

Chlorination of Carboxylic Acid Derivatives. X. Chlorine Substitution on the Alcohol Chain of Aliphatic C₂–C₈ Alkyl Chloro-, Dichloro- and Trichloroacetates

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Many investigations have been published on the chlorination of aliphatic alkyl acetates,¹ but few on the chlorination of alkyl chloroacetates. Waddle and Adkins have studied the chlorination of butyl trichloroacetates² and Gayler and Waddle the chlorination of propyl trichloroacetates.³ The monochloro products of these esters were saponified and analyzed as the corresponding alcohols.

The present paper reports the isomer distributions of the monochloro products formed in liquid phase chlorinations of aliphatic C₂–C₈ alkyl

Table 1. The relative quantities^a of monochloro isomers formed in the chlorinations of aliphatic C₂–C₈ *n*-alkyl acetates (A), chloroacetates (C), dichloroacetates (D) and trichloroacetates (T).

Chain length	Substrate	Isomeric monochlorinated esters							
		1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl
C ₂	A	170	100						
	C	175	100						
	D	156	100						
	T	134	100						
C ₃	A	46	116	100					
	C	32	107	100					
	D	23	105	100					
	T	19	104	100					
C ₄	A	29	94	179	100				
	C	17	69	163	100				
	D	11	61	151	100				
	T	9	60	150	100				
C ₅	A	27	68	161	179	100			
	C	15	54	159	195	100			
	D	12	50	141	183	100			
	T	8	40	107	153	100			
C ₆	A	21	62	132	173	182	100		
	C	15	48	126	188	193	100		
	D	9	41	104	161	174	100		
	T	7	38	89	148	166	100		
C ₇	A	22	63	128	154	171	176	100	
	C	15	47	113	143	173	178	100	
	D	9	40	101	140	171	175	100	
	T	7	35	83	125	155	158	100	
C ₈	A	22	65	127	151	166	176	182	100
	C	15	44	113	141	159	175	179	100
	D	9	40	97	129	145	163	164	100
	T	7	32	82	118	132	145	152	100

^a Relative to the ω -chloro isomers (= 100); the values of acetic acid derivatives (A) are taken from an earlier paper.¹ Values are averages of two independent experiments and agree to within $\pm 4\%$.

