hydroxide in 25 ml. of ethanol was refluxed under nitrogen with 2.8 g. (0.01 mole) of β-phenyl-β-bromopropiophenone.[5] After filtering to remove the sodium bromide, the solution was placed in the ice-box. The crystalline product thus obtained was filtered and recrystallized from fresh ethanol. Three grams (62%) of the product was obtained; m. p. and mixed m. p. (with product obtained from addition of *p*-chlorobenzeneselenol to chalcone) 105°.

Reaction of β-Phenyl-β-benzeneselenopropiophenone with Alkali.—Five-tenths of a gram (0.0013 mole) of the ketoselenide was dissolved in 15 ml. of ethanol to which 2.5 ml. of 20% sodium hydroxide had been added. The solution was allowed to stand at room temperature for one hour and then diluted with water. Benzalacetophenone (mixed m. p.) was recovered from the reaction, and the characteristic odor of the selenol was evident in the filtrate after acidification.

Reaction of β-Phenyl-β-benzeneselenopropiophenone with Phenylhydrazine.—Five-tenths of a gram (0.0013 mole) of the selenide was refluxed for 15 minutes with 0.5 g. (0.0045 mole) of phenylhydrazine in 15 ml. of glacial acetic acid. 1,3,5-Triphenylpyrazoline crystallized from the solution on dilution with water and cooling. After recrystallization from ethanol, the pure product melted at 134° and showed no depression of melting point when mixed with an authentic sample prepared from benzalacetophenone and phenylhydrazine.[6]

Attempted Addition of Benzeneseleninic Acid to Benzalacetophenone.—Benzeneseleninic acid and its nitrate were prepared according to the procedure of Pyman.[7] The products obtained melted at 118-120° and 114-115°, respectively. Previous investigators have reported melting points of 121° and 124-125° for the free acid and 112° for the nitric acid salt.[7a,b]

Equivalent quantities of benzeneseleninic acid and benzalacetophenone were dissolved in ethanol and allowed to stand at room temperature for several hours. The only product isolated from the reaction was the unreacted ketone (mixed m. p.). No addition product was obtained when benzene or glacial acetic acid was used as the solvent nor when benzeneseleninic acid nitrate was employed in the reaction.

The authors are grateful to Parke, Davis and Company for arranging for the pharmacological testing.

Summary

Aryl selenols undergo 1,4-addition to chalcones without the aid of a catalyst. The course of reaction is analogous to that previously described for the addition of thiols to α,β-unsaturated carbonyl compounds. The resultant γ-ketoselenides are crystalline, sharp melting compounds which decompose into their original components on treatment with dilute alkali. Refluxing these addition products with phenylhydrazine in glacial acetic acid gives rise to the selenium-free 1,3,5-triarylpyrazolines.

No addition product was obtained from benzalacetophenone and benzeneseleninic acid or its nitrate.

Ames, Iowa Received July 5, 1950

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[5] Vorländer and Tubandt, *Ber.*, **37**, 1644 (1904).

[6] Knorr and Laubmann, *ibid.*, **21**, 1205 (1888).

[7] (a) Pyman, *J. Chem. Soc.*, **115**, 166 (1919); (b) Stoecker and Krafft, *Ber.*, **39**, 2197 (1906).

[Contribution from the Department of Chemistry of the University of California at Los Angeles]

Allylic Rearrangements. XXXI. The Reaction of Butenyl Chlorides with Diethylamine and Triethylamine

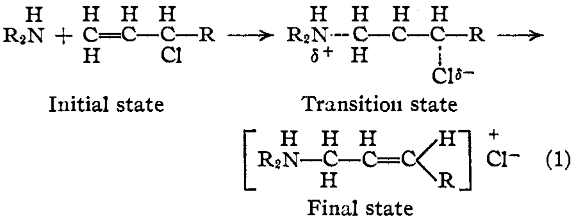
By William G. Young, I. D. Webb[1a] and Harlan L. Goering[1b]

The reaction of α- and γ-ethylallyl chlorides with secondary amines has been described by Meisenheimer and Link,[2] and is of interest due to the abnormal substitution product resulting from secondary chloride. These workers showed that the same product was obtained from either allylic chloride, and identified the product as the γ-ethylallyl isomer by reduction to the corresponding *n*-amylamine. Thus it was established that the primary halide yielded normal products, whereas abnormal products were produced from the secondary chloride. More recently Jones, *et al.*,[3] have observed the formation of abnormal products from the reaction of diethylamine on the halides I (R = H or n-C_4H_9). Normal products were obtained with aniline, ammonia and ethylamine. The abnormal

$$RC{\equiv}CCH{=}CHCHClCH_3 \qquad I$$

products from I may arise from isomerization of an initially formed normal product since treatment of the normal secondary amine, from I (R = H) and ethylamine, with ethyl bromide gives the abnormal product, $RC{\equiv}CCHN(Et)_2CH{=}CHCH_3$.

Analogous to the cases mentioned above, we have known for some time that the reaction of α-methylallyl chloride (II) with diethylamine results in an abnormal substitution product. Due to the lack of necessary evidence, especially kinetic evidence, any conclusions regarding the mechanism of the reactions leading to the abnormal products were necessarily speculative. However, as has been previously suggested,[4] the available facts could be accommodated by an abnormal bimolecular substitution (S_N2') mechanism formulated in equation (1).



$$R_2\overset{H}{N} + \underset{H}{\overset{H}{C}}{=}\overset{H}{C}-\underset{Cl}{\overset{H}{C}}-R \longrightarrow R_2\overset{H}{N}\cdots\underset{\delta+}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{\vdots\,Cl^{\delta-}}{\overset{H}{C}}-R \longrightarrow \left[R_2N-\underset{H}{\overset{H}{C}}-\overset{H}{C}{=}C\begin{matrix}H\\R\end{matrix}\right]^+ Cl^- \quad (1)$$

In view of recent explanations advanced for the non-existence of the S_N2' mechanism[5,6] and the more recent demonstration of its operation in the

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[2] Meisenheimer and Link, *Ann.*, **479**, 211 (1930).

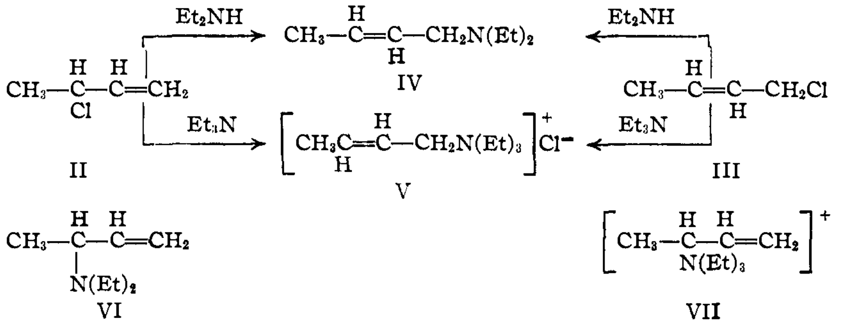
[3] Jones, Lacey and Smith, *J. Chem. Soc.*, 940 (1946).

