132°, $[\alpha]_D$ +10.27° (*c* 8.45, EtOH), +10.64° (*c* 8.96, EtOH). The melting point was unchanged on repeated chromatography.

The remaining 3.44 g. of alcohol product was converted to acid phthalate in the conventional manner. Crystallization from ethyl acetate–pentane gave 0.51 g. of apoisobornyl acid phthalate, m.p. 173–174°, m.p. reported[19] for *dl*-acid phthalate, 174–175°. The remainder of the acid phthalate was saponified and converted to acetate; 3.05 g., b.p. 109° (25 mm.), n^{25}_D 1.4597.

Inspection of the infrared spectrum of the acetate showed a similarity with the spectra of mixtures of apoisobornyl, *exo*-camphenilyl and β-fenchoisocamphoryl acetates.[9] The absence of α-nopinyl acetate was indicated by the absence of characteristic absorption peaks at 8.9, 9.35, 10.2 and 10.8 μ. The infrared spectrum of the acetate was compared with a mixture, 49.7% apoisobornyl and 50.3% β-fenchoisocamphoryl acetate, and with a mixture, 76.2% β-fenchoisocamphoryl, 19.1% apoisobornyl and 3.4% *exo*-camphenilyl acetate, these mixtures being available from other work.[9] By comparison of optical densities at 8.7 and 9.3 μ, an estimate of the composition of the acetate mixture was reached. This was 50% β-fenchoisocamphoryl, 43% apoisobornyl and 7% *exo*-camphenilyl acetates. On this basis, the calculated[9] n^{25}_D is 1.4598, compared to the observed n^{25}_D 1.4597.

Saponification of 2.67 g. of the acetate mixture and careful chromatography of the alcohol afforded 1.015 g. (45%) of apoisoborneol, m.p. 131–132°, $[\alpha]_D$ +13.44° (*c* 8.60, EtOH). Further elution with pentane and pentane–10% ether gave 1.250 g. of a low-melting alcohol, m.p. 54–58°, $[\alpha]_D$ +0.18° (*c* 7.73, EtOH). The *dl*-β-fenchoisocamphorol has[9,28] m.p. 60–61°.

Preparation of an acid phthalate from 0.965 g. of the alcohol, m.p. 54–58°, gave 1.43 g. of β-fenchoisocamphoryl acid phthalate, m.p. 129–131° (m.p.[19] of *dl*-β-fenchoisocamphoryl acid phthalate 130–131°).

An earlier solvolysis of α-nopinyl *p*-bromobenzenesulfonate in 80% aqueous dioxane gave rise to a product which was converted directly to acid phthalate, m.p. 154–156°, markedly depressed by admixture of β-nopinyl acid phthalate, m.p. 156°. No appreciable quantity of neutral material remained after the conversion to acid phthalate. Saponification of the acid phthalate and chromatography gave alcohol fractions, m.p. 133–134° and m.p. 141°. Conversion of some of the 133–134° alcohol fraction to *p*-bromobenzenesulfonate gave rise to a material which behaved in acetolysis identically with apoisobornyl *p*-bromobenzenesulfonate.[9] The integrated rate constant for acetolysis at 25° fell from 6.0×10^{-4} sec.$^{-1}$ to 3.4×10^{-5} sec.$^{-1}$ between 36 and 92% solvolysis, 24% being the zero point for the run.

Solvolysis of β-Nopinyl *p*-Bromobenzenesulfonate in 60% Acetone.—A solution of 9.3 g. of β-nopinyl *p*-bromobenzenesulfonate in 300 ml. of 60% acetone was refluxed for 30 hours with 7 g. of calcium carbonate. The product was worked up as in the case of the α-nopinyl *p*-bromobenzenesulfonate, and then it was chromatographed. Elution with pentane gave initially a small fraction which may have contained apocyclene. Elution with pentane–10% ether gave 1.634 g. of pure apoisoborneol, m.p. 139–141°, $[\alpha]_D$ +14.12° (*c* 8.44, EtOH), m.p. unchanged on repeated chromatography, m.p. on admixture with the apoisoborneol from the α-nopinyl *p*-bromobenzenesulfonate, 132–134°.

The remaining alcohol was acetylated to give 0.95 g. of the acetate, b.p. 109° (25 mm.), n^{25}_D 1.4594. Examination of the infrared absorption spectra of the acetate mixture and that of the acetate from the solvolysis of α-nopinyl *p*-bromobenzenesulfonate, and comparison of the peak intensities at 8.65, 8.85 and 9.25 μ led to an estimate of 68% β-fenchoisocamphoryl, 30% apoisobornyl and 2% *exo*-camphenilyl acetates in the mixture. This leads to a calculated n^{25}_D 1.4592.

Conversion of some of the 139–141° alcohol to *p*-bromobenzenesulfonate gave rise to a material which behaved just as does apoisobornyl *p*-bromobenzenesulfonate in acetolysis.

Acetolysis of α-Nopinyl *p*-Bromobenzenesulfonate.—A solution of 8.5 g. of α-nopinyl *p*-bromobenzenesulfonate in 450 ml. of 0.1 *N* sodium acetate in acetic acid was heated at 100° for 7 hours. The acetate, after pentane extraction, was reduced with lithium aluminum hydride in ether in the usual way, and the alcohol was chromatographed.

The first two pentane fractions contained 221 mg. of apocyclene, identified[9] by the infrared absorption of its carbon disulfide solution by means of the characteristic absorption peak at 12.4 μ. Further elution with pentane yielded 1.068 g. of apoisoborneol, m.p. 139–141°. Elution with pentane and pentane–10% ether then gave 610 mg. of the oily alcohol, very predominantly β-fenchoisocamphorol.

