Dehydroacetoxylation and Acetate Transesterification in the Reactions of *erythro*- and *threo*-Methyl 3-(Substituted acetoxy)-2-halogeno-3-phenylpropanoates with Triethylamine

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The response of the rate of triethylamine-induced dehydroacetoxylation of methyl *threo*-3-acetoxy-2-halogeno-3-phenylpropanoate to the influence of substituents in the leaving group points to a change in mechanism from $(E1cB)_i$ to a concerted process of the carbanion type. On the other hand, the *erythro*-isomers seem to undergo elimination exclusively through a carbanionic pathway. The effect of the acetoxy substituents upon the competitive transesterification is discussed.

We have previously obtained kinetic and stereochemical evidence for the triethylamine-promoted dehydroacetoxylation of methyl *erythro*- and *threo*-3-acetoxy-2-halogeno-3-phenylpropanoates (**1**; R = Me) in methanol pointing to the operation of an *E*1cB process of the irreversible type.[1] We have also found that transesterification of the leaving group competed for the substrate to a small extent.

The present paper extends these studies to the influence of substituents on the methyl portion of the acetoxy group upon both the elimination and the transesterification reactions of (**1**) with methanolic triethylamine.

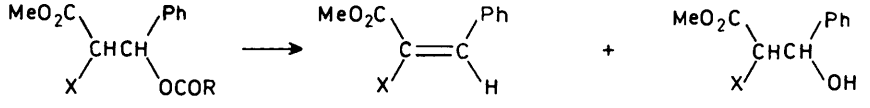
Results

The reaction of (**1**) with methanolic triethylamine afforded the corresponding olefin (**2**) along with the products of cleavage of the acetate ester. The product composition was determined by g.l.c. analysis of the reaction mixtures after 8 half-lives. Control experiments showed that the compounds were stable under the chromatographic conditions. G.l.c. analysis of the product showed the presence of the isomeric olefins (**2**), the corresponding halogenohydrins (**3**), methyl 2,3-epoxy-3-phenylpropanoate (**5**), and a fourth compound (less than 10%) with retention time longer than that for the *trans*-epoxide but shorter than that for the methyl *threo*-halogenohydrin. The peak corresponding to the product of transesterification arising from the acetyl portion of the ester was superimposed on that of the solvent.

In separate experiments under identical kinetic conditions it was shown that the halogenohydrins (**3**) were partially transformed into a mixture of the isomeric epoxy esters, which presumably arise from internal displacement of halide ion, and the fourth product. When this mixture was kept for an additional 48 h, g.l.c. analysis indicated that the unidentified compound had been converted into the epoxy esters (**5**). This was also observed when the 'infinity' solutions of the product of reaction with the 2-halogeno compounds were left for the same additional length of time. Nevertheless, as the analysis also showed that some of (**3**) had been converted into olefin, the end points of these reactions were considered as obtained after 8 half-lives. We assumed that the product from (**3**; X = Br) was 2-bromo-3-phenylpropiolactone (**6**); however, since attempts to prepare this compound independently were unsuccessful, no definitive structural assignment was made.

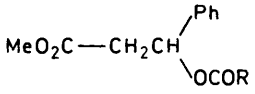
The kinetics were followed to at least 85% completion and were found to obey pseudo-first-order rate laws for the appearance of the corresponding olefin when a 25-fold excess of triethylamine was used. The reactions were carried out at a buffer concentration within a range which showed that the amine is the only reactive basic nucleophilic species in elimination and transesterification reactions under these conditions.[2] The second-order rate constants, calculated as usual from those of first order, are composites of elimination and transesterification rates. The elimination (k_E) and transesterification (k_T) components of the overall reaction were estimated from the product ratio of olefin to transesterification product.

