

Haloaldehyde Polymers XXXV. ^1H , ^{19}F , and ^{13}C NMR Spectra and Stereochemistry of Bornyl Esters of Fluorochlorobromoacetic Acid

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ABSTRACT: The optical resolution of FCIBrCCO₂H (FCBAA), an intermediate to fluorochlorobromoacetaldehyde, was carried out by fractional crystallization of its strychnine salt, and 8 samples of optically enriched FCBAA were prepared. The optical purities of the FCBAA samples ranged from 67% (+) to 35% (–) based on ^{19}F NMR studies on their (–)-borneol esters. ^1H and ^{13}C NMR spectra of the borneol ester were also investigated in detail using two-dimensional NMR technique. The optical rotations of the fluorochlorobromomethane samples, which were converted from the strychnine salt of FCBAA by thermal decarboxylation, were plotted against the enantiomer excesses of the parent FCBAA, and a good linear relation was obtained.

KEY WORDS ^{19}F NMR Spectroscopy / Two Dimensional NMR / Fluorochlorobromoacetaldehyde / Fluorochlorobromoacetic Acid / Fluorochlorobromomethane / (–)-Borneol / Diastereomer Excess / Optical Resolution / Thermal Decarboxylation / ^{35}Cl – ^{37}Cl Isotope Effect /

Fluorochlorobromoacetic acid (FCBAA) has become an important intermediate to us. It was used for the preparation of fluorochlorobromoacetaldehyde and for the decarboxylation to fluorochlorobromomethane (FCBM) and the deuteromethane.^{1–3}

Polymerizations of chloral and other perhaloacetaldehydes have been extensively studied by Vogl and his coworkers since 1963.^{4–6} Some years ago it was recognized that polychloral and several other poly(perhaloacetaldehyde)s only exist in purely isotactic form, and that polychloral, when initiated with chiral initiators, could be prepared in optically active form based on one-handed helicity of the polymer chain.^{5,7,8} Perhaloacetaldehydes could be prepared with a wide range of size and shape of the side

group and there would be still a great possibility in their polymerization. The basis of the present study results from our interest in the synthesis and polymerization of optically active fluorochlorobromoacetaldehyde to chiral poly(fluorochlorobromoacetaldehyde), a polymer that is expected to have optical activity not only based on the chiral side group but also on macromolecular asymmetry.^{1,7,8}

FCBAA was synthesized from chlorotrifluoroethylene (CTFE) in four steps in a yield of about 30%. The optical resolution of FCBAA was carried out by fractional crystallization of its strychnine salt in methanol and an optical purity of about 66% (83/17 mixture of antipodes) was achieved in four recrystallizations in a yield of 20% (6% based on CTFE).³ Further improvement in the optical purity was

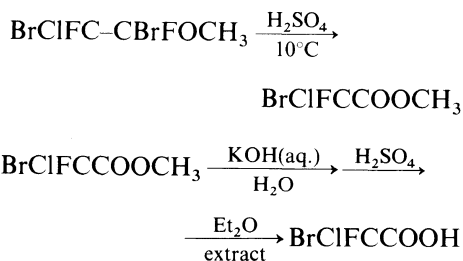
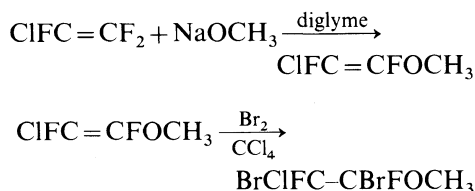
difficult because of the yield loss of the salt during recrystallization. Consequently, much of our work was done with optically enriched FCBA and its derivatives.

The exact identification of the optical purity of the enantiomeric composition required a reliable method for the determination of the optical purity. We found that the optical purity of FCBA could be determined by ^{19}F NMR spectroscopy of its [(1*S*)-endo]-(-)-borneol ester. The bornyl esters were readily prepared by esterification of FCBA with borneol in benzene using azeotropic removal of water. The esterification was selfcatalyzed and did not require additional acid catalysts, and no racemization was observed.³

It was the objective of this work to carefully analyze the bornyl esters by NMR spectroscopy which provides a quantitative basis of our decarboxylation studies as well as for the synthesis and polymerization of optically active fluorochlorobromoacetaldehyde.

