neopentane transmission limits also need to be measured.

Acknowledgment.—We must again express our appreciation to the University of Michigan for the extended loan of their fluorite spectrograph and to the University of Minnesota for the loan of a hydrogen arc and other equipment. We are indebted to Howard Carter and Dorothy Iker for experimental assistance.

Grateful acknowledgment is made to the American Petroleum Institute and the National Bureau of Standards for the loan of the samples measured in this investigation.

Summary

Limits of vacuum ultraviolet transmission through an 0.13 mm. cell are given for a number of very pure saturated hydrocarbons. The limits depend somewhat on chain length, but more on branching and cyclization. For the non-cyclic paraffins, the limits seem to be determined almost entirely by the maximum number of alkyl substituents on any carbon–carbon bond in the molecule. Limits for some other solvents, for some unsaturated compounds, and for a number of solids are also included. The liquid limits in compounds of a given type are mainly determined by the positions of the first strong absorption band and so are probably closely related to the ionization potentials. The transmission limit of a compound may be used as a partial criterion of purity.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

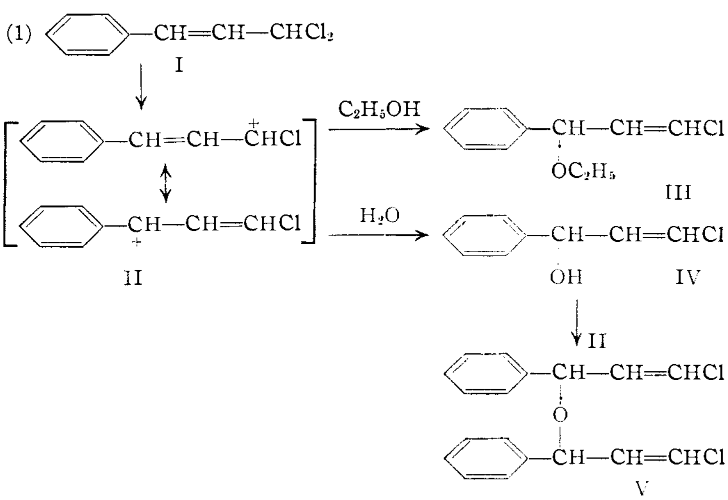
Allylidene Halides. III. A Spectrophotometric Study of Solvolysis Reactions of Cinnamal Chloride[1]

BY LAWRENCE J. ANDREWS

In an earlier publication[2] certain observations and proposed mechanisms regarding the hydrolysis and ethanolysis of cinnamal chloride were presented. Although cinnamal chloride has been reported to react with water to yield cinnamaldehyde, it was found that the main product of the reaction at room temperature was bis-(γ-chloro-α-phenylallyl) ether. Only from reactions run under reflux was a considerable quantity of aldehyde isolated. It has also been reported that cinnamal chloride reacts with sodium ethoxide in ethanol solution to form 1-chloro-3-ethoxy-3-phenyl-1-propene.[3] That the reaction also occurred rapidly in absolute ethanol in the absence of sodium ethoxide was confirmed by spectrophotometric procedures.

These and other observations were accounted for on the assumption that cinnamal chloride, a propenylbenzene derivative, undergoes an S_N1 type solvolysis losing chloride ion to form a resonating ionic intermediate which reacts with solvent to form an allylbenzene derivative (see equation 1).

(1)



This paper presents the results of an extension of this work designed to elucidate further the proposed reaction mechanisms. The report that the reaction of cinnamal chloride with sodium ethoxide in absolute ethanol proceeds with complete allylic rearrangement to form 1-chloro-3-ethoxy-3-phenyl-1-propene (III) could be accounted for entirely in terms of the S_N1 type mechanism. In view of a recent observation[4] it seemed important to establish whether or not any of this rearrangement should be ascribed to a bimolecular reaction in which ethoxide ion attacks the dihalide at the double bond adjacent to the phenyl group (equation 2). In addition to a consideration of this question this paper presents further information concerning the factors favoring the production of cinnamaldehyde during the solvolysis of cinnamal chloride.