The reactions of methyl 3-acetoxy-3-phenylpropanoate and its α-substituted acetoxy derivatives (**4**) with triethylamine in methanol led exclusively to loss of the acetyl group with formation of methyl 3-hydroxy-3-phenylpropanoate (**7**). Rate constants were obtained by measuring the ratio of alcohol to starting material by the quenching g.l.c. method.



threo and *erythro* (**1**) *E* and *Z* (**2**) (**3**)

X = Br or Cl, R = Me, ClCHCH$_3$, CH$_2$Cl, CHCl$_2$, CCl$_3$, or CH$_2$Br

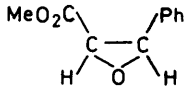


(**4**)

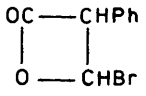
Table 1. Second-order rate coefficients for elimination of $MeO_2CCHBrCH(OCOR)Ph$[a] with triethylamine[b]–triethylamine hydrochloride[c] in methanol at 30 °C

	threo		*erythro*	
R	10^3k_E[d]	% Z[e]	10^3k_E[d]	% Z[e]
Me	0.960	99.0	0.842	98.8
CHClMe	2.85	97.4	1.72	92.0
CH_2Br			2.75	94.5
CH_2Cl	4.80	97.1	2.93	91.0
$CHCl_2$	13.3	98.5	4.32	87.3
CCl_3	44.8	99.3	5.13	86.3

[a] 0.002M. [b] 0.050M. [c] 0.020M. [d] In $dm^3\ mol^{-1}\ s^{-1}$. [e] Based on the ratio Z/E.



(5)



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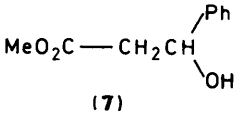


(7)

Discussion

From Table 1 it is seen that the sequence of reactivities for various leaving groups and the relative magnitudes of their influence on the elimination rates of the *threo*-2-bromo compounds are typical of an *E*2 process having a transition state of carbanionic type.[3] The fact that the reaction with the *threo*-isomers occurs with virtual (≥ 97%) stereospecificity, affording the *Z*-olefin according to the antiperiplanar configuration required for a concerted elimination[4] from conformation (a) (see later),[5] lends partial support to this interpretation. However, the kinetic behaviour of the unsubstituted acetoxy substrates (**1**; X = Br or Cl; R = Me) under similar conditions,[1] as well as that with methanolic sodium methoxide,[6] had been rationalised in terms of an irreversible *E*1cB mechanism. It is possible that enhanced nucleofugality caused by the presence of halogens in the acetoxy group results in a changeover in mechanism from a rate-determining ionisation to a concerted reaction on the *E*1cB-like side of the mechanistic spectrum.[3,7]

The effects of leaving group on reactivity of the *threo*- and *erythro*-isomers are compared in Tables 1 and 2. Two explanations can be offered for the fact that the enhanced electron-withdrawing ability of the leaving group affects the reactivity of the *erythro*-compounds to a smaller extent than for the *threo*-isomers. First, the elimination could follow a concerted pathway through a transition state near the carbanion end with a large component of proton transfer and a very small degree of cleavage of the bond to the acetoxy group. Alternatively, although the response of the rates of elimination to the influence of change in the leaving group is not large, it is higher than that expected purely from inductive stabilisation of the remote incipient 2-carbanion. Only a very slight rate-increasing effect (factor 1.12) upon the irreversible carbanionic elimination of methyl *erythro*-2-bromo-3-halogeno-3-phenylpropanoate under similar conditions was observed when the 3-halogen was varied from bromine to chlorine.[1]

The behaviour of the *erythro*-acetoxy substrates (**1**) might be understood on the basis of a mechanism involving assistance to ionisation by weak intramolecular interaction of the 2-proton with the carbonyl oxygen of the leaving group. This proposal agrees with the previous suggestion that the apparently unexpected reactivity of these compounds in methoxide-induced eliminations is a consequence of interaction between the 2-hydrogen and the acetoxy group.[6] However, the fact that the relative magnitudes of the effect of substitution in the acetoxy group on the rate of elimination fall in the sequence of abilities to induce increase of the electrophilic character of the carbonyl carbon seems to argue against this picture. It would be possible to explain these results if we were to assume that the propensity of the carbonyl oxygen to interact with the 2-hydrogen may be assisted by the nucleophilic approach of the reagent or the solvent to the carbonyl carbon. The negative net charge on the ester oxygen would then be increased, increasing attraction between the latter and the proximal hydrogen. Thus the observed order of reactivities could be a reflection of the enhanced susceptibility of the carbonyl carbon to the approach of the nucleophile as electronegative substituents are added to the leaving group. However, since the assumed interaction between hydrogen and the carbonyl oxygen is not well enough established this explanation is only tentative.

