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Allylidene Halides. II. The Structure and Reactivity of Cinnamal Chloride

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As a continuation of previous work[1] on the structure and reactivity of dihalides obtained by the reaction of α,β-unsaturated carbonyl compounds with phosphorus pentachloride, the dichloride prepared from cinnamaldehyde has been investigated. This compound has previously been characterized by oxidative procedures as cinnamal chloride[2] and is reported to give cinnamaldehyde on hydrolysis.[3] However, the products obtained in other solvolytic reactions of the dichloride appear to have the allylic configuration of 3-phenyl-1,3-dichloropropene rather than that of cinnamal chloride.[4]

In an attempt to decide which of the isomeric structures should be assigned to the dichloride a comparison of the solvolysis rates of benzal chloride and of the cinnamaldehyde derivative has been made. Since cinnamal chloride is a vinylog of benzal chloride it might be anticipated that the two compounds would display similar reactivities. The results of this work again suggest 3-phenyl-1,3-dichloropropene as the correct structure. For this reason it seemed necessary to reinvestigate the structure of the cinnamaldehyde derivative by other than oxidative procedures.[5]

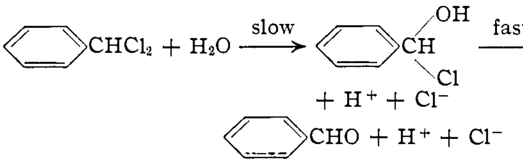
This paper, then, presents in addition to the results of studies of the relative reactivities of benzal and cinnamal chlorides toward solvolysis, the results of a spectrophotometric study of the structure of the latter compound and some of its solvolysis products.

The Hydrolysis of Benzal and Cinnamal Chlorides.—Previous studies[6] have shown that benzal chloride undergoes solvolysis in aqueous ethanol or acetone at a measurable rate with the liberation of two moles of hydrogen and chloride ions per mole of dichloride. For comparison with similar data obtained for cinnamal chloride the previous rate studies have been extended in this Laboratory to determine the effect of varying water concentration on the rate of solvolysis of benzal chloride in aqueous ethanol. It has been found that even when the water concentration of the solvent is as high as 50 volume per cent., the reaction proceeds at a measurable rate at 25°. In absolute ethanol the reaction at 25° is too slow to permit rate measurements.

The compound designated as cinnamal chloride, on the other hand, reacts very rapidly even with absolute ethanol; and in 50 volume per cent. aqueous ethanol the reaction is so fast that the rate is not measurable. However, in these reactions only one mole of hydrogen ion is liberated per mole of dichloride at room temperature. In practice it has been found possible to determine the equivalent weight of cinnamal chloride by direct titration with sodium hydroxide solution of a weighed sample dissolved in ethanol or acetone.

In Table I are presented data for a typical rate run on the solvolysis of benzal chloride in aqueous ethanol. The rate constant, k, has been calculated from equation (1) on the assumption that the reaction proceeds according to equation (2).[7]

$$k = \frac{2.303}{t} \log \frac{(C_6H_5CHCl_2)_{t=0}}{(C_6H_5CHCl_2)_{t=0} - \left(\frac{H^+}{2}\right)_t} \quad (1)$$



(2)

The several runs with benzal chloride are summarized in Table II.

TABLE I

THE SOLVOLYSIS OF BENZAL CHLORIDE IN 50 VOLUME PER CENT. AQUEOUS ETHANOL AT 25°

Time, hr.	(H^+) mole/liter	$(\varphi CHCl_2)$ mole/liter	$\log \frac{(\varphi CHCl_2)_{t=0}}{(\varphi CHCl_2)_t}$	k, hr.$^{-1}$
0		0.0530		
2	0.0027	.0503	0.02202	0.0254
11.5	.0133	.0397	.1265	.0253
23.6	.0478	.0291	.2606	.0254
48.8	.0756	.0152	.5428	.0256
76.6	.0907	.0077	.8389	.0252
				Av. 0.0254[a]

[a] Based on eight measurements.

