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^{1}H NMR AND IR SPECTRA OF METHYL DICHLOROPROPANOATES AND BUTANOATES

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Abstract—Methyl dichloropropanoates and butanoates were synthesized and their ^{1}H NMR and IR spectra were studied. Comparisons were made with the spectral characteristics of corresponding monochlorocompounds. Special attention was given to the elucidation of the characteristic spectral features associated with particular chlorine substitution patterns. The ^{1}H NMR of erythro and threo methyl 2,3-dichlorobutanoates were analyzed using a computer program MAOCON, a modified LAOCOON 3 program. In the spectrum of the threo form the order of the chemical shifts of protons on asymmetric carbons seems to be opposite to that reported in earlier literature. Also vicinal coupling constants J_{23} were found to be greater than those reported earlier.

In an earlier paper[1] we reported the IR, ^{13}C NMR and ^{1}H NMR behavior of methyl esters of all the isomeric monochlorocarboxylic acids from propanoic to hexanoic acid. As a logical extension we have carried out systematic investigation of a number of chlorinated esters in order to elucidate the spectral differences (IR, ^{1}H NMR, ^{13}C NMR and mass spectral) caused by introduction of a second chlorine substituent, substitution pattern of the two chlorine atoms and variations in the chain length. The stereochemical differences in configuration are reflected in the spectra of diastereomeric forms.

In this paper the IR and ^{1}H NMR spectra of methyl dichloropropanoates and butanoates are considered by comparing them with those of corresponding monochloroesters. 2,3-Dichlorobutanoate displays two diastereomeric forms, namely, erythro and threo isomers originating from the existence of two asymmetric carbon atoms. The differences observed in the spectra of these diastereomeric structures are discussed. The sensitivity of ^{1}H NMR and ^{13}C NMR towards differences in stereochemical configurations is well established, though the papers illustrating NMR spectral differences of diastereomers are few in number. Differences observed in the ^{1}H NMR spectra of diastereomers reflect differences in the average stereochemical environment of the protons. Extension of the carbon chain increases the number of different chlorine combinations since the generation of two asymmetric carbon atoms results in the occurrence of diastereomeric forms. Several diastereomeric pairs occur with dichloropentanoates and hexanoates. To learn about the possible general spectral tendencies exhibited by a certain diastereomeric form, further investigations are being carried out and a more concise discussion will be given later.

EXPERIMENTAL

Materials and Methods. Methyl 2,2-dichloropropanoate and methyl 2,2-dichlorobutanoate were obtained by synthesizing[2] corresponding acids and converting them to esters by the usual H_2SO_4-methanol method. Methyl 2,3-dichloropropanoate, methyl 3,4-dichlorobutanoate and racemic erythro methyl 2,3-dichlorobutanoate were prepared by chlorination[3] of unsaturated esters. Racemic erythro 2,3-dichlorobutanoic acid[3] was converted to racemic threo form[4] which after esterification gives threo methyl 2,3-dichlorobutanoate. Methyl 3,3-dichloropropanoate was synthesized by HCl addition to propiolic acid (Fluka AG).[1,4] Methyl 2,4-dichlorobutanoate was obtained when 4-chlorobutanoyl chloride (Merck) was chlorinated with sulfuryl chloride.[5] Methyl 3,3-dichlorobutanoate was prepared according to the directions given in a German patent.[6] Methyl 4,4-dichlorobutanoate was the main product when 4-chlorobutanoyl chloride was chlorinated. After distillation this and the preceding compounds were purified by preparative GLC before spectral analyses. Fig. 1 illustrates the gas chromatographic elution order of the above compounds.

^{1}H NMR spectra were run with 60 MHz Perkin–Elmer R 12 B Spectrometer in carbon tetrachloride solutions (5–10%) with TMS as a reference material.

IR spectra were recorded on a Perkin–Elmer 283 Infrared Spectrometer. 5 μl samples of pure esters were used in a standard Perkin–Elmer liquid cell.

GLC analyses were carried out by use of a glass capillary column connected to a Varian 2400 gas chromatograph.

RESULTS AND DISCUSSION

^{1}H NMR Spectra. ^{1}H NMR shifts for dichloroesters are given in Table 1. The spectra were compared with those of the corresponding monochloroesters.[1] The signal position of the methoxy group protons varies between 3.67 and 3.90 δ slightly downfield from that reported for corresponding monochloroesters. Introduction of a second chlorine atom to C_2 seems to have the greatest effect on the OCH_3 group resonance and in fact greater than with introduction of the first chlorine.