Table 2. Second-order rate coefficients for elimination of *erythro*-$MeO_2CCHClCH(OCOR)Ph$[a] with triethylamine[b]–triethylamine hydrochloride[c] in methanol at 30 °C

R	10^3k_E[d]	% Z[e]
Me	1.67	98.2
CH_2Cl	6.30	98.6
$CHCl_2$	11.3	99.1
CCl_3	17.3	100.0

[a] 0.002M. [b] 0.050M. [c] 0.020M. [d] In $dm^3\ mol^{-1}\ s^{-1}$. [e] Based on the Z/E ratio.

Although there is a marked stereospecificity in the reaction with the 2-bromo substrates leading to the *Z*-olefin, that with the *erythro*-isomer shows a modest increase in the proportion of *E*-olefin when the basicity of the acetate is weakened. We suggest that this result is the expected consequence of elimination from the *erythro*-compounds through the intermediacy of an anionic species. A high degree of stereospecificity will result when the rate of rotation of the intermediate to attain the configuration leading to the more stable olefin exceeds that of departure of the leaving group. That rotation could be favoured by the possibility of carbanionic stabilisation by hyperconjugation. Thus, the stereochemistry of the reaction might be the result of a balance between hyperconjugative stabilisation and leaving-group ability.[8,9] On the other hand, better leaving groups may depart directly from the carbanion geometries arising from the ground-state conformations. Thus the isomeric composition of the elimination product might be a measure of the relative tendencies towards carbanion hyperconjugation and leaving group expulsion. This proposal has precedent in a similar tendency shown by triethylamine-promoted elimination from *erythro*-2,3-halogeno analogues which, together with the kinetic evidence, was previously accounted for in terms of a rate-determining deprotonation, $(E1cB)_I$.[1]

It had also been observed[1] that for pairs of substrates with a common leaving group the degree of stereospecificity of elimination with the *erythro*-dihalogeno compounds was a function of the inductive capacity of the 2-halogen to stabilise an anionic intermediate. The present results with (**1**; X = Cl) seem to favour this assumption since the enhanced stabilising influence of chlorine with respect to bromine should increase the lifetime of the intermediate and hence increase the possi-

Table 3. Second-order rate coefficients for transesterification of *erythro*-$MeO_2CCHXCH(OCOR)Ph$[a] with triethylamine[b]–triethylamine hydrochloride[c] in methanol at 30 °C

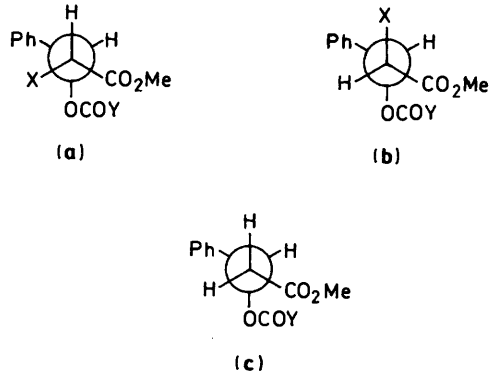
	10^3k_T[d]	
R	X = Br	X = Cl
Me	0.08[e]	0.07[f]
ClCHMe	0.88	
CH_2Br	8.45	
CH_2Cl	8.93	14.3
$CHCl_2$	65.3	141
CCl_3	104	323

[a] 0.002M. [b] 0.050M. [c] 0.020M. [d] In $dm^3\ mol^{-1}\ s^{-1}$. [e] Standard deviation ± 0.07. [f] Standard deviation ± 0.03.