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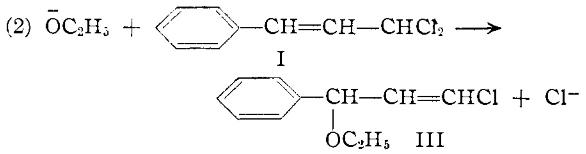
(1) Most of the material in this paper was presented before the Organic Division of the American Chemical Society, Atlantic City, New Jersey, April, 1947.

(2) Andrews and Linden, THIS JOURNAL, **69**, 2091 (1947).

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

(4) Kepner, Young and Winstein (manuscript submitted for publication) have demonstrated that such a reaction occurs between malonic ester anion and α-methylallyl and α-ethylallyl chlorides.

(2)



The Reaction with Alcoholic Sodium Ethoxide.—The kinetics of the reaction of cinnamal chloride in ethanolic sodium ethoxide solutions were followed spectrophotometrically by noting the rate of disappearance of the absorption maximum at 260 mμ (see Fig. 1). This change in spectrum is characteristic of the rearrangement of a propenylbenzene to an allylbenzene type structure.[2] First order rate constants (k) were calculated from equation (3) in which d_{260} mμ represents the optical density of the solutions at 260 mμ.[5]

$$k = \frac{2.303}{t} \log \frac{(d_{260\,\mathrm{m}\mu})_{t=0}}{(d_{260\,\mathrm{m}\mu})_t} \qquad (3)$$

The runs were performed using solutions in which the ethoxide ion concentration was zero or very high with respect to the dichloride concentration. Under these circumstances if any appreciable contribution of a bimolecular reaction of the type represented in equation (2) occurred, values of k obtained from run to run should increase with increasing sodium ethoxide concentration.

The data for a typical run are given in Table I. In Table II are presented the results of several runs which illustrate that the value of k does not increase with increasing ethoxide ion concentration. Indeed when the ethoxide ion concentration was raised to 1 M, the value of k was reduced.[6] Apparently the bimolecular rate constant is too small to account for the formation of an appreciable quantity of product by the process given in equation (2).

TABLE I

THE REACTION OF CINNAMAL CHLORIDE IN ETHANOLIC SODIUM ETHOXIDE (22.6°)

$(RCl_2) = 2.11 \times 10^{-5}$ M; (NaOEt) = 0.547 M

Time, hr.	d_{260} mμ	k
0	0.406	
0.167	.382	0.36
.516	.338	.35
1.23	.255	.38
2.21	.184	.36
2.95	.143	.35

Av. based on eleven readings 0.36

TABLE II

RATE CONSTANTS FOR THE REACTION OF CINNAMAL CHLORIDE IN ETHANOLIC SODIUM ETHOXIDE

$RCl_2 \times 10^5$ mole/liter	NaOEt mole/liter	k^a	Av. temp., °C.
2.34	....	0.36	22.3
5.46	....	.39	22.5
2.26	0.1018	.37	22.3
2.11	.547	.36	22.6
2.56	1.068	.25	22.0

[a] The values of k are considerably lower than that obtained previously[2] at 25° using volumetric methods for analyzing samples. However, the absolute ethanol used in earlier work was an old sample which apparently contained enough water to catalyze the ethanolysis rate markedly.

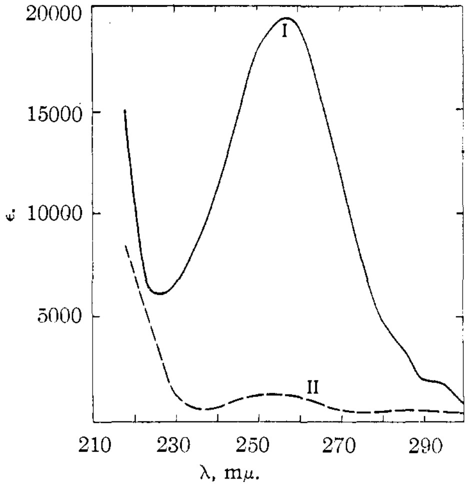


Fig. 1.—The absorption spectrum of cinnamal chloride in absolute ethanol: curve I measured immediately after preparation of the solution; curve II measured twenty hours later.

