A, C–O repulsion integrals were approximated by C–C integrals at the same distance.

The effective nuclear charge on oxygen was adjusted empirically and the value is given in Table V.

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Solvent and Salt Effects on the Products from Polar Chlorination of the Linear Pentenes

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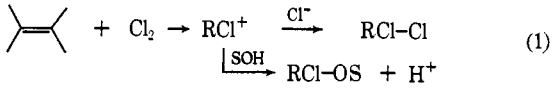
Abstract: Product distributions from chlorination of *cis*-2-, *trans*-2-, and 1-pentene in methanol, ethanol, formic acid, *t*-butyl alcohol, acetic acid, and trifluoroacetic acid have been determined as well as the effects of added lithium chloride, lithium acetate, lithium perchlorate, and lithium formate in acetic acid and lithium chloride in methanol. For the 2-pentenes, addition in each case gives both vicinal dichloride and solvent-incorporated product, each in a stereospecifically *trans* fashion. For the latter product type, both possible positional isomers are formed with a slight preference for attachment of solvent adjacent to the methyl group. For 1-pentene, dichloride is accompanied by both the normal and anti-Markovnikov solvent-incorporated products. For all three olefins, the relative effectiveness of the hydroxylic solvents in diverting intermediates from dichloride formation is in the order listed above. In acetic acid for the 2-pentenes, large concentrations of lithium chloride are required to give modest increases in the amount of dichloride formation, whereas lithium perchlorate has negligible effect on the product composition. The results are interpreted in terms of initial formation of a chloronium ion–chloride ion intimate ion pair. *trans*-Dichloride formation in the absence of added chloride ion occurs by reorientation and collapse of this ion pair. The immediate precursors of solvent-derived products cannot be precisely determined and two possibilities are discussed.

Chlorination of olefins in nonpolar solvents has recently been shown to be a more complex process than previously believed[1] because variations in olefin structure and concentration can lead to reaction through either polar or free-radial intermediates.[2] Use of radical inhibitors allowed isolation and study of the polar process even in nonpolar solvents.[3] Radical reaction can also be avoided by use of polar solvents which support formation of charged intermediates. However, most common polar solvents, such as alcohols and carboxylic acids[4a] as well as many nonhydroxylic solvents,[4b,c] are nucleophilic as well and can divert a portion of the reaction toward formation of products which incorporate solvent. In fact, this observation lent considerable support to the early formulation of a two-step mechanism for halogenation as shown in eq 1 where RCl^+ represents some type of positively charged



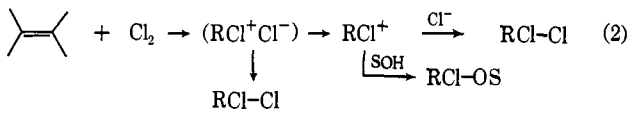
(1)

intermediate formed by attack of chlorine on the double bond; RCl–Cl, the dichloride product; and RCl–OS, the solvent-incorporated product.[5a] Significant questions can be asked concerning the attack of chlorine on the olefin which leads to RCl^+, concerning the structure of RCl^+, and concerning the characteristics of the second, product-determining step(s). Considerable direct kinetic evidence in polar solvents (especially acetic acid), albeit for deactivated olefins, has elucidated the electrophilic nature of the first step in some detail;[5] relative reactivity data for simple olefins in nonpolar solvents are also consistent with electrophilic attack, although *via* a rather symmetrical transition state with little development of positive charge on carbon.[3] Evidence as to whether RCl^+ is better formulated as an α-chlorocarbonium ion or as a bridged chloronium ion has appeared more recently. The chloronium ion formulation (or an unsymmetrical version thereof[5a]) has been advanced to explain the formation of significant amounts of anti-Markovnikov products and rearrangement products in several polar chlorinations[6] and to explain certain exclusively *trans* additions.[3,7] Fahey and Schubert,[8] using a stereochemical criterion, have recently shown that RCl^+ may be either bridged or open dependent on the stability of the open ion.

In contrast, knowledge concerning the product-forming steps is meager. Consideration of the reaction

(1) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **70**, 3364 (1948).
(2) M. L. Poutsma, *ibid.*, 87, 2161, 2172 (1965).
(3) M. L. Poutsma, *ibid.*, 87, 4285 (1965).
(4) (a) G. Williams, *Trans. Faraday Soc.*, 37, 749 (1941); (b) F. C. Weber, G. F. Hennion, and R. R. Vogt, *J. Am. Chem. Soc.*, 61, 1457 (1939); (c) I. G. Dinulescu, M. Avram, C. T. Jijovici, M. Farcasiu, and C. D. Nenitzescu, *Chem. Ind.* (London), 840 (1964).
(5) (a) See P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., Amsterdam, 1966, Chapter 6, for a recent review; (b) H. P. Rothbaum, I. Ting, and P. W. Robertson, *J. Chem. Soc.*, 980 (1948), and previous papers.
(6) P. Ballinger and P. B. D. de la Mare, *ibid.*, 1481 (1957).
(7) H. J. Lucas and C. W. Gould, Jr., *J. Am. Chem. Soc.*, **63**, 2541 (1941), and references therein.
(8) R. C. Fahey and C. Schubert, *ibid.*, 87, 5172 (1965).

in light of recent physical organic theory suggests that eq 1 may require expansion *at least* to eq 2 in which the first intermediate is an ion pair consisting of RCl^+ and the chloride ion derived from the same chlorine molecule.[9] Such an ion pair could then form products by a



(2)

variety of pathways parallel to those which have been elegantly demonstrated from solvolysis studies in which ion pairs are formed by heterolytic dissociation of a covalent bond rather than by electrophilic attack of an addend on an unsaturated molecule.[10] In the simplest scheme, the ion pair could collapse directly to dichloride, a process analogous to ion-pair return in solvolysis studies,[10] or dissociate to form free RCl^+ ions which would react competitively with nucleophilic species in solution. Only a few cases have appeared in which authors have attempted to compare the ionic intermediates in solvolyses to those in electrophilic addition. de la Mare and Salama[11] have compared chlorination of isobutylene in water with hydrolysis of 1,2-dichloro-2-methylpropane and concluded that a common intermediate is most likely involved. Fahey and Lee[12a] have invoked the formalism of ion pairs to explain the stereochemistry of addition of hydrogen chloride to 1-phenylpropyne in acetic acid.

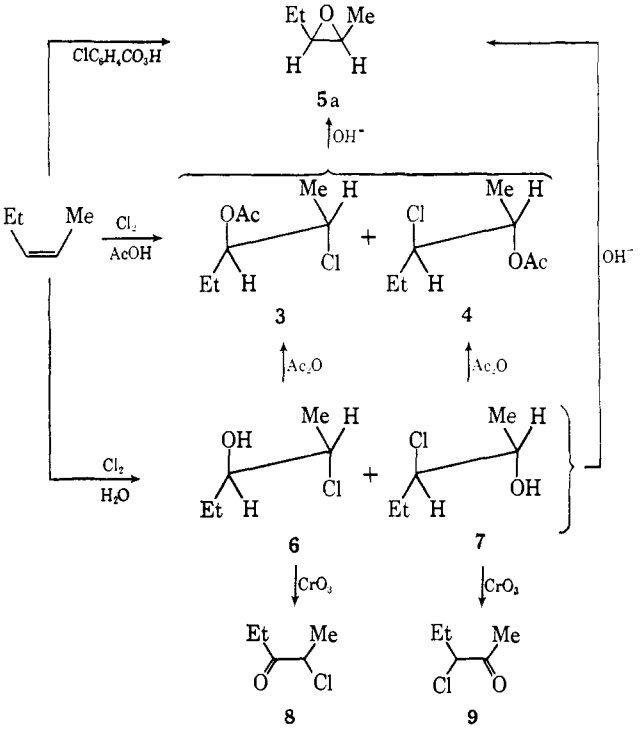
An initial experimental approach would be determination of the source of the two chlorine atoms in the dichloride product; *i.e.*, in an operational sense not related to any mechanistic considerations, one can ask whether these two chlorine atoms are derived from the same or different chlorine molecules. This operational question has been considered by van der Linde and Havinga[13] for bromination of phenanthrene in methanol. The initial product was found to be 9-bromo-10-methoxy-9,10-dihydrophenanthrene; the dibromide is formed only in later stages of reaction as bromide ions (the by-product of methoxybromide formation) build up in the reaction mixture. In mechanistic terms, we suggest that this result shows that, if ion pairs are formed at all, ion-pair return is negligible. A second approach would be determination of the dependence of the ratio of solvent-derived product to dichloride on added salts and on the nature of the solvent. Although many individual values of such ratios are reported,[14] no systematic quantitative study seems to have been made.