[4] Kepner, Winstein and Young, This Journal, **71**, 115 (1949).

[5] Catchpole, Hughes and Ingold, *J. Chem. Soc.*, 8 (1948).

[6] Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 86.

condensation of sodium malonic ester with α-methylallyl and α-ethylallyl chlorides,[4] the abnormal product formation in the reactions of amines with certain allylic halides was of considerable interest. The investigation of this phenomenon in the reactions of the butenyl chlorides with diethylamine and triethylamine is the subject of this paper.



When γ-methylallyl chloride (III) and α-methylallyl chloride (II) reacted with diethylamine, either in benzene solution or without solvent, both halides yielded the same product. This product was shown to be N-diethyl-γ-methylallylamine (IV) by reduction to *n*-butyldiethylamine. The primary halide (III) was converted to (IV) in 85% yield by allowing a mixture of the halide and diethylamine to stand at room temperature for 2 days. The secondary halide (II) reacted somewhat slower and produced the abnormal substitution product (IV) in 82% yield when a mixture of the halide and diethylamine was refluxed for 36 hours. A careful examination of the product from the secondary chloride revealed that no detectable amount of the normal substitution product, N-diethyl-α-methylallylamine (VI) was formed under the conditions employed.

Similar to the results mentioned above, the reaction of α-methylallyl chloride (II) with triethylamine in benzene gave only the abnormal product (V), which was identical with the product from γ-methylallyl chloride and triethylamine. This reaction was considerably slower than the reaction with diethylamine. The primary halide was converted to γ-methylallyltriethylammonium chloride (V) in 74% yield by refluxing a benzene solution of the halide and triethylamine for 2 days. The secondary halide required a 13-day reflux period for a 21% conversion to V. The structure of γ-methylallyltriethylammonium chloride was established by reduction to *n*-butyltriethylammonium ion, isolated and identified as the picrate.

Inasmuch as abnormal products could arise from a rearrangement of α-methylallyl chloride (II) prior to substitution or a rearrangement of initially formed normal products, the stabilities of these compounds were investigated under conditions of the corresponding reactions. The normal substitution product for the reaction of α-methylallyl chloride (II) and diethylamine, N-diethyl-α-methylallylamine (VI), and the normal product for II and triethylamine, α-methylallyltriethylammonium ion (VII) were prepared from α-methylallylamine.[7] The structure of α-methylallylamine had previously been established by reduction to *s*-butylamine.[7] α-Methylallylamine was alkylated with ethyl iodide to give a good yield of N-diethyl-α-methylallylamine (VI). The structure of this compound was confirmed by catalytic reduction to N-diethyl-*s*-butylamine. α-Methylallyltriethylammonium (VII) iodide was obtained quantitatively from VI by alkylation with ethyl iodide. The structure of the quaternary compound is apparent from its method of synthesis and from the fact that it is different from the γ-methylallyl isomer.

Available evidence indicates that secondary allylic chlorides are quite stable toward thermal rearrangement. It has been shown that α-methylallyl chloride is unchanged after 3 hours at 85°,[4] and Meisenheimer[2] observed that α-ethylallyl chloride was unchanged by heating the halide in the presence of diethylaniline for 7 hours at 100°. In the present work we have found α-methylallyl chloride to be stable toward rearrangement under conditions required for reaction with diethylamine. When the reaction of α-methylallyl chloride with diethylamine in petroleum ether was interrupted after *ca.* 50% reaction (3 days at 60°), the unreacted halide was found to be >99% α-methylallyl chloride. The allylic halide was also essentially unchanged when a homogeneous solution of the halide in benzene containing N-diethyl-α-methylallylamine (VI) hydrochloride was kept at 75° for 3 days. In this experiment the recovered allylic halide was found to be >95% α-methylallyl chloride. The N-diethyl-α-methylallylamine was also unchanged and recovered in 60% yield as the picrate. These experiments ruled out the possibility of a rearrangement of the halide prior to substitution in the reaction of α-methylallyl chloride with diethylamine. Under the more strenuous conditions required for reaction with triethylamine, α-methylallyl chloride underwent extensive rearrangement. When a solution of the halide in benzene over γ-methylallyltriethylammonium (VII) chloride was kept at 75° for 3 weeks, the recovered halide was found to be rearranged to the extent of about 50%. In this experiment the γ-methylallyltriethylammonium ion was completely decomposed and the only product isolated was a 13% yield of triethylamine. Thus, the abnormal product arising from the reaction of α-methylallylamine and triethylamine may be partially due to an initial rearrangement of the halide.

N-Diethyl-α-methylallylamine (VI) was found to be stable toward thermal rearrangement. It was found by refractive index measurements that the pure amine was unchanged after 1 week at 100°. When a methanolic solution of the amine was kept at 100° for 1 week, a pure picrate derivative of the original amine was obtained in 67% yield. The amine was found to be stable toward acid-catalyzed solvolysis or rearrangement in polar solvents and the amine hydrochloride was found to be stable in non-polar solvents under the conditions of the

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(7) Krueger and Schwarcz, THIS JOURNAL, 63, 2512 (1941).

reaction of α-methylallyl chloride and diethylamine. When methanolic and aqueous solutions of the amine containing two equivalents of *p*-toluenesulfonic acid were kept at 50° for 1 week, the unchanged amine was isolated in yields of *ca.* 60% as the picrate. Similarly, N-diethyl-γ-methylallylamine (IV) was recovered unchanged after refluxing an aqueous solution of the amine hydrochloride for 3 days. The experiment wherein N-diethyl-γ-methylallylamine (VI) hydrochloride was recovered unchanged from a benzene–α-methylallyl chloride solution has been mentioned. The amine hydrochloride was also recovered unchanged in >75% yield after keeping a homogeneous benzene solution at 75° for 3 days.

α-Methylallyltriethylammonium (VII) iodide was found to be stable toward rearrangement or decomposition in polar solvents as the unchanged ion was isolated from methanolic and aqueous solutions after ten days at 100°. However, the quaternary iodide, as well as the chloride, underwent extensive decomposition in benzene, chloroform or a benzene–α-methylallyl chloride mixture. The greater stability of the quaternary salts in polar medium is expected from a consideration of the charge type of decomposition reactions.[8] Indeed Halban[9] has shown that the decomposition of triethylsulfonium bromide is some two hundred times as rapid in non-polar solvents as in methanol, and Hughes and Ingold[10] have observed that the decomposition of *t*-butyldimethylsulfonium hydroxide in aqueous solution is accelerated by the addition of alcohol to the solvent.

The decomposition of α-methylallyltriethylammonium chloride in a mixture of α-methylallyl chloride and benzene has previously been mentioned. The quaternary chloride, as well as the iodide, underwent complete decomposition when suspended in benzene and heated to 75° for 2 weeks. In these experiments a low yield (4 to 11%) of the rearranged quaternary ion, γ-methylallyltriethylammonium ion, was isolated as the picrate.