Concentrated Ethanol Solutions of Cinnamal Chloride.—After a concentrated solution of cinnamal chloride in absolute ethanol stood at room temperature for several days, cinnamaldehyde was detected in the higher boiling fractions isolated on distillation of the products. To investigate the conditions contributing to the formation of cinnamaldehyde in concentrated solution, an ethanol solution approximately 0.3 M in cinnamal chloride concentration was prepared at room temperature and samples were removed and diluted for spectrum measurement from time to time. The absorption curves for the several samples are presented in Fig. 2, along with that of cinnamaldehyde for comparative purposes.[7]

Immediately after preparation the ethanol solution of cinnamal chloride showed the characteristic maximum at 260 mμ (Fig. 2, curve I). After twenty-two hours (curve III) the calculated extinction coefficient at 260 mμ had fallen markedly. At this point the absorption maximum at 285 mμ, characteristic of cinnamaldehyde, began to develop. After one hundred and nineteen hours curve IV was obtained. No further change in the absorption curve was noted. At this point the

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[5] Branch and Tolbert, THIS JOURNAL, **69**, 523 (1947), have used a similar method of measuring reaction rates of other systems. Allylbenzene derivatives show meager light adsorption at 260 mμ.[2] The measured optical densities were not, however, corrected on this basis since the corrections were well within the error of the measurements.

[6] This is contrary to the expected salt effect in an S_N1 type solvolysis. However at this high concentration of ethoxide ion the activity of the solvent may be reduced sufficiently to hamper its participation in the rate-determining process of separating chloride ion from the organic halide.

[7] The cinnamaldehyde spectrum in ethanol is not markedly altered by introducing into the solution hydrogen chloride in concentrations comparable to that of the aldehyde.

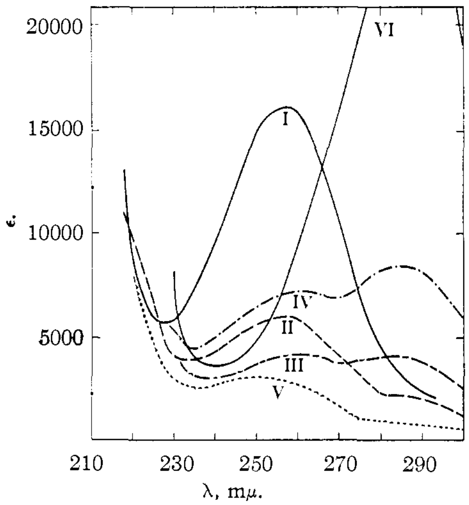
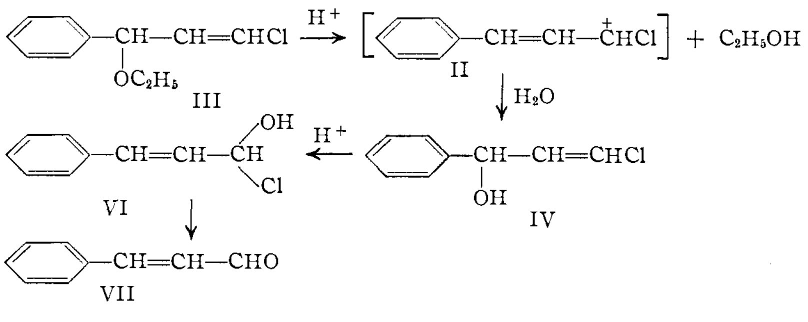


Fig. 2.—Spectrophotometric determination of the reaction of cinnamal chloride in ethanol (original cinnamal chloride concn. 0.346 *M*): curve I measured immediately after preparation of the solution; curves II, III, IV measured three, twenty-two and one hundred and nineteen hours later, respectively. Curve V is for a solution originally 0.34 *M* in cinnamal chloride and 0.6 *M* in sodium ethoxide (measured fifty-one hours after preparation). Curve VI is cinnamaldehyde (ϵ_{285} = 25,300).

peak at 285 mμ was pronounced, and the height of the maximum at 260 mμ had increased as compared to that of Curve III.

