Substitution at a Saturated Carbon Atom. XVI. Supporting Evidence for Discrete, Distinct Allylically Related Ion Pairs[1]

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Abstract: Kinetic and product studies of the competitive reactions of α- and γ-methylallyl chloride with cosolvent water and phenoxide ion in 60, 40, and 25% aqueous dioxane are reported and interpreted in terms of a reaction mechanism which includes distinct, allylically related ion pairs as discrete intermediates. Particularly compelling evidences against an alternative, competitive SN1–SN2 rationalization of the data include (a) the observed product spread on solvolysis; (b) an authentic example of an "SN2′" reaction; and (c) the "carbonium-ion-like" solvent dependence of the bimolecular rate of reactions of γ-methlyallyl chloride with phenoxide ion [m_G = 0.760 (solvolysis); m_G = 0.565 (bimolecular phenoxide attack)].

Among the vagaries of modern physical organic chemistry have been the "product spreads" observed on solvolysis of isomeric, allylically related halides.[3] Thus, for example (on buffered solvolysis in aqueous organic solvents), γ-methylallyl chloride gives a relatively larger precentage of the unrearranged γ-methylallyl alcohol (than of the isomeric α-methylallyl alcohol) than does the isomeric α-methylallyl chloride. This phenomenon appears to be quite general.[3]

An immediate and obvious conclusion deriving from the observation of product spreads follows; both isomeric halides cannot be reacting solely *via* a single common intermediate.

The traditional explanation for the existence of product spreads has invoked the operation of simultaneous SN1 and SN2 reactions; for example, in solvolysis of α- and γ-methylallyl chloride the relatively unhindered primary isomer has been presumed to undergo simultaneous bimolecular attack by solvent, leading to an excess of unrearranged solvolysis product, competitive with ionization to an intermediate (common with that produced from the isomeric α-methylallyl chloride), which produces both allylically related solvolysis products.

Although such an explanation might be intellectually tenable if a single or a limited number of instances of the phenomenon in question had been recorded, the very generality[4] of the phenomenon bespeaks against it. That a concurrence of competitive SN1 and SN2 reactions should be observed across a wide spectrum of solvent, temperature, and even of substrate types is inconsistent with all notions of chemical selectivity; selective reactions should not, in general, be nearly quantitatively parallel in their effects to changes in conditions.

As a corollary to these thoughts the very generality of the phenomenon of product spreads leads one to speculate that their existence may presage the existence of high energy (and therefore unselective) intermediates as the precursors of products.

An attractive alternate explanation for the general existence of product spreads invokes the involvement of a high-energy (and therefore unselective), discrete intermediate from each of the allylically related chlorides which in turn may react further to furnish either (1) with solvent, an excess of unrearranged solvolysis product, or (2) a common intermediate capable of giving rise to both allylic solvolysis products. Thus if the initially formed ion pair from the primary γ-methylallyl chloride (P^+Cl^-) were distinctly different from that derived from the isomeric α-methylallyl chloride (S^+Cl^-), both serving as a precursor to a further common intermediate (represented for simplicity as R^+Cl^-), product spreads could be rationalized without doing violence to the notions of chemical selectivity.

When we first began our (herein reported) studies with the isomeric α- and γ-methylallyl chloride, the evidence for discrete, distinct allylic ion pairs, which constitutes the subject matter of the previous two manuscripts (XIV[5] and XV[6]) in this series, had not been amassed, nor had our now-published studies with 2-octyl mesylate been completed.[7,8] The work described in this paper was undertaken in an attempt to implicate discrete allylically related ion pairs as the species responsible for the observed product spreads in the solvolysis reactions of α- and γ-methylallyl chloride. It had been our hope that, by the use of a solvent of sufficiently great ionizing power, the isomeric substrates might, on competitive substitution with solvent and externally added nucleophile, be induced to give rise to "borderline behavior," the behavior which we then recognized as necessary for a successful kinetic differentiation between the ion-pair mechanism and alternatives. This goal was never achieved. Even in 25% aqueous dioxane (75% water) γ-methylallyl chloride reacted with sodium phenoxide at a rate cleanly first-order in the concentration of nucleophile ("SN2").

While our primary objective was never realized the accumulated data do provide powerful support for the thesis advanced in the first paper of the present group,[5]

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(2) Acknowledgment is made by this author to the staff, students, and faculty of the Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, Zürich, Switzerland, for the use of their facilities and for their gracious hospitality during the writing of portions of this manuscript.

(3) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

(4) Product spreads appear to be invariantly present in the reactions of the allylic pair, α- and γ-methylallyl chloride,[3] under conditions as divergent as water–silver oxide, water–0.5 *M* sodium carbonate, 50% acetone–calcium carbonate, 45% ethanol–0.5 *M* sodium carbonate, ethanol, and acetic acid–silver acetate.

(5) R. A. Sneen and W. A. Bradley, *J. Amer. Chem. Soc.*, **94**, 6975 (1972).

(6) R. A. Sneen and P. S. Kay, *ibid.*, **94**, 6983 (1972).

(7) R. A. Sneen and J. W. Larsen, *ibid.*, **88**, 2593 (1966).

(8) R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 362 (1969).

Table I. Rate Constants for Reactions of α- and γ-Methylallyl Chloride (SCl and PCl) in Aqueous Dioxane at 50.1°

	% dioxane	[Salt]	k_1, sec^{-1} × 10^5	k_2, l. mol^{-1} sec^{-1} × 10^4 [a]
[SCl]				
0.0117	60		2.68 ± 0.03	
0.0100	60	0.0400 NaOPh	5.90 ± 0.08	9.0
0.0121	60	0.400 NaOPh	29.1 ± 1.6	6.7
0.0100	60	0.043 NaOH	3.05 ± 0.10	0.98
0.0119	50		10.3 ± 0.7	
0.0118	50		10.5 ± 0.5	
0.0122	50	0.0226 $LiClO_4$	9.8 ± 0.41	
0.0120	50	0.0168 $LiClO_4$	13.0 ± 0.2	
[PCl]				
0.0125	60		2.59 ± 0.02	
0.0098	60	0.043 NaOH	5.93 ± 0.21	8.8
0.0115	60	0.044 $NaClO_4$	2.91 ± 0.10	
0.0095	60	0.04 NaOPh	28.9 ± 1.0	75

[a] Calculated by subtracting the no-salt first-order rate from the observed pseudo-first-order rate and dividing the result by the average nucleophile concentration.