The above facts rule out the possibility of a rearrangement of the halide, or of initially formed normal substitution products in the reaction with diethylamine. In the reaction with triethylamine this is not the case as rearrangement of the halide, as well as decomposition and rearrangement of the normal substitution product, have been observed under the conditions of the reaction and the mode of formation of the abnormal product is ambiguous.

In the reaction of α-methylallyl chloride with diethylamine, it clear that the actual process of substitution gives rise to the abnormal product, as would be expected from the S_N2' process. As this mechanism requires second order kinetics, the kinetic form of the reaction was investigated. The specific second order rate constant, k_2, for the reaction in dry benzene was evaluated from the integrated form of equation 2, where *a* is the allylic halide concentration, *b* the diethylamine concentration, and *x* the concentration of reactants which have reacted.

$$dx/dt = k_2(a - x)(b - x) \qquad (2)$$

These rate constants showed a marked downward drift, particularly during the later stages of the reaction. Specific third order constants, assuming a reaction first order in halide and second order in diethylamine, were also evaluated and showed a considerable drift. It was found, however, that the data were consistent with a bimolecular process wherein two moles of diethylamine were consumed for each mole of halide (eqn. 3). The second order rate constants, k_2', evaluated from the integrated form of equation (3), showed no trends throughout the course of a rate run. Two kinetic runs are summarized in Table I.

$$dx/dt = k'_2(a - x)(b - 2x) \qquad (3)$$

The instantaneous second order rate constants at zero time, which are included in the table for each run, were evaluated graphically. A large scale plot of concentration of reacted halide, *x*, against time, *t*, was prepared for each kinetic run and the slopes of the resulting curves were measured at the origin with a tangent meter. As shown in equation 4, this measurement gave the initial velocity v_0 directly. The instantaneous rate constants were evaluated from the relationship shown in equation 5.

$$[dx/dt]_{t=0} = v_0 \qquad (4)$$
$$v_0/(RX)_0(Et_2NH)_0 = k_2 \qquad (5)$$

TABLE I

RATE OF REACTION OF α-METHYLALLYL CHLORIDE WITH DIETHYLAMINE IN BENZENE AT 62.7 ± 0.1°

Run I $(RCl)_0 = 0.793$ *M*, $(Et_2NH)_0 = 0.733$ *M*

Time, hr.	$(b - x)$ ml. 0.100 *N* acid	$(b - 2x)$ ml. 0.100 *N* acid	$(a - x)$ ml. 0.100 *N* acid	10^2k_2,[a] liter/mole hr.	$10^2k'_2$,[b] liter/mole hr.
0	14.65	14.65	15.86		2.2[c]
4.75	13.51	12.37	14.72	2.26	2.33
10.75	12.57	10.49	13.78	1.96	2.11
22.0	11.08	7.51	12.29	1.85	2.20
30.7	10.14	5.99	11.35	1.82	2.13
50.4	9.13	3.61	10.34	1.40	2.26
				Mean	2.21 ± 0.07[d]
Run II $(RCl)_0 = 0.397$ *M*; $(Et_2NH)_0 = 0.745$ *M*					
0	14.90	14.90	7.94		2.3[c]
4.9	14.26	13.62	7.30	2.35	2.52
16.0	13.08	11.26	6.12	2.34	2.54
25.0	12.48	10.06	5.52	2.14	2.41
42.2	11.50	8.10	4.54	2.04	2.45
67.8	10.60	6.30	3.64	1.87	2.44
90.3	10.22	5.54	3.26	1.63	2.25
114.3	9.60	4.30	2.64	1.67	2.53
				Mean	2.45 ± 0.07[d]

[a] Value calculated from integrated form of equation 2. [b] Value calculated from integrated form of equation 3. [c] Instantaneous rate constant at zero time. [d] Mean deviation.

The reaction scheme indicated by the kinetics is one wherein one mole of diethylamine is consumed in a bimolecular substitution reaction (eqn. 6) and a second mole of diethylamine is subsequently converted to diethylammonium ion (eqn. 6b). As shown in Table I, the reaction was followed until the unreacted diethylamine concentration

$$Et_2NH + CH_2{=}CHCHClCH_3 \longrightarrow (Et_2NHCH_2CH{=}CHCH_3)^+ + Cl^- \qquad (6)$$

$$(Et_2NHCH_2CH{=}CHCH_3)^+ + Et_2NH \longrightarrow Et_2NH_2^+ + Et_2NCH_2CH{=}CHCH_3 \qquad (6b)$$

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[8] Hughes, *Trans. Faraday Soc.*, 603 (1941).

[9] Halban, *Z. physik. Chem.*, **67**, 129 (1909).

[10] Hughes and Ingold, *J. Chem. Soc.*, 1571 (1933).

$(b - 2x)$, was approximately equal to the product concentration, (x). The kinetics show that over these ranges of concentrations reaction 6b proceeds essentially to completion. This is probably due to a combination of the relative basicity of diethylamine and N-diethyl-α-methylallylamine (IV) and the relative solubilities of the amine hydrochlorides in benzene. Throughout the course of the reaction an amine hydrochloride separates from the benzene solution. It seems probable that diethylamine hydrochloride is less soluble in benzene than the hydrochloride of IV and this may be an important factor in shifting the equilibrium of reaction 6b to the right.

In order to obtain supplementary evidence concerning the rate dependence on diethylamine concentration, two experiments were carried out in which the initial α-methylallyl chloride concentration was held constant and the diethylamine concentration varied by a factor of *ca.* six. The rate dependence on amine concentration was evaluated from the initial reaction velocities (v_0). The results of these experiments are summarized in Table II. These data show that at constant halide concentration a 6.26-fold increase in amine concentration results in a 5.4-fold increase in the rate and thus demonstrate a first order dependence in amine. The difference of about 15% in the instantaneous second order constants in the two experiments is probably largely due to the necessary change in the medium as the amine concentration is changed. The initial solvent was *ca.* 10% diethylamine in Run 3 and about 2% amine in Run 4.

TABLE II

REACTION VELOCITIES OF α-METHYLALLYL CHLORIDE WITH DIETHYLAMINE IN BENZENE AT 74.9°

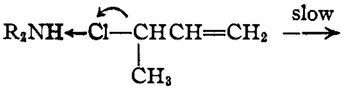
Run	RCl, *M*	Et_2NH, *M*	10^2, *v* mole/liter hr.	10^2k_2,[a] liter/mole hr.
3	0.980	0.852	3.18	3.8
4	.980	.136	0.59	4.4

$[(RCl)_3(Et_2NH)_3]/[(RCl)_4(Et_2NH)_4] = 6.26 \quad V_1/V_2 = 5.4$

[a] Instantaneous specific second order rate constant at zero time.