When the concentration of cinnamal chloride in ethanol is relatively high, the reaction to form 1-chloro-3-ethoxy-3-phenyl-1-propene (III) is accompanied by the formation of a considerable quantity of hydrogen chloride. This fact suggests that the concentration of acid in the medium is sufficiently high to promote the conversion of the ether to cinnamaldehyde as follows

(4)

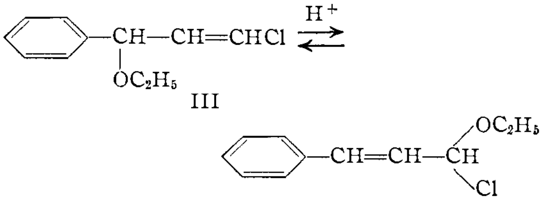


III II IV VI VII

Even traces of water in the solution would account for the formation of a considerable quantity of cinnamaldehyde. The fact that the quantity of cinnamaldehyde formed in the reaction studied reached a fixed value is consistent with the idea that at this point all of the water in the medium had been consumed. One would anticipate from earlier results[2] that the reaction product of the ionic intermediate (II) with water would be α-phenyl-γ-chloro-allyl alcohol (IV). However, other work has shown that allylic alcohols are interconvertible in acid solution[8] which suggests the mechanism for conversion of α-phenyl-γ-chloro-allyl alcohol to cinnamaldehyde given in equation (4).

The reformation of a peak at 260 mμ (Fig. 2, curve IV) may have resulted from the establishment of an equilibrium between isomeric chloroethers

(5)



III VIII

The latter compound (VIII) should display an absorption spectrum similar to that of cinnamal chloride. No attempt was made to isolate this material from the complex mixture of reaction products.

In view of these results it was expected that no cinnamaldehyde should be formed if the ethanol solution of cinnamal chloride were basic during the course of the reaction. Curve V (Fig. 3) representing the spectrum of an ethanol solution originally 0.3 *M* in cinnamal chloride and 0.6 *M* in sodium ethoxide concentrations and measured fifty-one hours after preparation confirmed this prediction. No cinnamaldehyde formed during this or a longer time interval.[9]

The Hydrolysis of bis-(γ-Chloro-α-phenylallyl) Ether.—The fact that cinnamal chloride reacts with cold water to form bis-(γ-chloro-α-phenylallyl) ether (V) but reacts with hot water to form considerable amounts of cinnamaldehyde suggested that the ether should be converted to cinnamaldehyde by heating with water. The presumption that the reaction would be markedly catalyzed by acid is verified by the curves of Fig. 3. Curve I shows the spectrum of a sample of the pure ether in ethanol. Curves II and III represent, respectively, the spectra in ethanol of the products obtained by refluxing a small quantity of the ether with water and with 1 *N* hydrochloric acid for one-half hour. Curve III shows that a large quantity of cinnamaldehyde (absorption maximum at 285 mμ) formed in the acid medium, while Curve II suggests that some cinnamalde-

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[8] See for example (a) Young, Nozaki and Warner, THIS JOURNAL, **61**, 2564 (1939); (b) Braude, Jones and Stern, *J. Chem. Soc.*, 396 (1946).

[9] The low peak at 250 mμ in curve V has a higher extinction coefficient than would be expected for an allylbenzene derivative. However, it is possible that impurities absorbing in this range might form in a strongly basic solution over long periods of time.

hyde may have formed even in neutral solution. The mechanism for conversion of the ether (V) to cinnamaldehyde is undoubtedly similar to that detailed in equation (4) for the formation of cinnamaldehyde from 1-chloro-3-ethoxy-3-phenyl-1-propene (III).

Experimental

Materials.—Cinnamal chloride and bis-(γ-chloro-α-phenylallyl) ether were prepared as described previously.[2] The sample of cinnamaldehyde used for absorption spectrum measurement was a freshly distilled portion of material obtained from Paragon Testing Laboratories. A freshly opened sample of Commercial Solvents absolute ethanol was used (better than 99.7% pure).

Ultraviolet Absorption Spectra.—These measurements were made using a Beckman Spectrophotometer (Model DU). The extinction coefficients as plotted in Figs. 1–3 were calculated from the expressions $\epsilon = d/lc_1$ or $E^{1\%}_{1\,\text{cm.}} = d/lc_2$, in which d is the measured optical density, l the cell width, c_1 the molar concentration and C_2 the concentration in g. per 100 ml. of solvent. In all cases c_1 and c_2 values were taken as the concentration of cinnamal chloride in the freshly prepared solutions.

