system in the benzotrifluoride molecule. This situation is apparently reversed when the cases of *m*-xylene and the 1,3-bis-(trifluoro)-compounds are considered, *viz.*, the fractional positive volume change exceeds the fractional negative change in *B*. It will be noted in Table IB that the values of ΔR_D are roughly constant for the *m*-fluoro and *m*-chloro compounds and the same applies to the *p*-compounds except for *p*-chlorobenzotrichloride. The latter compound has a rather low ΔR_D in view of the data on the other compounds of similar nature. It is notable that in all cases of the di-substituted compounds in which large + ΔR_D deviations occur one of the substituents is fluorine. This atom because of its small size, large electro-negativity and low polarizability would give rise to a large coulombic repulsion for other bonded electronegative atoms and would have low com-pensatory attraction arising from dispersion forces. The larger chlorine atom has a lower electronegativity and a higher polarizability and as such might give rise to a smaller *relative* volume increment than would the fluorine atom.

The bonded fluorine atom should contribute to the London[10] dispersion forces about the same as bonded hydrogen atoms and yet in spite of the large dipole moment of benzotrifluoride and 1,3-bis-(trifluoromethyl)-benzene the boiling point of the former is roughly 8° lower than that of toluene and of the latter roughly 23° lower than that of *m*-xylene. The first order factor in deter-mining boiling points in normal liquids is the force arising from the interaction of instantaneous

atomic dipoles with dipoles induced in neighboring polarizable systems. Since in first approximation this force varies as $1/r^6$, it is evident that a very small change in *r* will have a considerable influence on the interaction energy, and in cases of systems of essentially the same distribution and magnitude of polarizability within a molecule it may be generally expected that the substance with largest intermolecular distances will have the lower boiling point. In the cases of *m*-xylene and 1,3-bis-(trifluoromethyl)-benzene the ratio of the average intermolecular separations at 30° is about 1/1.15 and for toluene and benzotri-fluoride at 30° the ratio is about 1/1.10. The molar volume at the respective boiling points of the compounds would be more instructive in the above connection than the data at 30°; how-ever, to the knowledge of the authors, such data are not available for the fluorine compounds. The fact that the substances listed with largest intermolecular distances are the lowest boiling of the pairs considered can hardly be regarded as coincidence although it is recognized that the entire line of reasoning relating to the boiling point and intermolecular distance has serious quantitative limitations.

Summary

The electric moments of a number of organic fluorine compounds have been measured and dis-cussed in relation to the structure of the mole-cules. The effect of fluorine on some physical characteristics of molecules is briefly considered.

(10) F. London, *Trans. Faraday Soc.*, **33**, 8 (1937).

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Allylic Rearrangements. XXIV. Abnormal Bimolecular Substitution. The Condensation of Butenyl and Pentenyl Chlorides with Sodium Malonic Ester

BY RICHARD E. KEPNER,[1a] S. WINSTEIN AND WILLIAM G. YOUNG

Recent work[1b,c] on nucleophilic displacement reactions of allylic systems has indicated that bimolecular (S_N2) reactions produce unrear-ranged products (eqn. 1). An abnormal bimolec-ular (S_N2') mechanism (eqn. 2) has been pro-posed[2] and, while some of many conversions in the literature may involve this mechanism at least

$$R-\overset{H}{\underset{H}{C}}=\overset{H}{\underset{H}{C}}-C-X + Y^- \longrightarrow$$

$$R-\overset{H}{\underset{H}{C}}=\overset{H}{\underset{H}{C}}-C-Y + X^- \quad (1)$$

$$Y^- + R-\overset{H}{\underset{H}{C}}=\overset{H}{\underset{H}{C}}-C-X \longrightarrow$$

$$R-\overset{H}{\underset{Y}{C}}-\overset{H}{\underset{H}{C}}=CH + X^- \quad (2)$$
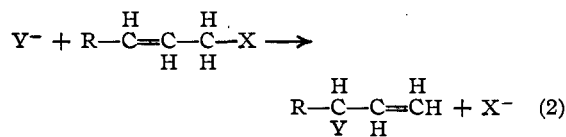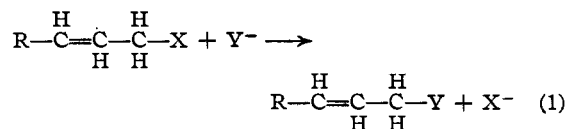
partly, no completely satisfactory evidence for its operation has so far appeared.

