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Determination and application of Winstein-Grunwald M and Y values in bridged polycyclic systems

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DETERMINATION AND APPLICATION OF WINSTEIN-GRUNWALD μ AND γ
VALUES IN BRIDGED POLYCYCLIC SYSTEMS

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AUGUST, 1970

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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ABSTRACT

The rates of solvolysis of 3-nortricyclyl p-bromobenzenesulfonate (nortricyclyl brosylate) have been determined (at 25.0⁰) in the solvents acetic acid, methanol, and acetic acid and methanol with various small amounts of added water. First order rate constants were obtained by u.v. absorbance, conductometric and titrimetric techniques. All rate constants obtained, with the exception of the titrimetric data, were fairly reproducible and agreed with the previously reported data (where available).

Numerical values of \underline{m} from the Winstein equation: $\log k/k_0 = \underline{m}Y$ were calculated from experimental data for solvolysis reactions of nortricyclyl brosylate in each of the solvent sets. These \underline{m} values fell in a range of 0.40-0.69. U.V. absorbance and conductometric data were employed in \underline{m} value calculations. Results of titrimetric method were inconsistent and were disregarded. Calculated values of \underline{m} were in the expected range for a secondary substrate. A range of \underline{m} values was observed depending on solvent and analytical technique employed. The range of \underline{m} values suggested that less attention should be focused on absolute value of \underline{m} and greater attention should be directed to the linear correlation fit of $\log k$ vs. Y plot (used to determine \underline{m}). Correlation coefficient data are presented which substantiate this conclusion.

The rates of solvolyses of exo-(cis) and endo-(trans)-3-chloro-exo-5-norborn-5-yl-2,4-dinitrobenzene thioether in acetic acid were

also studied using conductometric analytical techniques. The experimentally observed rate constant of the endo-(trans) compound was higher than that of the exo-(cis) compound. These rates determined by others in 70% aqueous dioxane show the cis compound to be more reactive than the trans. It is assumed that these latter results are the "normal" results and that the results in acetic acid indicate that this solvent is a poor one for determination of stereochemical structure. A rationalization for the reactivity ratio reversal in acetic acid is advanced.

HISTORICAL

The Winstein mY Equation

The study of solvolytic reactions by Grunwald and Winstein¹ indicated a linear free energy relationship between ionizing power of various solvents and the log of the rate constants of solvolytic reactions carried out in these same solvents. Through observation of the variation of rates of solvolysis of a selected compound (known to solvolyze by an S_N1 mechanism) in a variety of selected solvents the following equation was developed.

$$\log (k/k_0) = \underline{m}Y \quad (1)$$

In equation (1), Y refers to the "ionizing power"¹ of the solvent and \underline{m} is a measure of the sensitivity of the solvolyzing substrate to the ionizing power of the solvent. *t*-Butyl chloride, known from previous studies to solvolyze by essentially a unimolecular process, was chosen by Grunwald and Winstein as the standard substrate ($\underline{m} = 1.00$). The solvent, 80% ethyl alcohol (80 vol. of alcohol plus 20 vol. of water), because of its wide usage and intermediate ionizing power, was selected as the standard solvent ($Y = 0$). Thus, for any substrate, $\log k_0$ corresponds to the rate for that substrate in 80% ethanol. Values of Y are determined for solvents by measuring $\log k$ with $\log k_0$ known for *t*-butyl chloride in that solvent and solving for Y in equation (1) with $m = 1.00$ (see Table I). Thus, the statement that $\log k_0$ corresponds to rate in 80% ethanol essentially sets $Y = 0.00$ for 80% ethanol (2):

Table I¹

SOLVOLYSIS RATES OF t-BUTYL CHLORIDE AND Y VALUES FOR SOLVENTS

<u>Compound</u>	<u>Solvent</u>	δ	Temp. C.	E^+ kcal	$k(\text{sec.}^{-1})$	<u>Ref.</u>	<u>Y</u>
(CH ₃) ₃ CCl	Absolute EtOH	25.0		25.97	9.70×10^{-8}	Table II	-1.974
	90% EtOH, N _{H₂O} = 0.262				1.73×10^{-6}	6	-0.727
	80% EtOH, N _{H₂O} = 0.448			23.06	9.24×10^{-6}	6	0.000
	70% EtOH, N _{H₂O} = 0.582				4.07×10^{-5}	6	0.644
	60% EtOH, N _{H₂O} = 0.684				1.27×10^{-4}	6	1.139
	50% EtOH, N _{H₂O} = 0.765			22.92	3.67×10^{-4}	6	1.604
	40% EtOH, N _{H₂O} = 0.829				1.29×10^{-3}	6	2.151
	80% (CH ₃) ₂ CO ₂			22.6	1.94×10^{-6}	6	
	5% (CH ₃) ₂ CO, N _{H₂O} = 0.987				2.57×10^{-2}	7	3.449
	48.61 wt. % H ₂ O in dioxane			22.8	1.81×10^{-4}	8, 11b	1.292
	H ₂ O-MeOH, N _{H₂O} = 0.000			25.0	8.20×10^{-7}	8, Table II	-1.052
	H ₂ O-MeOH, N _{H₂O} = 0.070				1.75×10^{-6}	8	-0.722
	H ₂ O-MeOH, N _{H₂O} = 0.175				4.33×10^{-6}	8	-0.329
	H ₂ O-MeOH, N _{H₂O} = 0.230				7.14×10^{-6}	8	-0.112
	H ₂ O-MeOH, N _{H₂O} = 0.282				1.13×10^{-5}	8	0.088
	H ₂ O-MeOH, N _{H₂O} = 0.346				2.12×10^{-5}	8	0.361
	H ₂ O-MeOH, N _{H₂O} = 0.432				5.28×10^{-5}	8	0.757
	H ₂ O-MeOH, N _{H₂O} = 0.497				9.75×10^{-5}	8	1.023
	H ₂ ^c				3.3×10^{-2}		3.56
	HCOOH ^b			22.9 ^a	1.1×10^{-3}	9a	2.08
	AcOH, 0.025 M KOAc			26.43	2.13×10^{-7}	Table II	-1.633
	AcOH-Ac ₂ O, N _{AcOH} = 0.042						
	0.017 M KOAc			26.4 ^a	4.77×10^{-9}	Table II	-3.287

Table I (cont'd.)

-
- a Value used by the authors.
 - b An average value calculated from data at lower temperatures.
 - c Obtained by extrapolation.

$$\log \left[\frac{(k)_{t\text{-Butyl-Cl}/80\% \text{ EtOH}}}{(k)_{t\text{-Butyl-Cl}/80\% \text{ EtOH}}} \right] = \underline{m}Y \quad (2)$$

$$\log 1 = \underline{m}Y = 0$$

$$\text{but, } \underline{m} = 1.00$$

$$\therefore Y \text{ must be } = 0.00$$

Determination of \underline{m} values (Table II) was carried out utilizing the solvent Y values. Since the Y values are based on the *t*-butyl chloride solvolytic results, the substrate \underline{m} value essentially indicates the response of that substrate to variations in Y as compared to *t*-butyl chloride. E.g., α -methylallyl chloride (Expt. 5, Table IIa) responds 89.4% as well to Y changes as does *t*-butyl chloride.

The discussion of \underline{m} - Y relationships above is purely operational. It is desirable to have these related on a mechanistic (theoretical) basis also. Analysis of \underline{m} values in relation to simple structural features of compounds reveals an obvious trend. Those compounds which, from steric or energetic considerations (normally tertiary or highly hindered systems), would be expected to follow S_N1 solvolytic mechanisms exhibit a high (ca. unity) value of \underline{m} , e.g., *t*-butyl bromide, α -phenylethyl chloride, and 1-bromobicyclo[2.2.2]octane (Table II). In contrast, substrates expected to proceed via bimolecular or S_N2 solvolytic processes show relatively small values of \underline{m} (0.2-0.4, see first 9 values, Table IIc, all primary substrates). Values of \underline{m} appear consistent with the assumption that \underline{m} is a measure of the sensitivity of solvolytic rate of a substrate to the ionizing power of the solvent (assuming that Y measures ionizing power) and that this sensitivity arises because of stabilization of

Table IIa¹

CORRELATION OF SOLVOLYSIS RATES IN VARIOUS SOLVENTS

<u>No.</u>	<u>Compound</u>	<u>Temp.</u> <u>° C.</u>	<u>m</u>	<u>log k₀</u>
1	<u>t</u> -Butyl chloride	25.0	1.000	-5.034
2	<u>t</u> -Butyl bromide	25.0	0.917	-3.476
3	Neopentyl bromide	95.0	.712	-7.248
4	α -Methylnopentyl <u>p</u> -bromo- benzenesulfonate	70.0	.706	-2.837
5	α -Methylallyl chloride	25.0	.894	-6.314
6	Benzhydryl chloride	25.0	.757	-2.779
7	α -Phenylethyl chloride ^a	50.0	1.195	-3.808
8	<u>n</u> -Butyl bromide	59.4	0.392	-5.972
		75.1	0.331	-5.419

^a Solvents: 1, ethanol; 2, 80% ethanol; 3, 50% ethanol; 4, water; 5, methanol; 6, acetic acid; 7, 90% ethanol; 8, 60% ethanol; 9, 30% ethanol.

Table IIB²

CORRELATION OF SOLVOLYSIS RATES IN VARIOUS SOLVENTS

<u>Compound</u>	<u>Temp.</u> <u>° C.</u>	<u>Solvents</u> ^a	<u>log k_o</u>	<u>m</u>
Methyl bromide	50.00	1,2,3,4	-5.779	0.258
Methyl benzenesulfonate	50.00	1,4,5	-4.536	.228
Ethyl Bromide	55.00	1,2,3,4	-5.898	.343
Ethyl benzenesulfonate	50.00	1,4,5,9	-4.781	.279
Ethyl <u>p</u> -toluenesulfonate	50.00	1,2,3,5	-5.062	.262
Isopropyl bromide	50.00	1,2,3,4	-5.906	.544
Isopropyl <u>p</u> -bromobenzene- sulfonate	70.00	1,2,5	-2.750	.408
<u>t</u> -Butyl bromide	25.00	1,2,7,8	-3.472	.940
Benzyl chloride	50.00	1,2,3,5	-5.594	.425
Benzyl <u>p</u> -Toluenesulfonate	25.05	1,2,5	-3.449	.394
<u>trans</u> -2-Bromocyclohexyl- <u>p</u> -bromobenzenesulfonate	50.00	1,2,3,5,6	-5.159	.701
<u>trans</u> -2-Methoxycyclohexyl <u>p</u> -bromobenzenesulfonate	50.00	1,2,3,5,6	-5.539	.493

^a Solvents: 1, ethano; 2, 80% ethanol; 3, 50% ethanol; 4, water; 5, methanol; 6, acetic acid; 7.90% ethanol; 8, 60% ethanol; 9, 30% ethanol

Table IIc³m-VALUES IN VARIOUS SOLVENTS

<u>Compound</u>	<u>° C.</u> <u>Temp.</u>	<u>m (Aqueous</u> <u>Alcohol)</u>	<u>Apparent m</u> <u>(RCOOH)</u>
Methyl bromide	50	0.26	
Methyl tosylate	75	0.23 ^a	0.30
Ethyl bromide	55	0.34	
Ethyl iodide	50	0.27	
<u>n</u> -Propyl chloride	101.6	0.39	
<u>n</u> -Propyl bromide	95	0.34 ^b	
Ethyl benzenesulfonate	50	0.28	
Ethyl tosylate	50	0.26	0.44 ^c , 0.37 ^d
<u>n</u> -Butyl brosylate	60	0.32 ^e	0.38
Isopropyl bromide	50	0.54	
Isopropyl brosylate	70	0.41	0.66 ^c
2-Pentyl tosylate	58.2	0.41 ^b	0.68
3,3-Dimethyl-2-butyl brosylate	70	0.71	0.83 ^c
<u>tert</u> -Butyl chloride	25	1.00	1.00
<u>tert</u> -Butyl bromide	25	0.94	
1-Bromobicyclo[2.2.2]octane	100	0.88	0.92
Benzyl chloride	50	0.43	0.66
Benzyl bromide	25	0.39	
<u>p</u> -Methylbenzyl chloride	50	0.57	
Allyl chloride	44.6	0.40	
α -Phenylethyl chloride	50	0.81	

^a Value for methyl benzenesulfonate at 50° C. used.

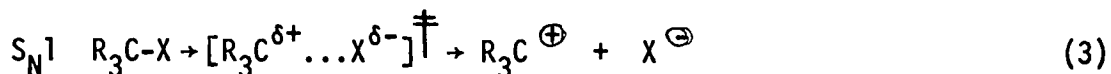
^b Assumed value.

^c at 25° C.