TABLE II

THE SOLVOLYSIS OF BENZAL CHLORIDE IN AQUEOUS ETHANOL AT 25° AS A FUNCTION OF WATER CONCENTRATION

Volume % water in solvent	$(\varphi CHCl_2)_{t=0}$ mole/liter	k, hr.$^{-1}$
50	0.0530	2.54×10^{-2}
33.3	.0530	3.69×10^{-3}
16.7	.0525	4.8×10^{-4}

Table III illustrates the rapidity with which cinnamal chloride reacts at room temperature

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(1) Andrews, THIS JOURNAL, **68**, 2584 (1946).

(2) Straus, *Ann.*, **393**, 285 (1912).

(3) Charon and Dougoujon, *Compt. rend.*, **136**, 94 (1903).

(4) Straus and Berkow, *Ann.*, **401**, 121 (1913).

(5) The ambiguity of the results of such methods as applied to allylic compounds has been illustrated by Young, McKinnis, Webb and Roberts, THIS JOURNAL, **68**, 293 (1946).

(6) Olivier and Weber, *Rec. trav. chim.*, **53**, 869 (1934).

(7) This treatment does not consider the possibility that benzal chloride may react with ethanol in the medium to produce a chloroether. Since the results are successfully interpreted by equation (1), it would appear that little chloroether is formed or that if formed it undergoes rapid decomposition to give benzaldehyde, ethanol and hydrogen chloride.

with 50 volume per cent. aqueous ethanol. Table IV presents data for the rate of reaction of cinnamal chloride in absolute ethanol. The rate constants, *k'*, were calculated from equation (3),

$$k' = \frac{2.303}{t}\log\frac{(\mathrm{CinnCl_2})_{t=0}}{(\mathrm{CinnCl_2})_{t=0} - (\mathrm{H^+})_t} \qquad (3)$$

TABLE III

THE SOLVOLYSIS OF CINNAMAL CHLORIDE IN 50 VOLUME PER CENT. AQUEOUS ETHANOL AT 25°

Original Cinnamal Chloride Concentration = 0.01762 *M*

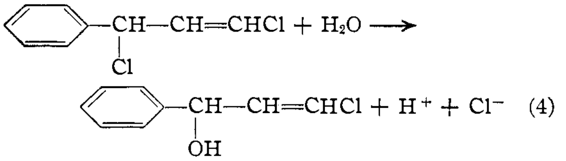
Time, hr.	$(\mathrm{H^+})$ mole/liter
0.17	0.01751
0.58	.01776
1.17	.01751
26.9	.01748

TABLE IV

THE REACTION OF CINNAMAL CHLORIDE WITH ABSOLUTE ETHANOL AT 25°

Time, hr.	$(\mathrm{CinnCl_2})$	$(\mathrm{H^+})$	$\log\frac{(\mathrm{CinnCl_2})_{t=0}}{(\mathrm{CinnCl_2})_t}$	k'
0	0.01556			
0.62	.00947	0.00609	0.215	0.802
1.32	.00570	.00986	.436	.763
2.08	.00356	.01200	.640	.706
3.45	.00113	.01443	1.139	.755
6.25	.00024	.01532	...	...
23.08	.00017	.01539	...	...

Thus under conditions of hydrolysis which favor the conversion of benzal chloride to benzaldehyde, the compound designated as cinnamal chloride displays a reactivity in line with that to be expected of benzhydryl chloride.[8] Indeed the reactivity toward solvolysis of the cinnamaldehyde derivative could satisfactorily be explained on the supposition that reactions of the type represented by equation (4) were occurring.



