The Kinetics and Mechanisms of Additions to Olefinic Substances. Part XI.[1] Stereochemistry of Addition of Chlorine Acetate and of Chlorine to Some Unsaturated Compounds

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The proportions of diastereoisomeric acetoxy-chlorides formed by addition of chlorine acetate to methyl cinnamate and to some of its derivatives, to phenanthrene, to acenaphthylene, and to cyclohexene have been estimated in acetic acid as solvent under a number of conditions. In a number of cases the ratios differ markedly from those of the same products formed by addition initiated by electrophilic chlorine in the same solvents. Different carbonium ion intermediates must be involved in the reactions initiated by the two reagents: the mechanisms of these reactions are discussed. It is concluded that the reactions initiated by chlorine acetate involve sequences in which the products come largely from chloronium ions, whereas those initiated by chlorine involve sequences in which the products often come from zwitterionic intermediates.

CHLORINE ACETATE (sometimes called acetyl hypochlorite) has been known for a long time;[2] and Bockemuller[3] regarded it as the intermediate responsible for the formation of acetoxy-chlorides from chlorine and olefinic substances in acetic acid. This rather natural interpretation of the formation of these products is now known[4,5] not to be generally correct. Yet there is good kinetic evidence for the participation of chlorine acetate in the chlorination of crotonic acid by hypochlorous acid in the presence of added acetate ions,[6] and from this and the hydrolysis constant of chlorine acetate in slightly aqueous acetic acid,[7] it can be estimated[5] that chlorine acetate is a more reactive electrophile than molecular chlorine. The same is true for aromatic substitution,[7,8] where it has been shown that both molecular chlorine acetate and its protonated form can be effective as electrophiles.

Apart from these studies, there has been little work done on the reaction paths followed in additions initiated by chlorine acetate. In particular, the kinetics and stereochemistry of the reactions were not known at the inception of the present work. In our own[9] and in related[10] studies, acetoxy-chlorides have been recognised from reaction initiated by chlorine in acetic acid with unsaturated compounds of various kinds; so we have now examined the corresponding reactions initiated by chlorine acetate, and have extended them to cover a wider range of olefinic compounds. The results now reported extend those which were given in our preliminary communication;[11] they throw new light on the mechanism of addition of chlorine, as well as establishing some aspects of the mechanism of addition of chlorine acetate. Most compounds discussed in this paper react too rapidly for conventional kinetic studies, which we plan to make on suitable systems.

EXPERIMENTAL

I.r. spectra were recorded by using a Perkin-Elmer 237 grating spectrometer, ^{1}H n.m.r. spectra by using a Varian A60 or a Varian T60 instrument, with tetramethylsilane as internal reference, and u.v. spectra by using a Unicam SP 800 spectrophotometer. Microanalyses are by Dr. A. D. Campbell and his staff, University of Otago, Dunedin. Mass spectral analyses are by Professor R. Hodges, Massey University of Manawatu, Palmerston North, New Zealand, and by Dr. P. D. Woodgate of this Department.

Some of the materials and methods have been described in earlier papers.[1,7-9] Methyl *trans*-cinnamate, from *trans*-cinnamic acid, was recrystallised from ethanol at −10°, and had b.p. 260° at 760 mmHg, m.p. 36° (lit.,[12] 35°). *cis*-Cinnamic acid was prepared essentially as described by Stoermer.[13] The sodium salt (10 g) was irradiated in water by using a low intensity mercury arc lamp (Hanovia photoreactor) for 125 h. The crude product obtained by neutralising the solution with hydrochloric acid was shown by ^{1}H n.m.r. spectroscopy to contain 20% of the *cis*-isomer. The filtrate was evaporated. The residue was extracted with diethyl ether and on removal of solvent and recrystallisation from a mixture of diethyl ether and n-hexane gave *cis*-cinnamic acid, m.p. 57—58° (lit.,[13] 58°). Esterification of this gave methyl *cis*-cinnamate, purified by elution through a short column of silica gel (' S,' Riedel de Haen) with diethyl ether–n-hexane (1 : 9); its purity was established by t.l.c. and by its ^{1}H n.m.r. spectrum.

p-Methoxy-, m.p. 174° (lit.,[14] 174—174·6°), *p*-methyl-, m.p. 196° (lit.,[14] 198·2—199°), *p*-chloro-, m.p. 248° (lit.,[14] 249—250°), and *p*-nitro-*trans*-cinnamic acid, m.p. 286—289° (lit.,[14] 287—289°), were prepared by the methods given in the literature,[14] and gave the corresponding methyl esters having m.p.s: *p*-MeO, 86—87° (lit.,[15] 85—86°); *p*-Me, 56°

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[3] W. Bockemuller and F. W. Hoffmann, *Annalen*, 1935, **519**, 165.
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[5] P. B. D. de la Mare and R. Bolton, ' Electrophilic Additions to Unsaturated Systems,' Elsevier, 1966, ch. 6.
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[9] P. B. D. de la Mare and R. Koenigsberger, *J. Chem. Soc.*, 1964, 5327; P. B. D. de la Mare, A. Singh, E. A. Johnson, R. Koenigsberger, J. S. Lomas, V. Sanchez del Olmo, and A. M. Sexton, *J. Chem. Soc.* (*B*), 1969, 717.
[10] (*a*) M. C. Cabaleiro and M. D. Johnson, *J. Chem. Soc.* (*B*), 1967, 565; (*b*) M. D. Johnson and E. N. Trachtenberg, *ibid.*, 1968, 1018.
[11] P. B. D. de la Mare, C. J. O'Connor, M. J. Rosser, and M. A. Wilson, *Chem. Comm.*, 1970, 731.
[12] J. Kendall and J. E. Booge, *J. Amer. Chem. Soc.*, 1916, **38**, 1712.
[13] R. Stoermer, *Ber.*, 1909, **42**, 4865.
[14] T. A. Wittstruck and E. N. Trachtenberg, *J. Amer. Chem. Soc.*, 1967, **87**, 3803.
[15] G. P. Schiemenz and J. Thobe, *Chem. Ber.*, 1966, **99**, 2663.

(lit.,[15] 55—56°); *p*-Cl, 76° (lit.,[16] 76—76·5°); *p*-NO_2, 155—156° (lit.,[15] 155—157°).

p-Methyl-*cis*-cinnamic acid was prepared essentially by Wittstruck and Trachtenberg's method; [14] it was separated from the mixture of isomers by extraction with n-hexane in a Soxhlet apparatus, and when crystallised from n-hexane had m.p. 77° (lit.,[14] 77·5—79°). From it was prepared *methyl* p-*methyl*-cis-*cinnamate* by the usual procedure; the crude product was passed through a short column of silica gel (' S,' Riedel de Haen) with diethyl ether–n-hexane (1 : 9). After removal of the solvent the residue was crystallised from light petroleum (b.p. 40—60°) at −10° to give the required ester, m.p. 28—30° (Found: C, 74·7; H, 6·8. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·9%). *p*-Chloro-*cis*-cinnamic acid was prepared similarly; [17] fractional precipitation from water gave first the pure *trans*-acid, and then a mixture containing 66% of the *cis*-isomer. This was extracted with water in a Soxhlet apparatus for 2 h; after partial evaporation of the extract, the pure *cis*-acid crystallised out and on recrystallisation from aqueous acetone had m.p. 110° (lit.,[14,17] 110, 114—116°). Its methyl ester had m.p. 30—31° (lit.,[10] 25°).

After photolysis of methyl *p*-nitro-*trans*-cinnamate (13 g) in ethanol (1 l) at *ca.* 40° for three days, the solvent was removed *in vacuo*, and the residue was shown by ^{1}H n.m.r spectroscopy to contain *ca.* 40% of the required *cis*-isomer. The product was treated several times with n-hexane, and removal of solvent from the extracts gave a yellow solid (8 g) which was dissolved in chloroform (30 ml) and chromatographed on alumina deactivated with dilute acetic acid. Elution with diethyl ether–n-hexane (1 : 4) gave *methyl* p-*nitro*-cis-*cinnamate* as pale yellow crystals which after crystallisation from n-hexane had m.p. 86—88° (Found: C, 57·9; H, 4·4; N, 6·8. $C_{10}H_9O_4N$ requires C, 58·0; H, 4·4; N, 6·8%).

