capillary tubes. Rearrangement of **1b** was followed chromatographically during dimerizations, rate constants being calculated from smoothed plots of **1b** and **5** *vs.* dimerization and cross plots of dimerization *vs.* time. A fraction of mixed dimers enriched in **1b** was also isolated by low pressure simple distillation to verify the rate of rearrangement without correction for continued formation.

2,3-Dichlorobutadiene. Redistilled **10** was inhibited and heated in a sealed container for **48** hr (60°) and found to contain 24% dimers, composition 22% **11**, 51% **12**, and 27% **13**. The first two products were found to react with piperidine. Monomer was evaporated and **13** largely crystallized by addition of hexane and cooling, mp 93–96°, after one recrystallization (lit.[1] 98–99°). Distillation of the residue, 79–90° (<2 mm), produced a fraction from which crystals of **11** slowly separated. These were used to seed a lower temperature crystallization to produce **11**, mp 54–60°, and leave a residue containing 78% **12**. The nmr spectrum of **13** showed a single peak at 2.89; for **11**, sharp $=CH_2$ peaks at 5.76 and 5.61, and broad methylene multiplets centered at 3.05 and 2.38; for **12**, $=CH_2$ at 5.62, 5.48, methylenes at 3.09, 2.60, and 2.34. Spectral and material balance calculations confirmed the chromatographic composition. Dimerization rates were also measured at room temperature as for chloroprene. Decomposition of **11** was measured at 160°, using the crude distillation mixture, which precluded accurate measurement of products.

Butadiene. From a dip-leg cylinder of commercial CP butadiene 10 months old from the date of filling, liquid butadiene was removed into a cooled flask. Trichlorotrifluoroethane containing a small amount of tetrachlorobutane internal standard was added, butadiene removed under reflux, and the resulting solution chromatographed with 30° initial column temperature. Vinylcyclohexene and cyclooctadiene peaks were verified by comparison to known samples and by mass spectroscopy, *trans*-divinylcyclobutane only by mass spectroscopy. A small peak which was probably the cis isomer was too small for positive identification

Cross-Dimerization of Chloroprene and Cyclopentadiene. An inhibited solution of 3.9 g of freshly distilled cyclopentadiene and 14.5 g of chloroprene was aged at room temperature and intermittently analyzed over 300 hr time. New peaks were observed at 6.2 and 8.2 min retention time with relative rates of formation calculated to be 0.20 and 0.013 relative to dicyclopentadiene assuming that the compounds were cross dimers. A relative rate for chloroprene was estimated at 0.0024 compared to 0.0016 calculated from Table III. For preparative purposes, a mixture of 96 g of chloroprene and an equal weight of partially dimerized cyclopentadiene was refluxed for 2 hr at 45–55°, allowed to stand overnight, and distilled. Analysis indicated 60 g of dicyclopentadiene, 12 g of **14a**, 1.1 g of the unidentified material, and negligible amounts of chloroprene dimers. Redistillation provided **14a**, 74–76° (17 mm), nmr $=CH$ at 6.12, 5.88, $=CH_2$ at 5.04, 4.87, bridgehead CH at 3.14, 2.85, exo protons at 2.95, 1.90, bridge protons at 1.42, 1.25, and the endo proton at 1.02. Splitting patterns were very similar to **14c**.[14] The small amount of remaining cross dimer was not isolated from the residue, but was found to remain unchanged when heated with piperidine.

The Use of Added Sodium Azide as a Mechanistic Probe for Solvolysis Reactions

Douglas J. Raber,[1a] J. Milton Harris,[1b] Robert E. Hall,[1c] and Paul v. R. Schleyer*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received August 14, 1970*

Abstract: The solvolysis of 2-propyl tosylate, 2-adamantyl tosylate, and 1-adamantyl bromide in 80% ethanol and 75% dioxane in the presence of sodium azide has been investigated in order to gain information on the role of solvent in solvolytic reactions of secondary substrates. Failure to observe a rate–product correlation for 2-adamantyl tosylate and 1-adamantyl bromide indicates nonidentity of the rate-determining and product-determining steps and the absence of nucleophilic solvent participation. However, the observed rate–product correlations for the solvolysis of simple, unhindered secondary derivatives (2-propyl tosylate, 2-octyl brosylate) are consistent with nucleophilic solvent participation in the solvolysis of these compounds. The ion pair hypothesis of Sneen is analyzed, and it is concluded that his data do not demand the intermediacy of ion pairs in the solvolysis of 2-octyl derivatives. The stability–selectivity relationship for carbonium ion reactions in the presence of azide ion has been extended to considerably less reactive substrates. The available evidence demonstrates the limiting nature of 2-adamantyl solvolysis.

The technique of adding strong nucleophile (*e.g.*, lyate ion or azide ion) to a solvolysis medium as introduced by Hughes and Ingold[2] affords a direct measure of the tendency of a substrate to react by a unimolecular or bimolecular pathway. The characterization of a reaction as unimolecular (SN1) or bimolecular (SN2) has been of fundamental importance in the study of the mechanism of solvolysis. The molecularity of the reaction with solvent cannot be determined, but inferences may be made from the kinetic order of the reaction with added nucleophile.[3]

When an added nucleophile produces a marked rate enhancement, a bimolecular displacement process is indicated. The use of sodium azide permits additional information to be derived from product composition; the product of attack by lyate ion is indistinguishable from the normal solvolysis product, but attack by azide ion leads in contrast to an isolable alkyl azide. The combination of kinetic and product data permits the

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[1] (a) National Institutes of Health Postdoctoral Fellow, 1968–1970; (b) National Institutes of Health Postdoctoral Fellow, 1969–1970; (c) A. B. Thesis, Princeton University, 1970.

[2] (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1969; (b) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

[3] Ingold and his coworkers discussed several approaches to this problem.[2] These are: studies of mass law effects, salt effects, and variations in structure, nucleophile, and solvent. One of the most powerful tools was shown to be the use of added azide ion.

determination of the relationship between the rate-determining step and the product-determining step.