The Structure of Cinnamal Chloride.—It has been demonstrated that a distinction between isomeric derivatives of allylbenzene and propenylbenzene may be made by examination of the ultraviolet absorption spectra of the compounds.[9] Accordingly the spectrum of cinnamal chloride has been determined in cyclohexane solution.[10] This spectrum has been compared with those of cinnamyl chloride, propenylbenzene and allylbenzene measured in cyclohexane solution. The spectra of benzal and benzyl chlorides and of α-phenylethyl chloride have been measured in the same solvent to establish the nature of the absorption of α-chlorotoluene derivatives. The results of these studies, presented in Figs. 1 and 2, indicate that the reaction product of cinnamaldehyde and phosphorus pentachloride must be, if not pure, very nearly pure cinnamal chloride. The

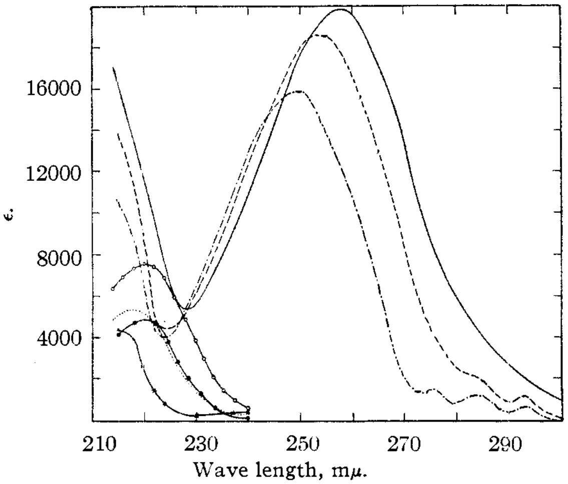


Fig. 1.—Absorption spectra of propenylbenzene, allylbenzene, and toluene derivatives in cyclohexane: — cinnamal chloride; ---- cinnamyl chloride; —·—·— propenylbenzene; -x-x-x- allylbenzene; -●-●-●- benzyl chloride; -O-O-O- benzal chloride; ...... α-phenylethyl chloride.

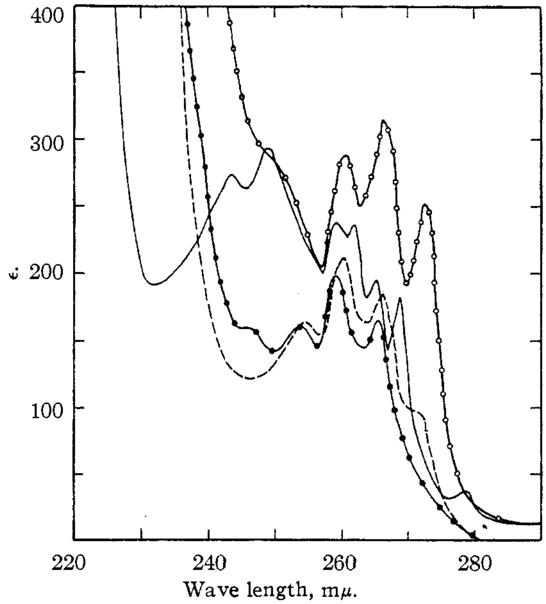


Fig. 2.—Absorption spectra of toluene derivatives in cyclohexane: — allylbenzene; --- benzyl chloride; -O-O-O- benzal chloride; -●-●-●- α-phenylethyl chloride.

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[8] Farinacci and Hammett, THIS JOURNAL, **59**, 2542 (1937).

[9] (a) Braude, Jones and Stern, *J. Chem. Soc.*, 396 (1946); (b) Campbell, Linden, Godshalk and Young, THIS JOURNAL, **69**, 880 (1947).

[10] A non-hydroxylic solvent was chosen to avoid complications resulting from the high reactivity of the dichloride. Assuming that the cinnamal chloride is a mixture of allylic isomers, it does not seem likely that a non-polar solvent would contribute to the mobility of any equilibrium existing between the two compounds, *cf.* Burton, *J. Chem. Soc.*, 1650 (1928).

spectrum of cinnamal chloride does not display the fine structure associated with the low absorption maxima from 240–280 mμ of the toluene and allylbenzene derivatives (Fig. 2). On the other hand, the spectrum of the cinnamaldehyde derivative shows the characteristic high maximum in the range 250–270 mμ characteristic of propenylbenzene derivatives (Fig. 1). The magnitude of the extinction coefficient is sufficiently high to indicate that there can be no large amount of isomeric material present. The important maxima and minima of the several compounds as represented in Fig. 1 are listed for convenience in Table V. Outside of slight shifts in the magnitude and wave lengths of the absorption maxima the curves (Figs. 1 and 2) obtained for cyclohexane solutions of propenylbenzene and allylbenzene are very similar to those obtained previously[9b] from ethanol solutions of these two compounds.

