

water was added and the gummy product recrystallized from alcohol yielding 1.3 g. (60%), m. p. 139–141°. A mixed melting point of this synthetic material with Schorigin's compound showed no depression.

*Anal.* Calcd. for  $C_{35}H_{30}O_2$ : C, 87.1; H, 6.27. Found: C, 86.8; H, 6.30.

### Summary

1. The rearrangement of the diphenylmethyl ether of *o*-cresol or the direct introduction of the

diphenylmethyl group under mild conditions involves the para position of the *o*-cresol.

2. 2-Methyl-4,6-di-(diphenylmethyl) phenylacetate has been synthesized and found to be identical with Schorigin's product obtained by heating diphenylcarbinol and *o*-cresol in an acetic-sulfuric acid medium.

DURHAM, NEW HAMPSHIRE

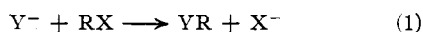
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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND HARVARD UNIVERSITY]

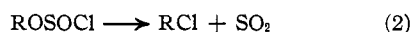
## Allylic Rearrangements. XIII. Kinetics and Mechanisms of the Conversion of Crotyl and Methylvinylcarbinyl Chlorides to Acetates and Ethyl Ethers<sup>1</sup>

BY JOHN D. ROBERTS, WM. G. YOUNG AND S. WINSTEIN<sup>2</sup>

Many investigators, notably Hughes, Ingold and collaborators,<sup>3</sup> have demonstrated that the mechanisms of nucleophilic replacement reactions at a saturated carbon atom may be classified into three general types. One mechanism, designated as  $S_N2$  is the familiar<sup>4</sup> bimolecular, usually second-order, substitution of an electron-donor such as hydroxide ion, alkoxide ion or acetate ion for the halide or a similar group as in equation (1), the replacement resulting in a complete Walden inversion.



Another mechanism, designated as  $S_Ni$ , involves the internal rearrangement of an intermediate compound to give the final product with retention of configuration. An illustration of this mechanism is furnished in equation (2) by the rearrangement of the intermediate from an alcohol and thionyl chloride to produce a chloride and sulfur dioxide.



The third mechanism, designated as  $S_N1$ , is comprised of an electrophilic attack of solvent on halogen or similar groups to yield an unfree<sup>3,5</sup> carbonium ion which subsequently reacts rapidly with an electron donor to yield the final product.

(1) Most of the material of this paper was presented before the Organic Division at the St. Louis and Atlantic City meetings of the American Chemical Society, April and September, 1941.

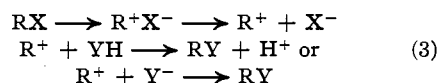
(2) National Research Fellow at Harvard University, 1939–1940.

(3) (a) Cowdrey, Hughes, Ingold, Masterman and Scott, *J. Chem. Soc.*, 1252 (1937); (b) Bateman, Church, Hughes, Ingold and Taher, *ibid.*, 979 (1940).

(4) (a) Olson, *J. Chem. Phys.*, **1**, 418 (1933); (b) Bergmann, Polanyi and Szabo, *Z. physik. Chem.*, **20**, 161 (1933).

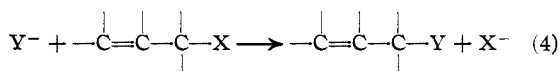
(5) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 172.

Equation (3) represents the sequence of these reactions.



A variation of the  $S_N1$  type of reaction involves the electrophilic attack of such a reagent as silver ion on a halogen group to produce the unfree carbonium ion intermediate.<sup>3,6</sup>

The application of the foregoing types of mechanisms to the replacement reactions of allylic systems<sup>7</sup> has been of great value in explaining the phenomenon of the allylic rearrangement.<sup>7d</sup> The recognition of the possibility of the simultaneous operation of both  $S_N1$  and  $S_N2$  processes, according to equations (4) and (5), has been used to correlate various results with the assumption that the

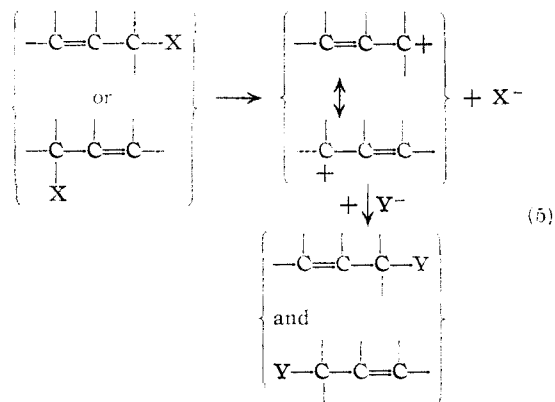


$S_N2$  reaction is normal and the  $S_N1$  reaction yields a mixture, the same mixture resulting from either starting allylic isomer.

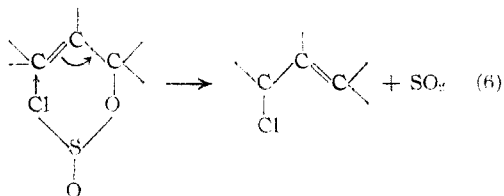
For example, the formation of similar but not identical bromide mixtures from the action of hydrogen bromide on crotyl alcohol and methylvinylcarbinol has been explained in this way.<sup>7a</sup>

(6) Ref. 5, p. 138.