It is clear from the kinetic experiments, together with the other facts presented concerning the abnormal product formation, that the reaction of diethylamine and α-methylallyl chloride involves a bimolecular substitution reaction where the actual process of substitution gives rise to an abnormal product. We interpret these data in terms of an S_N2' mechanism wherein the nucleophilic attack is on the γ-carbon atom. From the product studies it is apparent that the abnormal bimolecular substitution process (S_N2') operates essentially exclusive, if not entirely so, of the normal (S_N2) substitution process.

Another conceivable process, other than the S_N2' mechanism, which could possibly account for abnormal product formation and be consistent with the facts, is shown by equation (7). This process involves a bimolecular reaction wherein the amine, by hydrogen bonding, functions as an electrophilic reagent and assists the ionization of the allylic chloride to yield a carbonium ion. The ion would necessarily have to coördinate with amine to give only the γ-methyl isomer, rather than a mixture of isomers, to be consistent with the facts. The

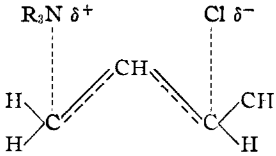


$$R_2NH \leftarrow Cl{-}\underset{\displaystyle CH_3}{\underset{|}{C}}HCH{=}CH_2 \xrightarrow{\text{slow}}$$

$$R_2NH + Cl^- + [CH_3CH{=\!=}CH{=\!=}CH_2]^+ \xrightarrow{\text{fast}} IV \quad (7)$$

latter requirement, as well as a consideration of the medium and the charge type for such a reaction appears to make such a process unlikely. Termolecular processes, wherein one molecule of amine by hydrogen bonding assists the departure of the chloride ion as a second amine molecule attacks the γ carbon atom, have also been considered and ruled out by the kinetic form of the reaction.

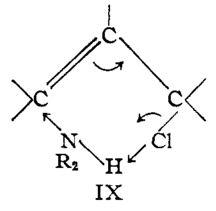
Various interesting aspects of the S_N2' mechanism arise from a geometrical consideration of the process. It appears that an attractive stereopath for the approaching nucleophilic agent and for the leaving chloride ion corresponds to a geometry in the transition state as shown in VIII. Contrary to the linear transition state formulated by Dewar[7]



VIII

for the S_N2' mechanism, the present formulation proposes a configuration wherein the α-, β- and γ-carbon atoms form a nearly equilateral triangle. *p*-Orbitals are used to form the bonds with the entering and leaving entities. The entering amine, partially bonded to the γ-carbon atom, and the leaving chloride ion, partially bonded to the α-carbon atom, are on the same side of the plane of the carbon atoms or in a *cis* configuration. The possibility of this configuration has been pointed out to us by Professor S. Winstein, who suggested that such an arrangement may be most suitable for satisfying the electronic requirements of the α-carbon atom in its transformation from a tetrahedral to a trigonal configuration. The indicated orientation for the approaching nucleophilic agent provides for the high electron density to the α-carbon atom at the opposite side from which the chloride ion is leaving, facilitating the conversion of the orbital bonding chlorine to a *p*-orbital and the accompanying rehybridization of the other α-carbon orbitals.

The juxtaposition of the entering and leaving groups, as formulated in VIII provides a basis for constructive speculation with regard to various aspects of the S_N2' mechanism. A modification of the S_N2' mechanism which has previously been suggested[5] as shown in IX may operate in the reaction of diethylamine and α-methylallyl chloride.



IX

This formulation features a decrease in the chemical inertia by internal hydrogen bonding and is geometrically satisfactory on the basis of a transition state with a configuration as shown in VIII. As the mode of abnormal product formation in the reaction with triethylamine proved to be ambiguous, it is not known if the type of internal hydrogen bonding depicted in IX is essential for the operation of the S_N2' mechanism in reactions with amines or to what extent this mechanism contributes. This aspect of the problem is being investigated further.

A possible explanation for the exclusive γ-carbon atom attack (S_N2') in the reaction of α-methylallyl chloride with a neutral nucleophilic agent (diethylamine) is suggested by the configuration proposed in VIII. When the attacking nucleophilic reagent is neutral, the S_N2' process involves a transition state wherein energy of stabilization is derived from the coulombic attraction of the adjacent partially positive entering group and partially negative leaving group. On the other hand, with an entering negatively charged nucleophilic agent, the transition state for a S_N2' mechanism would be destabilized by electrostatic repulsions between the partially negative entering and leaving groups. The magnitude of such energies may well be of such proportions as to play an important role in determining the substitution process. In this connection it is of interest to note that with negatively charged nucleophilic reagents α-carbon attack (S_N2) seems to be the general rule. For example, reagents such as acetate ion or ethoxide ion[11,12] give normal products exclusively with α-methylallyl chloride. In the reaction of α-methylallyl chloride with diethylmalonate ion there is competition between normal and abnormal substitution with the normal substitution predominating. On the other hand, in these laboratories we have observed several reactions, in addition to the ones presented in this paper, which give abnormal products. All of these cases involve uncharged nucleophilic reagents such as primary and secondary amines and thiourea. These reactions are being scrutinized further; however, indications are that in several cases the abnormal products are formed by an S_N2' process.

Experimental[13]

α- and γ-Methylallyl Chlorides.—The butenyl chlorides were prepared by previously described methods.[4] The properties of the chlorides were as follows: α-methylallyl chloride, b.p. 63.2–63.5°, n^{20}_{D} 1.4150; and γ-methylallyl chloride, b.p. 84°, n^{20}_{D} 1.4350.

Conversion of α-Methylallyl Chloride (II) to N-Diethyl-γ-methylallylamine (IV). A. (Without Solvent).—A solution of 20 g. (0.22 mole) of II and 48 g. (0.66 mole) of diethylamine was heated under reflux for 36 hours. Dilute alkali (0.3 mole) was added to the reaction mixture. The organic layer was separated and the aqueous layer extracted twice with 50-ml. portions of ether. The combined organic layers were dried over magnesium sulfate and finally over potassium hydroxide, and fractionated with an efficient column. After a forerun of ether and diethylamine, the following fractions were collected:

Fraction	B. p., °C.	Wt., g.	$n^{22.3}_{D}$
1	95–137	1.0	1.4291
2	137	4.0	1.4291
3	137–138	4.0	1.4291
4	138	6.0	1.4291
5	138	3.0	1.4291
6	138	3.0	1.4291
Residue	137	3.0	1.4322 (dark)

The yield of product was 23 g. (82%). This single alkylation product was shown to be IV by reduction (see below).

Anal. Calcd. for $C_8H_{17}N$: C, 75.52; H, 13.47. Found: C, 75.10; H, 13.60.

The picrate was formed in methanol and recrystallized from the same solvent, m.p. 81.5–83° (clear melt).

Anal. Calcd. for $C_{14}H_{20}N_4O_7$: C, 47.19; H, 5.66. Found: C, 47.20; H, 5.70.