We have studied the product distributions from chlorination of the three isomeric linear pentenes in a variety of hydroxylic solvents with and without added salts. The results, although they tend to raise more questions than they answer, give some insight into the nature of the product-determining steps.[14a]

Results

Products in Acetic Acid. Chlorination of *cis*-2-pentene in acetic acid (1.0 *M* solution) to 5–10% conversion at 25° produces four products (**1**–**4** in order of increasing retention time), detectable by glpc analysis, in a ratio of 3:52:12:33. The first was identified as 3-chloro-1-pentene (**1**); the other potential substitution products 4-chloro-*cis*- and 4-chloro-*trans*-2-pentene made up <10% of **1** (just at the limits of detection). The second product was shown by analytical and spectral data to be a 2,3-dichloropentane, and, by analogy to results for the 2-butenes,[3,7,8] is assigned as the product of *trans* addition, *threo*-2,3-dichloropentane (**2**). The final two products gave analytical and spectral results expected for the vicinal chloroacetates. Since each is converted by base to *cis*-2,3-epoxypentane (**5a**), the *threo* configuration is proven for both. The positional isomerism was determined by relation of these chloroacetates to the corresponding chlorohydrins. Chlorination of *cis*-2-pentene in acetone–water gives, in addition to dichloride **2**, a pair of *threo*-chlorohydrins (**6** and **7**), both converted by base to *cis*-epoxide **5a**. Oxidation of the chlorohydrins to the easily identified 2-chloro-3-pentanone (**8**) and 3-chloro-2-pentanone (**9**) established

Chart I



(9) A somewhat similar formulation has been suggested which involves an intermediate in which the original chlorine–chlorine bond is still intact: P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger, *J. Chem. Soc.*, 5285 (1961), and ref 5a.

(10) H. L. Goering, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), 21, 109 (1960); S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, 80, 459 (1958), and previous papers in this series; S. Winstein, B. Appel, R. Baker, and A. Diaz, "Organic Reaction Mechanisms," Special Publication No. 19, The Chemical Society, London, 1965, p 109.

(11) P. B. D. de la Mare and A. Salama, *J. Chem. Soc.*, 3337 (1956).

(12) (a) R. C. Fahey and D. J. Lee, *J. Am. Chem. Soc.*, 88, 5555 (1966); (b) *ibid.*, 89, 2780 (1967).

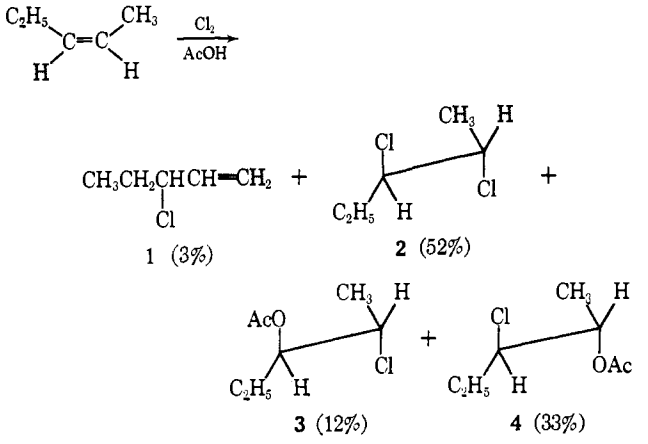
(13) J. van der Linde and E. Havinga, *Rec. Trav. Chim.*, 84, 1047 (1965).

(14) See, for example, H. R. Ing, *J. Chem. Soc.*, 1393 (1948); C. F. Irwin and G. F. Hennion, *J. Am. Chem. Soc.*, 63, 858 (1941), and previous papers.

(14a) NOTE ADDED IN PROOF. Since the completion of this work, a study of salt effects on the rate and products from chlorination of methyl *trans*-cinnamate in acetic acid has appeared: M. C. Cabaleiro and M. D. Johnson, *J. Chem. Soc., B*, 565 (1967). A similar formalism was invoked involving a set of isomeric ion pairs which collapsed to dichloride or reacted with solvent. The nonstereospecific addition points to an open carbonium ion in the cinnamate case and the ion pairs postulated to be in equilibrium differ from each other by an internal rotation about the C–C bond in the carbonium ion. In the pentene case, this route is not available to the bridged chloronium ion and an actual reorganization of the two ions within the ion pair must occur to achieve *trans* addition. The time scales for these two types of "isomerization" of intimate ion pairs may well be different.

6 as *threo*-2-chloro-3-pentanol and **7** as *threo*-3-chloro-2-pentanol. Since acetylation of **6** gave **3**, and of **7** gave **4**, product **3** is then *threo*-2-chloro-3-acetoxypentane and product **4** is *threo*-3-chloro-2-acetoxypentane. These transformations are outlined in Chart I. The chemical assignments were confirmed by nmr spectroscopy since $J_{H_1-H_2}$ = 6.8 cps for the less abundant product **3** and 6.2 cps for the more abundant **4**. Since J has been shown to be inversely related to the electronegativity of X in CH_3CHX– systems,[15] this result is consistent with the structural assignments.

Analogous chlorination of *trans*-2-pentene gives the same substitution product **1**, a different dichloride assigned as *erythro*-2,3-dichloropentane (**10**), and two



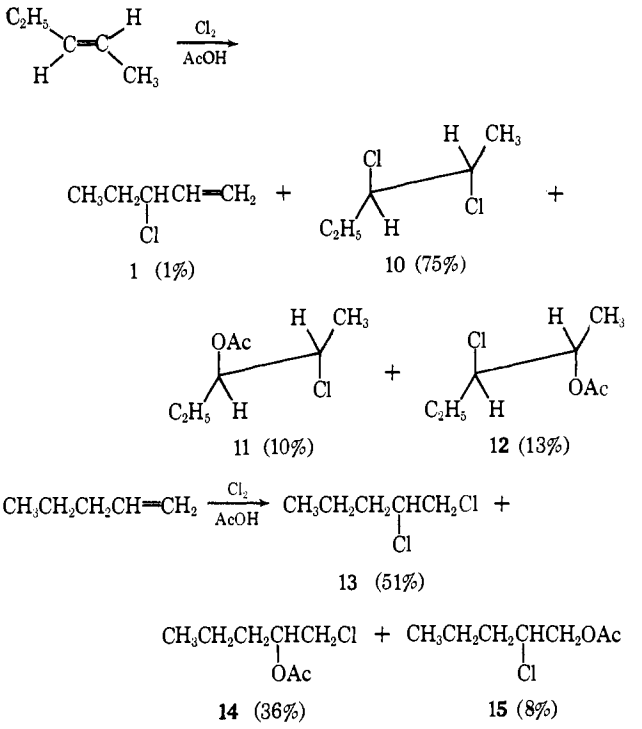
different chloroacetates **11** and **12**. Conversion of a mixture of **11** and **12** to *trans*-2,3-epoxypentane (**5b**) demonstrated the *erythro* configuration, and nmr evidence analogous to that presented above allowed assignment of **11** as *erythro*-2-chloro-3-acetoxypentane and **12** as *erythro*-3-chloro-2-acetoxypentane. Since all six distinct addition products (**2–4**, **10–12**) could be separated by glpc analysis, the addition process could be shown to be >99% stereospecifically *trans* for each olefin.

Chlorination of 1-pentene in acetic acid proceeds in similar fashion to give minor amounts of unidentified substitution products, 1,2-dichloropentane (**13**), the expected solvent-incorporated product 1-chloro-2-acetoxypentane (**14**), and also the anti-Markovnikov product 2-chloro-1-acetoxypentane (**15**). The positional isomerism of **14** and **15** was demonstrated by nmr spectroscopy (see Experimental Section).

Effects of Extent of Conversion and Added Salts. Chlorination of *cis*- and *trans*-2-pentene in acetic acid was carried out at conversions ranging from 2 to 30%; product compositions are shown in Tables I and II. The four products detected in each case by glpc analysis account for all the chlorine introduced as shown by use of an internal standard; owing to inaccuracy in measuring exactly the amount of chlorine introduced, the "yield" values given are probably ±10%. No significant trends in product composition with varying extent of conversion were observed.

At the highest conversions shown in Tables I and II, the final [(HCl) + (Cl^-)] concentration would have been *ca.* 0.12 *M* for the *cis* isomer and *ca.* 0.05 *M* for the

(15) N. S. Bhacca and D. H. Williams, "Applications of Nmr Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 52.



trans based on the amount of chlorine introduced and the fraction of chloroacetates formed. To determine the effects of larger amounts of added salts, the results shown in Tables III and IV for the 2-pentenes were ob-

Table I. Chlorination of *cis*-2-Pentene in Acetic Acid[a]

Convsn, %	Products, %[b,c] 1	2	3	4	Yield, %[d]
4	2.9	52.2	12.1	32.7	...
5.5	2.9	53.6	11.6	32.0	87
14	2.8	53.1	12.1	32.0	110
29	2.9	53.4	11.9	31.7	115

[a] 1 *M* solution under oxygen treated with chlorine at 25.0°. [b] Normalized to 100% for products listed. [c] **1** = 3-chloro-1-pentene, **2** = *threo*-2,3-dichloropentane, **3** = *threo*-2-chloro-3-acetoxypentane, and **4** = *threo*-3-chloro-2-acetoxypentane. [d] From glpc analysis with internal standard based on chlorine introduced.