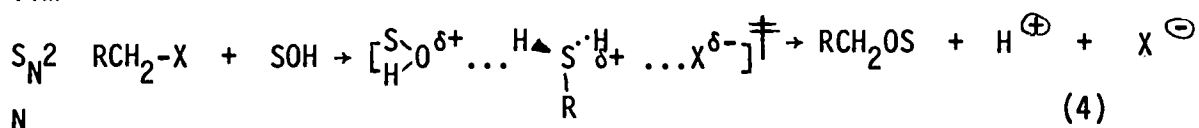
^d at 75° C.

^e Value for n-butyl benzenesulfonate used.

the highly charged activated complex which forms during the course of an S_N1 solvolytic mechanism. This would be expected to be much more dependent on the ionizing power of the solvent than would the activated complex which forms when S_N2 mechanisms are followed (Ingold prediction of solvent polarity effects on nucleophilic substitutions⁴, equations (3) and (4)).



lim



With reference to the charge separation in the two activated complexes illustrated above, Wiberg states, "... the charge separation might be expected to be about the same in both activated complexes, [but] the radius of the second (4) would be expected to be greater than that for the first (3), leading to a smaller susceptibility toward the ionizing power of the solvent for the S_N2 process."⁵ This is in agreement with the physically fundamental Kirkwood treatment which indicated that the solvolytic stabilization of ionic species is inversely proportional to the radius⁶.

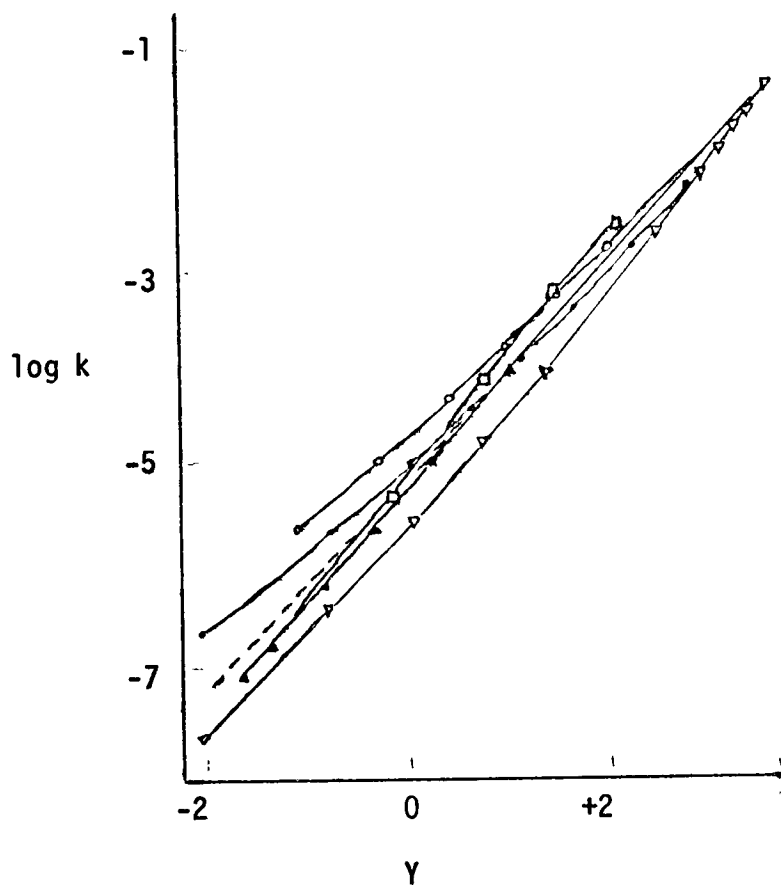
Further rate studies performed by Winstein⁷ indicated that the ionizing power of the solvent was not the sole influence exerted by the solvent on the observed rate. A study of ρ Y correlations for various compounds in a series of solvent mixtures indicated that ρ for one substrate was not a constant but varied with the nature of

the solvent system under study (Table III). Variation in \underline{m} for α -phenylethyl chloride is apparent in Fig. 1

The slope of each line should reveal a value of \underline{m} unique for α -phenylethyl chloride (at 25° C.). Inspection of Fig. 1 immediately reveals the observed variation in \underline{m} . An explanation for this moderate dispersion of values for \underline{m} , in terms of subtle and very specific solute-solvent interactions, is found in Kosower⁸.

A study of the variation in specific substrate solvolytic rate in various solvents, not explainable in terms of variation in ionizing power $[Y]$ of the solvent, is the work of Grunwald, Winstein and Jones, as described by Wiberg⁹. Various substrates were each solvolyzed in carboxylic acidic solvents and then in aqueous alcohol solvents. The acid and aqueous alcohol solvents were of equal ionizing power $[Y]$ value. The ratio of rate constants, if of purely S_N1 processes, should be equal or nearly equal unity in the ideal case. That this is clearly not so is shown in Table IV. The observed ratios reinforce the conclusion that a feature of the solvent, other than that of the ionizing power, plays a significant role in the solvolysis reactions of many compounds. Note that those substrates of relatively low \underline{m} values (Table II) exhibit a large $k[\text{aq. alcohol}]/k[\text{acid}]$ ratio (Table IV). This behavior is consistent with the previous interpretation of magnitudes of \underline{m} in terms of predominance of $S_N1^{(3)}$ and $S_N2^{(4)}$ mechanisms since primary (and, to a lesser extent, secondary) substrates would be expected to have higher $k[\text{aq. alcohol}]/k[\text{acid}]$ ratios than would

Figure 1⁸



Plots of $\log k$ for the solvolysis of 1-phenylethyl chloride at 25.0° versus Y in $C_2H_5OH-H_2O$, \bullet ; CH_3OH-H_2O , \circ ; dioxane- H_2O , \blacktriangle ; $CH_3COOH-H_2O$, \triangle ; $CH_3COOH-HCOOH$, \square . The dashed line is the least squares line for all of the data

Table III⁸m-VALUES FOR ALKYL HALIDE SOLVOLYSIS^a

<u>Compound</u>	<u>Solvent Mixtures</u> ^b	<u>m</u>	<u>Ref.</u>
1-Phenylethyl chloride	10-100% C ₂ H ₅ OH-H ₂ O	0.966	369
	50-100% CH ₃ OH-H ₂ O	0.912	369
	0-16M H ₂ O in CH ₃ COOH	1.136	369
	0-100% CH ₃ COOH-HCOOH	1.194	369
	10-90% dioxane-H ₂ O	1.136	369
1-Phenylethyl bromide	40-100% C ₂ H ₅ OH-H ₂ O	0.817	370
	50-100% CH ₃ OH-H ₂ O	0.843	370
	0-8M H ₂ O in CH ₃ COOH	1.245	370
	30-90% dioxane-H ₂ O	1.014	370
<u>t</u> -Butyl bromide	40-100% C ₂ H ₅ OH-H ₂ O	0.941	370
	60-100% CH ₃ OH-H ₂ O	0.947	370
	0-100% CH ₃ COOH-HCOOH	0.946	370
	0-8M H ₂ O in CH ₃ COOH	1.067	370
	40-90% dioxane-H ₂ O	0.921	370
Benzhydryl chloride	80-100% C ₂ H ₅ OH-H ₂ O	0.740	371
	90-100% CH ₃ OH-H ₂ O	0.820	371
	60-90% dioxane-H ₂ O	1.049	371
	0-4M H ₂ O in CH ₃ COOH	1.561	371
Benzhydryl Bromide	0-4M H ₂ O in CH ₃ COOH	1.687	371
Trityl fluoride	40-100% C ₂ H ₅ OH-H ₂ O	0.890	371
	40-70% (CH ₃) ₂ CO-H ₂ O	1.58	371
Triphenylsilyl fluoride	50-83.4% (CH ₃) ₂ CO-H ₂ O	0.468	371

^a At 25.0° C.^b Percentages by volume of first-named component.

Table IV¹⁰EFFECT OF SOLVENT NUCLEOPHILICITY ON SOLVOLYSIS RATES^a

Compound	T	m(aq. alcohol)	$\frac{k(\text{aq. alcohol})}{k(\text{RCOOH})}$	
			$\text{CH}_3\text{CO}_2\text{H}$	HCO_2H
Methyl bromide	50 ⁰	0.26		200
Methyl tosylate	75	0.23	97	55
Ethyl bromide	55	0.34		80
Ethyl tosylate	50	0.26	80	18
<u>n</u> -Propyl chloride	102	0.39		~ 30
<u>n</u> -Propyl bromide	95	0.34		63
<u>n</u> -Butyl brosylate	60	0.32	30	20
<u>i</u> -Propyl bromide	50	0.54		20
<u>i</u> -Propyl brosylate	70	0.41	6	2
2-Pentyl tosylate	58	0.41	4	0.4
t-Butyl chloride	25	(1.00)	(1)	(1)
1-Bromobicyclo[2.2.2]- octane	100	0.88	0.7	0.5
Benzyl chloride	50	0.43	58	4
Benzyl tosylate	25	0.39	30	
α -Phenethyl chloride	50	0.81	2.5	
Allyl chloride	45	0.40		40

^a The data were taken from S. Winstein, E. Grunwald, and H.W. Jones, J. Am. Chem. Soc., 73, 2700 (1951) and from A. Streitwieser, Jr., Chem. Revs., 56, 571 (1956).

tertiary substrates due to the nucleophilicity of the solvent Winstein Grunwald, and Jones² have indicated the nucleophilic character of the solvent [N] by the proposal of the following equation (5). Systematic developments of N values, however, have not been carried out.

$$d \ln k = \underbrace{\left(\frac{\alpha \ln k}{\alpha Y} \right)_N}_{\underline{m}} dY + \underbrace{\left(\frac{\alpha \ln k}{\alpha n} \right)}_{\text{nucleophilic contribution}} dN \quad (5)$$

In view of the observed variation in solvolytic rate accompanying alteration of nucleophilic character of solvent employed, the fundamental basis of the Winstein $\underline{m}Y$ correlation [$\log k = \underline{m}Y + \log k_0$] is substantially limited. Theoretical correlations are likely significant if one stays within a narrow range of solvent variations; e.g. aqueous alcohols cannot be directly compared to carboxylic acids and one should not vary the per cent compositions vastly even within a single alcohol-water solvent pair. The ratios given in Table III are, at least, a qualitative means of determining the existence of nucleophilicity of solvent in the solvolysis of a particular substrate.

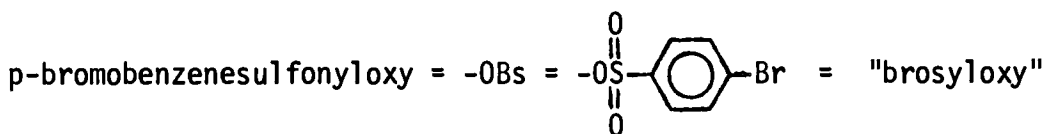
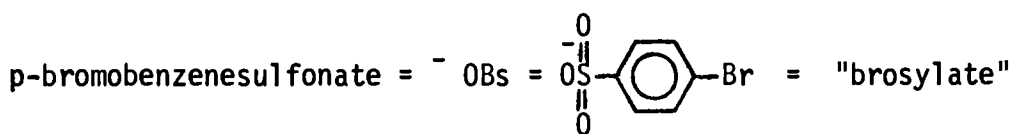
In summary, Kosower states "... experience with $\underline{m}Y$ correlations suggests that they are useful (a) for predicting rates in solvents for which direct rate determinations would be inconvenient or impossible, (b) for reaching qualitative conclusions about mechanisms of solvolysis reactions, and (c) as a means for evaluating subtle substituent effects in closely related compounds in solvolytic reactions."⁸

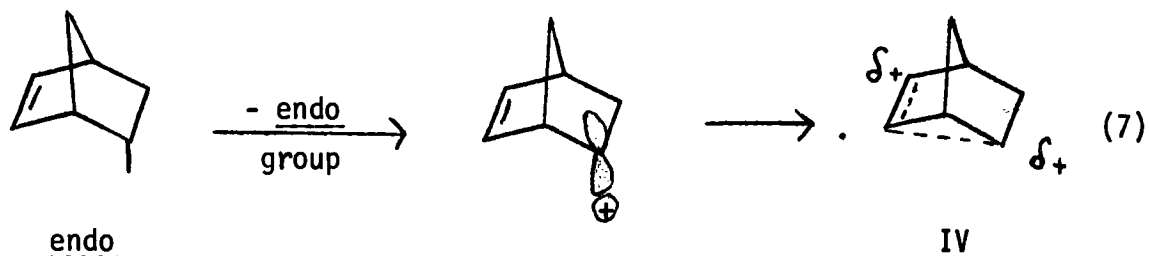
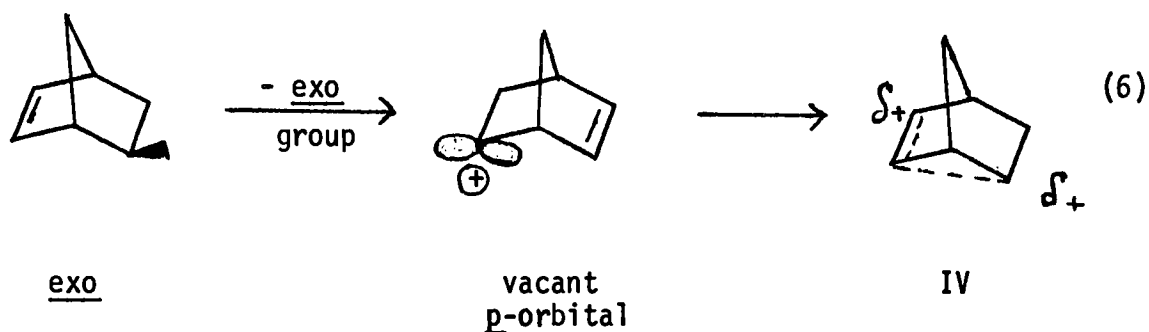
A more detailed and fundamental discussion of linear free energy relationships of solvents is that of Grunwald and Leffler¹¹.