Table 4. Second-order rate coefficients for transesterification with triethylamine[a]–triethylamine hydrochloride[b] in methanol at 30 °C

	10^3k_T[c]	
R	$MeO_2CCHBrCH(OCOR)Ph$[d] (*threo*)	$MeO_2CCH_2CH(OCOR)Ph$[d]
Me	0.003[e]	0.006 53
ClCHMe	1.00	
CH_2Cl	3.78	3.77
$CHCl_2$	33.5	33.7
CCl_3	57.0	59.0

[a] 0.050M. [b] 0.020M. [c] In $dm^3\ mol^{-1}\ s^{-1}$, [d] 0.002M. [e] Standard deviation ± 0.003.



bility of anion hyperconjugation. This will favour the appropriate geometry leading to the more stable olefin.[8,9]

Tables 3 and 4 show that the acetate transesterification reaction is accelerated by inductive removal of electrons from the acetoxy group; this is consistently represented by an acyl-transfer reaction proceeding through a rate-limiting nucleophilic attack of the reagent on the carbonyl carbon, followed by further reaction. Acyl-transfer reactions of this type with strongly basic amines are believed to proceed with rate-determining attack of the amine to give a dipolar addition compound, followed by rapid expulsion of the oxyanion.[10]

Alternatively, esters with acidic α-hydrogen have been shown to undergo solvolysis by an *E*1cB process involving collapse of the ester enolate ion through a ketenoid transition state.[11] However, the effect of the electron-withdrawing substitution in the acetoxy group should be insufficient to make this mechanism likely. Thus, the present reaction may be most simply described as following the normal associative $B_{Ac}2$ route with initial formation of the tetrahedral addition intermediate, which subsequently breaks down in a fast step involving loss of acetyl and separation of the corresponding oxyanion.

The data reported in Tables 3 and 4 reveal that the reactivity of the 2-bromo acetates shows a variable dependence upon the configuration of the substrate. The observed differences between the components of each pair of diastereoisomers might be thought to be steric in origin. Probably the transition states for the reaction corresponding to each diastereoisomer are configurationally related to their respective dominant ground-state conformations.[5] Thus a likely explanation for these observations might be that the *gauche* interaction between the incoming nucleophile reagent and the 2-halogen would make the transition state arising from conformation (a) for the *threo*-configuration somewhat disfavoured with respect to conformation (b) for the *erythro*-isomer.

However, the close parallel between the rates of reaction of the model compounds (**4**) (c) and those of the *threo*-2-bromo substrates (Table 4) indicates that the reactivity of the former is lower than that expected by application of such a stereochemical argument. This view is based on the assumption that the rates of transesterification are not affected by the polar influence of the 2-halogen. However, the kinetic evidence (Table 3) shows some sensitivity to the acyl-transfer reactivity of the *erythro*-compounds to the halogen identity; this increases with addition of further halogen atoms to the acetoxy group. It appears that part or all of the activating influence of the 2-halogen could be related to its remote location from the acetoxy group [see (b)]. However it is rather difficult to imagine how the halogen could possible exert its polar influence only when it is distant from the reactive site. The present evidence does not allow a complete explanation of this behaviour. We intend to explore this matter further by analysing the reactions of related systems.

Experimental

G.l.c. analyses were carried out with a Varian 3 700 spectrometer equipped with a flame-ionisation detector and a CDS 111 integrator. U.v. spectra were recorded with a Beckmen DB instrument. ^1H N.m.r. spectra were determined with a Varian EM 360 L spectrometer.

