stirred for 15 min at −78°C. The clear, colourless, still cold solution was poured into a mixture of 400 ml of 2% (v/v) ice/sulphuric acid. The reduction product was extracted from the aqueous phase in a continuous liquid/liquid extractor with diethyl ether for 12 h; the extract was dried over magnesium sulphate, filtered and concentrated on a rotary evaporator under reduced pressure. The residue was distilled using a short-path distillation head. Yields of methyl fluorochlorobromoacetaldehyde hemiacetal (HFCBA) as high as 92% were obtained; most commonly, the yields were between 75% and 85%.

The ratio of fluorochlorobromoacetaldehyde hydrate to methyl fluorochlorobromoacetaldehyde hemiacetal was determined by ^{1}H n.m.r. spectroscopy. 2-Fluoro-2-chloro-2-bromoethanol (FCBE) and fluorochloroacetaldehyde (FCAA) were identified by g.c. *Note*: Upon injection into the g.c. apparatus, the hydrate and hemiacetal of FCBA or FCAA decomposed into water or methanol and the aldehyde.

2-Fluoro-2-chloro-2-bromoethanol and 2-fluoro-2-chloroethanol as by-products

A mixture of MFCBA (6.1 g, 29.8 mmol) and diethyl ether (10 ml) was cooled in an ice bath to 0°C and LAH (1.0 M in diethyl ether) (16.4 ml, 16.4 mmol) was added over a 30 min period. After an aqueous work-up, the residue was distilled using a short-path distillation column; 2.3 g (b.p. = 38–43°C/11 mmHg) of a clear, colourless, mobile liquid were collected. The product was analysed by g.c. and ^{1}H n.m.r. spectroscopy; it was an 85/15 mixture of 2-fluoro-2-chloro-2-bromoethanol (FCBE) and 2-fluoro-2-chloroethanol (FCE), respectively.

The ^{1}H n.m.r. spectrum (acetone-d$_6$) showed δ: FCBE, 4.05, 4.10, 4.20 and 4.25 ppm (HO–C$\underline{\text{H}}_2$–) and 5.55, 5.60 and 5.65 ppm ($\underline{\text{H}}$O–CH$_2$–); FCE, 6.10, 6.15, 6.20, 6.55, 6.60 and 6.65 ppm ($\underline{\text{H}}$FClC–).

Diisobutylaluminium hydride (DIBAL-H) reduction of MFCBA

A dry, three-necked, 250 ml round-bottomed flask was equipped with a magnetic stirrer, pressure-equalized addition funnel, thermometer and flow control adaptor, which was connected by a 'T' joint to an argon cylinder. The argon flow was monitored by a bubbler. The round-bottomed flask was charged with MFCBA (12.4 g, 60.4 mol) and dry dichloromethane (DCM) (50 ml), and was cooled in a dry ice/acetone bath. Into the septum-capped addition funnel was placed DIBAL-H, 1.0 M in DCM (66.5 ml, 66.5 mol), with a dry syringe. The DIBAL-H solution was added over a period of 70 min. During the addition, the reaction temperature was not allowed to exceed −70°C; the solution was stirred for 15 min at −78°C and was poured into 150 ml of ice/water containing 2% (v/v) sulphuric acid. The aqueous phase was extracted with diethyl ether in a continuous liquid/liquid extractor (18 h); the extract was dried over magnesium sulphate, filtered under nitrogen and concentrated on a rotary evaporator. The residue was distilled using a short-path distillation head. A clear, colourless liquid was collected (9.2 g, b.p. = 59–76°C/90 mmHg). The product was analysed by g.c., which showed it to contain 3% diethyl ether, 12% MFCBA and 85% HFCBA. The overall yield of HFCBA was 8.3 g, 41.7 mmol, or 69%.