Table II. Product Compositions of Solvolyses of α-Methylallyl Chloride (SCl) in 60% Aqueous Dioxane at 80.4° with Added Sodium Phenoxide[a]

[SCl]	[NaOPh]	SOH[b]	POH[b]	SOPh[b]	POPh[b]	[POH]/[SOH]	[POPh]/[SOPh]	m[c]
0.09943		27.8	10.3			37/63		
0.0986	0.020						41/59	
0.0868	0.040	9.89	4.97	0.45	0.22	34/66	33/67	
0.0914	0.080	6.2	3.8	3.9	1.3	38/62	25/75	
0.0912	0.200	2.75	1.30	6.8	1.9	32/68	22/78	14.0
0.0929	0.320	1.85	0.94	8.6	1.8	33/67	17/83	13.9
0.0888	0.400	1.36	0.74	8.8	1.8	35/65	17/83	14.5
0.0898	0.200[d]					34/66		

[a] S = secondary = γ-methylallyl; P = primary = α-methylallyl; R = α-methylallyl + γ-methylallyl. [b] Moles × 10^4 in analyzed aliquot. [c] Slope of a plot of [ROPh]/[ROH] *vs.* $[NaOPh]_{av}$. [d] NaOH, *M*.

Table III. Product Compositions of Solvolyses of γ-Methylallyl Chloride (PCl) in 60% Aqueous Dioxane at 80.4° with Added Sodium Phenoxide

[PCl]	[NaOPh]	SOH[a]	POH[a]	SOPh[a]	POPh[a]	[POH]/[SOH]	m[b]
0.1045						56/44	
0.1002	0.110	0.70	0.80	0	12.8	53/47	142
0.1014	0.150	0.35	0.58	0	12.6	63/37	144
0.0993	0.150	0.33	0.54	0	14.0	62/38	
0.1083	0.200	0.18	0.34	0	15.4	65/35	202
0.1015	0.200	0.19	0.49	0	13.5	72/28	133

[a] Moles × 10^4 in analyzed aliquot. See footnotes to Table II. [b] Slope of a plot of [ROPh]/[ROH] *vs.* $[NaOPh]_{av}$.

that discrete, distinct allylic ion pairs intervene generally in these substitution reactions.

We shall here interpret the data in terms of an ion-pair mechanism, pointing out when appropriate the features of these studies which are only with difficulty reconcilable with alternative schemes.

Results

The experimental approach chosen to investigate the possibility that product spreads on solvolysis of allylically related halides may have their cause in the intermediacy of discrete, allylically related ion pairs involved kinetic and product studies of the solvolysis, in 60% aqueous dioxane, of α- and γ-methylallyl chloride in the presence of varying concentrations of added sodium phenoxide. Selected experiments with the primary γ-methylallyl chloride were also undertaken in the solvent systems 40 and 25% aqueous dioxane.

Before these data are presented it behooves us to present and to comment briefly upon the solvolytic behavior of α- and γ-methylallyl chloride on solvolysis in 60% aqueous dioxane in the absence of a perturbing nucleophile. In fact, under these conditions the chlorides are found to solvolyze at nearly identical rates (Table I), although a sizable product spread is observed (Tables II and III). Thus γ-methylallyl chloride furnishes 56% of the corresponding primary alcohol whereas the secondary chloride, α-methylallyl chloride, furnishes only 33% of this rearranged primary alcohol. Accordingly a product spread of 56% − 33% = 23% is observed.

Of prime importance in supporting conclusions later to be drawn from the data presented in this paper is the fact that both allylic chlorides undergo rearrangement, concomitant with solvolysis, to furnish the isomeric allylic chloride; starting with either isomer isolation, after partial solvolysis, of unreacted allyl chloride reveals the presence of its rearrangement product. The extent of rearrangement is particularly significant from α-methylallyl chloride. Data are given in Table IV.

Consider first the product data derived from solvolyses of the secondary α-methylallyl chloride in 60%

Table IV. Isomerization of α-Methylallyl and γ-Methylallyl Chloride in 60% Aqueous Dioxane at 80°

Starting isomer	% solvolysis[a]	% isomerization[b]
γ-Methylallyl chloride	83	4
α-Methylallyl chloride	69	17

[a] Determined by titrating inorganic chloride. [b] Amount of the isomeric allylic chloride in the total unreacted covalent chloride.

aqueous dioxane at 80° in the presence of varying concentrations of added sodium phenoxide (Table II). The major products of the reaction are α- and γ-methylallyl alcohol and α- and γ-methylallyl phenyl ether. Smaller amounts of C-alkylation products (the corresponding α- and γ-methylallylphenols) and of butadiene[9] were also formed but were not routinely analyzed for.

The invariance of the ratio of primary (POH) and secondary (SOH) solvolysis products, [POH]/[SOH], with varied nucleophile concentration is particularly worthy of note. This constancy is consistent with a reaction scheme which assumes that both solvolysis products, POH and SOH, arise by solvent attack on a single common intermediate and this tentative conclusion is reinforced by the last entry in Table II where it will be seen that 0.200 *M* NaOH is equally ineffective in changing the solvolysis product ratio.

In contrast should be noted the variation in the ratio [POPh]/[SOPh] with varied phenoxide concentration. More significant perhaps than the variation itself is the fact that at higher concentrations of phenoxide the ratio in question appears to level off toward a constant value; above ~0.3 *M* NaOPh a constant ratio of 17/83% of the rearranged primary γ-methylallyl phenyl ether to the unrearranged secondary ether is formed.

The decreasing value of this ratio at lower phenoxide concentrations is apparently to be ascribed to the aforementioned rearrangement of α- to γ-methylallyl chloride, competitive under these conditions with the bimolecular (see Table I) attack by phenoxide which produces, largely, unrearranged α-methylallyl phenyl ether. (γ-Methylallyl chloride, in turn, reacts facilely in bimolecular fashion to furnish exclusively unrearranged γ-methylallyl phenyl ether) (Tables I and III).

On the other hand, the residual 17% of rearranged γ-methylallyl phenyl ether, formed bimolecularly (Table I) at higher phenoxide concentrations, cannot be ascribed to this cause and must be recognized as an authentic example of the S$_N$2′ reaction, bimolecular nucleophilic substitution with allylic rearrangement.[12] (An alternate explanation to that usually accepted to accommodate the operationally defining conditions of the S$_N$2′ reaction will be presented below.)

The last column of Table II establishes that the phenyl ethers and solvolysis products are formed competitively from a common species; *i.e.*, a plot of [ROPh]/[ROH] *vs.* [NaOPh] is linear.