Preparation of Authentic Samples.—The halogenohydrins methyl *erythro*-2-bromo-3-hydroxy- and 2-chloro-3-hydroxy-3-phenylpropanoates were prepared as described by de la Mare.[12] Methyl *threo*-2-bromo-3-hydroxy-3-phenylpropanoate was obtained according to the reported procedure.[13] The alcohol methyl 3-hydroxy-3-phenylpropanoate was obtained by Reformatsky reaction followed by transesterification of the ethyl ester with methanolic sodium methoxide. The acetoxy compounds (**1**; X = Br or Cl, R = Me) were prepared following the method previously reported.[6] The acetoxy compounds (**1**; X = Br or Cl; R = ClCHMe, CH_2Br, $CHCl_2$, or CCl_3) and (**4**; R = Me, CH_2Cl, $CHCl_2$, or CCl_3) were obtained by acylation of the corresponding halogenohydrin or alcohol (6.5 mmol), respectively, with the appropriate acyl halide (16 mmol) in dimethylformamide at 30 °C. After the reaction was complete (1—3 h) the mixture was poured into aqueous 0.1M-hydrochloric acid (25 ml) and extracted with carbon tetrachloride (40 ml). The solvent was evaporated off and the products (90—100% yield) were purified as follows. The 2-bromo- and 2-chloro-3-acetoxy compounds were chromatographed on silica gel with hexane–carbon tetrachloride (1:3) as eluant, with the exception of the *erythro*-2-bromo-3-bromoacetoxy, 2-bromo-3-trichloroacetoxy, and 2-chloro-3-trichloroacetoxy compounds, which were recrystallised from methanol, and

Table 5. ^{1}H N.m.r. spectra of $MeO_2CCHXCH(OCOR)Ph$ in carbon tetrachloride

X	R		Chemical shifts[a] 3-H	2-H	OCOR	CO_2Me	$J_{2,3}$/Hz
Br	CH_2Cl	*erythro*	5.92	4.33	3.82	3.69	10.2
		threo	5.98	4.36	3.92	3.48	9.5
	$CHCl_2$	*erythro*	5.95	4.37	5.71	3.73	10.2
		threo	5.97	4.42	5.77	3.49	9.5
	CCl_3	*erythro*	5.92	4.35		3.71	10.2
		threo	5.96	4.48		3.52	9.5
	CHClMe	*erythro*[b]	5.89	4.32	4.13[c] 1.56[d]	3.69	10.2
			5.89	4.32	4.18[c] 1.56[d]	3.69	10.2
		threo[b]	5.95	4.50	4.03[e] 1.64[f]	3.50	9.0
			5.95	4.50	4.03[e] 1.66[f]	3.50	9.0
	CH_2Br	*erythro*	5.86	4.27	3.76	3.68	10.0
Cl	CH_2Cl	*erythro*	5.87	5.38	3.82	3.65	8.8
	$CHCl_2$	*erythro*	5.83	4.41	5.67	3.70	9.5
	CCl_3	*erythro*	5.89	4.45		3.68	9.5

[a] δ Values. [b] Equimolecular mixture of (*R*)- and (*S*)-3-(3-chloropropanoyloxy) compounds. [c] 1 H, q, *J* 7.0 Hz. [d] 3 H, d, *J* 7.0 Hz. [e] 1 H, q, *J* 6.8 Hz. [f] 3 H, d, *J* 6.8 Hz.

Table 6. ^{1}H N.m.r. spectra of $MeO_2CCH_2CH(OCOR)Ph$ in carbon tetrachloride

R	Chemical shifts (δ) 3-H	2-H		OCOR	CO_2Me	*J*/Hz $J_{2,3}$ (*trans*)	$J_{2,3}$ (*cis*)	$J_{2,2}$ (*gauche*)
Me	5.87	2.82	2.49	1.93	3.51	8.0	5.6	15.4
CH_2Cl	5.95	2.88	2.54	3.86	3.54	8.3	5.6	15.4
$CHCl_2$	5.99	2.96	2.66	5.72	3.52	8.4	5.6	15.1
CCl_3	6.02	3.02	2.66		3.57	8.3	5.5	15.8

of the *threo*-2-bromo-3-trichloroacetoxy compound, which was recrystallised from hexane. The 3-acetoxy-3-phenylpropanoates (**4**; R = Me, CH_2Cl, or $CHCl_2$) were chromatographed on silica gel (in carbon tetrachloride); (**4**; R = CCl_3) was recrystallised from hexane. Analytical data were as follows.

