Chlorination of αβ-Unsaturated Carbonyl Compounds. Part V.† Mechanism of Chlorination of αβ-Unsaturated Ketones in Methanol and in Trifluoroacetic Acid

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The kinetics and products of the reaction of chlorine with 1-phenyl-3-arylprop-2-enones and with 4-arylbut-3-en-2-ones in methanol have been studied. The reactions involve predominant *trans*-addition of the elements of methyl hypochlorite to the double bond with little formation of dichlorides, and are interpreted in terms of the formation of an open or partially-bridged carbocation which is captured by the solvent mainly prior to appreciable rotation about the carbon–carbon bond. Some catalysis by hydrogen chloride is apparent in the reaction with 4-phenylbut-3-en-2-one and is believed to involve the formation of acetals prior to reaction with chlorine. In contrast the reaction of 1,3-diphenylprop-2-enone and of 4-phenylbut-3-en-2-one with chlorine in trifluoroacetic acid gives appreciable yields of the expected dichlorides, probably through a mechanism involving ion-pairs.

THE available information regarding the reaction of chlorine with olefins in hydroxylic solvents other than acetic acid is sparse. Thus, whereas there have been extensive kinetic[1] and stereochemical[2] studies on reactions of chlorine with αβ-unsaturated carbonyl compounds in acetic acid, no investigation has been reported on the kinetics or stereochemistry of these reactions in other hydroxylic solvents.

This paper describes studies of the stereochemistry of the products of chlorination of several αβ-unsaturated ketones of the type ArCH⁚CHCOX (Ar = Ph, 4-$MeOC_6H_4$, or 4-$NO_2C_6H_4$, X = Me or Ph) in methanol both in the presence and absence of electrolytes under kinetically controlled conditions, and also the results of a less detailed study of the products of reaction of chlorine with some of the same olefins in trifluoroacetic acid.

RESULTS

(i) *Chlorination in Methanol.*—Only two products were obtained from the reaction of each of the αβ-unsaturated carbonyl compounds with chlorine in methanol in the absence of added electrolytes. These are the corresponding *erythro*- and *threo*-methoxy-chlorides ArCH(OMe)CHClCOX, the yields of which are shown in Table 1. In the presence of added lithium chloride or hydrogen chloride, only slight diversion to the formation of the dichlorides, *erythro*- and *threo*-ArCHClCHClCOX was observed (Table 1). The products obtained in the presence of added sodium methoxide are also shown in Table 1.

The structures of the methoxy-chlorides were determined from elemental analyses and ^1H n.m.r. spectroscopy. The ^1H n.m.r. chemical shifts and coupling constants of the products are shown in Table 2. In each case the spectra of the crude reaction product showed singlets in the region τ 6·68—6·90, characteristic of the presence of *C*-methoxy-groups. That these methoxy-groups were bonded to the benzylic carbon was established by dehydromethoxylation reactions which gave the corresponding α-chloro-αβ-unsaturated ketone ArCH⁚CClCOX of known structure.

The diastereoisomeric products were identified from their coupling constants $J_{\alpha\beta}$ according to the method described earlier for the products of reaction of chlorine with methyl

TABLE 1

Products and kinetics of the reaction of chlorine (0·003M) with the ketones ArCH⁚CHCOX (0·003M) in methanol at 0°

				Product (%)				
			Added	Dichlorides		Methoxy-chlorides		
X	Ar	Configuration	electrolyte (M)	*threo*	*erythro*	*threo*	*erythro*	k_2/l mol^{-1} s^{-1}
Me	Ph	*trans*	None			26	74	3·22 [a]
Me	Ph	*trans*	LiCl (0·01)	1	4	23	72	3·88
Me	Ph	*trans*	HCl (0·01)		2	31	67	7·0
Me	Ph	*trans*	NaOMe (0·003)			13	87	0·80
Me	Ph	*cis*	None			61	39	
Me	4-$MeOC_6H_4$	*trans*	None			21 [b]	79 [b]	*ca.* 60 [c]
Me	4-$NO_2C_6H_4$	*trans*	None			19 [d]	81 [d]	0·060 [d]
Ph	Ph	*trans*	None			11	89	3·15
Ph	Ph	*trans*	LiCl (0·01)	1	3	9	87	3·78
Ph	Ph	*trans*	HCl (0·01)	1	2	8	89	3·87
Ph	Ph	*trans*	NaOMe (0·01)			9	91	
Ph	Ph	*trans*	NaOMe (0·003)					0·70
Ph	Ph	*cis*	None			58	42	
Ph	4-$MeOC_6H_4$	*trans*	None			7 [b]	93 [b]	*ca.* 64 [e]
Ph	4-$NO_2C_6H_4$	*trans*	None			9 [d]	91 [d]	0·007 [f]

[a] Autocatalytic; extrapolated rate coefficient at zero time. [b] $[Cl_2]$ = 0·0015M. [c] [olefin] = 0·002M, $[Cl_2]$ = 0·0015M. [e] $[Cl_2]$ = 0·006M. [e] $[Cl_2]$ = 0·005M. [f] With $[HClO_4] = 7·2 \times 10^{-4}$M.