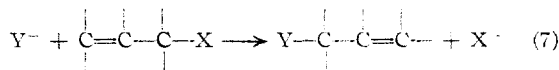
(7) (a) Young and Lane, *THIS JOURNAL*, **60**, 847 (1938); (b) Arcus and Kenyon, *J. Chem. Soc.*, 1912 (1938); (c) Ref. 5, p. 315; (d) After the completion of this manuscript, the paper by Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941), appeared, which reports unpublished work in similar directions to the experiments we report in this article. The conclusions drawn by Hughes are in substantial agreement with our own.



A special form of the  $S_Ni$  mechanism would account for the results obtained by Meisenheimer and Link<sup>8</sup> on the reactions of the  $\alpha$ - and  $\gamma$ -ethylallyl alcohols with thionyl chloride. It was reported that the primary isomer gave principally secondary chloride and from the secondary isomer mostly primary chloride was obtained. These reactions may be explained by a rearrangement involving addition of the halogen to the  $\gamma$ -carbon atom, simultaneous shift of the double bond and elimination of sulfur dioxide as shown in equation (6).



This indicated special form of the  $S_Ni$  mechanism suggests a possible abnormal  $S_N2$  reaction,<sup>9</sup> illustrated in equation (7), involving an attack by an electron donor at the  $\gamma$ -carbon atom, a shift of the double bond and elimination of a group, all occurring simultaneously.<sup>10</sup>



Indeed, the work of Meisenheimer and Beutler<sup>11</sup> on the reactions of cinnamyl chloride with potassium acetate in acetic acid seems to verify that such an abnormal  $S_N2$  reaction does occur.

These investigators found that in solutions of low concentration of potassium acetate, the kinetics of the reaction with cinnamyl chloride in

(8) Meisenheimer and Link, *Ann.*, **479**, 211 (1930).

(9) (a) Winstein, Dissertation, California Institute of Technology, 1938; (b) Hughes, *Trans. Faraday Soc.*, **34**, 185 (1938).

(10) A mechanism leading to the same result but requiring preliminary addition of a nucleophilic reagent to one of the ethylenic carbons has been proposed by Ogg, *This Journal*, **61**, 1946 (1939).

(11) Meisenheimer and Beutler, *Ann.*, **508**, 58 (1933).

acetic acid were between first- and second-order. At high concentrations of potassium acetate there was obtained a mixture of esters containing a considerable fraction of phenylvinylcarbonyl acetate and, in fact, this fraction of abnormal ester did not decrease with increasing acetate concentration as would be expected if it were produced only by a first-order reaction. Using rate constants which Meisenheimer and Beutler found to fit their data, it is possible to calculate that only 7% of the reaction proceeds by the first-order path at 50° if one starts with an acetic acid solution which is 1 *N* in cinnamyl chloride and 1.5 *N* in potassium acetate, whereas 35% of abnormal product was actually isolated. Hence, even if the  $S_N1$  reaction produced only abnormal product, the experimentally found composition seemingly cannot be explained unless an abnormal  $S_N2$  reaction is assumed. However, in the work of Meisenheimer and Beutler,<sup>11</sup> there was no consideration of ionic strength and specific salt effects, so that the large bimolecular contribution to the kinetics may have been only apparent. It is possible that a reinvestigation of this situation would disclose that the conversion of cinnamyl chloride to ester in acetic acid is almost exclusively solvolytic in character. Evidence in favor of this possibility is that cinnamyl chloride gives only cinnamyl acetate on treatment with potassium acetate in acetic anhydride, a solvent sure to be unfavorable<sup>3</sup> for the operation of an  $S_N1$  mechanism.

We have begun investigations designed to show the relative tendencies for  $S_N1$  and  $S_N2$  mechanisms in typical allylic cases and to formulate generalizations as to the products to be expected from the reactions by these mechanisms. In this paper we present the results so far obtained on the conversion of crotyl and methylvinylcarbonyl chlorides to ethyl ethers and acetates with special attention being given to any possible abnormal  $S_N2$  reaction.

**Simultaneous First- and Second-Order Reactions.**—If, in a conversion of a halide to ether or acetate, both second-order and first-order reactions are proceeding, an apparent bimolecular constant,  $K_2$ , calculated by equation (8) where  $a$  is the original concentration of halide,  $b$  the original concentration of alkoxide or acetate salt,  $x$  the concentration of inorganic halide produced at time,  $t$ , will show a drift in a rate run. So

$$K_2 = \frac{1}{t(a-b)} \ln [b(a-x)]/[a(b-x)] \quad (8)$$

also will  $K_1$  calculated on the basis of a reaction first-order with respect to organic halide. If only a second-order reaction according to equation (1) is proceeding, then  $K_2$  equals  $k_2$  the specific second-order rate constant. Similarly, if only a first-order reaction is proceeding,  $K_1$  will equal  $k_1$  the specific first-order rate constant. If both first- and second-order contributions are important, equation (9) is useful.