Reaction Rate of Cinnamal Chloride in Alcoholic Sodium Ethoxide Solution.—Samples of cinnamal chloride were weighed into volumetric flasks and were dissolved to the mark in absolute alcohol. Aliquots of these solutions were taken immediately and diluted to measured volume with ethanol or freshly prepared standard sodium ethoxide solutions to obtain the desired concentrations of reactants. Portions of the final solutions were transferred to absorption cells and the optical densities at 260 mμ determined spectrophotometrically from time to time. The solvent blank used in the spectrum measurements was either absolute ethanol or an ethanolic sodium ethoxide solution of the same concentration as was used in the run underway. Since no device for controlling the temperature of the cell housing was available, the spectrophotometer was used in a small closed room the temperature of which changed only a few tenths of a degree over a one-day interval. The ethanol and sodium ethoxide solutions were allowed to reach the temperature of this room before preparation of the solutions for rate measurement.

Changes in the Spectrum of 0.3 *M* Ethanolic Cinnamal Chloride.—Twenty-five ml. of 0.346 *M* cinnamal chloride solution was prepared by dissolving 1.619 g. of the dichloride in ethanol. From time to time 1-ml. samples were removed and diluted for spectrum measurement.

To test the effect of sodium ethoxide on the reaction 1.595 g. of cinnamal chloride was dissolved to a volume of 25 ml. in 0.610 *M* sodium ethoxide solution (0.341 *M* cinnamal chloride). Samples were taken occasionally, diluted, and the spectra of the dilute solutions measured against blanks having the same sodium ethoxide concentrations.

Conversion of bis-(γ-Chloro-α-phenylallyl) Ether to Cinnamaldehyde.—A sample of ether (0.0016 g.) was treated with 5 ml. of 1 *N* hydrochloric acid and a second sample (0.0014 g.) with 5 ml. of water. The two mixtures were refluxed for one-half hour and were cooled quickly and diluted to 50 ml. with absolute ethanol. The spectra of the resulting solutions were measured against an absolute ethanol blank. The product from the acid run absorbed so strongly that it was necessary to dilute a 10-ml. sample of the ethanol solution to 100 ml. to make optical density readings. Using the measured optical density at 285 mμ (0.190) for the final solution and the extinction coefficient of pure cinnamaldehyde in ethanol (25300) one can estimate that in acidic medium 0.38 × 10^{-5} mole of cinnamaldehyde was formed from 0.0016 g. (0.50 × 10^{-5}) mole of ether.

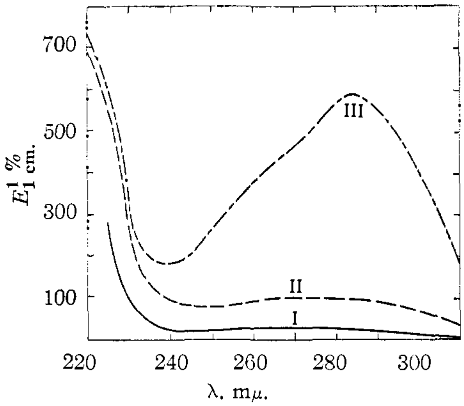

Fig. 3.—Spectrophotometric observation of the reaction of bis-(γ-chloro-α-phenylallyl) ether in hot aqueous media: curve I, pure ether (V) in absolute ethanol; curve II, the product of reaction in neutral solution; curve III, the product of reaction in acid solution.

Summary

Previous studies on the mechanisms of solvolysis reactions of cinnamal chloride have been extended. The reaction of the dichloride in alcoholic sodium ethoxide solution to form 1-chloro-3-ethoxy-3-phenyl-1-propene has been shown to be S_N1 in type. None of the product appears to form by a bimolecular reaction between ethoxide ion and the dichloride.

The formation of cinnamaldehyde in concentrated ethanol solutions of the dichloride has been attributed to the action of acid in the medium on the ether formed as the primary reaction product. The degree to which cinnamaldehyde is formed is limited by the amount of water contained as impurity in the solvent. It has also been shown that bis-(γ-chloro-α-phenylallyl) ether, obtained by the reaction of cinnamal chloride with water at room temperature, forms cinnamaldehyde on refluxing with dilute hydrochloric acid.

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