Synthesis of racemic FCBA

All glassware was dried overnight at 120°C, rapidly assembled and cooled under a flow of dry argon. The dehydrating mixture (a mixture of concentrated sulphuric acid and phosphorus pentoxide) was prepared in a tared round-bottomed flask equipped with a magnetic stirrer, capped with a septum and placed under a dry argon atmosphere. The flask was chilled in a dry ice/acetone bath, HFCBA was added and the mixture was then warmed to room temperature. A short-path distillation head was attached to the flask and FCBA was distilled at atmospheric pressure using an oil bath. The second fractional distillation was done through a 15 cm Vigreux column. Typical yields of FCBA were between 60 and 70%, but a yield of 85% has also been obtained

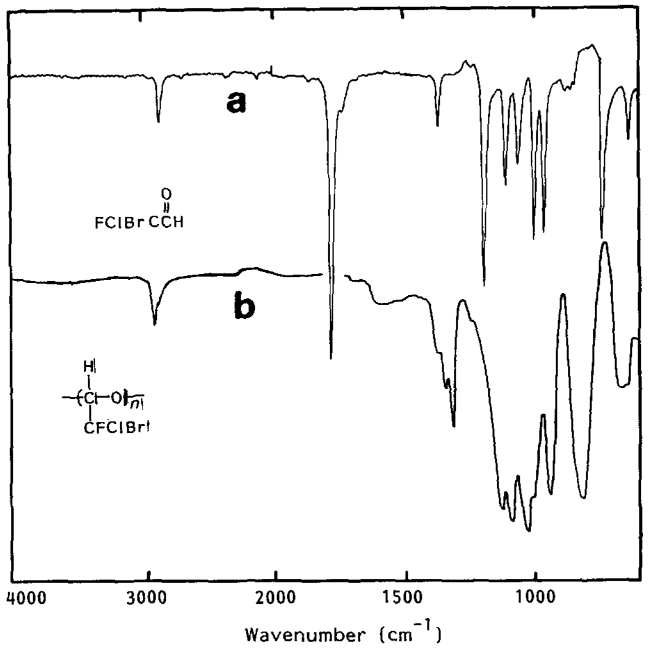


Figure 1 (a) I.r. spectrum (neat) of fluorochlorobromoacetaldehyde. (b) I.r. spectrum of polyfluorochlorobromoacetaldehyde (KBr pellet)

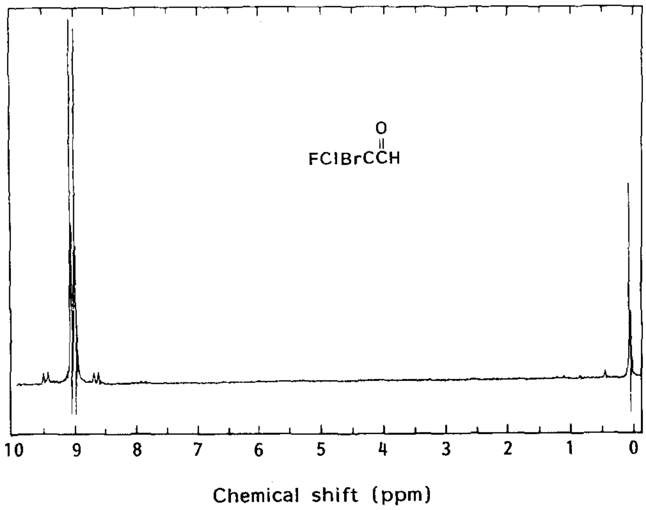


Figure 2 ^{1}H n.m.r. spectrum of fluorochlorobromoacetaldehyde

(b.p. = 80–81°C). The elemental and spectral analyses of FCBA gave the following results. The i.r. spectrum of FCBA showed absorptions at 2840 cm^{-1} (C–H stretching), 1755 cm^{-1} (C═O stretching), 1350 cm^{-1} (C–H bending) and 1170 cm^{-1} (C–F stretching) (*Figure 1a*). The ^{1}H n.m.r. spectrum of FCBA (acetone-d$_6$) showed the O═C$\underline{\mathrm{H}}$ proton as a doublet at 9.20 and 9.27 ppm, $^3J_{\mathrm{HF}}$ = 6.1 Hz (*Figure 2*). The ^{13}C n.m.r. spectrum of FCBA (acetone-d$_6$) showed δ: 96.07 and 110.11 ppm (FClBr$\underline{\mathrm{C}}$–), $^1J_{\mathrm{CF}}$ = 316.20 Hz; and 179.56 and 180.80 ppm (O═$\underline{\mathrm{C}}$H–), $^2J_{\mathrm{CF}}$ = 27.94 Hz. The ^{19}F n.m.r. spectrum (benzene-d$_6$, CFCl$_3$ internal reference, 178 ppm full width) showed δ: −77.52 ppm ($\underline{\mathrm{F}}$ClBrC–). The ^{19}F n.m.r. spectrum (benzene-d$_6$, CF$_3$COOH external reference, 23.7 ppm full width) showed δ: 0.72 and 0.79 ppm ($\underline{\mathrm{F}}$ClBrC–), $^3J_{\mathrm{HF}}$ = 5.86 Hz.

