Substitution at a Saturated Carbon Atom. XIV. The Case for Discrete, Distinct Allylically Related Ion Pairs[1]

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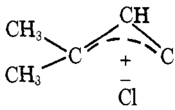
Abstract: Kinetics and product distributions accompanying the competitive substitutions by solvent and added external nucleophile into α,γ-dimethylallyl chloride have been determined under three related sets of conditions. In each case the data are beautifully correlated by the predictions of the ion-pair mechanism of nucleophilic substitution (in two of them, with *no* adjustable parameters). These conditions are (1) azide ion in absolute ethanol (36°), $m = 33$, $x = 4.0$; (2) thiocyanate ion in absolute ethanol (36°), $m = 6.6$, $x = 4.0$; and (3) azide ion in 90% aqueous ethanol (27°), $m = 12.0$, $x = 2.3$. It is to be noted that a prediction of the ion-pair mechanism, that the quantity, $x = k_{-1}/k_s$ (for a given substrate at constant solvent and temperature), be independent of the nature of the nucleophile, is gratifyingly confirmed experimentally by the first two sets of experiments ($x = 4.0$). Experiments with optically active substrate, levorotatory α,γ-dimethylallyl chloride, establish that (1) racemization of substrate accompanies solvolysis ($k_\alpha/k_t > 1$); (2) solvolysis product is completely racemic; and (3) azide or thiocyanate product is formed with (partial) optical activity. The ion-pair scheme, if it is to remain consistent with these stereochemical observations, must be expanded to include *asymmetric allylically related ion pairs*. Attempts are made to accommodate each of the three sets of data to the predictions of a competitive SN1–SN2 scheme, with limited success. A telling argument against this alternative interpretation of the data is advanced on the basis of nearly "limiting" solvent dependence of its presumed bimolecular "SN2" rate with azide ion.

The development of the current theory of nucleophilic substitution reactions[3] and a recognition of the importance of ion pairs as intermediates in these substitutions have depended heavily on observations gleaned from experiments using allylic substrates. In fact, the first published suggestion,[4] derived from experimental observations, that organic ion pairs might be significant intermediates in organic reactions stems from the observations of Young, Goering, and Winstein that solvolysis of α,α-dimethylallyl chloride (in solvent acetic acid) is accompanied by an intramolecular rearrangement, largely unaffected by added chloride ion, to its allylic isomer, γ,γ-dimethylallyl chloride. These data were interpreted by the authors, tentatively, in terms of an allylic ion-pair intermediate common to both rearrangement and substitution.



These early observations have since been buttressed by numerous subsequently reported experiments, emanating especially from the laboratories of Winstein[5] and of Goering[6] (where the emphasis has been heavily on allylic substrates), to such an extent that organic ion pairs have ceased to be an oddity in the lexicon of organic chemists and have assumed the status of accepted intermediates. It may be mentioned in passing that the cumulative experiments, out of both laboratories, constitute, conceptually and experimentally, among the most elegant and aesthetically pleasing in the literature of physical organic chemistry.

Our attention to allylic substrates (which dates publically to 1960)[7] has accordingly been strongly influenced by the evidence that ion pairs influence their behavior.

This interest in allylic substrates was intensified by our recognition (dating to 1963)[8] that certain apparent "SN2" and "borderline" substitutions at a saturated carbon atom might have as their mechanism a reversible formation of ion pair (R^+X^-), followed by attack of the nucleophilic agent on that ion pair.

$$RX \rightleftarrows R^+X^- \xrightarrow{k_N[N]} NR$$

The available compelling evidence that ion pairs intervene in selected reactions of allylic substrates made these as substrates particularly attractive for such investigations. Accordingly we initiated investigations, with particular attention to rates and product distributions, into the behavior of a number of allylic substrates toward competitive solvent and added external nucleophile attack. In this and the accompanying two papers[9,10] we describe our experiments utilizing (1) α,γ-dimethylallyl chloride in solvents absolute ethanol and 90% aqueous ethanol with added azide and thiocyanate ion (this manuscript, paper XIV); (2) α,α- and γ,γ-dimethylallyl chloride in 80% aqueous acetone[9] as well as α-methyl-γ-phenylallyl 2,6-dichlorobenzoate in numerous aqueous organic solvent mixtures and toward numerous nucleophiles (paper XV);[9] and (3) α-methyl- and γ-methylallyl chloride in various organic solvents and toward a variety of external nucleophiles,

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(3) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, Chapter 6.

(4) W. G. Young, S. Winstein, and H. L. Goering, *J. Amer. Chem. Soc.*, **73**, 1958 (1951).

(5) See, for example, S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

(6) See, for example, H. L. Goering, N. D. Nevitt, and E. F. Silversmith, *ibid.*, **77**, 5026 (1955).

(7) R. A. Sneen, *ibid.*, **82**, 4261 (1960).

(8) H. Weiner and R. A. Sneen, *Tetrahedron Lett.*, **No. 20**, 1309 (1963).

(9) R. A. Sneen and P. S. Kay, *J. Amer. Chem. Soc.*, **94**, 6983 (1972).

(10) R. A. Sneen and J. V. Carter, *ibid.*, **94**, 6990 (1972).

Table I. Experimental Data and Predictions of the Ion-Pair Mechanism for the Competitive Reactions with Solvent and Tetra-*n*-propylammonium Azide of α,γ-Dimethylallyl Chloride in Absolute Ethanol at 36.0°

$[(n\text{-Pr})_4NN_3] \times 10^2$	% RN_3, exptl	% RN_3, calcd[a]	$k_{exptl} \times 10^4$, sec^{-1}	k_{NS}[b] $\times 10^4$, sec^{-1}	k_{ip}[c] $\times 10^4$, sec^{-1}	k_{SN2}[d] $\times 10^4$, sec^{-1}
			1.33 ± 0.01	1.33		
1.90	38.4	38.6	2.29 ± 0.05	1.42	2.06	2.32
3.86	58.6	56.2	2.97 ± 0.10	1.50	2.72	3.41
5.90	67.7	67.2	3.78 ± 0.17	1.60	3.41	4.72
11.20	79.2	78.8	4.70 ± 0.20	1.83	4.94	8.61

[a] Calculated from eq 2 with $m = 33.0$. [b] Calculated from the relation $k_{NS} = k_{NS}^0(1 + b[N])$ with $b = 3.37$. [c] Calculated from eq 1 with $m = 33.0$, $x = 4.0$, $b = 3.37$. [d] Calculated from eq 1 with $m = 33.0$, $x = \infty$, $b = 3.37$.