$$\frac{dx}{dt} = k_1(a - x) + k_2(a - x)(b - x) \quad (9)$$

The fraction of reaction  $F_1$  which has proceeded by a first-order reaction at any fraction conversion can be shown to be given by equation (10).

$$F_1 = k_1/(k_2x) \ln (k_1 + k_2b)/[k_1 + k_2(b - x)] \quad (10)$$

**Rate Work on the Conversion of Crotyl Chloride to Crotyl Ethyl Ether.**—The reaction of crotyl chloride with sodium ethoxide in absolute ethanol displayed second-order kinetics, the first-order reaction which gives rise to hydrogen chloride in the absence of sodium ethoxide being slow enough to enable very good isolation of the second-order reaction. One main source of crotyl chloride was employed and no large rate trends were noticed.<sup>12</sup> Table I summarizes a typical run. Table II summarizes the rate constants obtained at 25.00°, using various original concentrations without attempt to keep ionic strength constant. There is some trend in  $K_2$  with original concentrations, as is usually found in work of this kind.<sup>13</sup> The change of  $K_2$  with the water content of the alcohol from pure alcohol to 10% water, is not very extensive and has about the magnitude of the change of  $K_2$  with concentrations of sodium ethoxide from 0.6 to 0.06 *M*.

Crotyl chloride in alcohol at 25.00° slowly produces hydrogen chloride and the rate of this solvolytic process was followed. Also, the effect on the solvolytic reaction of adding water was noted. Table IV summarizes the measurements on the solvolytic reaction while Table III presents a typical run.

The usual increase<sup>3,14</sup> in the rate of solvolysis of a halide with increase in the water content of

(12) Mr. L. Andrews has found in preliminary work that crotyl chlorides prepared in various ways give somewhat variable rate constants. It seems likely that some preparations contain *cis*-crotyl chloride and that an increase in rate is associated with these.

(13) (a) Hecht, Conrad and Brückner, *Z. physik. Chem.*, **4**, 273 (1889); (b) Segaller, *J. Chem. Soc.*, **103**, 1154 (1913), **103**, 1421 (1913), **105**, 106 (1914); (c) Quayle and Royals, *THIS JOURNAL*, **64**, 226 (1942).

(14) (a) Farinacci and Hammett, *ibid.*, **59**, 2542 (1937); (b) Olson and Halford, *ibid.*, **59**, 2644 (1937); (c) Hughes, *J. Chem. Soc.*, 255 (1935).

the alcohol solvent is noticed with crotyl chlorides. What fraction of the first-order reaction observed in the absence of sodium ethoxide is due to an  $S_N1$  process (equation 3) and what fraction is due to an  $S_N2$  process (equation 1), involving

TABLE I

THE REACTION OF NaOEt WITH CROTYL CHLORIDE IN ABSOLUTE ALCOHOL  
*a*, 1.008 *N*; *b*, 1.218 *N*

<i>t</i> , hr.	NaOEt, ml. HCl	Crotyl chloride, ml. HCl	$K_2$
0	61.32	50.79	
0.47	56.91	46.38	0.165
1.23	51.39	40.86	.159
2.02	46.30	35.77	.165
3.12	41.25	30.72	.163
4.37	36.96	26.43	.161
6.75	31.30	20.77	.157
9.33	27.16	16.63	.155

Mean 0.161 ± 0.003

TABLE II

SUMMARY OF RATE CONSTANTS FOR THE REACTION OF CROTYL CHLORIDE WITH SODIUM ETHOXIDE

Run	<i>a</i>	<i>b</i>	H <sub>2</sub> O moles/liter	$K_2$
1	1.01	1.22	0	0.161
2	0.50	0.61	0	.171
3	.50	.24	0	.199
4	.20	.24	0	.189
5	.48	.12	0	.222
6	.09	.11	0	.214
7	.09	.06	0	.231
2	.50	.61	0	.171
8	.50	.60	0.55	.178
9	.48	.58	2.67	.209
10	.41	.50	5.62	.229

TABLE III

THE SOLVOLYTIC REACTION AT 25.00° OF 0.487 *M* CROTYL CHLORIDE IN H<sub>2</sub>O-ALCOHOL (9.99 ML. H<sub>2</sub>O IN 103.3 ML. SOLUTION)

<i>t</i> , hr.	ML NaOH (38.07 ml. for completion)	$K_1 \times 10^4$
3.9	0.20	(1.35)
20.5	0.96	1.25
29.4	1.34	1.22
45.9	2.08	1.22
73.5	3.24	1.21
140.8	6.10	1.24

Mean 1.23 ± 0.01

TABLE IV

VARIATION OF RATE OF ALCOHOLYSIS OF CROTYL CHLORIDE AT 25.00° WITH WATER CONTENT OF THE ALCOHOL

H <sub>2</sub> O, mole/liter	$K_1 \times 10^4$
0	1.84
0.55	2.66
3.74	8.1
5.35	12.3

alcohol or water molecules as the attacking reagents, remains to be seen.<sup>15</sup>

From the constants given in Tables II and IV, it is clear that in the reaction of crotyl chloride with aqueous-alcoholic solutions of sodium ethoxide or sodium hydroxide it is necessary to use low concentrations of base and considerable water in the solvent to attain serious proportions of first-order reaction.