Introduction of a second chlorine at the terminal CH_2Cl group of the monochloroesters[1] causes a constant downfield shift of 2.3 ppm the terminal $CHCl_2$ group resonance signal appearing at about 6.0 δ. It seems to show a small diamagnetic shift with increasing carbon chain; 6.07 δ for 3,3-dichloropropanoate and 5.92 δ for 4,4-dichlorobutanoate. This tendency was clearly demonstrated by our experiments with methyl dichloroacetate 6.45 δ, methyl 5,5-dichloropentananoate ~5.8 δ and methyl 6,6-dichlorohexanoate ~5.8 δ for terminal $CHCl_2$ group resonances.

The determination of the exact resonance position of the CH_2Cl group of dichloroesters is complicated by the overlapping of this resonance with that of the ester OCH_3 group.

The ^{1}H NMR spectra of erythro and threo 2,3-dichlorobutanoates were analyzed as ABX spin systems

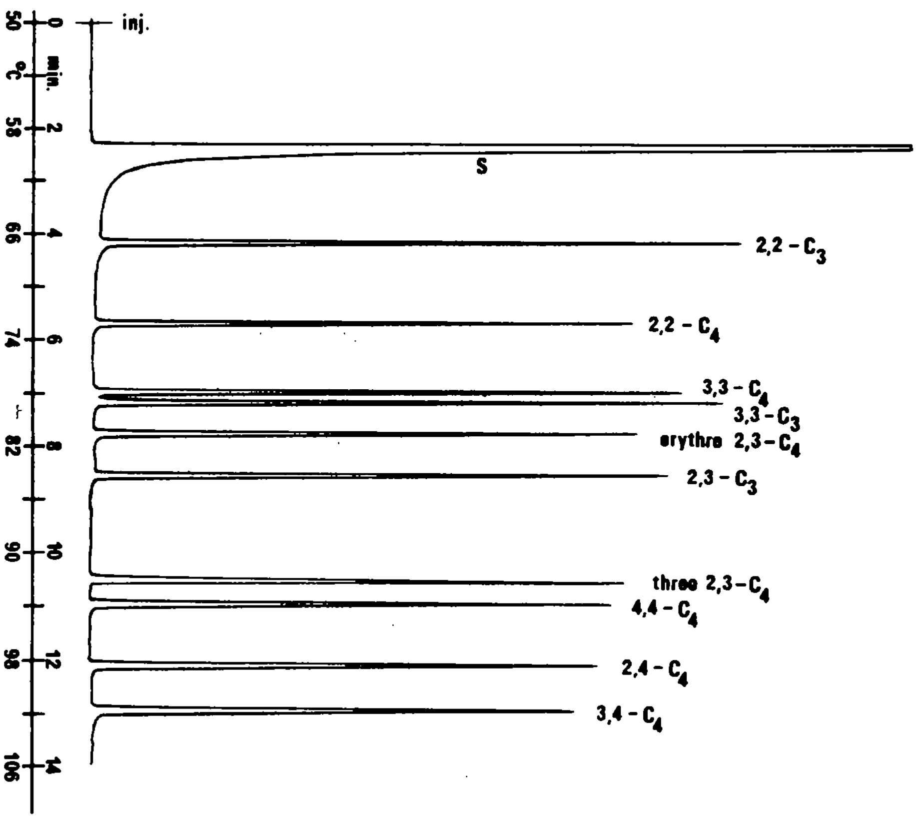

Fig. 1. Gas chromatogram of a mixture of methyl dichloropropanoates and butanoates. Column (165 ft × 0.012 in. I.D. 5% Carbowax 20 M) programmed from 50°C at 4C°/min. Carrier gas N_2 and flow rate 1.4 ml/min.

Table 1. ^1H NMR shifts of methyl dichloropropanoates and butanoates.