We were unsuccessful in preparing *p*-methoxy-*cis*-cinnamic acid or its methyl ester by photolysis of the corresponding *trans*-compounds. Instead, these compounds were prepared *via* *p*-hydroxy-*trans*-cinnamic acid, obtained by the method of Overberger *et al.*,[18] m.p. 205—210° (lit.,[18] 210—211°). This was acetylated with acetic anhydride in pyridine to give *p*-acetoxy-*trans*-cinnamic acid, m.p. 205° (lit.,[18] 205—206°). This was photolysed in a mixture of acetone and methanol for three days. The crude product contained *ca.* 60% of the *cis*-isomer, as judged by ^{1}H n.m.r. spectroscopy. The brown solid obtained by removal of the solvent was treated repeatedly with n-hexane–diethyl ether (9 : 1). The crude *cis*-acid hydrolysed on standing with excess of concentrated aqueous sodium hydroxide for 2 h. The reaction mixture was neutralised and extracted exhaustively with diethyl ether. Evaporation of the dried ether extracts gave *p*-hydroxy-*cis*-cinnamic acid as a solid which after crystallisation from acetone–chloroform had m.p. 129—132° (lit.,[19,20] 126—127, 130—131°). Attempted methylation by the use of diazomethane failed in our hands, and we found that this compound undergoes isomerisation readily. Methylation with a slight excess of methyl iodide and anhydrous potassium carbonate, however, gave methyl *p*-methoxy-*cis*-cinnamate, still containing a small proportion (<10%) of the *trans*-isomer (Found: C, 68·8; H, 6·5. Calc. for $C_{11}H_{12}O_3$: C, 68·7; H, 6·3%).

The ^{1}H n.m.r. spectra of these acids and their methyl esters are recorded for reference purposes in Table 1.

Acenaphthylene (K and K Laboratories) was purified through its picrate, m.p. 201°, and was recrystallised from

TABLE 1

^{1}H N.m.r. spectra of cinnamic acids and their derivatives, $R^1C_6H_4CH{:}CHCO_2R^2$

Geometric isomer	R^1	R^2	Chemical shifts (τ) [a] 2-H	3-H	ArH	Me (R^1)	Me (R^2)	Coupling constants $J_{2,3}$/Hz [a]	Solvent
trans	*p*-HO	H	3·7	2·3	3·1, 2·45			16·0	$(CD_3)_2CO$
cis	*p*-HO	H	4·15	3·1	3·1, 2·2			12·4	$(CD_3)_2CO$
trans	*p*-MeO	H	3·6 (3·6)	2·1 (2·4)	3·0, 2·4	6·0		16 (16) [b]	CF_3CO_2H
trans	*p*-AcO	H	3·5	2·3	2·8, 2·25	7·7		16·0	$(CD_3)_2CO$
cis	*p*-AcO	H	4·05	3·1	2·9, 2·3	7·7		12·4	$(CD_3)_2SO$
trans	*p*-Me	H	3·6 (3·5)	2·3 (2·4)	2·8, 2·5	7·6		16 (16) [b]	$CDCl_3$
cis	*p*-Me	H	4·2 (4·1)	3·0 (3·1)	2·8, 2·5	7·7		12·5	$CDCl_3$
trans	H	H	3·6 (3·5)	2·2 (2·3)	2·8—2·4(m)			16 (16) [b]	$CDCl_3$
cis	H	H	4·0 (4·0)	3·1 (3·0)	2·8—2·4(m)			12·5	$CDCl_3$
trans	*p*-Cl	H	3·5 (3·5)	2·3 (2·3)	2·6, 2·3			16 (16) [b]	$(CD_3)_2CO$
cis	*p*-Cl	H	4·0 (4·0)	2·8 (3·0)	2·7, 2·5			12·5	$CDCl_3$
trans	*p*-O_2N	H	3·3 (3·3) [b]	2·3 (2·3) [b]	2·0, 1·7			16 (16) [b]	$(CD_3)_2SO$
cis	*p*-O_2N	H	(3·7)	(2·8)					$CDCl_3$
trans	*p*-MeO	Me	3·7	2·4	3·2, 2·5	6·2	6·2	16·0	$CDCl_3$
cis	*p*-MeO	Me	4·15	3·1	3·1, 2·3	6·2	6·2	12·4	$CDCl_3$
trans	*p*-Me	Me	3·6	2·4	2·9, 2·6	7·6	6·2	16·1	$CDCl_3$
cis	*p*-Me	Me	4·2	3·2	3·0, 2·5	7·7	6·3	12·4	$CDCl_3$
trans	H	Me	3·6	2·3	2·5—2·9(m)		6·2	16·0	$CDCl_3$
cis	H	Me	4·1	3·1	2·8—2·4(m)		6·4	12·4	$CDCl_3$
trans	*p*-Cl	Me	3·6	2·4	2·6		6·2	16·0	$CDCl_3$
cis	*p*-Cl	Me	4·1	3·1	2·7, 2·5		6·3	12·5	$CDCl_3$
trans	*p*-O_2N	Me	3·5	2·3	2·3, 1·8		6·2	16·1	$CDCl_3$
cis	*p*-O_2N	Me	3·9	3·0	2·4, 1·8		6·3	12·4	$CDCl_3$

[a] Values are from this work, for $CDCl_3$ solutions except where otherwise stated. Literature values [14,21] are in parentheses; they refer to Me_2CO as solvent and were extrapolated to infinite dilution. [b] Spectra in Me_2SO.

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[19] W. A. Roth and R. Stoermer, *Ber.*, 1913, **46**, 260.

[20] A. J. Meritt and L. Preedman, U.S. Pat. 3,094,471/1963 (*Chem. Abs.*, 1964, **60**, P1655b).

95% ethanol; m.p. 94° (lit.,[21] 92—93°). Its ^{1}H n.m.r. spectrum (CCl_4) showed no evidence of signals at τ 5·8. Cyclohexene (B.D.H.) was fractionally distilled, a column packed with glass helices being used, b.p. 82° at 760 mmHg. *trans*-1,2-Dichloroacenaphthene was prepared from acenaphthylene and benzene iododichloride according to the method of Cristol *et al.*,[22] and had m.p. 68—69° (lit.,[22] 67—68°). Its ^{1}H n.m.r. spectrum (CCl_4) contained a singlet at τ 4·32. *cis*-1,2-Dichloroacenaphthene was prepared from acenaphthylene and chlorine in benzene as also recommended by Cristol *et al.*;[22] it had m.p. 116° (lit.,[22] 116°) and its ^{1}H n.m.r. spectrum (CCl_4) had a singlet at τ 4·48, well resolved in this solvent from that of its geometric isomer. *trans*-1-Acetoxy-2-chlorocyclohexane was prepared from the chlorohydrin [23] by acetylation with acetic anhydride and sulphuric acid.[24] The distilled product had b.p. 91—92° at 9 mmHg, (lit.,[4] 98·0—98·5 at 12 mmHg); its ^{1}H n.m.r. spectrum (CCl_4) had a singlet at τ 7·92. This was well resolved from the corresponding singlet at τ 8·05 attributable to *cis*-1-acetoxy-2-chlorocyclohexane which we obtained in admixture with its isomer by first preparing 2-chlorocyclohexanone from *trans*-2-chlorocyclohexanol by oxidation with sodium dichromate and sulphuric acid.[25] The ketone was reduced with t-butylmagnesium chloride and the resulting mixture of alcohols was acetylated in the usual way to give the required mixture of acetates.

Solutions of chlorine acetate were prepared by stirring a solution of chlorine in the required solvent with dried, finely divided mercuric acetate. The mixture was then filtered and distilled under reduced pressure, first and last fractions being discarded. This procedure gave colourless samples containing up to 0·30M-chlorine acetate, determined by adding a known volume to excess of aqueous potassium iodide and titrating the liberated iodine with standardised sodium thiosulphate. Chlorinations were carried out by mixing appropriate volumes of solutions of the unsaturated compound and of the chlorinating agent dissolved in acetic acid, or in aqueous acetic acid, and reactions were allowed to proceed in the dark at 25°, normally for the time required for complete reaction.

Two methods for working-up the products were used; in one, the solvent together with any volatile material was removed by evaporation at low pressure; benzene was then added and evaporated off, and the residue was made up to an appropriate volume in the solvent required for spectroscopic examination. In the second, the reaction mixture was added to a sufficient volume of diethyl ether, and the acetic acid and any added electrolytes were extracted out by exhaustive washing with water. The ether extract was then dried ($MgSO_4$) and the solvent was removed under reduced pressure. These two methods were shown to give the same results within experimental error for methyl *trans*-cinnamate, phenanthrene, and acenaphthylene, and no evidence for isomerisation was found when esterifying pure samples of substituted cinnamic acids, including the *cis*-isomers.