Table II. Chlorination of *trans*-2-Pentene in Acetic Acid[a]

Convsn, %	Products, %[b,c] 1	10	11	12	Yield, %[d]
2	1.1	79.2	7.8	11.8	...
8	1.0	75.8	9.6	13.5	97
12	1.2	76.9	8.9	12.9	98
17	1.1	76.4	9.5	13.0	98
26	1.2	75.9	9.6	13.3	104

[a] 1 *M* solution under oxygen treated with chlorine at 25.0°. [b] Normalized to 100% for products listed. [c] **1** = 3-chloro-1-pentene, **10** = *erythro*-2,3-dichloropentane, **11** = *erythro*-2-chloro-3-acetoxypentane, and **12** = *erythro*-3-chloro-2-acetoxypentane. [d] From glpc analysis with internal standard based on chlorine introduced.

tained. In these cases, the indicated amount of salt was added to the olefin–solvent mixture before chlorination to 5–10% conversion. Use of an internal standard in occasional runs again showed satisfactory material balances. For *cis*-olefin, addition of the common ion salt lithium chloride led to a steady increase in dichloride formation from *ca.* 52% with no added chloride to

Table III. Effects of Added Salts on Chlorination *cis*-2-Pentene in Acetic Acid[a]

Salt	Concn, *M*	Products, %[b,c] 1	2	(3 + 4)	(16d + 17d)	[3]/[3 + 4]
LiCl	0	3.0	51.6	45.3		0.28
	0	2.8	51.5	45.7		0.28
	0.2	2.6	55.0	42.3		0.28
	0.3	2.4	55.2	42.5		0.27
	0.5	2.4	57.0	40.7		0.29
	0.8	2.1	60.4	37.5		0.30
	0.8	2.2	59.7	38.1		0.30
	1.0	2.3	63.2	34.5		0.28
	1.2	1.9	63.4	34.6		0.29
	1.5	1.8	65.4	32.8		0.30
	1.5	1.9	66.1	32.0		0.29
	1.8	2.1	69.0	28.8		0.29
	1.8	1.8	69.6	28.6		0.30
LiOAc	0.15	3.0	53.1	43.8		0.27
	0.15	2.7	53.4	43.9		0.29
	0.75	2.9	51.3	45.9		0.29
	1.05	2.8	50.1	47.1		0.30
$LiClO_4$	0.2	2.7	51.3	45.9		0.28
	0.2	3.0	50.9	46.1		0.30
	0.8	2.8	51.7	45.5		0.30
	1.0	2.8	52.9	44.3		0.30
	1.8	3.0	57.4	39.7		0.31
LiO_2CH	0.56	3.0	50.8	43.4	2.8	0.30
	0.78	2.9	50.0	43.4	3.7	0.30
	1.00	3.1	49.7	42.7	4.6	0.31

[a] 1 *M* solution under oxygen treated with chlorine at 25.0° to 5–10% conversion. [b] Normalized to 100% for products listed. [c] **1** = 3-chloro-1-pentene, **2** = *threo*-2,3-dichloropentane, **3** = *threo*-2-chloro-3-acetoxypentane, **4** = *threo*-3-chloro-2-acetoxypentane, **16d** = *threo*-2-chloro-3-formyloxypentane, and **17d** = *threo*-3-chloro-2-formyloxypentane.

Table IV. Effects of Added Salts on Chlorination of *trans*-2-Pentene in Acetic Acid[a]

Salt	Concn, *M*	Products, %[b,c] 1	10	(11 + 12)	(18d + 19d)	[11]/[11 + 12]
LiCl	0	1.2	75.2	23.6		0.43
	0	1.2	75.7	23.0		0.43
	0	1.3	75.8	22.8		0.42
	0.1	1.3	75.2	23.5		0.42
	0.2	0.9	76.3	22.9		0.42
	0.2	1.1	75.6	23.3		0.41
	0.4	1.2	76.4	22.5		0.42
	0.7	1.0	76.2	22.8		0.43
	0.7	0.9	76.7	22.4		0.43
	1.0	0.8	78.5	20.6		0.42
	1.0	0.9	78.2	20.9		0.42
	1.0	0.9	77.4	21.6		0.43
	1.3	0.9	78.1	21.1		0.43
	1.6	0.9	78.9	20.2		0.42
	1.8	0.8	81.5	17.8		0.42
	1.8	0.9	78.3	20.8		0.43
	1.8	0.9	80.3	18 8		0.43
LiOAc	0.15	1.2	75.8	22.9		0.42
	0.5	1.6	73.0	25.5		0.43
	0.75	0.9	76.2	22.9		0.42
	0.9	1.1	70.5	28.3		0.43
	1.05	1.2	71.6	27.3		0.42
$LiClO_4$	0.2	1.0	76.6	22.4		0.43
	0.2	1.0	75.4	23.6		0.42
	0.8	1.3	73.3	25.5		0.44
	0.8	1.0	73.0	26.0		0.43
	1.0	0.9	75.0	24.0		0.43
	1.8	1.2	77.4	21.4		0.43
LiO_2CH	0.33	1.3	72.1	25.6	0.9	0.42
	0.56	1.3	71.4	25.8	1.5	0.42
	0.78	1.3	70.0	26.4	2.3	0.42
	1.00	1.3	67.8	27.9	2.9	0.43

[a] 1 *M* solution under oxygen treated with chlorine at 25.0° to 5–10% conversion. [b] Normalized to 100% for products listed. [c] **1** = 3-chloro-1-pentene, **10** = *erythro*-2,3-dichloropentane, **11** = *erythro*-2-chloro-3-acetoxypentane, **12** = *erythro*-3-chloro-2-acetoxypentane, **18d** = *erythro*-2-chloro-3-formyloxypentane, and **19d** = *erythro*-3-chloro-2-formyloxypentane.

Table V. Effects of Added Salts on Chlorination of 1-Pentene in Acetic Acid[a]

Salt	Concn, *M*	Products, %[b,c] 13	14	15
LiCl	0	51.0	35.5	7.7
	0.2	54.8	32.7	7.7
	0.8	61.8	28.5	6.0
	1.8	69.0	23.7	4.6
LiOAc	0.2	52.7	34.5	7.5
	1.05	44.9	39.7	11.4
$LiClO_4$	0.2	50.8	34.1	8.2
	1.8	49.0	25.2	5.2

[a] 1 *M* solution under oxygen treated with chlorine at 25.0° to 5–10% conversion. [b] Normalized to 100% for **13–15** plus two minor (supposed) substitution products. [c] **13** = 1,2-dichloropentane, **14** = 1-chloro-2-acetoxypentane, and **15** = 2-chloro-1-acetoxypentane.

ca. 70% at 1.8 *M* lithium chloride; for *trans*-olefin, the corresponding change from *ca.* 76% to *ca.* 80% is barely greater than experimental error. In neither case was there a dramatic effect of added lithium acetate although the slight increases in chloroacetate formation seem real. Addition of the nonnucleophilic lithium perchlorate up to 1.8 *M* gave somewhat scattered results but no apparent trends in product composition. Addition of the noncommon ion salt lithium formate up to 1.0 *M* gave small amounts of vicinal chloroformate product (see results below in formic acid solvent). For the *cis*-olefin, this product was formed mainly at the expense of chloroacetate; however, for the *trans*-olefin, chloroacetate formation slightly increased along with chloroformate formation, both at the expense of dichloride. The presence of added salts did not change the ratio of positionally isomeric chloroacetates for either olefin. Less extensive results for 1-pentene (Table V) parallel those for *cis*-olefin rather closely, starting as they do from similar initial dichloride:chloroacetate ratios.

Other Solvents. Chlorination of *cis*-2-pentene in methanol and analysis by glpc revealed substitution product **1** and dichloride **2** as well as two new products **16a** and **17a**. The same two materials are obtained by methylation of chlorohydrins **6** and **7**, respectively; hence **16a** is *threo*-2-chloro-3-methoxypentane and **17a** is *threo*-3-chloro-2-methoxypentane. From *trans*-olefin are obtained **1**, dichloride **10**, and two products distinct from **16a** and **17a** assigned as *erythro*-2-chloro-3-methoxypentane (**18a**) and *erythro*-3-chloro-2-methoxypentane (**19a**). Product distributions with and without added salts are shown in Tables VI and VII; occasional use of an internal standard again indicated satisfactory material balances. The major products in each case are now the chloro ethers, and the effect of added lithium chloride in increasing dichloride formation is more dramatic, starting as it does from a lower base value.

Less extensive chlorination studies of *cis*-2-pentene were carried out in four additional hydroxylic solvents: ethanol, *t*-butyl alcohol, trifluoroacetic acid, and formic

Table VI. Chlorination of *cis*-2-Pentene in Methanol[a]

Added salt	Concn, *M*	Products, %[b,c] 1	2	(16a + 17a)	[16a]/[16a + 17a]	Yield,[d] %
None		0.6	8.2	91.3	0.32	107
		0.5	9.2	90.4	0.32	...
		0.6	7.8	91.7	0.31	105
LiCl	0.2	0.6	12.6	86.8	0.31	93
	0.6	0.7	20.8	78.5	0.32	97
	1.0	0.2	32.4	67.5	0.31	...
	1.4	0.6	36.7	62.6	0.31	...
	1.8	0.9	42.5	56.6	0.29	101

[a] 1 *M* solution under oxygen treated with chlorine at 25.0° to 5–10% conversion. [b] Normalized to 100% for products listed. [c] **1** = 3-chloro-1-pentene, **2** = *threo*-2,3-dichloropentane, **16a** = *threo*-2-chloro-3-methoxypentane, and **17a** = *threo*-3-chloro-2-methoxypentane. [d] From glpc analysis with internal standard based on chlorine introduced.