Compound	Chemical shift, (δ), multiplicity[a]				
	Protons attached to				
	$COOCH_3$	C_2	C_3	C_4	J (Hz)
2,2-C_3	3.89, s	-	2.28, s		
2,3-C_3 [b]	3.80, s	4.30, m	3.70(H_{3A}),c 3.89(H_{3B}),c		J_{23A}∿5.2, J_{23B}∿8.9, J_{3A3B}∿-11.0
3,3-C_3	3.70, s	3.18, d	6.01, t		J_{23}∿6.7
2,2-C_4	3.84, s	-	2.41, q	1.16, t	J_{34}∿7.1
2,3-C_4(E)	3.77, s	4.11, c	4.26, c	1.64, d	J_{23}∿9.2, J_{34}∿6.6
2,3-C_4(T)	3.78, s	4.35, c	4.38, c	1.65, d	J_{23}∿5.4, J_{34}∿6.9
2,4-C_4	3.77, s	4.48, m	2.37, m	3.67, t	J_{23}∿6.0, J_{34}∿6.1
3,3-C_4	3.73, s	3.30, s	-	2.35, s	
3,4-C_4 [e]	3.69, s	2.72(H_{2A}),c 3.01(H_{2B}),c	4.38, m	[illegible](H_{4A}),c [illegible](H_{4B}),c	J_{2A2B}∿-16.4, J_{2A3}∿7.6, J_{2B3}∿5.4, J_{4A4B}∿-12.8, J_{34A}∿8.4, J_{34B}∿4.1
4,4-C_4 [f]	3.64, s	2.52, c	2.52, c	5.88, m	J_{24}∿1.5, J_{34}∿5.6

[a] s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, c, complex absorption.

[b] Iterated parameters by MAOCON. They are in good agreement with parameters given in literature[15] for corresponding ethyl ester.

[e] Best fit values from a computer analysis by MAOCON.[7]

[f] Estimation of J_{23} by first order approximation did not give a satisfactory result due to the complex cumulated absorption of protons H_2 and H_3.

and computer simulation and iteration were performed by a modified LAOCOON 3 program called MAOCON.[7] Chartier and Vessière[8] have reported for these diastereomers the following parameters:

	$\delta_{H(4)}$	J_{34}	$\delta_{H(3)}$	J_{23}	$\delta_{H(2)}$	δ_{OCH_3}
Erythro	1.67	6.5	4.26	2.8	4.21	3.82
Threo	1.64	6.8	4.30	2.0	4.47	3.81

The chemical shifts of H(3) and H(2) in the case of the threo isomer are close to each other and $\delta_{H(3)}$ appears rather slightly downfield from $\delta_{H(2)}$. Figure 2 illustrates both the observed and iterated spectra for these diastereomers. The intensity distribution of the simulated AB part of the threo form with the approximation that $\delta_{H(2)}$ appears at lower field from $\delta_{H(3)}$ was opposite to that observed. Analyses of the spectra by MAOCON led to distinctively greater vicinal coupling constants J_{23} 9.2 Hz and 5.4 Hz for erythro and threo, respectively. Computer simulations with vicinal coupling constants 2.0 and 2.8 Hz reported by Chartier and Vessière[8] resulted in AB parts with a too narrow shift range compared with the experimental spectra.

Analyses of the vicinal coupling constants of methyl dichloropentanoates gave higher values and that led us to test higher values also for erythro and threo 2,3-dichlorobutanoates. This discrepancy between the vicinal coupling constants of Chartier and Vessière[8] and ours is too great to be attributed solely to different rotamer populations because both spectra were recorded in car-