Elemental analysis. Calculated for $C_2HBrClFO$: C, 13.70%; H, 0.58%. Found: C, 13.42%; H, 0.61%.

Fluorochloroacetaldehyde (FCAA) (formed as an impurity during the LAH reduction of MFCBA) was determined by spectroscopic and gas chromatographic analyses. The ^{1}H n.m.r. spectrum (carbon tetrachloride) of the forecut fraction showed δ: 5.90, 5.93, 6.49 and 6.52 ppm (FCl$\underline{\mathrm{H}}$CHO, 1H), $^2J_{\mathrm{HF}}$ = 51.3 Hz and $^3J_{\mathrm{HF}}$ = 2.7 Hz; and 9.50 ppm (FClHC–C$\underline{\mathrm{H}}$O, 1H) two overlapping doublets. The ^{19}F n.m.r. spectrum of the forecut fraction (acetone-d$_6$) showed δ: −155.83 and −156.44 ppm ($\underline{\mathrm{F}}$ClHC–CHO), $^2J_{\mathrm{HF}}$ = 51.32 Hz. $^3J_{\mathrm{HF}}$ was not observed since a 30 030 Hz window was used in the spectrum.

Polymerization of FCBA

Sulphuric acid as initiator. FCBA (1.3 g, 7.5 mmol) was placed in a dry septum-capped test tube, and sulphuric acid (0.0037 g, 0.04 mmol, 2.0 μl) was added. The initially formed two-phase mixture was mixed well; gelation occurred within 30 min. After one day at room temperature, the tube was opened, and poly(fluorochlorobromoacetaldehyde) (PFCBA) was isolated as a solid plug, which was readily crumbled into a powder. The powder was stirred in ethanol and then in acetone for 2 h each at room temperature and filtered. PFCBA was filtered and dried at 0.1 mmHg. The yield was 0.8 g (62%). The i.r. spectrum (KBr) showed absorptions at 2950 cm^{-1} (C–H stretching) and 1380, 1360 and 1340 cm^{-1} (C–H bending) (*Figure 1b*). Differential scanning calorimetry showed the onset of depolymerization at 140°C.

Elemental analysis. Calculated for $(C_2HBrClFO)_n$: C, 13.70%; H, 0.58%. Found: C, 13.51%; H, 0.61%.

Lithium tertiary butoxide (LTB) as initiator. FCBA (4.1 g, 23 mmol) was placed in a dry, septum-capped test tube, brought to 80°C in an oil bath and charged with 0.46 ml of LTB (1.0 M) in methylcyclohexane and mixed well. At 0°C, rapid polymerization took place; after one day at 0°C, PFCBA was isolated as a plug, which readily crumbled into a powder; it was stabilized by stirring for 24 h in 25 ml of concentrated HCl/methanol (1:9 v/v). The suspension was filtered and dried for one day at 0.1 mmHg to yield 0.27 g (7%) of stabilized polymer.

R(−)- *and* S(+)-*lithium-2-octanoxide (RLO and SLO) as initiators.* The RLO initiating solution (0.82 M) was prepared by dissolving *R*(−)-2-octanol (0.69 g, 5.3 mmol) in anhydrous methylcyclohexane (MCH) (3.0 ml) in a 15 ml round-bottomed flask. The solution was cooled in a dry ice/acetone bath and charged with n-butyllithium (1.6 M in hexanes) (3.2 ml, 5.1 mmol).

The SLO initiating solution (0.83 M) was prepared in a similar fashion using *S*(+)-2-octanol (0.71 g, 5.5 mmol), MCH (3.0 ml) and 1.6 M n-butyllithium (3.3 ml, 5.5 mmol). FCBA was injected into four argon-blanketed test tubes and held in an oil bath (*Table 1*).

The contents of the tubes were initiated and clear colourless solutions were obtained. The tubes were then placed in an ice bath where instantaneous polymerization occurred. After 16 h at 0°C, the PFCBA samples were isolated and stabilized by stirring them in 25 ml of methanolic HCl solutions each. After filtration, the colourless PFCBA powders were dried, extracted with acetone in a Soxhlet extractor and dried for 18 h at 0.1 mmHg and room temperature.

