Polar Additions to Olefins. I. The Chlorination of 2-Butene and 1-Phenylpropene

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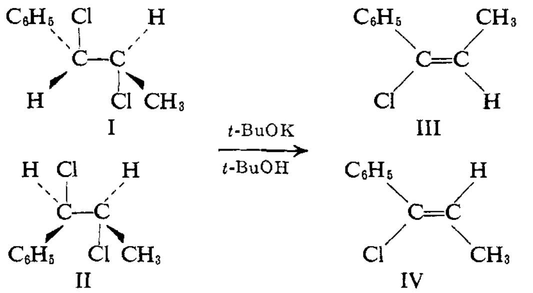
The chlorination of cis- or trans-2-butene in acetic acid yields 2,3-dichlorobutane and 3-chloro-2-butyl acetate by an exclusively trans-addition process. 3-Chloro-1-butene is also formed in small amounts. The chlorination of cis- and trans-1-phenylpropene in carbon tetrachloride and methylene chloride gives (2,3-dichloropropyl)benzene and 2-chloro-1-phenylpropene. (1-Acetoxy-2-chloropropyl)benzene is also formed when acetic acid is the solvent and (1-methoxy-2-chloropropyl)benzene is a major product in methanol. In all cases the kinetically controlled products are mixtures of stereoisomers and cis- and trans-1-phenylpropene give different product mixtures. The results provide further support for a bridged chloronium ion intermediate in the chlorination of 2-butene, but indicate that an open carbonium ion intermediate is involved in the chlorination of 1-phenylpropene.

Introduction

The available data on the stereochemistry of addition of molecular chlorine to olefins are quite limited. Lucas and Gould[1] have reported that *cis*- and *trans*-2-butene add chlorine exclusively *trans*.[2] In contrast to this, stilbene[3] and acenaphthylene[4] both give significant amounts of *cis* adduct with chlorine. All of these additions were carried out under nonpolar conditions. While there have been extensive kinetic studies of chlorination in acetic acid,[5] little is known about the kinetics in nonpolar media. de la Mare has recently emphasized the need for stereochemical data for chlorine addition under conditions where the kinetics are known.[6] It appears that the only case where the stereochemistry of chlorination in acetic acid has been examined is the study of phenanthrene by de la Mare and coworkers.[7] They found that addition of chlorine across the 9,10-bond occurs primarily *cis*. About 10% of the mixed product, acetoxychlorodihydrophenanthrene, was also formed, but the stereochemistry was not established. Clearly, more evidence on the stereochemistry of chlorination in hydroxylic solvents is needed. Also, there is an apparent difference in the stereochemistry of addition to symmetrical dialkyl olefins (2-butene) and aryl-substituted olefins (stilbene, acenaphthylene, and phenanthrene) which warrants further study. In the present paper we report on the stereochemistry of chlorination of the 2-butenes and 1-phenylpropenes, including studies in acetic acid as solvent.

Results

We shall consider first the identification of the products formed in the chlorination of 1-phenylpropene in various solvents. Under nonpolar conditions large amounts of *dl-erythro-* (I) and *dl-threo-*(1,2-dichloropropyl)benzene (II)[8] are formed. These were separated by preparatory v.p.c. and their n.m.r. spectra recorded. The structures are assigned from the products formed when a mixture of the dichlorides was treated with base under conditions for *trans* elimination. The products, 1-chloro-*cis*- (III) and 1-chloro-*trans*-1-phenylpropene[9] (IV), were identified on the basis of differences in their n.m.r. spectra. The C-2–H quartet occurs at τ 4.02 in one olefin and at 3.69 in the other. There is very little difference between the chemical shifts of olefinic protons located *cis* and *trans* to a chlorine,[10–12] but a phenyl group deshields a neighboring *cis* olefinic proton relative to a *trans* proton.[10,11] Thus, we may assign structure IV to the olefin with the C-2–H quartet at lowest field. This criterion has been tested previously and used to assign configurations for a number of styrene derivatives.[13] One dichloride reacts more rapidly than the other, yielding IV as the product. The *trans* stereospecificity of the elimination requires that this dichloride be assigned structure II. The slower reacting dichloride which eliminates to give olefin III is assigned structure I.



Isomeric 2-chloro-*trans*- (V) and 2-chloro-*cis*-1-phenylpropene[14] (VI) are found as minor products in the chlorinations of the 1-phenylpropenes. These were independently prepared by dehydrochlorination of (2,2-dichloropropyl)benzene and pure samples were

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[1] H. J. Lucas and C. W. Gould, *J. Am. Chem. Soc.*, **63**, 2541 (1941).

[2] This has been recently verified by Poutsma (*ibid.*, **87**, 2172 (1965)) for chlorination in nonpolar media under conditions where free-radical addition was completely suppressed.

[3] S. J. Cristol and R. S. Bly, *ibid.*, **82**, 142 (1960).

[4] S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *ibid.*, **78**, 4939 (1956).

[5] P. B. D. de la Mare, *Quart. Rev.* (London), **3**, 126 (1949); *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **47**, 126 (1950).

[6] P. B. D. de la Mare in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, pp. 93–95.

[7] P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger, *J. Chem. Soc.*, 5285 (1961).

[8] For simplicity, only one enantiomer of the *dl*-pairs will be illustrated here and throughout this paper.

[9] (1-Chloropropenyl)benzene.

[10] C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

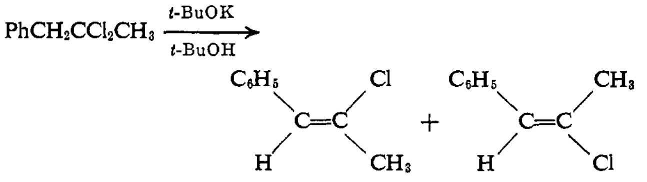
[11] L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881 (1960).

[12] M. Y. DeWolf and J. D. Baldeschwieler, *Mol. Spectry.*, **13**, 344 (1964).

[13] M. Barbieux, N. Defay, J. Pecher, and R. H. Martin, *Bull. soc. chim. Belges*, **73**, 716 (1964).