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† Part IV, ref. 2*d*.

[1] P. W. Robertson, N. T. Clare, K. J. McNaught, and G. W. Paul, *J. Chem. Soc.*, 1937, 335; P. W. Robertson, I. R. C. McDonald, and R. M. Milburn, *ibid.*, 1950, 2836.

[2] (*a*) M. C. Cabaleiro and M. D. Johnson, *J. Chem. Soc.* (*B*), 1967, 565; (*b*) M. D. Johnson and E. N. Trachtenberg, *ibid.*, 1968, 1912; (*c*) M. C. Cabaleiro, M. D. Johnson, B. E. Swedlund, and J. G. Williams, *ibid.*, p. 1022; (*d*) M. C. Cabaleiro, C. J. Cooksey, M. D. Johnson, B. E. Swedlund, and J. G. Williams, *ibid.*, p. 1026.

cinnamates in acetic acid.[2a] Thus, it has been assumed that each *erythro*-methoxy-chloride has a higher $J_{\alpha\beta}$ than the corresponding *threo*-isomer. However, the closer the values of the two coupling constants, the less reliable is the method. For example, with 2-chloro-3-methoxy-1,3-diphenylpropanone, $J_{\alpha\beta} = 8{\cdot}6$ and 9·6 Hz. Attempts to confirm the configuration by a study of the rates of dehydrochlorination of the two diastereoisomers instead showed that dehydromethoxylation occurred to give PhCH:CClCOPh. However, during the dehydromethoxylation of the *erythro*-diastereoisomer, equilibration took place to a mixture containing an *erythro* : *threo* ratio of 3·5 : 2·5, in accord with the former being the more stable diastereoisomer. A similar equilibration was observed during the corresponding dehydroacetoxylation of the acetoxy-chlorides PhCH(OAc)CHClCOPh.

TABLE 2

^{1}H N.m.r. spectra of products of the type ArCHYCHClCOX [a]

X	Ar	Isomer	Y	Chemical shift (τ) Hβ [a]	Hα [a]	X	$J_{\alpha\beta}$/Hz
Me	Ph	*erythro* [b]	OMe	5·48	5·76	6·88	8·6
Me	Ph	*threo* [b]	OMe	5·30	5·66	6·80	5·4
Me	4-MeOC_6H_4	*erythro* [b]	OMe	5·65	5·92	6·90	9·0
Me	4-MeOC_6H_4	*threo* [b]	OMe	5·56	5·84	6·78	5·8
Me	4-$NO_2C_6H_4$	*erythro* [c]	OMe	5·36	5·80	6·72	9·2
Me	4-$NO_2C_6H_4$	*threo* [c]	OMe	5·26	5·64	6·68	7·2
Ph	Ph	*erythro* [d]	OMe	4·60	5·72	6·90	9·8
Ph	Ph	*threo* [d]	OMe	4·38	5·72	6·75	8·6
Ph	4-MeOC_6H_4	*erythro* [b]	OMe	5·08	5·40	6·88	9·6
Ph	4-MeOC_6H_4	*threo* [b]	OMe	4·88	5·38	6·72	7·0
Ph	4-$NO_2C_6H_4$	*erythro* [c]	OMe	4·82	5·08	6·75	9·4
Ph	4-$NO_2C_6H_4$	*threo* [c]	OMe	4·60	5·06	6·62	7·2
Me	Ph	*erythro* [b]	Cl	4·84	5·38		10·2
Me	Ph	*threo* [b]	Cl	4·60	5·40		7·0
Ph	Ph	*erythro* [d]	Cl	3·90	4·36		10·0
Ph	Ph	*threo* [d]	Cl	3·88	4·38		8·6
Me	Ph	*erythro* [b]	CF_3CO_2	3·78	5·40		9·2
Me	Ph	*threo* [b]	CF_3CO_2	3·68	5·32		6·0
Ph	Ph	*erythro* [d]	CF_3CO_2	3·48	3·94		9·8
Ph	Ph	*threo* [d]	CF_3CO_2	3·30	3·84		7·6

C*H*X is β, C*H*Cl is α. [b] In CCl_4. [c] In $CDCl_3$. [d] In acetone.