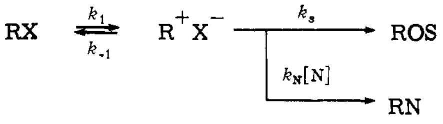
Table II. Experimental Data and Predictions of the Ion-Pair Mechanism for the Competitive Reactions with Solvent and Sodium Thiocyanate of α,γ-Dimethylallyl Chloride in Absolute Ethanol at 36.0°

[NaSCN] $\times 10^2$	% RSCN, exptl	% RSCN, calcd[a]	$k_{exptl} \times 10^4$, sec^{-1}	k_{NS}[b] $\times 10^4$, sec^{-1}	k_{ip}[c] $\times 10^4$, sec^{-1}	k_{SN2}[d] $\times 10^4$, sec^{-1}
			1.33 ± 0.01	1.33		
2.3	15.5	15.0	1.50 ± 0.02	1.43	1.60	1.65
5.5	32.2	26.8	1.81 ± 0.06	1.58	2.01	2.15
8.6	39.3	36.3	2.22 ± 0.06	1.72	2.46	2.70
15.3	51.5	51.6	3.03 ± 0.10	2.02	3.39	4.08
24.9	61.4	62.1	4.38 ± 0.09	2.44	4.87	6.47

[a] Calculated from eq 2 with $m = 6.60$. [b] Calculated from the relation $k_{NS} = k_{NS}^0(1 + b[N])$ with $b = 3.37$. [c] Calculated from eq 1 with $m = 6.60$, $x = 4.0$, $b = 3.37$. [d] Calculated from eq 1 with $m = 6.60$, $x = \infty$, $b = 3.37$.

especially phenoxide ion (paper XVI).[10] In this group of papers we shall attempt to reconcile all of the facts at our disposal, with regard to allylic substrates, and to assemble these facts into a generalized picture that is consistent with our ion-pair mechanism of nucleophilic substitution, predicts and rationalizes the example of an SN2′ reaction which these experiments have uncovered,[10] and rationalizes the observed "SN1-like" solvent and substrate dependence that is observed for certain bimolecular substitution reactions.

Both racemic and (in selected experiments) optically active α,γ-dimethylallyl chloride have been subjected to competitive substitution reactions by solvent (absolute and 90% ethanol) and added nucleophiles, either azide ion or thiocyanate ion. The kinetic data for those experiments in absolute ethanol, interpreted in terms of our generalized ion-pair mechanism,[11] are given in Table I [$(Pr)_4NN_3$ in absolute ethanol], and Table II (NaSCN in absolute ethanol). The ion-pair mechanism[11,12] in its simplest form is reproduced below.



Conditions necessary (if not necessarily sufficient)[16] to ensure operation of that mechanism are that the rate of reaction (k_{exptl}) be given by eq 1 and that products be determined simply by the linear relation (eq 2),

$$k_{exptl} = \frac{k_{NS}(x + 1)(1 + m[N])}{(x + 1 + m[N])} \quad (1)$$

$$[RN]/[ROS] = m[N] \quad (2)$$

where k_{NS} is the solvolysis rate in the absence of nucleophile (NS = no salt) but after correction for any normal salt effect on solvolysis (*vide infra*), $x = k_{-1}/k_s$, and $m = k_N/k_s$ (and is determinable experimentally from product distributions (eq 2)).[17] Experimentally we have established (Table III) that, to a very good approximation, the rate of solvolysis, k_{NS}, is accelerated moderately by those nonnucleophilic salts chosen as models to an extent empirically correlated by an equation linear in salt concentration, $k_{NS} = k_{NS}^0 \times (1 + b[N])$, where k_{NS}^0 is the rate constant of solvolysis in the absence of any added salt and b (= +3.0 to +3.7 for the model

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(11) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 362 (1969).

(12) Since the publication[11] in 1969 of the details of our study of the "borderline" behavior of 2-octyl mesylate toward solvent and azide ion, in 25 and 30% aqueous dioxane, and of our interpretation of these reactions as proceeding *via* the ion-pair mechanism, two alternative attempts to reconcile these data with traditional mechanisms (competitive, simultaneous SN1–SN2[13] or simple SN2[14]) have appeared in print from two independent laboratories. We have discussed each of these publications in detail in the Appendix to a recent publication[15] from our laboratory. We shall not repeat that discussion here but the interested reader is referred to that discussion.

(13) B. J. Gregory, G. Kohnstam, M. Paddon-Row, and A. Queen, *Chem. Commun.*, 1032 (1970).

(14) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 4821 (1971).

(15) R. A. Sneen and H. M. Robbins, *ibid.*, in press.

(16) In an earlier publication[11] we established that, mathematically, a linear product plot of [RN]/[ROS] *vs.* [N] would be consistent with the operation of competitive SN1–SN2 mechanisms only in the event that the ratios of bimolecular rate constants for formation of nucleophilic product/solvolysis product, k_{2N}/k_{2s}, equalled the corresponding unimolecular (carbonium ion) ratio, k_{1N}/k_{1s}. While this derivation is mathematically correct, it proves not to be a compelling criterion in practice. It remains a *necessary* criterion (if activities are proportional to concentrations) if the ion-pair mechanism is operative, but its demonstration does *not*, *per se*, exclude alternatives. Each case requires its own separate analysis. For example, see ref 13.

(17) We find it desirable to call to the reader's attention the differences among the defined quantities, m (or m_N), m_1, and m_G, which we have found it expedient to use in this manuscript. The symbol m (or m_N) retains its meaning from earlier publications[11] from our laboratory and is to be identified as the empirical slope of a plot of [RN]/[ROS] *vs.* [N]. Its theoretical definition in terms of the rate constants of an assumed scheme will then vary from scheme to scheme. In eq 1 and 2, for example, m is to be identified as the ratio, k_N/k_s, for the ion-pair mechanism in its simplest form.[11] In Scheme II of this manuscript, m is defined as k_N/k_2 (*vide infra*). The symbol m_1 is identified as the ratio, k_{1N}/k_{1s}, in Scheme I of this manuscript (*vide infra*). Finally, in an attempt to minimize confusion, we have elected to use the symbol m_G (Grunwald) for the substrate constant of the Grunwald–Winstein equation (see ref 36), which can then be expressed as log $(k_2/k_1) = m_G(Y_2 - Y_1)$. These formalisms will be used throughout this series of three manuscripts.[9,10]

Table III. Salt Effects on Solvolysis of α,γ-Dimethylallyl Chloride in Absolute Ethanol at 36° and in 90% Aqueous Ethanol at 27°

Salt	[Salt] × 10^2	$k_t \times 10^4$, sec^{-1}	b^a
		Absolute Ethanol	
		1.33 ± 0.01	
$NaClO_4$	2.3	1.42 ± 0.02	3.0
	5.0	1.53 ± 0.02	3.0
$(n\text{-Bu})_4NClO_4$	2.0	1.44 ± 0.03	4.1
	3.4	1.50 ± 0.03	3.7
	7.8	1.68 ± 0.03	3.4
		90% Aqueous Ethanol	
		8.40 ± 0.20	
$NaClO_4$	5.0	9.98 ± 0.30	3.8
	8.0	11.2 ± 0.4	4.2
NaCl	3.0	9.18 ± 0.20	3.1

[a] Calculated from the equation, $k_t = k_t^0(1 + b[\text{N}])$.[36]

salts in absolute ethanol) is fairly independent of the nature of the salt.[18,19]

Viable alternatives to the ion-pair mechanism as explanations of the apparent "borderline behavior" evidenced by the data of Tables I and II include (a) a *negative* (rather than positive) salt effect of nucleophile on the solvolysis rate of a traditional SN2 substitution;[20] and (b) competitive SN1 and SN2 reactions.