Solvolysis of the isomer and primary γ-methylallyl chloride in the presence of varying concentrations of sodium phenoxide (Table III) exhibits many of the same features shown by the secondary α-methallyl chloride; differences are perhaps of more interest and importance. In contrast to the behavior of α-methylallyl chloride, its isomeric γ-methylallyl chloride (1) produces *no* rearranged ether, α-methylallyl phenyl ether;[13] and (2) shows an increasing ratio of primary, unrearranged γ-methylallyl alcohol/α-methylallyl alcohol with increasing phenoxide concentration.

This latter observation appears but to be an artifact resulting from the hydrolysis of sodium phenoxide as can be seen from the data of Table V.[14]

Table V. Product Compositions of Solvolysis of γ-Methylallyl Chloride in 60% Aqueous Dioxane at 80.4° with Added Sodium Hydroxide

[PCl]	[NaOH]	SOH[a]	POH[a]	[POH]/[SOH]
				56/44
0.0058	0.0100	0.37	0.64	63/37
0.0231	0.0431	1.35	3.15	70/30
0.1075	0.1156	4.7	15.0	76/24

[a] Moles × 10^4 in analyzed aliquot. See footnotes to Table II.

$$\mathrm{OPh^- + H_2O \rightleftharpoons OH^- + HOPh}$$

Thus higher concentrations of sodium phenoxide have associated with them increased concentrations of sodium hydroxide; the latter reagent is capable of producing, in bimolecular fashion (Table I), increased percentages of γ-methylallyl alcohol. The product ratio data are quantitatively correlated quite adequately by this interpretation; accordingly *phenoxide as such is unable to affect the ratio of primary to secondary solvolysis products.*

As with the isomeric α-methylallyl chloride, the data of the last column of Table III indicate that a common species intervenes in the formation of phenyl ether and of solvolysis products.[15]

Additional evidence that the changing ratio of [POH]/[SOH] on solvolysis of γ-methylallyl chloride arises as a result of hydrolysis of sodium phenoxide and not as a result of a selective trapping by phenoxide ion of a reaction intermediate is provided by the data of Table VI where the ratio of [POH]/[SOH] appears to be independent of both the nature and concentration of competitive nucleophiles, which range from sodium azide through sodium thiocyanate, sodium phenoxide, aniline, pyridine, and sodium acetate. The relative efficiencies of these nucleophiles, as determined by the ratio, k_N/k_s (the slope of a plot of [RN]/[ROH] *vs.* $[\mathrm{N}]_{\mathrm{av}}$; see Table VI), decrease in the given order.

The kinetic data of Table I indicate that both allylic chlorides undergo bimolecular reactions with both phenoxide and hydroxide ion, the former being approximately ten times more effective toward both substrates.

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(9) The reluctance[10] to undergo elimination observed generally with allyl systems may well be associated with the dispersal of positive charge in the ion pair (*vide infra*), away from the α-substituents.

(10) Vernon[11] has reported the only other instance, to our knowledge, of the detection of elimination products from an allyl system by either a uni- or bimolecular process: namely, the formation of a small amount of butadiene from the reaction of α-methylallyl chloride with ethanolic sodium ethoxide.

(11) C. A. Vernon, *J. Chem. Soc.*, 4462 (1954).

(12) For an excellent recent summary of the status of the classical S$_N$2′ reaction, see F. G. Bordwell, *Accounts Chem. Res.*, 3, 281 (1970).

(13) This is a particularly significant result as it establishes that the ion-pair precursor of much of the solvolysis product (Scheme I) is *not* attacked by phenoxide ion; if it were, both isomeric phenyl ethers should be observed (as in solvolysis). See ref 5.

(14) An experiment described in the Experimental Section establishes that the concentration of hydroxide ion in a solution 0.20 *M* in sodium phenoxide (60% aqueous dioxane) is *ca.* 0.01 *M*.

(15) See Appendix of ref 8.

Table VI. Product Compositions of Solvolysis of γ-Methylallyl Chloride in 60% Aqueous Dioxane at 80.4° in the Presence of Various Nucleophiles

[PCl]	Nucleophile	[Nucleophile]	[POH]/[SOH]	% alcohol of total product	$(k_N/k_s)^b$
0.1045	None		56/44	100	
0.1009	NaN_3	0.0530	55/45	40	
0.1019	NaN_3	0.0726	58/42	34	
0.1013	NaN_3	0.1031	*a*	*a*	1500[c]
0.0733	NaSCN	0.1132	50/50	4.5	278
0.1025	NaSCN	0.0551	54/46	50	
0.1002	NaOPh	0.110	53/47	10.5	142
0.0992	$PhNH_2$	0.0735	58/42	38	
0.1030	$PhNH_2$	0.1345	61/39	17	59.0
0.1029	$PhNH_2$	0.1881	57/43	10	
0.1039	Pyridine	0.3153	57/43	20	15.2
0.1022	NaOAc	0.4668	59/41	42	3.32

[a] No alcohol products detectable. [b] Calculated from the formula $[RN]/[ROH] = k_N[N]_{av}/k_s$. Since every molecule of PCl consumes a molecule of nucleophile, $[N]_{av} = [N]_i - [PCl]_i/2$. [c] Estimated from unpublished data, J. V. Carter.

Furthermore the primary chloride (PCl) undergoes bimolecular attack at about ten times the rate of the secondary chloride (SCl).[16]

Finally, in an unsuccessful attempt to find evidence of "borderline" behavior [which would in turn have allowed definitive experiments[8] to be carried out for the positive identification of distinctly different primary and secondary ion pairs (P^+Cl^- and S^+Cl^-)], kinetic data were obtained for the reaction of γ-methylallyl chloride and sodium phenoxide in both 40% aqueous dioxane at 32.0° and in 25% aqueous dioxane at 10°. In both systems only strict second-order behavior was observed. These data are given in Tables VII and VIII, while product data for the reaction of γ-methylallyl chloride and phenoxide ion in 25% aqueous dioxane at 10° are given in Table IX.