**Isolation of Products of Reaction of Crotyl and Methylvinylcarbinyl Chlorides with Sodium Ethoxide in Absolute Ethanol.**—Crotyl chloride was converted to ether by treatment with sodium ethoxide in absolute ethanol under conditions where essentially second-order kinetics prevailed. When the original crotyl chloride concentration was approximately 0.7 *M* and the NaOEt was approximately 0.9 *M*, ether which was at least 99% crotyl ethyl ether with a maximum of 1% methylvinylcarbinyl ethyl ether was isolated.

No kinetic investigations on the reaction of methylvinylcarbinyl chloride with sodium ethoxide were carried out, but the product of the reaction under conditions favoring a bimolecular reaction was isolated. As shown in Table V the ether produced was at least 96% methylvinylcarbinyl ethyl ether with a maximum of 4% crotyl ethyl ether under the conditions used.

TABLE V

THE PRODUCTS OF REACTION OF ALLYLIC HALIDES WITH ABSOLUTE ALCOHOLIC NaOEt

Halide	Orig. NaOEt Concn. mole/l.	Orig. halide Concn. mole/l.	% Normal product	% Abnormal product
Crotyl chloride	0.9	0.7	100	0
3-Chloro-1-butene	1.8	1.3	>96	<4

It would certainly seem that the bimolecular reaction of sodium ethoxide with the primary and secondary 4-carbon chlorides proceeds without allylic rearrangement.

**Product of Reaction of Silver Acetate with the Butenyl Chlorides.**—The study of the kinetics of the reactions of the butenyl chlorides with acetate ion in acetic acid showed that it was impossible to isolate the bimolecular replacement reaction free of the solvolytic one, which in the case of an acetic acid solvent, will be more exclusively *S<sub>N</sub>1* than in absolute alcohol because of the large difference in basicity between acetic acid and ethyl alcohol molecules. In order to deter-

mine whether the products of such reactions could be accounted for quantitatively by a normal bimolecular reaction and a partially abnormal solvolytic one, it was necessary to have an estimate of the composition of the product arising from the *S<sub>N</sub>1* solvolytic reaction. Since there are many indications that reactions of halides with silver salts proceed similarly to *S<sub>N</sub>1* reactions in that an unfree carbonium ion is produced as an intermediate, the products of reaction of silver acetate with the butenyl chlorides were isolated and taken as an indication of what might be expected from the solvolytic mechanism.

Table VI contains along with other results the composition of the acetates produced from the two chlorides on treatment with silver acetate in acetic acid at 25°. A mixture of acetates is produced from either chloride as expected from a carbonium ion intermediate, but the mixtures are not quite identical. Thus, the primary chloride gives an acetate mixture which is about 63% primary and the secondary chloride gives a mixture which is only 56% primary. This spread seems to be real and Meisenheimer and Link<sup>8</sup> report a similar but somewhat smaller spread in the results from pentenyl chlorides.

TABLE VI

THE COMPOSITION OF BUTENYL ACETATES FROM THE REACTIONS OF CROTYL AND METHYLVINYL-CARBINYL CHLORIDES WITH VARIOUS ACETATES

Experimental method	Chloride used	Time of reaction, hr.	Composition of product		Yield, <sup>a</sup> %
			% primary acetate	% secondary acetate	
1 <i>M</i> Potassium acetate in acetic acid at 78.6°	primary	138	84	16	87
	secondary	48	51	49	31
	secondary	72	50	50	52
1 <i>M</i> Diphenylguanidium acetate in acetic acid at 78.6°	primary	51	88	12	68
	secondary	45	51	49	66
Potassium acetate in acetic anhydride at 100°	primary	192	100	0	63
Tetraethylammonium acetate in acetone at 58°	secondary	194	0	100	53
Silver acetate in acetic acid at 25°	primary	190	65	35	42
	primary	120	60	40	61
	secondary	120	56	44	59

<sup>a</sup> Yield based on the butenyl chloride, assuming reaction goes to completion.

This difference is an interesting one and will be considered more fully in later work. It may be due either to a second-order process in which acetate ion replaces chloride normally, or a termolecular process in which silver ion removes the chloride ion and acetate ion, or an acetic acid molecule simultaneously forms a bond to the carbon atom

(15) Preliminary work has shown that the solvolytic reaction of crotyl chloride in dry alcohol is considerably faster than the reaction of methylvinylcarbinyl chloride.