For a bimolecular (SN2) reaction the rate-determining step and the product-determining step are identical, and a quantitative agreement between rate and product data is expected. On the other hand, these two steps are different for an SN1 reaction, and a simple rate–product correlation is not expected [4]

In those situations for which SN1 behavior with azide ion is observed, it has been found that the amount of azide incorporation into the product varies with the stability of the intermediate carbonium ion.[2,5] Direct relationships between selectivity and stability of reactive intermediates have often been observed in organic chemistry.[6] These relationships have been qualitatively interpreted in terms of the ability of a relatively stable intermediate to discriminate between two different reaction pathways (*i.e.*, the ratio of the respective rate constants is not unity). For a highly unstable intermediate, however, the activation barrier should be very small; as this barrier approaches zero, the ratio of the rate constants for the two processes will approach unity (*i.e.*, little selectivity will be observed). Thus the ability of the intermediate to discriminate between possible reaction pathways should be directly related to its stability.

Sneen has shown[5] that a selectivity–stability relationship for carbonium ions could be placed on a more quantitative basis by plotting log $k_{\text{solvolysis}}$ *vs.* log $[k_N/k_W]$ (the ratio of the rate constants for reaction of the intermediate with azide ion and water, respectively) for a series of alkyl chlorides in 80% acetone. The solvolysis rate afforded an estimate of the stability of the resulting carbonium ion intermediate, and k_N/k_W provided a measure of its selectivity. This linear free energy relationship was found to correlate stability and selectivity over a wide range of reactivity.

Studies of solvolysis reactions in the presence of sodium azide have also been used to gain information on the role of ion pairs in these processes. Sneen has found evidence for ion pair intermediates in the solvolysis of simple secondary arenesulfonates with the use of a detailed analysis of kinetic data which appear to be intermediate between first and second order.[7] The work of Goering[8] and Winstein[9] with sodium azide afforded evidence for a series of ion pair intermediates in the solvolysis of benzhydryl derivatives. Added azide ion has also been used to probe the relationship between intermediates generated by solvolysis of isomeric cyclopropylcarbinyl and cyclobutyl arenesulfonates.[6a,11]

In this work we have attempted to extend the stability–selectivity relationship for carbonium ions found by Sneen,[5] and to utilize the effects of sodium azide to gain information on the mechanism of the reaction of secondary alkyl derivatives with solvent.

Results and Discussion

Rate–Product Correlations with Sodium Azide. Earlier studies[12,13] in our laboratories demonstrated that simple secondary substrates solvolyze with nucleophilic solvent participation, a process designated by the pseudo-first-order rate constant k_s. On the other hand, we have also shown that in the solvolysis of the more hindered 2-adamantyl derivatives such solvent assistance is largely absent.[13] In order to test further these conclusions, and to gain more insight into the nature of nucleophilic reactions at saturated carbon, we investigated the solvolysis of several substrates with sodium azide as added nucleophile.[14] In addition to 2-adamantyl tosylate, two model compounds were also examined. The bridgehead substrate, 1-adamantyl bromide, cannot be attacked at the rear; it must solvolyze by a k_c[13] mechanism. Isopropyl tosylate was chosen as a simple, open secondary substrate.

We felt that Ingold's[4a] criteria for a rate–product correlation would allow us to establish the nature of the reaction with azide ion. From these data inferences could then be made regarding the role of solvent in the solvolysis reactions without added nucleophile. If a second-order reaction with added strong nucleophile is not observed, then reaction with the less nucleophilic solvent should not be bimolecular either.[15] However, a second-order reaction with nucleophile may imply but does not demand a bimolecular reaction with solvent.

Our initial studies were carried out with 75% aqueous dioxane in order to allow comparison with Sneen's data on the 2-octyl system; Sneen has pointed out that in this solvent system 2-octyl brosylate "exhibits the defining characteristics of an SN2 reaction, bimolecular kinetics, and inversion of configuration."[7b] However, experimental difficulties were encountered in the use of this solvent. Unless oxygen is rigorously excluded from the system, the infinity titer increases with time, apparently as a result of an acid-catalyzed oxidation of the dioxane. Consequently, we used 80% aqueous ethanol for more precise and extensive studies; this solvent mixture offers the additional advantage that attack by the organic component leads to a stable product (an ethyl ether) rather than to an intermediate oxonium ion[7a] (as in the

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(4) (a) Reference 2a, p 450; (b) A. R. Olson and R. S. Halford, *J. Amer. Chem. Soc.*, **59**, 2644 (1937); A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 34.

(5) R. A. Sneen, J. V. Carter, and P. S. Kay, *J. Amer. Chem. Soc.*, **88**, 2594 (1966).

(6) (a) Z. Majerski, S. Borčić, and D. E. Sunko, *Tetrahedron*, **25**, 301 (1969); (b) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 22; (c) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 155.

(7) (a) H. Weiner and R. A. Sneen, *J. Amer. Chem. Soc.*, **87**, 287, 292 (1965); (b) R. A. Sneen and J. W. Larsen, *ibid.*, **88**, 2593 (1966); (c) R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 362 (1969); (d) R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 6031 (1969).

(8) H. L. Goering and J. F. Levy, *ibid.*, **86**, 120 (1964).

(9) Reference 10, p 121.

(10) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, **No. 19**, 109 (1965).

(11) K. L. Servis, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, Abstracts, ORGN 120.

(12) C. J. Lancelot and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4291, 4296 (1969); C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *ibid.*, **91**, 4294 (1969); P. v. R. Schleyer, and C. J. Lancelot, *ibid.*, **91**, 4297 (1969).

(13) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer *ibid.*, **92**, 2538 (1970); (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970); (c) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. L. Lancelot, *ibid.*, **92**, 2542 (1970); (d) S. H. Liggero, J. J: Harper, P. v. R. Schleyer, A. P. Krapcho, and D. E. Horn, *ibid.*, **92**, 3789 (1970); (e) J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93**, 2551 (1971).

(14) A preliminary account of this work has appeared in communication form: J. M. Harris, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92**, 5729 (1970).

(15) A referee has questioned this contention by pointing out that the solvent has a large molar concentration advantage over added azide ion. However, we show in the accompanying paper [D. J. Raber, J. M. Harris, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 4829 (1971)] that azide ions are much more ($\sim 10^3$) nucleophilic than water in direct displacement reactions; this compensates for the concentration disadvantage.