Methyl erythro-2-*bromo*-3-*chloroacetoxy*-3-*phenylpropanoate* (Found: C, 50.2; H, 3.8; Br, 23.2. $C_{12}H_{12}BrClO_4$ requires C, 49.9; H, 3.6; Br, 23.8%); *methyl* erythro-2-*bromo*-3-*dichloroacetoxy*-3-*phenylpropanoate* (Found: C, 39.6; H, 2.8; Br, 20.7. $C_{12}H_{11}BrCl_2O_4$ requires C, 39.0; H, 3.0; Br, 21.6%); *methyl* erythro-2-*bromo*-3-*trichloracetoxy*-3-*phenylpropanoate*, m.p. 75—76 °C (from MeOH) (Found: C, 35.8; H, 2.3; Cl, 25.6. $C_{12}H_{10}BrCl_3O_4$ requires C, 35.6; H, 2.5; Cl, 26.3%); *methyl* erythro-2-*bromo*-3-*bromoacetoxy*-3-*phenylpropanoate*, m.p. 52—53 °C (from MeOH) (Found: C, 37.8; H, 2.9; Br, 41.2. $C_{12}H_{12}Br_2O_4$ requires C, 37.9; H, 3.2; Br, 42.1%); *methyl* erythro-2-*bromo*-3-(3-*chloropropanoyloxy*)-3-*phenylpropanoate* (Found: C, 44.1; H, 3.8; Br, 21.8. $C_{13}H_{14}BrClO_4$ requires C, 44.7; H, 4.0; Br, 22.9%); *methyl* threo-2-*bromo*-3-*chloroacetoxy*-3-*phenylpropanoate* (Found: C, 48.9; H, 3.4; Br, 23.0. $C_{12}H_{12}BrClO_4$ requires C, 49.9; H, 3.6; Br, 23.8%); *methyl* threo-2-*bromo*-3-*dichloroacetoxy*-3-*phenylpropanoate* (Found: C, 39.1; H, 2.7; Br, 20.9. $C_{12}H_{11}BrCl_2O_4$ requires C, 39.0; H, 3.0; Br, 21.6%); *methyl* threo-2-*bromo*-3-*trichloroacetoxy*-3-*phenylpropanoate*, m.p. 48—49 °C (from hexane) (Found: C, 35.1; H, 2.5; Cl, 25.5. $C_{12}H_{10}BrCl_3O_4$ requires C, 35.6; H, 2.5; Cl, 26.3%); *methyl* threo-2-*bromo*-3-*bromoacetoxy*-3-*phenylpropanoate* (Found: C, 37.0; H, 3.2; Br, 41.5. $C_{12}H_{12}Br_2O_4$ requires C, 37.2; H, 3.2; Br, 42.1%); *methyl* threo-2-*bromo*-3-(3-*chloropropanoyloxy*)-3-*phenylpropanoate* (Found: C, 44.0; H, 3.7; Br, 21.9. $C_{13}H_{14}BrClO_4$ requires C, 44.7; H, 4.0; Br, 22.9%); *methyl* erythro-2-*chloro*-3-*chloroacetoxy*-3-*phenylpropanoate* (Found: C, 50.3; H, 4.3; Cl, 23.8. $C_{12}H_{12}Cl_2O_4$ requires C, 49.5; H, 4.2; Cl, 24.4%); *methyl* erythro-2-*chloro*-3-*dichloroacetoxy*-3-*phenylpropanoate* (Found: C, 43.6; H, 3.0; Cl, 31.9. $C_{12}H_{11}Cl_3O_4$ requires C, 44.3; H, 3.4; Cl, 32.7%); *methyl* erythro-2-*chloro*-3-*trichloroacetoxy*-3-*phenylpropanoate*, m.p. 53—54 °C (from MeOH) (Found: C, 39.5; H, 3.0; Cl, 38.6. $C_{12}H_{10}Cl_4O_4$ requires C, 40.0; H, 2.8; Cl, 39.4%); *methyl* 3-*acetoxy*-3-*phenylpropanoate* (Found: C, 65.3; H, 6.0. $C_{12}H_{14}O_4$ requires C, 64.9; H, 6.2%); *methyl* 3-*chloroacetoxy*-3-*phenylpropanoate* (Found: C, 56.5; H, 4.8; Cl, 13.0. $C_{12}H_{13}ClO_4$ requires C, 56.2; H, 5.1; Cl, 13.8%); *methyl* 3-*dichloroacetoxy*-3-*phenylpropanoate* (Found: C, 49.3; H, 4.0; Cl, 23.5. $C_{12}H_{12}Cl_2O_4$ requires C, 49.5; H, 4.2; Cl, 24.4%); *methyl* 3-*phenyl*-3-*trichloroacetoxypropanoate*, m.p. 43—45 °C (from hexane) (Found: C, 44.7; H, 3.2; Cl, 32.0. $C_{12}H_{11}Cl_3O_4$ requires C, 44.3; H, 3.4; Cl, 32.7%). ^{1}H N.m.r. data of the new compounds are shown in Tables 5 and 6.