TABLE VII

RESULTS OF KINETIC EXPERIMENTS WITH POTASSIUM ACETATE IN ACETIC ACID													
Run I (CrCl) (KOAc) = 1.017 = 0.973			Run II (CrCl) (KOAc) = 1.017 = 0.238			Run III (M.V.C.Cl) (KOAc) = 0.993 = 0.974			Run IV (M.V.C.Cl) (KOAc) = 0.993 = 0.226				
Time, hr.	$x$	$K_2$	Time, hr.	$x$	$K_2$	(dx/dt)	Time, hr.	$x$	$K_2$	(dx/dt)	Time, hr.	$x$	$K_1$
3	0.174	0.0709	2	0.032	0.0731	0.0150	2	0.061	0.0339	0.0294	2	0.022	0.0525
4	.219	.0710	4	.060	.0734	.0139	4	.117	.0342	.0274	4	.044	.0554
6	.299	.0720	6	.086	.0766	.0121	6	.169	.0351	.0241	6	.064	.0572
10	.415	.0720	10	.132	.0860	.0093	8	.216	.0357	.0220	8	.084	.0616
14	.497	.0718	14	.164	.0910	.0077	10	.260	.0364	.0218	10	.101	.0636
19	.572	.0720	18	.190	.0992	.0048	12	.298	.0368	.0185	12	.118	.0681
25	.630	.0695	24	.201	.1041	.00083							
48	.764	.0828											

losing the chloride ion. The possibility of a normal bimolecular substitution of acetate ion for chloride competing with the predominant process when silver acetate is being used, seems unlikely in view of the very low concentration of acetate ion and the relatively rapid action of silver acetate. Whether a third-order process ever contributes in reactions of silver salts is not yet clear. Still another likely explanation is that the inequality in the compositions of the acetate mixtures from the two halides is another indication of the lack of freedom of the carbonium ion being formed.<sup>16</sup>

#### Kinetics of Reaction of Butenyl Chlorides with Potassium and Diphenylguanidinium Acetates.

—The kinetic data on the reaction of potassium acetate with the butenyl chlorides in acetic acid at  $78.6 \pm 0.1^\circ$  are summarized in Table VII. The apparent second-order rate constant drifts upward in all the runs except in the one employing crotyl chloride with a high concentration of potassium acetate. This drift indicates a considerable amount of first-order reaction.

High concentrations of materials were employed in these rate measurements because it was desired to isolate reaction products using comparable conditions. Under these conditions potassium chloride precipitates, changing the ionic strength in the course of the reactions. Ionic strength effects and also specific salt effects are so serious in acetic acid that we were unable to treat the data of Table VII so as to obtain first- and second-order rate constants and to decide how much of the reaction proceeded by each of the two paths.

From the work of Steigman and Hammett<sup>17</sup> on the acetolysis of  $\alpha$ -phenylethyl chloride it appeared

(16) One might suppose that shielding by the chloride ion being extracted might favor the abnormal product but apparently this effect is overshadowed by the tendency for the cationic charge to favor the carbon atom losing the chloride ion while the chloride ion is still in the immediate vicinity.

(17) Steigman and Hammett, *This Journal*, **59**, 2536 (1937).

to us that diphenylguanidinium acetate was an ideal salt to use in place of potassium acetate since diphenylguanidinium chloride is soluble in acetic acid. Also, diphenylguanidinium chloride and acetate seem to have about the same salt effect, unlike some other salt pairs. Thus, rate measurements on the reaction of diphenylguanidinium acetate with the butenyl chlorides should be relatively free of trends due to change of ionic strength and change of the nature of the salt making up the ionic strength.

The rate measurements using diphenylguanidinium acetate are summarized in Table VIII. Run V is similar to Run I,  $K_2$  now being higher and drifting upward. The drift is small enough to indicate that crotyl chloride reacts predominantly by a second-order path. Run VI using methylvinylcarbinyl chloride and 0.9 *M* diphenylguanidinium acetate displays a  $K_2$  which drifts upward and a  $K_1$  which is constant.<sup>18</sup> Run VII using a lower concentration of acetate yields a  $K_2$  which drifts upward badly and a  $K_1$  with only a slight downward drift. Clearly methylvinylcarbinyl chloride undergoes a first-order reaction almost exclusively under conditions where crotyl chloride reacts predominantly by a second-order reaction. Runs VI and VII show the large trend in the first-order constant with ionic strength.

From Run V the rate constants for the first- and second-order reactions of crotyl chloride were estimated. By plotting  $x$  against  $t$ ,  $dx/dt$  at any time was obtained. A plot of  $dx/dt/(a-x)$  against  $(b-x)$  gives a straight line according to equation

(18) It would appear that no very serious amount of reaction of chloride ion with the unfree carbonium ion intermediate occurs nor is there much rearrangement of the halides. In either case drifts in the first-order constant for the secondary isomer would be found, unless some cancellation of effects accidentally takes place. Actually, from the work of Hughes and Ingold and co-workers,<sup>3b</sup> the intervention of chloride ion is less likely to occur in our system than with more complex ones. The intervention of chloride ion may be quite serious in the cinnamyl chloride work of Meisenheimer and Beutter,<sup>11</sup> however.