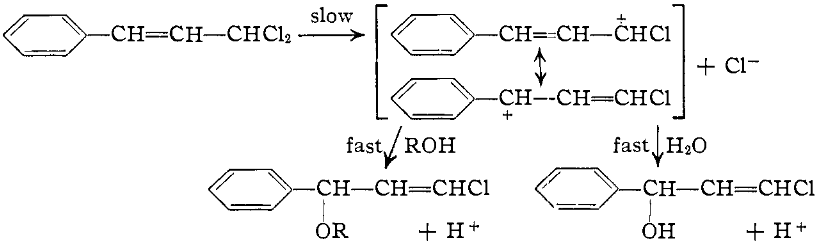
TABLE V

THE MAIN ABSORPTION MAXIMA AND MINIMA OF PROPENYLBENZENE, ALLYLBENZENE AND TOLUENE DERIVATIVES IN CYCLOHEXANE SOLUTION

Compound	λ max., mμ	ε max.	λ min., mμ	ε min.
Cinnamal chloride	258	19900	228	5300
Cinnamyl chloride	254	18600	224	4470
Propenylbenzene	250	15900	224	4000
Allylbenzene	216	4380	...	..
Benzyl chloride	220	4860	...	..
Benzal chloride	220	7600	...	..
α-Phenylethyl chloride	218	5380	...	..

The Products of Reaction of Cinnamal Chloride with Hydroxylic Solvents.—Studies to determine the structural nature of cinnamal chloride solvolysis products are now under way. A few preliminary observations will be noted here.

The rate data observed for the reaction of the dichloride with aqueous ethanol seem, in the light of previous studies of allylic systems,[11] best explained on the assumption that the solvolytic reaction is unimolecular (S_N1) in type and leads to allylic rearrangement (equation 5).



(5)

If cinnamaldehyde were formed by reaction of the ionic intermediate with water, two moles of hydrogen ion should be produced per mole of dichloride, which is contrary to the kinetic observations made at 25°.

Several attempts have been made to isolate the hydrolysis product of cinnamyl chloride. It has been observed that refluxing cinnamal chloride with water results in the production of cinnamaldehyde in low but appreciable yield. On the other hand, if the dichloride is shaken with water at room temperature, one obtains a crude product from which can be isolated only traces of cinnamaldehyde and a large amount of crystalline solid which at present writing appears to be bis-(γ-chloro-α-phenylallyl)-ether.[4] This is consistent with the rate studies which show that only one mole of hydrogen ion is generated per mole of dichloride in hydroxylic solvents.

The absorption spectra in cyclohexane solution both of the crude product and of the crystalline solid isolated from the reaction of cinnamaldehyde with cold water are presented in Fig. 3. The extinction coefficients are expressed as $E^{1\%}_{1\,\mathrm{cm.}}$ owing to the ambiguity as to the composition of the reaction product. The maximum at ca. 280 mμ for the crude product is characteristic of cinnamaldehyde.[12] The low magnitude of the extinction coefficient observed for this maximum has been taken as an indication that very little cinnamaldehyde was present. The crystalline solid shows an absorption curve characteristic of allylbenzene derivatives. This is consistent with the assumption that the solid is bis-(γ-chloro-α-phenylallyl) ether. If this is the correct structure for the compound the molar extinction coefficient at 215 mμ is 22200. Similarly the spectrum of a solution of cinnamal chloride in ethanol prepared several days before measurement may be interpreted on the basis that the solution contains a small amount of cinnamaldehyde and a larger

