rated, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue so obtained after evaporation was crystallized from ethanol giving colorless crystals of VIb, m.p. 203–204°; yield, *ca.* 68%.

Anal. Calcd. for $C_{19}H_{17}N_3O$: C, 75.24. H, 5.61; N, 13.86. Found: C, 75.54; H, 5.43; N, 13.90.

Action of Lithium Aluminum Hydride on Ia–Ic. General Procedure.—Lithium aluminum hydride (1.0 g.) was added to 50 ml. of dry ether. The mixture was refluxed for 15 min. and then 1.0 g. of each of the triazines (Ia–Ic) was added followed by 20 ml. of dry benzene. The reaction mixture was refluxed for 2 hr. and kept overnight at room temperature. It was poured into a cold saturated ammonium chloride solution and shaken in a separatory funnel. After separating the organic layer, it was dried over anhydrous sodium sulfate and filtered. After evaporation of the solvent, compounds IIk–IIm were obtained. The products were crystallized from ethanol. Compounds IIk–IIl gave no depression in melting point when each was mixed with an authentic sample.[3]

Anal. Calcd. for $C_{17}H_{17}N_3O$ (compound IIm): C, 73.11; H, 6.09; N, 15.05. Found: C, 72,95; H, 5.96; N, 14.78.

Action of *p*-Thiocresol on Ia–Ic. General Procedure.—The triazine (Ia–Ic, 1.0 g.) was heated (170–180°) with *p*-thiocresol (1.0 g.) for 1.5 hr. The reaction mixture was then cooled, washed several times with hot petroleum ether (b.p. 40–60°), and filtered. The products were crystallized from ethanol and proved to be IIk–IIm (melting point and mixture melting point with authentic samples[3]).

Action of Benzoyl Chloride on IIb.—Two grams of chloroform and 1.8 g. of benzoyl chloride were added to a solution of 1.25 g. of IIb in 2.0 g. of dry pyridine. The reaction mixture was heated (steam bath) for 1 hr. and kept overnight at room temperature. It was then poured into cold water. The oil obtained was extracted with benzene. The benzene extract was dried over anhydrous sodium sulfate, filtered, and evaporated. The colorless solid obtained after evaporation was washed with ethanol and recrystallized from the same solvent into colorless crystals of 3-oxo-5,6-diphenyl-2,4-dibenzoyl-2,3,4,5-tetrahydro-1,2,4-triazine, m.p. 182°; yield, *ca.* 81%.

Anal. Calcd. for $C_{31}H_{25}N_3O_3$: C, 76.38; H, 5.13; N, 8.62. Found: C, 75.67; H, 5.38; N, 8.61.

Action of Zinc and Acetic Acid–Alcohol Mixture on IIb.—To a solution of 1.0 g. of IIb in a mixture of 8 ml. of ethanol and 8 ml. of glacial acetic acid was added 0.6 g. of zinc powder. The reaction mixture was refluxed for 4 hr., filtered, then poured into cold water. The solid obtained was filtered, recrystallized from acetic acid, and proved to be unchanged IIb (melting point and mixture melting point). The yield was almost quantitative.

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Preparation and Thermal Rearrangement of Alkenyl 3-Alkenyloxy-2-butenoates. Catalysis of the Aliphatic Claisen Rearrangement by Ammonium Chloride

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The thermal rearrangements of allyl 3-allyloxy-2-butenoate and crotyl 3-crotyloxy-2-butenoate are shown to be first-order intramolecular reactions. The rate constants are $2.7 \times 10^{10}\ e^{-26,300/RT}$ and $5.3 \times 10^{11}\ e^{-28,000/RT}$ sec.$^{-1}$, respectively. The reactions have moderate rates at temperatures as low as 115°. The ΔS^* values of -11.3 and -5.4 e.u. are consistent with a cyclic transition state. All of the probable products and crossed products of the rearrangements have been prepared. No crossed products were detected by analysis of the products of a mixed rearrangement by gas–liquid partition chromatography and infrared spectroscopy. The rearrangements are accelerated to a small degree by heterogeneous catalysis by ammonium chloride. The operation of homogeneous catalysis by ammonium chloride or its dissociation products was excluded as an explanation of the increased rate by a proton magnetic resonance study of the rearrangements.

As a part of a continuing interest in thermal unimolecular reactions[3,4] we have studied the preparation and rearrangement of allyl 3-allyloxy-2-butenoate (1) and crotyl 3-crotyloxy-2-butenoate (2). Lauer and Kilburn[5] have reported the thermal rearrangement of ethyl 3-allyloxy-2-butenoate (3) to ethyl 2-allyl-3-oxobutanoate (6) at 150–200°. These workers also confirmed the report by Claisen[6] that this rearrangement took place at a lower temperature in the presence of ammonium chloride. No kinetic data on the rate of this rearrangement have been reported.

The purpose of this study was to establish the presumed intramolecular mechanism for the thermal rearrangement of allylic 3-alkenyloxy-2-butenoates to 2-alkenyl-3-oxobutanoates. A second objective was to define the role of ammonium chloride as a catalyst in the rearrangement. Due to the possibility of ester enol–ether interchange complicating this latter question, we chose to use the compounds **1** and **2** (where R = R′) in place of mixed ester enol–ethers such as **3**.