Thus many reported cases of reactions of allylic halides with nucleophilic reagents such as sodium malonic ester,[3] sodium acetoacetic ester,[4] sodium allyl benzene,[5] potassium phthalimide,[6] sodium

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(1) (b) Roberts, Young and Winstein, THIS JOURNAL, **64**, 2157 (1942); (c) Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

(2) (a) Winstein, Dissertation, California Institute of Technology, 1938; (b) Hughes, *Trans. Faraday Soc.*, **34**, 185 (1938); (c) Berg-mann, *Helv. Chim. Acta*, **20**, 590 (1937).

(3) (a) Staudinger, Kries and Schilt, *Helv. Chim. Acta*, **5**, 743 (1922); (b) Braun and Schirmacher, *Ber.*, **56**, 538 (1923); (c) Doran and Shonle, THIS JOURNAL, **60**, 2880 (1938).

(4) (a) Fischer and Lowenberg, *Ann.*, **475**, 183 (1929); (b) Ruzicka and Firmenich, *Helv. Chim. Acta*, **22**, 392 (1939).
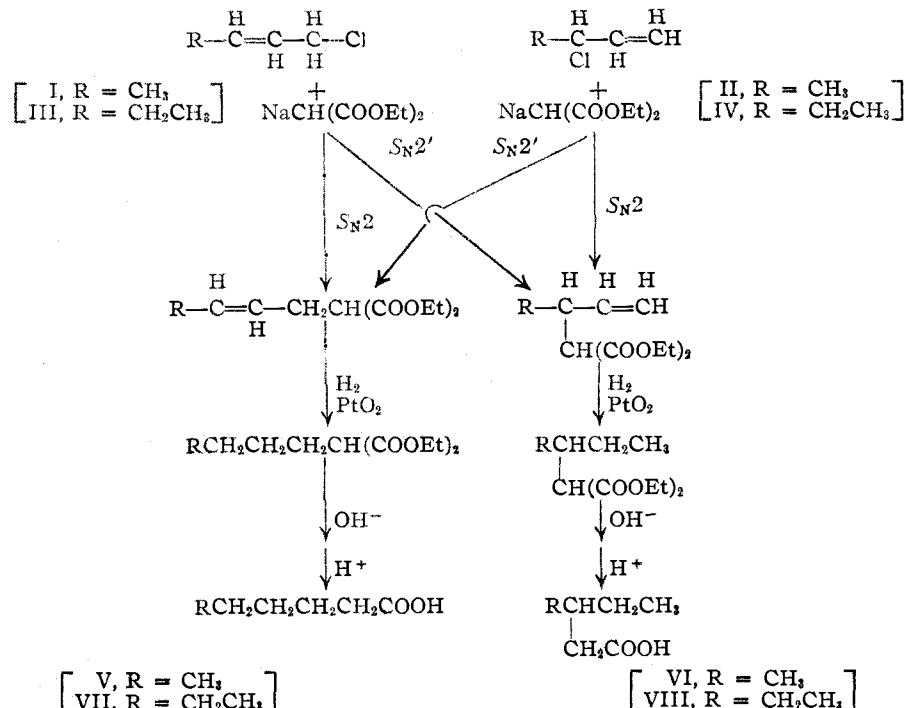
(5) Cope and Levy, THIS JOURNAL, **66**, 1684 (1944).

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

phenoxide[7] or the sodium enolates of ethyl isopropylidenemalonate and ethyl (1-methyl-propylidene)-cyanoacetate[8] afford no evidence for the operation of the S_N2' mechanism because of either the lack of kinetic evidence, the use of impure allylic halides, the probability of allylic rearrangement during the reaction, or extreme difficulty in detecting the presence of small amounts of abnormal product in certain cases.