Table I. Solvolysis of Alkyl Derivatives in 75% Aqueous Dioxane in the Presence of Sodium Azide

Substrate[a]	$[NaN_3]$	$k_{obsd} \times 10^5$, sec^{-1}	% RN_3	
			Obsd[b]	Calcd[c]
1-Adamantyl	0.00		0	
bromide, 100°	0.06		8	
	0.10		6	
2-Adamantyl	0.00	6.77 ± 0.10	0	0
tosylate, 75°	0.06	8.55 ± 0.32	12	21
	0.10	9.12 ± 0.80	10	26
2-Propyl	0.00	1.30 ± 0.04	0	0
tosylate, 50°	0.06	7.48 ± 0.06	83	83
	0.10	8.34 ± 0.50	87	85
2-Octyl	0.00	2.38	0	0
brosylate,[d] 65°	0.06	10.6	76	78
	0.10	16.0	84	85

[a] 0.02 *M* in all cases. [b] Determined titrimetrically. [c] Calculated by eq 3. [d] The values for 0.06 and 0.10 *M* NaN_3 were interpolated from the data in ref 7c.

Table II. Solvolysis of Alkyl Derivatives in 80% Aqueous Ethanol in the Presence of Sodium Azide

Substrate[a]	$[NaN_3]$	$k_{obsd} \times 10^5$, sec^{-1}	% RN_3		% ROH	% ROC_2H_5
			Obsd	Calcd[b]		
1-Adamantyl	0.00	12.6 ± 0.1	0.0	0	49	51
bromide,[c] 75°	0.02	13.0 ± 1.3	0.4	3	41	58
	0.04	13.2 ± 0.1	0.4	5	45	54
	0.06	14.2 ± 0.7	0.6	12	43	56
2-Adamantyl	0.00	1.94 ± 0.05	0.0	0	71	29
tosylate,[c] 75°	0.02	2.10 ± 0.01	0.1	8	68	31
	0.04	2.17 ± 0.01	0.4	11	66	33
	0.06	2.26 ± 0.01	0.7	16	65	34
2-Propyl	0.00	5.75 ± 0.06	0	0	100	
tosylate,[d] 50°	0.02	8.27 ± 0.29	31	30	69	
	0.04	12.5 ± 0.40	54	54	46	
	0.06	16.9 ± 0.20	65	66	35	

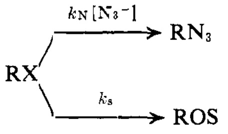
[a] 0.01 *M* in all cases. [b] Calculated by eq 3. [c] Products determined by gas chromatography. [d] Products determined titrimetrically.

case of dioxane or acetone) which is then partitioned between azide ion and water.

The kinetic results and product data for 75% dioxane are presented in Table I, and the data for 80% ethanol are given in Table II. The amount of product resulting from azide attack is readily obtained from the difference between the theoretical and experimental infinity titers; thus both rate and product data can be obtained from titration alone.[7] The distribution of all three products (alkyl azide, ether, and alcohol) from the aqueous ethanol solvolyses could be analyzed by gas chromatography; the azide incorporations so determined were in good agreement with those measured titrimetrically. Appropriate control experiments (see Experimental Section) indicated that all products were stable to the reaction conditions.

Examination of the data in Tables I and II shows the striking similarity of the behavior of the secondary 2-adamantyl tosylate and the tertiary 1-adamantyl bromide. On the other hand, the simple secondary substrates, 2-propyl and 2-octyl arenesulfonates, provide a sharp contrast. The latter compounds alone show a marked rate enhancement due to added azide, and a major diversion of product to alkyl azide.

Scheme I



Using the model depicted in Scheme I to represent a direct displacement reaction, the observed rate in the presence of azide ion is predicted by eq 1. Since the ratios of the rates and products are related by eq 2, combination of eq 1 and 2 gives eq 3, which explicitly states the rate–product correlation expected for Scheme I.

$$k_{obsd} = k_s + k_N[N_3^-] \qquad (1)$$

$$k_N[N_3^-]/k_s = \%\ RN_3/\%\ ROS \qquad (2)$$

$$\frac{k_{obsd}}{k_s} = 1 + \frac{\%\ RN_3}{\%\ ROS} \qquad (3)$$

In order to apply the criterion of a rate–product correlation it is necessary to determine the appropriate values of k_s (the other variables in eq 3 are measured directly experimentally). This can be done most conveniently by using eq 4,[10] but this necessitates estimation of the value of b.[16]

$$k_s = k_s^0(1 + b[N_3^-]) \qquad (4)$$

In all cases both the observed rate constants and the product ratios, RN_3/ROS, were found to be linear functions of the concentration of sodium azide. However, 2-adamantyl tosylate and 1-adamantyl bromide show very little rate enhancement due to added azide ion and only minor amounts of alkyl azide formation, especially in 80% ethanol (Table II). Furthermore, eq 3 *does not* relate rate and product data.[16] However, 2-propyl tosylate and 2-octyl brosylate show large effects on both rates and products, and these are correlated *quantitatively* by eq 3.[16] This indicates that the simple secondary substrates react by a mechanism in which the rate-determining step and the product-determining step are the same (*cf.* Scheme I). In the case of 2-adamantyl tosylate and 1-adamantyl bromide, however, eq 3 does not correlate rates and products, and the rate-determining step must be different from the product-deter-

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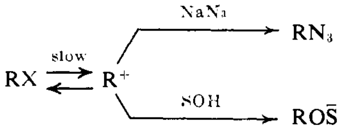
[16] Since salt effects in aqueous solvents usually are small (for example, b is 2–3 for 80% ethanolysis of 1-adamantyl bromide and 2-adamantyl tosylate), the simplest approach would be to ignore salt effects on k_s, *i.e.*, with $b = 0$, $k_s = k_s^0$. With small values of b and low salt concentrations, salt effect corrections are small and are in the range of the experimental errors in the observed rate constants.

mining step. On this basis the solvolysis of 1- and 2-adamantyl derivatives may be described by a process such as depicted in Scheme II. This scheme is clearly an oversimplification, however, since considerable evidence is available which indicates that free carbonium ions are not usually generated in solvolytic reactions, and some degree of association with the gegenion is involved.[10,17]

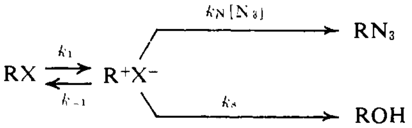
Scheme II



In this section we have discussed the behavior of added azide ion as a model for nucleophilic attack by solvent. Azide ion is a better nucleophile than typical solvolysis solvents.[18] Hence, if azide is found not to participate nucleophilically with a given substrate, it follows that solvent will not do so either; such is the case with 2-adamantyl tosylate. Tables I and II afford further evidence for our interpretation[12,13] of the role of solvent in secondary solvolyses: nucleophilic solvent assistance is relatively unimportant in the solvolysis of 2-adamantyl tosylate, but it is involved to varying degrees in the solvolysis of other secondary derivatives.