Table VII. Rate Constants for the Solvolysis of γ-Methylallyl Chloride in 40% Aqueous Dioxane at 30.2° with Added Sodium Phenoxide

[PCl]	[NaOPh]	$k_1 \times 10^4$ sec^{-1}	$k_2 \times 10^3$ l. mol^{-1} sec^{-1} [a]
0.01006	0.0	0.433 ± 0.031	
0.01035	0.0	0.390 ± 0.015	
0.01019	0.0513	3.50 ± 0.25	6.45
0.01020	0.0513	3.09 ± 0.07	5.80
0.01042	0.0769	4.19 ± 0.08	5.26
0.01024	0.1026	6.24 ± 0.35	5.97
0.01020	0.1026	5.27 ± 0.10	4.97
0.01039	0.1282	7.10 ± 0.17	5.43
0.01038	0.1282	7.01 ± 0.18	5.37
	$[NaNO_3]$		
0.01024	0.1002	0.421 ± 0.016	

[a] Calculated by subtracting the no-salt first-order rate constant from the observed first-order rate constant and dividing the remainder by the average sodium phenoxide concentration.

Discussion

Any mechanism which hopes to approximate the true mechanism of the investigated reactions of α- and γ-methylallyl chloride must be able to account for the following observations: (1) product spreads are evident over a wide spectrum of solvent nucleophilicity (acetic acid to ethanol) and solvent ionizing power (ethanol to water); (2) allylic rearrangement and solvolysis occur competitively; (3) a bimolecular nucleophilic attack with allylic rearrangement (an authentic "S_N2'" reaction) has been observed between phenoxide ion and γ-methylallyl chloride; and (4) the solvent sensitivity[18] of the bimolecular reaction between the substrate γ-methylallyl chloride and phenoxide ion ($m_G = 0.57$) approaches that of the solvolysis process ($m_G = 0.76$) (*vide infra*).

Table VIII. Rate Constants for Solvolysis of γ-Methylallyl Chloride in 25% Aqueous Dioxane at 10° with Added Sodium Phenoxide

[PCl]	[NaOPh]	$k_1 \times 10^4$ sec^{-1}	$k_2 \times 10^3$ l. mol^{-1} sec^{-1}
0.01025	0.0	0.130 ± 0.006	
0.01040	0.0608	1.15 ± 0.04	1.83
0.01034	0.0961	1.90 ± 0.11	1.94
0.01030	0.1044	1.93 ± 0.02	1.82
0.01067	0.1216	2.72 ± 0.13	2.22
0.01047	0.1946	3.06 ± 0.09	1.55
0.01035	0.196	4.05 ± 0.06	2.05
0.01029	0.192	3.94 ± 0.04	2.04
0.01042	0.200	3.75 ± 0.06	1.86
0.01038	0.300	6.07 ± 0.06	2.01
0.01037	0.300	4.57 ± 0.08	1.51
0.01040	0.298	5.27 ± 0.12	1.76
	$[NaNO_3]$		
0.01065	0.200	0.112 ± 0.003	
0.01022	0.300	0.133 ± 0.003	

We submit that *each* of these observations is beautifully consistent with an ion-pair mechanism involving discrete, distinct (presumably intimate) allylic ion pairs (P^+Cl^- and S^+Cl^-) derived reversibly from each of the isomeric covalent substrates, PCl and SCl, respectively. And we further submit that each of these observations is only difficultly reconcilable with a mechanism involving traditional, competitive S_N1 and S_N2 pathways.

We conclude, in perfect analogy with the mechanistic scheme which we advanced in paper XIV of this series[5] (to account for the kinetic, product, and stereochemical behavior of α,γ-dimethylallyl chloride), that the pres-

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(16) This value is to be contrasted with more typical primary to secondary ratios of approximately 50–100; for example, the bromide exchange in acetone with *n*-propyl bromide and isopropyl bromide has $k_p/k_s = 60$.[17] The situation here is reminiscent of that described in the preceding manuscript[6] where it was shown that the relative rates of (bimolecular) attack by azide ion into the primary γ,γ- and the secondary α,γ-dimethylallyl chloride were $k_{\gamma\gamma}/k_{\alpha\gamma} = 1.8$.

(17) P. B. D. de la Mare, *J. Chem. Soc.*, 3180 (1955).

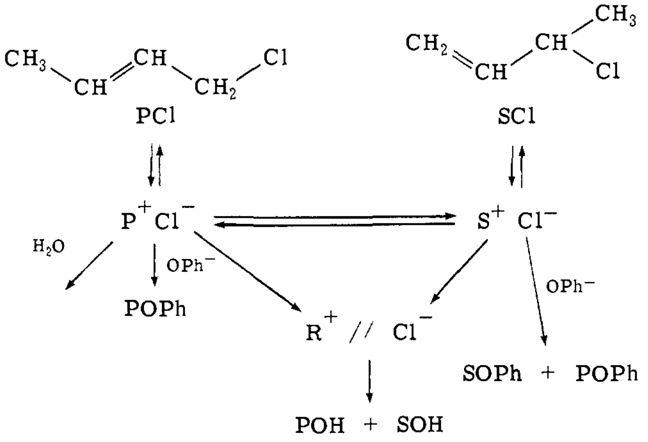
(18) In this and the accompanying two manuscripts the symbol m_G has been used to represent the substrate constant of the Grunwald–Winstein equation; *i.e.*, $\log (k_2/k_1) = m_G(Y_2 - Y_1)$. See ref 17 of ref 5 and ref 28 of ref 6.

Table IX. Product Compositions of Solvolyses of γ-Methylallyl Chloride in 25% Aqueous Dioxane at 10° with Added Sodium Phenoxide

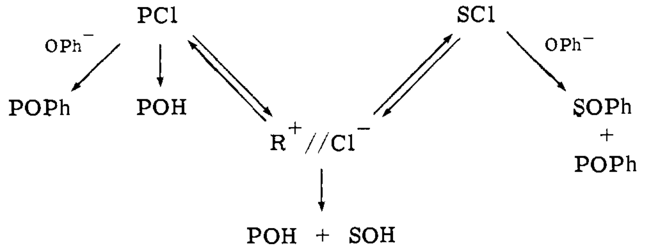
[PCl]	[NaOPh]	SOH[a]	POH[a]	[POH]/[SOH]	POPh[a]	P phenol[a,b]	m[c]
0.009822	0.01032	8.97	13.82	61/39	5.81	2.0	63
0.00995	0.02064	5.38	7.71	59/41	9.26	3.2	61
0.01162	0.04128	3.03	4.26	58/42	14.5	5.0	75
0.01101	0.0774	1.53	2.41	61/39	13.5	4.6	64

[a] Moles × 10^5 in analyzed aliquot. See footnotes to Table II. [b] *o*-(γ-Methylallyl)phenol. [c] Slope of a plot of [ROPh]/[ROH] *vs.* $[\text{NaOPh}]_{\text{av}}$.