The desired compounds (**1** and **2**) for this study were prepared by the conjugate addition of unsaturated alcohols to alkenyl 2-butynoates.[7] This addition should produce the isomer in which the CH_3– and H– have a *trans* relationship across the double bond conjugated with the ester carbonyl.[8] The infrared spectra of **1** and **2** support the assignment of the *trans* configuration, but are not completely conclusive. Lecomte and Naves have reported[9] that ionones and irones having a *trans* H–C═C–CH_3 structure show absorption at 984–999 cm.$^{-1}$. Compounds **1** and **2** have absorption bands at 995 and 990 cm.$^{-1}$, respectively, as would be expected. However, in the case of **1** the band is largely the result of out-of-plane bending vibrations of the allyl substituents.

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(1) A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Albany 10, Calif.

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(3) J. W. Ralls and C. A. Elliger, *Chem. Ind.* (London), 20 (1961).

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(8) W. J. le Noble, *J. Am. Chem. Soc.*, **83**, 3897 (1961).

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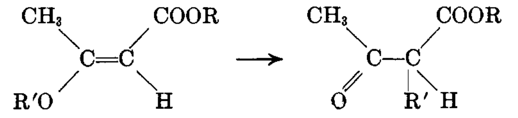


Reactants

1, $R = R' = \text{-}CH_2CH{=}CH_2$
2, $R = R' = \text{-}CH_2CH{=}CHCH_3$
3, $R = \text{-}CH_2CH_3;\ R' = \text{-}CH_2CH{=}CH_2$

Possible products

4, $R = R' = \text{-}CH_2CH{=}CH_2$
5, $R = R' = \text{-}CH_2CH{=}CHCH_3$
6, $R = \text{-}CH_2CH_3;\ R' = CH_2CH{=}CH_2$
7, $R = \text{-}CH_2CH{=}CHCH_3;\ R' = \text{-}CH(CH_3)CH{=}CH_2$
8, $R = \text{-}CH_2CH{=}CH_2;\ R' = \text{-}CH(CH_3)CH{=}CH_2$
9, $R = \text{-}CH_2CH{=}CHCH_3;\ R' = \text{-}CH_2CH{=}CH_2$
10, $R = \text{-}CH_2CH{=}CH_2;\ R' = \text{-}CH_2CH{=}CHCH_3$

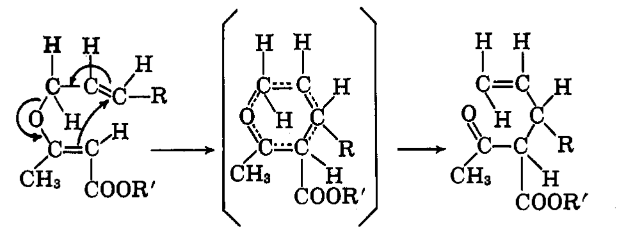
A configurational assignment determined by proton magnetic resonance (p.m.r.) ought to be possible either on the basis of the spin–spin coupling between the methyl protons and the proton on the C-2, or on the shielding value of the methyl protons if both geometrical isomers were available. Unfortunately in compounds **1** and **2** no spin coupling was observed and *cis* isomers, either pure or as a mixture, could not be obtained for correlation between shielding value and configuration.

An attempt to prepare a mixture of *cis*- and *trans*-allyl 3-allyloxy-2-butenoate by a different route gave only a single product. This was identical with the material prepared by the addition of allyl alcohol to allyl tetrolate. Jones and co-workers reported that the reaction of sodium mercaptides with ethyl 3-chloro-2-butenoates gave products of a displacement rather than of an elimination–addition mechanism.[10] Our results demonstrated that with unsaturated alkoxides the reaction apparently takes the elimination–addition sequence.

In order to determine the structure of the products from the rearrangements of **1** and **2**, the 2-substituted 3-oxobutanoates **4, 5, 7, 8, 9,** and **10** were prepared. The appropriate alkenyl 3-oxobutanoate was alkylated with allyl bromide or 3-chloro-1-butene. The reaction of sodium alkenyl acetoacetates with allylic secondary halides can take place by a SN2 or a SN2′ mechanism. Kepner and co-workers[11] found that when α-methylallyl and α-ethylallyl chlorides were used with sodium ethyl malonate the product contained 10 and 23%, respectively, of the compound resulting from the SN2′ mechanism. Using different starting materials and reaction conditions,[12] we found that about equal amounts of the two isomers resulted from the reactions using 3-chloro-1-butene. This estimation was made by analyzing the reaction mixture by gas–liquid partition chromatography (g.l.p.c.) and measuring peak areas. The yields on the preparation of the alkenyl 2-alkenyl-3-oxobutanoates and their physical properties are summarized in Table III. The alkylation of alkenyl acetoacetates with 3-chloro-1-butene gave very poor yields of a mixed product. Therefore, the thermal rearrangement of alkenyl 3-alkenyloxy-2-butenoates has considerable preparative utility. Double distillation at 25 mm. starting with compound **2** gave a 61% yield of compound **7** in a single small scale experiment.

The products of the thermal rearrangement of **1** and **2** were determined by a combination of g.l.p.c. and infrared absorption spectroscopy. At the same time, part of the information required to demonstrate the intramolecular nature of the rearrangement was obtained.

Three unimolecular reaction mechanisms can be written for the rearrangement of allylic 3-alkenyloxy-2-butenoates to 2-alkenyl-3-oxobutanoates: A. heterolytic enol–ether O–C bond breaking followed by recombination of contributing forms of ion-pair hybrids; B. homolytic enol–ether O–C bond cleavage followed by recombination of contributing forms of free-radical hybrids; C. concerted intramolecular, "thermo-reorganization"[13] reaction, *i. e.*,



In rearrangement of crotyl 3-crotyloxy-2-butenoate (**2**), mechanisms A and B would predict a mixed product consisting of crotyl 2-crotyl-3-oxobutanoate (**5**) and crotyl 2-(1-methyl-2-propenyl)-3-oxobutanoate (**7**). Mechanism C would predict that only **7** would result from the rearrangement.