The Ion Pair Mechanism. In the previous section we discussed solvolysis reactions in terms of classical S$_N$2 (Scheme I) and S$_N$1 (Scheme II) processes. It must be emphasized, however, that alternative interpretations of the data are possible. For example, Sneen has considered four possible mechanisms for the solvolysis of 2-octyl arenesulfonates: S$_N$1, S$_N$2, concurrent S$_N$1 and S$_N$2, and substitution at the stage of an intimate ion pair.[7] The latter mechanism, which was favored by Sneen, is depicted in Scheme III. According to this scheme, products are formed by a displacement reaction (by solvent or added nucleophile) on a reversibly formed ion pair. The observed rate constant must then be a complex function of all the individual rate constants (k_1, k_{-1}, k_N, and k_s). However, under conditions such that one of the individual steps becomes rate limiting, the predicted kinetic behavior would be indistinguishable from that expected for the corresponding situation illustrated in either Scheme I or Scheme II.

Scheme III



Sneen and Larsen proposed the ion pair mechanism to explain their observations that "when optically active 2-octyl mesylate was solvolyzed in the more aqueous system, 25° vol % aqueous dioxane (75% water) in the presence of sodium azide, 2-octyl azide was again obtained (along with 2-octanol) but in this solvent system the rate was found to be *nearly independent* of the concentration of sodium azide."[7c] This claim of only "a small dependence of rate on azide concentration"[7c] is not supported by the data. For example, in 25% dioxane containing 0.237 M sodium azide the total rate observed for 2-octyl mesylate was 2.5 times faster than the rate in the absence of azide ion (Table III, columns 1 and 2). From the product data and eq 3, a rate enhancement of 3.0 is expected for competing S$_N$2 processes (Table III, column 3). In 30% dioxane containing 0.311 M sodium azide (see Table III) the observed rate enhancement was 2.8, and a factor of 3.9 is calculated using eq 3. Sneen's treatment,[7] in effect, magnifies these small discrepancies (*e.g.*, 2.5 *vs.* 3.0 and 2.8 *vs.* 3.9) by the assumption of positive salt effects. It should be emphasized that the entire justification of the Sneen ion pair hypothesis is based on this discrepancy between rate and product data.

Table III. Observed and Predicted Rate Constants for the Solvolysis of 2-Octyl Mesylate in 25 and 30% Dioxane in the Presence of Sodium Azide[a]

$[NaN_3]$	k_{obsd}[b]	k_{SN2}[c,d]	k_{SN2} (positive[c,e] salt effect)	k_{SN2} (negative[c,f] salt effect)	$k_{ion\ pair}$[e,g]
		25% Dioxane			
0.000	2.21 ± 0.08				
0.0758	3.18 ± 0.12	3.34	3.79	3.29	3.23
0.113	3.76 ± 0.07	3.78	4.44	3.65	3.60
0.156	4.34 ± 0.17	4.38	5.39	4.17	4.08
0.237	5.18 ± 0.22	6.43	8.45	5.96	5.28
		30% Dioxane			
0.000	1.74 ± 0.04				
0.0543	2.43 ± 0.08	2.82	2.98	2.66	2.54
0.0571	2.26 ± 0.11	2.87	3.04	2.71	2.58
0.0979	2.67 ± 0.14	3.68	4.03	3.32	3.09
0.152	3.65 ± 0.14	3.83	4.46	3.25	3.34
0.199	3.73 ± 0.12	4.82	5.84	3.86	3.91
0.258	4.71 ± 0.08	5.65	7.20	4.19	4.42
0.311	4.91 ± 0.15	6.85	9.06	4.72	4.97

[a] Rate constants are all in $\sec^{-1} \times 10^4$. [b] Reference 7c. [c] From the product data[7c] using eq 3 and 4. [d] $b = 0$. [e] $b = 1.08$ for 25% dioxane and $b = 1.04$ for 30% dioxane. [f] $b = -0.3$ for 25% dioxane and $b = -1.0$ for 30% dioxane. [g] Using eq 5 where $x = 2.40$ for 25% dioxane and $x = 2.59$ for 30% dioxane. Since $m[N_3] = \%\ RN_3/\%\ ROH$, the product ratio[7c] for each experiment was used to calculate the corresponding rate constant.

Sneen's arguments in favor of the ion pair mechanism are cogently illustrated by Figure 1, a plot[7b,c] of k_{obsd}/k_{NA} *vs.* $[NaN_3]$, where k_{NA} is "the rate constant in the absence of azide ion."[7a] The open circles in Figure 1 represent what Sneen and Larsen[7b] call the "experimental points." The solid line was determined from eq 5[7]

$$\frac{k_{obsd}}{k_{NA}} = \frac{(x + 1)(1 + m[N_3^-])}{(x + 1 + m[N_3^-])} \qquad (5)$$

(derived by application of the steady-state approximation to Scheme III), where $m = k_N/k_s$ and $x = k_{-1}/k_s$. The value of m is an average determined from the product ratios, and the value of x is adjusted to obtain the best fit with the so-called experimental points. The dotted line in Figure 1 represents the values of k_{obsd}/k_{NA} (*i.e.*, k_{obsd}/k_s in our terminology) expected for an S$_N$2 reaction, which were calculated from the product data using eq 3; Sneen and Larsen calculated this line by

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(17) (a) A. F. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 1904 (1968); (b) A. Streitwieser and T. D. Walsh, *ibid.*, **87**, 3686 (1965); (c) V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *ibid.*, **91**, 7748 (1969).

(18) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

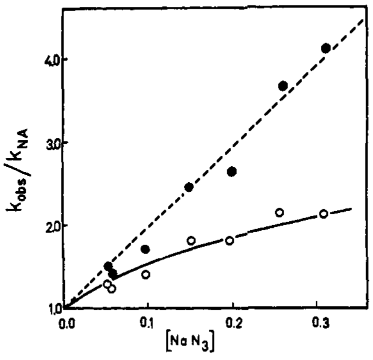


Figure 1. Plots of k_{obsd}/k_{NA} *vs.* [NaN$_3$] for 2-octyl mesylate in 30% dioxane. The solid line is that expected for the ion pair mechanism (Scheme III), and the dotted line is that expected for an SN2 process (Scheme I). The open circles represent values of k_{obsd}/k_{NA} calculated with eq 6 using b = 1.04, and the values represented by the filled circles were calculated with eq 6 using b = −1.0.