In analysing the reaction mixtures, we used ^{1}H n.m.r. spectroscopy, following the general procedure adopted by Johnson and his co-workers.[10] Normally the relative areas of the signals of the methoxycarbonyl groups were used to estimate product ratios, but in a number of cases these values could be checked from the areas of the signals from the acetoxy-groups and from those from the αβ-protons; satisfactory (±3 units %) and often excellent agreement was obtained. In the experiments with added water, where chlorohydrins were formed from the cinnamates, the yields of chlorohydrin were determined from the sum of the areas of the signals for the methoxycarbonyl protons less the sum of the areas of the signals for the acetoxy-protons. Use of this method depends on achieving complete reaction and on the absence of concomitant substitution; both were checked (a) by the fact that reaction without added water gave agreement between the expected areas for the signals of the two groups and (b) because no extraneous signals appeared in the products in the presence of added water.

The four possible racemic chlorohydrins (1 and 2;

TABLE 2

^{1}H N.m.r. spectra of derivatives, $R^1C_6H_4CH(OR^3)\ CHClCO_2R^2$, of 3-aryl-2-chloro-3-hydroxypropanoic acid

Isomer [see formulae (1) and (2)]	R^1	R^3	R^2	Chemical shifts (τ) * 3-H	2-H	Me (R^1)	Me (R^2)	Me (R^3)	Coupling constants $J_{2,3}$/Hz
erythro	*p*-MeO	Ac	Me	4·0	5·4	6·2	6·2	8·0	8·5
threo	*p*-MeO	Ac	Me					7·9	
erythro	*p*-MeO	H	Me	5·0	5·6		6·2		8·5
erythro	3-Cl, 4-OMe	Ac	Me	(4·0)	(5·4)		(6·2)	(7·95)	
				3·9	5·4	6·1	6·2	8·0	9(8·5)
threo	3-Cl, 4-OMe	Ac	Me	3·95	5·4			(7·9)	8·5
erythro	*p*-Me	Ac	Me	(3·9)	(5·4)		(6·2)	(8·0)	
				4·0	5·4	7·7	6·3	8·0	8(8·5)
threo	*p*-Me	Ac	Me				(6·4)	(7·9)	
				3·8	5·4	7·7	6·4	7·9	8(8)
erythro	*p*-Cl	Ac	Me	3·9 (3·9)	5·4 (5·4)		6·2 (6·2)	8·0 (7·9)	8(8)
threo	*p*-Cl	Ac	Me	3·8 (3·8)	5·4		6·3 (6·3)	7·9 (7·9)	7(7)
erythro	*p*-O_2N	Ac	Me	3·8 (3·8)	5·4 (5·4)		6·2 (6·2)	7·9 (7·9)	8(8)
threo	*p*-O_2N	Ac	Me	3·8	5·4		6·3 (6·3)	7·8 (7·8)	7·5
erythro	*p*-O_2N	H	Me	4·8	5·6		6·2		7·5
threo	*p*-O_2N	H	Me	4·7	5·6		6·2		5

* Values are from this work in $CDCl_3$ except where otherwise stated. Literature values [10] are in parentheses and refer to CCl_4 as solvent.

[21] A. R. Katritzky and F. J. Swinborne, *J. Chem. Soc.*, 1965, 6707.

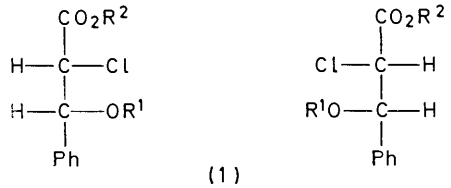
[22] S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *J. Amer. Chem. Soc.*, 1956, **78**, 4939.

[23] G. H. Coleman and H. F. Johnstone, 'Organic Syntheses,' Wiley, New York, 1941, Coll. Vol. I, p. 158.

[24] S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, *J. Amer. Chem. Soc.*, 1948, **70**, 816.

[25] L. T. Sandborn, 'Organic Syntheses,' Wiley, New York, 1941, Coll. Vol. I, p. 340.

$R^1 = R^2 = H$) which could be formed by addition of hypochlorous acid to cinnamic acid have been described.[1]



(1)
(*erythro*)

(2)
(*threo*)

Under all the conditions for which we record the addition of chlorine acetate to methyl *cis*- and *trans*-cinnamate, the only signals detected in the ^1H n.m.r. spectra of the products obtained from the reaction and isolated as indicated above were those of the two racemates (1 and 2; $R^1 = Ac$, $R^2 = Me$); reaction in the presence of sufficient added water gave products with additional signals attributable to the corresponding chlorohydrins (1 and 2; $R^1 = H$, $R^2 = Me$). The products from the substituted methyl cinnamates have extraneous signals. Spectral characteristics are in ref. 1 and Table 2.

TABLE 3

Product proportions and ratios of *trans* : *cis*-addition for the reaction of chlorine acetate (0·01M) with methyl cinnamates ($RC_6H_4CH{:}CHCO_2Me$; 0·01M) in acetic acid at 25°

Geometrical isomer	R	Added electrolyte	Product proportions: 3-acetoxy-3-aryl-2-chloropropanoates (1) and (2) *erythro*	*threo*	*trans* : *cis* ratio
trans	*p*-MeO		84	16	5·3
trans	*p*-MeO	NaOAc [a]	86	14	6·1
trans	*p*-Me		61	39	1·6
trans	*p*-Me	NaOAc [a]	63	37	1·7
trans	H		62	38	1·6
trans	H	NaOAc [a]	64	36	1·8
trans	H	$HClO_4$ [b]	67	32	2·1
trans	*p*-Cl		60	40	1·5
trans	*p*-Cl	NaOAc [a]	61	39	1·6
trans	*p*-O_2N		77	23	3·3
trans	*p*-O_2N	NaOAc [a]	78	22	3·5
trans	*p*-O_2N	$HClO_4$ [b]	73	27	2·7
cis	*p*-MeO		88	12	0·14
cis	*p*-MeO	NaOAc [a]	87	13	0·15
cis	*p*-Me		74	26	0·35
cis	*p*-Me	NaOAc [a]	72	28	0·39
cis	H		65	35	0·54
cis	H	NaOAc [a]	64	36	0·56
cis	H	$HClO_4$ [c]	67	33	0·50
cis	*p*-Cl		69	31	0·45
cis	*p*-Cl	NaOAc [a]	63	37	0·59
cis	*p*-O_2N		46	54	1·2
cis	*p*-O_2N	NaOAc [a]	40	60	1·5

[a] 1·0M; Results with added 0·1M NaOAc have been shown from representative cases to be similar. [b] 0·1M. [c] 0·3M.

The mass spectra of the mixtures of acetates from the reaction of chlorine acetate with methyl cinnamate gave the only indication we have been able to obtain that the product of the reversed orientation of addition, methyl 2-acetoxy-3-chloro-3-phenylpropanoate, can be detected in such reaction mixtures; the amount is $\gtrsim 5\%$.

The reaction of chlorine acetate with methyl *p*-methoxy-*trans*-cinnamate is complicated because some substitution can occur in the aromatic ring. This gives 3-acetoxy-2-chloro-3-(3-chloro-4-methoxyphenyl)propanoates, in which the aromatic signals are no longer a doublet, but instead a multiplet easily recognisable in admixture with the normal adduct. By experiments in which varying ratios of chlorine acetate and olefinic compound were used, it was shown that the aromatic substitution occurs after the addition, and does not compete appreciably with it if the concentration of the olefinic compound is kept in excess by a factor of two of that of the chlorine acetate. The results for this compound recorded in the later Tables were obtained with equimolecular concentrations of reagents, when the main not been so fully characterised, but they also showed no reaction involves addition to the *p*-methoxycinnamate. The corresponding *cis*-ester gave less difficulty of this kind, as is expected since *cis*-olefins generally react with electrophiles more rapidly than do their *trans*-isomers.[5]

In Table 3 we record product ratios for the reaction of chlorine acetate with methyl cinnamates and their derivatives in acetic acid at 25°. They have been estimated as indicated above, and the proportions are subject to the provisos and assumptions that we have indicated.

In Table 4 we show the effect of added water on the product proportions, which with sufficient water include chlorohydrins as well as acetoxy-chlorides.