The optical rotation of the powders was measured in suspension using an isorefractive mixture of carbon tetrachloride and carbon disulphide, 60/40 v/v. The results are shown in *Table 2*.

Table 1

Run no.	MCH (ml)	FCBA (g)	FCBA (mmol)	FCBA (ml)	Holding temperature (°C)	Initiator Type	Initiator (mmol)
I	1.00	1.82	10.38	1.00	85	RLO	0.10
II	1.00	1.82	10.38	1.00	85	SLO	0.10
III	1.00	1.83	10.44	1.00	65	RLO	0.10
IV	1.00	1.81	10.32	1.00	65	SLO	0.10

Table 2

Run no.	Unextracted (g)	Unextracted Yield (%)	Extracted (g)	Extracted Yield (%)	$[\alpha]_D^{22}$ (deg)
I	1.38	76	0.71	39	$+12\pm20$
II	1.29	70	0.15	8	$+13\pm20$
III	1.42	78	0.75	41	–
IV	1.33	74	0.19	10	$+10\pm20$

Table 3

Run no.	PFCBA (g)	PFCBA Yield (%)	Initiator	$[\alpha]_D^{22}$ (deg)
V	1.60	75	PPh_3	$+2\pm6$
VI	1.13	50	TMA(−)αM	$+4\pm10$
VII	1.57	66	STRY	$+20\pm20$
VIII	1.41	61	TMA(+)αAc	$+10\pm20$

Table 4

Run no.	PFCBA (g)	PFCBA Yield (%)	Initiator	$[\alpha]_D^{22}$ (deg)
IX	0.80	47	TMA(+)αAc	-2.5 ± 6
X	0.94	59	RLO	-1.0 ± 15
XI	0.93	61	SLO	$+6.5\pm10$

Table 5

MCH (ml)	FCBA (g)	FCBA (mmol)	Conc. (M)	LTB (mmol)	T_{polym} (°C)	Yield[a] (%)
0.60	3.32	18.93	7.82	0.19	66.0	53
1.00	2.05	11.69	5.49	0.12	60.0	50
2.00	1.24	7.07	2.64	0.07	48.5	45
2.50	0.83	4.73	1.60	0.10	40.0	5

[a] Yield of PFCBA after work-up

Triphenylphosphine (*PPh_3*), *strychnine* (*STRY*), *tetramethylammonium* (−)-*α-methoxymandelate* (*TMA*(−)*αM*) *and tetramethylammonium* (+)-*α-acetylmandelate* (*TMA*(+)*αAc*) *as initiators.* Polymerization of FCBA was carried out as described above with the initiators indicated. The optical rotations were measured in suspension using an isorefractive mixture of carbon tetrachloride and carbon disulphide, 60/40 v/v (*Table 3*).

Tetramethylammonium (+)-*α-acetylmandelate* (*TMA-*(+)*αAc*), R(−)-*lithium-2-octanoxide* (*RLO*) *and S*(+)-*lithium-2-octanoxide* (*SLO*) *as initiators.* The polymerization of FCBA was carried out with several initiators (*Table 4*).

Determination of the ceiling (*polymerization*) *temperature* (T_c) *of FCBA*

The polymerization temperature was measured in the following way. With a dry syringe the appropriate amount of solvent and monomer was transferred into a 15 mm × 120 mm test tube; the mixture was heated to 80°C in an oil bath and the initiating solution (1.0 mol%) was added with a syringe. The oil bath was allowed to cool slowly and the onset of turbidity in the initiated solution was taken as the polymerization temperature[12] (*Table 5*).

RESULTS AND DISCUSSION

Perfluorinated esters are known to be selectively reduced by LAH in diethyl ether at −78°C to the corresponding perfluoroaldehyde[30]. After decomposing the reaction product in water, a mixed hydrate/hemiacetal was obtained. This reduction technique is also successful for other perhaloacid esters[6,8–10].

FCBA synthesis

We found that MFCBA could be reduced by LAH in diethyl ether at −78°C to its hydrate/hemiacetal (HFCBA) (*Table 6*). G.c., ^{1}H and ^{19}F analysis of HFCBA produced in this way and also analysis of its aldehyde showed that between 2 and 5% of the bromine of the fluorochlorobromomethyl group had been reduced to the hydrogen compound (FClHCCHO), and the bromine atom removed. This side-product is undesirable for our purpose since it contains an active hydrogen and can interfere with the polymerization of FCBA by acting as a chain-transfer agent.