The reactions of allylidene chlorides[9] seemingly offered an example of the mechanism at first sight, but later work[10] has indicated that these re-

$$R—\overset{H}{\underset{H}{C}}=\overset{H}{\underset{H}{C}}—\overset{}{\underset{}{C}}—Cl \qquad\qquad R—\overset{H}{\underset{Cl}{C}}—\overset{H}{\underset{H}{C}}=CH$$

$$\begin{bmatrix} I, R = CH_3 \\ III, R = CH_2CH_3 \end{bmatrix} \qquad + \qquad\qquad + \qquad \begin{bmatrix} II, R = CH_3 \\ IV, R = CH_2CH_3 \end{bmatrix}$$

$$NaCH(COOEt)_2 \qquad NaCH(COOEt)_2$$

$$S_N2' \qquad S_N2'$$

$$S_N2 \qquad\qquad S_N2$$

$$R—\overset{H}{\underset{H}{C}}=C—CH_2CH(COOEt)_2 \qquad\qquad R—\overset{H}{C}—\overset{H}{\underset{CH(COOEt)_2}{C}}—\overset{H}{C}=CH$$

$$\downarrow H_2 \quad PtO_2 \qquad\qquad\qquad \downarrow H_2 \quad PtO_2$$

$$RCH_2CH_2CH_2CH(COOEt)_2 \qquad\qquad RCHCH_2CH_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad \underset{CH(COOEt)_2}{}$$

$$\downarrow OH^- \qquad\qquad\qquad\qquad \downarrow OH^-$$

$$\downarrow H^+ \qquad\qquad\qquad\qquad \downarrow H^+$$

$$RCH_2CH_2CH_2CH_2COOH \qquad\qquad RCHCH_2CH_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad \underset{CH_2COOH}{}$$

$$\begin{bmatrix} V, R = CH_3 \\ VII, R = CH_2CH_3 \end{bmatrix} \qquad\qquad \begin{bmatrix} VI, R = CH_3 \\ VIII, R = CH_2CH_3 \end{bmatrix}$$

actions can best be explained by other means. Carroll[11] reported the formation of CH_3COCH_2-$CH_2CH=CHC_6H_5$ in the treatment of α-phenylallyl alcohol with acetoacetic ester, and Wilson[12] has suggested that this rearranged product may result from the S_N2' mechanism. However, Kimel and Cope[13] found that the observed product was formed by successive ester interchange and cyclic rearrangement of the unsaturated ester.

Bergmann[2c] claims that the abnormal bimolecular mechanism operates in the reaction of optically active α,γ-dimethylallyl chloride with sodium malonic ester or sodium diphenylmethide, in this way accounting for the complete loss of optical activity. The same product results from either a normal or abnormal bimolecular attack on α,γ-dimethylallyl chloride, and thus it was impossible for Bergmann to prove the operation of the S_N2' mechanism from the structure of the product. In this article is reported some further work on displacement reactions of allylic halides which is pertinent to the question of the operation of an abnormal bimolecular mechanism. The conversions in question involved the action of sodium malonic ester on γ-methylallyl (I), α-methylallyl (II), γ-ethylallyl (III) and α-ethylallyl (IV) chlo-

(7) (a) Claisen and Tietze, *Ber.*, **59B**, 2344 (1926); (b) Reichstein and Trivelli, *Helv. Chim. Acta*, **16**, 968 (1933).

(8) Cope, Hoffman and Hardy, THIS JOURNAL, **63**, 1852 (1941).

(9) (a) Strauss and Berkow, *Ann.*, **401**, 121 (1913); (b) Kirrmann, *Compt. rend.*, **199**, 1228 (1934); (c) Kirrmann and Grard, *ibid.*, **190**, 876 (1930); (d) Kirrmann, Pacaud and Dosque, *Bull. soc. chim.*, [5] **1**, 860 (1934).

(10) Andrews, THIS JOURNAL, **69**, 3062 (1947).

(11) Carroll, *J. Chem. Soc.*, 704, 1266 (1940); 507 (1941).

(12) Wilson, *Trans. Faraday Soc.*, **37**, 631 (1941).

(13) Kimel and Cope, THIS JOURNAL, **65**, 1992 (1943).

rides. These chlorides are similar to the one employed by Bergmann[2c] but normal and abnormal bimolecular mechanisms give different products.