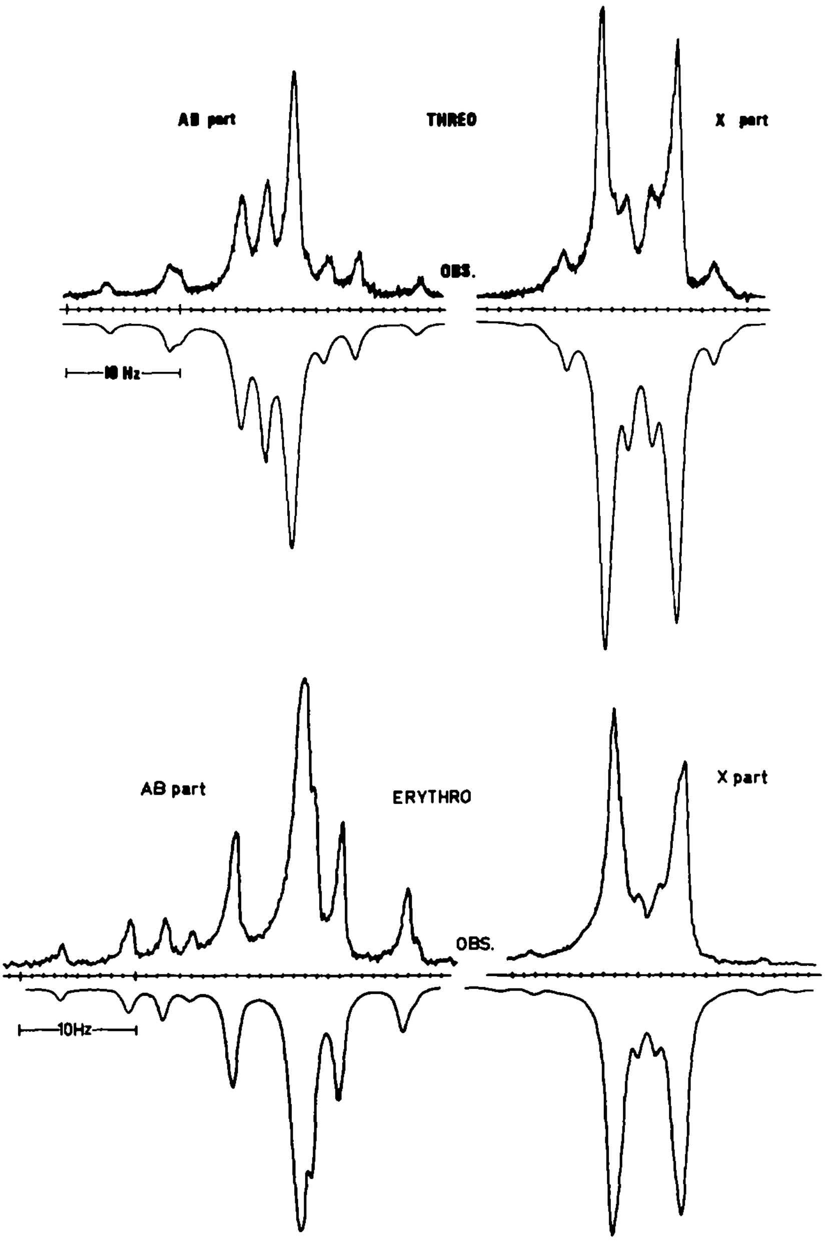

Fig. 2. The observed and iterated ^{1}H NMR spectra of methyl 2,3-dichlorobutanoates.

bon tetrachloride solutions. The chemical shifts as well as the best fit values for coupling constants are presented in Table 1. The calculated spectra in Fig. 2 were computed by using these parameter values.

IR Spectra. Our interest is mainly directed to revealing those spectral details associated with a particular chlorine substitution and to those indicating dependence on the chlorine number. The spectra of the esters of C_3 and C_4 acids require a chapter by themselves because of the great relative proportion of carbomethoxyl group and the possible ability of two chlorine atoms to effect (more) profoundly the relative rotamer populations by steric crowding in these very short molecules. With long chain esters, the carbon chains are folded with no regular manner giving rise to the existence of several rotational isomers, the absorptions of which will deviate from each other to some extent at least in regions associated with C–C streching and C–H bending vibrations.[9] The spectra of the liquid samples are then to be taken as summations over the various rotamers. In heavily substituted non-folded small molecules, however, steric interactions may influence considerably the mutual relative stabilities of the possible rotamers resulting in an energetically favoured rotamer pair or even a dominating single rotamer the spectrum being then more or less that of two or one rotamer only.[10]

Characteristic IR absorptions are listed in Table 2. The carbonyl stretching absorption occuring near 1750 cm^{-1} is as expected the most intense band in the spectra. Two electronegative chlorine substituents seem to cause only a very slight shift to higher frequency compared with corresponding monochloroesters.[1]

C–H Streching vibrations give rise to three absorption bands in the 3000 cm^{-1} region,[9,11] namely, at ~ 3000 cm^{-1}, at ~2957 cm^{-1} and at ~2845 cm^{-1}, the 2957 cm^{-1} band being of highest intensity and the 2845 cm^{-1} band that of lowest intensity. Any specific absorption due to the C–H stretching of the ester methyl group could not be recognized.

The C–H bending vibrations of methylene group have been extensively investigated with n-paraffins.[9] The resulting absorption bands are most frequently observed at 1460–1465 cm^{-1} and at 720 cm^{-1}.[11] Only 2,2-dichlorobutanoate displays a poorly resolved band at slightly lower frequency ~1455 cm^{-1} the others showing only weakly discernible shoulders. On the other hand these weak absorptions can equally be attributed to C–Me asymmetric bending. A methylene group next to a carbomethoxyl group is expected to absorb at a lower frequency[9] and compounds 3,3-dichloropropanoate, 3,3-dichlorobutanoate and 3,4 dichlorobutanoate (and in 4,4-dichlorobutanoate as an unresolved shoulder) show a weak absorption band near 1410 cm^{-1} (possible) for this bending vibration. The neighbouring electronegative chlorine substituents may, of course, also influence both the frequency and the intensity of this band. The quite strong bands occuring between these weak absorptions near 1440 cm^{-1} are typical of methyl esters arising from O–CH_3 symmetric bending.[12]