Pairs of the diastereoisomeric dichlorides 2,3-dichloro-1,3-diphenylpropanone and 3,4-dichloro-4-phenylbutan-2-one were obtained free from the corresponding methoxy-chlorides by the reaction of the appropriate olefins with chlorine in chloroform. The chemical shifts (Table 2) assigned to the aliphatic protons are in good agreement with those observed for the 2,3-dichloro-3-phenylpropionaldehydes.[2d] The configurations of the dichlorides were also assigned from consideration of $J_{\alpha\beta}$ and were confirmed by a comparison of the rates of dehydrochlorination of the pure *erythro*-dichloride with that of a 1 : 1 mixture of the *erythro*- and *threo*-dichlorides. No isomerisation of the *erythro*-dichlorides was apparent.

The kinetics of the reactions of the olefins with chlorine in methanol, with and without the added electrolytes, were measured under conditions comparable with those used for the product studies. The reactions were all first order in each reagent, and the second-order rate coefficients are shown in Table 1.

(ii) *Chlorination in Trifluoroacetic Acid*.—The reaction of chlorine with 1,3-diphenylprop-2-enone and 4-phenylbut-3-en-2-one in trifluoroacetic acid gave appreciable yields of the diastereoisomeric dichlorides (Table 3), with smaller proportions of the trifluoroacetoxy-chlorides $PhCH(CF_3CO_2)CHClCOX$. The influence of added electrolytes on the product proportions is shown in Table 3. The same trifluoroacetoxy-chlorides were obtained in much higher yield by the reaction of the two olefins with chlorine in the presence of a large excess of sodium trifluoroacetate. The diastereoisomeric pairs were separated from the dichlorides by t.l.c. and were identified as a pair from their elemental analyses and ^{1}H n.m.r. spectra (Table 2). That the trifluoroacetoxy-group was attached to the benzylic carbon was evident from the low proton resonance of the benzylic (β-)hydrogen atom in the region τ 3·30—3·78. In all cases, the values of $J_{\alpha\beta}$ are sufficiently different to justify assignment of the configurations in the manner described above. We thus assign the *erythro*-configuration to those trifluoroacetoxy-chlorides with the higher coupling constants.[2a]

TABLE 3

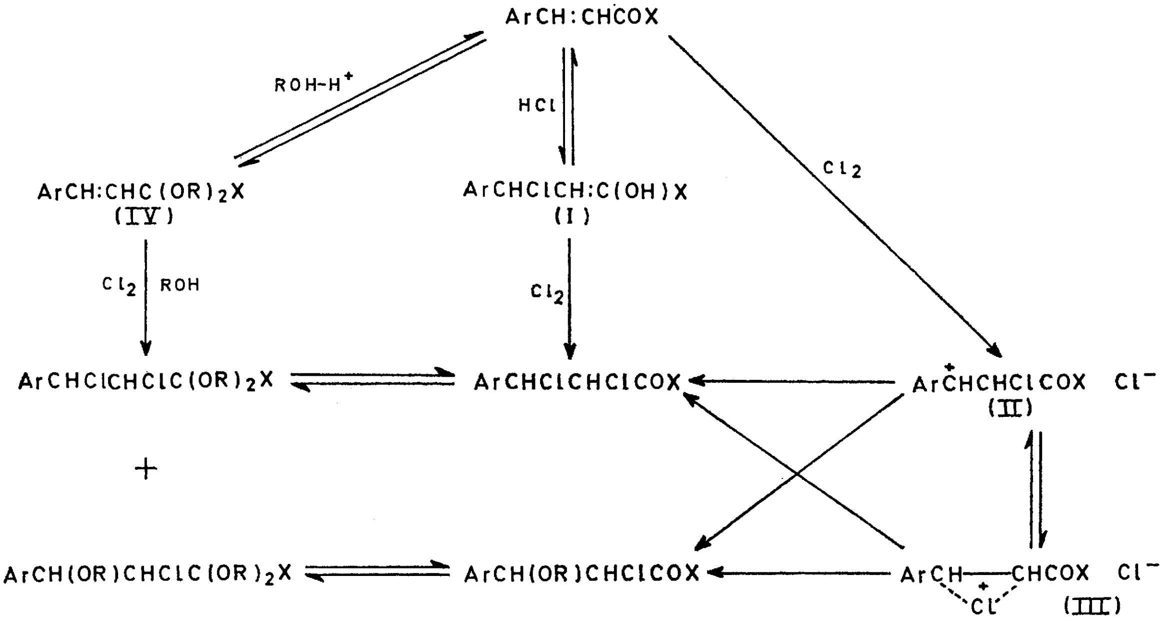
Products of reaction of chlorine with *trans*-PhCH:CHCOX [a] in trifluoroacetic acid at 20°