The products of the displacement reactions were directly hydrogenated, saponified and decarboxylated to yield saturated monocarboxylic acids. The acids which may result from the butenyl chlorides are n-caproic acid (V) and β-methylvaleric acid (VI), and from the pentenyl chlorides are n-heptanoic acid (VII) and β-ethylvaleric acid (VIII). The acid product from each halide was carefully fractionated and various of the distillation fractions converted to benzyl amine salts to yield a semiquantitative estimate of the composition. The estimates thus obtained indicated less than 1% of abnormal product from each of the primary chlorides (I and III). With α-methylallyl chloride (II), there was estimated 10% of abnormal product when the condensation with sodium malonic ester was carried out at the reflux temperature of the alcoholic solution and 6% when the condensation was carried out at room temperature. With α-ethylallyl chloride (IV) the abnormal product was estimated at 23%.

The original chlorides (I–IV) were very carefully purified so that the production of abnormal products cannot be due to impurity of starting materials. Also, the chlorides are quite stable to thermal rearrangement, so this possible cause for production of abnormal products can be eliminated. It was shown by refractive index measurements that the pure chlorides without a solvent are unchanged after three hours at 80°. Actually, we should be concerned about rearrangements in ethanol, the solvent employed for the condensa-

tions. However, we should expect rearrangement in ethanol to be accompanied by very extensive solvolysis and this, as will be discussed shortly, is quite slow relative to the rate of the reaction with sodium malonic ester.

Ruling out impurity and rearrangement of the halides, there is still another conceivable mode of production of abnormal products besides the S_N2' mechanism. This would be by way of a rate-determining ionization of the halide followed by very successful competition by malonic ester anion for the allyl carbonium ion. This we are able to rule out on the basis of kinetic experiments with α-ethylallyl chloride (IV), the halide which gave rise to the most abnormal product. The rate of solvolysis of this chloride in absolute ethanol and the rate of the condensation with diethyl malonate ion in absolute ethanol were both determined at 50.00°. The first order constant, k_1, observed for solvolysis of *ca.* 0.3 M chloride was 4.96 × 10^{-4} hr.$^{-1}$, the same order of magnitude as that previously observed for α-methylallyl chloride,[14] 2.11 × 10^{-4} hr.$^{-1}$ at 40°. The condensation of α-ethylallyl chloride with diethyl malonate ion gave excellent second-order kinetics, the results of a typical run being summarized in Table I and the results of several runs in Table II.

TABLE I

CONDENSATION OF α-ETHYLALLYL CHLORIDE WITH SODIUM MALONIC ESTER IN ABSOLUTE ETHANOL AT 50.00°

α-EA-Cl = 0.6461 M NaCH(COOEt)$_2$ = 0.1625 M

t, hr.	NaCH(COOEt)$_2$ at time, t, mole/liter	α-EA-Cl reacted at time, t, mole/liter	k_2
0.0	0.1625	0.0	...
0.25	.1470	.0155	...
0.75	.1312	.0313	0.353
2.00	.1002	.0623	.362
2.75	.0851	.0774	.368
3.75	.0711	.0914	.353
4.75	.0581	.1044	.357
6.75	.0410	.1215	.348

Mean 0.357 ± .005

TABLE II

SUMMARY OF RATE CONSTANTS FOR THE REACTION OF α-ETHYLALLYL CHLORIDE WITH SODIUM MALONIC ESTER

| Run	α-EA-Cl, mole/liter	NaCH(COOEt)$_2$, mole/liter	k_2
1	0.3391	0.3586	0.349
2	.3495	.3268	.366
3	.1655	.6279	.325
4	.6461	.1625	.357

From the second-order rate constant, k_2, listed in Tables I and II, it is clear that the bimolecular reaction with malonic ester anion is much faster than the first-order solvolysis. In fact, one can calculate[1a] for an experiment at 50° with initially 2 M reagents that at complete reaction only 0.5% of the α-ethylallyl chloride has reacted by a solvo-

lytic first-order mechanism. Thus, even if solvent does not compete with malonic ester anion, a maximum of 0.5% abnormal product could be accounted for by a solvolytic mechanism.

It is clear from the above arguments that the abnormal product observed in the case of the secondary chlorides (II and IV) arises from a bimolecular displacement process involving attack on the γ-carbon atom. Similarly this must have contributed to the reaction of α,γ-dimethylallyl chloride studied by Bergmann, but one would hardly anticipate sufficient contribution to account for complete racemization.