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(28) G. Komppa and S. Beckmann, *Ann.*, **537**, 140 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XXXIV. The Reaction of Trimethylamine with α-Methylallyl Chloride[1a,b]

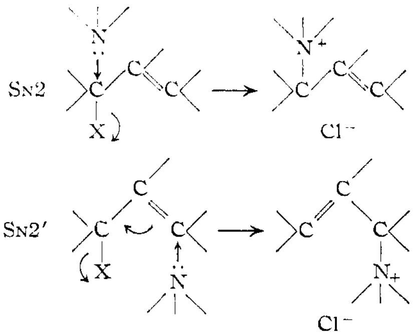
BY WILLIAM G. YOUNG, ROBERT A. CLEMENT[1c] AND CHIN-HUA SHIH

RECEIVED NOVEMBER 30, 1954

A study has been made of the bimolecular displacement reaction between trimethylamine and α-methylallyl chloride in acetone solution. The reaction was found to consist of simultaneous SN2 and SN2′ displacements. Reaction rates and thermodynamic functions of activation for the two modes of displacement are presented.

Introduction

Bimolecular nucleophilic displacement upon an allylic system may proceed by two mechanisms: normal displacement, SN2, and abnormal displacement, SN2′, as illustrated below for the general case with an unspecified nucleophile, N, and an unspecified leaving group, X. The possibility of SN2′ displacement upon allylic systems was recognized,[2] on theoretical grounds, prior to conclusive experimental demonstration. Experimental validation of the theory first was provided when it was



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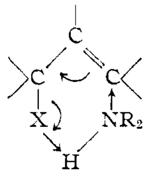
(1) (a) A preliminary report of this work appeared in *Science*, **115**, 488 (1952); (b) acknowledgment is made of the partial support of this research by a National Science Foundation Grant; (c) Standard Oil Company of California, Research Fellow, 1952.

(2) (a) E. D. Hughes, *Trans. Faraday Soc.*, **34**, 185 (1938); (b) S. Winstein, Ph.D. Dissertation, California Institute of Technology, 1938.

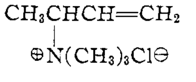
demonstrated that the reactions of malonate ion with α-methylallyl chloride and α-ethylallyl chloride occur, in part, by S_N2' displacements,[3] and that the reaction of diethylamine with α-methylallyl chloride proceeds exclusively by S_N2' displacement.[4] Subsequently, additional cases of S_N2' displacements have been reported by numerous investigators.[5]

In this Laboratory, interest in allylic systems has been concerned, in part, with their displacement reactions with amines. It has been pointed out[4] that, with secondary amines, an important factor in promoting S_N2' displacement might be a specific hydrogen-bond interaction between the entering and leaving groups, as illustrated for the general case. An attempt to evaluate the importance of such an effect by observing the course of displacement upon α-methylallyl chloride by triethylamine was inconclusive.[4] The present work was undertaken to obtain conclusive evidence concerning the importance of a specific hydrogen-bonded interaction in the S_N2' displacement of amines upon allylic systems. If S_N2' displacement is observed with tertiary amines, then it is clear that this interaction is not of fundamental importance. To this end, the reaction of trimethylamine with α-methylallyl chloride in acetone was examined.



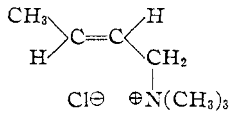
Results

The three isomeric trimethylbutenylammonium chlorides that could result reasonably from reaction between α-methylallyl chloride and trimethylamine were synthesized independently and characterized. Trimethyl-α-methyallylammonium chloride (I) would result from normal, S_N2, displacement of trimethylamine on α-methylallyl chloride. Either trimethyl-*trans*-γ-methylallylammonium chloride (II) or trimethyl-*cis*-γ-methylallylammonium chloride (III), or a mixture of the two, would result from abnormal S_N2' displacement.

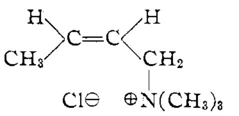


$$\underset{\oplus N(CH_3)_3Cl^{\ominus}}{CH_3CHCH{=}CH_2}$$

I

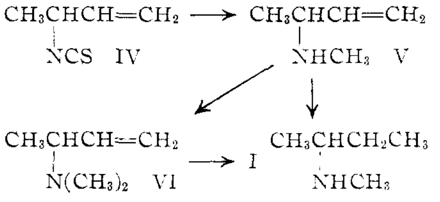


II



III

Trimethyl-α-methylallylammonium chloride (I) was prepared as follows. α-Methylallyl isothiocyanate (IV) was converted to N-methyl-α-methylallylamine (V) by reduction with lithium aluminum hydride, and the identity of V was established by catalytic hydrogenation to N-methyl-*s*-butylamine. Reductive methylation converted V to N,N-dimethyl-α-methylallylamine (VI), and quaternization of VI with methyl chloride yielded I.



The trimethyl-γ-methylallylammonium chlorides, II and III, were prepared by displacement reactions of trimethylamine on the corresponding butenyl chlorides, *trans*-γ-methylallyl chloride and *cis*-γ-methylallyl chloride, respectively, in ether solution. Experience in this Laboratory indicates that with primary allylic halides, displacements in non-ionizing media proceed without geometric isomerization of the allylic system.

The isomeric trimethylbutenylammonium chlorides were characterized by their infrared spectra. At 11.16 μ, II and III have absorption maxima of identical intensity, while I has an absorption maximum of much weaker intensity. At 10.20 μ, I has an absorption minimum, and II and III have absorption maxima, all three absorptions being of different intensities. These spectral characteristics were employed in the estimation of the products from the reaction of α-methylallyl chloride with trimethylamine.

In order that product studies and kinetic studies might be interrelated, product from the reaction of α-methylallyl chloride and trimethylamine in acetone was obtained under the conditions of the kinetic studies. Under these conditions the isolation of virtually quantitative yields of product which gave correct elementary analyses showed that the product was entirely trimethylbutenylammonium chloride and the infrared spectra showed that it was a mixture of allylic isomers.

Since II and III have identical extinction coefficients at 11.16 μ a calibration curve of optical density *vs.* percentage normal product was prepared by measuring the optical densities of synthetic mixtures of I and II at this wave length. The percentages of normal product (I) in the product mixtures were determined at this wave length by relating the optical densities of the product mixtures to this calibration curve. The percentages of the two abnormal products (II and III) in the product mixtures were determined at 10.20 μ where I, II and III have different extinction coefficients. At this wave length Beer's law was applied to the three component system, and the resulting equations were solved by utilizing the results of the analyses at 11.16 μ. The compositions of the product mixtures obtained in this manner are recorded

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(3) R. E. Kepner, S. Winstein and W. G. Young, THIS JOURNAL, **71**, 115 (1949).