The first alternative, in the present instance, can, we believe, be effectively eliminated. Thus one calculates that for such an explanation to account satisfactorily for the data of Table I, azide ion must here have a *negative* or rate-retarding salt effect on solvolysis (at 0.112 *M*), $b = -2.23$, to predict properly SN2 behavior.[21,22] Similarly, as seen from Table II, thiocyanate ion must have a *positive* salt effect on solvolysis (at 0.25 *M*), $b = +0.96$, to predict properly SN2 behavior. These divergences become even more compelling when it is recognized that a single salt effect, $b = +3.37$, just that predicted by model salts (Table III), is able to accommodate data, by the ion-pair mechanism, for *both* nucleophiles, azide and thiocyanate ion, whose nucleophilicities differ by a factor of 5 ($m_{N_3^-} = 33$; $m_{SCN^-} = 6.6$),[17] and *to do so for both nucleophiles with a single value of the parameter*, $x = k_{-1}/k_s = 4.0$. This quantity, x, is of course predicted, by the ion-pair mechanism, to be independent of the nature of the nucleophile and the adherence of predicted and observed rate data of Tables I and II (using in both cases $x = 4.0$) is evidence of the fact that this requirement of the ion-pair mechanism is satisfactorily and satisfyingly met.[23,24]

With the use of two separate nucleophiles, the only adjustable parameter of the ion-pair scheme, $x = k_{-1}/k_s$, ceases to be adjustable and there remain no degrees of freedom: x, determined from data using one nucleophile (say azide ion), must correlate data for a second nucleophile (say thiocyanate ion); b is determined from model salts; m is determined from product data.

Before considering whether the second alternative to the ion-pair mechanism, competitive, classical SN1 and SN2 reactions, is consistent with the available data it is desirable to outline the results of certain stereochemical experiments which we have conducted. Three experiments will be outlined here. (1) Loss of optical activity of a solution of optically active α,γ-dimethylallyl chloride (absolute ethanol, no nucleophile, 27°) was a first-order process, $k_\alpha = 1.15 \pm 0.03 \times 10^{-4}\ \text{sec}^{-1}$, some 2.32 times as fast as the rate at which acid is produced under these conditions (*i.e.*, $k_\alpha/k_t = 2.32$).[25] After 10 half-lives the reaction mixture is, within experimental error, devoid of optical activity (control experiments establish that optically active solvolysis product would not racemize under these conditions). (2) In the presence of 0.10 *M* tetra-*n*-propylammonium azide the reaction mixture first inverts its sign of optical activity (rotation$_{\text{init}}$ = −2.9 mdeg, rotation$_{\sim 3000\ \text{sec}}$ = ±0.0 mdeg, rotation (max)$_{\sim 8000\ \text{sec}}$ = +1.1 mdeg) and ultimately reverts, after some 50 half-lives of substitution, to a value indistinguishable from 0 (310 mμ). (Allylic azides are known to undergo intramolecular rearrangements,[26] which in the system under consideration would lead to racemic product.)[27] (3) In the presence of 0.25 *M* sodium thiocyanate (ethanol, 27°), the initially levorotatory solution (285 mμ) of α,γ-dimethylallyl chloride (rotation$_{\text{init}}$ = −4.3 mdeg) first inverts its sign (rotation$_{\sim 3200\ \text{sec}}$ = ±0.0 mdeg; rotation (max)$_{\sim 5500\ \text{sec}}$ = +3.4 mdeg) and then levels off gradually until, after some 50 half-lives of substitution, rotation = +0.7 mdeg. (Here one undoubtedly sees evidence of an intramolecular rearrangement of thiocyanate to isothiocyanate of the type studied by Fava and his coworkers.[28])

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[18] Robbins[15] reports the following positive salt effects for solvolysis of α-phenylethyl bromide in absolute ethanol (at 50°): sodium perchlorate, $b = 4.00$; potassium acetate, $b = 4.00$; tetra-*n*-butylammonium perchlorate, $b = 4.77$. For α-*p*-tolylethyl chloride in absolute ethanol at 50° he reports: sodium perchlorate, $b = 4.43$; sodium acetate, $b = 3.87$. Numerous other examples of positive salt effects are given in the Appendix to ref 15.

[19] Since a plot of [RN]/[ROS] *vs.* [N] (slope = m from eq 2) is linear, the suggested plot of eq 1 is equivalent to a plot of

$$k_{\text{exptl}} = \frac{k_{\text{NS}}(x + 1)(1 + [\text{RN}]/[\text{ROS}])}{(x + 1 + [\text{RN}]/[\text{ROS}])}$$

In other words, the only quantity upon which any salt effect has not been explicitly measured and included is x. See ref 20 and 25 of ref 15.

[20] Note that it is not here a question of what, if any, salt effects might be exerted by nucleophile on the k_N process of an assumed classical SN2 mechanism; any such effect is automatically included in the kinetic expression by virtue of the necessary relationships between rate enhancements and product distributions. The salt effect of concern is that on the solvolysis process, k_s. See ref 19 with $x = \infty$. See also ref 20 and 25 of ref 15.

[21] Thus, assuming only bimolecular, SN2-type reactions, $4.70/1.33[1 + b(0.112)] = 1 + 33(0.112)$, whence $b = -2.23$.

[22] For these same data a positive salt effect of $b = 22.6$ would have to be operative to predict SN1 behavior.

[23] This also serves as a rather demanding, if indirect, validation of our approach to salt effect corrections; since azide ion is some five times more effective as a nucleophile than is thiocyanate ion, five times the concentration of the latter are required to effect the same percentages of incorporation and, accordingly, salt effect corrections for this nucleophile are some five times larger. The required internal consistencies are not insignificant.

[24] Actually, in practice, the quality of the correlation of kinetic data proves not to be particularly sensitive to the exact choice of x and to assert that $x = 4.00$ is probably to say no more than that $3 \leq x \leq 6$. That it is neither zero (SN1) nor infinite (SN2) has already been established.

[25] It will be recognized that the structure of the substrate, α,γ-dimethylallyl chloride, is such that a suprafacial 1,3-allylic shift effects racemization.

[26] A. Gagneux, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, **82**, 5956 (1960).

[27] That ultimately no activity is detectable serves to confirm that the solvolysis product, here as in the absence of added azide ion, is racemic.

[28] A. Fava, "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, New York, N. Y., 1966, p 414.

It will be apparent that the two types of substitution products formed competitively in these stereochemical studies, solvolysis product on the one hand and alkyl azide or thiocyanate on the other, are formed in processes of *fundamentally different stereochemistries. All* of the solvolysis product (within experimental error) must be formed from a racemic or meso precursor. Much of the azide or thiocyanate product must be formed from optically active precursors. An obvious explanation, that alkyl azide (or thiocyanate) is formed exclusively by SN2 attack on covalent substrate while solvolysis product arises exclusively *via* a carbonium ion or ion-pair pathway, is untenable if the evidence for borderline kinetics presented and discussed above is accepted.