The methyl *trans*- and *cis*-2,3-epoxy esters (**5**) have been reported previously but their configurations were poorly characterised.[14] They were obtained by reactions of methyl *erythro*- and *threo*-2-bromo-3-hydroxy-3-phenylpropanoate (**3**; X = Br), respectively, with sodium methoxide in methanol as described elsewhere for the preparation of epoxy amides.[15] Configurations were assigned on the basis of ^{1}H n.m.r. coupling constants and literature precedent.[16] Methyl *trans*-2, 3-epoxy-3-phenylpropanoate showed δ(CCl_4) 3.85 (1 H, d, *J* 1.7 Hz, 3-H), 3.21 (1 H, d, *J* 1.7 Hz, 2-H), and 3.62 (3 H, s, CO_2CH_3); methyl *cis*-2,3-epoxy-3-phenylpropanoate showed δ(CCl_4) 3.99 (1 H, d, *J* 4.8 Hz, 3-H), 3.54 (1 H, d, *J* 4.8 Hz, 2-H), and 3.34 (3 H, s, CO_2CH_3).

Kinetic Procedures.—Rates were measured at 30 ± 0.03 °C. The kinetics of reaction with the 3-acetoxy-2-halogeno com-

pounds were followed by monitoring the absorption maximum of the olefin [(**2**; X = Br) at 286 nm; (**2**; X = Cl at 284 nm)]. The reaction was started by adding a 0.007M-solution (20 ml) of the substrate in methanol (prepared immediately before use) to triethylamine (0.007M)–triethylamine hydrochloride (0.028M) (50 ml) in the same solvent. Portions (5 ml) were removed and quenched at various times by dilution with aqueous 0.1M-hydrochloric acid (100 ml). For reactions with a small ratio of elimination of transesterification the dilution factor was about 10, in order to reduce the experimental error of the spectroscopic determination. This made only a very slight contribution to the optical density at the corresponding wavelengths, and the transparency of the starting materials were demonstrated in each case. Infinity absorbances were taken at 8 half-lives. Quantitative analysis of the product mixture was carried out by g.l.c. with a glass column filled with OV-17 on silanised Chromosorb (180 °C). Attempts to use unsilanised systems led to decomposition of the products.

The products were identified by comparison of their retention times with those of authentic samples. Analyses were performed by calibrating the detector responses for given weights of authentic samples against a known weight of standard. Second-order rate coefficients were calculated by division of those of first order by the base concentration. The elimination and transesterification constants were calculated from equation (1) and (2) respectively

$$k_E = k_{obs.}/[1 + (\%\ \text{transesterification})/(\%\ \text{elimination})] \quad (1)$$

$$k_T = k_{obs.} - k_E \quad (2)$$

The reactions with the model compounds (**4**) were initiated by mixing triethylamine (0.07M)–triethylamine hydrochloride (0.028M) in methanol (2.5 ml) with a freshly prepared solution of the substrate (0.007M) in methanol (1 ml). Samples (1 μl) were withdrawn *via* a Hamilton syringe and quenched by injection into the g.l.c. column (5% OV-101 Chromosorb WHP; 160 °C). Quantitative determinations were performed by converting the peak area ratios of product to starting material into molar ratios. The second-order rate constants were obtained in the usual manner.

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