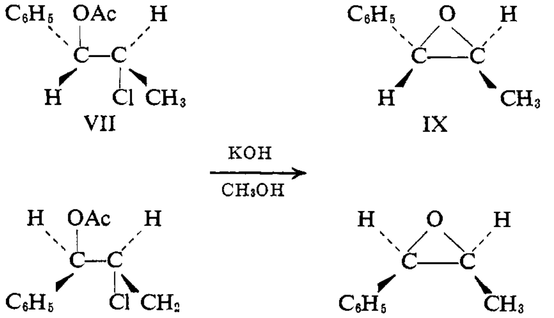
[14] (2-Chloropropenyl)benzene.

isolated by preparative v.p.c. The n.m.r. spectra of the two olefins differ in the aromatic region, the resonance for one isomer occurring as a complex, many-line pattern while that for the other isomer is a narrow, single peak. The complex aromatic resonance may be associated with halogen substituted *cis* to the phenyl group as evidenced by the fact that *cis*-β-bromostyrene[15] and the methyl esters of β-chloro- and β-bromo-*trans*-cinnamic acids[16] give complex patterns for the ring protons, but styrene,[17] a variety of β-substituted (including β-bromo) *trans*-styrenes,[17] and the methyl ester of cinnamic acid[16] all give single peaks in the aromatic region. The 2-chloro-1-phenylpropene giving the many-line pattern is assigned structure V and the one yielding only a single peak is assigned structure VI.



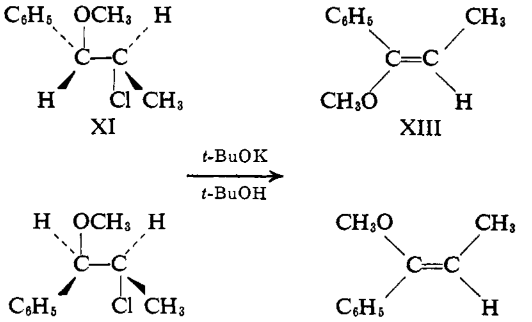
V VI

When the chlorination of the 1-phenylpropenes was carried out in acetic acid, small amounts of *dl-erythro*- (VII) and *dl-threo*-(1-acetoxy-2-chloropropyl)benzene[18] (VIII) were obtained. These were prepared in quantity by the treatment of a mixture of the dichlorides I and II with silver acetate. Since the chloro acetates could not be separated by v.p.c., they were identified by comparing the behavior of mixtures containing varying amounts of the two isomers. When mixtures containing VII and VIII in the ratio 1:1, in one case, and 5:3, in another, were treated with methanolic potassium hydroxide, *trans*- (IX) and *cis*-1-phenylpropene oxide (X) were formed in ratios of 1:1 and 5:3, respectively. This shows that the chloro acetates react stereospecifically with base and indicates that the isomer present at highest concentration in the second mixture is the *erythro* adduct VII.



VII IX VIII X

Chlorination of 1-phenylpropene in methanol yields mainly *dl-erythro*- (XI) and *dl-threo*-(1-methoxy-2-chloropropyl)benzene[19] (XII). Mixtures of these chloro methyl ethers were isolated from the addition products by preparative v.p.c. Upon dehydrochlorination with potassium *t*-butoxide in *t*-butyl alcohol, mixtures of 1-methoxy-*cis*- (XIII) and 1-methoxy-*trans*-1-phenylpropene (XIV) were obtained. One isomer eliminated much more rapidly than the other and gave XIV as the product of elimination. In experiments with different mixtures of XI and XII (1:3 and 3:1), complete reaction led to corresponding ratios of XIII and XIV. Since the elimination is stereospecifically *trans*, the structures may be assigned as indicated. The structures of the olefins are assigned on the basis of the chemical shifts of the C-2-H protons. The differential shielding between olefins *cis* and *trans* to a methoxy group is less than that for a phenyl group.[10] Since a proton *cis* to phenyl is deshielded, the isomer whose resonance is at lowest field is assigned structure XIV.



XI XIII XII XIV

The *meso*- and *dl*-2,3-dichlorobutanes obtained in the chlorination of the 2-butenes are known and have been previously identified.[1] Authentic *dl-threo*-3-chloro-2-butyl acetate was prepared from the corresponding alcohol. The chloro acetate formed in the chlorination of *cis*-2-butene was identical with this material, while the acetate formed with *trans*-2-butene had a slightly different n.m.r. spectrum and a shorter retention time on v.p.c.

Quantitative studies of the chlorination of the 2-butenes were carried out by passing a 1:1 mixture of chlorine and oxygen[20] into a solution of the 2-butene in acetic acid at 22–25°. Samples were removed at intervals during the period of the chlorine addition. They were worked up and analyzed by v.p.c. In the range from 20 to 90% reaction, the product compositions were found to be as shown in Table I. The principal products are those from *trans* addition to the olefin. The contamination by *cis* adducts does not exceed the values expected on the basis of the isomeric contaminations (≤ 1%) of the 2-butenes used in these studies. No significant variation in the product com-

Table I

	From *trans*-2-butene, %	From *cis*-2-butene, %
$CH_2{=}CHCHClCH_3$	1.3–1.7	2.7–3.2
$CH_3CHClCHClCH_3$	72–75	≤0.4
meso	≤0.5	53–54
dl		
$CH_3CHOAcCHClCH_3$	23–25	≤0.4
erythro	≤0.5	42–44
threo		

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(15) D. Seyferth, L. G. Vaughan, and R. Suzuki, *J. Organometal. Chem.*, **1**, 437 (1964).

(16) H. Kasiwagi, N. Nakagawa, and J. Niwa, *Bull Chem. Soc. Japan*, **36**, 410 (1963).

(17) H. Kasiwagi and J. Niwa, *ibid.*, **36**, 405 (1963).

(18) α-(1-Chloroethyl)benzyl acetate.

(19) α-(1-Chloroethyl)benzyl methyl ether.

(20) Used to suppress free-radical addition. See ref. 2.