(4) W. G. Young, I. D. Webb and H. L. Goering, *ibid.*, **73**, 1076 (1951).

(5) (a) M. J. Kland-English and C. L. Wilson, *Abstracts of Papers, Am. Chem. Soc.*, **119**, 48M (1951); (b) L. H. Amundsen and W. F. Brill, *ibid.*, 58m; (c) B. D. England and E. D. Hughes, *Nature*, **168**, 1002 (1951); (d) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 3555 (1953); (e) R. W. Kierstead, R. P. Linstead and B. C. L. Weedon, *ibid.*, 1803, and previous papers; (f) G. Stork and W. N. White, THIS JOURNAL, **75**, 4119 (1953); (g) P. B. D. de la Mare, E. D. Hughes and C. A. Vernon, *Nature*, **169**, 672 (1952).

in Table I. The absolute precision in the percentage of normal product present in the product mixtures (column 2, Table I) is better than 1%. Because the relative properties of II and III in the product mixtures were assigned on the assumed validity of Beer's law these latter values (columns 3 and 4, Table I) are less accurate, an absolute accuracy of 2% being estimated for them.

TABLE I

THE COMPOSITION OF TRIMETHYLBUTENYLAMMONIUM CHLORIDES FROM THE REACTION OF α-METHYLALLYL CHLORIDE AND TRIMETHYLAMINE IN ACETONE SOLUTION[a]

Temperature,[b] °C.	Normal product[c] I, %	Abnormal product[c] II, %	III, %
40.1	32	62	6
49.7	29	63	8
75.2	28	65	7

[a] Initial concentrations are: α-methylallyl chloride, 0.2097 mole/l.; trimethylamine, 0.3989 mole/l. (this reaction is bimolecular under these conditions). [b] Temperature variation is less than 0.1°. [c] Each value represents the average result of two determinations. The product mixtures were isolated after reaction times noted: 40.7°, 35.4 and 75.7 hr.; 75.2°, 7.8 and 23.7 hr. I is trimethyl-α-methylallylammonium chloride; II, trimethyl-*trans*-γ-methylallylammonium chloride; III, trimethyl-*cis*-γ-methylallylammonium chloride.

The decrease of normal product with increase in temperature, although slight, appears to be real. The significant features of Table I, however, are the relative insensitivity of product composition to temperature, and the appearance of both II and III as constituents of the abnormal portions of the product mixtures.

Because of the lability of allylic systems, it was necessary to establish that abnormal product (II and III) was produced directly by reaction between α-methylallyl chloride and trimethylamine, and that it did not arise from (a), rearrangement of α-methylallyl chloride to the γ-methylallyl chlorides prior to reaction, or (b), rearrangement of normal product (I) subsequent to reaction. Unreacted butenyl chloride isolated from the reaction of α-methylallyl chloride with insufficient trimethylamine was found to be at least 91% and probably exclusively α-methylallyl chloride. This observation and the bimolecular nature of the kinetics (see later) eliminated possibility (a). Possibility (b) was eliminated by the observation that normal product (I) was stable under the conditions of reaction.

The kinetics of the reaction of α-methylallyl chloride and trimethylamine in acetone were shown to be first order with respect to each of the reactants, second order over-all. The reaction was followed by analysis for chloride ion produced in the quaternization reaction, and the rate constants were calculated from the integrated form of the usual second-order rate expression given in equation 1. In equation 1, a is the initial concentration

$$k_2 = (2.303/b - a)(1/t) \log [(b - ay)/(1 - y)] - C \quad (1)$$

of α-methylallyl chloride, b is the initial concentration of trimethylamine, y is the fraction of α-methylallyl chloride reacted at time t, C is a constant of integration, and k_2 is the specific second-order rate constant for the production of ionic chloride. In the calculation of rate constants, C was determined by finding the least squares intercept for the straight line defined by a plot of log $[(b - ay)/(1 - y)]$ *vs.* time. The rate constants thus secured are recorded in Table II. A typical rate run is given in Table III.

TABLE II

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF α-METHYLALLYL CHLORIDE WITH TRIMETHYLAMINE IN ACETONE

Run	(RCl)[a]	(NMe_3)[a]	Temp.,[b] °C.	k_2[c]	Avg. dev.
1[d]	0.1968	0.427	49.5	0.052	0.001
2[d]	.0988	.432	49.5	.053	.002
3[d]	.0988	.216	49.5	.053	.002
4[e]	.2097	.411	40.1	.0288	.0006
5[e]	.2097	.408	49.7	.0552	.0006
6[e]	.2097	.406	75.2	.283	.006

[a] Units of concentration are mole/l. [b] Temperature is in °C., variation is less than 0.1°. [c] Units of k_2 are $(\text{mole/l.})^{-1}$ $(\text{hr.})^{-1}$. From 10 to 14 points were taken during the course of each run in the range of 10 to 90% reaction. [d] k_2 uncorrected for solvent expansion. [e] Average of two runs; k_2 corrected for solvent expansion.

TABLE III

THE REACTION OF α-METHYLALLYL CHLORIDE WITH TRIMETHYLAMINE IN ACETONE AT 40.1°[a]

Time, hr.	Thiocyanate titer, ml.	Fraction reacted	k_2[b]
0.00	4.551	0.000	0.0299
5.72	4.232	.0835	.0229
17.45	3.800	.1965	.0300
25.75	3.566	.258	.0287
30.47	3.480	.280	.0269
54.08	2.939	.422	.0272
69.35	2.648	.498	.0276
94.60	2.278	.595	.0278
125.4	1.939	.683	.0281
197.7	1.423	.819	.0291
383.9	0.942	.945	.0288
1010.0			
Expt. inf.	0.731	1.000	
Calcd. inf.	0.701		

Average k_2, 0.0282 ± 0.0007[c]

[a] Initial concentration of α-methylallyl chloride, 0.2097 (mole/l.); of trimethylamine, 0.412 (mole/l.); temperature is constant within 0.1°. [b] Units of k_2 are $(\text{mole/l.})^{-1}$; uncorrected for solvent expansion. [c] Average deviation.