		Product (%) Dichlorides		Trifluoroacetoxy-chlorides	
X	Electrolyte (M)	*erythro*	*threo*	*erythro*	*threo*
Me	None	45	50	4	1
Me	LiCl (0·5)	40	47	11	2
Me	HCl (0·05)	45	51	3	1
Me	CF_3CO_2Na (0·5)	39	40	17	4
Ph	None	43	46	9	2
Ph	LiCl (0·5)	38	41	18	3
Ph	HCl (0·5)	57	42		
Ph	$LiClO_4$ (0·5)	37	40	21	2
Ph	CF_3CO_2Na (0·5)	30	37	29	4

[a] [Olefin] = 0·05M; $[Cl_2]$ = 0·05M.

DISCUSSION

Catalysis and Autocatalysis of Chlorine Addition.—The chlorination of αβ-unsaturated carbonyl compounds of the type ArCH:CHCOX differs from that of simple olefins not only because of the considerable influence of the aryl groups on the stability and structure of the cationic transition states and intermediates, but also because of the possibility of direct participation of the carbonyl group before, during, and after reaction with chlorine. Thus, the reaction of chlorine with cinnamaldehyde in acetic acid was found [2d] to be autocatalytic owing to a specific catalysis by hydrogen chloride through formation of a more reactive chloro-enol (I; X = H) (Scheme 1). In the presence of sufficient base to suppress the autocatalysis, the products were much the same as found for *trans*-cinnamic acid and methyl *trans*-cinnamate in acetic acid, *i.e.* almost equal mixtures of dichlorides and acetoxy-chlorides. These were believed to be formed through a direct addition of chlorine and a concurrent mechanism involving the formation of a chlorine-containing cationic intermediate (II; X = H, OH, or OMe), which can undergo limited rotation about the carbon–carbon bond, and of a chloronium ion (III; X = H, OH, or OMe), before being captured by chloride ion or solvent.



Scheme 1

Autocatalysis by hydrogen chloride formed during the reaction has also been observed [3,4] in the chlorination of 3-(3-nitrophenyl)-1-phenylprop-2-enone in acetic acid, but no significant acid catalysis is evident in the present studies in methanolic solution either as autocatalysis or in the presence of an excess of hydrogen chloride (Table 1). Such catalysis does occur in the reaction of chlorine with 4-phenylbut-3-en-2-one, but the very low yield of dichlorides formed under conditions where the acid-catalysed reaction accounts for at least 50% of the total reaction, rules out any significant contribution of a chloro-enol (I; X = Me) as an intermediate. On the other hand, the product from the reaction of 4-phenylbut-3-en-2-one with chlorine, with and without added hydrochloric acid or lithium chloride, is contaminated with acetals of the dichlorides and methoxy-chlorides shown in Table 1. The character of the products formed under these conditions supports a mechanism in which the substrate first forms acetal (IV; X = Me) or hemiacetal which reacts with chlorine at a rate greater than that of the substrate. Thus, the ratio of *erythro*- to *threo*-products from 4-phenylbut-3-en-2-one is greater in the presence of sodium methoxide, which suppresses the autocatalysis, than it is under autocatalytic or catalytic conditions when the acetals are formed. We have also observed that the reaction of chlorine with cinnamaldehyde in methanol is even more complicated by acetal formation and autocatalysis, whereas in the reaction of chlorine with 1,3-diphenylprop-2-enone in methanol, acetal formation is negligible.

Mechanism of the Uncatalysed Reactions with Chlorine in Methanol.—As expected for an electrophilic reaction of chlorine with the substrates,[1] the reaction rates are very susceptible to the nature of the *para*-substituent of the aromatic ring attached to the olefinic carbon. The rate increase on changing from 3-(4-nitrophenyl)-1-phenylprop-2-enone to the 4-methoxyphenyl compound is *ca.* 10^4, that on changing from 4-(4-nitrophenyl)but-3-en-2-one to the 4-methoxyphenyl compound is *ca.* 10^3, indicating that each of the reactions has a high ρ value comparable with those observed for the chlorination of methyl *trans*-cinnamates and *trans*-cinnamic acids. The role of acetals in the reactions of the above 4-substituted compounds has not been investigated in detail.

Chlorine is undoubtedly the effective electrophile in these reactions, because hydrogen chloride and chloride ion do not have the retarding effect that would be expected if methyl hypochlorite, formed *via* equation (1),

$$\mathrm{Cl_2 + MeOH \rightleftharpoons MeOCl + HCl} \qquad (1)$$

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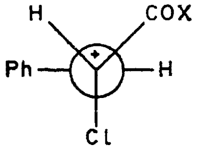
[3] P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 1045, 888.