Two possible explanations would seem to remain: (1) an elaboration of the ion-pair mechanism;[11] and (2) competitive SN1–SN2 reactions. Let us here diagram these two alternative reaction schemes, including in each sufficient detail to account qualitatively for all of the experimental evidence, and derive for each relationships which may allow it to be tested quantitatively against experimental data. Those facts for which the correct scheme must be able to account include: (1) a rate of reaction less than that predicted if all product alkyl azide (or thiocyanate) were formed bimolecularly; (2) a route for racemization of starting material concomitant with solvolysis (since $k_\alpha/k_t > 1$); (3) totally racemic solvolysis product; (4) at least partially optically active alkyl azide (or thiocyanate); and (5) the absence of reversibly formed carbonium ions (since k_α is constant with the time and added chloride ion does not depress k_t, Table III). For this scheme (Scheme I) one derives the following relationships.

$$k_\alpha = k_1:\ k_{NS} = k_t = k_1/(1 + 2k_{-1}/k_{1s});$$

$$k_\alpha/k_t = 1 + 2k_{-1}/k_{1s};\ [RN]/[ROS] = m_1[N] + (k_{2N}/k_1)[(k_\alpha/k_t) + m_1[N]]\ (\text{where } m_1 = k_{1N}/k_{1s}) \quad (3)$$

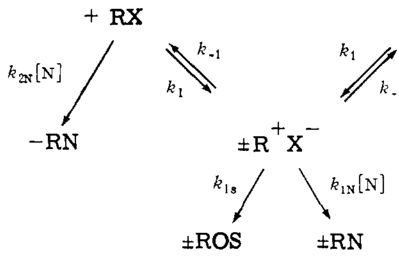
$$\frac{k_{\text{exptl}}}{k_{NS}} = (1 + [RN]/[ROS])/(1 + m_1[N]/k_\alpha/k_t) \quad (4)$$

Note that by virtue of the relationships in eq 3, the quantities k_α/k_t, k_{2N}/k_1, and m_1 cannot all be chosen independently. One derives for Scheme II simply eq 1 and 2, where $x = k_{-1}/k_2$ and $m = k_N/k_2$.[17] Furthermore one has

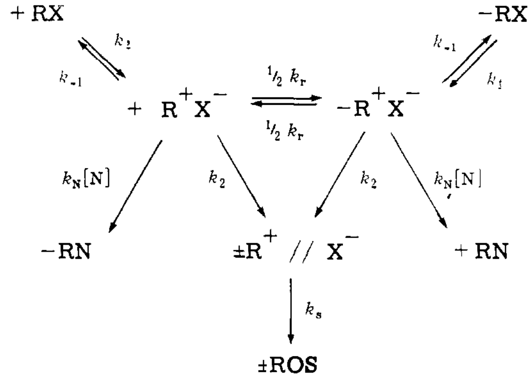
$$k_\alpha = k_1(1 + k_r/k_2)/(x + 1 + k_r/k_2)$$

$$k_t = k_{NS} = \frac{k_1}{(x + 1)}\frac{k_\alpha}{k_t} = \frac{(1 + k_r/k_2)(x + 1)}{(x + 1 + k_r/k_2)}$$

Scheme I. Competitive SN1–SN2 Mechanisms[29]



Scheme II. Elaborated Ion-Pair Mechanisms[30, 31]



The problem reduces, then, to one of establishing whether the available data are better correlated by the equations derived from the simultaneous classical SN1–SN2 mechanism or by those derived from the expanded ion-pair scheme, if such a choice is possible. The ability of the latter to correlate the kinetic and product distribution data (in absolute ethanol) has already been established (Tables I and II). In Tables IV and V we attempt to correlate the data by the equations appropriate to the SN1–SN2 scheme.[32] We have

Table IV. Comparison of Experimental Data with Predictions of the Competitive SN1–SN2 Scheme for the Reactions with Solvent and Tetra-*n*-propylammonium Azide of α,γ-Dimethylallyl Chloride in Absolute Ethanol at 36.0° ($k_{2N}/k_1 = 7.0$)

$[(n\text{-Pr})_4NN_3] \times 10^2$	% RN_3, exptl	$k_{\text{exptl}} \times 10^4$, sec^{-1}	m_1,[a] calcd	k_{calcd}[b] $\times 10^4$, sec^{-1}
		1.33 ± 0.01		
1.90	38.4	2.29 ± 0.05	14.6	2.06
3.86	58.6	2.97 ± 0.10	16.2	2.86
5.90	67.7	3.78 ± 0.17	13.6	3.68
11.2	79.2	4.70 ± 0.20	10.0	5.94

[a] Calculated from eq 3 with $k_{2N}/k_1 = 7.0$ and $k_\alpha/k_t = 2.32$. [b] Calculated from eq 4 with m_1 from the preceding column, $k_\alpha/k_t = 2.32$, and $k_{NS} = 1.33 \times 10^{-4}(1 + 3.37[N_3^-])$.

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(29) Alternatives, embodying the features of competitive SN1–SN2 reactions, include: (1) the deletion of the k_{-1} processes with introduction of a direct pathway for racemization between +RX and −RX (the racemic ion pair, $\pm R^-X^-$, might then be replaced by a dissociated carbonium ion); and (2) the insertion of a second intermediate, formed irreversibly from $\pm R^+X^-$, as the immediate precursor of ±ROS and ±RN (that intermediate might be a dissociated carbonium ion or a solvent-separated ion pair, $R^-//X^-$.

(30) The factor of ½ preceding the rate constant, k_r, is introduced to simplify subsequent derivations. It proves convenient to assume that a racemic intermediate, $\pm R^+X^-$, is formed during this overall inversion. The rate constant for the formation of this hypothetical, racemic intermediate is then k_r, while the rate of inversion is just $\frac{1}{2}k_r$.

(31) Alternatives include: (1) the replacement of the solvent-separated ion pair $\pm R^-//X^-$ by a dissociated carbonium ion; and (2) the deletion of the steps k_r with the concomitant introduction of two processes, k_{-2}, the reversal of solvent-separated to intimate ion pair. Our preference for the direct racemization route between intimate ion pairs rather than *via* the solvent-separated ion pair will be given below.

(32) The calculated rate constants of Table V for the experiments with NaSCN would approximate more closely the experimental rate constants if a smaller value of the rate ratio, k_{2N}/k_1, had been chosen. However, in view of the relationship between the assumed mechanism and predicted optical purity (see ref 44), one can calculate that, for competitive SN1–SN2 reactions and assuming $k_{2N}/k_1 = 1.0$, the initially produced thiocyanate (and/or isothiocyanate) from solvolysis of optically active α,γ-dimethylallyl chloride in the presence of 0.25 *M* NaSCN (ethanol, 27°) must have (an absolute value of) molecular rotation greater than that of the chloride by a factor of more than 4. An assumed value of $k_{2N}/k_1 = 0.5$ would require that this ratio be greater than 7. Even the value of 4 seems unrealistically high on the basis of experiments with optically active 2-octyl brosylate and sodium thiocyanate in 75% aqueous dioxane (365 mμ).[33]

(33) Unpublished work, H. Weiner.

Table V. Comparison of Experimental Data with Predictions of the Competitive SN1–SN2 Scheme for the Reactions with Solvent and Sodium Thiocyanate of α,γ-Dimethylallyl Chloride in Absolute Ethanol at 36.0° (k_{2N}/k_1 = 1.0)[c]

[NaSCN] × 10^2	% RSCN, exptl	$k_{\text{exptl}} \times 10^4$, sec^{-1}	m_1,[a] calcd	$k_{\text{calcd}}{}^{b} \times 10^4$, sec^{-1}
		1.33 ± 0.01		
2.3	15.5	1.50 ± 0.02	5.44	1.61
5.5	32.2	1.81 ± 0.06	6.00	2.04
8.6	39.3	2.22 ± 0.06	4.81	2.40
15.3	51.5	3.03 ± 0.10	4.00	3.28
24.9	61.4	4.38 ± 0.09	3.27	4.70

[a] Calculated from eq 3 with $k_{2N}/k_1 = 1.0$ and $k_\alpha/k_t = 2.32$. [b] Calculated from eq 4 with m_1 from the preceding column, $k_\alpha/k_t = 2.32$ and $k_{NS} = 1.33 \times 10^{-4}(1 + 3.37[\text{SCN}^-])$. [c] See ref 32.

attempted to be as judicious as possible in our choice of parameters.[34] (Incidentally, attempts to correlate the data by the alternative SN1–SN2 schemes of footnote 29 were generally less sucessful.)