Table II. Product Distribution in the Chlorination of 1-Phenylpropene

Solvent	Product Composition, % I	II	V	VI	VII or XI	VIII or XII
			trans-1-Phenylpropene			
CCl_4[a]	38–39	45–46	0.7–0.9	15	...	...
CH_2Cl_2[a]	55–56	28–29	1.4–2.1	14–15	...	...
AcOH[b]	27	38–39	0.4–0.8	5.8–6.2	20–21	7–8
CH_3OH[a]	8.5–10.2	7.6–7.8	<0.1	0.4–0.5	65	16–19
			cis-1-Phenylpropene			
CCl_4[a]	61–64	27–30	4.4–5.0	3.7–4.1	...	...
CH_2Cl_2[a]	62–63	21–23	9.3–11.1	5.7–6.5	...	...
AcOH[b]	48–50	14	5.6–6.3	0.9–1.4	15–17	13–15
CH_3OH[a]	8.5–9.0	7.0–8.7	0.7–0.9	0.2–0.3	23	58–60

[a] At 0–5°. [b] At 22–25°.

position with the per cent conversion was observed so that these results reflect the kinetically controlled product composition.

Chlorine addition to the 1-phenylpropenes was studied in a variety of solvents. A procedure similar to that used for the 2-butenes was followed and samples were analyzed by v.p.c. A wide variety of samples was also analyzed by n.m.r. and these results showed good agreement with the v.p.c. determinations. The isomeric chloro acetates were not separated by the v.p.c. conditions used here, so the ratio of these products was determined from the n.m.r. spectra of the individual samples. The product compositions found in the range from 10 to 80% conversion are summarized in Table II.

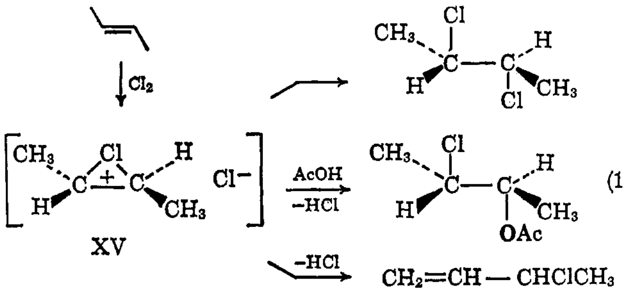
The product distributions from additions carried out in carbon tetrachloride and methylene chloride showed no consistent variations with the per cent reaction. Since the *cis*- and *trans*-1-phenylpropenes give different product compositions, this means that the products are stable under the reaction conditions. The situation for addition in acetic acid was similar, with the exception that the amount of V formed in the addition to *trans*-1-phenylpropene varies from 0.4 to 0.8% as the reaction proceeds. Accordingly, our estimate of this product must reflect a large uncertainty. The chloro methyl ethers formed in the additions in methanol show no large variations in composition with the extent of reaction, indicating that they are stable to the reaction conditions. The dichlorides are formed in about equal amounts in methanol, and there does seem to be a slight increase in the dichloride with increasing conversion. It was conceivable that some interconversion might be occurring in methanol containing hydrogen chloride. In a control experiment, a known mixture of I, II, V, and VI was added to methanol containing hydrogen chloride at a concentration equal to the maximum concentration obtained during the chlorination experiments. The solution was allowed to stand for an interval greater than the usual reaction period. The mixture was then worked up and analyzed in the usual fashion. The composition was unchanged, indicating that the products are stable under these conditions. It thus appears that the product distributions of Table I do reflect the kinetically controlled product composition. The small variations are probably due to the formation of hydrogen chloride during the course of the reaction, which leads to increased dichloride formation as the addition proceeds. It is clear, however, that this increase constitutes only a fraction of the total dichloride formed and that dichloride formation is not dependent upon the presence of hydrogen chloride.

It is important to add that, in all of these additions, no isomerization of the starting olefin occurred during the course of the addition as evidenced by both the v.p.c. and n.m.r. analyses.

Discussion

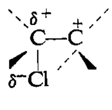
Our data show that the 2-butenes give the same *trans* stereospecificity for chlorination in acetic acid as has been observed under nonpolar conditions, but that the 1-phenylpropenes add nonstereospecifically in both polar and nonpolar solvents. With these results at hand, we are in a better position to discuss certain aspects of the chlorination of olefins.

We consider first the results for addition to the 2-butenes in acetic acid. The products may be accounted for by a mechanism of the type proposed by Lucas and Gould,[1] involving a rate-determining formation of a chloronium ion (XV) which reacts further to form the observed products. A mechanism of this type, illustrated with *trans*-2-butene, is shown in eq. 1. The intermediate is shown here as an ion pair, as is appropriate for weakly dissociating solvents, such as acetic acid. Both the addition to form exclusively the *trans*-dichloride and the substitution to give 3-chloro-1-butene (rather than 2-chloro-2-butene) are consistent with a bridged ion intermediate but not with an open carbonium ion intermediate.

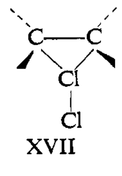


(1)

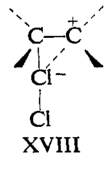
de la Mare has suggested[6] that the intermediate involved in the product-determining step for olefin chlorination might alternatively be formulated as structures XVI, XVII, or XVIII. For addition to the