The bimolecular nature of the reaction may be ascertained by a comparison of runs 1, 2 and 3 in Table II. Variations in the initial concentrations of the reactants had no effect on the second-order rate constants. The precision with which the reaction fitted second-order kinetics is illustrated in Table III. This precision supports the conclusion drawn previously that α-methylallyl chloride does not rearrange prior to reaction.

The homogeneity of the reaction was well established. To check the possibility of heterogeneous reaction on the glass surface, the rate of reaction in the presence of glass wool was compared to the rate in the absence of glass wool. Agreement within experimental error was obtained. That there was no heterogeneous reaction on the surface of the precipitated product was inferred from the kinetic data, for in no case was precipitation of product attended by a change in the rate constant.

From the kinetic data, it is apparent that the reaction is homogeneous and bimolecular in nature. Since normal product I and abnormal product (II plus III) are produced directly in the reaction, it follows that the reaction of α-methylallyl chloride and trimethylamine involves simultaneous S_N2 and S_N2′ displacements. This situation is conveniently expressed in equation 2 where v is the reaction velocity, $k_{\mathrm{S_N2}}$ is the specific second-order rate

$$v = k_{\mathrm{S_N2}}(\mathrm{RCl})(\mathrm{R_3N}) + k_{\mathrm{S_N2'}}(\mathrm{RCl})(\mathrm{R_3N}) = k_2(\mathrm{RCl})(\mathrm{R_3N}) \quad (2)$$

constant for the S_N2 displacement which produces normal product, $k_{\mathrm{S_N2'}}$ is the specific second-order rate constant for the S_N2′ displacements which produce abnormal products, and k_2 is the specific second-order rate constant for the over-all production of ionic chloride.[6] With the aid of data in Table I it is possible to separate k_2 into its component parts, $k_{\mathrm{S_N2}}$ and $k_{\mathrm{S_N2'}}$. The results of this separation are given in Table IV.

TABLE IV

SPECIFIC SECOND-ORDER RATE CONSTANTS FOR NORMAL AND ABNORMAL DISPLACEMENT

Temp.,[a] °C.	$k_{\mathrm{S_N2}}$[b]	$k_{\mathrm{S_N2'}}$[b]
40.1	0.0092	0.0196
49.7	.0160	.0392
75.2	.079	.204

[a] Deviation in temperature is less than 0.1°. [b] Units of k are (mole/l.)$^{-1}$(hr.)$^{-1}$; corrected for solvent expansion.

TABLE V

THERMODYNAMIC FUNCTIONS OF ACTIVATION

Function[a]	Type of displacement S_N2	S_N2′
E^*	13.4	14.5
ΔH^* (49.7°)	12.8	13.9
ΔS^* (49.7°)	−45	−38

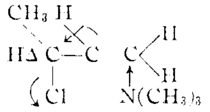
[a] Units are: E^* and H^*, kcal./mole; S^*, cal./mole/°A.

The thermodynamic functions of activation for the S_N2 and S_N2′ displacements now can be calculated from the data in Table IV. The results are given in Table V—the experimental energy of activation, E^*, was calculated from the Arrhenius equation, $k = Ae^{-E^*/RT}$, by plotting log k vs. $1/T$, and then calculating the slope by the method of least squares. The heat of activation, ΔH^*, was derived from E^* by the relationship $\Delta H^* = E^* - RT$, and the entropy of activation, ΔS^*, was calculated from the absolute reaction rate equation.[7] As would be expected, quaternization by S_N2′ displacement shares with quaternization by S_N2 displacement the characteristics of a low energy of activation and a large negative entropy of activation.

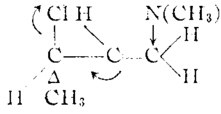
Conclusions

In this work it has been demonstrated unambiguously that the reaction of trimethylamine and α-methylallyl chloride proceeds simultaneously through S_N2 and S_N2′ displacements. Thus, the S_N2′ displacements of amines on α-methylallyl chloride, and by extension, on allylic systems in general, do not require the operation of a specific hydrogen-bond interaction between the entering and leaving groups. It seems likely, however, that such an interaction does promote S_N2′ displacement, and hence makes allylic systems more susceptible to S_N2′ displacement by secondary amines than by tertiary amines.

Both *cis* and *trans* isomers have been identified in the product of S_N2′ displacement of trimethylamine on α-methylallyl chloride. Similarly, *cis* and *trans* isomers have been noted in the products of the S_N2′ displacements of ethoxide ion and thiophenoxide ion on 3,3-dichloro-1-propene.[8] This duality of product from S_N2′ displacement is to be expected wherever possible, and probably arises from the duality of conformation about the α-carbon atom of allylic systems which may obtain at the moment of reaction. This situation is illustrated for the S_N2′ displacement of trimethylamine on α-methylallyl chloride. A *cis* orientation is assumed between the entering and leaving groups as such an orientation appears most likely,[4,5f] but the result is not dependent on this condition. Conformation VII leads to the *trans* isomer (II in this case), and conformation VIII leads to the *cis* isomer (III in this case.)



VII



VIII

Experimental

Commercial Materials.—The acetone employed in this work was Baker and Adamson C.P. acetone, dried over Drierite and distilled from Drierite; b.p. 56.6°. Trimethylamine (gaseous) was Eastman Kodak Co. White Label grade which was dried by passage through a drying tower of potassium hydroxide prior to use.