EXPERIMENTAL

Optically active FCBA and FCBM were prepared according to the previous paper.³ FCBA was prepared by a sequence of the following four steps starting with 1-chloro-1,2,2-trifluoroethylene.



Separation of the FCBA into the optical antipodes was carried out by fractional crystallization of the strychnine salt from methanol; an optical purity of about 66% could be achieved by four recrystallizations. The strychnine salt was converted into FCBM by thermal decarboxylation in water, ethylene glycol or deuterium oxide. Bornyl ester of the acid was synthesized by selfcatalyzed esterification with borneol.

NMR spectra of the bornyl esters of FCBA were measured in 10% CDCl_3 solution at 35°C. Sample solutions were filtrated, degassed, and sealed under nitrogen atmosphere in 5 mm NMR sample tubes. TMS (^1H and ^{13}C) and C_6F_6 (^{19}F) were used as internal standards. The spectra were recorded on a JEOL JNM-GX500 spectrometer. The spectral conditions (observed nucleus, broad-band decoupled nucleus, observed frequency, spectral width, data point, digital resolution, pulse width, pulse delay and number of scans) are listed in Table I.

In the ^1H COSY experiment was employed a recycle time of 5.0 s, with 4 transients being collected for each t_1 value. A total of 512 spectra, each consisting of 1024 data points,

Table I. Spectral conditions for NMR

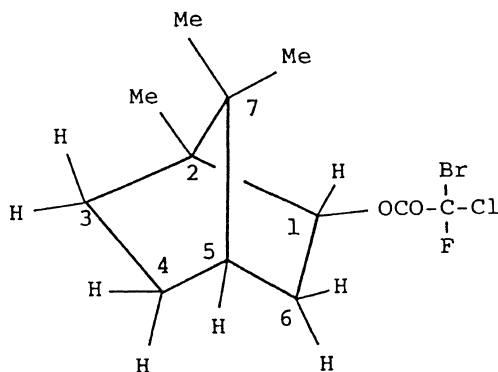
Obsd nuc.	Irradiation nuc.	Obsd freq.	Spectr. width	Data point	Digit. resoln.	Pulse width	Pulse delay	Scans
		MHz	Hz		Hz		s	
^1H	—	500.16	5000	32 K	0.31	45° (2.8 μs)	15	16
^{19}F	—	470.57	52000	128 K	0.79	45° (3.5 μs)	15	16
^{19}F	—	470.59	1000	16 K	0.12	45° (3.5 μs)	15	16
^{13}C	^1H	125.78	22500	128 K	0.35	45° (5.0 μs)	5	9044

were accumulated with a frequency range of 2500 Hz in both dimensions.

The ^{13}C - ^1H COSY experiment employed a recycle time of 4.0 s, with 16 transients being collected for each t_1 value. A total of 256 spectra, each consisting of 4096 points, were accumulated with a frequency range of 5000 Hz in ^{13}C axis and 2500 Hz in ^1H axis. The data matrix was zero-filled to 4096×512 points before Fourier transformation.

RESULTS AND DISCUSSION

Eight samples of bornyl esters of FCBAAs were examined by ^1H NMR spectroscopy. The ^1H chemical shifts measured in CDCl_3 at 35°C are summarized in Table II. The numbering system is shown below.



The peak assignments were made by 500 MHz ^1H COSY (Figure 1) starting from the signal at 5.06 ppm of the methine proton at 1-position (CH(C1)). Correlation peaks observed in the COSY spectrum are shown below.