For comparison, and to obtain values more strictly comparable with our own measurements involving electrophilic chlorine acetate, we have in part repeated and in part somewhat extended the estimates of Johnson and his co-workers [10] of the product ratios for chlorination by molecular chlorine in acetic acid at 25°. In all these cases, our observations of the ^1H n.m.r. spectra of the methyl 3-aryl-2,3-dichloropropanoates agree well with the previous values,* and we have accepted these workers' assignments of configuration. The results of both sets of measurements are given in Table 5. Agreement is in most cases satisfactory; the discrepancy in the example of methyl 2,3-dichloro-3-*p*-methoxyphenylpropanoate probably has come about because of the accompanying substitution mentioned above.

Subsidiary experiments were performed where necessary to show that (with the exception mentioned below) the product ratios have been determined under kinetic control. Thus methyl *erythro*-2,3-dichloro-, methyl *erythro*-3-acetoxy-2-chloro-, and methyl *erythro*-2-chloro-3-hydroxy-propanoate were each recovered unchanged after being allowed to stand for five days in acetic acid. So in the absence of

* The proviso must be recorded that in Table 1 of ref. 10*b* the chemical shifts for the α-C—H signals of the *threo*-3-aryl-2,3-dichloropropanoates with substituents *p*-CF_3, *p*-Cl, *p*-Me, *p*-MeO, 3-Cl-4-MeO, and 3,5-Cl_2-4-MeO are recorded as lying at τ *ca.* 4·36, below the corresponding values for the β-C—H signals. In those cases which we have re-examined, namely with substituents *p*-Cl, *p*-Me, *p*-MeO, and 3-Cl-4-MeO, we have found these signals to lie at τ *ca.* 5·36. This is consistent with pattern observed for the unsubstituted compound and for the *p*-nitro-derivative by both groups of workers.

TABLE 4

Product proportions, and ratios of *trans* : *cis*-addition, for the formation of acetoxy-chlorides and of chlorohydrins from chlorine acetate (0·01M) and methyl cinnamates ($RC_6H_4CH{:}CHCO_2Me$; 0·01M) in aqueous acetic acid at 25°

Geometrical isomer	R	Added water (%)	Added electrolyte	Product proportions * 3-Acetoxy-3-aryl-2-chloro-propanoates *erythro*	3-Acetoxy-3-aryl-2-chloro-propanoates *threo*	3-Aryl-2-chloro-3-hydroxy-propanoates *erythro*	3-Aryl-2-chloro-3-hydroxy-propanoates *threo*	*trans* : *cis* Ratio * Acetoxy-chlorides	*trans* : *cis* Ratio * Chloro-hydrins
trans	*p*-MeO	20		50	6	44	-	8·3	Large
trans	*p*-MeO	20	$HClO_4$ [a]	47	6	47	-	7·8	Large
trans	H	10	$HClO_4$ [b]	50	19	22	9	2·6	2·4
trans	H	20		51	18	21	10	2·8	2·1
trans	H	20	$HClO_4$ [a]	51	17	22	10	3·0	2·2
cis	H	1	$HClO_4$ [a]	67	33	t	t	0·49	i
cis	H	10		52	28	11	9	0·54	0·82
cis	H	10	$HClO_4$ [c]	43	24	26	7	0·56	0·27
cis	H	20		42	24	21	13	0·57	0·62
trans	*p*-O_2N	2·5		79	21	-	-	3·8	i
trans	*p*-O_2N	2·5	$HClO_4$ [a]	68	20	12	-	3·4	Large
trans	*p*-O_2N	5		74	19	7	-	3·9	Large
trans	*p*-O_2N	5	$HClO_4$ [a]	68	21	11	-	3·2	Large
trans	*p*-O_2N	10		76	16	8	-	4·7	Large
trans	*p*-O_2N	10	$HClO_4$ [a]	65	20	15	-	3·2	Large
trans	*p*-O_2N	15		69	15	16	-	4·6	Large
trans	*p*-O_2N	20		67	15	18	-	4·5	Large
trans	*p*-O_2N	30		63	12	25	t	5·2	Large
cis	*p*-O_2N	20		29	48	11	12	1·7	1·1

[a] 0·1M. [b] Mean of two concordant experiments with $HClO_4$ 0·2 and 0·5M. [c] 0·3M.

* t = Trace, - = not detected, i = indeterminate.

TABLE 5

Product proportions, and ratios of *trans* : *cis*-addition, for the reaction of chlorine with methyl cinnamates, $RC_6H_4CH{:}CHCO_2Me$, in acetic acid at 25°

Geometric isomer	R	Added electro-lyte (1·0M)	Product proportions [a] 3-Acetoxy-3-aryl-2-chloropropanoates (1) and (2) * *erythro*		3-Acetoxy-3-aryl-2-chloropropanoates (1) and (2) * *threo*		3-Aryl-2,3-dichloropropanoates * *erythro*		3-Aryl-2,3-dichloropropanoates * *threo*		*trans* : *cis* Ratio * Acetoxy-chlorides		*trans* : *cis* Ratio * Dichlorides	
trans	*p*-MeO		-	(-)	-	(-)	70	(77)	30	(23)	i	(i)	2·3	(3·4)
trans	*p*-MeO	LiCl		(-)		(-)		(81)		(19)		(i)		(4·3)
trans	*p*-MeO [b]	NaOAc		(22)		(t)		(50)		(26)		(Large)		(1·9)
trans	*p*-Me		17	(20)	5	(t)	27	(28)	51	(49)	3·4	(Large)	0·53	(0·57)
trans	*p*-Me	LiCl	21	(22)	t	(t)	45	(39)	34	(36)	Large	(Large)	1·3	(1·1)
trans	*p*-Me	NaOAc	41	(46)	5	(5)	21	(17)	33	(32)	8·2	(9·2)	0·64	(0·53)
trans	H		40	(41)	9	(7)	13	(12)	38	(40)	4·4	(5·9)	0·34	(0·30)
trans	H	LiCl		(40)		(6)		(24)		(30)		(6·7)		(0·80)
trans	H	LiOAc		(49)		(10)		(12)		(30)		(4·9)		(0·40)
trans	*p*-Cl		43	(42)	5	(5)	16	(15)	36	(39)	8·6	(8·4)	0·41	(0·39)
trans	*p*-Cl	LiCl	27	(28)	7	(4)	36	(35)	30	(28)	3·9	(7·0)	1·2	(1·25)
trans	*p*-Cl	NaOAc	50	(56)	14	(10)	14	(10)	22	(24)	3·6	(5·6)	0·64	(0·42)
trans	*p*-O_2N [c]		74, 80 [c]	(81)	7, 6 [c]	(5)	t	(t)	19, 14 [c]	(13)	10·6, 13·3 [c]	(16·2)	Small	(Small)
trans	*p*-O_2N [c]	LiCl	37	(26)	t	(t)	63	(70)	-	(t)	>30	(Large)	Large	(Large)
trans	*p*-O_2N [c,d]	NaOAc	90	(91)	5	(t)	-	(t)	5	(t)	18	(Large)	Small	(Small)
cis	*p*-MeO		t	(-)	-	(-)	79	(>90)	21	(<5)	i	(i)	0·26	(<0·05)
cis	*p*-MeO [b]	NaOAc	48		t		37		15		Small		0·40	
cis	*p*-Me		13		6		61		20		0·46		0·33	
cis	*p*-Me	NaOAc	32		16		40		12		0·50		0·30	
cis	H			(28)		(18)		(43)		(11)		(0·64)		(0·26)
cis	*p*-Cl			(24)		(13)		(52)		(11)		(0·54)		(0·21)
cis	*p*-Cl	LiCl	18		14		43		25		0·78		0·58	
cis	*p*-O_2N		23		56		16		t		2·4		Small	
cis	*p*-O_2N	NaOAc	26		65		9		-		2·5		Small	

* t = Trace, - = not detected, i = indeterminate. [a] Literature values[10] (initially $[Cl_2] = 10$ [olefin]) in parentheses. [b] Results may be affected by acetolysis of dichlorides; see text. [c] Initially $[Cl_2] = 10$[olefin]. [d] Other products were present in crude reaction mixture.

added salts under the reaction conditions used for electrophilic addition there is no equilibration between *threo*- and *erythro*-isomers. Although the corresponding *para*-substituted derivatives were not synthesised in pure diastereoisomeric forms, in all cases except that of the methoxy-substituted compound significantly different ratios of products were obtained in different reactions, and so here also equilibration between *threo*- and *erythro*-isomers has not been established.