***trans*-γ-Methylallyl Chloride and α-Methylallyl Chloride.**—Concentrated hydrochloric acid (2 l.) and anhydrous zinc chloride (2 lb.) were placed in a three-neck five-liter round-bottom flask fitted with a Tru-Bore stirrer and two Dry Ice condensers. Stirring was started, and the flask was immersed in a methanol-water-bath which was maintained at −20° to −10° during the addition of gaseous butadiene (615 g.) which required 30 minutes. The flask was then allowed to warm to 15°, the temperature maintained by the refluxing butadiene, and kept at this temperature, with stirring, for eight hours. Stirring was continued at room temperature overnight in the absence of the Dry Ice condensers. The organic layer was then separated, washed successively with water and aqueous potassium carbonate, dried over anhydrous potassium carbonate, and distilled through a glass-helices-packed column (100 cm. tall and 1.5 cm. in diameter) to yield α-methylallyl chloride (116 g., 11%), n^{25}D 1.4120, b.p. 63.5–64.2°, and *trans*-γ-methylallyl chloride (405 g., 39%), n^{25}D 1.4330, b.p. 84.2–84.8°.

***cis*-γ-Methylallyl Chloride.**—This compound was prepared by the method of Hatch and Nesbitt[9] and had b.p. 84.1° (758 mm.), n^{25}D 1.4360.

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[6] It should be noted that $k_{\mathrm{S_N2'}}$, is itself composite, consisting of the specific second-order rate constant for the production of II and that for the production of III. However, because of the uncertainty in the analyses for the relative proportions of II and III, $k_{\mathrm{S_N2'}}$, is treated subsequently as a single entity.

[7] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

[8] P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 3325, 3331 (1952).

[9] L. F. Hatch and S. S. Nesbitt, This Journal, **72**, 727 (1950).

α-Methylallyl Isothiocyanate (V).—This compound was prepared in 81% yield as described previously.[4] It had b.p. 150–156°, and the thiourea derivative obtained by reaction with ethanolic ammonium hydroxide melted 104° (lit.[4,10] 106–106.5°, 105°).

N-Methyl-α-methylallylamine (VI).—An excess 22.5 g. (0.6 mole) of finely divided lithium aluminum hydride and anhydrous ether (250 ml.) were placed in a three-neck round-bottom flask equipped with a mechanical stirrer, a dropping funnel and a reflux condenser fitted with a drying tube. The suspension was refluxed with stirring for two hours in order to provide a maximum concentration of soluble hydride. To the stirred, refluxing solution was added dropwise a solution of α-methylallyl isothiocyanate, 33 g. (0.29 mole) in an equal volume of anhydrous ether. After completion of the addition, stirring under reflux was continued overnight. The reaction mixture then was cooled in an ice-salt-bath, and water (50 ml.) was added with extreme caution to decompose the excess lithium aluminum hydride and to hydrolyze the reduction complex. Volatile components of the reaction mixture were stripped from inorganic material by rapid distillation under reduced pressure into a Dry Ice trap. An excess of dilute hydrochloric acid was added to the distillate, and the resulting solution was concentrated to near-dryness under reduced pressure to yield the amine hydrochloride as a viscous paste. Crude N-methyl-α-methylallylamine (20 g., 87%) was obtained from the hydrochloride by standard procedures.[11] Fractionation of the crude product through a twenty-inch Podbielniak column afforded pure N-methyl-α-methylallylamine, b.p. 76°, n^{25}_{D} 1.4092.

The phenylthiourea derivative of N-methyl-α-methylallylamine had m.p. 91–91.5°.

Anal. Calcd. for $C_{12}H_{16}N_2S$: C, 65.41; H, 7.32. Found: C, 65.22; H, 7.40.

N-Methyl-*s*-butylamine. (A).—A solution of methyl ethyl ketone (17 g., 0.236 mole), methylamine (21 g., 0.67 mole) and toluene (50 g.) was placed in a pressure bottle which was sealed and allowed to stand at room temperature for several days. The reaction product, imine, without isolation, then was hydrogenated at atmospheric pressure in the presence of platinum oxide catalyst. The toluene solution of amine which resulted was dried and fractionated through a Podbielniak Heli-Grid[12a] column to yield pure N methyl-*s*-butylamine (10.13 g., 50%), b.p. 78° (lit.[12b] 78–79°).

The phenylthiourea derivative of N-methyl-*s*-butylamine had m.p. 98°.

Anal. Calcd. for $C_{12}H_{18}N_2S$: C, 64.81; H, 8.16. Found: C, 64.86; H, 8.22.

(B).—A solution of N-methyl-α-methylallylamine (1.7 g.) in ether (30 ml.) was hydrogenated at atmospheric pressure over platinum oxide catalyst. The theoretical volume of hydrogen was taken up for the saturation of a single double bond. The reduction product, N-methyl-*s*-butylamine, was identified by its phenylthiourea derivative which had m.p. 98°, not depressed on admixture with the phenylthiourea derivative of authentic N-methyl-*s*-butylamine prepared by method A.

N,N-Dimethyl-α-methylallylamine (VII).—A solution of formaldehyde (35% aqueous, 18.9 g., 0.22 mole) and formic acid (90% aqueous, 57.8 g., 1.0 mole) was placed in a three-neck round-bottom flask equipped with a stirrer, a condenser and a dropping funnel. To this solution was added, dropwise, N-methyl-α-methylallylamine (17 g., 0.2 mole). The reaction was exothermic and was moderated by cooling the flask in an ice-bath. After addition of the amine was complete, the solution was refluxed gently for a period of 3.5 hr. At the end of this time the reaction mixture was cooled in an ice-bath while hydrochloric acid (12 *N*, 20 ml.) was added slowly. The resulting solution was concentrated to near dryness, and the crude amine was isolated[11] from the concentrate of amine hydrochloride in a 90% yield. Pure N,N-dimethyl-α-methylallylamine, b.p. 91° (lit.[13] 90–93°), n^{25}_{D} 1.4102, was obtained by fractionation of the crude amine through a Pobielniak[12a] column.

Trimethyl-α-methylallylammonium Chloride (I).—A mixture of N,N-dimethyl-α-methylallylamine (12 g.), methyl chloride (36 ml.) and ether (60 ml.) was sealed in a glass ampule (Dry Ice temperature) and the reaction was allowed to proceed for two days at room temperature. At the end of this time the ampule was opened (Dry Ice temperature), the crystalline product removed, washed repeatedly with acetone and dried under reduced pressure to give pure trimethyl-α-methylallylammonium chloride (16.7 g., 92%), m.p. 203° dec., as fine, white hygroscopic needles.