The rearrangement of **2** at 150° was found to be 87% complete in 10 minutes and essentially over in 30 minutes. The single product was crotyl 2-(1-methyl-2-propenyl)-3-oxobutanoate (**7**). This result excludes mechanisms A and B from consideration and makes mechanism C the only reasonable possibility for an unimolecular reaction.

The rearrangement of allyl 3-allyloxy-2-butenoate (**1**) at 150° gave 68% reaction in 10 min. and essentially complete reaction in 1 hr. The single, volatile, product was allyl 2-allyl-3-oxobutanoate (**4**).

When a mixture of **1** and **2** was heated at 150° for 1 hr. only **4** and **7** were formed. The absence of crossed products provided one part of the necessary information for the demonstration of the intramolecular nature of the rearrangement. In order for this to be a sufficient condition, the rate constants for the individual components of the mixed rearrangement must be comparable to allow time for possible interaction. Agreement in the values of the rate constants within one order of magnitude is generally required to detect crossed products conveniently.

The kinetics of the thermal change of **1** and **2** into **4** and **7** were studied at 115.1, 125.7, and 134.9° using an ultraviolet spectrophotometric method. The rate of disappearance of the absorption due to alkenyl alkenyl-

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[10] D. E. Jones, R. D. Morris, C. A. Vernon, and R. F. M. White, *J. Chem. Soc.*, 2349 (1960).

[11] R. E. Kepner, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **71**, 115 (1949).

[12] L. Ruzicka and G. Firmenich, *Helv. Chim. Acta*, **22**, 392 (1939).

[13] W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

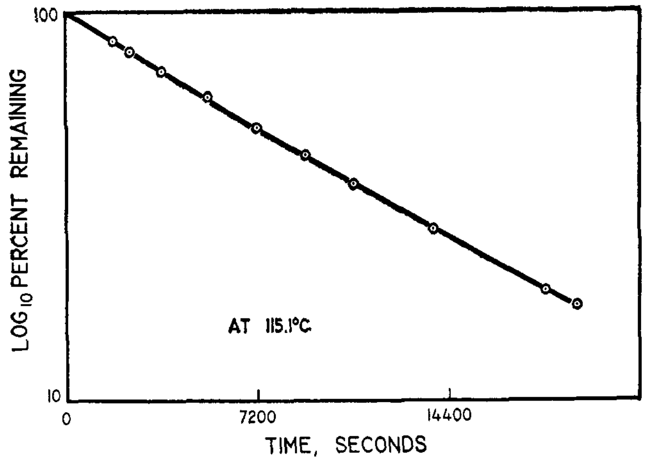
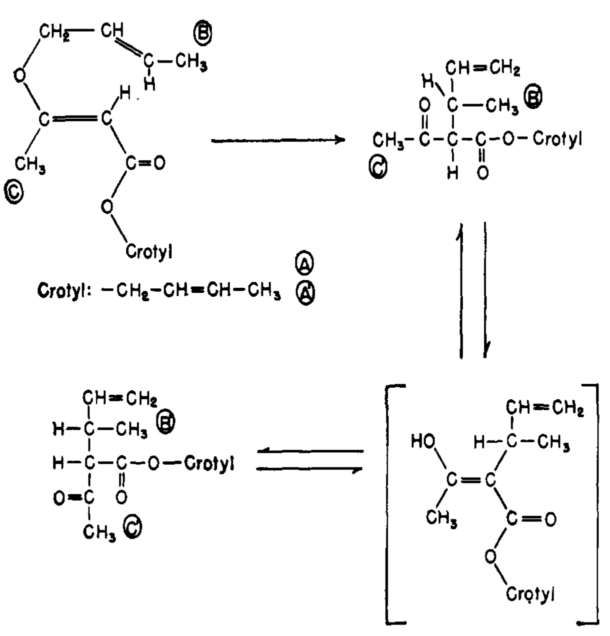


Fig. 1.—First-order plot of the rate of conversion of crotyl 3-crotyloxy-2-butenoate (2) to crotyl 2-(1-methyl-2-propenyl)-3-oxobutanoate (7).