B. (In Benzene).—A solution of 20 g. of II and 23 g. of diethylamine in 125 ml. of dry benzene was kept at 60° for 3 days. The reaction should have proceeded to *ca.* 50% completion as estimated using the second order rate constant of 0.02 liter mole^{-1} hour^{-1}. Dilute aqueous hydrochloric acid (0.3 mole) was added to the reaction mixture to dissolve the solid product, which had separated, and the unreacted amine. The aqueous extract was made basic and steam distilled. The oil layer in the distillate was taken up in ether, and the aqueous layer extracted with ether. After drying, the ether solution was fractionated. The single alkylation product, b.p. 137.5–139°, n^{20}_{D} 1.4301, weighed 13 g. (46%).

Conversion of γ-Methylallyl Chloride (III) to N-Diethyl-γ-methylallylamine (IV). 1. (Without Solvent).—A solution of 20 g. of III and 50 g. of diethylamine reacted exothermically. After standing for 2 days at room temperature, the product was worked up as in part A above. Fractionation gave 24 g. (85%) of a single alkylation product, b.p. 137–139°, n^{14}_{D} 1.4332–1.4340.

Identical picrates were obtained from three fractions, m.p. 77–79°. A single recrystallization from methanol raised the melting point to 78.5–82°. A mixture of this and the picrate derived from II, m.p. 81.5–83°, showed no depression of melting point.

2. (In Benzene).—A solution of 20 g. of III and 23 g. of diethylamine in 125 ml. of dry benzene was kept at 60° for 2 days. The product was isolated as in part B above. Fractionation yielded 15.5 g. (55%) of a single alkylation product, b.p. 137–139°, n^{17}_{D} 1.4323.

Calcd. for $C_8H_{17}N$: neut. equiv., 127. Found: neut. equiv., 129.

Reduction of N-Diethyl-γ-methylallylamine (IV) to *n*-Butyldiethylamine.—A solution of 12.7 g. (0.10 mole) of amine (IV) in 40 ml. of methanol was reduced in the presence of about 0.1 g. of Adams catalyst in a Burgess–Parr apparatus. About 3 hours was required for the absorption of 0.12 mole of hydrogen. The solution was filtered and fractionated. A considerable amount of hydrogenolysis was indicated by the amount of volatile amines (b.p. <80°) produced; however, a main fraction of 6.0 g. (45%) was obtained, b.p. 136.5; n^{20}_{D} 1.4133.

Calcd. for $C_8H_{19}N$: neut. equiv., 129. Found: neut. equiv. 131.

A picrate was formed in methanol and crystallized at low temperatures as fine yellow crystals, m.p. 47–48.5°.

Authentic ***n*-butyldiethylamine** was prepared by heating a mixture of 13.5 g. of butyl bromide and 20 g. of diethylamine overnight. The product was obtained in 90% yield and purified by fractionation, b.p. 134–135°, n^{20}_{D} 1.4135 (lit.[14] b.p. 136–137°).

The picrate of *n*-butyldiethylamine was prepared in the usual manner, m.p. 47–48.5°. When mixed with the picrate described above, the m.p. was not depressed.

Isolation of Unreacted α-Methylallyl Chloride (II).—A solution of 20 g. of II and 16 g. of diethylamine in 110 ml. of petroleum ether, b.p. 35°, was prepared in a pressure bottle and kept at 60° for 3 days. The unreacted amine was removed by extraction with dilute aqueous acid and the organic layer dried over potassium carbonate and frac-

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(11) Roberts and Young, Winstein, THIS JOURNAL, **64**, 2157 (1942).

(12) Catchpole and Hughes, *J. Chem. Soc.*, 4 (1948).

(13) Melting points and boiling points are not corrected.

(14) Hager and Marvel, THIS JOURNAL, **48**, 2689 (1926).

tionated. After removal of the solvent the following fractions were obtained:

Fraction	B. p., °C.	Ml.	$n^{20}D$
1	36–62	2.0	
2	62–63	10.4	1.4150
3	Residue	0.4	1.4205

The recovery of unchanged α-methylallyl chloride amounted to *ca.* 10.5 g. The quantity of the rearranged chloride, γ-methylallyl chloride (III), in the residue did not exceed 0.1 ml.

Stability of N-Diethyl-γ-methylallylamine (IV) Hydrochloride.—A solution of 20 g. of IV in 250 ml. of hydrochloric acid solution, just acid to methyl orange, was refluxed for 3 days. The amine was isolated and fractionated. A main fraction of 18.9 g. (95%), b.p. 138–139°, $n^{20}D$ 1.4307, of the unchanged amine was obtained.

Conversion of α-Methylallyl Chloride (II) to γ-Methylallyltriethylammonium (V) Chloride.—To a solution of 10 g. (1.11 moles) of II in 50 ml. of dry benzene was added 13.5 g. (1.33 moles) of fractionated triethylamine, b.p. 88.9°. After 1 day of reflux very little product had separated so another portion of triethylamine was added. After a total reflux period of 13 days during which time the solution darkened somewhat, 4.63 g. (21%) of crude V chloride had separated from solution, m.p. *ca.* 165° (dec.). The hygroscopic product was recrystallized one time from acetone–ethanol mixture, m.p. 174.5–175.5° (dec.).

Anal. Calcd. for $C_{10}H_{22}NCl$: N, 7.31. Found: N, 7.12.

The picrate was prepared from 0.50 g. of the quaternary chloride by treating a concentrated aqueous solution of the latter with an equivalent amount of 10% aqueous sodium picrate.[15] After a single recrystallization from aqueous ethanol, 0.910 g. (91%) of the picrate was obtained, m.p. 108–109°. An analytical sample was prepared by recrystallization to a constant melting point of 108.5–109.2° (clear melt).

Anal. Calcd. for $C_{16}H_{24}N_4O_7$: C, 49.99; H, 6.29. Found: C, 49.95; H, 6.28.

Conversion of γ-Methylallyl Chloride (III) to γ-Methylallyltriethylammonium (V) Chloride.—A solution of 10 g. of III and 13.5 g. of triethylamine in 50 ml. of dry benzene was heated under reflux. After 20 hours 8.9 g. of product had separated and was removed by filtration. The filtrate was refluxed an additional 28 hours and 6.6 g. of product obtained. The combined yield of 15.5 g. is 74% theory. The crude hygroscopic product, m.p. *ca.* 170° (dec.), after recrystallization from an acetone–ethanol mixture, melted at 175.5–176.5° (dec.).

Anal. Calcd. for $C_{10}H_{22}NCl$: N, 7.31. Found: N, 7.12.

The picrate of the quaternary amine was obtained in 90% yield after a single recrystallization from aqueous ethanol, m.p. 106–107°. An analytical sample was prepared by additional recrystallizations, m.p. 109–109.5° (clear melt). When this picrate was mixed with that derived from II, m.p. 108–109°, the mixture melted at 108–109°.

γ-Methylallyltriethylammonium (V) iodide was prepared from the quaternary chloride by treating a cold aqueous solution of 1.10 g. of V chloride with silver oxide in order to convert the quaternary chloride to the quaternary hydroxide. The solution was filtered and carefully neutralized, to congo red, with hydrogen iodide. The solution was concentrated to dryness and the solid residue recrystallized from ethanol–ethyl acetate mixtures. The yield was 1.55 g. (96%), m.p. 141–144°. An analytical sample, m.p. 143.4–144.5° (clear melt), was prepared by additional recrystallizations from the same solvent.