A feature of the mY equations that does not seem clear (upon examination of the literature) is the relationships of the m value (e.g., within any one structural class, primary vs. secondary vs. tertiary) to carbonium ion delocalization by neighboring aryl groups, σ -bonds or non-bonded electrons of nearby atoms. A realization of this and an appreciation of the systems and methods described below are the foundation of the ideas originating the research described in this thesis.

Bridged Polycyclic Systems of Interest

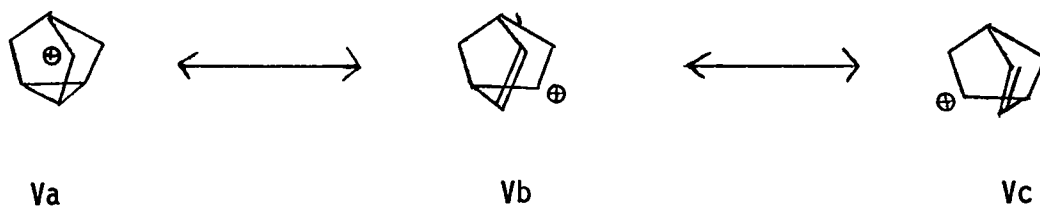
A substrate of interest in our research is 3-nortricyclyl p-bromobenzenesulfonate [nortricyclyl brosylate, I]. Winstein and co-workers¹² have compared the acetolysis rates (25^o) of saturated brosylate I to exo- and endo-norborneyl brosylates (II and III, respectively). The substrate of interest (I) is only slightly less reactive than exo-isomer (II) and both are substantially more reactive than endo-isomer (III).



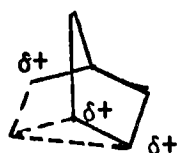


Judging from the nature of solvolysis products¹⁴ [$>90\%$ nortricyclyl] of the exo- and endo-isomers, it is assumed that both species pass through the delocalized cationic intermediate (IV) which has a very heavy concentration of positive charge on carbon atom 5. The rate of attainment of this structure is, however, much higher in the case of the exo-compound.

Explanation of the observed rate of the nortricyclyl derivative can, similarly, be explained in terms of sigma [σ]-p-orbital overlapping. This nortricyclyl cation might be depicted by the following resonance forms¹⁵:



Note that the combination of resonance forms Va-Vc would be effectively the same as the combination of resonance forms IV and IVb.

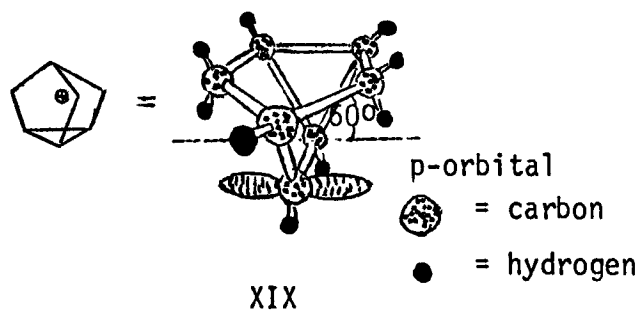


IVb

Formation of the above delocalized structure is dependent on effective overlap of the vacant p-orbital overlap with the σ -bond of the cyclopropyl ring, effectively a cyclopropyl cation^{15,16}. From Fig. 2, it is obvious that the location of the vacant p-orbital is oriented approximately 60° relative to the cyclopropyl ring σ -orbitals.

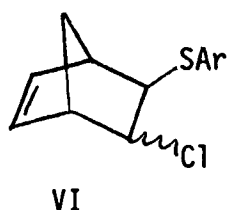
A possible explanation of the I, II, III reactivity sequence is that σ -p interaction in the nortricycyl system is much more facile than in the endo-norbornenyl system (90° vs. 60°) but is slightly less readily attainable than in the exo-norbornenyl system. A part of the explanation of the relative reactivities of exo-endo-isomers II and III may involve the known substantially greater reactivity of exo over endo derivatives in the corresponding saturated norbornyl systems^{17a,b}. Thus, part of the higher reactivity of exo-compounds may be due to σ -bond participation of the C_5 - C_6 bond (not directly related to double bond interaction) and, as has been pointed out¹⁸, the portions due to σ - and π -delocalization are not dissectable and which (if either) is more important is not clear.

FIGURE 2

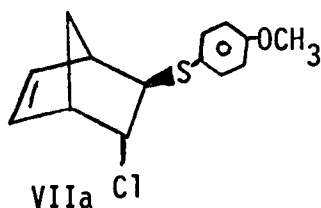


As would be expected for intermediates such as IV and IVb, the product formed by solvolysis in the nortricyclyl systems is mostly nortricyclyl derivative^{15,19}. The rate of formation of product from I relative to endo-norbornenyl isomer (II) justifies the invocation of direct cyclopropyl ring participation through limited σ -p interaction.

Another substrate system that is of interest to us is represented by general structure VI.



The solvolysis of a norbornenyl derivative of related importance has been reported by Cristol and co-workers²⁰. The particular solvolysis of interest is that of exo-2-p-thiocresoxy-endo-3-chloro-5-norbornene (VIIa) in 85% ethanol at 116.5^o C. The reported rate



constant was $6.6 \times 10^{-6} \text{ sec.}^{-1}$. This work alludes to the analogous exo-norbornenyl halide systems and concludes that the unreactive nature of the chloride (VIIa) is consistent with endo-chlorine behavior. Unreactive endo-chlorides are described in the rate studies of Roberts on the parent norbornenyl halide compounds²¹.

Analytical Techniques for Kinetic Analyses

In the kinetic analyses cited above for polycyclic systems and in related kinetic studies a variety of analytical techniques have been reported.

A technique of special interest to our kinetic procedures has been reported by Swain²². In this study, Swain followed an apparent first order solvolysis reaction of methyl *p*-toluenesulfonate in water. Absorption readings at 261 m μ at various intervals were reported. Decrease in absorption with time was observed. This decrease in absorption was anticipated in view of the fact that the ester solvolyzed had a characteristic extinction coefficient of 671 and the tosylate-anion had an extinction coefficient of 344. The rate constant for this system determined by this u.v. absorption method compared very well with the value determined conductometrically²³. Application of a modified technique of this type will be outlined in detail later in this thesis. Data measurements reported in the Swain investigation are reproduced in Table V.

In this report, Swain alludes (without pertinent details) to the usefulness of this ultra-violet technique in the study of methanolysis reactions. Extension of this technique to solvents absorbing in the ultra-violet region is also discussed by Swain. Universal application in ultra-violet sensitive solvent systems would, however, require the formulation of well chosen extraction schemes to effect transfer of solvolyzed material from an ultra-violet sensitive solvent to a transparent solvent.

Table V²²

Hydrolysis of 1.22×10^{-3} M Methyl Tosylate in Water
at 25^o

<u>Time, (hr.)</u>	<u>Absorbance</u>	<u>% unchanged</u>
0.0	0.791	100.0
5.0	0.746	87.9
9.0	0.709	77.9
18.0	0.645	60.6
24.0	0.611	51.5
32.0	0.570	40.4
44.0	0.526	28.6
55.0	0.498	21.0
67.0	0.471	13.7
290.0	0.420	0.0

$$k_1 = 7.91 \times 10^{-6} \text{ sec.}^{-1}$$

An ultra-violet study was also conducted by Sinnott²⁴. Sinnott has tabulated the observed extinction coefficient of methyl p-toluenesulfonate and p-toluenesulfonic acid in acetic acid solvent mixtures (Table VI). Sinnott's work lends support to general applicability of ultra-violet absorption analytical techniques to solvolytic studies.

In systems where ions are generated or destroyed during the course of solvolytic reaction, the reaction has been successfully studied through application of conductivity methods. The kinetic analysis of methyl p-toluenesulfonate in water, by R.E. Roberts²³ is such an example of this.

The classical method of following reaction rates in systems in which a strong acid is generated (usually mineral) is the titrimetric method. Winstein has extensively employed the titration method of analysis². Solvolysis rates, in acetic acid, are followed by titration of acidic solvolytic product with sodium acetate in acetic acid to a brom phenol blue end point². For solvolysis in alcohol, titrations were performed using alkali dissolved in the appropriate alcohol. Indicators used were brom thymol blue, methyl red, or phenolphthalein².

Table VI²⁴

Longest Wavelength Vibrational Sub-Band in Acetic Acid
0.1% in Water

<u>Solute</u> <u>1.49×10^{-2} M</u>	<u>λ_{\max}, mμ</u>	<u>$\epsilon \times 10^2$</u>	<u>Other Solute</u>
MeOTs	273.1	5.0	---
HOTs	272.6	3.3	---
HOTs	272.6	3.3	3.5×10^{-2} M HClO ₄
HOTs	272.2	1.7	4.2×10^{-2} M KOAc

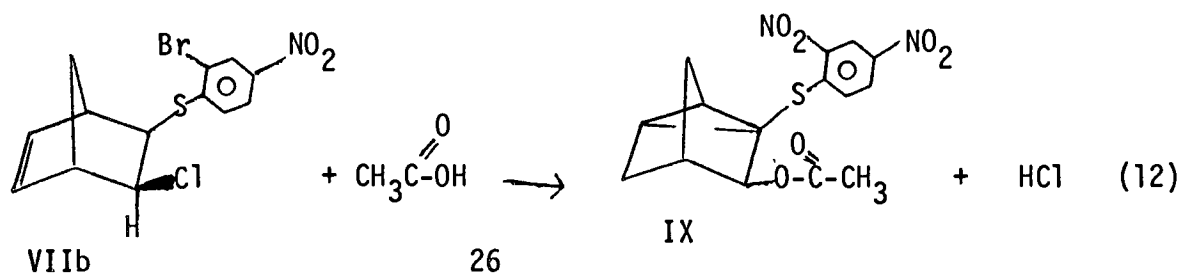
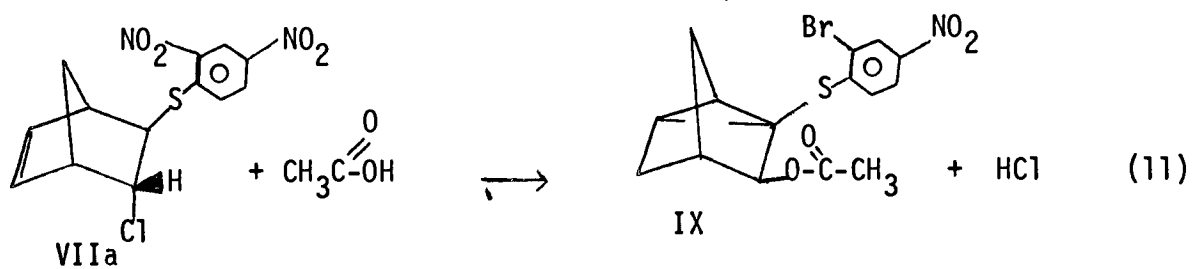
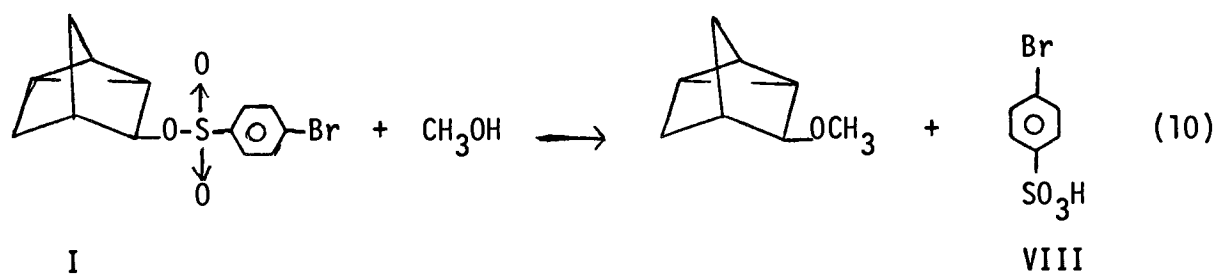
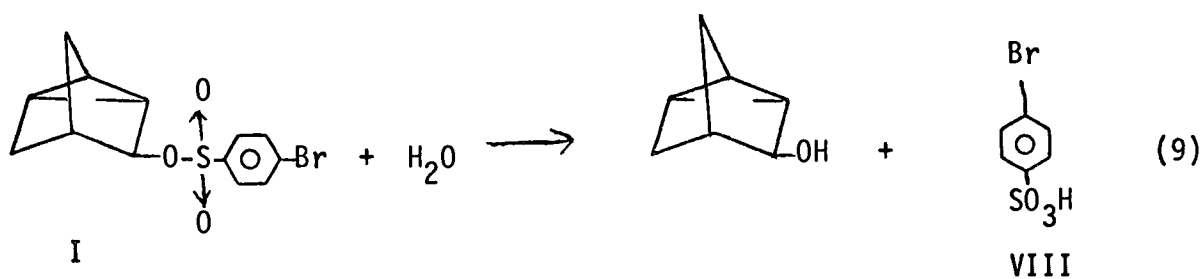
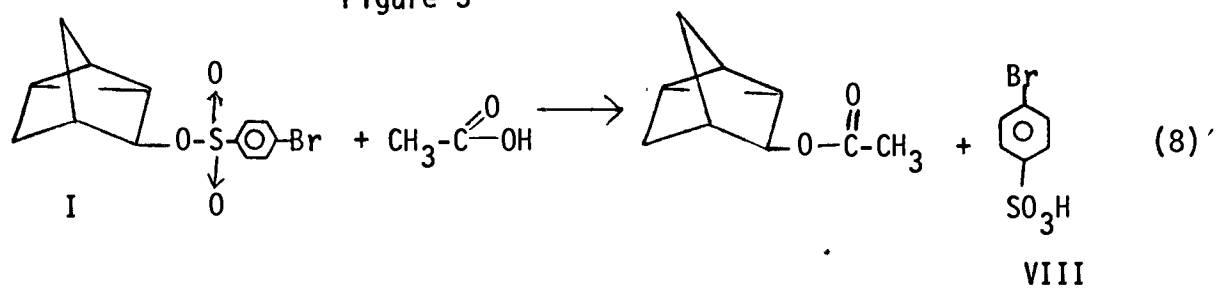
Longest Wavelength Vibrational Sub-Band in Acetic Acid
2.5% in Acetic Anhydride