2J : 3a—3e, 4a—4e, 6a—6e

3J : 1—6a, 1—6e, 3a—4a

3a—4e, 3e—4a, 3c—4e

4e—5, 5—6e

4J : 4e—6e

The pairs of methylene proton signals can also be seen clearly in the ^{13}C - ^1H COSY spectrum (Figure 2). The peaks due to the equatorial

Table II. ^1H NMR chemical shifts of bornyl ester of fluorochlorobromoacetic acid measured in CDCl_3 at 35°C

	ppm
CH(C1)	5.06
CH ₃ (C2)	0.926
CH ₂ (C3)-[a]	1.37
-[e]	1.99
CH ₂ (C4)-[a]	1.24
-[e]	1.79
CH(C5)	1.75
CH ₂ (C6)-[a]	1.13
-[e]	2.42
CH ₃ (C7)	0.904
	0.908

protons bonded to C4 and C6 carbons could be identified by the correlation peak due to 4J long-range coupling between these two protons through four bond planar "W" pathway. In both cases axial protons resonated at higher magnetic field than equatorial ones. Any peak splitting due to the diastereomeric isomers was not observed in the ^1H NMR spectra.

^{19}F NMR spectra of the bornyl esters showed two peaks at 98.1 and 98.2 ppm and the intensities of these two peaks varied depending on the sample (Figure 3). The lower-field peak is stronger in the spectra of esters of the acids which give (-)-FCBM by decarboxylation (Figure 3a), and the higher-field peaks is stronger in the case of esters of the acids which give (+)-FCBM (Figure 3b). Racemic mixture of the esters showed the two peaks of equal intensities (Figure 3c). These indicate that the two peaks are attributable to the diastereomers of the ester. Fractions of each isomer were determined from the intensity ratio of the peaks and summarized in Table III. The values of enantiomer excess (*e.e.*) of FCBM were estimated from the diastereomer fractions of the bornyl esters assuming that no racemization had occurred during the decarboxylation procedure of the strychnine salt of the acid (Table III). The plots of the *e.e.*'s against the optical rotations of the CHBrClF gave a