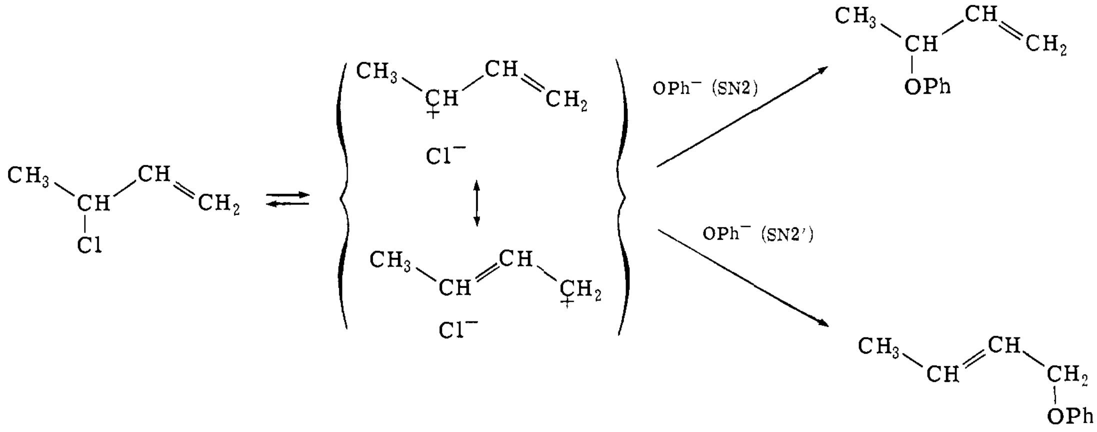
Scheme I



Scheme II



Scheme III



ently investigated reactions of α- and γ-methylallyl chloride are best described by Scheme I.[19]

The advantages which such a scheme has over a competitive SN1–SN2 picture can be more dramatically made if the alternative scheme (Scheme II) is also diagrammed. First it should be observed that the latter scheme, if it will account for the intramolecular rearrangement which accompanies solvolysis,[20] must also include at least one ion-pair intermediate (or transition state). The question then is not whether ion pairs are required, but rather how *many* ion pairs are required.

The ion-pair mechanism accounts for the continued observance of product spreads under greatly varied conditions of solvent-ionizing power rationally as the result of the relatively unselective reactions of a high-energy intermediate, the primary ion pair, P^+Cl^-; the competitive SN1–SN2 scheme would require that as solvolysis rates change by a factor of *ca.* 16,000 (ethanol to water)[22] the reactions of covalent substrate to give ion pairs and with nucleophile, solvent, must continue to compete. This requires a rather extraordinary (and traditionally unexpected)[25] near equivalence of the solvent sensitivities of the rates of an "SN2" and of an "SN1" process as a function of ionizing power.

The traditional SN2′ reaction has always struck us as an intellectually unreasonable[26] mechanism since it requires the unprovoked attack by nucleophile at the γ position of an allylic system, three atoms removed from the leaving goup. The "SN2′" mechanism becomes intellectually reasonable, it seems to us, when one assumes that it proceeds *via* an ion-pair mechanism as then the attack ceases to be unprovoked; when a redistribution of electron density, accompanying the initial formation of the intimate ion pair, induces (by resonance and/or induction) an electron deficiency at

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(19) We have chosen to represent the rearrangement process as proceeding *via* direct interconversion between P^+Cl^- and S^-Cl^- rather than *via* reversal from the species, $R^+//Cl^-$, in harmony with our similar conclusion for the α,γ-dimethylallyl chloride system. See ref 5.

(20) Solvolysis of α,α-dimethylallyl chloride in 75% aqueous dioxane is accompanied by *intramolecular* rearrangement to γ,γ-dimethylallyl chloride.[21] The α-methylallyl chloride system, being a potentially poorer carbonium ion, must then also undergo rearrangement by an intramolecular pathway.

(21) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 2504 (1954).

(22) $Y_{\text{EtOH}} = -2.03$;[23] $Y_{\text{H}_2\text{O}} = +3.49$;[23] $m_{\text{G}} = 0.760$ (γ-methylallyl chloride).[24]

(23) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 78, 2770 (1956).

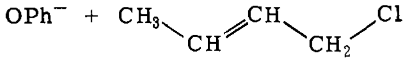
(24) Unpublished work, J. V. Carter.

(25) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969.

(26) This abhorrence is apparently shared by Professor Bordwell

the γ position, there exists a driving force for γ substitution (Scheme III). For the first time the S$_N$2′ mechanism becomes intellectually satisfying.[28]

Finally, let us turn to the experimentally observed solvent dependence of the bimolecular process



$$OPh^- + CH_3CH{=}CHCH_2Cl$$

Again, if the competitive S$_N$1–S$_N$2 mechanism is required to accommodate the observation that the rate of this process is dramatically accelerated ($k_{25\%}/k_{60\%} = 12.9$; $m_G = 0.57$)[18,29] by solvent-ionizing power it does so only by denying the traditional expectations of classical S$_N$2 theory: that the rate of reaction of a charged nucleophile with neutral substrate should be little changed ($m_G \simeq 0$) or, more probably, slightly decreased ($m_G < 0$) by an increase in solvent-ionizing power.[25] Yet the facts are that it shows a solvent sensitivity (based on the Grunwald–Winstein criterion)[18] of *ca.* 75% that of the solvolysis process. Truly this must be an ionic transition state.[30]

We conclude that, without exception, the chemical criteria uncovered in this study fit beautifully into the context of the ion-pair mechanism (Scheme I) and present severe difficulties to a cohesive explanation assuming any variations of a scheme involving competitive S$_N$1–S$_N$2 reactions (Scheme II).