Other pertinent cases of nucleophilic displacements with allylic compounds involve the action of amines on halides. Thus Meisenheimer and Link[15] found that α-ethylallyl chloride (IV) on treatment with diethylamine or methylaniline yielded abnormal products, the same ones derived from γ-ethylallyl chloride (III). Also, Webb has found in these laboratories that α-methylallyl chloride II yields, on reaction with diethylamine, an abnormal product identical with the one from γ-methylallyl chloride (I). While these reactions are being scrutinized further, the indications are that abnormal product arises from bimolecular processes involving attack on the γ-carbon atom.

In the case of the abnormal displacement reactions, it is still not clear to what extent a mechanism of the type symbolized in IX contributes.
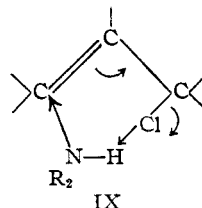
IX

Just as this manuscript was being completed, Jones, Lacey and Smith[16] reported the formation of an abnormal product from the action of diethylamine on the halides X (R = H or n-C$_4$H$_9$).

RC≡CCH=CHCHClCH$_3$ RC≡CCH=CHCH$_2$Cl
      X   XI
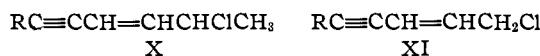
Normal products were obtained with aniline, ammonia and ethylamine. The halides XI (R = H or n-C$_4$H$_9$) yielded normal products even with diethylamine. The case of the abnormal product may be analogous to the cases of Meisenheimer and Link and Webb. However, abnormal product from X may arise from isomerization of normal product since treatment of normal product from X (R = H) and ethylamine with ethyl bromide gives the abnormal product.

Among the factors favoring abnormal product formation, Jones, Lacey and Smith emphasize basic strength of the nucleophilic reagent, in this way accounting for the formation of abnormal product with only diethylamine (and not NH$_3$

(14) Young and Andrews, THIS JOURNAL, **66**, 421 (1944).

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

(16) Jones, Lacey and Smith, *J. Chem. Soc.*, 940 (1946).

$C_2H_5NH_2$ or $C_6H_5NH_2$). We feel that in cases of competing modes of attack (in this case α vs. γ) by a *limited* series of reagents, the dependence of rate on basic strength for each mode will be different. Thus a correlation of the ratio of the two rates with basic strength may become possible for a *limited* series of reagents. However, on this basis we do not expect a sharp difference between diethylamine and the other amines employed by Jones and co-workers, for the gap in basic strength is large between aniline and ethylamine and small between ethylamine and diethylamine.

One factor which is certain to be serious in a case of competing attacks such as the present competition between α- and γ-attacks is the steric one. Thus, primary halides will suffer α-attack more rapidly than the secondary halides, at least partly or largely for steric reasons. It is interesting that on this basis alone, without considering resonance effects and steric effects in the γ-attacks, the general behavior of the various halides can be correlated. The primary halides I, III and XI (R = H or n-C_4H_9) give normal products and similarly Meisenheimer and Link[15] obtained normal product from cinnamyl chloride and ethylaniline. On the other hand, the secondary halides II, IV and X (R = H or n-C_4H_9) give partly or largely abnormal products with certain reagents.

Experimental

α- and γ-Methylallyl Chlorides.—A mixture of the chlorides was prepared from a mixture of the alcohols and purified by standard methods.[17] The chlorides used had the following properties: α-methylallyl chloride, b. p. 63.2–63.5° (750 mm.), $n^{20}D$ 1.4151, and γ-methylallyl chloride, b. p. 58.5–59.0° (300 mm.), $n^{20}D$ 1.4351.

α- and γ-Ethylallyl Chlorides.—The α-ethylallyl alcohol, b. p. 113–113.5° (750 mm.), $n^{25}D$ 1.4223, d^{25}_4 0.8344, used as a source of the allylic chlorides was prepared from ethylmagnesium bromide and acrolein according to the method of Delaby[18] as modified by Prevost.[19] The pentenyl chlorides were prepared from the α-ethylallyl alcohol by means of phosphorus trichloride and pyridine at 0° using standard methods[17] and were fractionated through a 1.5 × 135 cm. helices packed column under reduced pressure. The properties of the chlorides[20] used were as follows: α-ethylallyl chloride, b. p. 55.0° (200 mm.), $n^{20}D$ 1.4253, $n^{25}D$ 1.4229, d^{25}_4 0.8933, M_D, obs. 29.81, calcd. 29.69, equiv. wt., obs. 104.6, 104.9, calcd. 104.6; γ-ethylallyl chloride, b. p. 71.8° (200 mm.), $n^{20}D$ 1.4404, $n^{25}D$ 1.4380, d^{25}_4 0.9089, M_D, obs. 30.20, calcd. 29.69, equiv. wt., obs. 105.2, 105.7, calcd. 104.6.