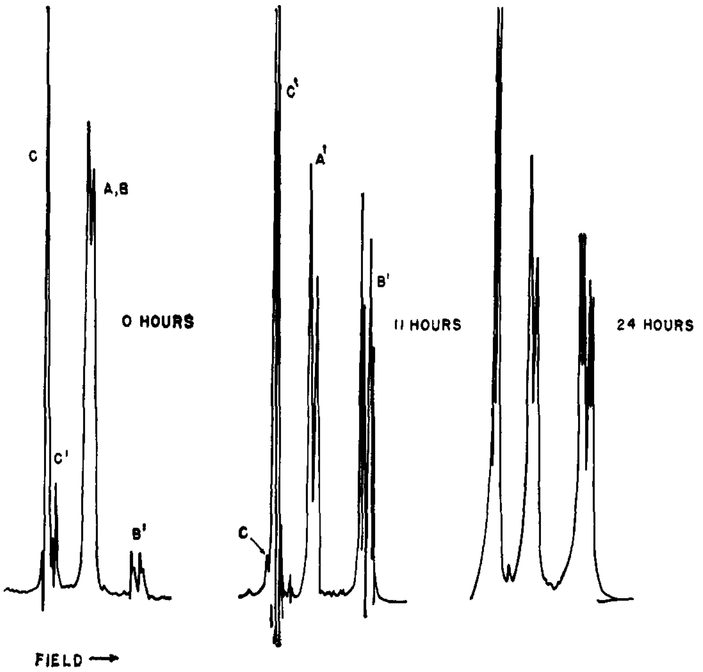


Fig. 2.—P.m.r. spectra for thermal rearrangement of crotyl 3- crotyloxy-2-butenoate (2) in the presence of NH_4Cl at 134.9°. The presence of approximately 15% of 7 in the zero time sample is believed to have resulted from the flame sealing of the p.m.r. sample tube without first cooling to −78° as was done with the ultraviolet kinetic samples.

oxybutenoates is first order out to about 70% reaction. Beyond this point, deviation from first-order behavior was observed due to accumulation of product in the neat samples. A plot of a typical kinetic run is shown in Fig. 1.

Measurement of the rate of rearrangement of 1 was complicated by a competing polymerization reaction. The heated capillary sample tubes produced a turbid suspension when broken under methanol for analysis. The nature of the solid material was not investigated. It was found that addition of 1% wt./wt. of butylated hydroxytoluene to the allyl 3-allyloxy-2-butenoate gave samples which showed no turbidity after heating. The kinetic results were no longer erratic and were about 23% slower than the uninhibited runs at 134.9°.

An accurate measure of the rate constants for the rearrangements at 150° was not possible with the equipment at hand due to the high rate of reaction at this temperature. The rate constants at 150° were estimated by extrapolation of the log k $vs.$ $1/T$ plot. The values for 1 and 2 at 150° were 6.9×10^{-4} and 19.8×10^{-4} sec.$^{-1}$, respectively. Since these rate constants are within an order of magnitude, the second criterion stated previously is fulfilled and the intramolecular nature of the rearrangement is conclusively demonstrated. The rate constants and derived thermodynamic data[14] of the rearrangements are summarized in Table I. The relatively large negative entropy of activation indicates that the transition state must be fairly well ordered and is consistent with the concerted intramolecular mechanism.

Table I

Rate Constants and Derived Thermodynamic Data

Compound	$k \times 10^5$, sec.$^{-1}$ 115.1°	125.7°	134.9°	E_a, kcal.	$A \times 10^{-11}$, sec.$^{-1}$	ΔS^*, 125.7°, e.u.
1	4.18	10.9	23.4	26.3	0.27	−11.3
2	9.35	24.6	55.6	28.0	5.3	− 5.4

The question of catalysis of these intramolecular reactions by ammonium chloride mentioned by the early investigators is intriguing. The thermal intramolecular reactions which have been studied carefully have no catalyst requirement.[15] The solubility of ammonium chloride in these esters is limited; so the possibility of heterogeneous catalysis must be considered.

Incorporation of ammonium chloride into heated samples of crotyl 3-crotyloxy-2-butenoate (2) did cause a small, but significant, increase in rate. There was no significant difference in rate among samples containing equal weights of three different particle sizes of ammonium chloride. There was no appreciable solubility of ammonium chloride in compound 7; so homogeneous catalysis by dissolved salt is not operating. Following

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[14] E. G. Foster, A. C. Cope, and F. Daniels, *J. Am. Chem. Soc.*, **69**, 1893 (1947).

[15] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 453.

the compositional changes of the samples containing ammonium chloride as a function of heating time by p.m.r. suggested a possible cause of the change in rate.

Figure 2 shows the portion of the room temperature p.m.r. spectra extending from about 7.8 to 9.2 τ for the reaction mixture resulting from the rearrangement of **2** into **7** in the presence of ammonium chloride after different periods of heating at 134.9°. Exact shielding values and spin–spin coupling constants are given in the Experimental. The gradual change in the relative intensity of the fine-split components of both the B doublet and C peak, but of no other peak in the spectra, suggested the presence of two conformers in which the structural change is confined to the nonester portion of the molecule. Since the concentration of the two species appears to approach a limiting ratio of 1:1, it seemed that two conformations of equal energy must be involved, the conformations being separated by an energy barrier of sufficient height not only to prevent averaging of the peaks by interconversion at room temperature but also to require an appreciable time at the reaction temperature to reach equilibrium. The abnormally low shielding value (7.03 τ) for the proton adjacent to the B′ methyl suggested that the conformations might be stabilized by the interaction of this proton with one of the carbonyl oxygens.

It was hoped that observation of the spectrum of **7** at an elevated temperature would reveal the interconversion rate to be sufficiently rapid to cause at least a partial coalescence of the doublets. However, below 150° no immediate change was apparent in the spectrum. At 150° no coalescence was observed, but the concentrations of the two species became equal within approximately 3 hr. After this time no further change was observed during an additional 4-hr. heating time at 150°.

In view of the slow rate of conversion initially observed at 134.9°, it was obviously fruitless to hope that rotational averaging of p.m.r. peaks could be observed. It now seems apparent that we are observing the two diastereoisomers of **7** (*each as an enantiomer pair*). A change in one of the two asymmetric centers could be effected by an enol–keto tautomerism. Since there is no evidence for the enol form in the p.m.r. spectra, either from line shapes or shielding values, it must be considerably less favored energetically. This is also consistent with the slow rate of interconversion observed.