Conclusions

In this series of three papers we have established (1) that the borderline behavior evidenced by azide and thiocyanate ion substitution into α,γ-dimethylallyl chloride is beautifully accommodated by the predictions of the ion-pair mechanisms *with no arbitrary parameters* (a common $x = 4.0$ for both nucleophiles).[5] These data can only with difficulty be accommodated by the predictions of competitive S$_N$1–S$_N$2 reactions and then only with an adjustable parameter. We have established (2) that the solvent sensitivity of nucleophilic substitution by azide into α,γ-dimethylallyl chloride ($m_G = +0.73$)[5] and by phenoxide ion into γ-methylallyl chloride ($m_G = +0.57$) is remarkably more like that expected of carbonium ion reactions ($m = 1.00$ and $m = 0.76$, respectively) than like that predicted by traditional S$_N$2 theory ($m_G \leq 0$ for both N_3^- and PhO^-).[25] We have established (3) that rates of bimolecular attack by nucleophile (N_3^-) into primary and secondary allylic substrates, α,γ- and γ,γ-dimethylallyl chloride, take place at virtually identical rates, independent of the extent of substitution at the reaction center.[6] We have established (4) that bimolecular attack by azide ion on the tertiary α,α-dimethylallyl chloride takes place (although it may be at the γ position *via* an "S$_N$2′" reaction) at a rate *ca.* $^1/_{10}$ that of bimolecular attack on the corresponding primary γ,γ-dimethylallyl chloride.[6] We have established (5) that an unequivocal example of mechanism S$_N$2′ (bimolecular nucleophilic attack on allylic substrate with rearrangement) is observed in the reactions of α-methylallyl chloride.

We submit that the cumulative evidence is overwhelming and irrefutable. All of these observations lead, singly and collectively, to the conclusion that all of the investigated allylic systems (with the possible exception of the methylphenyl system)[6] react *via* discrete, distinct, allylic ion pairs, species capable of retaining their asymmetry. The recognition of such species allows one to rationalize (1) borderline behavior with its associated stereochemical results; (2) the observed solvent sensitivity of bimolecular reactions; (3) the observed steric insensitivity; (4) the attack at tertiary carbon (and/or S$_N$2′ attack); (5) the observed S$_N$2′ reaction; and (6) product spreads.

Experimental Section

Preparation and Purification of Chemicals. γ-Methylallyl Chloride. γ-Methylallyl chloride was obtained from Aldrich Chemical Co. and from Columbia Organic Chemicals Co. The commercial material was contaminated with the isomeric α-methylallyl chloride. Purification was by vpc, using a 4 ft × $^1/_4$ in. (o.d.) stainless steel column packed with 10% (w/w) adiponitrile on 60–80 mesh Chromosorb W (HMDS treated), operating with a helium flow of 45–60 ml/min at temperatures ranging from 30 to 50°. Purity was at least 99%, as determined by vpc. Fresh material was collected before each experiment to ensure against isomerization.

α-Methylallyl Chloride. This material was also obtained commercially and was purified exactly as was γ-methylallyl chloride.

γ-Methylallyl Alcohol. Yellow label Eastman Organic Chemicals material was purchased and distilled once before use, bp 120–121°.

α-Methylallyl Alcohol. Commercial material, purchased from Columbia Organic Chemicals Co., was used without further purification.

α-Methylallyl Phenyl Ether. A mixture of 0.2 mol of phenol, 0.22 mol of α-methylallyl chloride, and 0.22 mol of potassium carbonate in 50 ml of dry acetone was refluxed for 8 hr. After cooling, 250 ml of water was added and the resultant solution was extracted with three 35-ml portions of ethyl ether. The ether-soluble fraction was washed with 10% sodium hydroxide and was then dried over magnesium sulfate. Distillation yielded 6 ml of material, bp 52° (1 mm). The infrared spectrum was consistent with the proposed structure.

γ-Methylallyl Phenyl Ether. This ether was prepared by exactly the same method used for the α isomer, using γ-methylallyl chloride in place of α-methylallyl chloride. The reaction yielded 13 ml of material, bp 66–68° (1.0–1.2 mm). The infrared spectrum was consistent with the proposed structure.

o-(α-Methylallyl)phenol. γ-Methylallyl phenyl ether was refluxed in mesitylene under nitrogen for 4 hr. Distillation of the reaction mixture gave the product, bp 63–65° at 0.3 mm. The infrared spectrum was consistent with the proposed structure.

o-(γ-Methylallyl)phenol. α-Methylallyl phenyl ether was refluxed in mesitylene under nitrogen for 4 hr. Distillation of the reaction mixture gave the product, bp 68° (0.45 mm).

Dioxane. Dioxane was purified by the method of Fieser,[31] stored over sodium, and distilled immediately prior to use.

Water. Distilled water was passed first through a Barnstead oxygen-removing column and then through a Barnstead mixed ion exchange bed.

Pentane. Crude pentane was shaken with numerous portions of concentrated sulfuric acid until the acid layer was colorless,

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(see ref 12) and, at one time, it was apparently even shared by Professor Ingold,[27] later one of its champions.

(27) A. G. Catchpole, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 8 (1948).

(28) See also ref 17 of R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 6031 (1969).

(29) From Tables III and IX the ratio of rates of phenoxide and solvent attack, k_{OPh^-}/k_s, as given by the slope of a plot of [ROPh]/[ROH] *vs.* [OPh$^-$], are 155 and 66 for 60% aqueous dioxane and 25% aqueous dioxane, respectively. Using an m value of 0.760 for the solvolysis of γ-methylallyl chloride[24] and Y values from the literature,[22,23] a value of 12.9 is calculated as the rate enhancement of phenoxide attack effected by the change in solvent.

(30) In our opinion the importance and utility of selectivity considerations in the diagnosis of reaction mechanisms have not been adequately appreciated. The competitive formation of diverse products under varying conditions should be recognized generally as good suggestive evidence for the intervention of high-energy, unselective intermediates in the reaction pathway.

(31) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath, Boston, Mass., 1941.

washed with water, dried over magnesium sulfate, filtered, and distilled through a 4-ft column packed with Heli-Pak.

Sodium Phenoxide. Sodium phenoxide was prepared in aqueous solution by adding equimolar amounts of phenol and sodium hydroxide to a volumetric flask, the sodium hydroxide being in the form of a standardized aqueous solution. Extreme care had to be taken to exclude oxygen from every step of the preparation to obtain solutions of sodium phenoxide which did not rapidly turn yellow.

Sodium Azide. The commercial salt (Fisher) was dissolved in hot water and the solution was filtered. After cooling to 0° the solution was diluted with ethanol, causing the salt to precipitate. This material was filtered and the filtrate was washed with acetone and stored in a desiccator over Drierite.