n-Caproic Acid.—This material was redistilled Eastman Kodak Company White Label material, b. p. 97.5–98.0° (10 mm.), $n^{20}D$ 1.4163. The benzylamine derivative was prepared according to the method of Buehler, Carson and Edds[21] and recrystallized from anhydrous ethyl acetate; m. p.[22] 71–71.5° (cor.).

Anal. Calcd. for $C_{13}H_{21}O_2N$: C, 69.92; H, 9.48. Found: C, 69.97; H, 9.64.

(17) Young and Lane. THIS JOURNAL, **59**, 2051 (1937).

(18) Delaby, *Compt. rend.*, **175**, 967 (1922).

(19) Prevost. *Ann. chim.*, [10] **10**, 113, 147 (1928).

(20) Prevost [*Compt. rend.*, **187**, 1052 (1928)] reported the following properties: α-ethylallyl chloride, $n^{23}D$ 1.4224, d^{24}_4 0.8966; γ-ethylallyl chloride, $n^{23}D$ 1.4347, d^{24}_4 0.9095.

(21) Buehler, Carson and Edds. THIS JOURNAL, **57**, 2181 (1935).

(22) Buehler. Carson and Edds[21] reported the melting point of the benzylamine salt of n-caproic acid to be 51.7–52.7°.

β-Methylvaleric Acid.—Secondary butyl bromide, b. p. 89–90° (750 mm.), $n^{25}D$ 1.4345, prepared from redistilled Eastman Kodak Company White Label 2-butanol, b. p. 99.0° (750 mm.), by means of phosphorus tribromide and pyridine at 0°, was condensed with malonic ester, b. p. 104–5° (25 mm.), in absolute ethanol according to the general method of Gilman and Blatt.[23] The condensation product was isolated but not purified and then hydrolyzed and decarboxylated as described by Blatt[24] to give β-methylvaleric acid, b. p. 93–94° (13 mm.), $n^{20}D$ 1.4158. The benzylamine derivative was somewhat hygroscopic and melted at 66–67° (cor.) after several recrystallizations from a mixture of anhydrous ethyl acetate and low-boiling petroleum ether.

Anal. Calcd. for $C_{13}H_{21}O_2N$: C, 69.92; H, 9.48. Found: C, 70.44; H, 9.52.

n-Heptanoic Acid.—Hydrolysis of Eastman Kodak Company White Label heptanoic anhydride yielded n-heptanoic acid, b. p. 109–110° (10 mm.), $n^{20}D$ 1.4225. The benzylamine derivative, recrystallized from a mixture of anhydrous ethyl acetate and low boiling petroleum ether, melted at 66.0–66.5° (cor.).

Anal. Calcd. for $C_{14}H_{23}O_2N$: C, 70.85; H, 9.77. Found: C, 71.72; H, 9.88.

β-Ethylvaleric Acid.—Diethylcarbinol, b. p. 115–115.2° (750 mm.), $n^{15}D$ 1.4126, prepared by the reaction of ethylmagnesium bromide with propionaldehyde, was converted to 3-bromopentane by treatment with phosphorus tribromide and pyridine at 0°. The 3-bromopentane, b. p. 116.5–116.8° (750 mm.), $n^{20}D$ 1.4444, was condensed with malonic ester[23] and the condensation product hydrolyzed and decarboxylated[24] to β-ethylvaleric acid, b. p. 104–105° (13 mm.), $n^{20}D$ 1.4250, in 40% over-all yield. The benzylamine derivative of β-ethylvaleric acid crystallized slowly from low boiling petroleum ether at room temperature. Since the derivative was extremely hygroscopic and difficult to handle the best melting point which could be obtained was 51–53°.