Anal. Calcd. for $C_{10}H_{22}NI$: C, 42.41; H, 7.83. Found: C, 42.45; H, 7.83.

***n*-Butyltriethylammonium Iodide.**—A solution of 20 g. of freshly distilled *n*-butyl iodide and 13.5 g. of triethylamine was heated on a steam-bath for *ca.* 30 hours. The resulting semi-solid solution was washed onto a filter with ether. The crude product, m.p. 204–205°, weighed 18.7 g. (60%). After recrystallization from an ethyl acetate–ethanol mixture the material melted at 204.5–205° (clear melt), (lit.[14] 205° (dec.)).

The picrate was prepared and purified in the usual manner, m.p. 110–110.5° (clear melt).

Anal. Calcd. for $C_{16}H_{26}N_4O_7$: C, 49.73; H, 6.78. Found: C, 49.84; H, 6.59.

Reduction of γ-Methylallyltriethylammonium Ion (V) to *n*-Butyltriethylammonium Ion.—γ-Methylallyltriethylammonium (V) chloride was reduced according to the method of Buchman and Howton.[15,16] The quaternary chloride (0.90 g., 0.0074 mole) was converted to the dibromide in chloroform. The dibromide, which was not crystallized, was dissolved in 10 ml. of water and shaken with 0.50 g. of palladium-on-barium sulfate and moist hydrogen. A total of 240 ml. (calcd. 234 ml.) of hydrogen was absorbed. After filtering, the solution was concentrated to dryness under reduced pressure. The residue was taken up in water and again concentrated to dryness in order to remove the excess hydrogen bromide. The residual solid quaternary salt was converted to the iodide by treating a cold aqueous solution with silver oxide, filtering and neutralizing the filtrate with hydrogen iodide. The iodide was isolated by concentration of the aqueous solution to dryness. The crude iodide was dissolved in ethanol and precipitated with ethyl acetate. The yield was 1.38 g. or 93%, m.p. *ca.* 195° (dec.). After recrystallization from an ethanol–ethyl acetate mixture the white solid melted at 203–204° (clear melt). When this compound was mixed with authentic *n*-butyltriethylammonium iodide, m.p. 203.5–204°, the m.p. was not depressed.

The quaternary iodide, obtained by the reduction of V, was converted to the picrate, m.p. 110–111° (clear melt). When this picrate was mixed with authentic *n*-butyltriethylammonium picrate, m.p. 110–111°, the m.p. was not depressed.

α-Methylallylamine.—This compound was prepared by a modification of the procedure described by Krueger and Schwarz.[7,17] γ-Methylallyl chloride (II) was converted to γ-methylallyl thiocyanate in 80% yield by the slow addition of II to a refluxing solution of ammonium thiocyanate in acetone. This conversion was also carried out in ethanol using potassium thiocyanate with somewhat lower yields in the single preparation carried out. The γ-methylallyl thiocyanate was quantitatively isomerized[18] to α-methylallyl isothiocyanate by rapid distillation. A thiourea derivative, m.p. 106–106.5° (lit. 105°), was obtained by treatment of the isothiocyanate with alcoholic ammonia.

α-Methylallyl isothiocyanate was hydrolyzed to α-methylallylamine by refluxing a well-stirred solution of the isothiocyanate in 20% hydrochloric acid for 9 hours. The stirring shortened the required reflux period considerably. The acid solution was concentrated to dryness under reduced pressure, treated with water and concentrated again to remove all of the excess acid. The free amine was obtained from the salt by standard procedures.[19] Fractionating with an efficient column gave a 30% yield (based on α-methylallyl isothiocyanate) of a fraction with constant boiling point and refractive index, b.p. 63.2–63.3°, $n^{20}D$ 1.4142 (lit.[7] b.p. 62.3°, $n^{20}D$ 1.4155–1.4150).

N-Diethyl-α-methylallylamine (VI).—A solution of 30 g. (0.423 mole) of α-methylallylamine and 135 g. (0.846 mole) of fractionated ethyl iodide was placed in a flask equipped with reflux condenser and ice-bath. The reaction was exothermic and the temperature was kept below the reflux temperature by intermittent cooling with an ice-bath. After the reaction had subsided, 27.4 g. (0.423 mole) of 87% powdered potassium hydroxide was added to the solution. The reaction was exothermic and maintained gentle reflux. After heating the reaction solution for 1 hour on a steam-bath, an equal volume of water was added and the resulting solution concentrated to dryness. The amine was isolated from the residual salt[19] and fractionated. A middle fraction with constant boiling point and refractive index weighed 35 g. (66%), b.p. 129.3°, $n^{20}D$ 1.4262.

Anal. Calcd. for $C_8H_{17}N$: C, 75.52; H, 13.47; N, 11.01. Found: C, 75.53; H, 13.64; N, 11.30.

The picrate was prepared in methanol and recrystallized from aqueous ethanol, m.p. 113.2–113.7° (clear melt).

Anal. Calcd. for $C_{14}H_{20}N_4O_7$: C, 47.19; H, 5.66. Found: C, 47.15; H, 5.57.

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[15] Howton, This Journal, **69**, 2555 (1947).

[16] Buchman and Howton, *ibid.*, **70**, 2517 (1948).

[17] See also Vladimirova and Petrov, *J. Gen. Chem.* (*U. S. S. R.*), **16**, 2141 (1946); *C. A.*, **42**, 108 (1948).

[18] Mumm and Richter, *Ber.*, **73B**, 843 (1940).

[19] Leffler, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons Inc., New York, N. Y., 1943, p. 24.

N-Diethyl-α-methylallylamine (VI) hydrochloride was prepared by dissolving VI in alcoholic hydrogen chloride or by passing dry hydrogen chloride through an ether solution of the amine. After removal of the solvent under reduced pressure the residual oil crystallized while standing overnight in a vacuum desiccator. The amine hydrochloride was obtained as a white solid with a slight greenish tinge after recrystallization from ethyl acetate. The compound was extremely hygroscopic and was identified by conversion to the picrate.

N-Diethyl-*s*-butylamine (**A**).—*s*-Butylamine (Eastman Kodak Co. white label) was alkylated with ethyl iodide by the procedure described above. The yield was 65%, b.p. 132°, n^{20}D 1.4128 (lit.[20] b.p. 131° for *d*-isomer).

(**B**).—A solution of 10 g. of fractionated *s*-butyl bromide and a threefold excess of diethylamine was heated to 90° for several days. Alkali was added to the reaction mixture and the amines separated and dried. The amines were separated by fractionation; yield 80%, b.p. 129–131°; n^{20}D 1.4128.

The picrate was prepared in the usual manner, m.p. 116–116.5° (lit.,[20] m.p. 117° for *d*-isomer).