TABLE VIII

DATA ON THE RATE OF REACTION OF DIPHENYLGUANIDIUM ACETATE WITH BUTENYL CHLORIDES IN ACETIC ACID

Run V (C-Cl) = 1.020 (D.P.G.OAc) = 0.921					Run VI (M.V.C.Cl) = 0.987 (D.P.G.OAc) = 0.925				Run VII (M.V.C.Cl) = 0.987 (D.P.G.OAc) = 0.222			
Time, hr.	$x$	$K_2$	( $dx/dt$ ) obs.	( $dx/dt$ ) calcd.	Time, hr.	$x$	$K_1$	$K_2$	Time, hr.	$x$	$K_1$	$K_2$
4	0.279	0.1040	0.0476	0.0478	4	0.138	0.0376	0.0439	2	0.032	0.0165	0.0795
8	.441	.1079	.0308	.0304	8	.253	.0370	.0474	4	.062	.0163	.0859
12	.541	.1090	.0206	.0215	12	.354	.0370	.0515	6	.090	.0160	.0929
16	.614	.1120	.0161	.0161	16	.437	.0365	.0554	8	.116	.0156	.0999
20	.672	.1176	.0128	.0123	20	.518	.0372	.0622	13	.173	.0148	.1325

(9). The intercept and slope give  $k_1$  and  $k_2$ , respectively:  $k_1$  is 0.017 and  $k_2$  is 0.074. Table VIII shows a comparison between  $dx/dt$  calculated for these constants and  $dx/dt$  obtained from the plot of the actual data. Clearly the values chosen for  $k_1$  and  $k_2$  reproduce the data well. Table IX summarizes the rate constants for the reactions of the butenyl chlorides.

TABLE IX

RATE CONSTANTS FOR REACTION OF BUTENYL CHLORIDES WITH DIPHENYLGUANIDIUM ACETATE IN ACETIC ACID AT 78.6°

Halide	Concn. OAc <sup>-</sup> , M	$k_1$	$k_2$
Secondary	0.925	0.037	...
Secondary	.222	.016	...
Primary	.921	.017	0.074

**Products of Reaction of Butenyl Chlorides with Potassium and Diphenylguanidium Acetates in Acetic Acid.**—Using conditions that had been explored kinetically, the products of the reactions in acetic acid were isolated and analyzed. Table VI includes the analyses of the products obtained from the reactions with initial concentrations of approximately 1 M. The two salts give about the same products.

The product of reaction of crotyl chloride with diphenylguanidium acetate was the result of a reaction, 36% of which was first-order, calculated by the use of equation (10) with  $b = 0.92$  and  $x$  at the time the reaction was interrupted equal to 0.85 (estimated by analogy with Run V, Table VIII). With the information we have so far, the best approximation to the product to be expected from the first-order reaction of crotyl chloride in acetic acid containing diphenylguanidium acetate, is the same mixture crotyl chloride gives with silver acetate (38% secondary acetate) in spite of some differences in the two reactions. The reaction employing silver acetate proceeds at a lower temperature and is heterogeneous. The unreacted crotyl ion may coordinate for the most

part with different reagents (acetic acid or acetate ion) in the two reactions.

If one assumes the second-order reaction gives only normal product, then a reaction which is 36% first-order should give 36(0.38) or 14% secondary ester. Actually 12% is obtained.

With potassium acetate 16% of secondary ester is obtained from crotyl chloride. However, the reaction was allowed to proceed more nearly to completion. This is expected to increase the fraction of the reaction proceeding by a first-order path and thus the per cent. of secondary ester obtained from crotyl chloride. Hence there is no evidence for an abnormal second-order reaction of crotyl chloride with acetate ion, the data being entirely compatible with a normal second-order reaction and a first-order reaction yielding a mixture.<sup>19</sup>

Methylvinylcarbinyl chloride gives with either diphenylguanidium or potassium acetate a mixture of acetates which is 51% crotyl acetate and only 49% secondary acetate. A completely first-order reaction might be expected as a first approximation to yield 56% crotyl acetate by analogy with the silver acetate reaction. Part of the difference between 51 and 56% may be due to a small contribution of a normal second-order reaction to the total reaction of the secondary chloride.

**Products of Reaction of Butenyl Chlorides with Acetates in Other Solvents.**—If, as it appears, the second-order reactions of the butenyl chlorides are completely normal and a reaction

(19) The failure to find the abnormal bimolecular mechanism seems to be in line with the usual inability of the isolated ethylenic linkage to be susceptible to attack by nucleophilic reagents. However, suitable variation in the structure of the allylic molecule may produce this mechanism.

After this article was submitted for publication we noticed that, in a general article on configurational changes in reactions at a saturated and unsaturated carbon atom, Bergmann [Bergmann, *Helv. Chim. Acta*, **20**, 590 (1937)] claims that this abnormal bimolecular mechanism operates in the reaction of sodium malonic ester and sodium diphenylmethide with active 2-chloropentene-3. It is still possible, however, that some other reason exists for the racemization observed by Bergmann and further confirmation of the mechanism would be desirable.

proceeds partly abnormally only when part of the reaction is  $S_N1$  in character, the proper choice of solvent should enable one to force certain replacement reactions to proceed entirely normally. Non-hydroxylic solvents are known to be unfavorable<sup>8,17</sup> for the solvolytic first-order reactions so that reactions in these solvents might be expected to be normal and quite useful synthetically.

As was expected, the reaction of methylvinylcarbinyl chloride with tetraethylammonium acetate in acetone gave an acetate with no detectable amount of crotyl acetate. Also, crotyl chloride and potassium acetate in acetic anhydride yielded an acetate with no detectable amount of secondary ester. These results are shown in Table VI.