<u>Solute</u> <u>1.75×10^{-2} M</u>	<u>λ_{\max}, mμ</u>	<u>$\epsilon \times 10^2$</u>	<u>Other Solute</u>
MeOTs	273.1	5.1	---
HOTs	272.7	3.5	---
HOTs	272.7	3.3	4.7×10^{-2} M HClO ₄
HOTs	272.2	1.6	4.0×10^{-2} M KOAc

RESULTS AND DISCUSSION

The solvolytic reactions of interest in our work are the following:

Figure 3



Kinetic analyses of the reactions of Eq. 8, 9 and 10 were initially studied by application of u.v. absorption techniques reported by Swain²² and Sinnott²⁴. An important energetic transition in the u.v. region is the $\pi \rightarrow \pi^*$ type²⁵. It was assumed that the benzene pi system of the p-bromobenzenesulfonyloxy (brosyloxy) group of I would provide such absorption. Based on Swain's report²² of an observable difference in extinction coefficients for methyl tosylate and the tosylate anion, one might anticipate a similar difference in the extinction coefficients of nortricyclyl brosylate (I) and the brosylate anion produced in the solvolytic reactions 8, 9 and 10.

Choice of ultra-violet technique was guided, essentially, by anticipation of absorption patterns (progress of solvolysis attended by a decrease in absorption) similar to those observed by Swain²² and by apparent technical simplicity (precision aliquot transfer was unnecessary and solvents of interest, acetic acid, methanol, and water, do not absorb in the ultraviolet region of interest²⁶).

Experimental results and pertinent data of nortricyclyl brosylate (I) acetolyses applying the u.v. method are shown in Table VII. Rate constants reported in Table VII were derived using u.v. absorbance data²⁷ applying a least-squares analysis (see Appendix IV) of \ln (Absorbance) vs. time; the slope of this plot constitutes the rate constant (Equation 13).²⁸

$$\ln (c) = kt \quad (13)$$

Table VII

 RATES OF SOLVOLYSIS OF NORTRICYCLYL BROSYLATE (I)
 USING U.V. ANALYTICAL TECHNIQUE

<u>Kinetic Run</u>	<u>Solvent</u>	<u>Temp. ° C.</u>	<u>Wavelength (mμ)</u>	<u>(10⁵) k (sec⁻¹)</u>	<u>Hours of kinetic run used in least squares program</u>
1,a	100% acetic acid	29.8	233	0.90	9
1,b	"	29.3	233	0.64	3
2,a	"	25.0	233	0.36	5
2,b	"	25.0	233	4.38	20
2,c	"	25.0	233	0.48	7
2,d	"	25.0	233	0.92	18
2,e	"	25.0	233	1.34	6
2,f	"	25.0	233	2.96	18
2,g	"	25.0	233	0.43	5
2,h	"	25.0	233	0.30	20
2,i	"	25.0	233	0.25	13
3,a	" ^a	25.0	233	0.92	21
3,b	" ^a	25.0	233	0.79	4
				$k_{\text{ave.}}^{(25^\circ)} = 1.19$	$(\sigma = 1.25)^b$
4,a	95.3%	25.0	233	2.03	5.5
4,b	"	25.0	233	1.60	12.0
				$k_{\text{ave.}}^{(25^\circ)} = 1.82$	$(\sigma = 0.4)^b$
5,a	95.0% acetic acid	25.0	233	3.72	4
5,b	"	25.0	233	2.76	>3
5,c	"	25.0	233	5.24	3
				$k_{\text{ave.}}^{(25^\circ)} = 3.91$	$(\sigma = 1.0)^b$
6,a	91.4% acetic acid	25.0	233	4.90	4
6,b	"	25.0	233	4.26	3
				$k_{\text{ave.}}^{(25^\circ)} = 4.58$	$(\sigma = 0.32)^b$

Table VII (Continued)

<u>Kinetic Run</u>	<u>Solvent</u>	<u>Temp. ° C.</u>	<u>Wavelength (mμ)</u>	<u>(10⁵)₁k^c (sec⁻¹)</u>	<u>Hours of kinetic run used in least squares program</u>
7,a	100% methanol	29.3	233	2.19	5
7,b	"	29.8	"	3.73	2
8,a	"	25.0	"	1.99	3
8,b	"	"	"	1.87	2.5
				$k_{\text{ave.}}^{(25^\circ)} = 1.93 (\sigma = 0.06)^b$	
9,a	98% methanol	"	"	2.04	4
				$k_{\text{ave.}}^{(25^\circ)} = 2.04$	
10,a	95% methanol	"	"	4.35	1.75
10,b	"	"	"	2.60	2.50
10,c	"	"	"	3.90	2.0
10,d	"	"	"	3.68	1
				$k_{\text{ave.}}^{(25^\circ)} = 3.634 (\sigma = 0.54)^b$	
11,a	90% methanol	29.3	"	6.88	2
				$k_{\text{ave.}}^{(25^\circ)} = 6.88$	

^a 1% acetic anhydride added.

^b standard deviation multiplied by 10⁵ (see appendix I).

^c rate constants are of the order of ca. 10⁻⁵ and have been multiplied by 10⁵ for ease of presentation in this table.

In application of a first-order rate relationship (Equation 13), any parameter which varies as C in Equation 13 to give the proper slope (k) may be used. The parameter used in the u.v. technique is absorbance²⁷.

That the u.v. kinetic data (Table VII) are meaningful results is shown in a later section of this thesis by obtaining very similar results by a conductometric method and by relating these results to the titrimetric method of Winstein.

Inspection of Table VII allows one to qualitatively evaluate certain groups of data. It is expected, since the acetolysis of nortricycyl brosylate should have substantial dependence on Y, that as the solvent medium becomes increasingly aqueous the rate of solvolysis should be increased². It is also of interest to note, in comparing the two solvent systems, that a consistent trend of increasing rate with increasing water composition of either aqueous acetic acid or aqueous methanol is obtained. In addition, a 5% (0 to 5%) increment of water added to acetic acid effects 3.3 fold rate enhancement (kinetic runs 2a to 5c, Table VII), whereas in the methanol system (kinetic runs 8a - 10d, Table VII) the same solvent increment results in a 1.9 fold rate increase.

Interpretation of these rate enhancements caused by added water could possibly be due to increased solvent nucleophilicity. Pure acetic acid is of extremely low nucleophilic character²⁹. Water added to the acetic acid would be expected to lead to large gains in nucleophilic character. In contrast, methanol would be expected to already possess relatively high nucleophilic character²⁹.

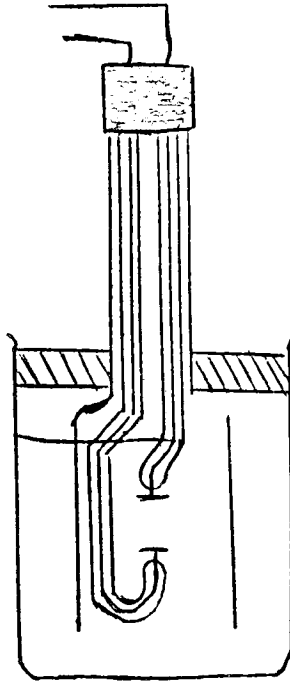
Nucleophilicity of methanol would, therefore, not be altered significantly (relative to acetic acid) by introduction of small increments of water.

It is perhaps surprising that, even qualitatively, that the rate trends with solvent composition are so consistent. This conclusion is in view of the work of Sinnott²⁴ published during the course of our work. Sinnott indicated that acetolyses of this type could be followed by determining absorbance change due to p-toluene-sulfonic acid formation (from alkyl tosylates) in the undissociated state. The Swain procedure²² is the opposite; comparison of alkyl tosylate absorbance to that of tosylate anion. One would expect in the work of this thesis that the acetic acid data with modest aqueous increments would be acceptable (Sinnott²⁴), but that the aqueous methanol conditions would put conditions between the Sinnott-Swain spectrum of conditions. This fear, however, does not seem justified in view of Table VII and the m discussions for nortricycyl brosylate (I) below. All data obtained by the u.v. technique appear acceptable.

It was essential to cross check the reliability of the u.v. method of analysis by measuring the same rate constants by another technique. The method chosen was the conductivity procedure similar to that used by Roberts²³. A conductivity analytical technique would be an efficient laboratory procedure since use of the conductivity cell (Fig. 4) would obviate the need for aliquot transferral. Aliquot transferral may result in an introduction

FIGURE 4³⁰

conductivity cell



of an undetermined quantity of water into the solvolytic system and is extremely time consuming. In addition, the solvent of interest (acetic acid) has a relatively low specific conductance³¹.

Pertinent data and calculated rate constants derived using the conductometric method of analysis are summarized below in Table VIII. The reported rate constants are obtained by following the \ln of conductance (mhos) with time (in analogy to the absorbance data techniques described above).

The rate constants of Table VIII qualitatively show the same trend as described for kinetic analyses using the u.v. absorption method (Table VII); that is, as aqueous content of solvent media increased, rate enhancement is observed.

Table IX displays a direct comparison utilizing data obtained by each method in the same solvent compositions (three different sets). The comparison for any one set shows good agreement, considering the major differences in the methods, and the agreement is well within experimental error. It does seem, however, that the constants obtained using the conductometric technique are consistently higher than rates calculated from u.v. data.

The acetolysis rate for nortricyclyl brosylate has been alluded to many times in the literature³²; the absolute rate, to our knowledge, has not been reported. The rate constant for nortricyclyl brosylate can only be calculated from other absolute data reported^{33,36} and by making use of the relative reactivities, the form in which such rates are often reported^{34,35}.