The possibility that chlorohydrins arise by hydrolysis of acetoxy-chlorides was excluded also; thus, for example, acetoxy-chloride mixtures from the methyl *p*-methoxy- and *p*-nitro-cinnamates showed no signs of hydrolysis after being allowed to stand for five days in acetic acid containing 20% water. Chlorohydrin mixtures were similarly not acetylated in acetic acid, and dichlorides did not solvolyse in acetic acid.

The possibility that added acetate ion could initiate a displacement reaction to produce acetoxy-chlorides from dichlorides under the conditions of the chlorination and product isolation was excluded for all cases except that of the methyl 2,3-dichloro-3-*p*-methoxyphenylpropanoates. This case is complicated because, as we have already noted, with excess of chlorine, substitution occurs in the aromatic ring. It has been reported [10] that the products obtained by using a nine-fold excess of chlorine do not undergo solvolysis in acetic acid; but we have found that a mixture of dichlorides obtained from methyl *p*-methoxy *trans*-cinnamate and an equimolecular amount of chlorine, although stable in acetic acid over the time used for chlorination, decomposed in the presence of sodium acetate to give a mixture of acetoxy-chlorides together with an unidentified product having ^{1}H n.m.r. signals at τ 5·0 and 5·65.

Even with the most reactive of our olefinic compounds, the order in which the reagents were added made no difference to the product ratios.

These studies provide internal evidence also that the *cis*-olefins are not converted to the *trans*-compounds under the conditions of reaction. In one case, this was checked separately: the product from addition of 0·5 mol. equiv. of chlorine acetate to methyl *p*-chloro-*cis*-cinnamate contained no methyl *p*-chloro-*trans*-cinnamate. It was also noted that in experiments with mixtures of *cis*- and *trans*-cinnamates the *cis*-isomers reacted faster than the *trans*-isomers, as expected.

The reactions of cyclohexene with chlorine acetate in acetic acid gave only *trans*-1-acetoxy-2-chlorocyclohexane as established by the ^{1}H n.m.r. spectrum of the product. The signal attributable to the *cis*-isomer was not detected, and this must be present in $<1\%$.

The products from the reaction of acenaphthylene with chlorine acetate were also identified by ^{1}H n.m.r. spectroscopy. Associated through the areas of the respective signals (in the ratio 3 : 1 : 1) are an acetoxymethyl singlet at τ 7·84 and two alicyclic doublets (J 6·5 Hz) centred at τ 3·67 and 4·32. These clearly characterise *cis*-1-acetoxy-2-chloroacenaphthene, with a dihedral angle of 0° between the C–C–H planes of the coupled hydrogen atoms (J, from the Karplus [26] relationship, expected to be *ca.* 7 Hz). Similarly associated are an acetoxymethyl singlet at τ 7·95 and two alicyclic doublets (J 1·5 Hz) centred at τ 3·33 and 4·48. These characterise trans-1-*acetoxy*-2-*chloroacenaphthene* (J expected to be *ca.* 2 Hz), which was obtained as crystals, m.p. 94—95°, from the reaction of acenaphthylene with t-butyl hypochlorite in acetic acid (Found: C, 67·7; H, 4·6. $C_{14}H_{11}O_2Cl$ requires C, 68·2; H, 4·5%), τ 7·91 (OAc), 4·43 ($J_{1,2}$ 1·2 Hz, 2-H), 3·40 ($J_{1,2}$ 1·2 Hz, 1-H).

The relative chemical shifts of the acetoxymethyl signals for these two compounds (*trans* τ 7·95; *cis* τ 7·84 *) accord with those which we have assigned [9] to the corresponding 9-acetoxy-10-chloro-9,10-dihydrophenanthrenes (*trans* τ 8·25; *cis* τ 7·9). Since the stereochemistry is established in the former through ^{1}H n.m.r. spectroscopy, these results provide independent confirmation of our assignment in the latter series. Previously, our conclusions had been based on mechanistic arguments; ^{1}H n.m.r. spectroscopy does not provide an unambiguous assignment for the dihydrophenanthrene system, since the preferred conformations of both diastereoisomers would be expected to have coupling constants (J *ca.* 2 Hz) corresponding with a dihedral angle between the C–H bonds of *ca.* 60°.

Chlorinations of phenanthrene and of acenaphthylene were carried out similarly. Results from this and earlier work [9] are summarised in Table 6, along with those for the corresponding additions of chlorine acetate. They refer to reactions carried out under kinetic control; in separate

TABLE 6

Adduct proportions,[a] and ratios of *trans* : *cis*-addition, for the reactions of chlorine acetate and of chlorine with phenanthrene and with acenaphthylene

Compound	Reagent	Added electrolyte (0·1M)	Adduct proportions: Acetoxy-chlorides *cis*	Acetoxy-chlorides *trans*	Dichlorides *cis*	Dichlorides *trans*	*trans* : *cis* Ratio: Acetoxy-chlorides	Dichlorides
Phenanthrene	ClOAc		50	50			1·0	
Phenanthrene	ClOAc	NaOAc	50	50			1·0	
Phenanthrene [b]	Cl_2		8	18	59	15	2·4	0·27
Phenanthrene [b]	Cl_2	LiCl	6	17	65	12	2·7	0·20
Phenanthrene [b]	Cl_2	NaOAc	8	27	55	10	3·2	0·18
Phenanthrene [b]	Cl_2	NaOAc [c]	7	38	50	5	5·0	0·12
Acenaphthylene	ClOAc		25	75			3·0	
Acenaphthylene	ClOAc	NaOAc	33	67			2·0	
Acenaphthylene	Cl_2		3	9	51	37	3·75	0·71
Acenaphthylene	Cl_2	LiCl	1·2	8·8	<8	>82	7	>7
Acenaphthylene	Cl_2	NaOAc	1·5	10·5	51	37	7·0	0·73

[a] All reactions give also some substitution; details are in ref. 9 for phenanthrene and chlorine, but otherwise will be presented in a subsequent paper. [b] Results from ref. 9. [c] 1·0M.

* These chemical shifts are slightly concentration- and solvent-dependent, but the signals remain clearly resolved in mixtures.

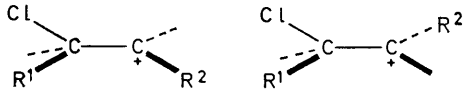
[26] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

experiments it was shown that all the products are stable in acetic acid and in acetic acid containing sodium acetate.

DISCUSSION

With aromatic compounds, chlorine acetate initiates rapid substitution reactions,[7,8] and the present work confirms that it is similarly effective in initiating additions to olefins. We have also shown by qualitative observation that the latter reactions involve electrophilic chlorine, just as the former do; for example, methyl-*p*-nitrocinnamate adds chlorine acetate much more slowly than methyl cinnamate does. Furthermore, the orientation of addition of chlorine acetate to methyl cinnamate has now been shown to be the same as that of the corresponding addition initiated by electrophilic chlorine.

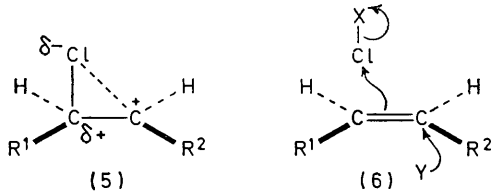
The stereochemical course of addition, however, reveals important differences between molecular chlorine acetate and molecular chlorine, and these throw insight into the detailed reaction paths taken by both reagents, permitting a revision of long-standing views concerning the course available in the latter case. We turn attention first to the reactions of cyclic systems, because here we eliminate a complexity which exists in acyclic systems, namely that any intermediate acyclic chlorocarbonium ion or related structural analogue formed in a conformation such as (3) can undergo the interconversion (3) ⟶ (4) to an extent which depends on its lifetime and on the energy barrier



(3) (4)

resisting free rotation about the newly formed single bond. The result of this interconversion can be to alter the discrimination that the two faces of the carbonium centre can show towards the nucleophile. We accept, with other workers,[10,27,28] that such rotational interconversions are probably important in some additions to acyclic systems; but for cyclic cases they are precluded.