References to Tables I, II, IV, and V will make it apparent that, with one exception, the data are about as well correlated by the assumed competitive SN1–SN2 scheme as by the ion-pair scheme; that exception is the highest concentration azide point (0.112 *M*) where the procedure which we have used leads to a calculated rate constant of 5.94 × 10^{-4} sec^{-1} (assuming competitive SN1–SN2 reactions) compared with the experimental value of 4.70 × 10^{-4} sec^{-1} and the value predicted by the ion-pair mechanism, 4.94 × 10^{-4} sec^{-1}. This, of course, is just where one expects maximum deviation from the predictions of the competitive SN1–SN2 scheme if the ion-pair mechanism is operative (at high nucleophile concentrations), but it is also at a concentration of nucleophile where salt-effect-induced deviations are maximized. A *significantly* reduced value of the ratio, k_α/k_t, from 2.32 to 1.27 could account for the discrepancy ($m_1 = 9.95$; $k_{2N/k_1} = 10.1$). A significantly decreased value of the ratio, k_{2N}/k_1, from 7.0 to 3.69 could account for the discrepancy ($m_1 = 18.0$; $k_\alpha/k_t = 2.32$). Or a significantly reduced value of the salt effect constant, *b*, from 3.37 to 0.76 could account for the discrepancy ($m_1 = 9.95$; $k_{2N}/k_1 = 7.0$; $k_\alpha/k_t = 2.32$).[35] Any one of these changes would make considerably less satisfactory the correlation of the data at the lower concentration azide runs.

Thus, although these available data from our studies in absolute ethanol seem somewhat better correlated by the predictions of the ion-pair scheme, it seems that the competitive SN1–SN2 scheme cannot as yet be convincingly ruled out. It was for this reason that we chose to repeat certain of these experiments in the solvent system 90% aqueous ethanol. Rates of reaction and product distributions for the competitive substitutions of solvent and added nucleophile (NaN_3) at 27° in this solvent system were studied. The data are given in Table VI together with the values calculated assuming the ion-pair mechanism [$m = 13.0$; $x = 2.5$; $b = 3.76$ (see Table III)]. As expected the solvolysis reaction is considerably faster in this better ionizing solvent ($Y_{100\%} = -2.0$; $Y_{90\%} = -0.73$),[36] even before correction for the lower temperature (27°) at which these experiments in aqueous ethanol were performed. One can estimate that, at comparable temperatures, α,γ-dimethylallyl chloride would solvolyze at a rate faster by a factor of 19.1 in the aqueous solvent.[36,37] Also expected is that the reaction in the aqueous solvent is more "SN1-like" ($x = 4.0$ in absolute ethanol → $x = 2.3$ in 90% ethanol) and that azide ion is somewhat less effective as a nucleophile ($m = 33$ in ethanol → $m = 13.0$ in 90% ethanol). What might not have been predicted is that the reaction continues to exhibit a second-order component. The fact that it does will be seen to have important mechanistic consequences.

Table VI. Experimental Data and Predictions of the Ion-Pair Mechanism for the Competitive Reactions with Solvent and Sodium Azide of α,γ-Dimethylallyl Chloride in 90% Aqueous Ethanol at 27.0°

[NaN_3] × 10^2	% RN_3, exptl	% RN_3, calcd[a]	$k_{\text{exptl}} \times 10^4$, sec^{-1}	$k_{NS}{}^{b} \times 10^4$, sec^{-1}	$k_{ip}{}^{c} \times 10^4$, sec^{-1}	$k_{SN2}{}^{d} \times 10^4$, sec^{-1}
			8.40 ± 0.20	8.40		
4.0	32.5	32.4	11.9 ± 0.3	9.65	12.5	14.3
6.0	42.3	41.9	15.0 ± 0.4	10.29	14.6	17.8
8.0	49.2	49.0	17.7 ± 0.3	10.92	16.6	21.4
10.0	53.6	54.5	19.5 ± 0.7	11.56	18.7	25.5

[a] Calculated from eq 2 with $m = 12.0$. [b] Calculated from the relation $k_{NS} = k_{NS}{}^{0}(1 + b[\text{N}])$ with $b = 3.76$. Calculated from eq 1 with $m = 12.0$, $x = 2.3$, $b = 3.76$. [d] Calculated from eq 1 with $m = 12.0$, $x = \infty$, $b = 3.76$.

We have also investigated stereochemical features of these reactions in 90% aqueous ethanol. As in the anhydrous solvent solvolysis here also furnishes racemic solvolysis product (presumably now a mixture of alcohol and ethyl ether), the polarimetric rate constant being only slightly larger than the titrimetric constant ($k_\alpha/k_t = 1.23$). Obviously rearrangement is less of a problem here. Reaction of α,γ-dimethylallyl chloride (27°, 90% ethanol) in the presence of 0.10 *M* sodium azide gave polarimetric results (at 310 mμ) quite analogous to those described for pure ethanol: rotation$_{\text{init}}$ = −7.7 mdeg → rotation$_{\sim 600\text{ sec}}$ = ±0.0 → rotation (max)$_{\sim 3000\text{ sec}}$ = +3.0 mdeg → rotation$_{50\text{ half-lives}}$ = ±0.0. It is clear that alkyl azide, as initially formed, is significantly optically active.

In Table VII the ability of simultaneous SN1–SN2 mechanisms to correlate the kinetic and product data

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[34] Our procedure has been to solve the rate equation (eq 4) (assuming $k_\alpha/k_t = 2.32$, the experimental value) for m_1 and then to use this value of m_1 to solve, from the product distribution equation, eq 3, for the ratio, k_{2N}/k_1. A set of m_1 and k_{2N}/k_1 values was thus determined for the various experimental runs. An approximate average of the so-determined k_{2N}/k_1 ratios was then chosen and the same two equations were used to calculate, for each experimental run, the corresponding m_1 values and the rate constant.

[35] It should be mentioned that, mathematically, correlations by the ion-pair mechanism are considerably more demanding since the data are subject to an additional mathematical constraint, that *x* of that mechanism must be independent of nucleophile. If simplicity is to be valued as a valid scientific criterion, the ion-pair scheme is certainly, mathematically, the simpler.

[36] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948).

[37] R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 790 (1956).

for these studies in 90% aqueous ethanol is tested (k_α/k_t = 1.23; b = 3.76; k_{2N}/k_1 = 5.0). Without exception the correlation is good.

Table VII. Comparison of Experimental Data with Predictions of the Competitive S$_N$1–S$_N$2 Scheme for the Reactions with Solvent and Sodium Azide of α,γ-Dimethylallyl Chloride in 90% Aqueous Ethanol at 27.0° (k_{2N}/k_1 = 5.0)

[NaN$_3$] × 10^2	% RN$_3$, exptl	$k_{\mathrm{exptl}} \times 10^4$, sec^{-1}	m_1,[a] calcd	k_{calcd}[b] × 10^4, sec^{-1}
		8.40 ± 0.20		
4.0	32.5	11.9 ± 0.3	4.87	12.4
6.0	42.3	15.0 ± 0.4	4.45	14.6
8.0	49.2	17.7 ± 0.3	4.33	16.8
10.0	53.6	19.5 ± 0.7	3.64	19.3

[a] Calculated from eq 3 with k_{2N}/k_1 = 5.0 and k_α/k_t = 1.23. [b] Calculated from eq 4 with m_1 from the preceding column, k_α/k_t = 1.23 and $k_{NS} = 1.33 \times 10^{-4}(1 + 3.76[N_3^-])$.