a slightly different but equivalent method.[7c] According to Sneen and Larsen, "...the experimental data are well correlated by the ion pair mechanism but deviate considerably (especially at higher salt concentrations) from the rate constants calculated for a true SN2 process."[7b]

However, this conclusion is open to criticism. Sneen and Larsen's values of k_{obsd}/k_{NA} were calculated using eq 6 in which the magnitude of k_{NA} is calculated by assuming a positive salt effect.[7b,c]

$$\frac{k_{obsd}}{k_{NA}} = \frac{k_{obsd}}{k^0(1 + b)[N_3^-]} \tag{6}$$

Although one might expect a positive salt effect for both SN1 and SN2 solvolyses as a consequence of charge generation in the transition state,[2] in actual fact examples of *negative* salt effects have been reported, especially for solvolyses in highly aqueous solvents.[19] Presumably such negative salt effects are the result of predominating decreases in the activity coefficients of neutral organic substrates.[19b] Sneen and Larsen evaluated the expected magnitude and sign of the sodium azide salt effect from the observed salt effects due to added NaBr, NaNO$_3$, and LiClO$_4$.[7c] This may not be a reliable procedure since salt effects are highly dependent on the nature of the added salt.[19] For example, the salt effects on both the activity coefficient and the hydrolysis rate of γ-butyrolactone vary not only in magnitude but also in sign with the identity of the added salt.[19b] In addition, the rate increases observed by Sneen and Larsen[7c] with bromide, nitrate, and perchlorate ions might, to some extent, be due to SN2 processes involving these ions. By assuming a negative salt effect (b = −1.0, to be contrasted with the value of b = 1.04 used by Sneen and Larsen[7c]) for the reaction in 30% dioxane, eq 6 was used to calculate the values of k_{obsd}/k_{NA} represented by filled circles in Figure 1. The least squares straight line through these circles is virtually identical with the dotted line representing an SN2 reaction. Thus, in contrast to Sneen's contention,[7] the experimental data can also be described adequately in terms of SN2 processes.

Table III provides an alternative comparison. Sneen and Larsen's treatment is given in column 6, and the SN2 results for a negative salt effect correction are shown in column 5. While the ion pair treatment gives statistically somewhat better agreement with experiment, it should be observed that this treatment involves use of an adjustable parameter, x, and rather arbitrarily chosen values for b.

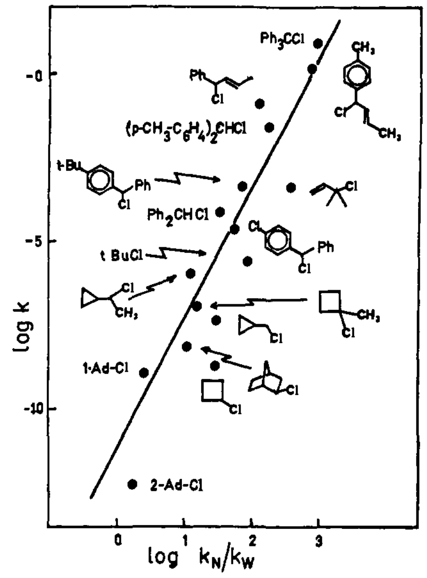


Figure 2. Stability–selectivity plot for carbonium ions derived from the solvolysis of alkyl chlorides in 80% acetone at 25°.

It is apparent that rather than being "nearly independent of the concentration of sodium azide,"[7c] the rates of 2-octyl mesylate in 25 and 30% dioxane are entirely compatible with competing SN2 processes. On this basis, although there is considerable evidence implicating ion pairs in solvolysis reactions,[17] we cannot accept the view that "...the operation of this [ion pair] mechanism was demonstrated unequivocally"[7d] for 2-octyl mesylate in these two solvent systems.[20–22]

Azide Ion as a Quantitative Probe for Carbonium Ion Processes. Sneen, Carter, and Kay[5] have discussed a linear free energy relationship between carbonium ion stability and azide incorporation. When log k for solvolysis in the absence of azide ion (a measure of carbonium ion stability) was plotted against log k_N/k_S (a measure of azide incorporation) for a series of alkyl

(19) (a) E. F. Duynstee, E. Grunwald, and M. L. Kaplan, *J. Amer. Chem. Soc.*, **82**, 5654 (1960); (b) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, pp 150–155.

(20) Professor K. L. Servis (private communication) has found that in the range 0.1–0.4 M, the activity of sodium azide deviates substantially from its concentration. Both Sneen's work[7] and our own utilize the relationship between rate and product data; consideration of activity is implicit in these treatments.

(21) J. L. Kurz and J. C. Harris, [*J. Amer. Chem. Soc.*, **92**, 4117 (1970)] have recently published evidence against the generality of Sneen's ion pair hypothesis. However, these authors considered the ion pairs to have a full positive charge on carbon. It is likely that ion pairs, especially the tight ion pairs discussed by Sneen, have a considerable degree of bonding character between the carbon atom and the gegenion; thus the assumption of a full positive charge on carbon may not be valid. See ref 13a, footnote 8.

(22) B. J. Gregory, G. Kohnstam, M. Paddon-Row, and A. Queen [*Chem. Commun.*, 1032 (1970)] have also criticized Sneen's ion pair mechanism. These authors argued in favor of competing SN2 and SN1 mechanisms, the latter taking place through dissociated carbonium ions. Substantial evidence is available[12,13] which shows that dissociated carbonium ions are not expected to intervene in the solvolysis of simple secondary substrates. In addition, the magnitudes of their variable parameter, β, needed to obtain agreement between rate and product data, are entirely unrealistic. As will be shown in Figure 2, were secondary aliphatic derivatives to solvolyze by carbonium ion mechanisms, very low selectivity ratios between azide ions and water would be expected corresponding to values of β on the order of 10^{-2}. Such realistic values of β, some two orders of magnitude less than those used by Gregory, *et al.*, do not give the agreement of rate and product data necessary to support their proposed mechanistic interpretation.