The change in the reaction environment due to this change in the amount of the diastereoisomer initially formed in greatest abundance could cause the observed slight acceleration in rate in the presence of ammonium chloride. The rate of rearrangement of allyl *p*-tolyl ether at 170° is increased 100-fold in changing solvent from tetradecane to *p*-chlorophenol.[16]

A possible catalyst for the tautomerization is hydrogen chloride formed by the dissociation of ammonium chloride. The dissociation vapor pressure of ammonium chloride has not been studied at temperatures below 160.4° where it is 1 mm.[17] At the temperature of the rearrangement (115–135°), the dissociation pressure would be very low, but might be sufficient to cause catalysis. However, samples of **7** prepared by rearranging **2** at 150° in the absence of ammonium chloride showed the same ratio of diastereoisomers as catalyzed experiments. The change in diastereoisomer ratio is therefore a result of heating and is not caused by ammonium chloride dissociation products. The slight increase in the rate of rearrangement of **2** to **7** must be due to heterogeneous catalysis.

The study of the effect of ammonium chloride on the rearrangement of **1** to **4** was more difficult due to the competing polymerization reaction observed in the absence of inhibitors. Although the ultraviolet data showed considerable scatter (Table II), a moderate acceleration of rate in samples containing ammonium chloride was observed. Due to the variability of the side reaction, the data as to the effect of mesh size were not sufficiently precise to draw meaningful conclusions. However, in six of the eight samples at various heating times the rate of reaction in the 80–100-mesh samples was greater than in the 18–35-mesh samples.

TABLE II

REARRANGEMENT OF ALLYL 3-ALLYLOXY-2-BUTENOATE CATALYZED BY AMMONIUM CHLORIDE (NO BUTYLATED HYDROXYTOLUENE) AT 134.9°

Heating time, min.	No NH_4Cl	% **1** remaining			
		18–35	35–60	60–80	80–100 mesh
30		41.8	41.4		38.6
45			30.1		28.9
60	38.0	33.7	33.0	33.0	30.3
90	29.3	21.6	21.5	19.7	18.8
120	18.0	12.4	12.6	11.4	11.2
150	15.6	8.2	7.3	7.2	7.5
180	14.6	7.6	7.2	6.7	6.5
210		7.6	7.7	8.0	8.1
240	12.8	6.2	6.2	6.4	6.3

Examination was made by p.m.r. of a heated sample of **1** in long tubes containing a limited amount of ammonium chloride at the bottom. In this situation, heterogeneous catalysis would make little contribution to a change in rate, but any effect due to ammonium chloride dissociation products would be evident. Within experimental error, the degree of rearrangement based on the relative intensities of the methyl peaks was the same in both the neat and ammonium chloride containing tubes at 30 min. and at 3 hr. at 134.9°.

A study of the heterogeneous catalysis by ammonium chloride on the rearrangement of **1** was made using the inhibitor in the rearranging ester. The results were corrected for the small contribution of the inhibitor and the product to the absorption at 234 mμ. There was no significant difference among the four particle sizes; the average catalytic effect was larger than with the crotyl compound (**2**). The apparent convex curvature seen in the plot of data for samples containing ammonium chloride is probably due to different efficiencies of mixing by diffusion at the different time intervals.

Since the operation of homogeneous catalysis is eliminated by the insolubility of ammonium chloride in the rearranging esters and no evidence for catalysis by ammonium chloride dissociation products was obtained, the only reasonable explanation for the change in rate is heterogeneous catalysis. The experimental method

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[16] E. F. Wolfarth, Ph.D. thesis, The Ohio State University, 1962; *Dissertation Abstr.*, **22**, 3415 (1962).

[17] H. Rassow, *Z. anorg. allgem. Chem.*, **114**, 117 (1920).

used in this study employing static systems and small-sized samples is not sufficiently sensitive to distinguish among the small differences in rate with the different particle sizes. The actual catalytic effect was so small that a more intensive study using flow systems was not undertaken.

Experimental

Allyl Tetrolate.—A solution of 19 g. of tetrolic acid[18] and 30 ml. of freshly distilled allyl alcohol in 50 ml. of benzene was treated with 1.0 g. of p-toluenesulfonic acid monohydrate. The mixture was heated and distilled slowly for 2.5 hr. during which time 52 ml. of cloudy distillate was collected. An additional 30 ml. of benzene and 20 ml. of allyl alcohol were added and the distillation continued for 2 hr. At the end of this period, the distillate was clear and had b.p. 94°. After standing at 25° for 18 hr., 0.278 g. of sodium carbonate was added. The mixture was filtered, the solid rinsed with benzene, and the benzene removed by distillation at atmospheric pressure. The residue was distilled at reduced pressure through a vacuum-jacketed Vigreux column. The fraction boiling at 82–84° (38 mm.) was collected in two fractions: 11.2 g., n^{24}_{D} 1.4550, and 11.08 g., n^{24}_{D} 1.4551. The yield was 79%. G.l.p.c. (on a 10 ft. × $^1/_8$ in. silicone-stearic acid column at 123° and 12 ml./min. helium flow rate) showed that the product (retention time, 12.8 min.) was at least 99% one component; infrared, 3.24 (w), 3.39 (m), 4.34 (m), 4.46 (s), 5.84 (s), 6.06 (m), 7.25 (m), 7.34 (m), 7.95 (s), 9.07 (m), 9.31 (s), 10.02 (m), 10.62 (m), 12.38 (m), 13.28 (m) μ.