XVI

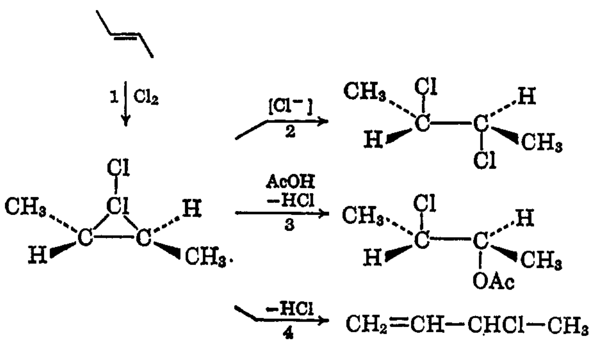


XVII



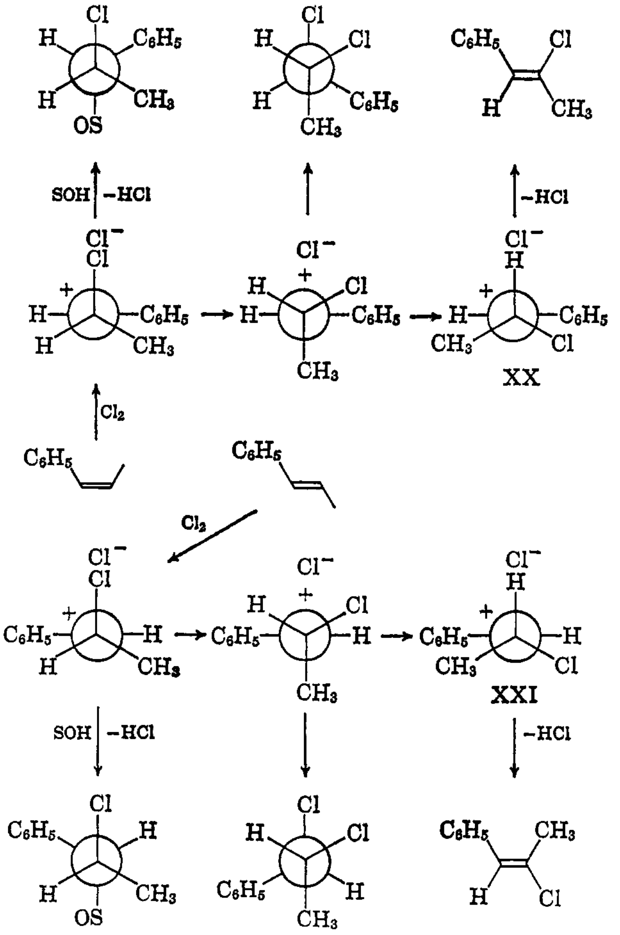
XVIII

2-butenes, the present evidence does not rule out XVI as the intermediate, so long as it is assumed that the interaction indicated by the dotted line is strong enough to preclude collapse to *cis* adduct. Our results do have a bearing on the possible intermediacy of structures XVII and XVIII. Let us assume that chlorine reacts with *trans*-2-butene forming an intermediate of the type represented by structure XVII and that this species is involved in the product-forming steps as illustrated in eq. 2. It does not appear stereochemically feasible, in this mechanism, for both chlorines of the product dichloride to have been derived from this intermediate and at the same time to have *trans* addition to the olefin. Thus, some other source of chloride is required in step 2, as is indicated in eq. 2. The only sources of chloride in our system are hydrogen chloride (formed in steps 3 and 4) and molecular chlorine. If hydrogen chloride is involved in step 2, we would expect the amount of dichloride formed to increase as the reaction progresses and the hydrogen chloride concentration increases, but this is not observed (Table II). If a second molecule of chlorine attacks the intermediate in a fashion leading to *trans* addition, then there must be formed in step 2 an ionized and dissociated molecule of chlorine. This would certainly require that step 2 be slower than step 1. However, olefin chlorinations in acetic acid follow a rate law which is first order in the chlorine concentration,[5] and this is inconsistent with step 2 being rate determining. We feel, therefore, that a mechanism of the type illustrated in eq. 2 does not represent a reasonable alternative to the mechanism of eq. 1. An analogous argument may be given against an intermediate such as XVIII being important in product formation. The mechanism of eq. 1, involving a chloronium ion intermediate, remains the simplest scheme consistent with the data on the chlorination of 2-butene.



(2)

Turning to the results obtained with the 1-phenylpropenes, we see that the products are those expected from carbonium ion reactions, but the lack of stereospecificity indicates an open rather than a bridged ion intermediate. A different product distribution is obtained from *trans*- than from *cis*-1-phenylpropene, showing that the two additions do not involve one common intermediate. This is hardly surprising, since ion pairs should intervene in these solvents, and different ion pairs would be formed from the two olefins. We note that in all solvents chlorination of *trans*-1-phenylpropene gives mainly 2-chloro-*cis*-1-phenylpropene as the substitution product, while *cis*-1-phenylpropene gives primarily 2-chloro-*trans*-1-phenylpropene. Also, with the exception of the additions in methanol, the dichloride formed in largest quantity is usually the *cis* addition adduct. Preferential *cis* collapse of ion pairs is not unreasonable. Moreover, if the proton eliminations which give V and VI involve the counterion (chloride ion), as is indicated in some solvolytic eliminations,[21] the steric preference in the elimination is plausibly explained in terms of the ion-pair conformations XX and XXI, which should undergo preferential *cis* elimination. This type of *cis* elimination is analogous to that found when deuterium-labeled 2-butyl tosylates are solvolyzed in media of low basicity.[21b] One might also expect that nucleophilic solvents should attack the ion pair preferentially from the side opposite to that occupied by the chloride ion. In acetic acid and methanol there does seem to be a tendency for the mixed product to be formed preferentially *trans*.



Although the qualitative nature of the product distribution can be rationalized in terms of ion-pair intermediates, a simple mechanism encompassing the chlorination of both *cis*- and *trans*-1-phenylpropene cannot be implied from the results. Thus, we might ask whether any two products are derived from a single intermediate which is common in the addition to both olefins. If this were the case, the ratio of the two products would be the same, independent of the olefin being studied. If one constructs a table of all possible combinations of product ratios, it is found that significantly different ratios are obtained from the two different olefins in any given solvent. Only two exceptions are found. The ratio of I to VIII is very nearly the same for both olefins when the chlorination is

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[21] (a) M. Cocivera and S. Winstein, *J. Am. Chem. Soc.*, **85**, 1702 (1963); (b) P. S. Skell and W. L. Hall, *ibid.*, **85**, 2851 (1963).

carried out in acetic acid, and the two dichlorides are formed in the same ratio with each olefin for the chlorination in methanol. The fact that most product ratios are different for the two olefins suggests that the corresponding mechanisms may have little in common. It is thought that the rate for rotation about carbon–carbon single bonds can be comparable to the rate of ion-pair collapse.[22] This could well be true in the present case. If so, each of the conformations of the ion pairs must be considered separately. Each conformer could collapse to products at a different rate and interconversion of the conformers would occur at different competing rates. This description necessarily implies a complex mechanism in terms of which the chlorination of *cis*- and *trans*-1-phenylpropene would understandably give different product ratios.