Table VII. Chlorination of *trans*-2-Pentene in Methanol[a]

Added salt	Concn, *M*	Products, %[b,c] 1	10	(18a + 19a)	[18a]/[18a + 19a]	Yield,[d] %
None		0.5	15.6	83.9	0.41	99
		0.5	15.6	83.9	0.42	110
		0.6	15.6	83.8	0.42	102
LiCl	0.2	0.5	19.5	80.0	0.42	86
	0.6	0.4	27.4	72.2	0.42	110
	1.0	0.5	35.6	63.9	0.42	109
	1.4	0.4	42.7	56.8	0.42	109
	1.8	0.5	49.2	50.3	0.42	94

[a] 1 *M* solution under oxygen treated with chlorine at 25.0° to 5–10% conversion. [b] Normalized to 100% for products listed. [c] **1** = 3-chloro-1-pentene, **10** = *erythro*-2,3-dichloropentane, **18a** = *erythro*-2-chloro-3-methoxypentane, and **19a** = *erythro*-3-chloro-2-methoxypentane. [d] From glpc analysis with internal standard based on chlorine introduced.

acid. In each case the major products were as expected: **1**, **2**, and a pair of products which incorporated solvent. The structure of ethyl ethers **16b** and **17b** were assigned by analogy with the results in methanol. Treatment of chlorohydrins **6** and **7** with isobutylene in the presence of an acid catalyst gives *t*-butyl ethers **16c** and **17c** identical with those produced by chlorination in *t*-butyl alcohol. Reaction of the chlorohydrins with trifluoroacetic anhydride gives esters **16e** and **17e**. In the case of formic acid, esters **16d** and **17d** could not be resolved by glpc analysis but the presence of both was indicated by two low-field singlets in the nmr spectrum at 7.98 and 8.07 ppm. In formic and trifluoroacetic acids, additional products with retention times similar to **1** are observed in variable amounts; however, these were also slowly formed from the olefin and acid without chlorine and hence are assumed to be the result of acid-catalyzed addition of the solvent to the olefin.[16] Analogous chlorinations of *trans*-2-pentene in the same solvents gave a comparable set of solvent-incorporated products, unique from **16** and **17**, to which the *erythro* structures **18** and **19** have been assigned. 1-Pentene also produces a pair of solvent-incorporated products **20** and **21**; however, except for the acetates, these could not be completely resolved either by glpc or nmr analysis and hence only a sum of (**20** + **21**) could be determined. A summary of results appears in Table VIII.

Table VIII. Chlorination of Pentenes in Nucleophilic Solvents[a]

Solvent[b]	From *cis*-2- [16 + 17]/[2][c]	[16]/[16 + 17][c]	From *trans*-2- [18 + 19]/[10][c]	[18]/[18 + 19][c]	From 1- [20 + 21]/[13][c]
Formic acid[d]	3.6	(0.29)[e]	1.6	...	3.4
Trifluoroacetic acid	0.2	0.39	0.09_5	0.47	0.2
Methanol	10.7[f]	0.32[f]	5.4[g]	0.42[g]	11.2
Ethanol	4.3	0.32	2.3	0.41	3.9
t-Butyl alcohol	1.0	0.26	0.45	0.39	1.4
Acetic acid	0.87[h]	0.28[h]	0.30[i]	0.42[i]	0.85[i]
Ethyl ether	0.05	0.2	0.04_5	0.31	0.3
Acetic anhydride	0.2_8	0.27	0.09	0.40	0.4_4[k]

[a] 1 *M* solution under oxygen treated with chlorine at 25.0° to 5–10% conversion; averages of at least two runs. [b] Hydroxylic solvents listed in order of decreasing dielectric constant. [c] **16** = *threo*-2-chloro-3-OS-pentane, **17** = *threo*-3-chloro-2-OS-pentane, **18** = *erythro*-2-chloro-3-OS-pentane, **19** = *erythro*-3-chloro-2-OS-pentane, **20** = 1-chloro-2-OS-pentane, **21** = 2-chloro-1-OS-pentane, **2** = *threo*-2,3-dichloropentane, **10** = *erythro*-2,3-dichloropentane, and **13** = 1,2-dichloropentane. [d] 0.2 *M* olefin; limit of solubility. [e] Based on nmr spectrum of isolated sample. [f] Average from Table VI. [g] Average from Table VII. [h] Average from Tables I and III. [i] Average from Tables II and IV. [j] [21]/[20 + 21] = 0.18. [k] [21]/[20 + 21] = 0.06.

Chlorinations were also performed in two nonhydroxylic solvents, acetic anhydride and diethyl ether. In the former, the expected[4b] acetates (**16f–21f**) were detected, and in the latter, the expected[4c] ethyl ethers (**16b–21b**). These results are also shown in Table VIII.

Discussion

Acetic Acid as Solvent. Since significant dichloride formation occurs at the very beginning of the chlorination reaction when no chloride ion has as yet built up in solution (as shown by extrapolation of product ratios to zero conversion), this dichloride (52% from *cis*-2-pentene, 75% from *trans*-2-pentene, and 51% from 1-pentene) must derive both its chlorine atoms from the original attacking chlorine molecule. This conclusion is supported by the surprisingly small increases in dichloride formation even at concentrations of added

(16) H. B. Knight, R. E. Koos, and D. Swern, *J. Am. Chem. Soc.*, 75, 6212 (1953); P. E. Peterson, *ibid.*, 82, 5834 (1960).

lithium chloride as high as 1.8 *M*. Thus any mechanistic proposal must allow for partitioning of the originally formed intermediate(s) between direct dichloride formation (without intervention of external chloride ion) and chloroacetate formation, as well as account for the failure of high concentrations of lithium perchlorate to change this ratio significantly. On the other hand, it must allow for the small, but definitely real diversion of some intermediate(s) from chloroacetate formation to dichloride formation by added lithium chloride. And finally, it should encompass the effects of added lithium formate and the concomitant formation of chloroformate product.

Since electrophilic attack of chlorine on the olefin produces a pair of ions, we will turn to solvolysis studies for a reaction model. A general scheme of ionic intermediates generated during solvolysis of halides, tosylates, etc. has been developed by Winstein and co-workers.[10] The first proposed intermediate **22**, pictured as two ions in contact solvated but not separated by solvent molecules and termed an intimate ion pair, can be detected if process k_{-1}, internal return, produces an observable change in RX such as racemization or allylic rearrangement. Further separation of ions produces the solvent-separated ion pair **23** which can be

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+X^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R^+\|X^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} R^+ + X^-$$

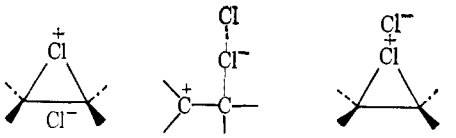
22 **23** **24**

k_s SOH k_s' SOH k_s'' SOH

ROS ROS ROS

detected by exchange studies with foreign nucleophiles or which can be diverted from ion-pair return (k_{-2} and k_{-1}) by added salts such as lithium perchlorate (the special salt effect), whereas **22** cannot be so intercepted. Finally, ultimate separation may produce free ions (**24**) whose presence is indicated by common ion rate depression *via* k_{-3}. Capture by solvent may occur at all stages (k_s, k_s', and k_s'') although k_s is often small because of the special geometry of the systems studied. In general, the more stable R^+ is, the further along this dissociation sequence a given solvolysis will proceed before product formation occurs.