Anal. Calcd. for $C_7H_8O_2$ (124.13): C, 67.73; H, 6.49. Found: C, 67.7; H, 6.66.

Crotyl Tetrolate.—Under essentially the same conditions as those described previously, 21 g. of tetrolic acid and 25 g. of crotyl alcohol (Distillation Products, practical grade)[19] reacted to give 22.95 g. of product, b.p. 48–50.5° (0.7 mm.), n^{25}_{D} 1.4597. G.l.p.c. analysis showed the material to be about 90% pure. A sample was prepared for analysis by preparative g.l.p.c. (5 ft. × 0.25 in. diethylene glycol adipate at 120°, 50 ml./min. helium flow rate, retention time, 33 min.), n^{26}_{D} 1.4578; infrared, 3.32 (m), 3.40 (m), 4.36 (m), 4.47 (s), 5.86 (s), 6.91 (m), 7.27 (m), 7.97 (vs), 8.73 (w), 9.18 (s), 9.40 (s), 10.31 (s), 11.05 (m), 12.32 (w), 13.28 (s) μ.

Anal. Calcd. for $C_8H_{10}O_2$ (138.16): C, 69.54; H, 7.30. Found: C, 69.5; H, 7.36.

Allyl 3-Allyloxy-2-butenoate (**1**). **A.**—Thirty milliliters of 1 *N* sodium allyloxide in purified allyl alcohol was stirred at 21–24° with a Teflon-coated magnetic stirring bar while 3.72 g. of allyl tetrolate was added over 30 min. After an additional stirring period of 30 min., 30 ml. of ether and 35 ml. of water were added at 3–5°. The two layers were separated; the ethereal layer was washed with portions of dilute NaCl solution until the washings were neutral to pH paper. The organic layer was dried over anhydrous Na_2SO_4 and the lower boiling components were removed by evaporation in a Rotovac unit at 24-mm. pressure and a final bath temperature of 55°. The liquid residue was distilled. The fraction boiling at 70–71° (0.8 mm.) was collected, m.p. 15–18°. The product weighed 2.66 g. (49%) and had n^{24}_{D} 1.4790; it gave no immediate color with $FeCl_3$ in 95% ethanol; p.m.r., 3.72, 4.40, 4.54, 5.04, 5.51 (J = 5.1), 5.72 (J = 5.1), and 7.77 τ.

Anal. Calcd. for $C_{10}H_{14}O_3$ (182.21): C, 65.91; H, 7.75. Found: C, 66.0; H, 7.78.

B.—A solution of 10.3 g. of mixed *cis*- and *trans*-3-chloro-2-butenoic acids,[20] m.p. 43–91°, was esterified with allyl alcohol essentially as previously described for the preparation of allyl tetrolate. Distillation of the crude ester gave 9.06 g., b.p. 75–82° (23 mm.), n^{24}_{D} 1.4705.

Anal. Calcd. for $C_7H_9O_2Cl$ (160.6): C, 52.35; H, 5.65. Found: C, 52.4; H, 5.69.

A solution of 1.3 g. of clean sodium in 40 ml. of allyl alcohol was prepared and cooled in an ice bath. A mixture of 8.77 g. allyl *cis*- and *trans*-3-chloro-2-butenoate and 10 ml. of allyl alcohol was added with stirring over a period of 70 min. There was an immediate formation of a solid. The mixture was kept at 25° for 16 hr. The solid was removed by filtration and washed with several portions of ether. The dried solid weighed 3.27 g. (103% of the theoretical NaCl). The filtrate and rinsings were combined and washed with three portions of dilute NaCl solution. The ether was evaporated and the residue distilled at reduced pressure to yield fraction 1, 0.2 g., b.p. 69° (0.8 mm.), n^{25}_{D} 1.4784; fraction 2, 2.80 g., b.p. 70–71° (0.8 mm.), n^{25}_{D} 1.4785; fraction 3, 4.75 g., b.p. 71° (0.75 mm.), n^{25}_{D} 1.4785. All fractions solidified on cooling in an ice bath. The yield was 7.75 g. (78%). The infrared spectrum of fraction 2 was identical with that of the sample prepared in part A.

Crotyl 3-Crotyloxy-2-butenoate (**2**).—Freshly distilled crotyl alcohol (25 ml.) was treated with 0.575 g. of clean sodium to give a 1 *M* solution of sodium crotyloxide. Then, 3.76 g. of crotyl tetrolate, b.p. 46–47° (0.7 mm.), was added and the reaction carried out as described for the preparation of **1**, part A. Distillation of the crude product provided 2.74 g. (65%) of liquid, b.p. 92–94° (0.5 mm.), n^{25}_{D} 1.4727. No color was observed with $FeCl_3$ in 95% ethanol. The infrared spectrum of the freshly distilled sample showed no ketonic absorption; p.m.r., 3.94, 4.75, 5.12, 5.61 (J = 4.0), 5.81 (J = 3.6), 7.79, and 8.31 (J = 5) τ.

Anal. Calcd. for $C_{12}H_{18}O_3$ (210.26): C, 68.55; H, 8.62. Found: C, 68.6; H, 8.70.