It has been reported previously that diethyl ether slurries of LAH do not cause the reduction of bromine in mixed perhaloesters at −78°C[6,9].

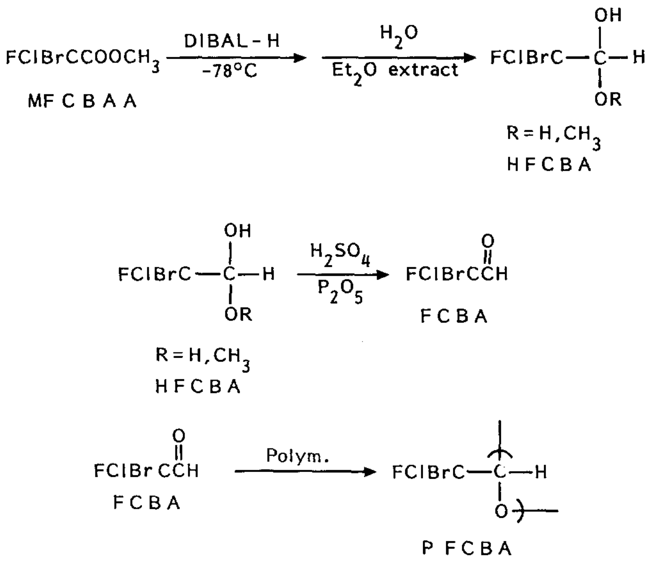
In 1981 Brown[31] reviewed the scope of LAH reduction of alkyl halides in tetrahydrofuran (THF) and found that clear solutions of LAH in THF were much more reactive towards halide reduction than slurries of LAH (see also ref. 32).

Brown[33] has shown that the reduction of alkyl halides with DIBAL-H (an electrophilic 'acidic' reducing agent) is considerably slower than the reduction of alkyl halides with LAH (a nucleophilic 'basic' reducing agent), and Winterfeldt[34] has shown that DIBAL-H can selectively reduce esters to their corresponding aldehydes at low temperatures.

Table 6 LAH reduction of MFCBA (product analysis)

MFCBA (g)	Product b.p. (°C/mmHg)	Et_2O^a (%)	Hydrate^a (%)	Acetal^a (%)	FCBE^b (%)	FCAA^b (%)
0.5	29–50/104	15	75	8	–	2
21.1	50–75/104	3	78	16	1	2
0.9	75–78/104	1	12	80	5	2
0.2	31–43/82	19	75	4	–	2
23.8	43–73/82	4	73	20	1	2
20.6	42–71/59	3	73	21	1	2
0.7	50–52/85	10	88^c		–	2
17.2	52–74/85	2	95^c		1	2

[a] Determined by ^1H n.m.r. spectroscopy
[b] Determined by g.c.
[c] Analysed by g.c. only



Scheme 1 Synthesis of fluorochlorobromoacetaldehyde

Table 7 ^{13}C n.m.r. spectrum of HFCBA^a. Carbon types:

$FClBr\overset{1}{\underline{C}}\text{–}\overset{2}{\underline{C}}H(OH)_2$ $FClBr\overset{3}{\underline{C}}\text{–}\overset{4}{\underline{C}}HOH(O\overset{5}{\underline{C}}H_3)$
$FClH\overset{6}{\underline{C}}\text{—}\overset{7}{\underline{C}}H(OH)_2$ $FClH\overset{8}{\underline{C}}\text{–}\overset{9}{\underline{C}}HOH(O\overset{10}{\underline{C}}H_3)$

Carbon type	δ (ppm)	$^1J_{FC}$ (Hz)	$^2J_{FC}$ (Hz)
1	120.68	310.32	
1	106.91		
2	94.31		27.94
2	93.07		
3	118.40	313.26	
3	104.50		
4	100.65		27.94
4	99.41		
5	56.20		
6	118.20	308.91	
6	104.63		
7	95.29		27.94
7	94.05		
8^b	–		
8^b	–		
9	98.75		29.42
9	97.45		
10	49.87		

[a] Solvent:benzene-d_6, Internal reference: TMS
[b] Not observed due to low intensity

We found that MFCBA was readily reduced with DIBAL-H in dichloromethane at −78°C; HFCBA was obtained in good yield. N.m.r. spectroscopy and g.c. analysis showed that neither fluorochlorobromoethanol, fluorochloroacetaldehyde, nor other reduction products were formed.