Table IV. Solvolysis Rates and k_N/k_W Ratios for Alkyl Chlorides in 80% Aqueous Acetone at 25° in the Presence of Sodium Azide

Substrate	k, sec^{-1}	Ref	k_N/k_W	Ref
Triphenylmethyl	8.75×10^0	*a*	1000	*b*
1-*p*-Tolyl-2-butenyl	1.58×10^0	*c*	815	*d*
1-Phenyl-2-butenyl	1.34×10^{-1}	*c*	130	*e*
p,p'-Dimethylbenzhydryl	2.70×10^{-2}	*f*	180	*g*
p-tert-Butylbenzhydryl	4.77×10^{-4}	*h*	74	*i*
α,α-Dimethylallyl	4.26×10^{-4}	*j*	390	*d*
Benzhydryl	7.27×10^{-5}	*k*	34	*l*
p-Chlorobenzhydryl	2.31×10^{-5}	*m*	56	*n*
tert-Butyl	1.97×10^{-6}	*o*	74	*p*
1-Methylcyclopropylcarbinyl	1.11×10^{-6}	*q*	12	*r*
1-Methylcycobutyl	1.15×10^{-7}	*s*	15	*r*
Cyclopropylcarbinyl	4.81×10^{-8}	*t*	31	*r*
exo-Norbornyl	7.00×10^{-9}	*u*	11	*v*
Cyclobutyl	1.81×10^{-9}	*w*	28	*r*
1-Adamantyl	1.10×10^{-9}	*x*	2.5	*y*
2-Adamantyl	5.30×10^{-13}	*z*	1.7	*y*

[a] Estimated from the rate in 85% acetone [C. G. Swain, C. B. Scott, and K. H. Lohman, *J. Amer. Chem. Soc.*, **75**, 136 (1953)] assuming $m = 1$. [b] E. A. Hill, *Chem. Ind.* (*London*), 1696 (1965). [c] Estimated from the rates of the paranitrobenzoate in 60, 70, and 80% dioxane [R. A. Sneen, *J. Amer. Chem. Soc.*, **82**, 4261 (1960)] using a Cl/OPNB ratio of 3×10^4. [d] Reference 5. [e] R. A. Sneen and A. M. Rosenberg, *J. Amer. Chem. Soc.*, **83**, 900 (1961). [f] Estimated from the rate at 0° [L. C. Bateman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 974 (1940)] assuming a rate increase of a factor of 20. [g] A. R. Hawdon, E. D. Hughes, and C. K. Ingold, *ibid.*, 2499 (1952). [h] M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *ibid.*, 971 (1940). [i] Reference 2b. [j] F. B. Miles, *J. Amer. Chem. Soc.*, **89**, 2488 (1967); **90**, 1265 (1968); P. G. Gassman and J. M. Hornback, *ibid.*, **89**, 2487 (1967); P. G. Gassman, J. M. Hornback, and J. L. Marshall, *ibid.*, **90**, 6238 (1968). [k] S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, **79**, 4146 (1957). [l] M. G. Church, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 966 (1940). [m] Reference 10, p 109. [n] Reference 8. [o] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956). [p] L. C. Bateman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 960 (1940). [q] Estimated from the rate of 1-methylcyclobutyl chloride (footnote *s*) using the rate ratio of 9.65 found in 50% ethanol [E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 2719 (1961)]. [r] Reference 6a. [s] Calculated from the rates in 80% ethanol [H. C. Brown and M. Borkowski, *J. Amer. Chem. Soc.*, **74**, 1894 (1952)] and 50% ethanol (Cox, *et al.*, footnote *q*). [t] Calculated from the rates in 80% ethanol (Brown and Borkowski, footnote *s*) and 50% ethanol (Cox, *et al.*, footnote *q*). [u] Estimated from the rate in 80% ethanol [P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 3901 (1967)] assuming $m = 0.75$. [v] J. M. Harris and D. J. Raber, unpublished results. [w] Estimated from the rate of cyclopropylcarbinyl chloride (footnote *t*) using the rate ratio of 3.76×10^{-2} found in 50% ethanol (Cox, *et al.*, footnote *a*). [x] Calculated from the rates in 50% ethanol [P. v. R. Schleyer and V. Buss, *J. Amer. Chem. Soc.*, **91**, 5880 (1969)] and 80% ethanol: P. v. R. Schleyer and R. D. Nicholas, *ibid.*, **83**, 182 (1961). [y] This work. [z] Estimated from the rate of the bromide in 80% ethanol[13b] using $m = 1.03$ for the bromide[13a] and using a Br/Cl ratio of 40.

halides, a good straight line was obtained.[5] The basis of the stability–selectivity relationship lies in the expectation that a difference in rate constants for attack on an intermediate by two different reactants should diminish as the stability of the intermediate decreases. In the limit, a highly unstable intermediate would have no activation barrier for collapse to products, the rates of attack by two competing reactants would depend only on their concentrations, and the ratio of the respective rate constants would be unity.

We have extended Sneen, Carter, and Kay's treatment[5] to include a number of considerably less reactive substrates, among these some secondary derivatives which would not afford resonance stabilized cations. Table IV presents a summary of results for solvolysis in 80% acetone together with the effects of added azide ion for alkyl derivatives felt to react by carbonium ion pathways, and the table includes the available data from the literature. When data for the solvolysis of the appropriate chlorides in 80% acetone were not available, the rate constants were estimated by standard methods as described in the table. The values of k_N/k_W, when not given in the original literature, were calculated from the product distributions using eq 7.[7c]

$$\frac{k_N}{k_W} = \frac{\%\ RN_3[H_2O]}{\%\ ROH[NaN_3]} \tag{7}$$

A log–log plot of the data in Table III is presented in Figure 2. A reasonably good straight line is obtained for a range of solvolytic reactivities varying over 13 powers of ten (thus extending Sneen's range by 7 powers of ten). The correlation coefficient for the least squares line is 0.886; the standard deviation in log k is 0.52, and the standard deviation in log k_N/k_W is 0.02.

Certain limitations on this linear free energy relationship must be considered. First, it does not predict the anticipated limiting value of unity for the k_N/k_W ratio of a highly unstable carbonium ion. For example, an alkyl chloride solvolyzing at a rate similar to that of 2-adamantyl chloride is predicted by the line in Figure 2 to show an inverse selectivity (*i.e.*, $k_N/k_W < 1$).[23] Thus, although the plot in Figure 2 amply demonstrates the stability–selectivity relationship, it cannot apply to the entire range of carbonium ion stability. On the basis of this theory the experimental points for less reactive alkyl chlorides would be expected to approach the vertical axis asymptotically, and thus a curve rather than a straight line should best describe the stability–selectivity relationship.