Allyl 2-Allyl-3-oxobutanoate (**4**).—Addition of 2.3 g. of clean sodium in portions to 50 ml. of allyl alcohol produced a pale yellow solution. This was cooled to 20°, and 14.2 g. of allyl acetoacetate[21] was added over 30 min. A solution of 13.3 g. of freshly distilled allyl bromide in 50 ml. of petroleum ether (b.p. 60–68°) was stirred and cooled in an ice bath. The solution of sodium allyl acetoacetate was added over a period of 70 min. A copious white precipitate formed during the addition. The suspension was stirred for 30 min. at 0°, at 25° for 30 min., and at 50–55° for 30 min. The mixture was transferred to a separatory funnel, and ether and water were added. The layers were separated and the aqueous layer was extracted with ether. The ethereal solution was washed with water until the wash water was neutral to pH paper. The organic phase was dried and evaporated to a small volume. Distillation gave three fractions: 0.35 g., b.p. 30–60° (1.3 mm.), n^{23}_{D} 1.4600; 9.49 g., b.p. 64–68° (1.2 mm.), n^{23}_{D} 1.4563; and 2.26 g., b.p. 68–69° (1.2 mm.), n^{23}_{D} 1.4582. Fractions 2 and 3 were combined and redistilled to give 10.2 g., b.p. 64–66.5° (0.8 mm.), n^{23}_{D} 1.4514. The analytical sample was prepared by g.l.p.c. (retention time 51.3 min.) using conditions described subsequently for analysis of rearrangement mixtures; p.m.r. 3.74, 4.48, 4.56, 5.15, 5.42 (J = 5.1), 6.57 (J = 7.2), 7.46 (J = 7.2), and 7.84 τ.

The remaining substituted acetoacetates listed in Table III were prepared essentially as described previously except that equimolar amounts of allyl acetoacetate and crotyl acetoacetate[21] and the alkenyl halides were used. When the alkenyl halide was 3-chloro-1-butene, the reaction mixture was heated under reflux for 2 hr. using a bath controlled at 95–100°. The purified products of the preceding reactions did not change in composition under the conditions of g.l.p.c. used. The use of g.l.p.c. to analyze mixtures was, therefore, a valid method.

TABLE III

PROPERTIES OF ALKENYL 2-ALKENYLOXY-3-OXOBUTANOATES

Compound	Yield, %	B.p. (mm.), °C.	n^{25}_{D}	Analysis, % Calcd. C	Calcd. H	Found C	Found H
4	65	65–66.5 (0.75)	1.4514	65.9	7.74	65.9	7.75
5	6	85–87 (1.3)	1.4587	68.6	8.62	68.2	8.52
7	6	84–85 (1.3)	1.4540	68.6	8.62	68.4	8.69
8	6	70–72 (0.6)	1.4527	67.3	8.22	67.1	8.23
9	59	72–74 (0.6)	1.4554	67.3	8.22	67.1	8.23
10	6	72–74 (0.8)	1.4543	67.3	8.22	67.2	8.24

Crotyl 2-(1-Methyl-2-propenyl)-3-oxobutanoate (**7**).—A 25-ml. round-bottomed flask was charged with 7.62 g. of **2** which was contaminated with a small per cent of crotyl tetrolate (infrared) and fitted with an U-shaped Claisen head. The vapor path from liquid surface to side arm was 17 cm. The flask was heated in a silicone oil bath and the rearrangement product dis-

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[18] L. A. Carpino, *J. Am. Chem. Soc.*, **80**, 599 (1958).

[19] Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

[20] L. F. Hatch and R. H. Perry, *J. Am. Chem. Soc.*, **77**, 1136 (1956).

[21] W. Kimel and A. C. Cope, *ibid.*, **65**, 1992 (1943).

tilled at 25-mm. pressure. A 0.5-ml. forerun was collected at 123–133° (bath temp. 195–197°). The major fraction (6.13 g.) was collected at 140–146° (bath temp., 200–218°). The infrared spectrum showed 95% loss of the 12.2 μ absorption and trace $-$C≡C$-$ absorption. Redistillation of 6.10 g. of the major fraction gave 1 ml., boiling at 134–137° (23 mm.). The major fraction (4.63 g., 61%) was collected at 139–141° (bath temp. 210–224°). This material had $n^{26}\text{D}$ 1.4540 and identical infrared spectrum with that of the g.l.p.c. purified product from the alkylation of crotyl acetoacetate with 3-chloro-1-butene; p.m.r., 3.98, 4.75, 4.83, 5.16, 5.46, 5.60, 6.83 ($J \sim 10$), 7.03 ($J = 6.1$), 7.86, 7.91, 8.24 ($J = 5.1$), 8.93, 9.03 ($J = 6.3$) τ.

There was a trace peak in the g.l.p.c. purification of allyl 2-allylacetoacetate (retention time. 36 min.) when the column was run at 140°. -The pot residue (2.19 g.) from the original distillation showed a larger proportion of this component. A portion was collected from the g.l.p.c. separation. The compound showed a negative $FeCl_3$ test in 95% ethanol solution. The infrared spectrum was consistent with the structure **allyl 2,2-bis-(allyl)-3-oxobutanoate,** 3.26 (w), 3.37 (w), 3.42 (w), 5.75 (m), 5.84 (s), 6.10 (m), 6.94 (m), 7.05 (m), 7.37 (m), 7.58 (w), 7.82 (m), 8.02 (m), 8.28 (s), 8.47 (m), 8.75 (m), 9.52 (w), 10.06 (m), and 10.83 (m) μ.

Anal. Calcd. for $C_{13}H_{18}O_3$ (222.27): C, 70.24; H, 8.16. Found: C, 70.2; H, 8.26.