We will attempt to apply a similar model to the chlorination reaction. The initial dichloride formation, which occurs when the external chloride ion is negligible and which is not decreased by added lithium perchlorate, must come from collapse of intimate ion pairs, a process analogous to intimate ion-pair return k_{-1}. Since dichloride is formed in a stereospecifically *trans* fashion, one can reasonably picture this intimate ion pair immediately preceding product formation as **25**, a bridged chloronium ion and a chloride ion in position for *trans* nucleophilic ring opening. However, the chloride ion is initially formed at the other face of the double bond and must somehow migrate through the plane originally described by the carbon atoms of the olefin to be in position for product formation. From studies of additive chlorination of naphthalene and phenanthrene in acetic acid, in which case considerable *cis* addition occurs (and hence an open rather than bridged ion is implicated), de la Mare[9] has suggested as an initial intermediate a species **26** in which chlorine–chlorine bonding is retained and which can collapse directly to



25 **26** **27**

cis-dichloride.[17] We would suggest that a comparable early intermediate in our cases might also be the ion pair **27**; whether **26** or **27** is of lower energy seems an open question. Whatever the exact formulation, de la Mare[18] has implied more recently that *trans*-dichloride formation by a totally "internal" route is impossible because the conversion of **26** (or **27**) to a species geometrically suited for *trans* attack (we suggest **25**) without intervention of solvent or salts is unreasonable. However, our results leave little doubt that such a rearrangement of one intimate ion pair (or partially bonded species) to another without passage through a species divertible by lithium perchlorate must be possible in our system. Again drawing on solvolysis studies for models, we would point out that both extremes have been observed. Goering and co-workers[19] have found that migration of phthalate ion from one face of the cyclohexenyl cation system to the other which occurs in acetonitrile is totally intercepted in ethanol. In contrast in a somewhat analogous geometrical arrangement, Allred[20] has observed nondivertible rearrangement between the 4-methoxy-1-pentyl and 5-methoxy-2-pentyl *p*-bromobenzenesulfonates during solvolysis through the O-methyl-2-methyltetrahydrofuranium ion. That the competition between geometrical rearrangements and chemical capture of intimate ion pairs is a closely balanced one, we note that sodium azide completely eliminates racemization (migration of the anion from one face of the benzhydryl cation to the other is required) of *p*-chlorobenzhydryl *p*-nitrobenzoate in 80% aqueous acetone at 99.6°,[21] whereas it does not for *p*-chlorobenzhydryl chloride at 25° in the same solvent.[22]

This internal return route to product accounts for only part of the products in the chlorination without added salts. Further inquiry must be made as to the source of the chloroacetate. To account for the increase in dichloride formation caused by added lithium chloride, one is initially tempted to propose that dissociation beyond the intimate ion-pair stage must occur. In fact, even solvent-separated ion pairs would not be sufficient since their exchange with lithium chloride ion pairs would be an identity reaction and would not affect a product-determining competition between k_{-2} and k_s'. Thus dissociated ions would need to be postulated and the increased dichloride formation would be operationally analogous to external return or common ion rate depression (Scheme I).

(17) The recent spectral observation of transient species assigned to charge-transfer complexes of olefins with chlorine suggests an even earlier energy minimum at least in nonpolar solvents: J. E Dubois and F. Garnier, *J. Chim. Phys.*, **63**, 351 (1966).

(18) P. B. D. de la Mare, M. D. Johnson, J. S. Lomas, and V. Sanchez del Olmo, *J. Chem. Soc., B*, 827 (1966).

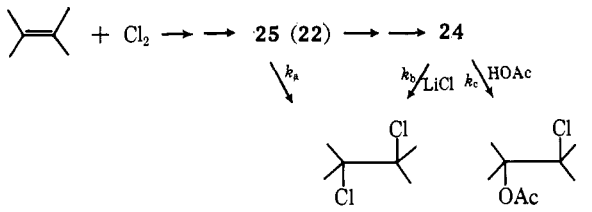
(19) H. L. Goering and E. F. Silversmith, *J. Am. Chem. Soc.*, 77, 1129 (1955); H. L. Goering, T. D. Nevitt, and E. F. Silversmith, *ibid.*, 77, 5026 (1955); H. L. Goering, J. T. Doi, and K.D. McMichael, *ibid.*, **86**, 1951 (1964).

(20) E. L. Allred and S. Winstein, *ibid.*, **89**, 3998 (1967).

(21) H. L. Goering and J. F. Levy, *ibid.*, **86**, 120 (1964).

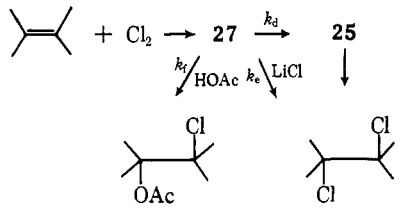
(22) A. Diaz, Ph.D. Thesis, University of California, Los Angeles, Calif., 1965.

Scheme I



However, as a second alternative, we can examine Scheme II involving only intimate ion pairs. The

Scheme II



originally formed **27** could competitively reorient to form **25** which is now sterically favorably disposed for and committed to dichloride formation or suffer nucleophilic attack by acetic acid or lithium chloride at the backside. A somewhat analogous model involving a number of ion pairs has been proposed by Fahey and Lee[12a] for hydrochlorination of 1-phenylpropyne in acetic acid. It was hoped that differentiation between these extremes of behavior might be obtained from results with an added foreign nucleophile which should generate a third product type. Such a nucleophile must be stable to molecular chlorine (hence bromide or azide would be questionable) and must be derived from an acid stronger than acetic to avoid its complete protonation in the medium (hence cyanide would be questionable). As a compromise between these criteria and strong nucleophilicity, formate was chosen although we do not know the equilibrium constant for the lithium formate–acetic acid system in acetic acid. If Scheme I applies, chloroformate should be formed at the expense of chloroacetate with no change in dichloride, whereas, if Scheme II applies, dichloride should also be decreased. In reality, the results for *cis*-2-pentene approximate those expected for Scheme I whereas those for *trans*-2-pentene do not fit either in that chloroacetate is actually *increased* by added lithium formate (Tables III and IV); hence no conclusion can be drawn.

At this point it must be noted that the present study required use of salt concentrations orders of magnitude greater than those normally considered in solvolysis studies and hence any specific salt effects considered have a general medium effect superimposed on them. This probably accounts for the strange results obtained with lithium formate and *trans*-2-pentene. In fact the almost identical product distributions obtained in acetic acid and in 1.8 *M* $LiClO_4$ in acetic acid are even more surprising in this context since a considerable medium change must be traversed here. In summary then, intimate ion pairs have been shown to be a significant source of dichloride, but more data are required to fix the source(s) of chloroacetate and the point of intervention of added lithium salts.

To consider the effects of added lithium chloride more quantitatively, if Scheme II applies, then we can write eq 3 where $k_f' = k_f[\text{HOAc}]$ which is relatively con-

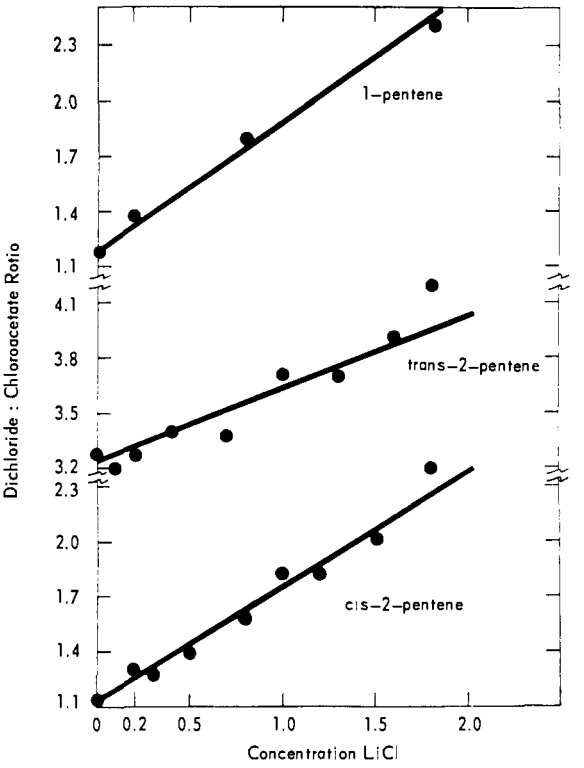


Figure 1. Dependence of product distributions on lithium chloride concentration for chlorination of the linear pentenes in acetic acid at 25.0°.

stant compared to [LiCl]; in other words the product

$$\frac{[\text{dichloride}]}{[\text{chloroacetate}]} = \frac{k_d + k_e[\text{LiCl}]}{k_f[\text{HOAc}]} = \frac{k_d}{k_f'} + \frac{k_e}{k_f'}[\text{LiCl}] \quad (3)$$

ratio is a linear function of lithium chloride concentration with a nonzero intercept. If the step (**27** → **25**) is significantly reversible, a more complex expression results but the slope formalism remains the same. For Scheme I a more complex equation arises but a qualitatively similar slope formalism is retained. Plots of eq 3 are shown in Figure 1 and are relatively linear with $k_e/k_f' = 0.62$ for *cis*-2-pentene, 0.45 for *trans*-2-pentene, and 0.71 for 1-pentene. Assuming a relatively constant acetic acid concentration, $k_e/k_f \sim 9.5$, 7.0, and 11.0, respectively. These plots are not exact enough to draw rigid mechanistic conclusions, but the term k_e/k_f should approximate the relative nucleophilicities of lithium chloride and acetic acid toward the chloronium ion.

Implicit in this discussion has been the assumption that the rate-determining step involves olefin and chlorine but not the nucelophilic component. Such a third-order reaction has been observed recently[12b] for hydrochlorination of 3-hexyne in acetic acid. The dramatic effects of small quantities of added chloride ion on product composition in that case[12b] compared to our minor effects at much higher concentrations support our basic assumption.