The terminal methyl group displays the symmetrical bending absorption at 1380 cm^{-1}. A neighbouring chlorine substituent is known to enhance the intensity by changing the polarizability of the terminal methyl.[13]

The intensity of the doublet bands at ~1360 and ~1380 cm^{-1} is in erythro 2,3-dichlorobutanoate comparatively higher than in the threo form. Further the erythro form gives rise to a medium sized absorption band at 1054 cm^{-1} and a strong band at 1027 cm^{-1} which are entirely missing from the spectrum of the threo form. The most intense of the C–O single bond vibrations is usually the highest asymmetric streching frequency near 1220 cm^{-1} for normal saturated esters. The C–O single

Table 2. Characteristic IR absorptions of methyl dichloropropanoates and butanoates

Compound	Bands (cm^{-1}), intensity [a]								
2,2-C_3	3005 w sp	2960 m sp	1750 s b	1445 s sp	-	1380 s sp	1345 w sh	1275 s b	660 s sp
2,3-C_3	3005 w sp	2955 m sp	1750 s b	1440 s sp	-	-	1360 m sp	1200 s b	700 s sp
3,3-C_3	3015 w b	2955 m sp	1740 s b	1440 s sp	1410 m sp	-	1365 s sp	1230 s b	695 s sp
2,2-C_4	2990 w sp	2955 w sp	1750 s sp	1440 m sp	-	1380 w sp	1345 w sh	1250 s sp	830 m sp
2,3-C_4,E	2995 m sp	2955 m sp	1750 s sp	1440 s sp	-	1380 m sp	1360 m sp	1170 s sp	655 s sp
2,3-C_4,T	2990 w sp	2955 m sp	1750 s sp	1440 m sp	-	1380 w sp	1360 w sp	1290 s sp	805 m sp 750 m sp
2,4-C_4	3000 w b	2955 w sp	1750 s sp	1440 m sp	-	-	1365 w b	1170 m sp	725 w sp
3,3-C_4	3000 w b	2955 w sp	1750 s sp	1440 m sp	1410 w b	1380 m sp	1355 m sp	1205 s sp	660 m sp
3,4-C_4	3000 w b	2955 m sp	1740 s sp	1440 m sp	1410 w b	-	1370 m sp	1215 m b	790 m sp
4,4-C_4	3000 w b	2955 m sp	1740 s sp	1440 s sp	1415 m sh	-	1370 m sp	1200 s sp	755 s sp
	Note b	Note b	Note c	Note d	Note e	Note f	-	Note g	Note h

[a] s, strong; m, medium; w, weak; sp, sharp; b, broad; sh, shoulder.
[b] C–H streching, unspecified.
[c] carbonyl streching.
[d] O-Methyl symmetric bending.
[e] –CH_2CO– scissoring
[f] C-Methyl symmetric bending.
[g] The strongest band in the C–O streching region.
[h] The strongest band in the C–Cl streching region.

bond of carbomethoxyl group is stiffer than the other C–O single bonds due to resonance which tends to localize the higher vibration in the C–O bond.[9] This absorption is visible in all spectra. The 1054 cm^{-1} band in the spectrum of erythro form is ascribable to O–CH_3 asymmetric vibration. It is known to be more sensitive to branching changes in the alcohol part of the ester than the higher frequency vibration.[9] This lower band is met near 1050 cm^{-1} in acetates of primary alcohols and frequently it appears in the spectra of other saturated esters of primary alcohols but usually not as clear as in the acetates. The streching frequency involves some interaction with all the C–C bonds in the molecule. There should, therefore, be some difference in the stereochemical environments of the $COOCH_3$ groups in the favoured conformations of erythro and threo forms.

On the basis of IR data and the ^{1}H NMR parameters we suggest the preferred conformations of erythro and threo 2,3-dichlorobutanoates to be those presented in Fig. 3.

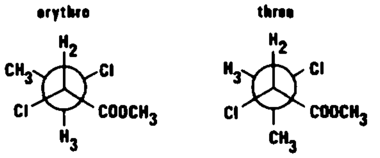

Fig. 3. Preferred conformations for racemic erythro and threo methyl 2,3-dichlorobutanoates.

The differences observed in the chlorine absorption region[14]560–830 cm^{-1} are given in Table 2 in which the strongest absorption bands of this region are listed in the last column.

Sinclair *et al.*[11] have studied the IR spectra of long-chain fatty acid esters and according to them an estimate of the mean chain length may be obtained from the determination of the intensity of 720 cm^{-1} methylene rocking band. This band was not even observable in the spectra of these short molecules.

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