A test for crossed products in the rearrangement of mixed allyl 3-allyloxy-2-butenoate (**1**) and crotyl 3-crotyloxy-2-butenoate (**2**) was made by preparing three sets of capillary tubes containing: (a) 5 μl. of **1**, (b) 5 μl. of **2**, (c) 5 μl. each of **1** and **2**. The tubes were cooled, flame sealed, and inverted and centrifuged several times to mix the contents. One set of tubes was heated for 10 min. at 150° 1 ±, and the infrared spectrum taken. Tube a showed 42% unchanged **1** from the decrease of the 12.2-μ absorption, tube b showed 12.5% unchanged **2**. After heating another set of tubes for 1 hr. at 150°, the 12.2-μ absorption had disappeared in all three tubes. The mixture in tube c was analyzed by g.l.p.c. (5 ft. × 0.25 in. 20% diethyleneglycol adipate on 30–60-mesh firebrick column, column temperature, 115–116°, helium flow rate 65 ml./min., thermal conductivity detector). The retention (g.l.p.c.) times for the compounds of interest in this analysis are: **1**, 66 (partially rearranged on column), **2**, 106 (partially rearranged); **4**, 52; **5**, 148, **7**, 105; **8**, 55; **9**, 92; and **10**, 81.

There were only two large symmetrical peaks, at 50 and at 90 min. in the tube c sample. The material from these peaks was collected and the infrared spectra determined. The material collected over the 44–64-min. period was identical in spectrum with that of a sample of allyl 2-allylacetoacetate. The material collected over the 82–118-min. period was identical in infrared spectrum with that of a sample of crotyl 2-(1-methyl-2-propenyl)-3-oxobutanoate.

The heating bath for the kinetic studies was a rapidly stirred silicone fluid in an insulated steel beaker. The bath had one nonregulated (250 w.) and one regulated (100 w.) immersion heater. Temperature control was maintained at ±0.1° by use of a Yellow Springs Instrument Co., Inc., Thermistemp unit with a metal-cased sensing probe. The samples were inserted and removed from the heated bath by a vertically traveling and oriented brass rod. The rod was bored with horizontal holes in which the capillary samples tubes were retained with spring clips.

The kinetic samples were prepared by delivering 10–20 μl. of compound to 1.5–2.0-mm. i.d. × 50 mm. soft glass capillary tubes. The tubes were centrifuged in a special capillary tubing head (catalog no. 927) for the International Clinical Centrifuge Model CL. The tubes were then cooled in a drilled aluminum block resting on solid carbon dioxide. The cold tubes were rapidly flame sealed into 3.0–3.5-cm. lengths.

The tubes were heated the requisite time (stopwatch) and then quenched with cold water. The residual silicone fluid was carefully wiped off and the tubes were placed in volumetric flasks one-third to one-half filled with methanol. The tubes were crushed with a stirring rod, the rod was rinsed with methanol, and the solutions were diluted to volume at 25°. The ultraviolet spectra were measured, after further dilutions when necessary, by use of 1-mm. cells in the Cary Model 14 and 1-cm. cells in the Cary Model 11 spectrophotometer. All runs were made on a time schedule in which the measurements were made 2 hr. after crushing the sample tubes. Actually, the time of measurement was not critical; solutions stored at 1.5° and −34° in the dark or at 25° in the light for 48 hr. did not change significantly. When butylated hydroxytoluene was used in samples of allyl 3-allyloxy-2-butenoate, the ultraviolet measurements were corrected for contributions of the additive and of the product to the absorption at 234 mμ. The rate constants were calculated from the slope of the line resulting from the plot of log concentration *vs.* time.[22]

In the catalysis study, reagent grade NH_4Cl was ground with a mortar and pestle and sized with brass sizing screens. The glass capillary tubes were charged with 8.7 or 20 mg. of NH_4Cl, tapped gently to drop the solid to the bottom, and filled and sealed as described previously.

The solubility of NH_4Cl in the esters was determined by heating about 500 mg. of ester with 50 mg. of NH_4Cl in sealed tubes at 134.9° for 8 hr. The supernatant liquid was drawn off, and extracted with three portions of water. The water was evaporated at 25–45° and the residue weighed. In no case was any significant amount of NH_4Cl found.

To determine if the products of the catalyzed reactions were the same as those of the uncatalyzed, tubes of the rearranging esters in the presence and absence of NH_4Cl were heated, and the contents analyzed by infrared and g.l.p.c. methods. Except for slight differences in the early trace amount g.l.p.c. peaks, the catalyzed and uncatalyzed samples were identical.

The infrared spectra were determined by use of a Beckman IR-5 spectrophotometer. The samples were run as liquid films between NaCl plates. The film thickness was not measured; it was not the same for all compounds.

P.m.r. spectra were obtained at 60 Mc. with a Varian DP-60 spectrometer system equipped with a base-line stabilizer and integrator. Peak positions determined by interpolation from a modulation side band whose frequency was counted over a 10-sec. interval, are believed to be accurate within 1 c.p.s. Kinetic samples were run at 29° or at 150° as neat liquids in 4-mm. i.d. thin wall borosilicate sample tubes which had been flame sealed. Reference spectra of the reactants **1** and **2** and the products **4** and **7** were taken at 29° in 5–10% solution in CCl_4 which contained approximately 1% tetramethylsilane as an internal reference. Some of these spectra were integrated to confirm purity and to aid in the identification of certain peaks. Shielding values in tau units and approximate spin–spin coupling constants were determined.

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[22] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961.