Again, a definitive choice between the two proposed mechanisms to account for these data from studies in 90% aqueous ethanol appears not to be possible. The simultaneous S$_N$1–S$_N$2 picture seems equally able to account for the data, *until one compares certain values of these data* (90% ethanol) *with those discussed previously* (100% ethanol). In particular let attention be focused on the rate ratio, k_{2N}/k_1. The competitive S$_N$2–S$_N$1 mechanism correlates data most effectively both in absolute ethanol (Y = −2.0)[36] (Table IV) and in 90% aqueous ethanol (Y = −0.73)[36] (Table VII), where the solvolysis rate changes by a factor of 19, *with a virtually unchanged* k_{2N}/k_1 *ratio* (k_{2N}/k_1 = 7.0 in absolute ethanol; k_{2N}/k_1 = 5.0 in 90% aqueous ethanol).[38] If in fact we are observing a true, S$_N$2-type, bimolecular attack by nucleophile azide ion on covalent substrate, α,γ-dimethylallyl chloride (the competitive S$_N$1–S$_N$2 scheme), it is rather remarkably accelerated by the ionizing power of the solvent to virtually the same extent as is the ionization process, k_1. Expressed in terms of the Grunwald–Winstein equation[36] for solvolysis reactions (which was certainly never intended for this purpose), α,γ-dimethylallyl chloride has an m_G value[17] (*toward azide ion*) of +0.73! (m_G = +1 = limiting behavior.)[36,39,40] To say the least, such a solvent-sensitive bimolecular nucleophilic displacement reaction by negative nucleophile, azide ion, on neutral substrate, α,γ-dimethyllallyl chloride, is not predicted by the traditional theory.[41]

We conclude either (1) these "S$_N$2" reactions are rather extraordinarily similar, in their solvent-sensitivity dependence, to carbonium ions or substrates exhibiting limiting behavior, or (2) the competitive S$_N$1–S$_N$2 mechanism is not operative.

If the ion-pair mechanism is to remain a satisfactory alternative to a competitive S$_N$1–S$_N$2 scheme as a rationalization of the available data, it must be able to account for the continued ability of a negative nucleophile, azide ion, to compete effectively with an ionization pathway in a solvent of substantially increased ionizing power. There would appear to be at least two aspects to the answer. First, an ion-pair substrate for nucleophilic attack, already having achieved a measure of charge separation, R^+X^-, must of necessity extend that charge separation in its subsequent reaction with nucleophile, whether with neutral solvent or negative azide ion; after all an anion, X^-, is being liberated. And second, a relatively unstable intermediate, which an ion pair certainly is, should be relatively unselective (Hammond postulate)[42] in its subsequent reactions, whether with azide ion, solvent, or in further ionization.[43]

We shall arrive at a similar conclusion that ion pairs derived from allylic substrates have a remarkable propensity, in their reactions with negatively charged nucleophiles, to behave in a manner reminiscent of carbonium-ion-like reactions, from completely independent evidence to be assembled in the succeeding paper (XV).[9] And we shall provide another example, in paper XVI,[10] of an allylic substrate, the primary γ-methylallyl chloride, whose bimolecular displacement reaction (with phenoxide ion) is remarkably accelerated by solvent ionizing power.

It may have become apparent, to the thoughtful reader, that an alternative experimental differentiation between the ion-pair mechanism, on the one hand, and the competitive S$_N$1–S$_N$2 mechanism, on the other, might lie in their differing predictions as to the optical purity of the derived optically active alkyl azide (or thiocyanate) emanating from the optically active precursor, α,γ-dimethylallyl chloride. The predictions are, in fact, significantly different[44] but the presently

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(38) These ratios will change somewhat as one modifies assumptions for the treatment of data. No set of reasonable assumptions, however, leads to calculated k_{2N}/k_1 ratios, for these two sets of experiments, which are not remarkably similar in value.

(39) Thus, assuming competitive S$_N$1–S$_N$2 reactions, and salt effects on solvolysis of b = 3.37 (100% ethanol) and b = 3.76 (90% ethanol) as used in the calculations of Tables I, II, IV, and VII (see Table III), $(k_{\mathrm{exptl}}/k_{NS} - 1)/[N] = k_{2N}/k_{NS}$ or $(k_{2N}/k_{NS})_{100\%} = 14.1$ (at $[N_3^-]$ = 0.112 M, Table I) and $(k_{2N}/k_{NS})_{90\%} = 6.9$ (at $[N_3^-]$ = 0.100 M, Table VI). Since $(k_{NS})_{90\%}/(k_{NS})_{100\%} = 19.1$ (*vide supra*), $(k_{2N})_{90\%}/(k_{2N})_{100\%} = (6.9)\cdot(19.1)/(14.1) = 9.3$. Further, since $Y_{90\%} - Y_{100\%} = 1.35$,[36] (log 9.3)/(1.35) = 0.73 = m_G.[40]

(40) It is especially to be noted that these conclusions about the solvent sensitivity of the presumed bimolecular component of the reaction are virtually independent of any reasonable treatment of salt effects. As has been demonstrated,[39] if positive salt effects on solvolysis are assumed and estimated from model salts, $(k_{2N})_{90\%}/(k_{2N})_{100\%} = 9.3$ and m_G = +0.73. If, on the other hand, salt effects are assumed in both solvent systems to be nonexistent (b = 0), one calculates (Tables I and VI) that $(k_{2N})_{90\%}/(k_{2N})_{100\%} = 11.1$ and m_G = +0.82. Finally, if one assumes that the salt effect in each solvent system is of just that magnitude necessary to ascribe *all* alkyl azide formation to a bimolecular process, $(k_{2N})_{90\%}/(k_{2N})_{100\%} = 9.55$ and m_G = +0.77.

(41) See, for example, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N.Y., 1969, Chapter 7.

(42) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).

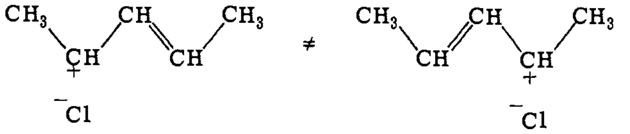
(43) Incidentally it has frequently been asked of us why, if the ion-pair mechanism be operative, ionic properties are not more evident. Here they rather abundantly are. However, this should not be interpreted to mean that we believe that all ion pairs, derived from all manner of precursors (primary, secondary, tertiary, allylic, etc.), must therefore, indiscriminately, display this same high level of "carbonium-ion-like" behavior. Actually we believe that ion pairs derived from secondary substrates (*e.g.*, 2-octylsulfonates)[11] and, especially, primary and methyl substrates will prove to have considerably more covalent character and therefore will be less "carbonium-ion-like" in their behavior. In other words we believe that the extent of charge separation in ion pairs will prove to be a function of the stability of the derived carbonium ions, tertiary ion pairs being considerably more ionic than primaries.