The contrasting behavior of the 2-butenes and 1-phenylpropenes deserves some comment. If the results are interpreted in terms of carbonium ion intermediates, it must be concluded that bridged ions are involved in additions to the 2-butenes, but that open ions are involved, though perhaps not exclusively, with the 1-phenylpropenes. The present results, taken together with the earlier evidence on stilbene,[2] acenaphthylene,[3] and phenanthrene,[4] and the recent report that cyclohexene adds chlorine exclusively *trans*,[23] show that chlorine is quite effective in bridging to a secondary carbonium ion center, but that such bridging is severely reduced or eliminated when the carbonium center is in conjugation with an aromatic ring. A similar explanation has been given for the steric course of the reaction of the stilbene dichlorides with silver acetate[24] and for the stereochemistry of the chlorination of stilbene and cyclohexene with iodobenzene dichloride as the chlorinating agent.[25]

Since chlorine does not appear to bridge effectively to a phenyl-substituted carbonium center, one might expect that chlorine bridging to a tertiary carbonium carbon would also be weak. However, there is some evidence that chlorine participation is important in such cases.[26] Just how strong the interaction is remains unclear, and, in this regard, it would be of interest to know the steric course of dichloride formation for an olefin chlorination which formally proceeds *via* a tertiary carbonium ion intermediate. There does not at present appear to be any evidence on this point.

Experimental Section

Materials. *trans*-1-Phenylpropene was purchased from Aldrich Chemical Co. *cis*-1-Phenylpropene was prepared as described previously.[27] For quantitative studies both olefins were purified by v.p.c., sealed in ampoules under nitrogen, and stored in a refrigerator until used. Chlorine, oxygen (extra dry), and the 2-butenes (C.P. grade) were obtained from Matheson Co. Chlorine was passed through a sulfuric acid trap prior to use. Spectroquality methylene chloride and pentane were purchased from Matheson Coleman and Bell, as was phenyl-2-propanone and an equilibrium mixture of 1-chloro-2-butene with 3-chloro-1-butene. 2-Chloro-2-butene was supplied by Columbia Chemicals Co. Authentic *dl*- and *meso*-2,3-dichlorobutane were prepared according to the method of Lucas and Gould.[1]

Chlorination of 1-Phenylpropene in Methylene Chloride. A solution of 23 g. (0.2 mole) of 1-phenylpropene (Aldrich Chemical Co. unpurified) in 100 ml. of methylene chloride was added to a reaction flask immersed in an ice bath. Light was excluded and chlorine was passed into the solution. Aliquots were removed and analyzed by v.p.c. and the reaction was stopped when 90% of the olefin had reacted. Evaporation of the methylene chloride gave 31 g. of crude product. Evolution of hydrogen chloride during the course of the addition was noted. The crude product mixture was purified by preparatory v.p.c. using column A at 130° with a helium flow of 250 ml./min. Fractions containing unreacted 1-phenylpropene, 2-chloro-1-phenylpropene, *dl-erythro*-(1,2-dichloropropyl)benzene, and *dl-threo*-(1,2-dichloropropyl)benzene, having retention times of 14, 23–28, 54, and 61 min., respectively, were collected. The n.m.r. spectra of the purified dichlorides are reported in Table III.

Dehydrochlorination of dl-erythro- (I) and dl-threo-(1,2-Dichloropropyl)benzene (II). A 4.8-g. (0.025-mole) sample of a mixture composed of I (60%) and II (40%) was placed in a 50-ml. reaction flask containing 5.0 ml. of 1.25 *M* potassium *t*-butoxide in *t*-butyl alcohol. The mixture was stirred at 25° for 1 hr. A 2-ml. aliquot was then removed, mixed with 10 ml. of water, and extracted with pentane. The pentane fraction was washed with dilute acid and dried over anhydrous magnesium sulfate. After filtration, the pentane was evaporated and the residue was analyzed by v.p.c. and by n.m.r. The composition was: I, 58%; II, 14%; III, 2%; and IV, 25%. The reaction was carried to completion by the addition of 15 ml. of 1.25 *M* potassium *t*-butoxide in *t*-butyl alcohol and stirring for 16 hr. The complete reaction mixture was then worked up in a fashion similar to that described above. Evaporation of the pentane gave 2.5 g. of crude product which analyzed for III and IV in the approximate ratio 3:2. The two components of this mixture were separated by preparatory v.p.c. on column A at 145° with a helium flow rate of 150 ml./min. Retention times were IV, 30 min. and III, 40 min. The n.m.r. spectra of the pure materials are given in Table III.

Preparation of 2-Chloro-trans- (V) and 2-Chloro-cis-1-phenylpropene (VI). A reaction flask was fitted with a stirrer, condenser, drying tube, and dropping funnel and immersed in an ice bath. Phosphorus pentachloride (125 g., 0.6 mole) was placed in the flask and 80 g. (0.6 mole) of phenyl-2-propanone was added over 3 hr. while the mixture was stirred. Stirring was continued for an additional 16 hr. after which the mixture was poured over ice. Methylene chloride was added and the organic layer was separated, washed with water, washed with dilute base, dried over anhydrous calcium chloride, treated with 1 g. of charcoal, and filtered. Evaporation of the methylene chloride left 95 g. of crude product which was analyzed by n.m.r. and found

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[22] C. J. Collins and B. M. Benjamin, *J. Am. Chem. Soc.*, **85**, 2519 (1936); S. Winstein, *ibid.*, **87**, 381 (1965).

[23] M. L. Poutsma, *ibid.*, **87**, 2161 (1965).

[24] S. Winstein and D. Seymour, *ibid.*, **68**, 119 (1946).