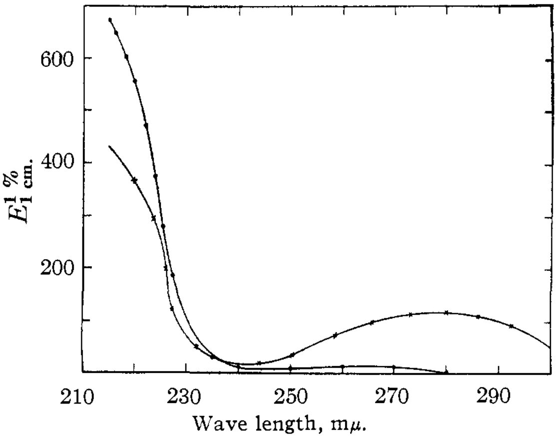


Fig. 3.—Absorption spectra of cinnamal chloride hydrolysis products in cyclohexane: -●-●- solid hydrolysis product; -x-x-x- crude hydrolysis product.

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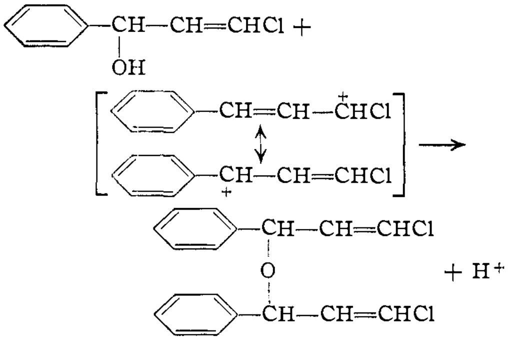
(11) (a) Hughes, *Trans. Faraday Soc.*, **37**, 627 (1941); (b) Roberts, Young and Winstein, THIS JOURNAL, **64**, 2157 (1942); Young and Andrews, *ibid.*, **66**, 421 (1944).

(12) Herzog and Hilmer, *Ber.*, **64B**, 1288 (1931).

quantity of some allylbenzene derivative (spectrum not shown). These observations seem consistent with the mechanism shown in equation (5). The formation of an ether in the reaction of cinnamal chloride with cold water could be accounted for on the assumption that the alcohol formed (equation 5) reacted with the carbonium ion intermediate as represented below



(6)

Experimental

Cinnamal Chloride.—This was prepared from phosphorus pentachloride and freshly distilled cinnamaldehyde according to the directions of Straus and Berkow.[4] The crude product was recrystallized several times from petroleum ether, m. p. 58–59°.

Benzal Chloride.—Eastman Kodak Company white label benzal chloride was redistilled and a fraction collected at 74–75° (6 mm.).

Propenylbenzene and Allylbenzene.—Pure samples of these compounds were kindly furnished by Dr. Tod Campbell.

α-Phenylethyl Chloride.—A sample, b. p. 91° (30 mm.), was kindly furnished by Dr. S. Winstein.

Cinnamyl Chloride.—A sample of b. p. 83–84° (1–2 mm.) was used.

Kinetic Studies.—The rate runs were made at 25° on solutions of benzal or cinnamal chloride in measured volumes of alcohol to which the appropriate measured volumes of water had been added. Final volumes of the reaction mixtures were calculated from density data for alcohol–water mixtures.[13] The exact procedures used have been outlined previously.[1] Samples withdrawn for analysis were titrated with alcoholic sodium hydroxide solution using methyl red indicator.

Ultraviolet Absorption Spectra.—The measurements were made on a Beckman Spectrophotometer (Model DU) equipped with a hydrogen discharge tube. Figures 1 and 2 present plots of the molar extinction coefficients as a function of wave length of the several substances measured. In Fig. 3 the extinction coefficients have been calculated as $E^{1\%}_{1\,\text{cm.}}$. Eastman Kodak Company white label cyclohexane was used without further purification as a solvent in this work.