### Experimental Part

**Crotyl and Methylvinylcarbinyl Chlorides.**—Mixtures of chlorides from Shell Development Corporation or prepared from the alcohols with concentrated hydrochloric acid were dried over calcium chloride or potassium carbonate, distilled once and then fractionated through a six-foot column of glass helices. The secondary chloride could be obtained at atmospheric or reduced pressure. For the primary chloride reduced pressure was employed. The pure chlorides: secondary b. p. 24.2–24.6° (178 mm.), 63.5° (750 mm.),  $n_D^{20}$  1.4150; primary b. p. 43.7–44.0° (177 mm.), 45.6–45.7° (191 mm.),  $n_D^{20}$  1.4351, were used in this work. One pair of chloride samples were kept in a cold room several months with no appreciable change in refractive index. After a year at room temperature, this pair of chlorides showed an increase of 0.0004 and 0.0013 in the refractive index for the primary and secondary chlorides, respectively. This change was largely due to other factors than isomerization for distillation at reduced pressure nearly restored the refractive indices to the old values.

**Rate of Conversion of Crotyl Chloride to Ether.**—Proper volumes of stock solutions of crotyl chloride and sodium ethoxide in absolute ethanol (Commercial Solvents Gold Shield), water, and absolute ethanol, all previously brought to temperature, were mixed in glass-stoppered Erlenmeyer flasks and kept at 25.00°. The volumes of the alcohol solutions were considered additive. When water was added, an approximate correction on the final volumes was estimated.<sup>20</sup> Aliquot portions of the reaction mixture were withdrawn from time to time and titrated with alcoholic hydrogen chloride or aqueous sodium hydroxide with phenolphthalein as the indicator.

The sodium ethoxide stock solution was freshly made up by dissolving cleaned sodium rinsed with absolute alcohol in absolute alcohol with protection against moisture and carbon dioxide. The solution was standardized before use.

**Preparation of Crotyl Ethyl Ether.**—A mixture of 92.5 g. of crotyl chloride in 800 ml. of ethanol and 700 ml. of approximately 2 *N* sodium ethoxide was kept ten days at 25° and then diluted with water to six times the volume.

The mixture was then extracted with 1000 ml., then 500 ml., and then 250 ml. of pure ether. The ether extracts were washed with a little water and dried over potassium carbonate. Some of the ether was distilled off at 34.1–34.4° through a Weston<sup>21</sup> type column using a good reflux ratio. The residue was distilled through a four-foot modified Podbielniak column. The fractions other than pure diethyl ether collected at 762 mm. were

Fr. 1	1.0 g.	34.1–65.0°	
Fr. 2	3.0 g.	65.0–77.1°	
Fr. 3	34.5 g.	77.1–77.6°	$n_D^{21}$ 1.3751
Fr. 4	3.0 g.	77.6–100.8°	
Fr. 5	68.5 g.	100.8–100.9°	$n_D^{21}$ 1.4038
Holdup	3.0 g.		

Fraction 3 was a constant-boiling mixture of alcohol and crotyl ethyl ether,<sup>22</sup> so fractions 1, 2, 3 and 4 were poured into 200 ml. of water and the ether separated with the aid of 100 ml. of pure carbon disulfide. The carbon disulfide layer was dried over potassium carbonate and distilled through the four-foot Podbielniak column. The fractions collected other than pure carbon disulfide were as follows at 765 mm.

Fr. 1	2.3 g.	46.7–100.7°	
Fr. 2	9.5 g.	100.7–100.9°	$n_D^{23}$ 1.4030
Holdup	2.0 g.		

There was no indication of methylvinylcarbinyl ethyl ether. A generous estimate of the amount of this ether would be one-third of Fraction 1. This places the proportion of secondary ether as less than 1% of the total. The yield of ether was 82%.

**Preparation of Methylvinylcarbinyl Ethyl Ether.**—A mixture of 63 g. of methylvinylcarbinyl chloride and 500 ml. of approximately 2 *N* sodium ethoxide in absolute ethanol was left two weeks at 25° and four days at 35°. The mixture was poured into 2.5 liters of water and the ether separated with the aid of 200 ml. of pure carbon disulfide and two 100-ml. portions more. The extracts were dried briefly over potassium carbonate and distilled through the four-foot Podbielniak column. The fractions collected at 760 mm. which contained other than water, alcohol and carbon disulfide were

Fr. 1	5.0 g.	46.9–76.4°	
Fr. 2	32.5 g.	76.4–76.8°	$n_D^{23}$ 1.3882
Holdup	3.5 g.		

The holdup was distilled through a short Vigreux column, 2.7 g. distilling 77–96° and having  $n_D^{23}$  1.3960. This indicated a maximum of 1.4 g. of crotyl ethyl ether out of a total of approximately 37.2 g. (53% yield) considering 2.0 g. of Fraction I as ether.

**Kinetic Experiments in Acetic Acid.**—The procedure used for the rate determinations was the same as that of Steigman and Hammett<sup>17</sup> except that the excess acetate ion was titrated with a solution of perchloric acid in acetic acid. The acetic acid solvent was purified by treatment with potassium permanganate and then triacetyl borate,<sup>23</sup> material, m. p. 16.6° being obtained. The potassium acetate was dried at 110–120° for three hours and the diphenylguanidine was Eastman Kodak Co. material.