[25] J. L. Cotter, L. J. Andrews, and R. M. Keefer, *ibid.*, **84**, 793 (1962).

[26] P. Ballinger and P. B. D. de la Mare, *J. Chem. Soc.*, 1481 (1957); J. G. Traynham and O. S. Pascual, *Tetrahedron*, **7**, 165 (1959); see also the discussion by de la Mare in ref. 6, p. 101.

[27] M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 3645 (1963).

Table III. N.m.r. Data

Compd.	Shift, τ	Multiplicity	J, c.p.s.	Rel. area
I	2.72	Singlet	...	5
	5.20	Doublet	8.0	1
	5.73	Approx. quintet	...	1
	8.32	Doublet	6.4	3
II	2.71	Singlet	...	5
	5.08	Doublet	5.7	1
	5.70	Approx. quintet	...	1
	8.59	Doublet	6.6	3
III	2.68	Singlet	...	5
	4.02	Quartet	7.3	1
	8.30	Doublet	7.3	3
IV	2.2–2.7	Complex	...	5
	3.69	Quartet	6.7	1
	8.09	Doublet	6.7	3
V	2.3–2.9	Complex	...	5
	3.72	Unresolved mult.	...	1
	7.86	Doublet	1.2	3
VI	2.86	Singlet	...	5
	3.40	Unresolved mult.	...	1
	7.81	Doublet	1.2	3
VII	2.75	Singlet	...	5
	4.19	Doublet	5.4	1
	5.80	Complex	...	1
	7.92	Singlet	...	3
	8.57	Doublet	6.5	3
VIII	2.75	Singlet	...	5
	4.31	Doublet	7.3	1
	5.81	Complex	...	1
	7.95	Singlet	...	3
	8.70	Doublet	6.6	3
IX	2.82	Singlet	...	5
	6.61	Doublet	1.8	1
	7.18	Quartet of doublets	5.0 1.8	1
	8.63	Doublet	5.0	3
X	2.79	Singlet	...	5
	6.12	Doublet	4.2	1
	6.85	Complex	...	1
	8.99	Doublet	5.2	3
XI	2.74	Singlet	...	5
	5.92	Complex	...	2
	6.75	Singlet	...	3
	8.55	Approx. doublet	6.5	3
XII	2.74	Singlet	...	5
	5.91	Complex	...	2
	6.77	Singlet	...	3
	8.78	Approx. doublet	6.5	3
XIII	2.74	Singlet	...	5
	5.33	Quartet	7.0	1
	6.46	Singlet	...	3
	8.34	Doublet	7.0	3
XIV	2.52–2.96	Complex	...	5
	4.78	Quartet	6.9	1
	6.55	Singlet	...	3
	8.25	Doublet	6.9	3
dl-threo-3-Chloro-2-butyl acetate				
	5.03	Complex (A)	4.5 (J_{AB})[a]	1
	5.99	Complex (B)		1
	7.97	Singlet	6.2 (J_{AY})[a]	3
	8.54	Doublet (X)		3
	8.73	Doublet (Y)	6.6 (J_{BX})[a]	3
dl-erythro-3-Chloro-2-butyl acetate				
	5.11	Complex (A)	4.8 (J_{AB})[a]	1
	5.97	Complex (B)		1
	7.99	Singlet	6.3 (J_{AY})[a]	3
	8.55	Doublet (X)		3
	8.73	Doublet (Y)	6.6 (J_{BX})[a]	3

[a] From spin decoupling experiments.

to contain primarily a 2:1 mixture of (2,2-dichloropropyl)benzene and 2-chloro-1-phenylpropene (*cis* and *trans* isomers). This material was diluted with 50 ml. of ethanol and added to a solution of 22 g. of potassium hydroxide in 150 ml. of ethanol. The mixture was stirred at 50° for 2 hr. and then worked up in water by extracting with methylene chloride. The organic layer was washed with dilute acid and dried over anhydrous magnesium sulfate. Evaporation of the methylene chloride gave an oil which was analyzed by n.m.r. and found to contain considerable unreacted dichloride. This material was then refluxed with 20 g. of potassium hydroxide in 150 ml. of ethanol for 3 hr. and worked up as before. A 63-g. yield of product was obtained which was analyzed by v.p.c. and n.m.r. and found to be primarily (75%) a 2:1 mixture of V and VI. Part of the crude product was purified by v.p.c. on column A at 120° with a helium flow of 200 ml./min. Retention times were: unidentified impurities, 33, 37, and 47 min.; VI, 57 min.; and V, 74 min. N.m.r. spectra (Table III) were obtained on the pure samples.

dl-erythro- (VII) and dl-threo-(1-Acetoxy-2-chloropropyl)benzene (VIII). A 4.0-g. (0.021-mole) sample containing I and II in the ratio of 5:3 was added to a mixture of 50 ml. of acetic acid and 3.5 g. (0.021 mole) of silver acetate. The mixture was stirred at 100° for 1.5 hr. The reaction mixture was worked up in water, followed by extraction with pentane. The pentane fraction was washed with dilute, aqueous sodium bicarbonate and dried over anhydrous potassium carbonate. After evaporation of the pentane, the crude product (4.5 g.) was analyzed by n.m.r. and found to contain approximately equal amounts of dichloride and chloro acetate. This mixture was treated further with 2.5 g. of silver acetate in 50 ml. of acetic acid for 2 hr. at 100°. After work-up as before, analysis showed that the dichloride had been completely reacted. The 3.8 g. of crude product obtained was purified by v.p.c. on column B at 170° with a flow of 100 ml. of helium/min. A 5:3 mixture of VII and VIII (retention time 23 to 37 min.) was isolated. In another analogous experiment, a 1:1 mixture of VII and VIII was obtained. The n.m.r. spectra reported in Table III were derived from these mixtures.