The tertiary amine was quantitatively converted to *s*-**butyltriethylammonium iodide** by heating a solution of amine with a twofold excess of ethyl iodide. The quaternary iodide was recrystallized from ethyl acetate–ethanol mixtures, m.p. 234–235° (dec.).

Anal. Calcd. for $C_{10}H_{24}NI$: C, 42.11; H, 8.48; N, 4.91; I, 44.50. Found: C, 41.75; H, 8.69; N, 4.68; I, 44.28 (Volhard).

The picrate of the quaternary amine was obtained as soft yellow crystals from ethanol–Skellysolve B mixtures, m.p. 157.5–158.5° (clear melt).

Anal. Calcd. for $C_{16}H_{26}N_4O_7$: C, 49.73; H, 6.78. Found: C, 49.48; H, 6.89.

Reduction of N-Diethyl-α-methylallylamine (VI) to N-Diethyl-*s*-butylamine.—A solution of 1.410 g. (0.011 mole) of VI in 5 ml. of methanol was reduced at room temperature and atmospheric pressure over 0.15 g. of Adams catalyst. The reduction required 0.0107 mole of hydrogen in excess of that required for the reduction of the catalyst, and was complete in 1 hour. The reduction product was identified as N-diethyl-*s*-butylamine by the picrate, m.p. 114.5–115.0°. When this picrate was mixed with authentic *N*-diethyl-*s*-butylamine picrate, m.p. 116–116.5, the m.p. was not depressed. When the picrate was mixed with that of the original amine, m.p. 113.3–114.0°, the mixture melted at 111.5–113°.

α-Methylallyltriethylammonium (VII) Iodide.—A solution of 2.3 g. of N-diethyl-α-methylallylamine (VI) and 6 ml. of fractionated ethyl iodide in a sealed tube was heated on a steam-bath overnight. The resulting semisolid solution was washed on to a filter with ether. The crude iodide, 5.1 g. (100%), was recrystallized from ethyl acetate–ethanol mixtures, m.p. *ca.* 173° (dec.).

Anal. Calcd. for $C_{10}H_{22}NI$: C, 42.41; H, 7.83; N, 4.95; I, 44.81. Found: C, 42.30; H, 8.08; N, 4.94; I, 44.74 (Volhard).

The picrate of the quaternary iodide, m.p. 172–173° (dec.), was prepared in the usual manner.

Anal. Calcd. for $C_{16}H_{24}N_4O_7$: C, 49.99; H, 6.29. Found: C, 49.76; H, 6.63.

α-Methylallyltriethylammonium bromide was prepared from the iodide by converting the latter to the quaternary hydroxide with silver oxide, filtering and neutralizing with hydrobromic acid. The hygroscopic bromide was obtained in 90% yield and recrystallized from ethyl acetate–ethanol mixtures, m.p. *ca.* 186° (dec.).

Anal. Calcd. for $C_{10}H_{22}NBr$: C, 50.84; H, 9.39. Found: C, 50.87; H, 9.27.

α-Methylallyltriethylammonium chloride was prepared in a similar manner. The white hygroscopic solid was recrystallized from an ethyl acetate–ethanol mixture. The material was not analyzed, but there is no question concerning its identity since with sodium picrate it gave pure α-methylallyltriethylammonium picrate.

Stability of N-Diethyl-α-methylallylamine (VI) (A).—Pure VI, n^{20}D 1.4263, was sealed in an ampule and kept at 100° for 1 week. The amine was unchanged as indicated by the refractive index, n^{20}D 1.4263.

(B).—A solution of 0.77 g. of VI in methanol was kept at 100° for 1 week. The solution, after treatment with 1.5 g. of picric acid followed by dilution with water, yielded the picrate derivative of the unchanged amine. After recrystallizing from ethanol–Skellysolve B mixtures, the picrate derivative weighed 1.45 g. (67%), m.p. 113–113.5°.

(C).—A solution of 0.77 g. (0.006 mole) of VI and 2.0 g. (0.011 mole) of *p*-toluenesulfonic acid monohydrate in 5 ml. of methanol was sealed in an ampule and kept at 50° for 2 days. The solution was placed in a distilling flask, 3.0 g. of potassium hydroxide in 5 ml. of water was added, and the amine distilled. To the 7 ml. of distillate collected was added 3.0 g. of picric acid, and the picrate derivative obtained was recrystallized from aqueous ethanol and from ethanol–Skellysolve B mixtures. The yield of purified picrate, m.p. 112.5–113.5° (clear melt), was 1.25 g. (58%). When mixed with the picrate of the original amine, m.p. 112.5–113.5, the m.p. was not depressed.

(D).—When the above experiment was carried out in water and kept at 50° for 1 week, 1.35 g. (63%) of the purified picrate, m.p. 112.5–113.5°, was obtained.

Stability of N-Diethyl-α-methylallylamine Hydrochloride in Benzene.—An homogeneous solution of 0.436 g. of N-diethyl-α-methylallylamine hydrochloride in 10 ml. of benzene was kept at 75° for 3 days. The solvent was removed under reduced pressure and the residual amine hydrochloride was converted to the picrate by the addition of aqueous sodium picrate solution. After recrystallization from aqueous ethanol and an ethanol–Skellysolve B mixture, the picrate derivative weighed 0.65 g. (69%), m.p. 113–114°. When mixed with authentic N-diethyl-α-methylallylamine picrate, the m.p. was not depressed.

Isolation of Unchanged N-Diethyl-α-methylallylamine and α-Methylallyl Chloride after Heating Together in Benzene.—A homogeneous solution of 0.870 g. of *N*-diethyl-α-methylallylamine hydrochloride and 18.55 g. of α-methylallyl chloride in 20 ml. of dry benzene in a pressure bottle was kept at 75° for 3 days. The solution was cooled and transferred into a flask with a side arm attached to a receiver. The solution was chilled for some time in a Dry Ice–acetone-bath and the system evacuated to *ca.* 1 mm., and sealed. The Dry Ice-bath was removed from the flask containing the solidified solution and placed around the receiver. In this manner the volatile material was vaporized and condensed at low temperatures.

The solid residue from the above distillation was taken up in a small amount of water and converted to the picrate derivative with aqueous sodium picrate. After recrystallizations from an aqueous ethanol solution and an ethanol–Skellysolve B mixture, 1.10 g. (58%) of picrate of the unchanged N-diethyl-α-methylallylamine was obtained, m.p. 113–114° (clear melt). When mixed with an authentic sample, m.p. 113–114°, the m.p. was not depressed.

The benzene solution of α-methylallyl chloride obtained in the above distillation was analyzed by careful fractionation with an efficient column. The following fractions were obtained:

Fraction	B. p., °C.	n^{20}D	Wt., g.
Total reflux	63.3	....	.....
1	63.3–64	1.4150	13.551
2	64–77.5	1.4578	1.157
3	77.5–79.0	1.4870	.923
4	79.0–80.0	1.4952	2.276
5	80.0	1.4970	12.709
Hold-up	....	1.4950	1.200

From the refractive index it was estimated that fractions one, two and three contain 14.30 g. of unchanged α-methylallyl chloride, b.p. 63.5°, n^{20}D 1.4150. The γ-methylallyl chloride, b.p. 84°, n^{20}D 1.4352, if present, could not be separated from the benzene; however, the maximum amount of this halide in the hold-up and fractions four and five was estimated as 1.20 g. from the refractive index of the various fractions. Thus the recovered halide 15.4 g. (83%) contained a maximum of 8% γ-methylallyl chloride and may not have contained any.