The Products of Reaction of Cinnamal Chloride with Water: (A) At Reflux Temperature.—A mixture of 100 cc. of water, 2.7 g. (0.027 mole) of calcium carbonate and 5 g. (0.0268 mole) of cinnamal chloride was refluxed for four hours. The cooled mixture was extracted with ether and the dried extract distilled. One gram of cinnamaldehyde, b. p. 135–136° (25 mm.), was recovered and identified as the semicarbazone (m. p. and mixed m. p. with authentic sample 214–215°). The small tarry residue left in the distilling flask was not investigated.

(B) **At Room Temperature.**—Eight grams (0.043 mole) of cinnamal chloride was shaken overnight with 150 cc. of water. The white solid changed to a heavy yellow oil which settled to the bottom of the shaking flask. Analysis of a sample of the aqueous phase showed that 0.0426 mole of hydrogen ion had been liberated in the reaction.[14] The oil was extracted in petroleum ether, and the dried ether phase was concentrated by distillation under vacuum. The residual oil (5.8 g.) slowly began to crystallize. The crystal mush was taken up in a small amount of ethanol, and a crop of fine white needles was filtered from the mixture. After three recrystallizations from ethanol the material showed a melting range of 93.8–95.8°.

In a second run carried out in a similar manner the yellow oil obtained from the petroleum ether solution was distilled under reduced pressure. About 2.0 g. of distillate (b. range 122–130° (7 mm.)) was obtained. This liquid contained a small amount of cinnamaldehyde as shown by semicarbazone formation (m. p. and mixed m. p. with authentic sample 214–215°). The residual greenish-yellow oil was treated with 15 ml. of ethanol. A crop of white crystals precipitated immediately (dry weight 1.93 g.). After three recrystallizations from ethanol, the small white needles melted 103–104°.

Both of the above-mentioned crystalline products, m. p. 93.8–95.8° and 103–104°, were non-acidic, contained halogen and gave negative tests for active hydrogen on treatment with ethylmagnesium bromide. Combustion analyses on both samples are in reasonable agreement with the postulated structure of bis-(γ-chloro-α-phenylallyl) ether. *Anal.* Calcd. for $C_{18}H_{16}OCl_2$: C, 67.71; H, 5.05. Found for sample of m. p. 93.8–95.8: C, 67.22; H, 5.25; for sample of m. p. 103–104°: C, 67.22; H, 5.18. The differences in melting points of the two samples should probably be attributed to differences in composition with respect to *cis–trans* isomers. Attempts at chloride analysis by use of sodium ethoxide give slightly low results, presumably because the chlorine atoms are attached to vinyl groups. The ether has been obtained previously in a similar manner[4] but has not previously been isolated in crystalline form. Further investigation of the structure and behavior of this substance is contemplated. The authors are indebted to Mr. Bruce Day for the combustion analyses.

Summary

Cinnamal chloride behaves in solvolytic reactions as if it were 3-phenyl-1,3-dichloropropene. A study of the ultraviolet absorption spectrum of the dichloride indicates, however, that the correct structure is cinnamal chloride. On the basis of kinetic measurements of the dichloride and studies of the nature of the reaction products it is concluded that the solvolysis reactions are accompanied by allylic rearrangement. Mechanisms consistent with those proposed previously for similar reactions of other types of allylic chlorides may be used to account for the observations.

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[13] "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio.

[14] Straus and Berkow[4] have reported that when an ether solution of cinnamal chloride is shaken with water, a second mole of hydrogen ion is liberated slowly. The implication is that under their experimental conditions the alcohol or other substance obtained as a primary reaction product slowly reacts in the acidic medium to form cinnamaldehyde. Preliminary experiments performed in this Laboratory indicate that when an aqueous suspension of cinnamal chloride is heated, more than one mole of hydrogen ion is liberated per mole of dichloride. This is consistent with the observation that larger amounts of cinnamaldehyde are isolated under reflux conditions than at room temperature.