Reaction of VII and VIII with Methanolic Potassium Hydroxide. A sample containing 0.32 g. (1.5 mmoles) of VII and VIII in a 5:3 ratio was added to 12 ml. of 0.5 *M* potassium hydroxide in methanol and stirred at room temperature for 1 hr. The temperature was then raised to 50° and stirring was continued for 15 min. The reaction mixture was then dumped into water and extracted three times with pentane. The combined pentane layers were washed with water and dried over anhydrous potassium carbonate. Evaporation of the pentane gave 0.18 g. (90%) of product which was analyzed by n.m.r. and found to contain *trans*- (IX) and *cis*-1-phenylpropene oxide (X) in a 5:3 ratio. In another experiment, a 1:1 mixture of VII and VIII gave equal amounts of the two epoxides. N.m.r. spectra of the epoxides are included in Table III.

Authentic 1-Phenylpropene Oxide. Chloroform (50 ml.) and sodium acetate (0.5 g.) were added to 8.5 ml. of 5.2 *M* peracetic acid in acetic acid (F. M. C. Corp.) and the mixture was cooled in an ice bath. A solution of 5.0 g. (0.042 mole) of 1-phenylpropene (Aldrich: 95% *trans*, 5% *cis*) in 20 ml. of chloroform was added over 20 min. The solution was stirred at 0° for 1 hr., allowed to stand at 0° for 12 hr., and then stirred at 25° for 12 hr. The reaction mixture was dumped into water and the chloroform layer was separated. The water layer was washed with chloroform and the two chloroform fractions were combined. After washing with dilute base and then water, the chloroform fraction gave a negative peroxide test with iodide. The solution was dried over anhydrous magnesium sulfate and the chloroform was evaporated. A 5.0-g. (88%) yield of product was obtained. The material gave the expected n.m.r. spectrum for *trans*-1-phenylpropene oxide (IX) contaminated by 6% *cis*-1-phenylpropene oxide (X).

dl-erythro- (XI) and dl-threo-(1-Methoxy-2-chloropropyl)benzene (XII). A solution of 8.7 g. (0.074 mole) of *trans*-1-phenylpropene (Aldrich, unpurified) in 50 ml. of methanol was stirred at 5–10° and a 1:1 mixture of chlorine and oxygen was passed in until chlorine was in excess. The mixture was poured into water and extracted twice with pentane. The combined pentane fractions were washed with dilute base and dried over anhydrous potassium carbonate. Evaporation of the pentane left a 13-g. yield of crude product. Part of this material was purified by v.p.c. using column B at 140° with a helium flow of 150 ml./min. A mixture of the methoxy chlorides eluting from 17 to 30 min. after injection was collected. Analytical v.p.c. and n.m.r. analyses of the mixture showed that XI and XII were present in a 3:1 ratio. A similar sequence of experiments starting with *cis*-1-phenylpropene gave the same products in a 1:3 ratio. The n.m.r. spectra of these compounds, as derived from the two mixtures, are given in Table III.

Dehydrochlorination of XI and XII. A 0.92-g. (5-mmole) sample composed of XI and XII in a 3:1 ratio was added to 3 ml. of 1.0 *M* potassium *t*-butoxide in *t*-butyl alcohol and stirred at 50°. After 2 hr. a 0.5-ml. sample was removed, shaken with water, and extracted with pentane. The pentane layer was separated and dried over anhydrous potassium carbonate. Evaporation of the pentane and analysis of the residue by v.p.c. showed that XI was still present while XII was about half-reacted to give a product later shown to be 1-methoxy-*trans*-1-phenylpropene (XIII) from its n.m.r. spectrum. An additional 10 ml. of 1 *M* potassium *t*-butoxide solution was added and stirring was continued at 50° for an additional 11 hr. A 1.0-ml. sample was then removed, worked up, and analyzed. All of the XII originally present had reacted to form XIII. About 17% of 1-methoxy-*cis*-1-phenylpropene (XIV) was also present and 58% of XI remained unreacted. The reaction mixture was heated at 80–90° for 6 hr., then cooled and worked up. Analysis of the product by v.p.c. showed the composition to be: XI, 7%; XII, 0%; XIII, 27%; and XIV, 66%. Another experiment with XI and XII in the ratio 1:3 gave similar results with complete reaction yielding XIII and XIV in the ratio 3:1. The n.m.r. spectra of XIII and XIV are given in Table III.

dl-threo- and dl-erythro-3-Chloro-2-butyl Acetate. A reaction flask was fitted with a gas inlet tube, drying tube, magnetic stirrer, and thermometer. Glacial acetic acid (50 ml.) was added and 4.5 g. of 2-butene was distilled into the flask. The mixture was stirred and protected from light, and chlorine was bubbled into the solution. The temperature was held between 22 and 27° with a water bath. When the chlorine was in slight excess, the addition was stopped and the reaction mixture was poured into water and pentane. The pentane layer was separated, washed with dilute sodium bicarbonate solution, and dried. The chloro acetates were isolated by preparatory v.p.c., the *threo* isomer being obtained from *cis*-2-butene and the *erythro* isomer from *trans*-2-butene. N.m.r. spectra were obtained on the pure materials, and spin decoupling techniques were employed to evaluate the spin coupling constants and their assignment. The data are reported in Table III.

Authentic *dl-threo*-3-chloro-2-butanol was prepared from *cis*-2-butene oxide according to the procedure of Lucas and Gould.[1] A 2.2-g. (0.02-mole) sample of the alcohol was stirred with 5.7 ml. of acetic anhydride in 17 ml. of pyridine at 100° for 1 hr. The reaction mixture was then mixed with 120 ml. of cold 2 *M* hydrochloric acid and the resulting mixture was extracted with three 20-ml. portions of methylene chloride. The combined methylene chloride extracts were washed with two 20-ml. portions of 5% aqueous sodium hydroxide and dried over anhydrous potassium carbonate. The methylene chloride was evaporated to yield 2.6 g. (87%) of the *threo* acetate, with a trace of methylene chloride still present. This material gave the n.m.r. spectrum reported in Table III. V.p.c. analysis (see procedure below) of mixtures showed that the acetate from chlorination of *cis*-2-butene had the same retention time as the authentic *threo* acetate, but that the adduct from *trans*-2-butene had a shorter retention time.