Our investigation of addition initiated by carriers of electrophilic chlorine to cyclic unsaturated compounds has so far been confined to a study of cyclohexene, phenanthrene, and acenaphthylene. With cyclohexene, we observe only *trans*-addition of Cl and OAc, whether the reaction is initiated by chlorine acetate or by molecular chlorine in acetic acid. This accords with behaviour reported in the literature; for example, addition of ClOH gives only *trans*-2-chlorocyclohexanol,[29] and of chlorine gives only *trans*-1,2-dichlorocyclohexane.[30] Stereospecificity in this sense would be expected for either of two types of mechanism: (i) reaction through a bridged chloronium * intermediate, which might but need not be symmetrical in character [see (5)] as we have discussed in earlier parts of this series; [32] (ii) reaction involving synchronous attack by the electrophile and the nucleophile on opposite sides of the molecule (6; the Ad3 mechanism).[5,33] We have no evidence to distinguish between these possibilities; evidence concerning rearrangements accompanying addition [32] is in our view the only evidence yet obtained relating unambiguously to the significance of bridging interactions (5, *etc.*) in our solvents, though Olah and his co-workers [34] have established that with certain structures under other conditions chloronium ions can be stable entities.



(5) (6)

The stereospecificity in the additions initiated by chlorine and by chlorine acetate to cyclohexene contrasts markedly with the behaviour of these reagents with phenanthrene and with acenaphthylene (Table 6); for these compounds, substantial proportions of *cis*-adducts, be they acetoxy-chlorides or dichlorides, can be recognised in all the reaction mixtures. Qualitatively this result can be rationalised whether *trans*-stereospecificity is determined by bridging or by synchronous addition; for the positive charge on the chlorocarbonium ion derived from these aromatic structures is delocalised and stabilised by resonance, thereby loosening any bridging, and also increasing the potential lifetime of the intermediate.

In passing, it should be noted that the results in Table 6 confirm that our experiments are carried out under kinetic control, in that neither during the reaction nor during the isolation do the products interconvert significantly. With different reagents different ratios of *trans* : *cis*-addition have been recorded for both substrates. Focusing attention first on the acetoxy-chlorides, formation of these with chlorine as the electrophile requires solvent capture by an intermediate. Clearly, both faces of the chlorocarbonium ion intermediate become accessible to the nucleophile, with *trans*- predominating over *cis*-addition. The proportion of *trans*-addition is then increased by the inclusion of acetate ions in the medium. This again is to be expected, especially if the Ad3 mechanism (6; X = Cl, Y = OAc^-) is marginally under observation.

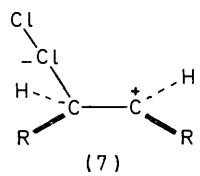
Addition initiated by chlorine acetate is, however, markedly less stereoselective, giving higher proportions of the *cis*-isomer. Added acetate ions now change very little the proportion of *trans*-addition, and such change as is observed is in the direction opposite to that found

* For a discussion of the history of this concept see ref. 31.

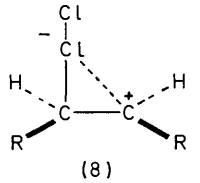
[27] R. E. Buckles, J. M. Badar, and R. J. Thurmaier, *J. Org. Chem.*, 1962, **27**, 4523.
[28] R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, 1965, **87**, 5172.
[29] P. D. Bartlett, *J. Amer. Chem. Soc.*, 1935, **57**, 224.
[30] M. L. Poutsma, *J. Amer. Chem. Soc.*, 1965, **87**, 2161.
[31] P. B. D. de la Mare, in P. De Mayo, ' Molecular Rearrangements Part 1,' Wiley, New York, 1963, p. 93.
[32] P. B. D. de la Mare and J. G. Pritchard, *J. Chem. Soc.*, 1954, 3910, 3990.
[33] R. C. Fahey, *Topics Stereochem.*, 1968, **3**, 237.
[34] G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, 1967, **89**, 4744.

with chlorine, and probably can be attributed to a minor environmental influence.

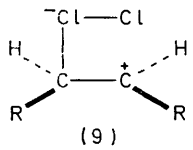
Both for phenanthrene and acenaphthylene, therefore, we have additions initiated by two different electrophiles, giving *inter alia* the same products in the same solvent in different proportions, and affected by added acetate ions in different ways. The two addition pathways leading to these products must therefore differ and cannot involve the same intermediates. The intermediates that have in the past been favoured by us in descriptions of the addition initiated by molecular chlorine include the open ion (3), the bridged ion (5), the ' open ' zwitterion (7), and the corresponding ' bridged ' zwitterion (8) (see ref. 4) and the geometrically different zwitterion (9).



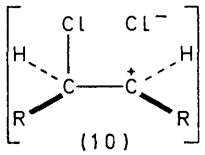
(7)



(8)



(9)

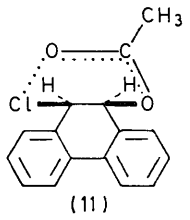


(10)

We have assumed that intermediates (7)—(9) precede (3) and (5) on the reaction path, that *trans*-acetoxy-chloride adducts could be derived from any of these intermediates, and that *cis*-acetoxy-chloride adducts must be derived from ' open ' ions, probably from chlorocarbonium ions approximating in structure to (3). Johnson and his co-workers' picture [10] uses primarily structures (3)—(5), and a direct addition involving an ion-pair (10) rather similar in geometry to (9) is invoked also to explain the formation of *cis*-dichlorides in certain cases. Interconversions of the type (3) $\rightleftharpoons$ (4) are permitted in their systems, but are prevented in those of ours which involve cyclic structures.

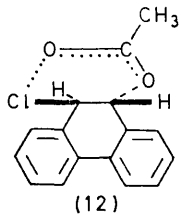
Our new results could be accommodated within the previous framework if it were assumed, as we proposed tentatively in our preliminary communication,[11] that both *cis*- and *trans*-addition of chlorine acetate to these rather rigid cyclic olefins could proceed through a ' direct ' mechanism, in which the geometrical representations of the transition states are indicated for phenanthrene in structures (11) and (12). Consideration of models shows that in both these possibilities, a six-membered transition state can be reached without substantial steric hindrance. Either possibility seems consistent [7,8] with the enhanced reactivity of chlorine acetate as compared with molecular chlorine, but neither seems particularly favourable from consideration of entropies of activation. A synchronous termolecular *trans*-addition (6; X = OAc, Y = HOAc) competing with a bimolecular *cis*-addition would circumvent the latter difficulty but would involve the assumption that the termolecular path used acetic acid and acetate ion quite indiscriminately.

An alternative, which requires revision of the reaction path involving molecular chlorine as the reagent, is that chlorine acetate reacts with the unsaturated compounds



(11)

hypothetical direct *cis*-addition



(12)

hypothetical direct *trans*-addition

to give as the only significant intermediate a chlorocarbonium ion, which for addition to cyclohexene and related systems must adopt the bridged form (5) in which one face of the developing carbonium centre is protected. For addition to aryl-substituted, unsaturated centres, however, the chlorocarbonium ion must be rather open, and must co-ordinate with the solvent or with other nucleophiles rather indiscriminately, since stereospecificity in the direction of *trans*-addition is not favoured by the inclusion of the better nucleophile in the medium. We then must ask, for reaction of molecular chlorine, what intermediate is involved that can be diverted by acetate ion towards *trans*-addition. Clearly, it cannot be the chlorocarbonium ion; a rational alternative is that the acetoxy-chlorides are derived from intermediates such as (7)—(9) in which the potential chloride ion is still playing a structural role.

If this is so, it seems likely also that diversion of the addition of molecular chlorine, to give dichlorides, in the direction of increased *trans*-addition (see Table 6; results with added LiCl) also comes about by attack on intermediates such as (7)—(9), rather than on intermediates such as (3) or (5).

It will be appreciated that these two possible interpretations of our new results, namely that chlorine acetate provided as the electrophile gives products of addition through transition states (11) and (12), or alternatively through chlorocarbonium ions (3) or (5), are very different in character; and for evidence to distinguish between them we have studied the addition of chlorine acetate to a series of substituted methyl cinnamates, it having been the study of these systems which led Johnson and his co-workers [10] to accept that direct *cis*-addition of molecular chlorine is significant.

We note first that the orientation of addition is the same as that of reaction initiated by molecular chlorine; no more than a trace ($\gtrsim$5%) of the products of reversed orientation could be detected by examination of the mass spectra of the product of reaction of methyl *trans*-cinnamate with chlorine acetate and comparison of this with mass spectra of appropriate synthetic mixtures. The reaction therefore is nearly regiospecific, though not completely so; it will be remembered that the reaction of

propene with hypochlorous acid in water gives 9% of the product $MeCH(Cl)CH_2OH$ of reversed (' generalised anti-Markownikoff ') orientation.[35]

As far as the stereochemistry of addition is concerned, such a transition state as (12) seems stereochemically possible for a *cis*-disubstituted olefin (largely because of the large size of chlorine and the flexibility of the Cl–O–C=O system); but it seems to us that it would be seriously disfavoured and probably precluded for the *trans*-disubstituted compounds. The results of Table 3 show that, uniformly through the series of substituted methyl cinnamates, the ratio of *trans*- to *cis*-addition is greater for the *trans*-isomer than for the *cis*-isomer. If *trans*-addition of chlorine acetate through (12) is unlikely for the *trans*-isomer, it is probably not important for the *cis*-isomer either. On these grounds we now consider that our earlier speculation [structure (12)] is not sustained.