In order to obtain a check on the amount of organic chloride in fractions four, five and the hold-up, these fractions were combined, diluted with an equal volume of ethanol and shaken overnight with excess aqueous silver nitrate. The 0.775 g. of dry silver chloride obtained corresponds to

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[20] Leithe, *Ber.*, **63**, 800 (1930).

0.490 g. of butenyl halide, indicating that the original estimate of 8% γ-methylallyl chloride was high and a more accurate maximum value would be 4%.

Decomposition of α-Methylallyltriethylammonium Chloride and Rearrangement of α-Methylallyl Chloride when Heated Together in Benzene.—This experiment was carried out in a similar manner to the one above with the exception that α-methylallyltriethylammonium chloride, 0.283 g., was used and the solution was kept at 75° for 17 days. The quaternary chloride did not dissolve in the solution and during the heating period the solution, as well as the solid material, turned dark. Upon cooling, white needles separated.

The non-volatile decomposition products were isolated as described in the preceding section. This material was not completely soluble in water. Treatment of the water-soluble components with sodium picrate gave 0.050 g. of a derivative which, after recrystallization from an ethanol–Skellysolve B mixture, melted at 169–171° (clear melt). This material was identified as triethylamine picrate by comparison with an authentic sample, m.p. 171–172.5° (clear melt). A mixture melted at 169–172°. Apparently the quaternary chloride was completely decomposed as no picrate derivate corresponding to either allylic isomer could be isolated.

Fractionation of the benzene solution showed that the α-methylallyl chloride had isomerized extensively. A total of 5.46 g. of unchanged α-methylallyl chloride was isolated but there was a considerable amount of organic halide which could not be separated from benzene and presumably was γ-methylallyl chloride. The amount of this isomer was estimated as 6.14 g. from the refractive index of the high boiling fractions and hold-up. Treatment of these combined fractions with silver nitrate yielded 11.00 g. of silver chloride corresponding to 6.97 g. of γ-methylallyl chloride. Thus the total butenyl chloride accounted for was about 63% and this material was about 53% γ-methylallyl chloride.

Decomposition of α-Methylallyltriethylammonium Chloride and Iodide in Benzene.—A suspension of α-methylallylammonium iodide, 0.65 g., in 10 ml. of benzene was refluxed for 2 weeks. Decomposition was indicated by the darkening of the solution and of the insoluble material. After removal of the solvent the residual oil was extracted with warm water and treated with sodium picrate solution. The picrate, which separated in an impure form, after recrystallization weighed 0.10 g. (11%), m.p. 107.5–108.5°. This material was shown to be γ-methylallyltriethylammonium picrate by comparison with an authentic sample, m.p. 109.5–110°, and by analysis. When mixed with an authentic sample, the mixture melted at 109–110°.

When the above experiment was repeated with α-methylallyltriethylammonium chloride, similar results were obtained. The picrate of the rearranged material, γ-methylallyltriethylammonium picrate, m.p. 105–107°, was obtained in 4% yield. Apparently the original quaternary salts were completely decomposed and rearranged as none of the original material could be isolated.

Stability of α-Methylallyltriethylammonium Ion (VII) in Aqueous and Methanolic Solutions. A.—An aqueous solution containing 0.200 g. of VII iodide was sealed in an ampule and kept at 100° for 10 days. Addition of 3 ml. of 20% sodium picrate yielded a picrate which was purified by recrystallizations from ethanol–Skellysolve B mixtures. The yield of purified picrate was 0.180 g. (66%), m.p. 170–173° (dec.). When this material was decomposed beside authentic α-methylallyltriethylammonium picrate, the decomposition point was identical with respect to time and temperature. A mixture also had an identical decomposition point.

B.—When the above experiment was carried out in methanol at 50° for 10 days, 0.200 g. (73%) of the purified picrate was obtained. This picrate had an identical decomposition point, *ca.* 170–173°, with respect to time and temperature as the picrate of the original α-methylallyltriethylammonium ion.

Kinetic Part.—The data presented in Tables I and II were obtained as follows. Solutions were made up by weighing samples of pure α-methylallyl chloride into a volumetric flask, and diluting with dry, thiophene free benzene. Diethylamine, b.p. 55°, was added from a pipet and the solution made up to the mark with pure benzene. All concentrations are given for 25°. Two-ml. aliquots were measured with a "normax" pipet and sealed into soft glass ampules. Analyses were performed by crushing the ampules under 50 ml. of water and titrating to the methyl red end-point with 0.1000 *N* hydrochloric acid. Time was recorded from the time that the ampules were placed in the thermostat maintained at 62.7 ± 0.1°.

For runs 3 and 4 the reaction solutions were made up as described above. In these runs 10-ml. aliquots were employed. Time was recorded from the time that the ampules were placed in the 74.9 ± 0.1° thermostat. At desired time intervals an ampule was removed from the thermostat and immersed in an ice-bath to quench the reaction. Analyses were performed as follows. The contents of the ampules were washed into a 50-ml. separatory funnel with about 15 ml. of distilled water. About 15 ml. of petroleum ether was added and the aqueous layer separated. The organic layer was washed twice with water and the combined aqueous layers were acidified with acetic acid to the phenolphthalein end-point. The chloride ion in the aqueous solution was titrated with silver nitrate using potassium chromate indicator for Run 3 and dichlorofluorescein for Run 4. The following data were obtained:

Run 3		Run 4	
t, min.	Ml. 0.1182 *M* silver nitrate	*t*, min.	Ml. 0.0118 *M* silver nitrate
1	0.00	0	0.0
54	3.19	60	6.0
83	4.55	60	6.0
112	6.12	94	8.7
145	7.70	112	10.7
180	9.08	112	10.4
		147	13.4
		164	14.5
		180	15.7
		197	16.8

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Summary

The reaction of diethylamine with either α- or γ-methylallyl chloride yields N-diethyl-γ-methylallylamine. The formation of the abnormal product from α-methylallyl chloride is not due to a rearrangement of the halide prior to substitution or a rearrangement of an initially formed normal substitution product. Kinetic studies show that the formation of the abnormal product involves a second order reaction.

The reaction of triethylamine and α-methylallyl chloride gives a low yield of a completely abnormal product, identical with the product obtained from γ-methylallyl chloride. The mode of abnormal product formation in this reaction is ambiguous inasmuch as α-methylallyl chloride and the normal substitution product are not stable under the conditions of the reaction.

Some aspects of the abnormal bimolecular displacement are discussed in terms of a proposed geometry for the transition state.

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