Quantitative Studies of the Chlorination of 2-Butene. A dry, 25-ml. reaction flask was fitted with a gas inlet tube, thermometer, drying tube, and magnetic stirring bar. Glacial acetic acid (10 ml.) was added, and 1.0 g. of 2-butene was condensed into the flask. The mixture was stirred, protected from light, and a 1:1 mixture of chlorine and oxygen was passed into the flask. The temperature was maintained between 22 and 25° with a water bath. Aliquots (1-ml.) were removed at intervals and shaken with 10 ml. of water and 1 ml. of pentane. The pentane layer was separated and washed with dilute sodium bicarbonate. This solution was then analyzed by v.p.c. using a 10-ft. × $^1/_8$ in. column packed with 3% polypropylene glycol on Chromosorb G. The temperature was programmed from 50 at 1.5°/min., and the helium flow rate was maintained at 18 ml./min. Retention times (in minutes) were: 2-butene and pentane, 0.5–2.0; 3-chloro-1-butene, 3.0; *dl*-2,3-dichlorobutane, 9.5; *meso*-2,3-dichlorobutane, 10.5; *dl-erythro*-3-chloro-2-butyl acetate, 22; and *dl-threo*-3-chloro-2-butyl acetate, 24. These conditions were not adequate to differentiate the isomeric chlorobutenes. For this purpose a 15 ft. × $^1/_8$ in. column packed with 20% SE-52 on Chromosorb P was used at 50° with a helium flow of 12 ml./min. Retention times (in minutes) for authentic samples were: 3-chloro-1-butene, 13; 2-chloro-2-butene, 17; and 1-chloro-2-butene, 25. The product mixtures from chlorination of the 2-butenes showed a peak at 13 min., but not at 17 or 25 min.

In control experiments, it was shown that product fractionation in the course of the work-up procedure does not lead to significant errors in the product composition.

Quantitative Studies of the Chlorination of 1-Phenylpropene. The procedure followed was similar to that used for the 2-butenes. In a typical experiment, 0.8 g. of the 1-phenylpropene and 5 ml. of solvent were used. Temperatures for additions in carbon tetrachloride, methylene chloride, and methanol were maintained at 0–5° by the use of an ice–water bath, while temperatures for additions in acetic acid were kept at 22–25° with a water bath. The reaction was complete in 5 to 6 min. Samples were removed during this interval and either evaporated directly (carbon tetrachloride and methylene chloride as solvent) or dumped into water and extracted with pentane (acetic acid and methanol as solvent). In the latter case, the pentane layer was separated, washed with water, and dried over anhydrous potassium carbonate. The pentane was evaporated and the residue was analyzed by v.p.c. and, in many cases, by n.m.r. also. The v.p.c. and n.m.r. analyses were in good agreement. V.p.c. analyses were carried out with a 4 ft. × $^1/_8$ in. column packed with 20% diethylene glycol succinate on Chromosorb P. The temperature was programmed from 75 at 1.5°/min., and the helium flow rate was 60 ml./min. The injection port temperature was maintained at 100° to avoid sample pyrolysis which occurred when higher temperatures were used. Retention times (in minutes) were: *cis*-1-phenylpropene, 4; *trans*-1-phenylpropene, 6.5; VI, 12; V, 14.5; XI, 18; XII, 20.5; I, 27; II, 29; and VII and VIII, 38. All of the samples obtained in acetic acid were analyzed by n.m.r. to obtain the ratio of VII to VIII.

To test the stability of the chlorination products in acidified methanol, a 0.7-g. sample containing I (58.7%), II (31.1%), V (1.6%), and VI (8.7%) was added to 5 ml. of 0.75 *M* methanolic hydrogen chloride and the mixture was stirred at 0°. A 1-ml. sample was removed after 6 min. and worked up in the usual fashion. V.p.c. analysis showed the composition to be: I (59.5%), II (30.0%), V (1.6%), VI (8.8%).

Using known mixtures, it was demonstrated that no significant product fractionation occurs during the isolation process.

V.p.c. Procedure. Preparatory v.p.c. separations were carried out on an Aerograph Autoprep chromatograph using column A (10 ft. × $^3/_8$ in.) or column B (4 ft. × $^3/_8$ in.) packed with 30% diethylene glycol succinate on Chromosorb P. An Aerograph Moduline Model 202 chromatograph equipped with thermal conductivity detectors and a linear temperature programmer was used for the analytical measurements. The columns and conditions for the analytical separations have already been described. Peak areas were integrated with a disk integrator installed on the recorder, and mole ratios were taken equal to peak area ratios. The validity of this procedure was checked with known samples for the experiments with the 2-butenes and was varified by independent n.m.r. analyses for the experiments with the 1-phenylpropenes.

N.m.r. Procedure. N.m.r. spectra were measured on a Varian HR-60 spectrometer using the side-band technique to calibrate peak positions. Peak areas were integrated electronically. Samples were measured as approximately 15% v./v. solutions in carbon tetrachloride, containing tetramethylsilane as an internal standard.

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Positive Halogen Compounds. XII.[1] Relative Reactivities of Hydrocarbons toward Alkoxy Radicals Determined by Direct and Indirect Methods[2]

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Relative reactivities of hydrocarbons toward t-butoxy radicals derived from t-butyl hypochlorite have been determined in dilute chlorobenzene solution by direct competition and indirectly from t-butyl alcohol–acetone yields. For several pairs one of which contains benzylic hydrogen the results are inconsistent, indicating a more complicated reaction path than previously assumed. It is shown that, in the cyclohexane–toluene system, the presence of toluene leads to increased yields of cyclohexyl chloride, although alcohol–acetone yields are additive. Results are consistent with a scheme in which attack on benzylic hydrogen occurs by two paths, one of which involves an unknown radical intermediate which can be intercepted by aliphatic hydrocarbons. A similar explanation is used to account for the enhanced reactivity of β-hydrogens in ethylbenzene and tetralin.

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(1) Preceding paper in this series: C. Walling, L. Heaton, and D. D. Tanner, *J. Am. Chem. Soc.*, **87**, 1715 (1965).

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