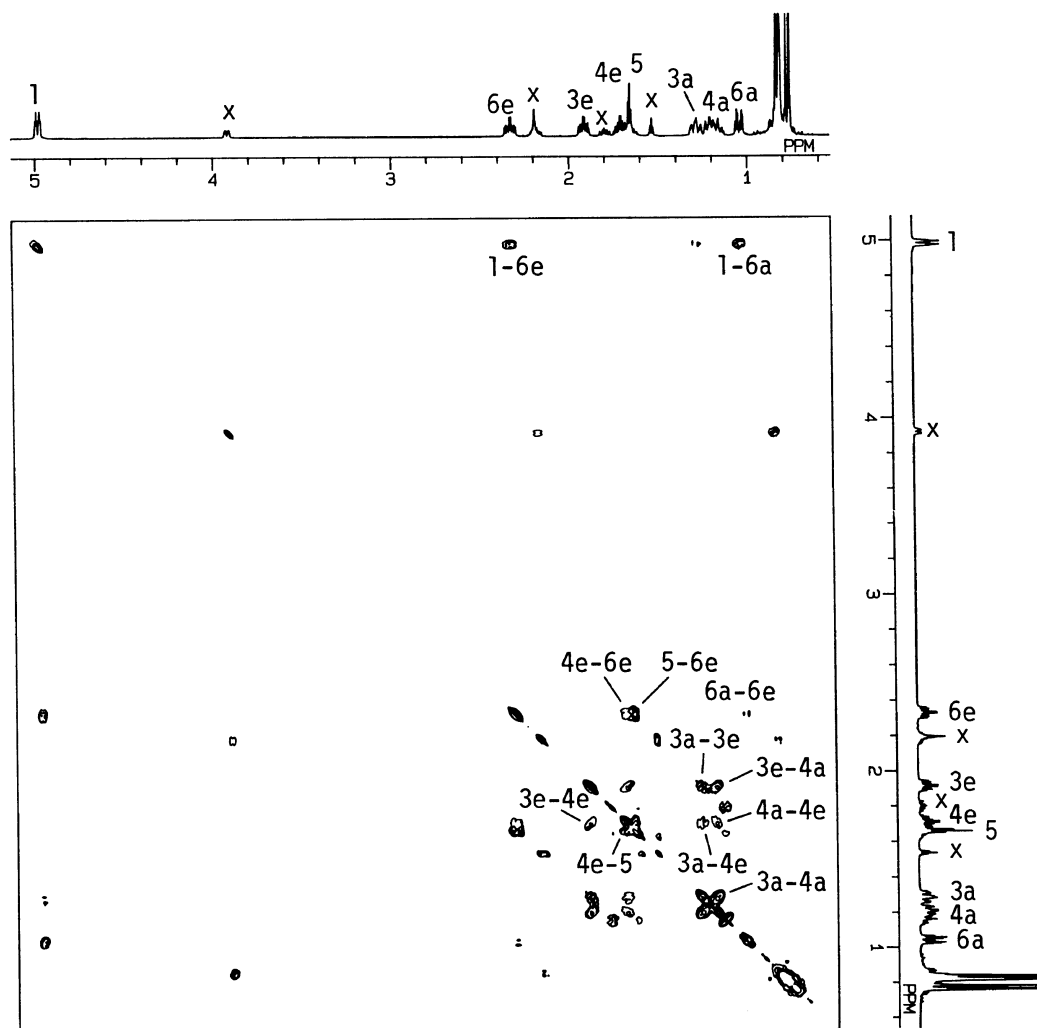


Figure 1. ^1H COSY spectrum of bornyl ester of fluorochlorobromoacetic acid measured in CDCl_3 at 35°C . (The peaks labelled x are due to the borneol contained as an impurity.)

good linear relation as shown in Figure 4. Extrapolation of the rotation to 100% *e.e.* gave an $[\alpha]_D^{20}$ of $+2.70^\circ$ for the pure antipodes.

The ^{19}F signals of both diastereomers of the bornyl ester split into two peaks, the intensity ratio of which is 3/1. The splitting should be due to the $^{35}\text{Cl}/^{37}\text{Cl}$ -isotope effect. Similar isotope effects of chlorine were reported recently on proton^{9,10} and carbon.¹¹

The bornyl esters were examined by ^{13}C NMR spectroscopy. The peak assignments

were made using ^{13}C - ^1H COSY spectrum (Figure 2) and the chemical shifts are summarized in Table IV. The chemical shifts of C2, C6, CO, CHBrClF , and CH_3 (attached to C2) carbons are sensitive to the diastereoisomerism and the chemical shift difference was the largest in the signals of C6 carbon. The diastereomer ratios determined from these signals coincided with each other (Table IV) and also with those determined from the ^{19}F NMR signals (Table III).