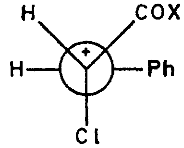
[4] B. E. Swedlund, personal communication.

were the reagent.[5] Moreover, sodium methoxide, which would be expected to increase the proportion of methyl hypochlorite present in solution, retards the rate of the reactions.

The products of reaction of 1,3-diphenylprop-2-enone and of 4-phenylbut-3-en-2-one with chlorine in methanol are consistent with the prior formation of a carbocation (II and/or III; X = Me or Ph) which undergoes only limited rotation about the carbon–carbon bond prior to capture by the solvent at the opposite side from the attached halogen.[6,7] Consequently, different mixtures of products are obtained from each *cis*- and each *trans*-isomer, in each case with that product arising from an effective *trans*-addition of the elements of methyl hypochlorite predominating. That the stereospecificity of this *trans*-addition is greater in the reactions of the *trans*-olefins is a consequence of the greater stability of the intermediate cations (II*t*; X = Me or Ph) [equally applicable to the bridged intermediate (III)], initially derived from the *trans*-olefins than those (II*c*; X = Me or Ph) [equally (III)] initially derived from the *cis*-olefins.

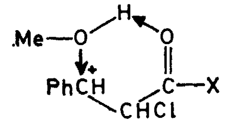


(II*t*)
[or (III*t*)]



(II*c*)
[or (III*c*)]

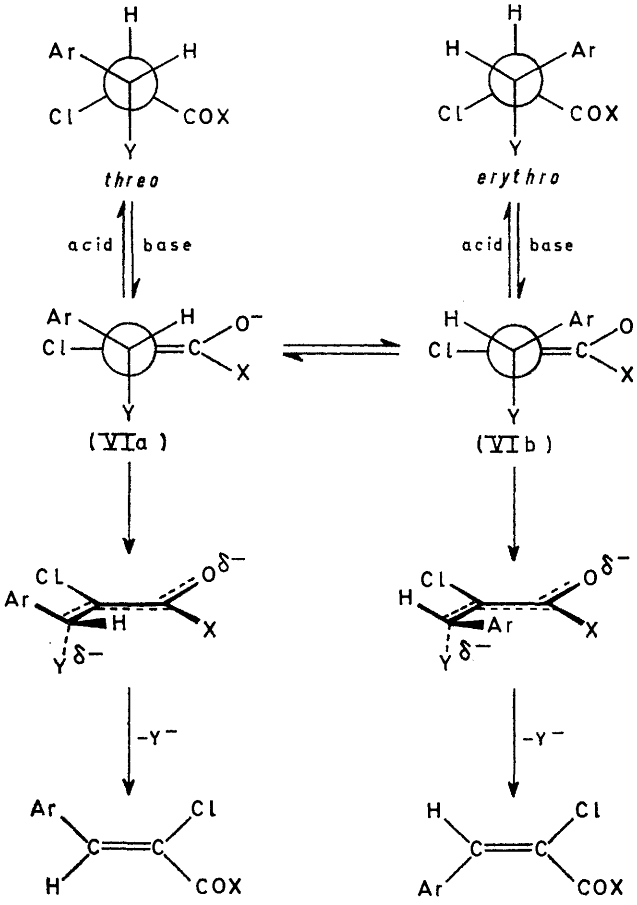
The present results do not distinguish unambiguously between an ' open ' intermediate cation (II) or one which can attain some chloronium character (III); however, under the conditions of adequate solvation, as in methanol, the lack of complete rotation prior to product formation does suggest that rotation is additionally hindered by some interaction between the cationic β-carbon and the α-chlorine or the carbonyl oxygen. The product distribution from the 4-nitro- and the 4-methoxy-derivatives of both *trans*-1,3-diphenylprop-2-enone and *trans*-4-phenylbut-3-en-2-one are very similar to each other and to those from the respective parent compounds. The relative stabilities of the open intermediates (II) from the 4-nitro- and 4-methoxy-derivatives would be expected to differ widely, and the extent of rotation prior to product formation would be expected to be greatest in that from the 4-methoxy-compound. For example, in the reaction of chlorine with the methyl *trans*-cinnamates in acetic acid, the extent of rotation prior to product formation is believed to increase markedly on going from the 4-nitro- to the 4-methoxy-derivative.[2b] Therefore it seems possible that the methanol solvates the intermediate sufficiently well to prevent rotation even in the case of the 4-methoxy-derivative, particularly if a six-centre interaction involving solvent and the carbonyl group [as in (V)] may take place. The extent of rotation would thus depend upon the period elapsing before such solvation is organised, which may well be relatively independent of the 4-substituent, but dependent on the nature of X.