The ^1H n.m.r. spectrum of HFCBA (neat) showed the methyl hemiacetal $-OC\underline{H}_3$ protons at 3.60 ppm; the $-C\underline{H}OH(OCH_3)$ proton was observed between 4.75 and 4.85 ppm as a multiplet (two overlapping doublets); the hydrate $-C\underline{H}(OH)_2$ as a doublet as 5.15 and 5.20 ppm, $J_{FH} = 3.4$ Hz. The OH peak position was variable depending on the solvent used for the measurement of the spectrum and the composition of HFCBA. The ^{13}C n.m.r. analysis of HFCBA is shown in *Table 7*. The ^{19}F n.m.r. spectrum of HFCBA (acetone-d_6) shows the fluorine resonance of $\underline{F}ClBrCCH(OH)_2$ at −65.74 ppm and $\underline{F}ClBrCCHOH(OCH_3)$ at −66.87 ppm. Fluorine/proton coupling was not observed since a 15015 Hz window was used. The compound obtained from the bromine reduction (HFClCCHO) was not observed in the ^{19}F spectrum since resonances of this type of fluorine atom ($\underline{F}ClHC-$) are found at the −155 ppm region and our spectral range covered only the range between +69 and −119 ppm (relative to $CFCl_3 = 0$ ppm).

The synthesis of FCBA from HFCBA was accomplished as follows. Sulphuric acid (conc.) as a dehydrating agent resulted in a 60% yield of FCBA when 1.8 mol of acid was used per mole of HFCBA. Higher ratios of sulphuric acid (2.4 and 6.2 mol per mole of HFCBA) gave no FCBA.

Dehydration of HFCBA using phosphorus pentoxide (1.5 mol per mole of HFCBA) resulted in a 54% yield of FCBA. The viscous two-phase system limited the effectiveness of stirring, resulting in a reduced yield.

The best dehydrating system was found to be a mixture of sulphuric acid and phosphorus pentoxide. Initially, the mixture of HFCBA and the dehydrating agents consisted of two phases, but, upon heating, a single phase was obtained. Optimization of this system resulted in the production of FCBA of high purity and in over 80% yield.

G.c. analysis of FCBA obtained by LAH reduction of MFCBA showed a lower-boiling impurity, which was characterized as the bromide reduction product, fluorochloroacetaldehyde (FCAA). FCAA was identified by n.m.r. spectroscopy of a FCBA 'forecut fraction' and was identified by g.c. to be present at a level of 6% in FCBA in this preparation.

FCBA polymerization

The polymerization of FCBA with sulphuric acid as initiator resulted in the formation of a solid plug of PFCBA. The polymerization was slow and it took 35 min for the mixture to form a gel of PFCBA at room temperature. The presence of FCAA (about 3%) appeared to have little effect on the polymerization of FCBA with sulphuric acid since its behaviour was similar to the behaviour of other perhaloaldehyde polymerizations using sulphuric acid as initiator[35-37].

It should be pointed out that sulphuric acid or other acids seemed to have no effect on FCBA in its impure state and do not cause polymerization; otherwise the dehydration from the HFCBA could not have been accomplished. The dehydration was also carried out near to or above the T_c of polymerization. Polymer-grade (<100 ppm protic impurities) FCBA (like other polymer-grade perhaloacetaldehydes) are much more sensitive towards polymerization (not only cationic but also anionic polymerization).

When purified, FCBA was treated with alkoxide, tertiary amine, or carboxylate initiators; an instantaneous polymerization (about 1 h to completion) resulted upon cooling (cryotachensic polymerization). The polymers were obtained as opaque solid plugs, which contained a hard glassy polymer portion near the surface and a brittle interior that readily crumbled into a powder. The ratio of the glassy fraction to the brittle fraction varied with the purity of the monomer. In general, the purer monomer gave a higher percentage of glassy polymer. When triphenylphosphine (TPP) was used as initiator, the polymer was obtained as a tough, translucent, homogeneous plug. D.s.c. analysis of PFCBA decomposition showed the onset of an endotherm at 140°C, indicating depolymerization of PFCBA.