Anal. Calcd. for $C_7H_{16}NCl$: C, 56.17; H, 10.78. Found: C, 56.08; H, 10.78.

Trimethyl-*trans*-γ-methylallylammonium Chloride (II).—An ether solution of *trans*-γ-methylallyl chloride and trimethylamine was sealed in a glass ampule and allowed to react at room temperature for 5.5 days. The ampule was opened, the white, crystalline product dissolved in chloroform, shaken with Norite for 24 hours at room temperature, and filtered. Pure trimethyl-*trans*-γ-methylallylammonium chloride was isolated as white, granular, hygroscopic crystals, m.p. 187.8–188.0° dec., by addition of acetone to the chloroform filtrate. A melting point depression was obtained on admixture with I.

Anal. Calcd. for $C_7H_{16}NCl$: Cl, 23.69. Found: Cl, 23.82.

Trimethyl-*cis*-γ-methylallylammonium Chloride (III).—An ether solution of *cis*-γ-methylallyl chloride and trimethylamine was sealed in a glass ampule and allowed to react for six days at room temperature. A chloroform solution of the crude, brown product was treated several times with Norite at room temperature before it yielded pure trimethyl-*cis*-γ-methylallylammonium chloride as white, granular, hygroscopic crystals, m.p. 184.5–185.0° dec., upon the addition of acetone. Melting point depressions were obtained upon admixture with I and II.

Anal. Calcd. for $C_7H_{16}NCl$: Cl, 23.69. Found: Cl, 23.54.

Kinetic Methods.—Stock solutions of trimethylamine in acetone were prepared by passing the approximate weight of trimethylamine, as a gas, into the approximate volume of absolute acetone *via* a drying tower of potassium hydroxide. Stock solutions of α-methylallyl chloride were prepared by mixing directly approximate weight of α-methylallyl chloride directly with the approximate volume of absolute acetone.

Equal aliquots (2.00 ml.) of each stock solution were pipetted into ampules, previously drawn out to permit easy sealing and containing a minimum of free space, which were then immersed in a Dry Ice-bath. The ampules were sealed off while in the Dry Ice-bath, shaken to mix the contents, and kept at Dry Ice temperature until transferred to the constant-temperature bath for reaction. Because of the volatile nature of the reactants, the concentrations of α-methyl allyl chloride and of trimethylamine in their respective stock solutions were determined before and after the series of ampules which constituted a rate run had been filled. The average values were employed as the concentrations of the reactants in their respective stock solutions. Perfect mixing was assumed, and the initial concentrations of the reactants in the kinetic ampules were taken as one-half of the average values determined for the stock solutions employed for that rate run. Trimethylamine was estimated by pipetting an aliquot of the stock solution into standard acid and back-titrating with standard base to the brom cresol purple end-point. α-Methylallyl chloride was estimated by pipetting an aliquot of the stock solution into alcoholic silver nitrate and then weighing the precipitated silver chloride after complete reaction (12 hr.).

The ampules constituting a run were immersed simultaneously in the constant-temperature bath, zero time being taken as the time of immersion. The zero-time titer was taken at this point. At appropriate time intervals, ampules were removed and quenched in Dry Ice. The ampules were broken in a dry beaker with clean pliers, the pliers washed successively with nitrobenzene (15 ml.) and water (20 ml.) which were added to the beaker which contained the crushed ampule and its contents. In succession, were added an indicator solution (7 ml.) composed of three parts of ferric alum indicator and four parts of nitric acid (6 *N*) by

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(10) J. Kreuger and M. Schwarz, THIS JOURNAL, **63**, 2512 (1941).

(11) M. T. Leffler, "Organic Syntheses," Col. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 24.

(12a) W. J. Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **13**, 639 (1941).

(12b) K. Löffler, *Ber.*, **43**, 2041 (1910).

(13) Elkerfeld, *Chem. Zentr.*, **83**, II, 159 (1912).

volume, and an aliquot (5.000 ml.) of standard silver nitrate solution (*ca.* 0.2 *N*). The excess silver nitrate was then back-titrated with standard thiocyanate solution (*ca.* 0.2 *N*). The silver nitrate precipitated silver chloride from the ionic quaternary chlorides present in the aqueous phase, while it had only a slight effect upon the unreacted α-methylallyl chloride present in the nitrobenzene phase.

Control experiments indicated that 1.3% of the α-methylallyl chloride present at zero time was analyzed as ionic chloride. This value was used in the calculation of theoretical infinity titers, but it was neglected in the calculation of rate constants, inasmuch as the error was significant only in the vicinity of zero time.

Isolation and Analysis of Product.—Ampules of α-methylallyl chloride and trimethylamine were made up as described under "Kinetic Methods." After reaction, the ampules were quenched in Dry Ice and opened. The solvent was removed from the cold ampules through a fine capillary tube, and the product was washed with absolute ether (25 ml.) which was removed in the same manner. Where necessary, the weight of the product was determined by noting the difference in the weight of the opened ampule before and after removal of product. In these cases it was necessary to dry the ampule and product at reduced pressure, and to close the ampule with rubber finger to protect the hygroscopic contents from atmospheric moisture during the weighing process.

In two experiments, there was isolated from the reaction of trimethylamine (0.399 *M*) and α-methylallyl chloride (0.210 *M*) a yield of crystalline product, 97.5% of theory for the formation of the trimethylbutenylammonium chlorides. The reactions were conducted at 75.2° and for periods of 100 and 126 hr., respectively. This crystalline material, without further purification, analyzed as 23.55% chloride ion (gravimetrically as AgCl), in good agreement with the 23.69% required by $C_7H_{16}NCl$. Evidence that this material was a mixture of the three isomeric trimethylbutenylammonium chlorides was provided by its infrared spectrum which fell entirely within the limits defined by the pure isomeric trimethylbutenylammonium chlorides.

All analyses by the infrared technique were performed on solutions of the trimethylbutenylammonium chloride(s), 10% by weight in chloroform. Optical density readings were taken on a Beckman Infrared spectrophotometer, IR2T.