The possibility that a nearly synchronous termolecular process leading to *trans*-addition is in competition with a similar, or with a bimolecular process leading to *cis*-addition, although difficult to exclude, does not explain why several pairs of substituted methyl *cis*- and *trans*-cinnamates give approximately the same ratio of products. This result in our opinion makes it likely that the attack by chlorine acetate often leads fairly directly to the chlorocarbonium ion, which in these aryl-substituted systems is most stable in the ' open ' form. On this basis, the results in Table 3 bear on the openness of this ion, and on the ease of interconversion of the type (3) $\rightleftarrows$ (4). If such an ion were formed and lasted sufficiently long in solution to reach its equilibrium conformational mixture before further reaction, both *cis*- and *trans*-isomers would give the same ratio of products. For the unsubstituted methyl cinnamates there are significant differences, though in terms of free-energy changes these are all small. If we take the situation in the methyl cinnamates as a standard of comparison, both methyl *cis*- and *trans*-*p*-nitrocinnamates give more *trans*-addition than expected. This is what would be predicted if bridging by chlorine were becoming more significant as electrons were withdrawn from the olefinic double bond; and this is what is expected from theory and experiment on bridged carbonium ions.[36] The other differences shown in Table 3 are probably too small for sensible interpretation.

The results of experiments with added nucleophiles fit satisfactorily into the above pattern. Added acetate ions make little difference to the product ratios (Table 3); and there is also very little effect from adding perchloric acid to the reaction medium. This result, we consider, justifies us in neglecting ion pairs in elaborating the intermediates important in determining the product ratios in these reactions, for if it were important for this purpose to consider the counter ion of our intermediates [(3)—(5), *etc.*], then this would no doubt be changed when perchloric acid was included in the medium. For this reason also, we prefer formulation (9) to the isomeric (10) in discussion of chlorine addition.

The results given in Table 4 show also the effect of adding water to the reaction medium. Considering first the ratio of *trans* : *cis*-addition in the acetoxy-chlorides, there is a general tendency for this to increase with an increase in the ionising power of the medium, both among the *trans*- and the *cis*-olefins. This would be expected if capture by the nucleophile became more rapid, the greater the ionising power of the medium.

Secondly, addition of sufficient water to the medium gives significant amounts of chlorohydrins associated with acetoxy-chlorides, though on a molar basis acetic acid is more effective than water in providing the nucleophile. Analyses of our four-component mixtures were not fully satisfactory; products both of *trans*- and of *cis*-addition could be recognised in most cases, and for the methyl *cis*- and *trans*-cinnamates the ratios of *trans* : *cis*-addition were similar in the two types of product, acetoxy-chloride and chlorohydrin. We are not sure whether the divergences in the other cases are real or the result of experimental difficulties; if real, they may indicate that chlorohydrin, and perhaps also acetoxy-chloride, can arise through a termolecular pathway.

Our proposed reaction path for addition of chlorine acetate to olefinic (including aromatic) systems can thus be formulated as in Scheme 1. In terms of Scheme 1, the results mentioned above are interpreted in terms of the following pathways for the formation of acetoxy-chlorides. 1. Cyclohexene adopts the path *via* the bridged intermediate (5) to the product of *trans*-addition. 2. Acenaphthylene and phenanthrene require the opening of the bridge, thus giving intermediate (3), to allow the formation of both *cis*- and *trans*-acetoxy-chlorides. 3. Methyl *trans*- and *cis*-cinnamate also require additionally the conversion of intermediate (3) into its conformational isomer (4) so that *erythro*- and *threo*-acetoxy-chlorides can be obtained from the two isomers in similar proportions. These are the main paths for most of the substituted methyl cinnamates. 4. Because of the greater importance of bridging in the intermediate derived from methyl *p*-nitro-*trans*-cinnamate, this compound makes rather greater use of reaction directly from (5). 5. Termolecular pathways using a component of the solvent as the nucleophile are possibly involved, particularly in the formation of chlorohydrins from relatively reactive olefins.

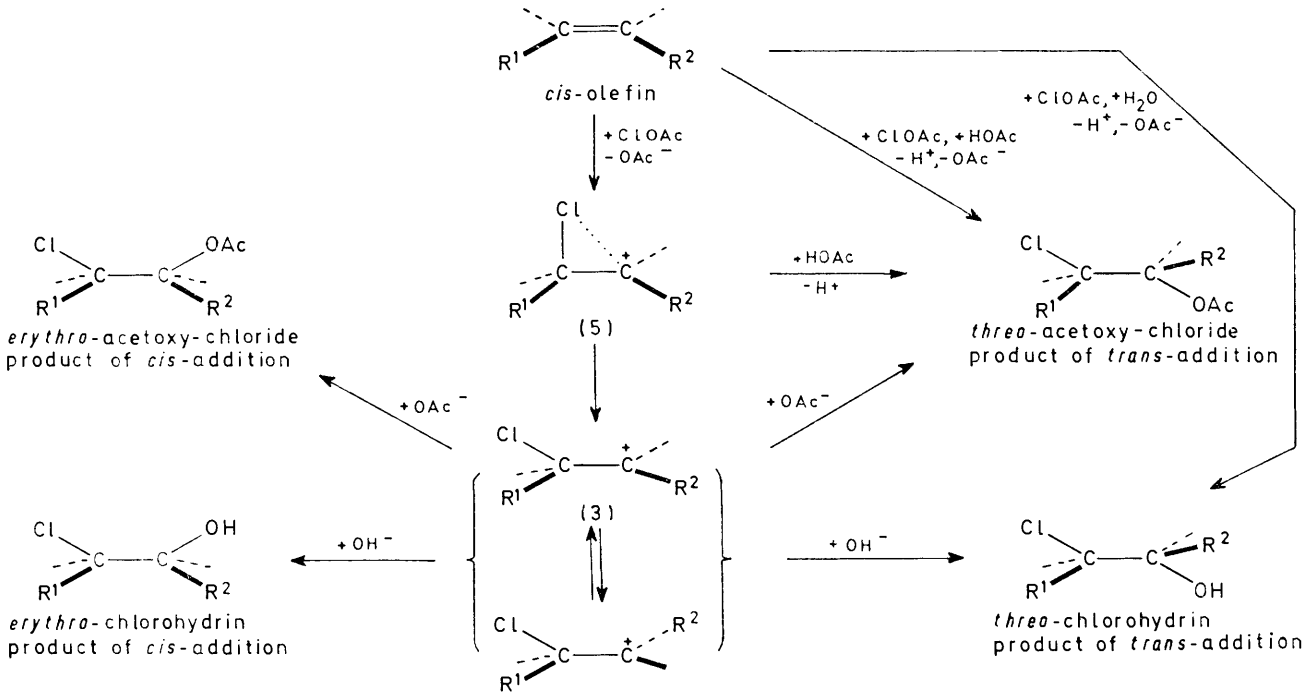
The rather high *erythro* : *threo* ratio in the reactions of both the methyl *p*-methoxycinnamates deserves comment. The ^1H n.m.r. spectra of the products from both the geometric isomers were so similar that we have little doubt that similar intermediates are concerned in the product-determining stage of these reactions, and hence that the equilibration (3) $\rightleftarrows$ (4) is substantially achieved before the nucleophile is picked up. The reason why the formation of the *erythro*-product is favoured may be because interaction between the π-electron systems of the aryl and the CO_2R groups holds the interconverting system (3) $\rightleftarrows$ (4) in a conformation favourable for completion of reaction in this way. In the

[35] L. Smith and S. Skyle, *Acta Chem. Scand.*, 1950, **4**, 39.
[36] S. Winstein, *Bull. Soc. chim. France*, 1951, C55.

compounds containing less powerfully electron-releasing groups, however, this interaction is reduced, and a more indiscriminate reaction is achieved.