Other Solvents. For all three isomeric pentenes, the relative ability of the hydroxylic solvents studied to interfere with the ion-pair route to dichloride and to give solvent-incorporated products was methanol >

ethanol > formic acid > *t*-butyl alcohol > acetic acid > trifluoroacetic acid. No fully satisfactory explanation can be given since the exact point of intervention of solvent in the reaction path is unknown (*vide supra*). This solvent order is not identical with that of any common measure of solvent properties. For example, the relative nucleophilicities should be *t*-butyl alcohol > ethanol > methanol > acetic acid > formic acid > trifluoroacetic acid. Thus a contribution from nucleophilicity nicely accounts for the position of trifluoroacetic acid and for the greater effectiveness of the alcohols compared to the acids, but does not explain the position of formic acid. In contrast, a dielectric constant order (formic acid > trifluoroacetic acid > methanol > ethanol > *t*-butyl alcohol > acetic acid[23]) which might have been expected to be related to an ion dissociation process fails for trifluoroacetic acid. The effectiveness of these solvents at promoting ionization (although in our case the ion-producing step should not affect the product distribution) as measured by the Smith–Fainberg–Winstein correlation[24] (formic acid > acetic acid > methanol > ethanol) is also not consistent. For the moment therefore the observed order can only have empirical synthetic significance.

The ability of nonhydroxylic solvents such as acetic anhydride and ethyl ether to lead to solvent-incorporated products has been recognized several times[4b,c] but deserves note.

Orientation. Nucleophilic ring openings of unsymmetrical three-membered rings, such as epoxides, can give either the more or less highly alkylated derivative depending on the reagent and reaction conditions; hence two extremes of behavior have been postulated: (1) a purely SN2 opening at the sterically favored, less highly alkylated carbon atom; and (2) a more carbonium ion-like opening to give the more highly alkylated derivative.[25] For the 2-pentene case, the factors are obviously closely balanced although steric factors should slightly favor attack adjacent to the methyl rather than ethyl group and carbonium ion stability should probably favor the 3-pentyl over the 2-pentyl cation.[26] In all solvents studied for both isomers, chlorination gives solvent attack mainly at C-2 and steric considerations probably are the dominant factor. Although epoxide opening would have made a good model, no good data seem to exist for as closely symmetrical a case as methyl *vs.* ethyl.[27] In the 1-pentene case, the significant portion of terminal solvent attack supports the chloronium ion formulation for here the two possible open carbonium ions are obviously of considerably different energy.

Experimental Section

Infrared spectra were determined as 10% carbon disulfide solutions on a Beckman IR-10 instrument. Nmr spectra were determined as 20% carbon tetrachloride solutions on a Varian A-60 instrument and results expressed in parts per million downfield from internal tetramethylsilane. Boiling points are uncorrected.

Materials. Commercial 1-pentene (Matheson Coleman and Bell, 99%) was distilled from calcium sulfate; glpc analysis revealed none of the 2 isomers. Commercial *cis*-2-pentene (Phillips Petroleum, 98%) apparently contained small amounts of 2-methyl-2-butene which reacts preferentially with chlorine;[3] hence both *cis*- and *trans*-2-pentene had to be synthesized (*vide infra*). Anhydrous acetic acid was prepared by addition of the calculated amount of acetic anhydride to react with the water present (determined by Karl Fischer titration), refluxing at least 12 hr, and distillation; Karl Fischer titration showed <0.015% water.[28] Lithium chloride was crystallized from methanol–acetone; the calculated amount was dissolved in distilled acetic acid to make a 2 *M* stock solution; acetic anhydride was added to destroy the residual water indicated by Karl Fischer titration and the solution heated just below reflux for 12 hr. A stock solution of lithium perchlorate was made from vacuum-dried salt and dried acetic acid. The solution of lithium acetate in acetic acid was prepared by use of the appropriate quantity of lithium carbonate and treatment with acetic anhydride.[28] Methanol was dried by distillation from magnesium and showed <0.022% water. *t*-Butyl alcohol was distilled from calcium sulfate. Formic acid was dried by distillation from boric anhydride.[29] Absolute ethanol, trifluoroacetic acid, acetic anhydride, and diethyl ether were not purified further.

trans-**2-Pentene.**[30] Ammonia (1 l.) was condensed into a 3-l., three-necked flask equipped with a stirrer, addition funnel, and dewar condenser filled with Dry Ice–acetone. Sodium (50.6 g, 2.2 g-atoms) was added in small pieces and the stirred mixture was held at reflux for 1.5 hr to effect solution of the sodium. 2-Pentyne (68 g, 1 mole, Farchan Research Laboratories) was added dropwise in 1 hr; occasional external cooling with a Dry Ice–acetone bath was required to maintain a controlled reflux rate. Solid ammonium chloride was added *cautiously* in small portions until the blue color was dispelled. About 2 l. of water was then added, very slowly with cooling at first, until all the solids dissolved; efficient stirring is required during this operation. The organic layer was separated, washed with dilute hydrochloric acid, dried over sodium sulfate, and distilled through an 18-in. spinning-band column to give 35.1–40.7 g (50–58%) of product, bp 36.5–37°. Glpc analysis (Perkin-Elmer column H, silver nitrate in diethylene glycol, at 25°) failed to reveal any *cis*-2-pentene, 1-pentene, or 2-pentyne.

cis-**2-Pentene.** A solution of 10 ml of 2-pentyne and 0.2 ml o quinoline in 50 ml of nonane was hydrogenated at 25° and *ca.* 30 psi over 1.0 g of Lindlar catalyst[31] until hydrogen consumption ceased (*ca.* 1 hr); after filtration of the catalyst, glpc analysis typically revealed <1% residual 2-pentyne and <1% pentane. Filtrates from 12 such runs were combined and distilled directly through an 18-in. spinning-band column to give, after a small forerun, 60.6 g (73%) of product, bp 36–38°, whose glpc analysis showed 98% purity with <1% each of 2-pentyne, *trans*-2-pentene, and pentane.

Identification of Products from Chlorination of *cis*-2-Pentene in Acetic Acid. Low-conversion quantitative runs (*vide infra*) gave four products A–D[32] as evidenced by glpc analysis (Perkin-Elmer column B, bis(2-ethylhexyl)sebacate). From preparative runs on a larger scale (*ca.* 0.35 mole of chlorine added to 1.0 mole of olefin in 3.5 moles of acetic acid) were isolated by a combination of distillation and preparative glpc (1) a pure sample of A, (2) a pure sample of B, (3) a pure sample of D, and (4) mixtures of C and D in varying proportions. Component A was identified as 3-chloro-1-pentene (**1**) by the *t*-butyl hypochlorite chlorination procedure of Walling and Thaler[33] with the use of Perkin-Elmer columns B and A (diisodecyl phthalate). This procedure also gave appropriate retention times to determine that chlorination produced very little (<10% of **1**) of either 4-chloro-*cis*- or 4-chloro-*trans*-2-pentene. Product B, bp 49–51° (21 mm), $n^{24}D$ 1.4446, 95% pure by glpc analysis, has been assigned as *threo*-2,3-dichloropentane (**2**).

Anal. Calcd for $C_5H_{10}Cl_2$: C, 42.6; H, 7.2; Cl, 50.3. Found: C, 42.8; H, 7.2; Cl, 49.4.

The gross structure is confirmed by the nmr spectrum: triplet at 1.08 ppm, J = 7 cps (CH_3CH_2–); doublet at 1.55 ppm, J = 7 cps (CH_3CHCl–); multiplet at 1.87 ppm (CH_3CH_2CHCl–); and com-

(23) A. Weissberger, Ed., "Technique of Organic Chemistry," Vol. VII, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1955.
(24) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, 83, 618 (1961).
(25) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).
(26) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *J. Am. Chem. Soc.*, 87, 5169 (1965); W. Pritzkow and K. H. Schöppler, *Chem. Ber.*, **95**, 834 (1962); these solvolysis data, of course, do not account for ground-state differences.
(27) A. Rosowsky in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part I, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964.
(28) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, 78, 2767, 2770 (1956).
(29) S. Winstein and H. Marshall, *ibid.*, 74, 1120 (1952).
(30) A. L. Henne and K. W. Greenlee, *ibid.*, **65**, 2020 (1943).
(31) H. Lindlar, *Helv. Chim. Acta*, 35, 446 (1952).
(32) In the Experimental Section all labeling of components of mixtures will be alphabetical in order of increasing retention time.
(33) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

plex multiplet at 3.7–4.4 ppm (-$CH_2CHClCHClCH_3$) with relative areas of 3.0:3.1:1.95:1.95. The *threo* assignment is based on analogy to the 2-butene–chlorine reaction.[3,7,8]

Infrared absorption at 1742 cm^{-1} and elemental analysis suggested mixtures of C and D, bp 80–82° (20 mm), $n^{24}D$ 1.4280, to consist of 2-chloro-3-acetoxypentane and 3-chloro-2-acetoxypentane.

Anal. Calcd for $C_7H_{13}ClO_2$: C, 51.1; H, 8.0; Cl, 21.5. Found: C, 50.9; H, 8.0; Cl, 21.7.