(44) For example, one calculates that, with 0.10 M sodium azide in 90% aqueous ethanol under kinetic conditions, the ion-pair mechanism predicts that the product azide be 91% optically active ([excess inverted RN]/[total RN] × 100) while the competitive S$_N$1–S$_N$2 scheme predicts that it be 58% optically pure. The appropriate equations, which are derived simply from the appropriate schemes, we give here for future reference. For the ion-pair scheme one has

$$\frac{[\text{excess inverted RN}]}{[\text{total RN}]} = \frac{m[\mathrm{N}] + 1}{m[\mathrm{N}] + 1 + k_r/k_2}$$

available data are insufficiently precise to warrant further discussion at this time.

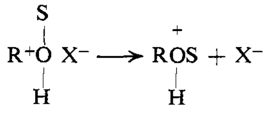
If then our demonstration that the ion-pair mechanism is operative in the substitution reactions of α,γ-dimethylallyl chloride in absolute and 90% aqueous ethanol is accepted, one must inquire as to the implications of that mechanism for allylic reactions in general. They are not inconsiderable. One must, above all, accept that "classical" intimate ion pairs exist; *i.e.*, that[45]



One might also ask at this point why, physically, discrete, distinct allylic ion pairs of the sort suggested here should have an energy barrier to conversion to more symmetrical species. One can reasonably suggest that as symmetry is achieved (with its presumed increased resonance energy), electrostatic stabilization is necessarily sacrificed as the C^+X^- distance is increased. Coupled with expected changes in solvation energies (both enthalpy and entropy), it seems to us not at all strange that a relative minimum in a free energy plot might exist between the covalent substrate and the symmetric (presumably solvent-separated) ion pair.

A consequence of the recognition of the existence of discrete allylic ion pairs is that, for the first time, the long-standing problem of product spreads observed, under most solvolytic conditions, on solvolysis of simple allylically related chlorides, becomes reasonable. They result from the rather indiscriminate behavior of the relatively high-energy intermediates, intimate allylic ion pairs, toward nucleophile (solvent) and further ionization (to solvent-separated ion pair). We shall return to this subject in the third paper of this present series.[10]

Our preferred reaction scheme for the system under discussion, α,γ-dimethylallyl chloride in ethanol and in 90% aqueous ethanol, suggests that the solvent-separated ion pair, once formed, is attacked at an appreciable rate only by solvent; externally added nucleophile, azide or thiocyanate ion, is unable to compete. This conclusion is buttressed experimentally, for a related system, by data in the third paper of this series.[10] One properly asks why. We believe that solvent-separated ion pair, by virtue of the solvent-separating solvent molecule(s), has available a route for solvolysis of particularly low energy, a route, presumably, of retention and that

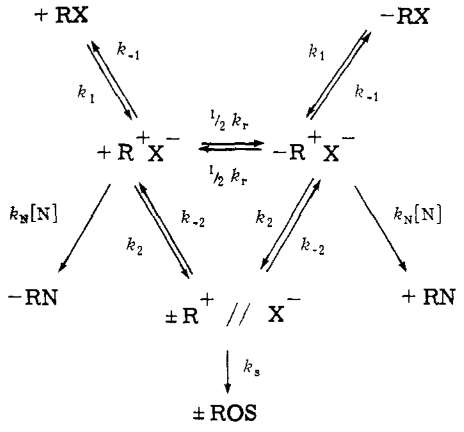


$$\underset{\displaystyle\text{H}}{\overset{\displaystyle\text{S}}{\text{R}^+\text{O}}}\ \text{X}^- \longrightarrow \underset{\displaystyle\text{H}}{\overset{+}{\text{ROS}}} + \text{X}^-$$

external nucleophile is simply not able to compete effectively with this collapse mechanism.[46] It is of more than passing interest that such a proposal provides a ready and satisfying alternative to backside nonclassical bridging as an explanation for much of what has traditionally been used to support the existence of nonclassical "ions," the observed retention of configuration on solvolysis.

Finally it seems desirable to explain, at least briefly, why we have chosen to suggest that racemization of optically active α,γ-dimethylallyl chloride proceeds at the intimate ion-pair state rather than *via* reversal from a racemic solvent-separated ion-pair species. If one expands the ion-pair scheme to include this possibility (Scheme III), the following relationships can be shown to exist[47]

Scheme III



$$\frac{k_{\text{exptl}}}{k_{\text{NS}}} = \frac{(x+1)(1+m[\text{N}])}{(x+1+m[\text{N}])} \qquad \frac{k_\alpha}{k_t} = \frac{(1+\gamma)(x+1)}{(\alpha+1+\gamma)}$$

$$x = \alpha(2\beta+1) \qquad m = (k_\text{N}/k_2)(2\beta+1)$$

where $\alpha = k_{-1}/k_2$, $\beta = k_{-2}/k_s$, and $\gamma = k_r/k_2$. On solving the equations, using the experimental data, one finds that, if k_r (or γ) = 0, the ratio, $\alpha = k_{-1}/k_2$, must increase on passing from 100 to 90% aqueous ethanol, a chemically unreasonable result. If on the other hand k_{-2} (or β) is assigned a value of 0, both α and γ decrease on passing from the poorer to the better ionizing solvent, consistent with chemical predictions. We conclude that racemization proceeds largely (if not exclusively) by way of the intimate ion-pair interconversion, $^1/_2k_r$.

Experimental Section

Preparation and Purification of Chemicals. α,γ-Dimethylallyl Alcohols. To the Grignard reagent prepared from *ca.* 3.4 g-atoms of magnesium turnings and 3.5 mol of iodomethane (Columbia Organic) at 0°, was added dropwise, with stirring under reflux, 3.5 mol of freshly distilled crotonaldehyde [Aldrich, bp 101–103° (760 mm)]. The reaction mixture was (subsequently) hydrolyzed with a cold saturated solution of ammonium chloride. The ethereal layer was decanted and the water layer was extracted with three 200-ml portions of fresh ether, which were then combined with the decanted ether and dried over anhydrous magnesium sulfate. Fractional distillation furnished, after removal of solvent

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For the competitive SN1–SN2 scheme one has

$$\frac{[\text{excess inverted RN}]}{[\text{total RN}]} = \frac{(k_{2\text{N}}/k_1)[\text{N}](1+[\text{ROS}]/[\text{RN}])}{1+(k_{2\text{N}}/k_1)[\text{N}]}$$

(45) This should in no way be interpreted to mean that we believe that "*non*classical" ion pairs do *not* exist; in fact we picture the solvent-separated species of the ion-pair scheme as symmetrical. Nor should this be interpreted to mean that we believe classical ion pairs are necessarily more stable than their nonclassical counterparts; our data suggest only that they are first formed.

(46) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 6031 (1969). Schleyer and his coworkers[14] have suggested a similar mechanism.

(47) It was for these derivations (and also those of ref 44) that we introduced tacitly the (perhaps) hypothetical racemic, intimate ion pair ($\pm\text{R}^+\text{X}^-$) in the ion-pair scheme above and defined its rate of formation from the optically active intimate ion pair as k_r (rate of racemization), rate of inversion then becoming $^1/_2k_r$.

ether, α,γ-dimethylallyl alcohol, bp 121–124° (lit.[48] bp 120–125°). Both nmr and ir spectra were consistent with the assigned structure.