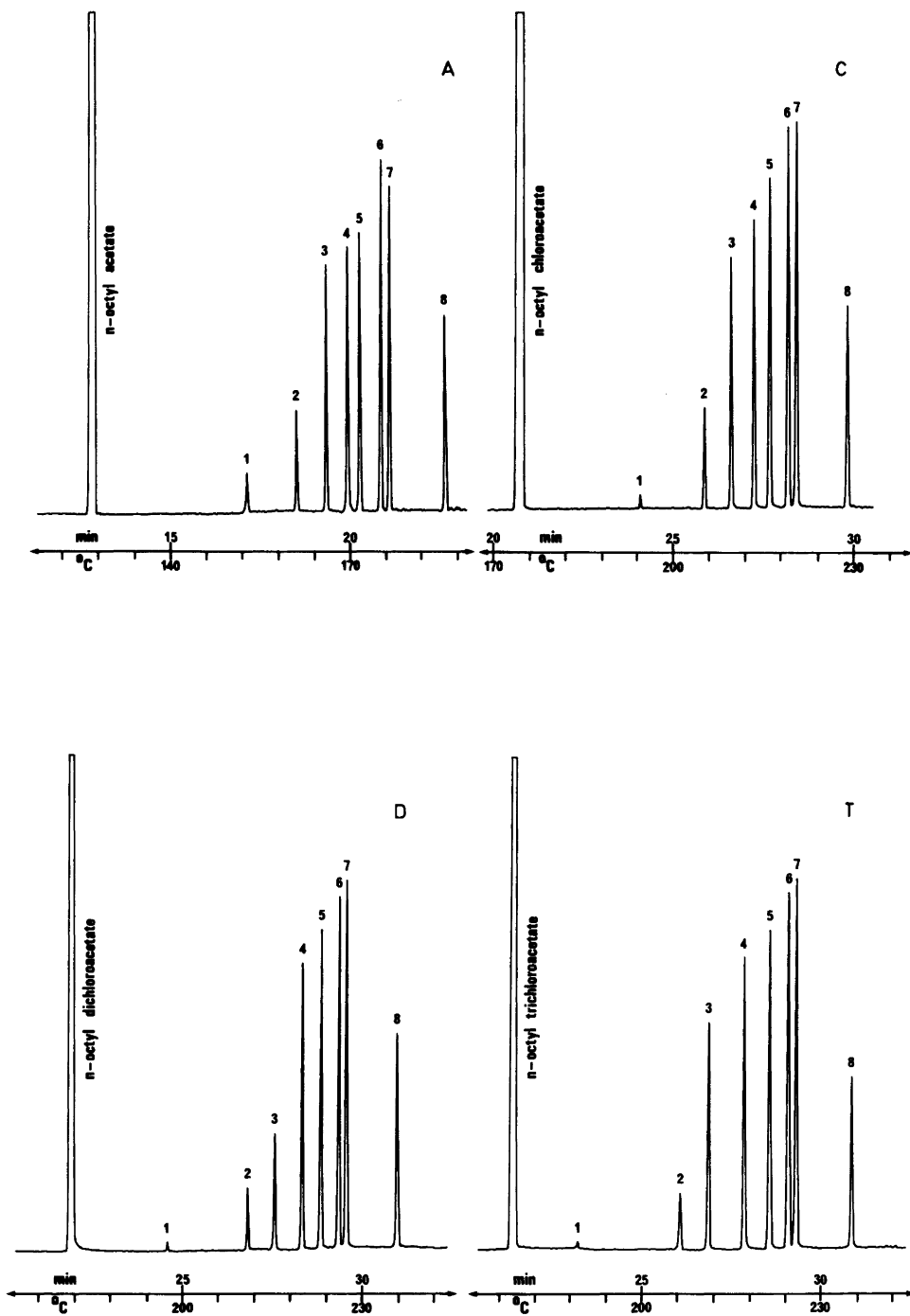


Fig. 1. Chromatograms of monochlorinated *n*-octyl acetates (A), chloroacetates (C), dichloroacetates (D) and trichloroacetates (T), analyzed on OV-351 quartz capillary column. Temperature programme from 50 °C at 6 °C/min. The peak number indicates the position of the Cl-substituent.

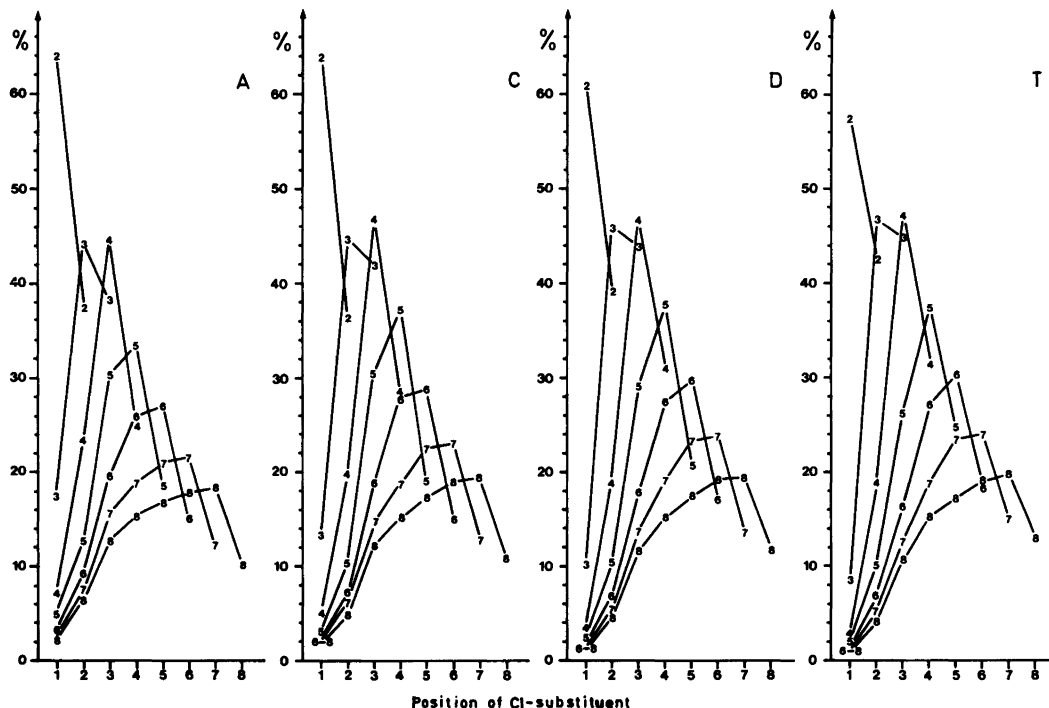


Fig. 2. Isomer distribution of monochlorinated C_2-C_8 *n*-alkyl acetates (A), chloroacetates (C), dichloroacetates (D) and trichloroacetates (T) based on GLC analyses. The numbers denote the alcohol chain length.

esters of chloroacetic, dichloroacetic and trichloroacetic acids. The results are compared with those of earlier chlorinations of acetic acid derivatives given in Ref. 1.