(21) Weston, *Ind. Eng. Chem., Anal. Ed.*, **5**, 179 (1933).

(22) Leping, *Bull. soc. chim.*, **89**, 864 (1926).

(23) Eichelberger and La Mer, *This Journal*, **55**, 3633 (1933).

(20) Data used are listed in Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 40.

**Analysis of Reaction Products in the Ester Preparations.**—In order to determine the composition of the esters produced in various conversions of the butenyl chlorides to acetates, runs were made using in each case, unless otherwise specified, 250 ml. of solution approximately 1 *N* in chloride and acetate. Final analysis of the esters with an accuracy of 2 or 3% was accomplished by distillation through a three-foot Podbielniak type column. The results are summarized in Table VI.

**Reaction of Potassium and Diphenylguanidinium Acetates with the Butenyl Chlorides in Acetic Acid.**—The reaction mixtures of dry base, dry acetic acid and butenyl chloride were held at 78.6° for the desired interval and then poured into ice-water. The acid was carefully neutralized with concentrated sodium hydroxide and the ester was extracted with ether. After being dried over potassium carbonate, the extracts were distilled. A blank experiment was carried out on methylvinylcarbinyl acetate which showed that the ester remained unchanged under the conditions of the experiment.

**Reaction of Crotyl Chloride with Potassium Acetate in Acetic Anhydride.**—A mixture of 25 ml. of crotyl chloride and 28 g. of dry potassium acetate and 300 ml. of fractionated acetic anhydride (b. p. 139.0–139.1°) was heated on a water-bath under reflux with efficient stirring. After the heating period, the mixture was quite dark. The volatile material was distilled (25–40°) at reduced pressure, the distillate was poured onto crushed ice and the mixture was allowed to stand for an hour to hydrolyze the anhydride. The resulting solution was neutralized and treated as in the previous case. On distillation of the ester, there was no evidence of secondary acetate.

**Reaction of Methylvinylcarbinyl Chloride with Tetraethylammonium Acetate in Acetone.**—A mixture of 41 g. of tetraethylammonium acetate prepared from the directions

of Steigman and Hammett,<sup>17</sup> 20 ml. of the butenyl chloride and 200 ml. of dried and fractionated Merck c. p. acetone was boiled under reflux. After heating, the volatile material was distilled from salts at reduced pressure, the receiver being cooled with a dry-ice-bath. The distillate was then fractionated. There was no evidence of any crotyl acetate in the product.

**Reaction of Silver Acetate with the Butenyl Chlorides in Acetic Acid.**—A mixture of 45 g. of silver acetate which had been recrystallized from water and dried over sulfuric acid for three days, 25 ml. of butenyl halide and 250 ml. of dry acetic acid was stirred at room temperature. At the end of the reaction period, excess sodium chloride was added, the mixture was filtered and the filtrate was treated as in the case of the runs with potassium acetate in acetic acid.

### Summary

The kinetics of conversion of crotyl and methylvinylcarbinyl chlorides to ethyl ethers and acetates and the compositions of the products of the conversions have been studied. The compositions of the products can be well accounted for on the basis that bimolecular replacement of the chloride group by an ethoxide or acetate ion gives rise only to normal product while solvolytic or  $S_N1$  type reaction gives rise to a mixture of allylic isomers.

By choosing conditions unfavorable for the  $S_N1$  type of reaction, it is possible to convert the butenyl halides to the corresponding pure acetates or ethyl ethers.

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## The Relation of Dielectric Properties to Structure of Crystalline Polymers. I. Polyesters

BY W. A. YAGER AND W. O. BAKER

The interpretation of dielectric properties in terms of molecular structure<sup>1,2</sup> may be attempted for assembles of macromolecules when knowledge of polymer constitution and structure permits recognition of polar groups and of their relative disposition. The following factors have been considered in the succeeding report of the dielectric behavior of linear polyesters.

The most probable source of orientation polarization in solids containing long chain molecules with polar linkages has been attributed to the rotational-vibrational (liberational) motion of

(1) P. Debye, "Polar Molecules," Chemical Catalog Co., New York, N. Y., 1929.

(2) C. P. Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, N. Y., 1931.

atomic groups rather than to the unified displacement of a given molecule.<sup>3,4</sup> Of course, potentials inhibiting rotation around most single bonds, especially the carbon-carbon bond,<sup>5</sup> prevent complete independence of the motion of polar groups from the size and form of their attached chains.

Also, in polymers, the loss component,  $\epsilon''$ , of the dielectric constant generally deviates from the value it should have at an absorption maximum on the Debye theory for a single relaxation time.<sup>6,7</sup>

(3) W. A. Yager, *Trans. Electrochem. Soc.*, **74**, 113 (1938).

(4) W. O. Baker and C. P. Smyth, *THIS JOURNAL*, **60**, 1229 (1938).

(5) See C. Gorin, J. Walter and H. J. Eyring, *ibid.*, **61**, 1876 (1939), and references therein.

(6) W. A. Yager, *Physics*, **7**, 434 (1936).

(7) R. M. Fuoss and J. G. Kirkwood, *THIS JOURNAL*, **63**, 385 (1941).