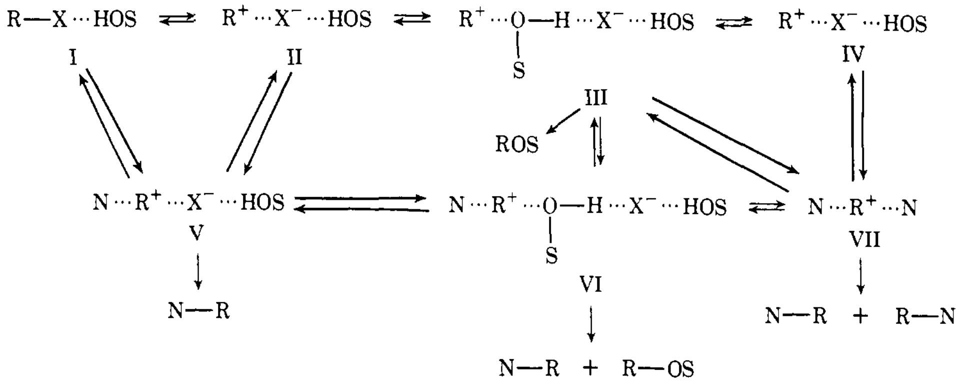
Similarly, this relationship fails to account for differences in ground-state energies of the alkyl halides. Many examples are known in which two or more substrates react, by rearrangement, to give the same solvolytic intermediate.[24] Clearly, two such compounds solvolyzing at highly different rates yet giving the same intermediate (and the same product distribution) could not both fall on the same line for a plot of log k *vs.* log k_N/k_W. This simply serves to indicate that solvolysis rates, although frequently used for this purpose, do not afford an entirely accurate estimate of the relative stabilities of carbonium ions. The solvolysis rate reflects not only the energy of the intermediate (more properly, the transition state) but also the energy of the ground state.

For a stability–selectivity relationship the stability of the intermediate is best defined as the energy difference between the intermediate and the products (*i.e.*, it is this difference which is assumed to influence the heights of the activation barriers for collapse to products and the differences between the barriers). This reasoning

[23] Sneen's original plot[5] gave the intercept with the vertical axis at a value of log k approximately equal to that corresponding to 1-adamantyl chloride. Inclusion of the additional points in Figure 2 results in a steeper slope and lower intercept for the least squares line.

[24] (a) J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, **73**, 2509 (1951); (b) R. G. Lawton, *ibid.*, **83**, 2399 (1961).

Scheme IV[a]



[a] N = either HOS or added nucleophile.

indicates that the best correlation will be obtained when solvolysis takes place without skeletal rearrangement.

A third possible deficiency lies in the nature of the intermediate which is diverted to product. For the sake of simplicity we have discussed these reactions in terms of carbonium ions since they all appear to be limiting with respect to nucleophilic solvent participation. However, Goering has presented evidence that *p*-chlorobenzhydryl chloride reacts with azide ion at the stage of a solvent-separated ion pair.[8] It is likely that different intermediates may be involved for the different alkyl chlorides and even that more than one intermediate may be involved for a single alkyl chloride.[8,9]

The importance of these limitations on the stability–selectivity relationship should not be overemphasized, however; they only serve to indicate that caution must be exercised in its interpretation. The stability–selectivity relationship can be of significant value in ascertaining the mechanism of solvolysis. The line in Figure 2 does correlate alkyl chlorides which solvolyze without nucleophilic solvent participation; it will be shown in the following paper that compounds solvolyzing by a k_s pathway do not fall on this line.[25] Adherence to this stability–selectivity relationship for carbonium ions provides further supporting evidence for the limiting nature of 2-adamantyl solvolysis.

Some Observations on the Detailed Mechanism of Solvolysis. The mechanistic possibilities for solvolysis are many. The traditional Winstein solvolysis scheme,[10] $R\text{-}X \rightleftharpoons R^+X^- \rightleftharpoons R^+ \| X^- \rightleftharpoons R^+ + X^-$, can be elaborated to show more explicitly the role of nucleophile and solvent. This results in the complicated mechanism shown in Scheme IV, which accommodates most of the possibilities.[26]

The basic Winstein intermediates, I–IV, have been modified to show electrostatic solvation of the leaving group, and Winstein's more recent formulation[15b] has been followed to show the solvent-separated ion pair, III, with the solvent playing a dual role, solvating both the anion (by hydrogen bonding) and the cation. In effect, the solvent molecule shown solvating the anionic portion of the intimate ion pair, II, has inserted itself between the two fragments to give III.

Species V, VI, and VII indicate the possibility of stable intermediates with solvation at the backside. These species may also possibly be transition states for direct displacements on I–IV. Whether V, VI, and VII are intermediates or transition states depends on the substrate structure, the nature of the nucleophile, and the reaction conditions.

Intermediate III provides a simple rationalization for the several cases of *retention* of configuration which have been observed; *e.g.*, in the solvolysis of 7-norbornyl arenesulfonates,[27a] the solvolysis[27b] of methyl substituted 2-adamantyl tosylates, and the phenolysis of α-phenethyl chloride.[28] If the structure of III is such that nucleophilic attack from the rear is inhibited (*i.e.*, VI does not form) and the rate of conversion to the "free" cation, IV (or to the symmetrically solvated VII), is slow, then simple collapse would convert III to VIII with retention of configuration. This seems to us preferable to Okamoto's formulation[28] of this retention process, collapse of a four-center intermediate.

The role of nucleophile (or solvent acting as nucleophile) is emphasized in Scheme IV. Direct displacement on I *via* V as transition state represents the classical S$_N$2 reaction.[29] Alternatively, V may be formed from II, as Sneen and Larsen have suggested.[7c] On the other hand, if ion-pair intermediates are involved in the solvolysis of simple secondary and primary substrates,[7,17] it may be that V and not II is the structure of the first intermediate.

The solvent-separated ion pair may be nucleophilically solvated (VI) or not (III). An interesting possibility is shown; VI can, in principle, collapse in two nonequivalent ways. If the nucleophile is present, the substitution product, N–R, should be inverted, but the solvolysis product, ROS may have appreciable retention of configuration.[30] Symmetrically solvated (VII) or totally nucleophically unsolvated (IV) species would give completely racemic product, a stereochemical result seldom actually observed in solvolysis.[4c]

A major problem remaining in the study of solvolysis reactions is the delineation of all of these mechanistic possibilities. Our work shows that nucleophilic sol-

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(25) See Raber, *et al.*, ref 15.

(26) *Cf.* V. J. Shiner, Jr., and R. D. Fisher, *J. Amer. Chem. Soc.*, **93**, 2553 (1971).

(27) (a) See Table IV, footnote *j*; (b) J. A. Bone and M. C. Whiting, *Chem. Commun.*, 115 (1970).