Kinetic Procedures. Rate constants were obtained by following the production of either acid or chloride ion. The acid concentration was determined by pipetting a standard volume of the reaction mixture into a quench and titrating with standard (0.01 *N*) sodium hydroxide to the end point of Phenol Red–Bromthymol Blue mixed indicator. Chloride ion concentration was determined by potentiometric titration. An aliquot of the reaction mixture was quenched in a two-phase mixture of 1 *N* nitric acid and diethyl ether and titrated with standard (0.01 *N*) silver nitrate to a constant voltage using either a Fisher titrimeter or a Beckman pH meter equipped with silver and calomel electrodes. The two-phase quench was found to be more effective than dilute nitric acid alone, since the unreacted organic chloride is extracted by the diethyl ether, eliminating drifting end points. Nitric acid is necessary since all phenoxide must be acidified to phenol; phenoxide reacts with silver nitrate to form a black precipitate in water.

Solutions whose reaction rates were determined by following acid production were prepared by dissolving weighed amounts of starting material and the appropriate salt in the solvent mixture in a 100-ml volumetric flask. Portions of this solution were placed in constricted, nitrogen-flushed 6-in. test tubes which were subsequently sealed and placed in a constant-temperature bath. This ampoule technique, as well as the use of dioxane freshly distilled from sodium and distilled, deoxygenated deionized water, was found necessary in order to obtain constant infinity titers. It was not necessary to use the ampoule technique when rates were followed by titration of chloride ion. Instead, the volumetric flask in which the solution was prepared was placed in the constant-temperature bath and aliquots were pipetted from it at regular intervals.

Due to solubility problems, in the more aqueous solvent systems the starting material had to be added to the dioxane and followed by addition of water. These solutions were very thoroughly shaken to ensure complete dissolution of the starting material. For the rates measured at 10°, the solvent mixtures containing sodium phenoxide were prepared and cooled to 0°. The starting material was added by syringe, the weight being obtained by difference, and the resulting solution was shaken for about 5 min before being placed in the constant-temperature bath.

Product Determination Procedures. Reaction mixtures for product studies were prepared by pipetting into a 25-ml volumetric flask an appropriate amount of dioxane, adding the starting material by syringe to the dioxane, and finally adding the necessary amount of an aqueous solution of the desired nucleophile. As dissolution of water in dioxane gives a small volume contraction, it was necessary to have on hand some separately prepared dioxane–water solvent of the proper composition, which was used to bring the volume of the reaction mixture to the mark of the flask. In the case of the product runs done at 10°, 50-ml volumetric flasks were used, and the starting material was added after the solvent mixture had been prepared and cooled to *ca.* 0°.

Product runs were analyzed by vapor-phase chromatography, using an F & M Model 609 gas chromatography equipped with a flame ionization detector and a Texas Instruments integrating recorder. It was necessary to use two sets of conditions to analyze each reaction mixture, one for determination of the solvolysis products and another for analysis of the products resulting from attack by nucleophile. For the solvolysis products, α- and γ-methylallyl alcohol, single-phase packing, Porapak Q, was found to give the desired separations. Three different stainless steel (s.s.) columns with 120–150 mesh Porapak Q were used in the studies: 6 ft × $^1/_8$ in. (o.d.), 4 ft × $^1/_4$ in. (o.d.), and 6 ft × $^1/_4$ in. (o.d.). The reason for using the different columns is that the high-boiling products in the reaction mixtures coat the packing and gradually destroy the separations. A 10 ft × $^1/_4$ in. (o.d.) copper column packed with 10% (w/w) FFAP on HMDS-treated Chromosorb W also gave good analyses of the alcohols. Conditions for the Porapak Q columns were: column oven temperature, 190°; nitrogen flow rate, 20 ml/min; hydrogen flow rate, 25 ml/min. For the FFAP column, conditions were: column over temperature, 100°; nitrogen flow rate, 25 ml/min; hydrogen flow rate, 25 ml/min. α-Methylallyl and γ-methylallyl phenyl ethers, and *o*-(α-methylallyl)- and *o*-(γ-methylallyl)phenols were analyzed on a 6 ft × $^1/_8$ in. (o.d.) stainless steel column packed with 20% diethylene glycol succinate on 60–80 mesh Firebrick, operated at 100–175° with a nitrogen flow rate of 30 ml/min and a hydrogen flow rate of 30 ml/min.

Work-up prior to analysis was limited to the extraction of water from the reaction mixture. Since both alcohols are water soluble, there is no way to extract them from dioxane. A portion of the reaction mixture to be analyzed was pipetted into a separatory funnel containing a milky solution of saturated potassium carbonate and a weighed amount of the appropriate internal standard. The resulting mixture was thoroughly shaken. If no solid potassium carbonate remained, more was added and the mixture was shaken again. When there was undissolved salt remaining, indicating the complete extraction of water, the organic layer was separated and placed in a 10-ml erlenmeyer flask with a ground-glass joint which was subsequently sealed with two silicone septums. Analyses were made by inserting a Hamilton syringe through the septums, drawing up 0.5–2.0 μl and injecting into the gas chromatograph. At least three separate injections were made for each determination, the average value being reported.

One advantage of the Porapak Q column packing is that water has an extremely short retention time. This made it possible to analyze most of the solutions for the alcohols without work-up. A control experiment (described in detail under Control Experiments) showed that the difference between results obtained with and without extraction of water was within experimental error. Only when the amount of alcohol present was very small were the solutions worked up, so as to concentrate the solution. Of course, all solutions analyzed using the other two columns were worked up.

The concentration of each desired product in the reaction mixture was determined by relating its peak area to that of a known amount of an internal standard; 1-propanol was used for the alcohols and either anisole or benzaldehyde for the products resulting from phenoxide attack. Since the flame-ionization detector is not linear in molarity, it was necessary to determine response factors for each compound to be analyzed. These were done by preparing standard mixtures of internal standards and compounds, analyzing them, and determining the constant by which the apparent value of the ratio of internal standard to compound has to be multiplied to obtain the true ratio. Listed in Table X are the response factors so obtained.