NMR Spectra of the Bornyl Ester of FCIBrCCOOH

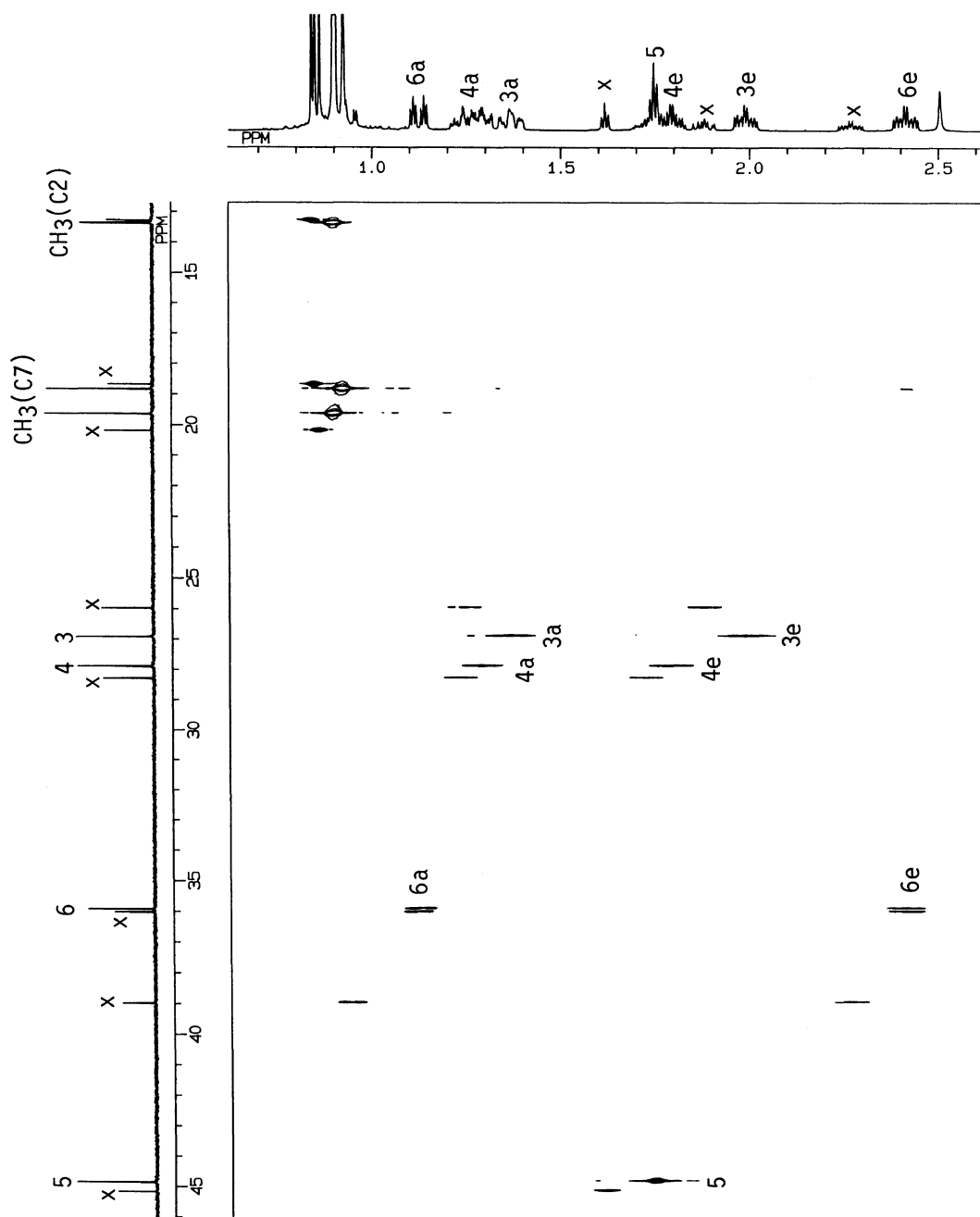


Figure 2. ^{13}C - ^1H COSY spectrum of bornyl ester of fluorochlorobromoacetic acid. (The peaks labelled x are due to the borneol contained as an impurity.)

Table III. Fractions of isomers of the bornyl esters of fluorochlorobromoacetic acid and optical rotations of the fluorochlorobromomethanes obtained from the acids

No.	Bornyl ester ^a		CHBrClF ^b		
	(+)	(-)	<i>e.e.</i> /%	$[\alpha]_D^{20}$	$[\alpha]_{365}^{20}/[\alpha]_D^{20}$
116 (racemic)	0.50	0.50	-0.6	0.00	—
160-1M	0.33	0.67	-34.6	-0.84	2.3
160-3/2M	0.39	0.61	-21.8	-0.59	2.1
160-3/3M+4M	0.52	0.48	+4.2	+0.28	2.2
	(0.54) ^c	(0.46) ^c			
160-3/4C	0.83	0.17	+67.4	+1.84	2.0
	(0.82) ^c	(0.18) ^c			

^a The isomers which gives (+)- and (-)-CHBrClF's are represented by (+) and (-), respectively. The fractions were determined from ¹⁹F NMR spectra.

^b The enantiomer excess (*e.e.*) was determined from the fractions of diastereomers of bornyl ester of fluorochlorobromoacetic acid assuming that no racemization had occurred during the decarboxylation procedure of the strychnine salt of the acid to CHBrClF.

^c Determination from the signal of the C-6 carbon.