(V)

Only in the presence of added chloride ion are the dichlorides observed in the products. The yields of these products are too low to be able accurately to apportion them between *erythro* and *threo*, but they are consistent with capture of the intermediate cations by the excess of chloride ion in solution rather than by the solvent.

Mechanism of the Uncatalysed Reaction with Chlorine in Trifluoroacetic Acid.—In trifluoroacetic acid, the products are principally the two dichlorides in almost equal yields. Indeed, the proportion of dichlorides in the products of chlorination of αβ-unsaturated carbonyl compounds increases in the solvent order: methanol < acetic acid < trifluoroacetic acid, in the same order as



SCHEME 2

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[5] P. B. D. de la Mare, *Quart. Rev.*, 1949, **3**, 126.

[6] R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, 1965, **87**, 5172.

[7] P. B. D. de la Mare and R. Bolton, ' Electrophilic Additions to Unsaturated Systems,' Elsevier, London, 1966, p. 92.

the increase in the role of ion-pairs. The addition of salts to the trifluoroacetic acid decreases the yield of dichlorides and increases the yields of *erythro*-trifluoroacetoxy-chlorides much more than of the *threo*-trifluoroacetoxy-chlorides. An acid-catalysed mechanism is indicated in the reaction of 1,3-diphenylprop-2-enone by the absence of trifluoroacetoxy-chlorides and the high yield of the *erythro*-dichloride in the presence of hydrogen chloride and the fact that the highest yields of both the trifluoroacetoxy-chlorides and the lowest yield of the *erythro*-dichloride are obtained in the presence of sodium trifluoroacetate.

Isomerisation and Dehydromethoxylation of Methoxy-chlorides.—One further reaction deserves comment. The isomerisation and dehydromethoxylation of the methoxy-chlorides in the presence of t-butoxide ion is particularly interesting, especially as dehydrochlorination does not appear to take place under these conditions. The reaction probably involves the formation of the corresponding enolate ion (VIa) [and (VIb)] which can undergo rotation about the carbon–carbon bond and then either return to the appropriate methoxy-chloride, or can lose methoxide ion stereospecifically, as shown in Scheme 2. Further studies of this reaction are in progress.

EXPERIMENTAL

Materials.—Methanol was purified by the method of Lund and Bjerrum,[8] b.p. 64·5—65°. Trifluoroacetic acid, lithium chloride, and lithium perchlorate were high quality commercial materials used without further purification (Carlo Erba or Fluka). Solutions of hydrogen chloride were prepared by passing the dry gas into methanol or trifluoroacetic acid. Sodium methoxide and sodium trifluoroacetate were prepared *in situ* by dissolving sodium metal in an excess of methanol or trifluoroacetic acid, respectively. Chlorine gas was washed with water and dried with sulphuric acid. *trans*-4-Arylbut-3-en-2-ones and *trans*-3-aryl-1-phenylprop-2-enones were prepared by condensation of the appropriate unsubstituted or 4-substituted benzaldehyde with acetophenone or acetone, respectively, in an alcohol–water alkaline solution, and the crude product was recrystallised from absolute ethanol. Examination of the ^{1}H n.m.r. spectra showed the absence of the corresponding *cis*-isomers. *trans*-PhCH:CHCOMe had m.p. 39—41° (lit.,[9] 41—42°), $J_{\alpha\beta}$ 16 Hz; *trans*-4-MeOC$_6$H$_4$CH:CHCOMe had m.p. 71—73° (lit.,[10] 73°), $J_{\alpha\beta}$ 18 Hz; *trans*-4-NO$_2$C$_6$H$_4$CH:CHCOMe had m.p. 107—109° (lit.,[11] 110°), $J_{\alpha\beta}$ 16·6 Hz; *trans*-PhCH:CHCOPh had m.p. 56—57° (lit.,[12] 57°), $J_{\alpha\beta}$ 16 Hz; *trans*-4-MeOC$_6$H$_4$CH:CHCOPh had m.p. 77—78·5° (lit.,[13] 76—78°), $J_{\alpha\beta}$ 16·4 Hz; *trans*-4-NO$_2$C$_6$H$_4$CH:CHCOPh had m.p. 161—163° (lit.,[14] 164·1—164·5°). *cis*-1,3-Diphenylprop-2-enone was prepared by exposing a solution of the *trans*-isomer in n-pentane to direct sunlight for five days, $\lambda_{max.}$ (pentane) 288 (log ε 3·90) and 252 nm (4·10) [lit.,[15] $\lambda_{max.}$ 290 (log ε 3·95) and 248 nm (4·15)], m.p. 44—46° (lit.,[15] 45—46°), $J_{\alpha\beta}$ 12 Hz. *cis*-4-Phenylbut-3-en-2-one was prepared by irradiation of the *trans*-isomer in ether with a mercury vapour arc lamp, $\lambda_{max.}$ (ethanol) 289 (log ε 4·51) and 228 nm (4·03) [lit.,[15,16] $\lambda_{max.}$ 308 (log ε 4·55) and 230 nm (4·15), $J_{\alpha\beta}$ 13 Hz].