Anal. Calcd. for $C_{14}H_{23}O_2N$: C, 70.85; H, 9.77. Found: C, 70.63; H, 10.11.

Condensation of α- and γ-Methylallyl and α- and γ-Ethylallyl Chlorides with Sodium Malonic Ester.—To a stirred solution of sodium ethoxide, prepared by adding 0.50 mole of freshly cut sodium to 250 ml. of absolute ethanol (99.96%), was added 0.50 mole of diethyl malonate, b. p. 104–105° (25 mm.), over a one-half hour period. To this stirred sodium malonic ester solution was added 0.50 mole of the allylic chloride over a one-half hour period and the mixture then refluxed for two hours to complete the condensation. The cooled reaction mixture was poured into 800 ml. of water, neutralized with carbon dioxide gas, and the condensation product isolated by extraction with diethyl ether. The diethyl ether was removed by distillation and the condensation product added to 100 ml. of 95% ethanol and reduced at atmospheric pressure using platinum oxide catalyst. The catalyst was removed by filtration and the reduction product hydrolyzed and decarboxylated as described by Blatt.[24] The organic acids were isolated by extraction with diethyl ether and then completely removed from the ether layer by extraction with sodium carbonate solution. The aqueous solution of the sodium salts was decolorized with carbon, filtered, and the resulting colorless solution acidified with sulfuric acid. The organic acids were again isolated by extraction with diethyl ether. The diethyl ether was removed by distillation and the organic acids were carefully fractionated into 2–3 g. fractions. A second run was made using α-methylallyl chloride (Method 2) in which the condensation of the chloride with sodium malonic ester was completed by allowing the mixture to stand at room temperature for one week instead of refluxing for two hours.

(23) Gilman and Blatt, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons. Inc., New York, N. Y., 1941, p. 250.

(24) Blatt. "Organic Syntheses," Coll. Vol. II, John Wiley and Sons. Inc., New York, N. Y., 1943, p. 416.

The products from the condensations with α-methylallyl chloride (Method 1), α-methylallyl chloride (Method 2), γ-methylallyl chloride, α-ethylallyl chloride and γ-ethylallyl chloride absorbed 92, 88, 93.5, 93.5 and 100%, respectively, of the theoretical amount of hydrogen, and the over-all yields of the saturated monocarboxylic acids were 89, 76, 80, 80 and 74%, respectively.

Fractionation of the saturated acids from the first condensation with α-methylallyl chloride with the aid of an estimated 25-plate 0.9 × 85 cm. platinum gauze-packed column similar to one described by Bower and Cooke[25] yielded 22 fractions (2–3 g. each) with a distillation temperature variation of 89–91° (10 mm.) and refractive index variation of $n^{20}D$ 1.4155–1.4157. Benzylamine derivatives of various distillation fractions were prepared by addition of approximately 0.25 ml. of benzylamine to 0.25 ml. of the acid. The resulting solid mass of crystals was recrystallized from a minimum volume (approximately 1 ml.) of a 50% mixture of anhydrous ethyl acetate and low boiling petroleum ether. From the melting point data for these derivatives, summarized in Table III, the amount of n-caproic acid, the abnormal product, was estimated to be 10 ± 3% of the total acid obtained. The loss of benzylamine derivative in the small amount of mother liquor was low but some difference in the solubility of the derivative of the normal and the abnormal products was a source of some uncertainty in the analysis, estimated at ±3%.

TABLE III

MELTING POINTS OF BENZYLAMINE DERIVATIVES OF α-METHYLALLYL CHLORIDE PRODUCTS

Distillation fraction	M. p., of benzylamine salt °C.	Mixed m. p. with β-methylvaleric acid salt, m. p. 66–67°	Mixed m. p. with n-caproic acid salt, m. p. 71–71.5°
2	66–67	66–67	
4	65–67	66–67	
12	66–67	66–67	
18	65.5–67	66–67	50–56
19	66–67	66–67	53–57
20	47–51	50–55	42–45
21	65–68	54–57	66–69
22	70–71	55–57	70–71

The second condensation with α-methylallyl chloride (Method 2) gave similar results and the amount of abnormal product was estimated by means of benzylamine derivatives to be 6 ± 3% of the total acid obtained.