Conversion of the mixture by base (*vide infra*) to *cis*-2,3-epoxypentane (**5a**), free from the *trans* isomer, showed both C and D to have the *threo* configuration. Only D, $n^{24}D$ 1.4274, could be obtained pure and its nmr spectrum showed triplet at 1.05 ppm, J = 7 cps (CH_3CH_2–); doublet at 1.30 ppm, J = 6.2 cps (CH_3CHX–); multiplet at 1.5–1.9 ppm (CH_3CH_2CHX–); singlet at 2.00 ppm (CH_3CO_2–); multiplet at 3.75 ppm (–CHCl–); and multiplet at 5.03 ppm (–CHOAc–), with relative areas of 3.0:3.15:1.95:0.9:1.0. The nmr spectrum of a 1:1 mixture of C and D showed the spectrum of D with a very similar, slightly shifted spectrum superimposed: overlapping triplets at 0.92 and 1.05 ppm, two doublets at 1.29 (J = 6.2 cps) and 1.43 ppm (J = 6.8 cps), a more complex multiplet at 1.4–1.9 ppm, two singlets at 2.00 and 2.04 ppm, and two broader multiplets centered at 3.9 and 4.9 ppm. The relationship of decreasing J with increased electronegativity of X in CH_3-CHX- systems[15] suggested that C is *threo*-2-chloro-3-acetoxypentane (**3**) and D is *threo*-3-chloro-2-acetoxypentane (**4**); these positional assignments were confirmed chemically (*vide infra*).

Conversion of Mixed *threo*-2,3-Chloroacetates to *cis*-2,3-Epoxypentane (5a). A 1:2 mixture of **3** and **4** (0.51 g, 3.1 mmoles) was stirred with 24 ml of 0.5 *M* potassium hydroxide in methanol solution for 1 hr at room temperature and then 15 min at 50°. The mixture was diluted with 75 ml of water and extracted with pentane to recover the organic products. Glpc analysis of the dried extract (Perkin-Elmer column B) showed no starting materials remaining and only a single peak corresponding to *cis*-2,3-epoxypentane (**5a**) free from the *trans* isomer. A small portion was isolated by preparative glpc, $n^{25}D$ 1.3910, and shown indeed to be the epoxide by comparison of its infrared spectrum with that of an authentic sample.

***cis*- (5a) and *trans*-2,3-Epoxypentane (5b).** To a solution of 10.5 g (0.15 mole) of commercial 2-pentene (Matheson Coleman and Bell), shown to be *ca.* 80% *cis* by glpc analysis, in 40 ml of methylene chloride was added with stirring a solution of 32.0 g (0.15 mole based on 81% assay) of commercial *m*-chloroperbenzoic acid (FMC Corp.) in 360 ml of methylene chloride. Addition required 1 hr during which occasional cooling was required to maintain the reaction at room temperature. After 20 min additional, the mixture was stirred with 50 ml of 10% aqueous sodium sulfite solution to destroy any excess peracid. The precipitated *m*-chloroperbenzoic acid was removed by filtration and the organic layer was washed with three portions of saturated sodium bicarbonate solution and dried over sodium sulfate. Glpc analysis (Perkin-Elmer column B) showed two peaks, E and F, in a ratio of *ca.* 1:4. Distillation gave four fractions, boiling between 79 and 86°, which totaled 9.15 g (71%) of product; however, since little separation of E and F had been effected, preparative glpc was used to obtain pure samples. E, $n^{24}D$ 1.3845 (lit.[34] $n^{20}D$ 1.3867), had an infrared spectrum corresponding to that reported[34] for *trans*-2,3-epoxypentane (**5b**); F, $n^{24}D$ 1.3918 (lit.[34] $n^{20}D$ 1.3942), had an infrared spectrum corresponding to that reported[34] for the *cis* isomer **5a**. To confirm this assignment, use of pure *cis*-2-pentene in an analogous preparation gave only *cis* epoxide.

Chlorination of *cis*-2-Pentene in Acetone–Water. Chlorine (25 g, 0.35 mole) was condensed in a trap and slowly swept into a mixture of 70 g (1.0 mole) of *cis*-2-pentene (98% commercial material from Phillips Petroleum), 200 ml of acetone, and 100 ml of water at 0°. The mixture was flooded with water and extracted with pentane. Glpc analysis (Perkin-Elmer column B) of the dried extract revealed a band corresponding to *threo*-2,3-dichloropentane (**2**) plus two new bands at longer retention time, G and H, in a ratio of *ca.* 1:2. Distillation gave 21 g of a mixture of **2**, G, and H, bp 134–147°. The dichloride was isolated by preparative glpc and confirmed as **2** by its infrared spectrum. The infrared spectrum of the mixture showed OH absorption at 3545 and 3450 cm^{-1} and hence G and H were tentatively assigned as the isomeric chlorohydrins. To confirm this, the mixture of **2**, G, and H was treated with 0.5 *M* methanolic potassium hydroxide for 15 min at room temperature. Usual work-up with water and pentane gave a dried extract whose glpc analysis indicated indicated complete conversion of G and H to *cis* epoxide **5a** as judged by use of the dichloride **2** present as an internal standard; hence G and H both have the *threo* configuration.

Acetylation of Mixed *threo*-2,3-Chlorohydrins. A 1:1 mixture of dichloride **2** and chlorohydrins G and H (G/H = 0.57) (1.44 g) was treated with 0.1 g of sodium acetate, 1 ml of acetic acid, and 3 ml of acetic anhydride for 5 hr at 100°. The mixture was diluted with water and extracted with pentane. Glpc analysis of the dried extract (Perkin-Elmer column B) showed the original dichloride **2** plus chloroacetates C and D (*vide supra*) with C/D = 0.58. The dichloride served as an internal standard to show that acetylation was quantitative and hence that no preferential loss of G or H had occurred. Hence C and G fall into the same positional isomer class whereas D and H have the other orientation.

Oxidation of Mixed *threo*-2,3-Chlorohydrins To a stirred solution of 1.2 g of the same dichloride–chlorohydrin mixture used above for the acetylation in 3 ml of ether was added at 0° a solution of 1 g of sodium dichromate in a mixture of 2 ml of sulfuric acid and 5 ml of water.[35] After 30 min, the layers were separated and the aqueous layer extracted with ether. The combined ether fractions were dried over sodium sulfate; glpc analysis revealed dichloride plus a new, more volatile material but no residual chlorohydrins; again consideration of the amount of dichloride indicated quantitative conversion. The new product could be only partially resolved into two components I and J by careful glpc analysis and preparative glpc gave only a mixture, $n^{24}D$ 1.4245, whose infrared spectrum showed strong absorption at 1720 cm^{-1} consistent with the expected α-chloro ketone structure. The nmr spectrum was a superposition of the expected spectra for 3-chloro-2-pentanone (**9**) as the major product J and 2-chloro-3-pentanone (**8**) as the minor product I in a ratio of I/J = 0.57. The bands for **9** are a triplet at 1.03 ppm, 7 cps (CH_3CH_2–); a multiplet at 1.75–2.15 ppm (CH_3CH_2CHCl–); a singlet at 2.27 ppm ($CH_3C(=O)$–); and a doublet of doublets at 4.08 ppm (-$CH_2C^*HClC(=O)$–). The bands for **8** are: a triplet at 1.07 ppm, J = 7 cps (CH_3CH_2–); a doublet at 1.58 ppm, J = 7 cps (-$CHClCH_3$); a multiplet at 2.70 ppm ($CH_3CH_2C(=O)C^*HCl$–); and a quartet at 4.30 ppm -$C(=O)CHClCH_3$). This combination of acetylation and oxidation of the chlorohydrins proves that chloroacetate C (**3**), chlorohydrin G (**6**), and chloro ketone I (**8**) all have chlorine in the 2 position while the corresponding D (**4**), H (**7**), and J (**9**) all have chlorine in the 3 position.

Identification of Products from Chlorination of *trans*-2-Pentene in Acetic Acid. Low-conversion quantitative runs gave four observable products, K–N, by glpc analysis (Perkin-Elmer column B). Product K had retention times equal to those of 3-chloro-1-pentene (**1**) on several columns and was so assigned. Products L, M, and N each had retention times similar to but distinct from those of B, C, and D (**2**, **3**, and **4**), respectively. From a preparative run distillation gave pure L and mixtures of M and N. Product L, bp 40–42° (21 mm), $n^{25}D$ 1.4433, had infrared and nmr spectra similar to but distinct from those of **2**; it is assigned as *erythro*-2,3-dichloropentane (**10**).

Anal. Calcd for $C_5H_{10}Cl_2$: C, 42.6; H, 7.2; Cl, 50.3. Found: C, 42.7; H, 7.2; Cl, 50.3.

Analysis of the nmr spectra of mixtures of M and N, bp 85–87° (21 mm), $n^{25}D$ 1.4260, exactly as above for C and D indicated the minor chloroacetate M to be *erythro*-2-chloro-3-acetoxypentane (**11**) and the major chloroacetate N to be *erythro*-3-chloro-2-acetoxypentane (**12**). Mixtures showed the expected ester carbonyl absorption at 1750 cm^{-1}.

Anal. Calcd for $C_7H_{13}O_2Cl$: C, 51.1; H, 8.0; Cl, 21.5. Found: C, 50.5; H, 8.0; Cl, 22.0

Treatment of a mixture of M and N with methanolic potassium hydroxide as above gave only *trans*-2,3-epoxypentane (**5b**); this confirms the *erythro* assignment.