In extending the description of addition of electrophiles to the reactions of molecular chlorine (Tables 5 and 6; Scheme 2) we must now accept that the unbridged intermediates concerned in Scheme 1 can make only minor contributions to the reaction paths, even for the formation of acetoxy-chlorides. Otherwise the acetoxy-chlorides would be formed in the same ratios from chlorine as from chlorine acetate. For the reasons discussed in sults on the chlorination of *cis*-2,2,5,5-tetramethylhex-3-ene [37] that in non-aryl substituted systems the intermediates leading to addition initiated by chlorine do not easily allow rotation about the originally ethylenic double bond.

Diversion of the reaction, towards the formation of *trans*-dichlorides by added chloride ions, is apparent even for the cyclic aryl-substituted olefins (Table 6) and even more so for the acyclic analogues (Table 5), since it is shown that the proportion of *trans*-dichloride is increased by addition of chloride ions. Similar diversion towards



SCHEME 1 Proposed reaction paths in additions to some olefinic substances initiated by chlorine acetate in acetic acid. For routes indicated as involving OAc^- or OH^-, the alternative possible involvement of HOAc or H_2O is postulated also

earlier papers,[9] we consider that *cis*-addition of molecular chlorine is an important process for reactions of acenaphthylene and phenanthrene, and so, in formulating Scheme 2, we attribute additional prominence to reaction from intermediate (9) to give *cis*-addition for addition to structures in which the olefinic system is stabilised by an attached aryl group.

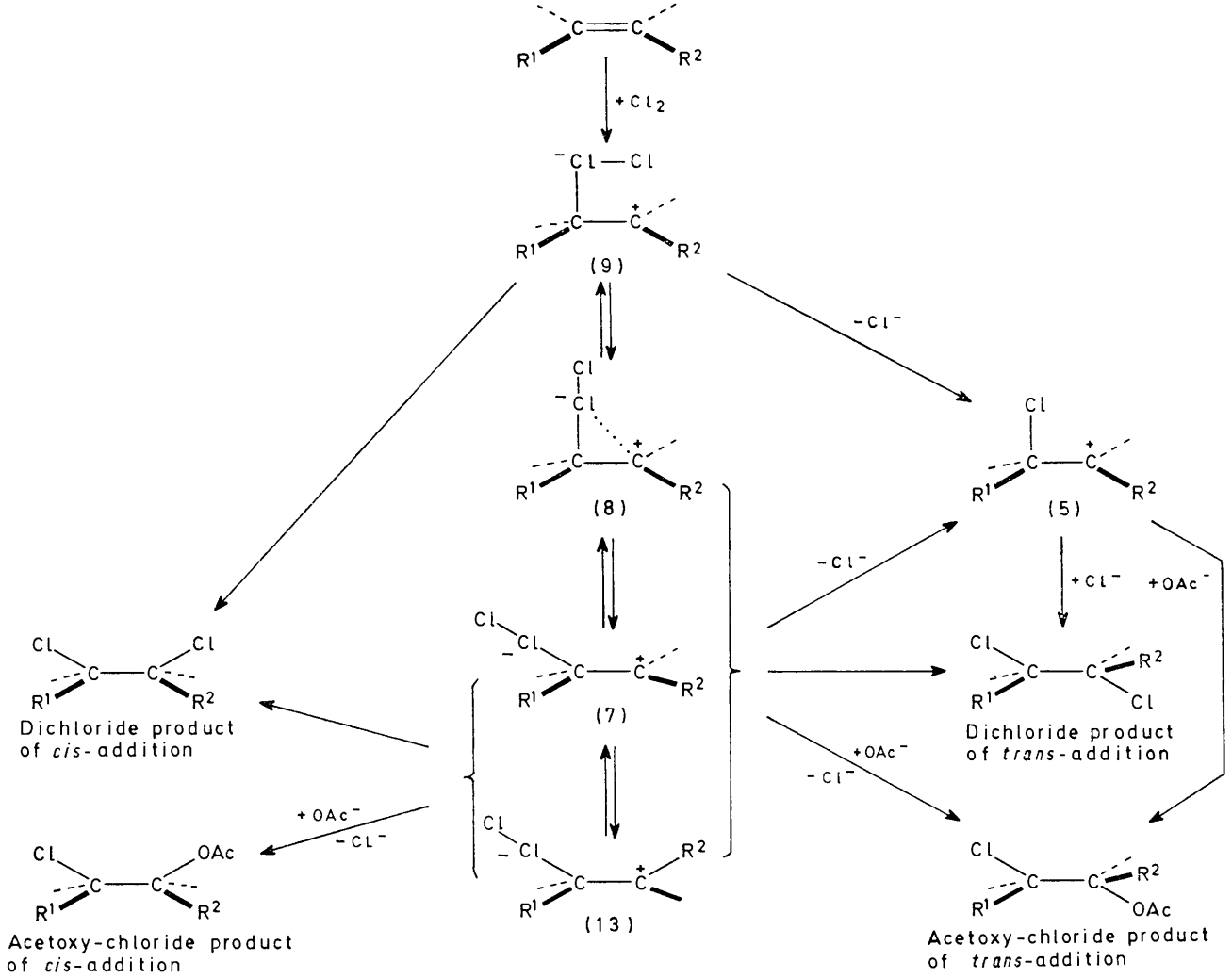
It is not precluded that this type of intermediate can also give some product of *trans*-addition; but the latter product is more characteristic of other bridged species, and becomes predominant for olefins in which the developing carbonium ion centre is not stabilised by aryl groups.[28] Two alternative possible pathways have been included to describe the stereospecific formation of the *trans*-products, one involving attack by a nucleophile on (8), and one involving the bridged chlorocarbonium ion (5). The latter is preferred by Fahey and Schubert [28] but their arguments are not compelling, since kinetic support is lacking for these fast reacting systems. Whichever of these paths is adopted, it is clear from Fahey's re- *trans*-acetoxy-chloride by added acetate ions is also evident in a number of cases, so paths of this kind leading from the intermediates (8) and (9) are included in Scheme 2.*

The formation of *cis*-acetoxy-chlorides from phenanthrene and acenaphthylene indicates that the intermediates (8) and (9) must open significantly for these substrates. They do not, however, give (3), since we now believe this to give very different product ratios, as

* A referee has asked us to comment on the fact that there is a major difference between phenanthrene and acenaphthylene in this respect, in that acenaphthylene gives much and phenanthrene little if any evidence for diversion. We have confirmed that both the adducts from acenaphthylene are stable to lithium chloride under our conditions of reaction and isolation, so we believe that the difference in behaviour is real. Qualitatively, it is reasonable that acenaphthylene should resemble the olefinic systems, since its double bond might be expected to be more olefin-like; it is indeed much more reactive than phenanthrene. We do not, however, think that as yet any satisfactory general theory exists to account for the relative ease with which different carbonium ion systems can be captured by nucleophiles.

[37] R. C. Fahey, *J. Amer. Chem. Soc.*, 1966, **88**, 4681.

in the reactions of chlorine acetate (Scheme 1), but instead through an intermediate such as (7). Results for the methyl cinnamates and for 1-phenylpropene [28] are adequately interpreted in terms of similar intermediates. It is probable that, in the acyclic systems stabilised by aryl substituents, such intermediates can undergo some rotation (7) ⇄ (13) but it is clear from the results of Table 5 that this equilibrium is usually by no means fully established. Thus neither *erythro*- and *threo*-dichlorides nor *erythro*- and *threo*-acetoxy-chlorides are formed in approximately the same proportion from similarly substituted *cis*- and *trans*-cinnamates, except for the case of the *p*-methoxy-derivatives, where the intermediate would be expected to be least stabilised by bridging chlorine.



SCHEME 2 Proposed reaction paths in additions to some olefinic substances initiated by molecular chlorine. For routes indicated as involving OAc^- or OH^-, the alternative possible involvement of HOAc or H_2O is postulated also

The formulations given in Scheme 2 are not meant to be exhaustive in terms of the possible ramifications of additions initiated by carriers of electrophilic chlorine. For example, we have not considered the various possible paths involving 1,2-shifts in chlorine-substituted carbonium ions, of which some examples have been given in earlier papers in this series; [32] and we have neglected ion-pair interchanges for the reason already mentioned, though ion pairs may be found to be significant in other cases. The overall picture for reaction with these reagents is that of reaction paths involving multiple intermediates all rather close in energy, and all liable in some circumstances to react with nucleophiles before reaching their most stable conformations. We believe that the present results, besides describing for the first time the behaviour of the reagent chlorine acetate, require a revision of the details of the intermediates to be considered in addition initiated by molecular chlorine in the direction now indicated. Further studies of both reagents are in progress; we hope to throw further light on the reactions of chlorine acetate by means of kinetic studies.

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