A calibration curve of optical density *vs.* composition was established at 10.20 μ with mixtures (volumetric) of stock solutions (10% by wt.) of trimethyl-α-methylallylammonium chloride (I), and trimethyl-*trans*-γ-methylallylammonium chloride (II) in chloroform. The optical densities of solutions (10% by wt.) of the three pure trimethylbutenylammonium chlorides, I, II and III, in chloroform were measured at 11.16 and from this data extinction coefficients for the three isomers at this wave length were calculated.

For analysis, the reaction product was isolated as described above. After the ether wash had been removed, the product was dissolved in chloroform and an aliquot of the homogeneous solution was transferred to a weighed flask. The chloroform was removed by evaporation under reduced pressure, the flask weighed again, and the correct amount of chloroform to make a 10% solution by weight of the product was added.

Stability of Trimethyl-α-methylallylammonium Chloride.—Trimethyl-α-methylallylammonium chloride (0.585 g.) was placed in an ampule which was then filled with an acetone solution of α-methylallyl chloride (0.210 *M*) and trimethylamine (0.399 *M*), sealed, and allowed to react at 75.2° for 32.88 hr. At the end of this time, 1.975 g. of crystalline material was isolated by the methods described under "Isolation and Analysis of Product." Of this total, 0.585 g. represents the trimethyl-α-methylallylammonium chloride initially added, and 1.390 g. represents the trimethylbutenylammonium chlorides produced by reaction. Since the trimethylbutenylammonium chlorides produced under these conditions consists of 28% trimethyl-α-methylallylammonium chloride (Table I), 49% of the total material isolated should have been trimethyl-α-methylallylammonium chloride if there were no rearrangement of the trimethyl-α-methylallylammonium chloride initially added. When the total material isolated was analyzed by the infrared technique, it was found to consist of 50% trimethyl-α-methylallylammonium chloride. The agreement between the calculated and experimental values is considered proof that trimethyl-α-methylallylammonium chloride is stable under reaction conditions. This experiment also shows that prototropic shifts activated by the quaternary ammonium group do not occur in this system in the presence of trimethylamine.

Analyses of Recovered Butenyl Chloride.—Trimethylamine (4.6 g.) was dissolved in anhydrous acetone (100 ml.) and to this solution was added a solution of α-methylallyl chloride (35.5 g.) in acetone (100 ml.). The total solution, contained in a pressure bottle, was immersed in the 75° bath for 76.75 hr. Upon removal from the bath, the pressure bottle was cooled in an ice-bath, the contents poured into 600 ml. of ice-water which contained 1 ml. of concentrated sulfuric acid, and the organic layer separated with the aid of pure toluene (70 ml., n^{25}D 1.4942). In order to remove acetone, the organic layer was washed five times with 20-ml. portions of 35% sodium bisulfite solution, sufficient ice being added to the extraction to maintain the temperature at 0°. The organic layer was then extracted once with an iced sodium carbonate solution (30 ml., 10%), and finally dried over anhydrous potassium carbonate. The dry toluene solution of recovered butenyl chloride was distilled through a 30-cm. center-rod column and distillates analyzed by refractive index methods.

In this analysis, material distilling intermediate between the boiling points of pure α-methylallyl chloride (64°, and pure γ-methylallyl chloride, 84°) was assumed to be mixtures of these two compounds, and a linear relationship between refractive index and weight composition was justifiably assumed.[14] Material distilling between the boiling points of pure γ-methylallyl chloride and toluene (111°) was assumed to be mixtures of these two components and was analyzed by reference to a calibration curve of refractive index *vs.* weight composition established with synthetic mixtures of the two pure components. The refractive indexes employed were: α-methylallyl chloride, n^{25}D 1.4120; γ-methylallyl chloride (the *trans* isomer), n^{25}D 1.4330; toluene, n^{25}D 1.4942. The butenyl chloride recovered (19.68 g.) analyzed as 91.0% α-methylallyl chloride, 9.0% γ-methylallyl chloride.

For control analyses, the butenyl chloride(s) was dissolved in absolute acetone (200 ml.) and then isolated and analyzed exactly as described above. From 25.95 g. of pure α-methylallyl chloride there was isolated 21.02 g. of butenyl chloride which analyzed as 91.0% α-methylallyl chloride and 9.0% γ-methylallyl chloride. From 25.92 g. of a mixture of α-methylallyl chloride (85.9%) and γ-methylallyl chloride (14.1%) there was isolated 19.70 g. of butenyl chloride which analyzed as 82.4% α-methylallyl chloride and 17.6% γ-methylallyl chloride.

The second control analysis indicates that reasonably accurate analyses may be made on mixtures of the butenyl chlorides which contain appreciable fractions of α-methylallyl chloride. The first control analysis indicates that the analysis of pure α-methylallyl chloride will indicate the presence of some (9%) γ-methylallyl chloride. The γ-methylallyl chloride thus indicated may be real, resulting from isomerization of α-methylallyl chloride, or, more probably, it may be artificial, resulting from the designation of material distilling between 84 and 111° as mixtures of α-methylallyl chloride and toluene. The identity of the analytical results obtained with pure α-methylallyl chloride and with butenyl chloride recovered from reaction with trimethylamine, strongly suggests that the recovered butenyl chloride is actually pure α-methylallyl chloride.

Thermal Expansion of Kinetic Solutions.—Aliquots of kinetic solutions of α-methylallyl chloride and trimethylamine were introduced into small-bore glass tubes which were sealed off in Dry Ice. The positions of the menisci were marked at room temperature (23°), at 40.1, 49.7 and at 75.2°. The tubes were opened, emptied and filled to the marks with water which was measured out from a microburet.

Homogeneity of Reaction.—The normal procedure for a rate run was employed except that half of the ampules contained dry Pyrex glass wool. At appropriate time intervals two ampules were quenched simultaneously and analyzed for ionic chloride. One of the ampules contained glass wool; the other did not.

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[14] D. B. Brandon, Ph.D. Thesis, U.C.L.A., 1950, p. 55.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Arylation of Unsaturated Systems by Free Radicals. III. The Action of Radical Generators upon Coumarin[1]

BY O. VOGL[2] AND CHRISTIAN S. RONDESTVEDT, JR.