Table X. Response Factors of Reaction Products from Solvolysis of α- and γ-Methylallyl Chlorides in Aqueous Dioxane with Added Phenoxide

Analysis conditions	Internal standard/compound[a]	Response factor[b]
4 ft × $^1/_4$ in. s.s. Porapak Q; 185°; N_2, 20 ml/min; H_2, 25 ml/min	*n*-PrOH/SOH *n*-PrOH/POH	1.49 1.64
6 ft × $^1/_4$ in. s.s. Porapak Q; 215°; N_2, 20 ml/min; H_2, 25 ml/min	*n*-PrOH/SOH *n*-PrOH/POH	1.38 1.46
8 ft × $^1/_8$ in. s.s. 20% DEGS on 60–80 mesh Firebrick programmed from 100° at 13 deg/min; N_2, 30 ml/min; H_2, 30 ml/min	PhOMe/POPh PhOMe/P phenol[c]	1.46 1.31
8 ft × $^1/_8$ in. s.s. 20% DEGS on 60–80 mesh Firebrick; 115°; N_2, 30 ml/min; H_2, 35 ml/min	PhCHO/POPh PhCHO/SOPh	1.47 1.55
10 ft × $^1/_4$ in. copper 10% FFAP on 60–80 mesh Chromosorb W (HMDS treated); 100°; N_2, 25 ml/min; H_2, 25 ml/min	*n*-PrOH/SOH *n*-PrOH/POH	1.58 1.36

[a] S = secondary = α-methylallyl; P = primary = γ-methylallyl. [b] The ratio of the peak areas of internal standard to compound is multiplied by the response factor to get the actual mole ratio. [c] *o*-(γ-Methylallyl)phenol.

Control Experiments. To ensure the validity of the data obtained, the following control experiments were carried out.

1. To check the efficiency of the work-up procedure various standard mixtures of the reaction products in aqueous dioxane were prepared, subjected to the work-up procedure, and analyzed. An example of the results obtained is the following experiment. Into 25 ml of 25% aqueous dioxane were weighed 2.37×10^{-4} mol of α-methylallyl alcohol and 2.35×10^{-4} mol of γ-methylallyl alcohol. After mixing, 20 ml of this solution was pipetted into a separatory funnel containing 125 ml of saturated potassium carbonate and 2.47×10^{-4} mol of 1-propanol. After thorough shaking, the organic layer was separated and analyzed by vpc, using the 20% DEGS column, giving 2.37×10^{-4} mol of α-methylallyl alcohol and 2.32×10^{-4} mol of γ-methylallyl alcohol. Thus in the most aqueous solvent used, the work-up procedure quantitatively accounts for the most water-soluble products produced in the reactions studied.

2. A standard mixture of α- and γ-methylallyl alcohol and 1-propanol in dioxane was analyzed both before and after addition of water to the solution, using the 6 ft × $^1/_8$ in. (o.d.) Porapak Q column. The actual ratio of primary to secondary alcohol in the mixture was 53.4% primary and 46.4% secondary. Analysis before addition of water gave a value of 52.3% primary alcohol, with an overall recovery of 93%. After adding some water to the solution, analysis showed 52% primary alcohol, with an overall recovery of 85%. A check of the 4 ft × $^1/_4$ in. (o.d.) Porapak Q column gave similar results. Thus the work-up procedure is not absolutely necessary when using Porapak Q columns for analysis.

3. To determine whether the ratio of primary to secondary alcohol changes during solvolysis of the chlorides, a product run was carried out in which aliquots of the reaction mixture were removed from the constant-temperature bath at various degrees of reaction and analyzed. The ratio of alcohols resulting from the solvolysis of α-methylallyl chloride in 60% aqueous dioxane at 80.4° was found to be constant from 20% reaction to 10 half-lives.

4. To show that the alcohols do not equilibrate under the conditions of the reaction the thermodynamically less stable isomer. α-methylallyl alcohol, was dissolved in 60% aqueous dioxane which was 0.1 *N* in hydrochloric acid. The solution was analyzed before being placed in the constant-temperature bath and again after a time equivalent to 16 half-lives for the solvolysis of α-methylallyl chloride. No trace of rearranged alcohol was found in either of these analyses.

5. In order to determine the extent of rearrangement of one allylic chloride to the other during a solvolysis reaction, the following experiment was carried out. A reaction mixture was prepared, placed in the 80.4° bath for a period of time which allowed only partial reaction, removed, and cooled. Titration for inorganic chloride revealed the per cent reaction. The solution was worked up by pouring into an excess of water and extracting with methylene chloride. The separated organic layer was dried over calcium chloride, filtered, and distilled through an 18-in. packed column. The distillation was stopped when *ca.* 3 ml of solution remained. Analyses were done on a 4 ft × $^1/_4$ in. (o.d.) stainless steel column packed with 10% adiponitrile on HMDS-treated Chromosorb W, attached to the F & M Model 609 gas chromatograph.

A control was carried out to find out if the work-up precedure would isomerize the chlorides. A mixture of the two chlorides containing 39.5% α-methylallyl chloride showed 38% α-methylallyl chloride after being subjected to the work-up procedure.

The following are the results which were obtained. A 0.0903 *M* solution of α-methylallyl chloride in 60% aqueous dioxane was allowed to react for *ca.* 3000 sec at 80.4°. The reaction was quenched by cooling. Titration for inorganic chloride showed that the solvolysis was 69% complete. Analysis of the chlorides by vpc showed that the unreacted chloride was 83% α-methylallyl chloride and 17% γ-methylallyl chloride. Analysis of the α-methylallyl chloride used to prepare the solution showed no (less than 0.1%) primary chloride.

Titration of a portion of a 0.1220 *M* solution of γ-methylallyl chloride in 60% aqueous dioxane which had reacted for about 3000 sec at 80.4° showed that the solvolysis was 83% complete. Analysis of the γ-methylallyl chloride used to prepare the solution showed a 1% impurity of α-methylallyl chloride. Analysis after 83% reaction showed 4.9%. Thus the chloride remaining, correcting for the small impurity, was 4% α-methylallyl chloride and 96% γ-methylallyl chloride.

6. To determine the approximate sodium hydroxide concentration in aqueous dioxane solutions of sodium phenoxide, readings on a Beckman pH meter for various solutions of sodium phenoxide in 60% aqueous dioxane were compared to the readings for solutions of sodium hydroxide in the same solvent. It was found that in this solvent, at room temperature, a 0.200 *M* solution of sodium phenoxide is about 0.01 *M* in sodium hydroxide.

Equipment. Glassware. All glassware was soaked in a base bath, then soaked in a dilute hydrochloric acid solution, rinsed with copious amounts of distilled water, and dried at 110° in a closed oven.

Constant Temperature Baths. Rates carried out at 30, 40, 50, and 60° were done in an 8-gallon oil bath, the temperature being controlled with a Sargent thermometer unit. This bath was also used for product studies carried out at 80°. All temperatures except 30° were constant to within ±0.02°. It was necessary to use cooling water to maintain a temperature of 30°, and the variance at that temperature was ±0.1°.

Rates and product studies carried out at 10° were done in an Ultra-Kryostat Type UK 15 N low-temperature bath built by Lauda Instruments, Inc. The variance at 10° was ±0.1°.