Reactions with Chlorine.—(a) *In methanol.* The αβ-unsaturated ketone was dissolved in methanol containing the appropriate amount of added electrolyte such that the initial concentrations of ketone and chlorine was *ca.* 0·003M. In the case of the very reactive ketones, such as the 4-methoxy-derivatives, substitution of the benzene ring follows the reaction of the double bond, and hence only 0·0015M chlorine was used. When the reaction was complete, the solution was poured into water and extracted with carbon tetrachloride. The carbon tetrachloride solution was washed with water, dried (Na$_2$SO$_4$), and evaporated under reduced pressure. The ^{1}H n.m.r. spectrum of the residue was recorded and the product proportions were calculated from the areas under the methoxy-proton singlet resonances and confirmed by consideration of the areas under the β-proton doublet resonances. Mixtures of diastereoisomeric methoxy-chlorides were also obtained by chlorination of the corresponding ketone with t-butyl hypochlorite in methanol.[2a] The *erythro*-methoxy-chlorides were separated from the mixture on silica gel by elution with carbon tetrachloride–light petroleum (2 : 1). *erythro*-2-Chloro-3-methoxy-1,3-diphenylpropanone had m.p. 53—55°; *erythro*-3-chloro-4-methoxy-4-phenylbutan-2-one was an oil (Found: C, 70·2; H, 5·5. C$_{16}$H$_{15}$ClO$_2$ requires C, 70·1; H, 5·6%); 4-NO$_2$C$_6$H$_4$CH(OMe)CHClCOPh (Found: C, 59·9; H, 4·4. C$_{16}$H$_{14}$ClNO$_4$ requires C, 60·1; H, 4·4%); PhCH(OMe)-CHClCOMe (Found: C, 62·3; H, 6·1. C$_{11}$H$_{13}$ClO$_2$ requires C, 62·2; H, 6·2%); 4-MeOC$_6$H$_4$CH(OMe)CHClCOMe (Found: C, 59·4; H, 6·1. C$_{12}$H$_{15}$ClO$_3$ requires C, 59·4; H, 6·2%); 4-NO$_2$C$_6$H$_4$CH(OMe)CHClCOMe (Found: C, 51·2; H, 4·7. C$_{11}$H$_{12}$ClNO$_4$ requires C, 51·3; H, 4·7%). The reactions in methanol were also carried out in the presence of external illumination, but no change was observed in the product composition.

(b) *In trifluoroacetic acid.* The αβ-unsaturated ketone (0·001 mol) was added to a solution of chlorine in trifluoroacetic acid (20 ml, 0·05M) at 20° with or without the appropriate amount of lithium chloride, lithium perchlorate, or sodium trifluoroacetate. After 1 h the mixture was poured into water and extracted with carbon tetrachloride. The extract was worked-up and examined as described above.

The mixtures of trifluoroacetoxy-chlorides were obtained by similar chlorination of the appropriate ketone in trifluoroacetic acid in the presence of an excess of sodium trifluoroacetate. The resulting oil was separated on silica gel by elution with benzene. The mixture of *erythro*- and *threo*-2-chloro-3-trifluoroacetoxy-1,3-diphenylpropanone was analysed (Found: C, 57·5; H, 3·3. Calc. for C$_{17}$H$_{12}$ClF$_3$O$_3$: C, 57·4; H, 3·4%). *erythro*- and *threo*-3-Chloro-4-trifluoroacetoxy-4-phenylbutan-2-one (Found: C, 48·9; H, 3·7. Calc. for C$_{12}$H$_{10}$ClF$_3$O$_3$: C, 49·0; H, 3·4%) were similarly treated.

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[8] H. Lund and J. Bjerrum, *Ber.*, 1931, **64**, 210.

[9] S. Gamboni, V. Theus, and M. Schinz, *Helv. Chim. Acta*, 1955, **38**, 255.

[10] A. Einhorn and J. P. Grabfield, *Annalen*, 1888, **243**, 363.