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Coumarin is arylated by free radicals from benzoyl peroxide, N-nitrosoacetanilide, 1-phenyl-3,3-dimethyltriazene and the correspondng *p*-nitro compounds. The 3-arylcoumarins are formed in much lower yields than when the arylating agent is a diazonium salt promoted by cupric chloride (Meerwein reaction). Acrylonitrile and acrylic acid are not arylated by N-nitrosoacetanilides nor 1-phenyl-3,3-dimethyltriazene, although the Meerwein reaction gives good yields. These results imply that *free* radicals are not intermediates in the Meerwein reaction.

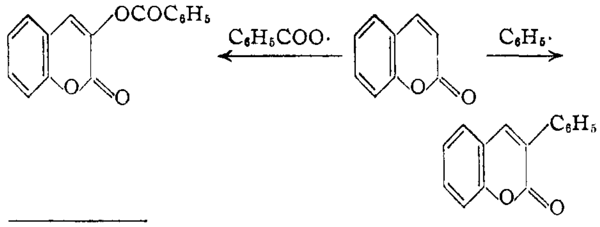
Aromatic rings are arylated by several different reagents, notably benzoyl peroxides, N-nitrosoacetanilides, 1-aryl-3,3-dimethyltriazenes and diazonium salts in alkaline medium.[3] These reagents are thought to decompose to free aryl radicals which then attack the aromatic ring. Quinones are arylated by diazonium salts, often in high yields.[4] Still less aromatic systems, such as found when olefinic double bonds are conjugated with vinyl, aryl, carbonyl and cyano groups, are attacked by diazonium salts in the presence of cupric chloride at *p*H 3 with substitution of aryl for hydrogen or addition of aryl and halide groups to the conjugated system.[1,5] This so-called Meerwein reaction has been regarded as a free-radical process,[6] though others have stated that carbonium ions are involved.[5,7-9]

To distinguish these possibilities, it was of interest to decompose known free radical generators in the presence of an olefinic double bond known to undergo the Meerwein reaction. Many of the common unsaturated systems, such as acrylonitrile and acrylic acid, are polymerized by benzoyl peroxide and N-nitrosoacetanilide.[10] Therefore, coumarin was selected for this study since it is not readily polymerized and since it also affords an opportunity to compare aromatic ring arylation with double-bond arylation. The less reactive radical generators also were tried with acrylonitrile and acrylic acid.

Aroyl Peroxides.—Meerwein[5] obtained a 26% yield of 3-phenylcoumarin and a 50% yield of 3-*p*-nitrophenylcoumarin from the corresponding diazonium salts in acetone solvent.[11] We obtained lower yields of 3-arylcoumarins when benzoyl and *p*-nitrobenzoyl peroxides were decomposed in the presence of coumarin in acetone, butanone, acetonitrile and ethyl acetate; the yield in glycol dimethyl ether solvent was nil.

A benzoxycoumarin was a by-product from benzoyl peroxide decompositions.[12] After the reaction product had been freed from the benzoic acid normally formed in peroxide decompositions, it exhibited bands in the infrared at 7.82, 8.45, 9.40 and 13.02 μ, in addition to the complete spectrum of 3-phenylcoumarin. The first two mentioned are said to be characteristic of benzoate esters.[13] These four bands disappeared upon alkaline hydrolysis, and an additional quantity of benzoic acid was formed; 3-phenylcoumarin was reformed upon acidification, but 3-hydroxycoumarin (or its tautomer) was not isolated. The benzoxy group is assumed to be in position 3, since this appears to be the most reactive site in the coumarin molecule for free radical attack. No evidence was obtained for any isomeric phenylcoumarins, hence the conjugated unsaturated "side chain" is more reactive toward radicals than the aromatic ring. The quantity of benzoate ester was larger when the decompositions were carried out in the higher-boiling

$$(C_6H_5COO)_2 \longrightarrow C_6H_5COO\cdot \longrightarrow C_6H_5\cdot$$



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[1] Paper II, C. S. Rondestvedt, Jr. and O. Vogl, THIS JOURNAL, **77**, 2313 (1955).

[2] On leave of absence from University of Vienna, Austria.

[3] For references, see C. S. Rondestvedt, Jr., and H. S. Blanchard, THIS JOURNAL, **77**, 1769 (1955).

[4] D. E. Kvalnes, *ibid.*, **56**, 2478 (1934); K. Schimmelschmidt, *Ann.*, **566**, 184 (1950).

[5] H. Meerwein, E. Buchner and K. van Emster, *J. prakt. Chem.*, **152**, 237 (1939).

[6] C. F. Koelsch and V. Boekelheide, THIS JOURNAL, **66**, 412 (1944).

[7] W. H. Brunner and H. Perger, *Monatsh.*, **79**, 187 (1948); W. H. Brunner and J. Kustatscher, *ibid.*, **82**, 100 (1951).

[8] F. Bergmann and D. Schapiro, *J. Org. Chem.*, **12**, 57 (1947), and previous papers.

[9] P. L'Ecuyer and C.-A. Olivier, *Can. J. Research*, **28B**, 648 (1950), and previous papers.

[10] A. T. Blomquist, J. R. Johnson and H. J. Sykes, THIS JOURNAL, **65**, 2446 (1943).

[11] C. S. Rondestvedt, Jr. and O. Vogl, *ibid.*, in press, have noted that solvents with no unsaturation are decidedly inferior.

[12] Benzoxylation frequently occurs when benzoyl peroxides are decomposed in the presence of reactive molecules. For example, P. D. Bartlett and S. G. Cohen, *ibid.*, **65**, 543 (1943), have observed incorporation of benzoxy groups into polymer molecules, although more commonly aryl groups are introduced [C. C. Price, R. W. Kell and E. Krebs, *ibid.*, **64**, 2508 (1942)]. Highly reactive aromatic systems are benzoxylated, rather than phenylated; R. L. Dannley and M. Gippin, *ibid.*, **74**, 332 (1952), obtained a mixture of α- and β-naphthyl benzoates by decomposition of benzoyl peroxide in naphthalene.

[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, Chapter 11.