α,γ-Dimethylallyl Chloride. The corresponding alcohol was treated with phosphorus trichloride (Mallinckrodt) in dry pyridine at 0°. The product was distilled from the reaction mixture and had bp 44° (55 mm) [lit.[48] bp 19–26° (20 mm)]. Spectra (nmr and ir) were consistent with the proposed structure. α,γ-Dimethylallyl chloride was stored over Dry Ice. Purity was established by the infinity acid titer (>98%) on ethanolysis.

α,γ-Dimethylallyl Ethyl Ether. The ether was prepared from the corresponding alcohol, ethyl iodide (Columbia Organic), and silver oxide according to the procedure described by Mislow.[49] Final purification was by vpc on a 6 ft × 0.25 in. column, 23% SE-30 on Gas Chromb Q (60–80 mesh). The assigned structure was consistent with its nmr and ir spectra.

α,γ-Dimethylallyl Thiocyanate. To 3.6 g of potassium thiocyanate (Baker reagent) in 100 ml of *N,N*-dimethylformamide (Matheson Coleman and Bell) was added 3.6 g of α,γ-dimethylallyl chloride. This mixture was allowed to stir at room temperature for about 18 hr after which it was poured into 500 ml of cold water and extracted with three 120-ml portions of pentane. The pentane extracts were dried over anhydrous magnesium sulfate and the pentane was removed under vacuum. The vpc trace indicated the presence of the solvents plus two major components. Both components were collected and both showed absorption in their respective ir spectra at 2090 cm^{-1}, the region characteristic of an organic isothiocyanate.[50,51] Reinjection, after several hours, of each of the "pure" components (presumably the allylic thiocyanate and its isomeric isothiocyanate) indicated that each had undergone partial rearrangement to its isomer.[28] Since the equilibrium has been established to lie far on the side of the isothiocyanate,[52] structures could be assigned. The thiocyanate proved to have the shorter retention time (*vide infra*).

α,γ-Dimethylallyl isothiocyanate (produced as described above) was conveniently purified by vpc (6 ft × 0.25 in. column 23% SE-30 on Gas Chromb Q). The nmr and ir spectra were consistent with the assigned structure.

α,γ-Dimethylallyl Azide. In 100 ml of *N,N*-dimethylformamide (Matheson Coleman and Bell) were placed 2.3 g of recrystallized sodium azide and 3.6 g of α,γ-dimethylallyl chloride. The mixture was stirred vigorously overnight because the sodium azide was not very soluble in the solvent. The reaction mixture was then poured into 500 ml of cold water and the aqueous solution was then extracted with three 125-ml portions of pentane. The combined pentane extracts were then dried over magnesium sulfate and the pentane was removed under vacuum. Final purification was by vpc under the conditions described above for the corresponding isothiocyanate. The compound exhibited a sharp peak in its ir spectrum at 2100 cm^{-1}, the region characteristic of organic azides.[53,54] The nmr spectrum was also consistent with the assigned structure.

(+)-α,γ-Dimethylallyl Alcohol. The resolution was accomplished by the procedure of Hills, Kenyon, and Phillips.[48] Purification was by fractional distillation, bp 120–122° (lit.[48] bp 119–120°).

(−)-α,γ-Dimethylallyl Chloride. Levorotatory chloride was prepared from dextrorotatory alcohol by the action of freshly distilled phosphorus trichloride in the presence of dry pyridine at 0°. The chloride was distilled from the reaction mixture, bp 19–26° (20 mm) [lit.[48] bp 19–26° (20 mm)], $[\alpha]_{310\ \text{m}\mu}$ −19.3° (*c* 0.725, 0.1) in absolute ethanol. Spectra (nmr and ir) were consistent with the proposed structure.

Ethanol. Commercial absolute ethanol (99.5%) was dried in accordance with the diethyl phthalate method of Manske.[55] New material was prepared periodically, its purity being checked routinely by the ethanolysis rate of α,γ-dimethylallyl chloride of each new batch.

Water. Distilled water was passed through a Barnstead bantam demineralizer (standard cartridge 0802).

Sodium Thiocyanate. Reagent grade sodium thiocyanate (Baker) was dried over Drierite and phosphorus pentoxide under vacuum and was then stored over Drierite in a vacuum desiccator.

Potassium Thiocyanate. Reagent grade potassium thiocyanate (Baker) was employed without further purification.

Sodium Perchlorate. The commercial salt (G. Fredrick Smith Chemical Co.) was dried in an oven (150°) overnight and was then stored in a vacuum desiccator with Drierite.

Lithium Chloride. The commercial material (Baker) was dried at 150° overnight and stored over Drierite.

Sodium Azide. The commercial material (Matheson Coleman and Bell) was dissolved in boiling water and the resulting solution was filtered. The cooled solution (0°) was diluted with 95% ethanol to initiate precipitation. The crystals were collected, washed four times with acetone, dried (at 100°) in vacuum, and stored in a desiccator over Drierite and phosphorus pentoxide.

Tetra-*n*-propylammonium Azide. This material was supplied by H. M. Robbins.[15] The extremely hydroscopic salt was stored over phosphorus pentoxide and was dried under vacuum at 150° for at least 24 hr, depending upon the size of the sample being used.

Kinetic Procedures. Titrimetric. An appropriate amount of substrate and salt was weighed into a 100-ml volumetric flask and sufficient solvent was added to bring the volume to 100 ml. In those experiments with 90% aqueous ethanol, 125 ml of the solvent mixture was pipetted into an erlenmeyer flask into which the desired salt had previously been weighed. The substrate was then weighed directly into a volumetric flask and sufficient salt solution was added to bring the solution to volume. The volumetric flask was then placed in a constant temperature bath and the solution was allowed to equilibrate to temperature (*ca.* 10–15 min). At appropriate time intervals aliquots were removed and quenched in 5 ml of absolute methanol at 0°. The acid concentration was determined by titration against standard sodium methoxide in methanol, using Bromthymol Blue as the indicator.

Polarimetric. Polarimetric studies utilized a Cary Model 60 recording spectropolarimeter which made possible the continuous observation of rotation with time. The solutions were prepared as previously described, introduced into either a 1- or 2-cm Cary cell, and then placed in the cell compartment of the instrument which maintained a temperature of 27.00 ± 0.05°. Blanks were taken before and after each run to ensure the base line stability. It was noted that severe movement of the cell in its holder could cause drastic shifts in the base line. Therefore solutions and blanks were transferred without removal of the cell from its holder. All measurements were made at either 310 or 280 mμ.

Isolation of Products. The solutions were prepared, as previously described, and placed in a constant temperature bath for *ca.* 10 half-lives. The reaction mixture was then poured into 500 ml of cold water and extracted with four 125-ml portions of pentane. The pentane extracts were dried over magnesium sulfate and filtered, and the pentane volume was carefully reduced under vacuum to *ca.* 3.5 ml. This material was subjected to vapor-phase chromatography on an Aerograph Model 202 and the retention times of the products were compared with the retention times of products whose structures were known. All analyses were accomplished successfully on a stainless steel 6 ft × 0.25 in. 23% SE-30 on Gas Chromb Q (60–80 mesh) column (column temperature, 100°; flow rate, 75 ml/min). The various α,γ-dimethylallyl derivatives investigated in this work had the following observed retention times (in minutes): alcohol, 2.88; ethyl ether, 3.52; thiocyanate, 9.0; isothiocyanate, 18.9; azide, 4.88.

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