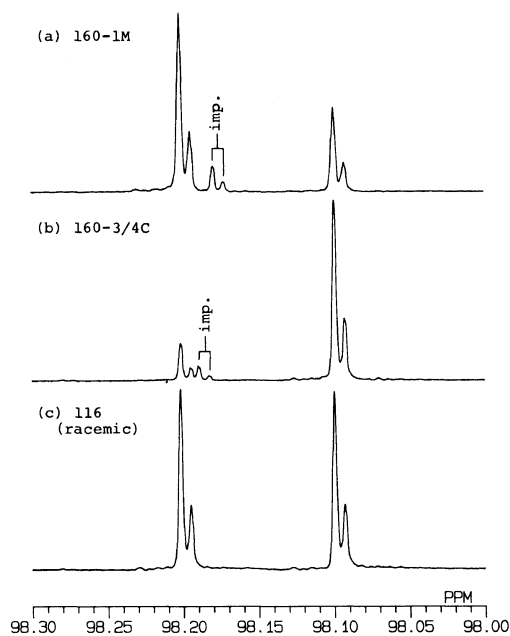


Figure 3. 470 MHz ¹⁹F NMR spectra of bornyl esters of fluorochlorobromoacetic acid measured in CDCl₃ at 35°C.

Optical resolution of CHBrClF as well as the bornyl ester on chiral column such as cellulose tris(3,5-dimethylphenylcarbamate) coated on silica gel was not successful. The anilide of bromotrifluoroacetic acid was par-

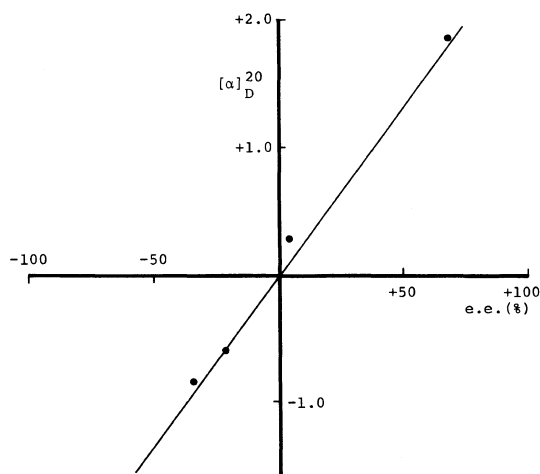


Figure 4. Plots of optical rotation of CHBrClF against the *e.e.* (%).

tially resolved on cellulose tris(4-*t*-butylphenylcarbamate) coated on silica gel. Extensive studies are being made on the optical resolution of various derivatives of FCBAAs using chiral HPLC stationary phases, and on the conversion of the resolved FCBAAs into the optically active fluorochlorobromoacetaldehydes and their polymerization. The results obtained in the present work will provide the basis for understanding

Table IV. ^{13}C NMR chemical shift of bornyl ester of fluorochlorobromoacetic acid (160–1M)

Carbon	$\delta(-)^a$	$\delta(-) - \delta(+)^a$	$(+)/(-)^a$
	ppm	ppm	mol mol $^{-1}$
C1(CH)	85.20	0	—
C2(q-C)	49.46	0.0220	32.4/67.6
C3(CH ₂)	26.92	0	—
C4(CH ₂)	27.91	0	—
C5(CH)	44.86	0	—
C6(CH ₂)	36.03	0.1103	33.4/66.6
C7(q-C)	48.21	0	—
CH ₃ (C2)	13.40	0.0165	29.9/70.1
CH ₃ (C7)	18.84	0	—
	19.64	0	—
C=O ^b	161.68	0.0082	n.d.
CBrClF ^c	96.27	-0.0799	31.5/68.5

^a The isomers which give (+)- and (-)-CHBrClF's are represented by (+) and (-), respectively.

^b $J_{\text{CF}} = 28.09$ Hz.

^c $J_{\text{CF}} = 314.89$ Hz.

the optical activity of poly(fluorochlorobromoacetaldehyde).

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