Identification of Products from Chlorination of 1-Pentene in Acetic Acid. Chlorination and glpc analysis in the usual fashion showed minor amounts of substitution products, and three major products O–Q. Since chlorination under oxygen in 1,1,2-trichlorotrifluoroethane gave only O as a significant product,[3] it was assigned as 1,2-dichloropentane (**13**). A combination of distillation and preparative glpc gave P (98.5% pure) and a mixture of P and Q containing 86% Q; each sample showed infrared absorption at 1740 cm^{-1}. The nmr spectrum of P showed complex absorption at

(34) H. van Risseghem, *Bull. Soc. Chim. France*, 1661 (1959).

(35) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, 83, 2951 (1961).

0.8–1.8 ppm ($CH_3CH_2CH_2CHX$–), a singlet at 2.01 ppm (CH_3CO_2–), a doublet at 3.53 ppm (–$CHXCH_2Y$), and a broadened quintet at 4.93 ppm (–CH_2CHXCH_2Y) in a ratio of 7.1:2.95:1.95:1.0. The nmr spectrum of the mixture rich in Q showed a complex multiplet at 4.1 ppm corresponding to three hydrogens in place of the distinct absorptions at 3.53 and 4.93 ppm in P. Since acetoxy is more deshielding than chlorine and tertiary hydrogens are more deshielded than secondary,[36] the only consistent assignment is that the major chloroacetate P is 1-chloro-2-acetoxypentane (**14**) and the minor chloroacetate Q is 2-chloro-1-acetoxypentane (**15**).

Methylation of *threo*-2,3-Chlorohydrins. A mixture of 0.5 g of mixed *threo*-2,3-chlorohydrins (**7**/**6** = 3.1), 0.1 ml of boron trifluoride etherate, and 1 ml of ether was treated at 0° with small portions of a cooled solution of diazomethane in ether[37] until the yellow color persisted. Glpc analysis (Perkin-Elmer column B) revealed as volatile products *ca.* 10% residual chlorohydrins (**7**/**6** = 3.3) plus *ca.* 90% of two new materials in a ratio of 3.2:1.0. Since materials of identical retention time were obtained by chlorination of *cis*-2-pentene in methanol, they are assigned as *threo*-3-chloro-2-methoxypentane (**17a**) (major) and *threo*-2-chloro-3-methoxypentane (**16a**) (minor)

***t*-Butylation of *threo*-2,3-Chlorohydrins.** A mixture of 9.0 g of mixed *threo*-2,3-chlorohydrins (**7**/**6** = 1.65), 0.8 ml of concentrated sulfuric acid, and 140 ml of methylene chloride was kept saturated with isobutylene at 0°. Occasional small aliquots were extracted with sodium carbonate solution and analyzed by glpc. The chlorohydrins gradually disappeared and were replaced by a new pair of peaks which, in a ratio of 1.90:1.00, made up 80% of the volatile material after 4 days. Since materials of identical retention time were obtained by chlorination of *cis*-2-pentene in *t*-butyl alcohol, they are assigned as *threo*-3-chloro-2-*t*-butoxypentane (**17c**) (major) and *threo*-2-chloro-3-*t*-butoxypentane (**16c**) (minor).

Trifluoroacetylation of *threo*-2,3-Chlorohydrins. A mixture of dichloride **2**, chlorohydrins **6** and **7**, and trifluoroacetic anhydride in excess was allowed to stand at room temperature for 2 hr. The same pair of products were formed in quantitative yield as detected by glpc analysis as were formed by chlorination of *cis*-2-pentene in trifluoroacetic acid (**16e** and **17e**).

Chlorination of *cis*-2-Pentene in Formic Acid. A partially miscible mixture of 108 ml (1 mole) of 98% *cis*-2-pentene and 400 ml of formic acid (commercial) was treated with 21.5 ml (liquid) (0.5 mole) of chlorine with stirring under oxygen at room temperature. The mixture was flooded with water and extracted with pentane and ether. The extracts were partially evaporated, taken up in benzene, washed with 10% sodium carbonate solution, dried over sodium sulfate, and again evaporated on a rotary evaporator. Glpc analysis of the residue revealed dichloride **2**, chlorohydrins **6** and **7**, several unidentified peaks, and finally a band corresponding in retention time to the major product of chlorination detected in low-conversion quantitative runs. Only 4.5 g of this material, bp 165–168°, $n^{24.5}$D 1.4323, could be isolated by distillation.

Anal. Calcd for $C_6H_{11}ClO_2$: C, 47.9; H, 7.4; Cl, 23.5. Found: C, 47.7; H, 7.3; Cl, 23.6.

The infrared spectrum showed a strong band at 1755 cm^{-1} and the nmr spectrum had two singlets at 7.8 and 8.07 ppm; this latter observation indicated the presence of both *threo*-3-chloro-2-formyloxypentane (**17d**) and *threo*-2-chloro-3-formyloxypentane (**16d**) although these were never resolved by glpc analysis.

(36) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, pp 54–55.

(37) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 165.

Chlorination of *trans* 2-Pentene in Various Solvents. Quantitative chlorinations of *trans*-2-pentene in methanol, ethanol, *t*-butyl alcohol, formic acid, and trifluoroacetic acid each gave mixtures of dichloride **10** and two new materials assigned the structures **18a–e** and **19a–e** by analogy to results for *cis*-2-pentene.

Chlorination of 1-Pentene in Various Solvents. Preparative chlorinations were carried out and mixtures of products **20a–e** and **21a–e** were isolated in each case by preparative glpc. Each pair could be only partially resolved by glpc. The infrared and nmr spectra were consistent with the assigned structures. The methyl singlets in **20a** and **21a**, the *t*-butyl singlets in **20c** and **21c**, and the formyl singlets in **20d** and **21d** were each too similar in position to allow quantitative resolution.

The structures of **20a–21a**, **20e–21e**, and **20f–21f** (same as **14** and **15**) were confirmed by methylation, trifluoroacetylation, and acetylation of a mixture of 1,2-chlorohydrins (prepared by chlorination in water–acetone) in a manner analogous to that described above for the *threo*-2,3 series.

Quantitative Chlorination Procedure. The appropriate quantities of olefin and solvent (or salt solution) (10 ml total) were measured into a 25-ml flask equipped with a magnetic stirring bar, gas inlet tube, and reflux condenser fitted with a drying tube; all glassware was dried in an oven and assembled hot under a slow oxygen stream. Chlorine was condensed in a calibrated tube by use of a Dry Ice–acetone bath and then swept into the stirred reaction mixture in 5–10 min by a slow stream of oxygen which had been passed through concentrated sulfuric acid. Temperature was maintained by a thermostated bath at 25.0° containing an immersible magnetic stirring motor. After reaction was complete, the reaction mixture was treated with 50 ml of water and extracted with five 5-ml portions of pentane. The dried extracts (sodium sulfate) were analyzed by glpc analysis; when used, the internal standard, nonane, was added prior to analysis. Control experiments showed that this extraction procedure isolated all the organic products while most of the hydroxylic solvent, which tailed badly during analysis, remained in the aqueous phase.

Analyses were performed on a Microtek 2500R instrument equipped with a flame ionization detector and 2-m Perkin-Elmer columns; column B was used for all quantitative work except that column O (silicone grease) was used for the 1-pentene–trifluoroacetic acid case. Areas were determined from the product of peak height and retention time except in the cases of unresolved peaks where a planimeter was used. Calibration factors for conversion of areas to molar quantities were determined directly from analysis of known mixtures of authentic materials for the cases: *cis*-2-pentene–acetic acid, *cis*-2-pentene–methanol, and 1-pentene–all six solvents. For the other products from the 2-pentenes in various solvents, the corresponding factor for the product derived from 1-pentene in that particular solvent was assumed to hold. The 1-pentene factors used in the formula (moles) = (f)(area)$\frac{1}{2}$ were f = 1.02 for methyl ethers, f = 0.83 for ethyl ethers, f = 0.65 for *t*-butyl ethers, f = 0.87 for acetates, f = 1.15 for formates, and f = 1.07 for trifluoroacetates where f = 1.00 for the dichloride.

Retention times on column B in minutes at a flow rate of *ca.* 200 ml/min for the *threo* series at 93° were: **1**, 4; **2**, 18; **3**, 43; **4**, 46; **16c**, 41; **17c**, 36; **16e**, 16; and **17e**, 17. At 73° retention times were: **2**, 39; **16a**, 28; **17a**, 31; **16b**, 45; **17b**, 47.5; and **16d** and **17d**, 35. For the corresponding *erythro* series at 93° they were: **10**, 15; **11**, 38; **12**, 41; **18c**, 49; **19c**, 46; **18e**, 14; and **19e**, 16. At 73° they were: **10**, 34; **18a**, 28; **19a**, 31; **18b**, 43; **19b**, 47; and **18d** and **19d**, 31. For the 1,2 series at 108° retention times were: **13**, 16; **14**, 38; **15**, 45; **20c**, 36; and **20d**, 31. At 88° they were: **13**, 32; **20a**, 28; and **20b**, 41. At 77° on column O they were: **13**, 21 and **20e**, 18.