Fractionation of the saturated acids from the condensation with α-ethylallyl chloride gave 21 fractions (2–3 g. each) with a distillation temperature variation of 100–108° (10 mm.). The refractive index of fractions 1–14 varied from $n^{20}D$ 1.4250–1.4254 and then decreased for fractions 15–17 until fractions 18–21 were constant at 1.4226. In this fractionation, the refractive indices, the boiling points and the odor all indicated the presence of n-heptanoic acid, the abnormal product, in fractions 15–21, inclusive. Benzylamine derivatives of various distillation fractions were prepared and recrystallized once from low-boiling petroleum ether and the minimum amount of anhydrous ethyl acetate necessary to dissolve the solid. From the melting point data for these derivatives, summarized in Table IV, the amount of n-heptanoic acid, the abnormal product, was estimated to be 23 ± 3% of the total acid obtained.

Investigation of the fractionated acids from the condensations with γ-methylallyl and γ-ethylallyl chlorides in a similar manner indicated that a generous estimate of the amount of abnormal product present in each case would be 1% of the total acid obtained.

Kinetic Studies.—The presence of a small amount of acidic impurity in the solutions resulted in a fast initial rate so that in each run the first determination was taken as a

(25) Bower and Cooke. *Ind. Eng. Chem., Anal. Ed.,* **15,** 291 (1943).

TABLE IV

MELTING POINTS OF BENZYLAMINE DERIVATIVES OF α-ETHYLALLYL CHLORIDE PRODUCTS

Distillation fraction	M. p., of benzylamine salt °C.	Mixed m. p. with β-ethylvaleric acid salt, m. p. 51–53°	Mixed m. p. with n-heptanoic acid salt, m. p. 66.0–66.5°
3	51–53		30–38
14	50–53		40–44
15	Obtained crystals at 0° which melted at room temp.		
16	Viscous oil		
17	60–63	37–41	63–65
18	65–66	38–41	65.5–66.5
19	66–66.5	37–42	66–66.5
20	66–66.5	37–40	66–66.5
21	65–66	36–40	65.5–66.5

blank and the rate constants calculated assuming this to be zero time.

(A) **Solvolysis of α-Ethylallyl Chloride in Absolute Ethanol.**—A sample of α-ethylallyl chloride was weighed into a 100-ml. volumetric flask and diluted to volume with absolute ethanol (99.96%). Approximately 13 ml. of this solution was sealed into each of a series of tubes which were maintained at 50.00°. At certain time intervals tubes were withdrawn from the thermostat, cooled quickly in an ice-bath and 10.00-ml. aliquots titrated to the first definite phenolphthalein end-point with standard sodium hydroxide solution.

(B) **Condensation of α-Ethylallyl Chloride with Sodium Malonic Ester in Absolute Ethanol.**—To a weighed sample (approximately 0.034 mole) of α-ethylallyl chloride in a 100-ml. volumetric flask was added 85 ml. of 0.44 M alcoholic sodium malonic ester solution and the resulting mixture diluted to volume with absolute ethanol (99.96%). The solution was mixed thoroughly and 10.00-ml. aliquots sealed in test-tubes and placed in a thermostat at 50.00° as rapidly as possible. The samples were removed from the thermostat at intervals, cooled rapidly in an ice-bath and the contents of the tube washed quantitatively into an excess of standard alcoholic hydrochloric acid. The excess hydrochloric acid was then titrated with standard sodium hydroxide solution using brom thymol blue indicator. Determinations of the initial concentration of the sodium malonic ester in the reaction mixture by analyzing one aliquot when the samples were immersed in the thermostat and by analyzing another aliquot which had been heated fifteen hours at 80° to complete the reaction agreed within 0.3%.

Summary

The products resulting from the condensation of sodium malonic ester with α- and γ-methylallyl and α- and γ-ethylallyl chlorides have been investigated. γ-Methylallyl and γ-ethylallyl chlorides reacted entirely to give products which would result from a normal bimolecular displacement. α-Methylallyl and α-ethylallyl chlorides reacted to give 10 and 23%, respectively, of the product which would result from an abnormal bimolecular displacement involving attack on the γ-carbon atom. Kinetic studies with α-ethylallyl chloride indicated that the abnormal product arises from a second-order reaction.

Abnormal bimolecular displacements are briefly discussed.