Table VIII

 RATES OF SOLVOLYSIS OF NORTRICYCLYL BROSYLATE
 AT 25⁰ C. USING CONDUCTOMETRIC TECHNIQUE

<u>Kinetic Run</u>	<u>Solvent</u>	<u>(10⁵) k^c</u>	<u>Hours of kinetic run used in least squares program</u>
12,a	100% Acetic Acid	0.78	25
12,b	" ^a	0.14	26
12,c	"	1.98	22
		$k_{\text{ave}}^{(25^0)} = 1.38$	$(\sigma = 0.72)^b$
13,a	95.3% Acetic Acid	3.80	7.3
13,b	"	2.04	5.5
13,c	"	1.60	8.0
		$k_{\text{ave}}^{(25^0)} = 2.51$	$(\sigma = 0.96)^b$
14,a	91.4% Acetic Acid	5.15	2.75
14,b	"	4.26	
		$k_{\text{ave}}^{(25^0)} = 4.71$	$(\sigma = 0.45)^b$

^a 1 eq. NaOAc added and 1% acetic anhydride.

^b Standard deviation multiplied by 10⁵.

^c Rate constants are of the order of 10⁻⁵ and have been multiplied by 10⁵ for ease of presentation in this table.

Table IX
 RATES OF SOLVOLYSIS OF NORTRICYCLYL BROSYLATE AT $25.0 \pm 0.1^\circ$

<u>Ultra-Violet Method $10^5 \times k$</u>	<u>Conductometric Method $10^5 \times k$</u>
1.19 \pm 2.50 ^a 100% Acetic Acid	1.38 \pm 1.44 ^{a,b}
1.82 \pm 0.80 ^a 95.3% Acetic Acid	2.51 \pm 1.92 ^a
4.57 \pm 0.64 ^a 91.4% Acetic Acid	4.71 \pm 0.90 ^a
Ave. Rate Constants: 100% Acetic Acid	(10 ⁵)k 1.29 ⁺ 2.50
95.3% Acetic Acid	2.16 \pm 1.92
91.4% Acetic Acid	4.65 \pm 0.90

^a Two standard deviations (see Appendix I).
^b Rate constants are of the order of 10⁻⁵ and have been multiplied by 10⁵ for ease of presentation in this table.

Brosylate Relative Reactivities

$$\frac{\text{nortricyclyl (I)}}{\text{exo-norbornenyl (II)}} = \frac{2}{7} \quad \text{Winstein}^{34}$$

Rate of acetolysis exo-norbornenyl brosylate (II) =

$$4.5 \times 10^{-5} \text{ sec.}^{-1} (25^0) \quad \text{Winstein}^{33}$$

$$\therefore (2/7) (4.5 \times 10^{-5} \text{ sec.}^{-1}) = 1.28 \times 10^{-5} \text{ sec.}^{-1} (25^0) \quad (14)$$

An alternative estimate of the rate constant for nortricyclyl brosylate (I) from reported data is accomplished by making use of the acetolysis rate of cyclohexyl brosylate.

$$\text{Relative Rate: } \frac{\text{nortricyclyl brosylate (I)}}{\text{cyclohexyl brosylate}} = \frac{2000}{10} \quad \text{Winstein}^{35}$$

Rate of acetolysis (25⁰), cyclohexyl brosylate =

$$1.71 \times 10^{-7} \text{ sec.}^{-1} \quad \text{Winstein}^{36}$$

∴ Rate of acetolysis (25⁰) nortricyclyl brosylate =

$$\frac{2000}{10} \times 1.71 \times 10^{-7} \text{ sec.}^{-1} =$$

$$3.42 \times 10^{-5} \text{ sec.}^{-1} \quad (15)$$

This latter procedure, however, produces an estimated rate constant in which one should have less confidence than for the result of first estimate. Cyclohexyl brosylate is a much less reactive brosylate than nortricyclyl (I) or exo-norbornenyl (II) brosylates. Therefore, the rate constant for the cyclohexyl brosylate was obtained by substantial extrapolation from rate data obtained at much higher temperatures³⁶. The former method involved only more reactive brosylates (I and II) and thus the calculation involves relative rates all at 25⁰. It is satisfying to see that the (calculated)

literature value^{33,34}, obtained by the presumably more reliable (first) method above, and both the u.v. absorption and conductometric results of this work (Table IX) agree extremely well. This not only establishes the methods of this thesis, but more accurately establishes the absolute rate constant for nortricyclyl brosylate (I).

Since kinetic analyses employing titrimetric procedures are reported for these systems³⁷, this method also was applied to the study of nortricyclyl brosylate (I) in several solvents systems (similar to those described in Tables VIII and IX). Experimental results obtained using this technique are shown in Table X.

Examination of these kinetic data (obtained using the titration technique, Table X) reveals serious inconsistencies in observed rates of reactions in methanol and aqueous methanol (run 16a to 20d). The decrease in rate observed in changing from 98.1% to 96.8% aqueous methanol (Table X, runs 17-18) and from 94.4% to 91.4% aqueous methanol (runs 19-20, Table X) are not at all consistent with well known expectations of increasing solvolysis rate with increasing Y value (and solvent polarity)¹. Such unlikely trends, the general lack of reproducibility in any one solvent composition (see especially Table X, 94.4% methanol data), large rate enhancements accompanying slight changes of solvent composition and substantial difficulties encountered in end-point interpretation lead one to place little confidence in data obtained using the titration technique. It is therefore of almost incidental importance that the titrimetrically obtained acetolysis rate constant for glacial (100%) acetic acid (Table X, run 15) agrees extremely well with both the (essentially

Table X

RATES OF SOLVOLYSIS OF NORTRICYCYL BROSYLATE
AT 25⁰ C. USING TITRIMETRIC ANALYTICAL TECHNIQUE

<u>Kinetic Run</u>	<u>Solvent</u>	<u>(10⁵)k^b</u>	<u>Hours of kinetic run used on least squares program</u>
15,a	100% Acetic Acid	1.19	20
15,b	"	0.91	20
15,c	"	1.39	
		$k_{ave}^{(25^0)} = 1.16$	$(\sigma = 0.064)^a$
16,a	100% Methanol	12.76	5
16,b	"	9.6	4
		$k_{ave}^{(25^0)} = 11.2$	$(\sigma = 1.58)^a$
17,a	98.1% Methanol	10.0	4
17,b	"	15.7	3
17,c	"	14.97	4
17,d	"	25.8	1.5
		$k_{ave}^{(25^0)} = 16.62$	$(\sigma = 5.7)^a$
18,a	96.8% Methanol	9.5	4.5
18,b	"	8.8	5.0
18,c	"	10.4	5.0
		$k_{ave}^{(25^0)} = 9.58$	$(\sigma = 0.67)^a$
19,a	94.4% Methanol	24.9	1.5
19,b	"	6.9	6.5
		$k_{ave}^{(25^0)} = 16.92$	$(\sigma = 9.0)^a$
20,a	91.4% Methanol	12.7	4
20,b	"	14.8	2
20,c	"	10.0	4
		$k_{ave}^{(25^0)} = 12.51$	$(\sigma = 2.0)^a$

^a Standard deviation (see appendix I).

^b These rate constants are of the order of 10⁻⁵ and have been multiplied by 10⁵ for ease of presentation in this table.

equal) rate constants obtained by the u.v. absorption and conductometric methods and with the value calculated from literature data (by the method in which more confidence is placed).

Having arrived at reasonable rate data for nortricycyl brosylate in various aqueous acetic acid and methanol mixtures (u.v. and conductivity methods), one can use these data (Tables VII and VIII) in the Winstein-Grunwald equation (1) to arrive at a value for \underline{m} . Using all of the data (all solvents, all methods except titrimetric) the graph of Fig. 5 is evolved (with a separate line drawn for each combination of a specific solvent and method set). One immediately notices the extreme similarity of all of the slopes of all of these lines despite the gross differences in these solvents (e.g., acetic acid vs. methanol)³.

Methanol (as a solvent system) does lead to an \underline{m} value somewhat different than observed in acetic acid (Tables XI and XII). This is similar to the "family of \underline{m} values" for a substrate described by Kosmer⁸. That some success can be obtained by putting the acetic acid and methanol solvent system data in the same correlation is shown below.

The ability to put all of these results on the same linear correlation is a feature to which very definite exception has been reported. The value of \underline{m} calculated from the least squares fit of all data (Table XII) indicates that the best approximation for the value of \underline{m} for nortricycyl brosylate (I) is 0.44 (\pm 0.15). The magnitude of this \underline{m} value is in the range of those observed for