Results. The monochlorinated products were determined by gas-liquid chromatography (GLC) and gas-liquid chromatography-mass spectrometry (GLC-MS). Fig. 1 presents the chromatograms of monochlorinated octyl acetates,¹ and chloro-, dichloro- and trichloroacetates. As can be seen, complete separation of the isomers was achieved on a polar column under suitable operating conditions. The products were eluted in direct order from 1-chloro to ω -chloro compounds, as were the corresponding alkyl acetates.¹ On polar OV-351 phase the retention times of the corresponding chloroalkyl esters increased in the order chloroacetate < trichloroacetate < dichloroacetate, except for 1-chloroalkyl esters where the trichloro isomers were eluted before the monochloro isomers (Fig. 1). A quite different elution order was observed on a non-polar SE-30 column.⁴

Fig. 2 illustrates the isomer distributions of monochlorinated products. The values for

chloroalkyl acetates are taken from an earlier paper.¹ The relative quantities are presented in Tables 1 and 2. As can be seen, the main products were always the ($\omega-1$)-chloro isomers. The deactivation at the 1-position increases with increase in the degree of chlorination of the adjacent acetoxy group⁵ (Table 2). The effect is smaller at positions further away. In the case of butyl acetate, for example, the substitution in the 2-position is 3.2 times as great as in the 1-position. The corresponding ratios in butyl chloro-, dichloro- and trichloroacetates are 4.1, 5.5 and 6.7, respectively.

The 1-chloroalkyl esters of chlorinated acetic acids are somewhat unstable. Hydrogen chloride is clearly lost during storage leading to the formation of unsaturated compounds, particularly in the case of 1-chloroalkyl trichloroacetates. Thus, if hydrogen chloride is lost during the chlorination^{1,6} or GLC analysis, the true proportions of monochlorinated products will be greater than those given in this paper.

Experimental. Aliphatic C_2-C_8 *n*-alkyl chloro-, dichloro- and trichloroacetates were prepared in our laboratory as described earlier.⁷

Table 2. The relative quantities^a of monochloro isomers formed in the chlorinations of aliphatic C₂–C₈ *n*-alkyl chloroacetates (C), dichloroacetates (D) and trichloroacetates (T).

Chain length	Substrate	Isomeric monochlorinated esters							
		1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl
C ₂	C	101	98						
	D	97	105						
	T	91	115						
C ₃	C	76	101	110					
	D	58	104	115					
	T	48	106	117					
C ₄	C	70	85	105	115				
	D	49	80	105	124				
	T	39	80	105	126				
C ₅	C	58	82	101	111	102			
	D	48	82	96	112	110			
	T	40	80	87	111	130			
C ₆	C	72	77	95	109	106	100		
	D	47	74	90	106	109	114		
	T	38	74	83	105	112	123		
C ₇	C	74	79	94	98	107	107	106	
	D	44	70	87	100	111	110	111	
	T	37	69	80	99	111	111	123	
C ₈	C	73	73	95	99	102	106	105	107
	D	50	71	90	99	102	108	105	117
	T	41	64	84	100	102	106	108	129

^aRelative (=100) to the corresponding isomers formed in the chlorination of *n*-alkyl acetates (see Table 1).

The chlorinations were carried out with chlorine in the liquid phase at room temperature.¹ The amounts of higher chlorinated products were only a few per cent and no chlorine substitution in the acid chain in chloro- and dichloroacetates could be observed.

GLC analyses were run on a Perkin-Elmer Model Sigma 3 instrument equipped with a fused silica OV-351 quartz capillary column (25 m × 0.32 mm I.D.), supplied by Orion Analytica (Espoo, Finland). The operating conditions used are given in Ref. 4.

GLC-MS data were recorded as described earlier.¹ The mass spectra will be published later.

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