The characteristics of FCBA polymerization seem to be between those of chloral and dichlorofluoroacetaldehyde. As in chloral polymerizations, no soluble PFCBA fraction could be isolated, as determined by exhaustive Soxhlet extraction of the polymer with acetone. It should be noted that soluble low-*MW* fractions ($DP \simeq 8$–12) of polydichlorofluoroacetaldehyde and polybromodichloroacetaldehyde have been isolated[5,8].

The stabilization of PFCBA was carried out by stirring a suspension of PFCBA in methanolic HCl at room temperature for 3 days.

When lithium alkoxides or the reaction product of FCBA and triphenylphosphine was used as initiator, a 75% yield of PFCBA was obtained; tertiary amine and carboxylates as initiators gave lower yields of polymer (about 65% and 60%, respectively). Exhaustive extraction with acetone resulted in a substantial decrease in the yield of PFCBA samples; the extracted yield of PFCBA ranged between 5% and 52%. These results indicate incomplete stabilization of the polymer end-groups (presumably alkoxides), which results in depolymerization. It was later found that a methanol wash after acid treatment was sufficient to render the polymer reasonably stable for storage at room temperature (for as long as six months). It should be mentioned that Corley[7] obtained bulk polychloral in 54% yield after exhaustive extraction of the polymer (stabilized by stirring for 2 days in 90/10 methanol/concentrated HCl(aq)) with methanol. The result of PFCBA stabilization parallels that of polychloral stabilization and shows a clear dependence on the initiator used for the polymerization.

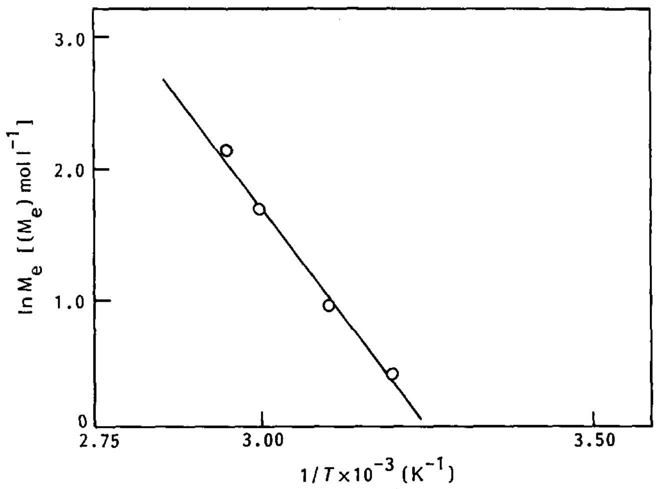


Figure 3 Determination of the polymerization (ceiling) temperature of fluorochlorobromoacetaldehyde: $\Delta H = -12.9$ kcal mol^{-1}, $\Delta S = -42.1$ cal mol^{-1} K^{-1}; 1.0 M, $T_c = 33$°C; neat, $T_c = 72$°C

The ceiling temperature (T_c) of the polymerization of FCBA was determined by visual observation of the cloud point, as has been done with other perhaloacetaldehyde polymerizations (*Figure 3*). Four solutions of FCBA of different concentrations were prepared, warmed in an oil bath to 80°C (above the expected threshold temperature of polymerization) and initiated with lithium tertiary butoxide (1.0 mol%). Slow cooling of the oil bath allowed an accurate determination of each threshold temperature; the polymerization temperature could be determined since the polymer precipitated out of solution. The thermodynamics of the polymerization was established based on previous work[12].

Polymerization of FCBA by chiral initiators resulted in the formation of PFCBA with only negligible optical activity (experimental error limits ranged from $\pm 5°$ to $\pm 25°$). These results are somewhat puzzling since chloral has been polymerized by many chiral initiators into polychloral samples with high optical rotations[7,22-26,28,29]. If stereo-selective polymerization of FCBA had occurred, one would expect the polymer to have a large optical rotation since the polymer would be optically active due to the asymmetric centre of the monomer unit and the macromolecular asymmetry of the polymer helix.

A preliminary X-ray powder diffraction investigation of PFCBA was carried out. It was found that PFCBA appeared to be more amorphous than is the partially crystalline[15] polychloral. X-ray diffraction studies of other perhaloaldehyde polymers indicated that they are partially crystalline and that their diffraction patterns were similar to that of polychloral[15,38].

The following conclusions may be drawn from our investigations: PFCBA is apparently isotactic; substantial stereo-selective polymerization of racemic FCBA by chiral initiators does not seem to occur since no optical activity of the PFCBA powder was found.

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