Figure 5a

ULTRA-VIOLET METHOD USING ACETIC ACID SOLVENT

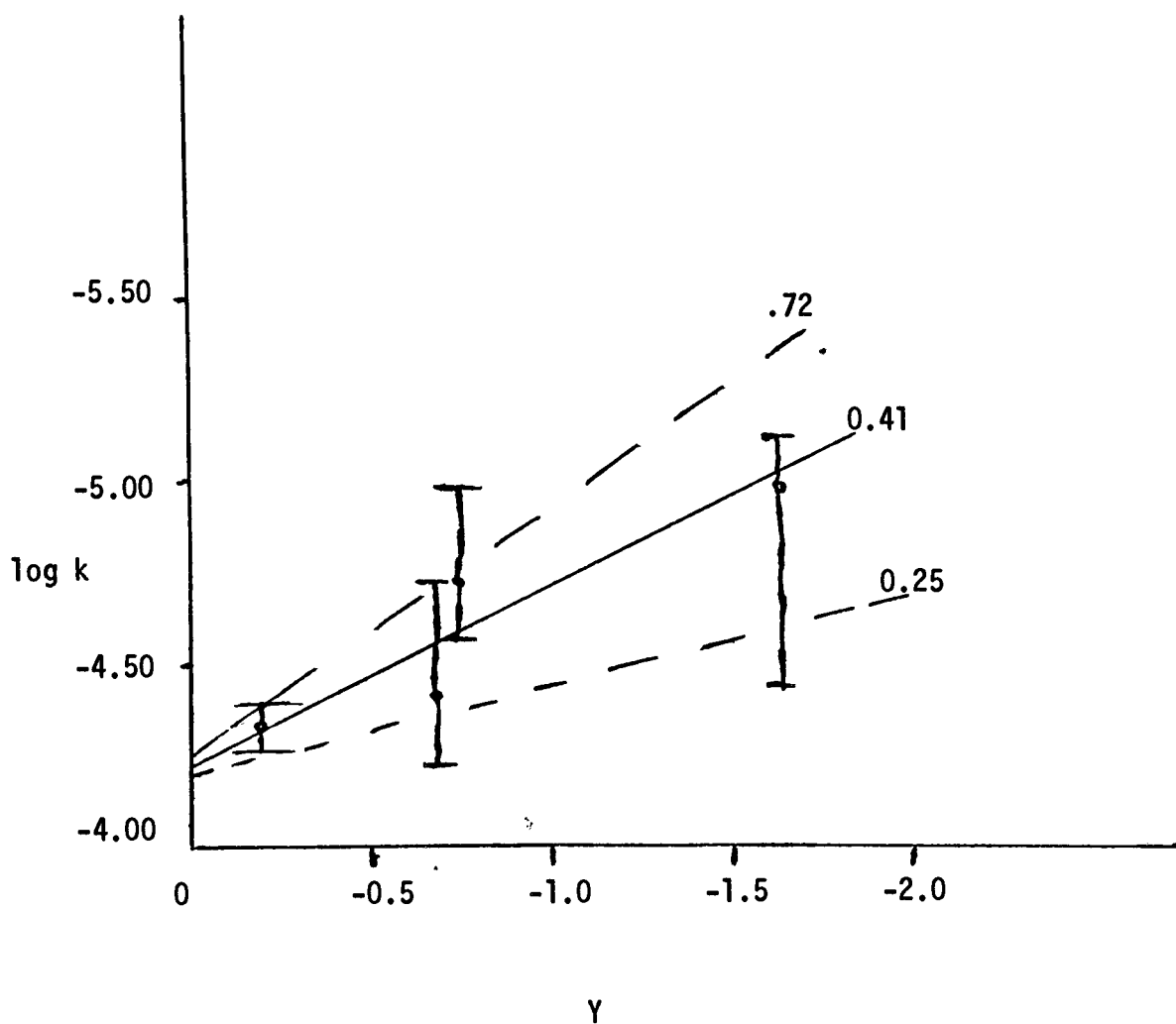


Figure 5b

CONDUCTIVITY METHOD USING ACETIC ACID SOLVENT

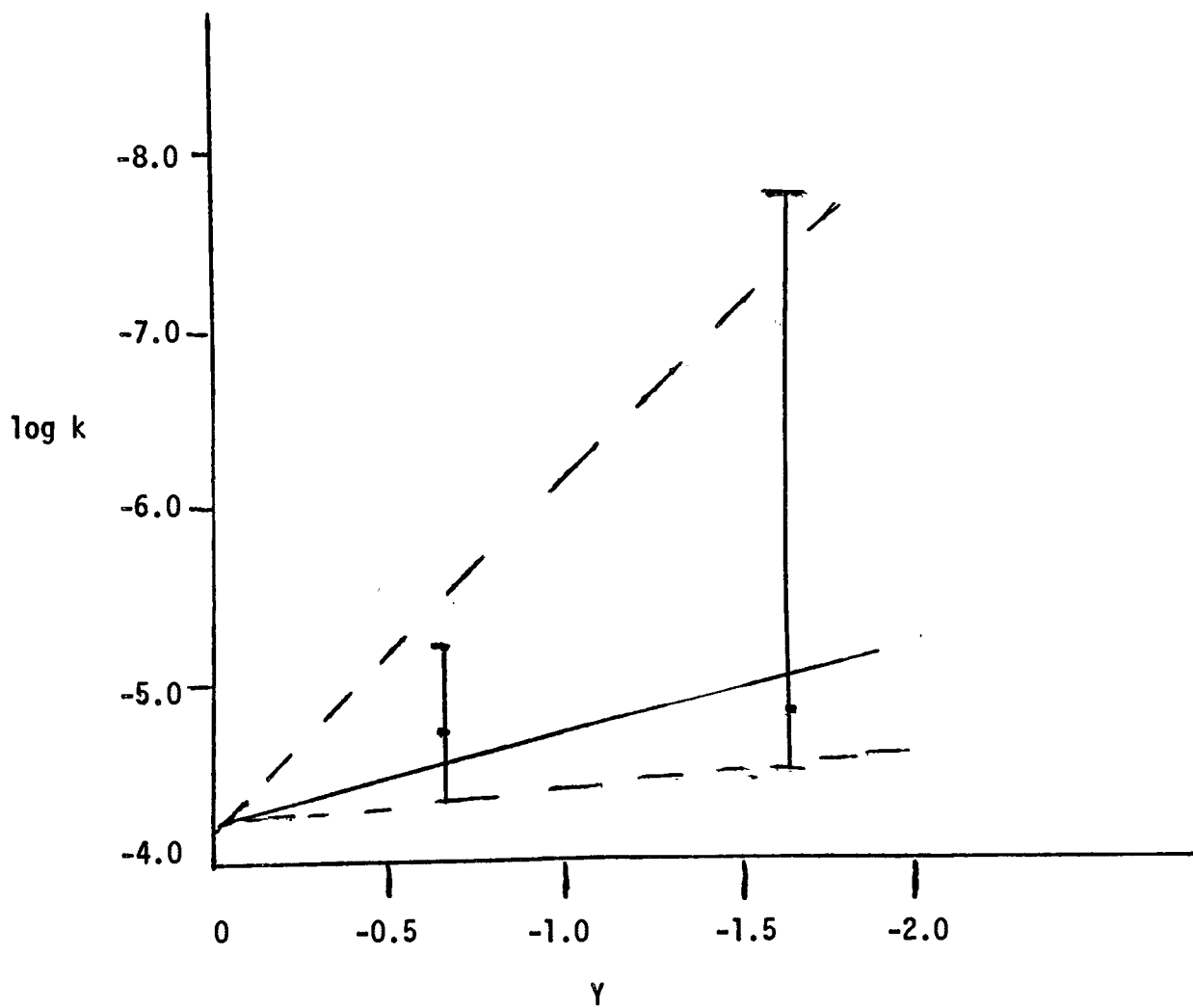


Figure 5c

AVERAGE OF CONDUCTIVITY AND ULTRA-VIOLET METHODS
USING ACETIC ACID SOLVENTS

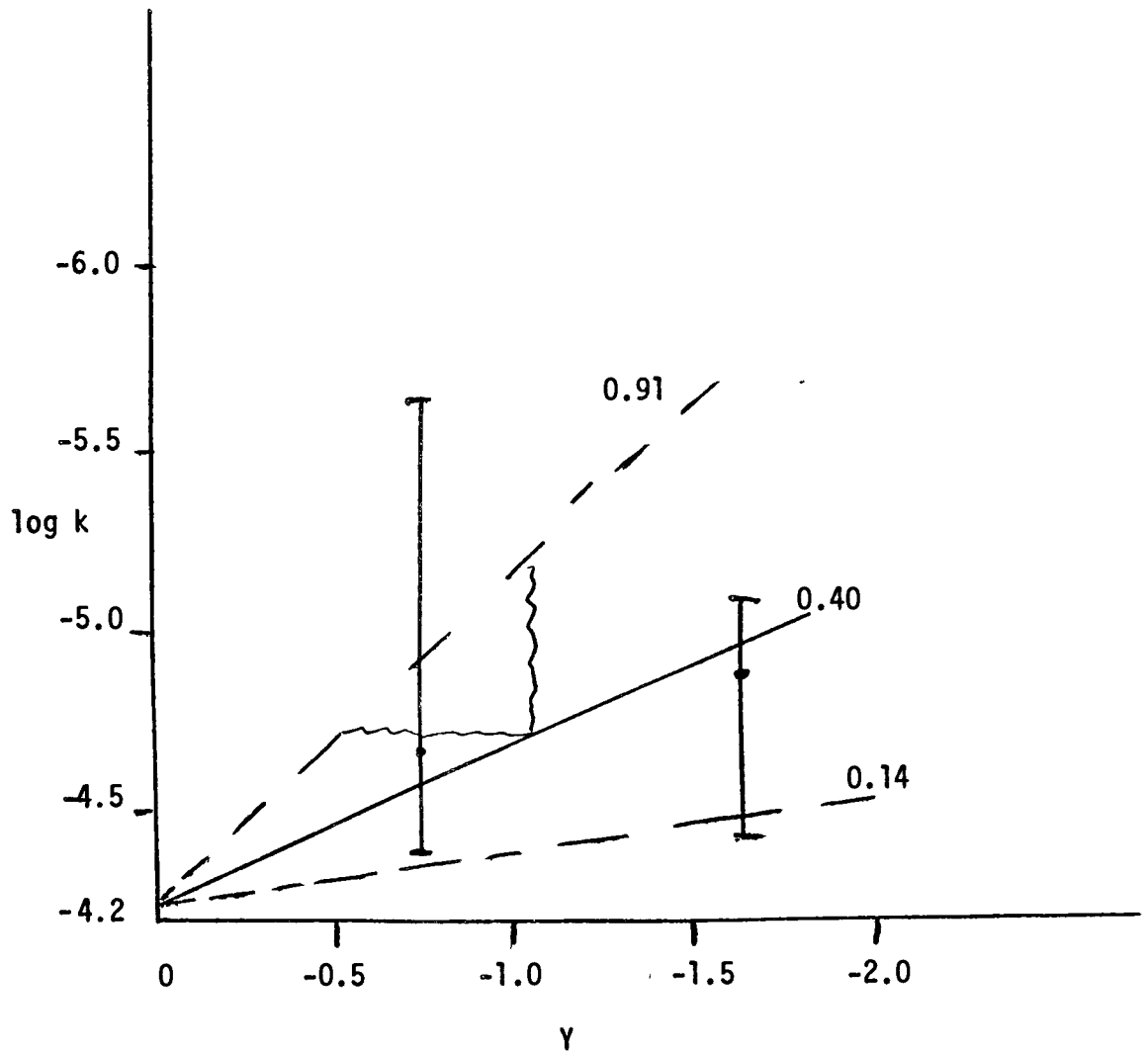


Figure 5d

ULTRA-VIOLET METHOD USING METHANOL SOLVENT

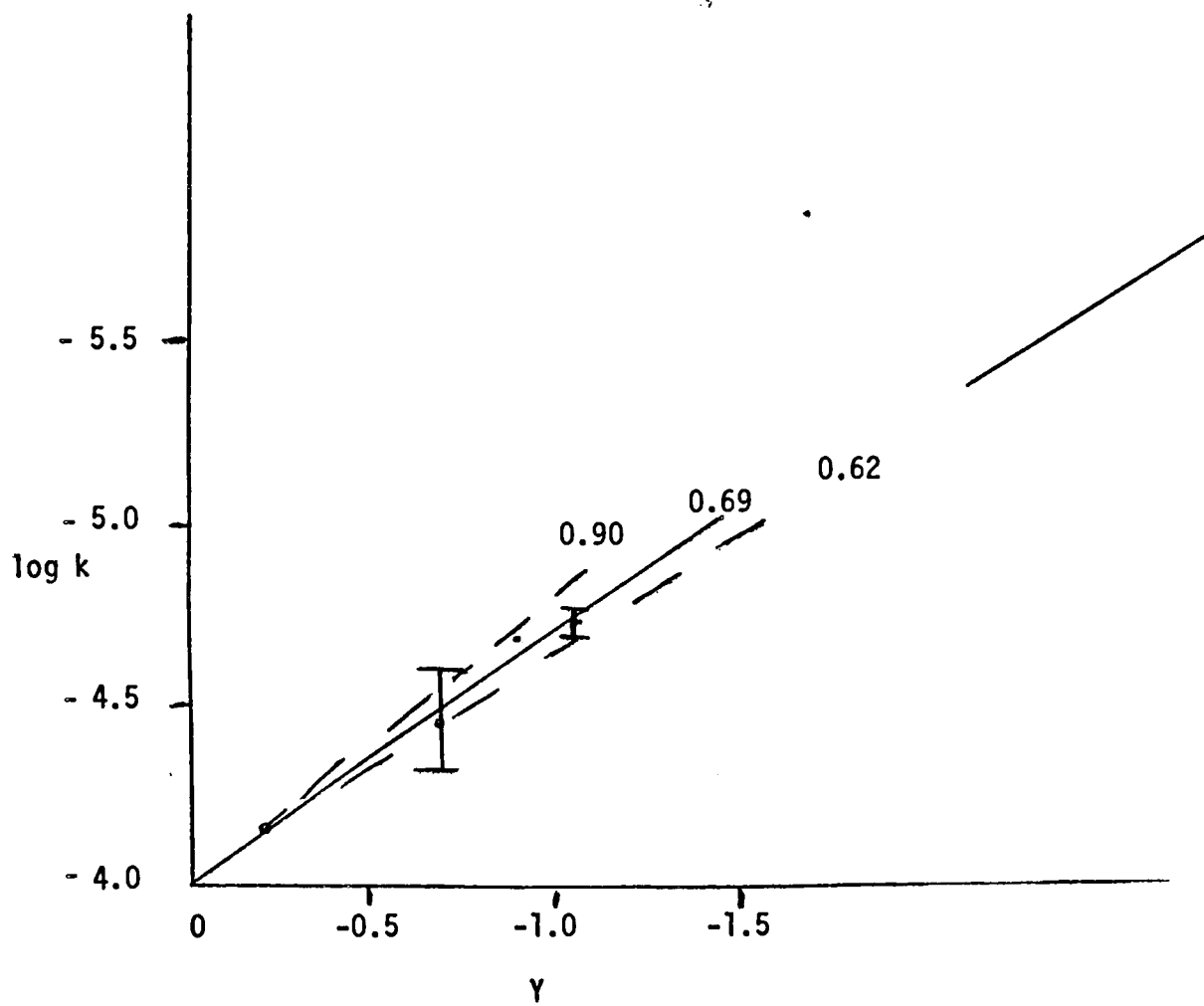


Figure 5e

ALL METHODS AND ALL SOLVENTS

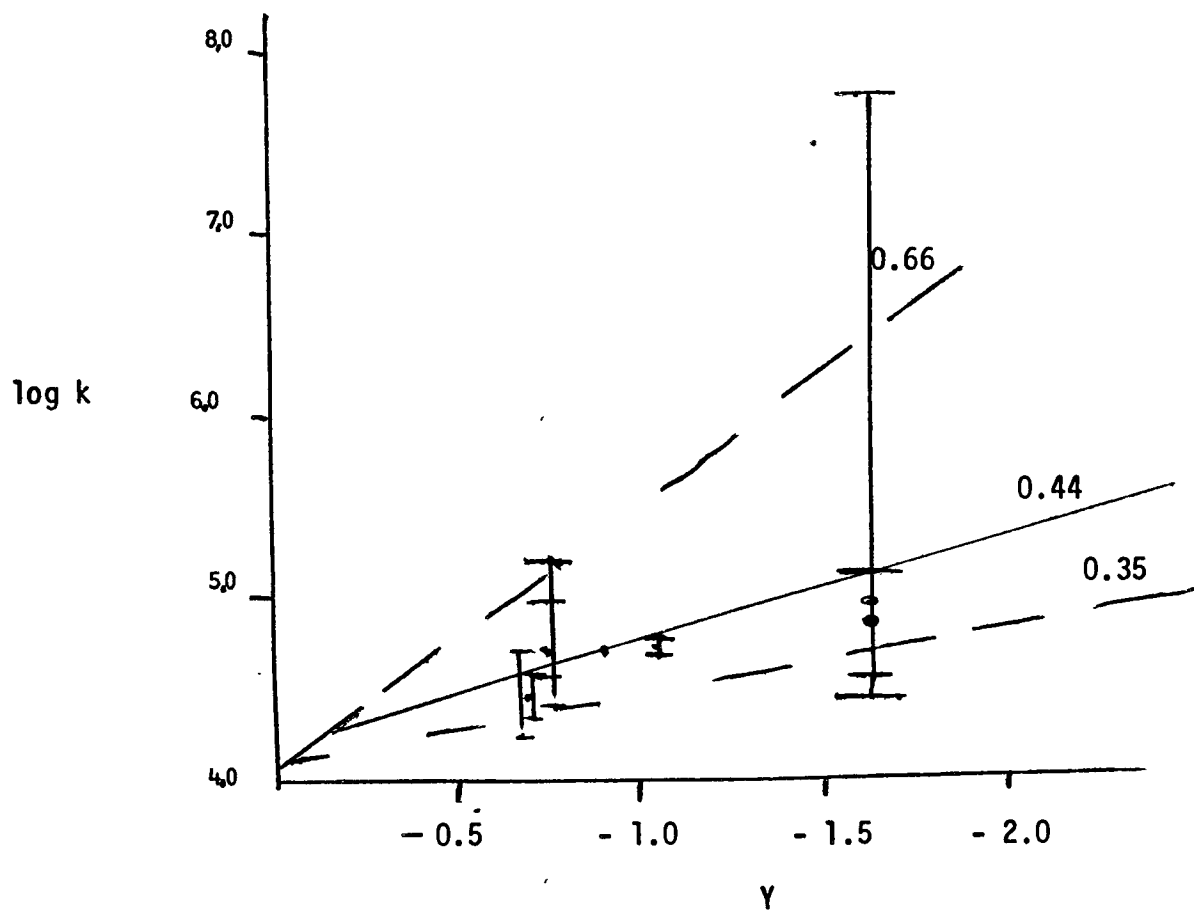


Table XI^a

DATA FOR LOG k vs. Y PLOT (Fig. 5)