[11] R. E. Corbett and C. L. Davey, *J. Amer. Chem. Soc.*, 1955, **77**, 296.

[12] H. P. Rothbaum, I. Ting, and P. W. Robertson, *J. Chem. Soc.*, 1948, 980.

[13] W. B. Black and R. E. Lutz, *J. Amer. Chem. Soc.*, 1955, **77**, 5134.

[14] D. S. Noyce and W. A. Pryor, *J. Amer. Chem. Soc.*, 1959, **81**, 618.

[15] R. E. Lutz and S. R. Jordan, *J. Amer. Chem. Soc.*, 1950, **72**, 4090.

[16] H. O. House, *J. Org. Chem.*, 1959, **24**, 1374.

(c) *In chloroform.* Chlorine was treated with the αβ-unsaturated ketones in the manner described for the methyl cinnamates to give PhCHClCHClCOMe (Found: C, 55·6; H, 4·6. $C_{10}H_{10}Cl_2O$ requires C, 55·6; H, 4·6%). *erythro*-2,3-Dichloro-1,3-diphenylpropanone was separated from the mixture of diastereoisomers by elution from silica gel with n-hexane–light petroleum (2 : 1). It had m.p. 115—116° (lit.,[17] 116°). Similarly separated was *erythro*-3,4-dichloro-4-phenylbutan-2-one, m.p. 73—76°.

Other Reactions.—(a) *Dehydrochlorinations.* *erythro*-2,3-Dichloro-1,3-diphenylpropanone (*ca.* 0·001 mol) was added to a solution of sodium t-butoxide in t-butyl alcohol (50 ml, 0·05M) and refluxed for 15 min. An aliquot portion (10 ml) was removed, poured into water, and extracted with carbon tetrachloride. The extract, when washed with water and worked-up as described above, was shown to contain *ca.* 30% unchanged *erythro*-dichloride. Similar treatment of a mixture containing both *erythro*- and *threo*-dichlorides (1 : 1) contained only traces of the *erythro*-dichloride. Similar results were obtained in the dehydrochlorination of the 3,4-dichloro-4-phenylbutan-2-ones.

(b) *Dehydromethoxylation.* (i) *erythro*-2-Chloro-3-methoxy-1,3-diphenylpropanone (0·275 g, *ca.* 0·001 mol) was heated under reflux with a solution of sodium t-butoxide in t-butyl alcohol (50 ml, 0·05M). After 3 h an aliquot portion was cooled, poured into water, and worked-up as described above. It contained (^{1}H n.m.r.) 19% 2-chloro-1,3-diphenylprop-2-enone and 81% of a mixture of *erythro*- and *threo*-2-chloro-3-methoxy-1,3-diphenylpropanone in the ratio 7 : 5. After 20 h the remaining reaction mixture was cooled and worked-up as described above. It contained a mixture of the two isomers of 2-chloro-1,3-diphenylprop-2-enone, $\lambda_{max.}$ (ethanol) 298 (log ε 4·03) and 247 nm (4·15) [lit.,[18] $\lambda_{max.}$ 300 (log ε 4·12) and 245 nm (4·20)]. Similar treatment of a mixture of *erythro*- and *threo*-2-chloro-3-methoxy-1,3-diphenylpropanone (3 : 2) for 3 h gave 37% 2-chloro-1,3-diphenylprop-2-enone.

(ii) *erythro*-3-Chloro-4-phenyl-4-methoxybutan-2-one (0·255 g, 0·0012 mol) was heated under reflux for 18 h with a solution of sodium acetate in ethanol (50 ml; 0·05M). The solution was cooled, poured into water, and worked-up as described above to give a mixture of the two isomers of 3-chloro-4-phenylbut-3-en-2-one, $\lambda_{max.}$ (ethanol) 292 (log ε 4·12), 229 (3·84), and 223 nm (3·85) [lit.,[18] $\lambda_{max.}$ 291 (4·19), 228 (3·91), and 222 nm (3·91)].

Kinetics.—The rates of reaction were measured by methods similar to those described earlier for the chlorination of methyl cinnamate in acetic acid.[2a] All rate measurements were carried out at 0°, and were found to be unaffected whether the runs were carried out in blackened or clear flasks.

Spectra.—^{1}H N.m.r. spectra were determined using a Varian A60 spectrometer with 20% w/v samples and tetramethylsilane as an internal reference.

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[17] T. Crowell, A. Wall, R. Kemps, and R. Lutz, *J. Amer. Chem. Soc.*, 1963, **85**, 2521.

[18] D. B. Denney and S. T. Ross, *J. Org. Chem.*, 1962, **27**, 1000.