(28) K. Okamoto, K. Komatsu, and H. Shingu, *Bull. Chem. Soc. Jap.*, **40**, 1677 (1967); K. Okamoto, T. Kinoshita, and H. Shingu, *ibid.*, **43**, 1545 (1970).

(29) In Winstein's solvolysis scheme,[10] such direct attack on covalent substrate is not explicitly indicated.

(30) Goering and Levy[8] have actually performed such an experiment. Optically active *p*-chlorobenzhydryl *p*-nitrobenzoate was solvolyzed in 80% acetone in the presence of sodium azide. Evidence showed that solvent-separated ion pairs intervened. The *solvolysis* product had net retention of configuration, and the azide product was also optically active. Unfortunately, the relative configuration of the azide product was not determined.

vent participation is involved in the overall solvolysis process. Whatever the mechanistic details, such solvent attack results in considerable rate enhancement for simple secondary substrates.

Experimental Section

Materials. 1-Adamantyl Bromide. Commercial 1-adamantyl bromide (Aldrich) was sublimed at 105° (10 mm) and 95° (0.15 mm), and was then recrystallized from pentane at −80°, mp 118.8–119.2° (lit.[31] mp 119–120°).

2-Adamantyl Tosylate. 2-Adamantyl tosylate was prepared from 2-adamantanol[32,33] with tosyl chloride in pyridine and recrystallized from pentane at −80°, mp 81.6–82.1° (lit.[33] 82.7–83.7°).

2-Propyl Tosylate.[34] 2-Propanol was distilled through a 6-in. Vigreux column (bp 82.0°) and converted to the tosylate with tosyl chloride in pyridine. The tosylate was recrystallized several times at low temperature before use.

1-Adamantyl Azide. An authentic sample of 1-adamantyl azide was prepared as described by Sasaki, Eguchi, and Toru.[35]

2-Adamantyl Azide. Following the procedure for 1-adamantyl azide,[35] a solution of 1.0 g of 2-adamantyl bromide, 9.4 g of sodium azide, and *ca.* 0.1 g of silver perchlorate in 100 ml of dry dimethyl sulfoxide was stirred at 100° for 48 hr. The reaction was monitored by glpc, and at the end of this time less than 1% of the starting material remained. The solution was poured into 100 ml of ice and water, and the crude crystalline product was collected by filtration and dried at reduced pressure. The product was dissolved in 150 ml of diethyl ether, and the ether solution was washed with two 50-ml portions of saturated sodium chloride solution and dried over sodium sulfate. Evaporation of the ether afforded a colorless solid, which was purified by two recrystallizations from aqueous methanol to give 0.30 g (36%) of 2-adamantyl azide: ir (CCl_4) $\bar{\nu}$ 2090 cm^{-1} (N_3); nmr (CCl_4) δ 3.75 (0.9 H, broad singlet), 1.9 (14.1 H, multiplet); mass spectrum, *m/e* 177 (M^+).

A sample of the azide was reduced with lithium aluminum hydride to give a yellow oil which was found to be identical (glpc) with an authentic sample of 2-adamantylamine.[36]

Ethanol. Ethanol was distilled from magnesium ethoxide as described by Lund and Bjerrum.[37]

Dioxane. Dioxane was purified by the method of Fieser.[38] The purified solvent was stored over sodium and distilled shortly before use.

Sodium Azide. Sodium azide (Aldrich) was dissolved in a minimum amount of hot water. The solution was filtered, and ethanol was added until clouding persisted. The solution was then cooled slowly to 0° and filtered. The inorganic salt was washed with acetone, dried *in vacuo* for 2 hr, and stored in a desiccator.

Kinetic Methods. Rates in 80% (v/v) aqueous ethanol in the absence of NaN_3 were determined conductimetrically with a Wayne-Kerr Model B331 impedence bridge, capable of 0.1% accuracy. The conductivity cells used had bright platinum electrodes, cell constants of 0.2–0.4, and a volume of approximately 25 ml. In a typical experiment enough substrate to make a 10^{-3} *M* solution was placed in the conductivity cell and 20 ml of solvent was added. The cell was then sealed and equilibrated with stirring for 5 min in the constant-temperature bath. The usual number of measurements taken was 15. The raw conductance data were then fitted to the first-order rate equation by means of a least squares computer program. Linear conductivity–concentration plots within the limits of experimental error were obtained. Also, there was excellent agreement between the rate constants determined conductimetrically and test titrimetric rate constants.

Rates in 75% (v/v) aqueous dioxane (both with and without sodium azide) and in 80% ethanol in the presence of sodium azide were determined titrimetrically. In a typical experiment 1.0 mmol of substrate was added to a 100-ml volumetric flask and the volume was brought to the mark with the desired premixed solution of sodium azide. About 5.1 ml of the solution was added to each of 18 ampoules, and the ampoules were sealed and immersed in a constant-temperature bath. Ampoules were removed from the bath at approximately equal intervals of per cent reaction, and were quenched by swirling in an ice–water bath. Two infinity ampoules were removed and quenched after 10 half-lives. The cold ampoules were brought to room temperature before titration. A 5-ml sample of the solution was pipeted from each ampoule and titrated with standardized aqueous sodium hydroxide using bromothymol blue as indicator. Rate constants were then calculated using a least squares computer program. All rate constants are the result of at least two independent determinations, with a mean deviation of 5% or less.

Product Determination. The amount of alkyl azide formed was determined from the difference between experimental and theoretical infinity titers or by glpc analysis. Agreement between the two methods was good. The chromatographic studies also allowed determination of ether and alcohol products; peak assignments were also checked by injection of authentic samples. A 5 ft × 1/8 in. FFAP (5% on Chromosorb W) column was used at an oven temperature of *ca.* 160°. Agreement between analyses at 10 and 20 half-lives demonstrated that the products were stable to the reaction conditions.

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(31) S. Landa and S. Hala, *Collect. Czech. Chem. Commun.*, **24**, 93 (1959).

(32) H. W. Geluk and L. L. M. A. Schlatmann, *Tetrahedron*, **24**, 5361 (1968).

(33) P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 182 (1961).

(34) R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953).

(35) T. Sasaki, S. Eguchi, and T. Toru, *Bull. Soc. Chem. Jap.*, **42**, 3613 (1969).

(36) H. Stetter, H. Held, and J. Mayer, *Justus Liebigs Ann. Chem.*, **658**, 151 (1962).

(37) H. Lund and J. Bjerrum, *ibid.*, **64**, 210 (1931).

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