U.V. Method (10 ⁵) k	Conductivity Method (10 ⁵)k	log k _{u.v.}	log k _{cond.}	log ave. k _(u.v. + cond.)	Y value	Solvent
1.19	1.38	-4.9244	-4.8602	-4.8894	-1.633 ^b	100% Acetic Acid
1.82	2.51	-4.7310	-4.600	-4.6655	-0.743 ^b	95.3% acetic acid
3.91		-4.4078		-4.4078	-0.687 ^b	95% acetic acid
4.58	4.71	-4.3391	-4.3269	-4.3325	-0.2045 ^b	91.4% acetic acid
1.923		-4.7160			-1.052 ^b	100% methanol
2.04		-4.6904			-0.89 ^b	98% methanol
3.634		-4.4396			-0.687 ^b	95% methanol
6.88		-4.1624			-0.200 ^c	90% methanol

^a All data reported at 25° C.

^b Reference no. 38

^c Reference no. 9, obtained by interpolation

Table XII

DEGREE OF CORRELATION BETWEEN SOLVOLYSIS
RATES AND Y VALUES

<u>Solvent</u>	<u>Analytical Method</u>	<u>m^a</u>	<u>Correlation Coefficient</u>
aq. Acetic Acid	U.V.	0.41 ^a ± 0.25 ^b	0.89 ^a
aq. Methanol	U.V.	0.69 ± 0.09	0.98
aq. Acetic Acid	U.V. and Cond.	0.40 ± 0.39	0.92
aq. Acetic Acid	Cond.	0.36 ± 0.90	0.98
All Solvents	All methods	0.44 ± 0.15	0.92

^a Obtained in least squares analysis.

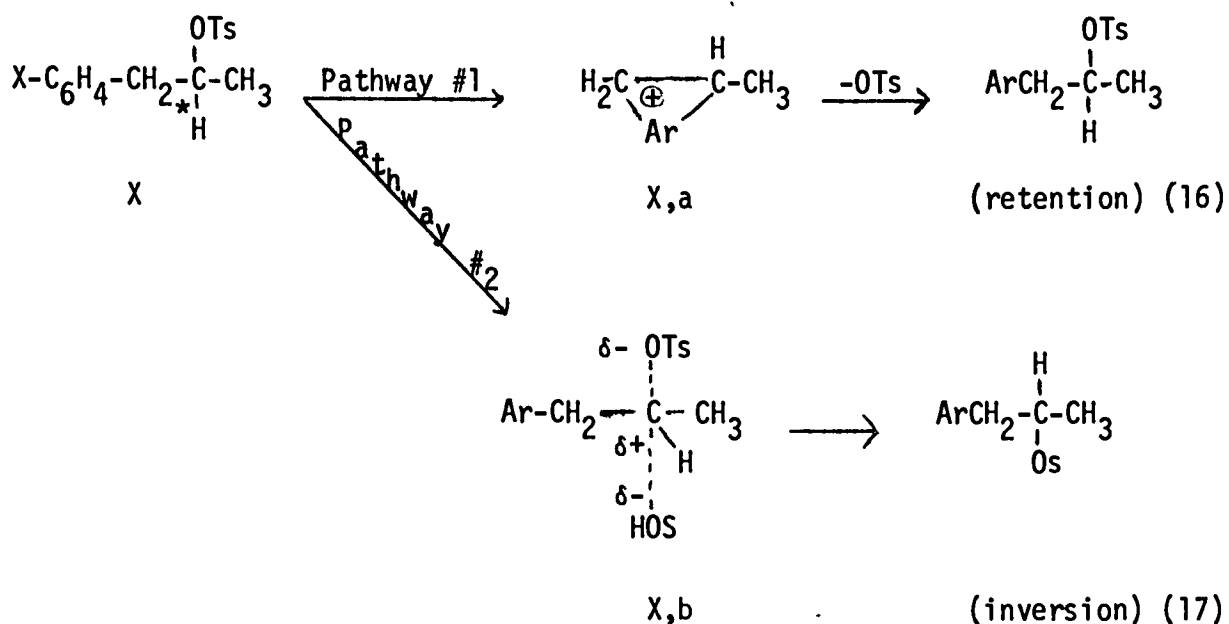
^b Obtained by average dispersion of slopes from Figs. 5a-e.

secondary substrates (e.g., isopropyl brosylate, $\underline{m} = 0.4$, Table IIB) and some aryl substituted compounds (e.g., benzyl tosylate, $\underline{m} = 0.39$, Table IIB). Thus one might conclude that the solvolysis of nortricyclyl brosylate (I) is not substantially of the LIM or S_N1 type², a conclusion that would not seem consistent with the well studied solvolytic pathway of this substrate (see discussion in Historical Section, p. 8). However many substrates, that would be expected to go through principally LIM or S_N1 processes (benzyl tosylate above) show low \underline{m} values (0.3-0.5), e.g., benzyl chloride and trans-2-methoxycyclohexyl brosylate (Table IIB). Several similar substrates (e.g., benzhydryl chloride, trans-2-bromocyclohexyl brosylate, α -phenylethyl chloride) have higher (0.7-0.9) \underline{m} values; these too would be expected to solvolyze by substantially S_N1 or LIM processes. Thus \underline{m} values seem to be a poor criterion for classifying substrate solvolysis mechanism; Winstein has said that \underline{m} simply means the substrate response to γ values². Thus, \underline{m} values closer to unity for nortricyclyl brosylate should not be anticipated because of the favorable conditions for first order solvolyses.

One might have been led to mechanistic conclusions regarding S_N1 reactions and \underline{m} values by systems containing phenyl groups. As number of phenyl groups increases, it is expected that corresponding increases in dependence on solvent ionizing power would be exhibited. This is apparently so as benzyl chloride has $\underline{m} = 0.43$ and benzhydryl chloride has $\underline{m} = 0.74$ (Tables IIC,a). Since, however, the degree to which this measures mechanism is not clear (see below), such conclusions are tenuous.

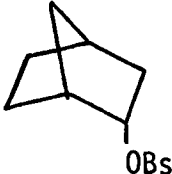
Winstein, with reference to the trans- β -bromocyclohexyl brosylate mY study², has pointed out that Y does seem to measure ionizing power of the solvent since this substrate gives a very good linear fit to Y over a wide range of solvent (acetic acid and alcohol - water mixtures). This linear fit is not found with other substrates, e.g., isopropyl bromide, especially with the acetic acid data. Thus Winstein concluded that since in the trans- β -bromocyclohexyl compound, trans-anti-bromine is the only source of nucleophilicity participation and the substrate is responding only to ionizing power but that in the solvolysis of substrates such as isopropyl bromides the substrate is responding to nucleophilicity of the solvent in addition to ionizing power. Thus the fit to linearity, rather than the value of the slope, m , is a better criterion for solvolysis mechanism. One should then note that, although there is a substantial range of m values for nortricycyl brosylate, the fit to linearity is good (see correlation coefficients, Table XI). For a poor fit to linearity, see Fig. 2 of Winstein, Grunwald and Jones². Nucleophilicity in the solvolysis of nortricycyl brosylate (I) is thus apparently the result of cyclopropyl participation and solvent does not participate nucleophilically in the process.

The nucleophilicity of solvent has been investigated recently by Schleyer^{39a,b} in another way (stereochemistry and Hammett ρ - σ studies).



Their study revealed the distinct possibility of two solvolytic pathways (Eq. 16 and 17). They also found that solvolyses were faster for this system in formic than in acetic acid (consistent with ρ values, see Table I). Both pathways, however, would be expected to have their rates accelerated by increasing ionizing powers of solvent. An interesting check of solvent participation would be the degree to which the substrate (X) of Schleyer's work would yield solvolysis data that would correlate well to one linear fit (including acetic acid and aqueous alcohol data).

Further confirmation of difficulties associated with ρ values and solvolysis mechanism is shown by the following: an ρ value (in a bridged system) is obtainable for endo-norbornyl brosylate (XV). This (XV) would be expected to solvolyze without substantial neighboring carbon (nucleophilic) participation^{37a}. An estimate of ρ can be obtained by calculating from the rate data reported by Winstein and Marshall³⁶.

<u>Compound</u>	<u>Solvent</u>	<u>(10⁷) k; 25° C.</u>
 (XV)	CH ₃ CO ₂ H	2.52
	HCO ₂ H	850.0

$$\log 850/2.52 = \log 336 = 2.5263 = \log k_{\text{HCO}_2\text{H}}/k_{\text{CH}_3\text{CO}_2\text{H}}$$

$$\Delta Y = Y(\text{HCO}_2\text{H}) - Y(\text{CH}_3\text{CO}_2\text{H}) \quad (\text{see Table I})$$

$$2.2563 = \underline{m}\Delta Y$$

$$2.5263 = \underline{m}(3.693)$$

$$0.683 = \underline{m}$$

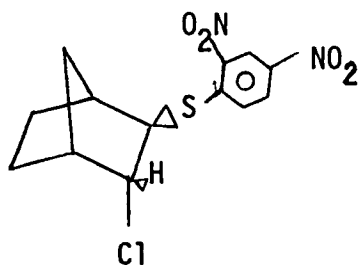
The magnitude of this \underline{m} value is of the order of the \underline{m} values of simple secondary substrates (Tables IIb and IIc). Nucleophilic solvent participation could only be known if plots of Y vs. $\log k$ were obtained in a variety of solvents (acetic acid and alcohol-water mixtures) and the fit to linearity determined (vide supra).

A final discredit to the use of \underline{m} values as an intrinsic measure of mechanism is Table XIII. Table XIII shows \underline{m} values close to those that were determined for nortricyclyl brosylate herein. The relationship of the solvolytic mechanism of substrates in Table XIII to that for nortricyclyl brosylate is not at all clear.

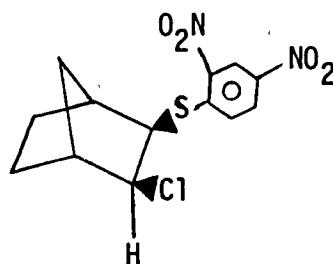
In conclusion, the work described above indicates that attempts to assign \underline{m} values by a superficial examination of structures (e.g., secondary) is extremely dangerous⁴¹. In addition, the mechanistic values of the \underline{m} value is extremely limited.

Kinetic studies were undertaken on endo-(VIIa) and exo-(VIIb)-3-chloro-exo-2-norborn-5-enyl 2,4-dinitrobenzene thioether.

Experimental objective in these studies was essentially differentiation between cis and trans isomers of these compounds through interpretation of kinetic behavior (see p. 20). Kinetic results obtained for solvolyses reactions studies are summarized in Table XIV.



VIIa



VIIb

Average calculated rate constants for solvolyses in 100% acetic acid were unexpected in terms of exo- (cis) reactivity relative to endo- (trans) reactivity (see Historical, p. 20). An expected ratio would have the exo-(cis)-chloro compound (VIIb) more reactive than the endo-(trans)-compound (see Table XV). Assumedly suppression of exo-chloro reactivity would result from solvent assistance not sufficiently provided by acetic acid solvent (low γ value). Acetic acid is generally classified as a poor nucleophile⁵. In addition, solvent nucleophilicity would aid reactivity of the trans compound (exo-solvent attack to displace endo-chlorine). Such nucleophilic solvent participation would assumedly be less important with the cis-compound (VIIb, exo-chlorine). If one assumes that reactivity ratios are "normal" in 70% aqueous dioxane (a solvent system more

TABLE XII I⁴⁰VALUES OF \underline{m} BETWEEN 0.45-0.50 FOR VARIOUS SUBSTRATES

	\underline{m}
triphenyl carbonyl acetate	0.48
triphenyl silyl fluoride	0.468
neophyl tosylate	0.50

Table XIV

Solvolytic Rates of endo-(VIIa) and exo-(VIIb)-3-Chloro-exo-2-norborn-5-enyl-2,4-dinitrobenzene Thioether in Acetic Acid at $40.0 \pm 0.1^\circ$

<u>run</u>	<u>trans solvent</u>		<u>run</u>	<u>cis solvent</u>	
	100% Acetic Acid	(10^6)k		100% Acetic Acid	(10^6)k
21,a		4.2	24,a		1.85
21,b		7.4	24,b		1.44
21,c		3.45			
22	97% Acetic Acid	1.15			

nucleophilic than acetic acid), then the ratio reversal must be due to a much greater suppression of the rate of solvolysis of the cis-compound than of the trans. This would be expected since the cis- would solvolyze mostly via $\text{Lim}(\text{S}_{\text{N}}1)$ processes. Both $\text{Lim}(\text{S}_{\text{N}}1)$ and $\text{S}_{\text{N}}2$ processes would be subject to suppression in acetic acid solvent (relative to 70% aqueous dioxane) but the effect would be much greater on the cis (exo-chloro) compound;⁴ i.e. on the $\text{Lim}(\text{S}_{\text{N}}1)$ process.

Thus it seems clear that acetic acid is a poor solvent for determining structures (exo- vs. endo-) by kinetic methods, especially when the model studies³ were done in aqueous alcohol. Aqueous dioxane would better approximate (especially via nucleophilicity) aqueous alcohol than would acetic acid.

Table XV⁴²

Rates of Solvolysis of endo (VIIa)- and exo (VIIb)-3-Chloro-exo-
2-norborn-5-enyl 2,4-dinitrobenzene thioether in 70% Aqueous
Dioxane (116.0 ± 3.0° C.)

endo
(trans)

$$k = 1.73 \times 10^{-5} \text{ sec.}^{-1}$$

exo
(cis)

$$k = 1.2 \times 10^{-4} \text{ sec.}^{-1}$$

EXPERIMENTAL

General Instrumentation

Ultra-violet absorptions for kinetic runs were obtained using the Hitachi Perkin-Elmer 139 UV-VIS Spectrophotometer with quartz cells. Complete u.v. spectra were obtained using the Perkin-Elmer model 450 UV-Visible-NIR Spectrophotometer with quartz cells for nortricyclyl brosylate (I) in acetic acid and methanol solvents.

Melting points were determined using Mel-Temp apparatus.

All temperatures are reported (m.p. and kinetic bath) as $^{\circ}$ C.

Conductivity cells used were Industrial Instrument products.

Cell constants (after plating) were determined as described by Skoog and West⁴³.

Plating of cells was affected by immersing cleaned (in dilute nitric acid) electrode cell in an aqueous solution of 3% platinum chloride and .02% lead acetate and attaching the cell to a low voltage power supply (3-4 volts). Current was allowed to run for ca. 30 seconds. Poles were then alternated. Current was again allowed to flow for 30 seconds. If light plating was not affected after one alternation of poles the above procedure was repeated.

The conductivity bridge used was a standard YSI (Yellow Springs Instrument Co., Inc.) model 31.

Solvent Purification

Acetic acid (b.p. 115-118⁰; lit. 118.1⁰ ⁴³) was fractionally distilled from a mixture of 800 ml. DuPont Reagent Grade acetic acid, ca. 40 g. sodium dichromate and 5 ml. of J.T. Baker reagent acetic anhydride.

Conductivity water (b.p. 100.0⁰; lit. 100.0⁰ ⁴⁵) was prepared as described by Swain²².

Methanol (b.p. 65.0⁰; lit. 64.7⁰ ⁴⁶) was purified by distillation from ca. 100 g. sodium hydroxide (per liter methanol) followed by distillation from ca. 50 g. benzoic acid (per liter methanol). The distillate collected was then subjected to drying procedure of Lund and Bjerrum as described by Fieser⁴⁷.

Nortricyclyl brosylate (I) was prepared by the method of Cristol and co-workers¹⁹. This brosylate (81.5-82.0⁰) was recrystallized from the minimum amount of hexane. Recrystallized material was stored in the freezer.

Kinetic Procedures

The general procedure followed for kinetic runs using the u.v. method was as follows: A carefully weighed sample of nortricyclyl brosylate (I) (m.p. 81.5-82⁰) was transferred to a volumetric flask (50 or 100 ml.). Sample weight of nortricyclyl brosylate, for different runs, varied between 30-50 mg. (0.9-1.5 x 10⁻⁴ moles) per 100 ml. solvent. The volumetric flask was filled to the mark with solvent (or solvent mixture). Flask and contents were shaken vigorously to effect complete dissolution.

The flask was next placed in a constant temperature bath set at $25.0 \pm 0.1^{\circ}$. After a thermal equilibration period (ca. 5-10 min.) and at selected time intervals thereafter a sample was withdrawn from the volumetric flask and placed in a 1.0 cm. quartz cell (with appropriate solvent in the reference cell). The P.E. 139 UV-VIS Spectrophotometer was balanced as described in the accompanying manual⁴⁸. Absorbance readings were then recorded and time of reading noted. All measurements were carried out at 233 m μ . This procedure is a modified procedure of that of Swain²² and Sinnott²⁴. The general procedure followed using conductivity method was initially the same as that described for the kinetic method above except that the contents of the volumetric flask were transferred to the conductivity cell (Fig. 4, p. 32). Solutions of brosylate were made up as described in the preceding section. Solutions of trans and cis chloro compounds (VIIa and VIIb) were ca. 30 mg. (1.1×10^{-4} moles) per 100 ml. of solvent. The cell was immersed in the kinetic bath ($25.0 \pm 0.1^{\circ}$ for nortri-cyclyl brosylate and $40.0 \pm 0.1^{\circ}$) for cis and trans chloro compounds (VIIa and VIIb). Conductivity readings were taken (after ca. 5-10 min. equilibration period) at various intervals directly from the attached conductivity bridge.

Procedure for kinetic runs analyzed titrimetrically was essentially that described for the u.v. method with the following modifications: Samples withdrawn from the volumetric flask were of known volume (volumetric pipette) and were transferred to an erlenmeyer flask cooled in ice bath and equipped with magnetic

stirring apparatus. Solvolytically generated strong acid was titrated with sodium carbonate in acetic acid (for kinetic runs employing acetic acid and aqueous acetic acid solvent mixtures) to a brom phenol blue (indicator prepared in acetic acid) endpoint. When methanol or aqueous methanol was used as solvent, two titrants were tried. For aqueous sodium hydroxide titrant, brom thymol blue indicator was used. The other titrant employed was sodium methoxide (sodium dissolved in methanol) with brom thymol blue indicator.

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A P P E N D I C E S

APPENDIX I

Use of Standard Deviation

Average rate constants and \bar{m} values reported in this thesis may be considered in the following form:

Arithmetic mean value $\pm 2\sigma$.

$$\text{where } \sigma = \frac{\sum(x - \bar{x})^2}{n}$$

where σ = standard deviation

x = individual rate constant

\bar{x} = average (arithmetic) rate constant

n = no. of rate constant measurements

Data in the above form fall within the 95% confidence level⁴⁹ based on a normal distribution. The magnitude of standard deviations is of interest in this thesis, also. A measure of relative sensitivities of analytical techniques employed can be derived reference to associated standard deviations.

APPENDIX II

Dependence of m on Temperature

Discussion of m values in this thesis is essentially restricted to m -substrate and m -solvent relationships. It is also of interest however, to note that m -temperature relationships do likewise exist. Grunwald and Winstein¹ describe the form of the relationship:

$$2.303 \gamma \frac{dm}{dT} = \frac{E^\ddagger - E_0^\ddagger}{RT^2}$$

where E^\ddagger is the activation energy in the solvent of interest, and,

E_0^\ddagger is the activation energy in 80% ethanol.

It is obvious from the above that rising temperatures create diminishing m values. The change in m values is, however, not substantial compared to change in m with change in substrate since $E^\ddagger - E_0^\ddagger$ is not large for most solvents.

APPENDIX III

Solvent Exchange Processes: N.M.R.

As described in this thesis, kinetic studies were performed using solvent mixtures of acetic acid and water and methanol combined with varying quantities of water. A complete kinetic survey of behavior of nortricycyl brosylate in these solvents would require reference to kinetically significant exchange processes occurring between acetic acid (or methanol) and water. These exchange processes which are extremely rapid can be conveniently studied by application of n.m.r. spectroscopic analytical techniques⁵⁰. The n.m.r. scan reveals a time averaged peak for the hydroxyl proton which is consistent with the rapid rate of the exchange process as contrasted with the significantly slower nuclear excitation rate.

APPENDIX IV

Least Squares Computer Program⁵¹

11111 CORREG (CORRELATION REGRESSION PROGRAM) 11.950 PMS

// JOB

// EQU. CORR.

*LIST ALL

*LOCN (DATE, 1962, PLOTTER)

C CORREG CORRELATION REGRESSION PROGRAM

C READ X(201),Y(201),PAGE(80)

L10=1

L101=5

READ(L10,21)PAGE

WRITE(LOUT,22)PAGE

50 SX = 0

SY = 0

SXY = 0

SXX = 0

SYY = 0

SXC = 0

SYC2 = 0

I = 1

5 READ(L10,13)PAGE,Y(I),X(I)

IF(PAGE)9,10,9

10 SX = SX + X(I)

SY = SY + Y(I)

XY = X(I)*Y(I)

SXY = SXY + XY

XX = X(I)*X(I)

SXX = SXX + XX

YY = Y(I)*Y(I)

SYY = SYY + YY

I = I + 1

GO TO 5

9 B = I - 1

XBAR =

XBAR = SX/XB

YBAR = SY/YB

B = (SXY - XBAR*SY) / (SXX - XBAR*SX)

A = YBAR - B*XBAR

SXC = SQRT((SXX/XB) - (XBAR**2))

SYC = SQRT((SYY/YB) - (YBAR**2))

WRITE(LOUT,12)

DO 6 I=1,

XY = X(I)*Y(I)

XX = X(I)*X(I)

YY = Y(I)*Y(I)

YC = A + B*X(I)

YC2 = YC*YC

SYC = SYC + YC

SYC2 = SYC2 + YC2

6 WRITE(LOUT,16)I,X(I),Y(I),XY,XX,YY,YC,YC2

4 WRITE(LOUT,951)

951 FORMAT(' ')

```

WRITE(LOUT,16) F, SX, SY, SXY, SXX, SYY, SYC, SYCZ
R2 = (B*(SXY-XBAR*SY))/(SYY-YBAR*SY)
XY=X(F)*Y(F)
WRITE(LOUT,951)
R = SQRT(R2)
SE2=SDY*SDY*(1.-R2)
SE=SQRT(SE2)
WRITE(LOUT,19) XBAR, YBAR, A, B
WRITE(LOUT,20) SDX, SDY
WRITE(LOUT,15) A, B
WRITE(LOUT,17) SE2, SE
WRITE(LOUT,18) R2, R
12 FURCAT(/ /3X,2F20.6,10X,1HX,19X,1HY,14X,2HX2,15X,2FX2,16Y,2FY2,11.
1212HYC,13X,3HYC2/)
13 FURCAT(12,21X,2E12.6)
15 FURCAT (/10X,5H YC =,F20.6,3H +,F20.6,2H X,/)
16 FURCAT (15,2F20.6,5E15.6)
17 FURCAT(/10X,5H SE2 =,F20.6,5X,5H SE =,F20.6/)
18 FURCAT(/10X,5H R2 =,F20.6,5X,5H R =,F20.6/)
19 FURCAT(10X,6HXBAR =,F20.6,2X,6HYBAR =,F20.6,2X,3HX =,F20.6,2X,
1913HY =,F20.6)
20 FURCAT(/10X,6HSDX =,F20.6,5X,6HSDY =,F20.6/)
21 FURCAT(10A1)
22 FURCAT(10I,60A1)
99 CALL EXIT
END

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