This is unlikely, since we get a different product distribution from the $(R_3Si)_2NOSiR_3 \rightarrow (R_3Si)_3N^+ \rightarrow O^- \rightarrow R_3SiN(R)SiR_2OSiR_3$ isomeric hydroxylamines **20** and **24**, which would form the same amine oxide intermediate by such a mechanism. An attempt was made to synthesize such a compound from $(Me_3Si)_3N$ and ozone (see Experimental Section).

(19) Raw rate data available upon request from the authors.

(20) (a) R. A. Abramovitch in "Organic Reactive Intermediates", S. P. McManus, Ed., Academic Press, New York, N.Y., 1973, Chapter 3; (b) S. P. McManus and C. V. Pittman, Jr. in *ibid.*, Chapter 4; (c) P. T. Lansbury in "Nitrenes", W. Lwowski, Ed., Interscience, New York, N.Y., 1970, Chapter 11.

(21) Y. Pocker in "Molecular Rearrangements", P. deMayo, Ed., Wiley, New York, N.Y., 1964, Chapter 1.

(22) The preference for methyl migration instead of *tert*-butyl migration to nitrogen in compounds **14** and **16** may be for steric reasons.

(23) It must be noted that in the compounds **5**, **6**, **8**, and **9** the methyl groups greatly outnumber the hydrogen or phenyl substituents and should be favored statistically by Scheme I by at least a factor of two and possibly more.

(24) A. P. Bassindale, A. G. Brook, P. F. Jones, and J. M. Lennon, *Can. J. Chem.*, **53**, 332 (1975).

(25) (a) P. P. Gaspar and B. J. Herold in "Carbene Chemistry", 2d ed, W. Kirmse, Ed., Academic Press, N.Y., 1971, Chapter 13; (b) R. West and R. Bailey, *J. Am. Chem. Soc.*, **85**, 2871 (1963); (c) T. J. Barton and J. Kilgour, *ibid.*, **96**, 7150 (1974).

(26) (a) R. West and J. M. Gaidis, *J. Am. Chem. Soc.*, **86**, 3609 (1964); (b) F. D. Lewis and W. B. Saunders, ref 20c, Chapter 3; (c) W. Lwowski, ref 20c, Chapter 12.

(27) C. Hurd, *Inorg. Synth.*, **1**, 87 (1939).

(28) R. West, M. Ishikawa, and R. Bailey, *J. Am. Chem. Soc.*, **88**, 4648 (1966).

(29) R. West and P. Boudjouk, *J. Am. Chem. Soc.*, **95**, 3987 (1973).

(30) U. Wannagat and O. Smrekar, *Monatsh. Chem.*, **100**, 750 (1969).

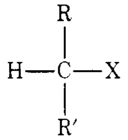
Correlation of Rates of Solvolysis of Secondary Tosylates with Tertiary Benzylic Derivatives[1]

Edward Norman Peters

Contribution from the Union Carbide Corporation, Chemicals and Plastics, Bound Brook, New Jersey 08805. Received October 28, 1975

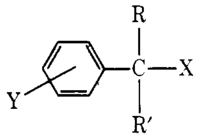
Abstract: A linear free-energy relationship, log $(k/k_0) = \rho\gamma^+$, with group constants, γ^+, was defined. The group constants are characteristic of the ability of a group to stabilize an adjacent cationic center. These groups can be aromatic or nonaromatic. The γ^+ for hydrogen was determined to be 2.53. This group constant allows for the first time the direct correlation of acetolysis of secondary tosylates with their analogous tertiary benzylic derivatives. Such correlations were found to be general, and excellent $\rho\gamma^+$ plots were obtained. This relationship was applied in the elucidation of anchimeric assistance and shown to be valuable in evaluating neighboring group effects.

From the pioneering work of Winstein and co-workers, rates of solvolysis for secondary substrates have been usually compared in terms of acetolysis of *p*-toluenesulfonates (**1**) (tosylates, X = OTs).[2] Brown, Gassman, Tanida, and other workers have investigated the rates of solvolysis of various tertiary benzylic systems, **2**.[3]



$$H-\overset{\displaystyle R}{\underset{\displaystyle R'}{C}}-X$$

1



2

In the solvolysis of benzyl derivatives, it is possible to increase the electron demand of the cationic center by varying the substituent on the aryl group. Thus, a linear free-energy relationship can be obtained by treatment of the kinetic data with the Hammett-Brown relationship:[4]

$$\log (k/k_0) = \rho\sigma^+ \tag{1}$$

Equation 1 is based on the fact that as the substituent, Y, is varied the logarithms of the rate constants for aromatic side chain reactions are linearly related to one another.

The substituent constant, σ^+, is characteristic only of the substituent on the aryl group in **2** and represents the ability of the substituent, Y, to attract and repel electrons by a combination of inductive and resonance effects.

Until now a unifying theory correlating rates of reaction of **1** with **2** was lacking. However, reported here is the application of a linear free-energy relationship for correlating rates of solvolysis of secondary substrates (**1**) with the corresponding tertiary benzylic analogues (**2**).

Results and Discussion

In the past solvolysis of tertiary benzylic derivatives have been used extensively in the evaluation of phenomena occurring in secondary substrates. However, such an approach has been questioned.[5] Indeed, one worker has suggested that this practice "can be treacherous".[5a] Other workers have cautioned against extraneous steric effects.[5b,c] Although these suggestions are intuitive, they appear somewhat questionable.[6]

In order to correlate nonaromatic with aromatic derivatives, a linear free-energy relationship was defined with group constants, γ^+, and is represented by:

$$\log (k/k_0) = \rho\gamma^+ \tag{2}$$

The group constant is characteristic of the ability of an entire group (for example, aryl or hydrogen) to stabilize an adjacent cationic center. The γ^+ values for aryl groups will be the same as the σ^+ values for the substituent on that aryl group.

Since the difference between **1** and **2** is a hydrogen group vs. an aryl group, a group constant for a hydrogen group is needed to correlate the solvolysis of secondary substrates with their analogous tertiary benzylic derivatives via eq 2.

This γ^+ value has to include a correction for the difference in leaving group and solvent.[7]

Group constants (nee substituent constants) are usually determined from the solvolysis of *tert*-cumyl chlorides; however, in certain cases indirect methods have been employed.[8] The 7-norbornyl system offers an alternative route to determine the γ^+ value for a hydrogen group.[9] Because of the importance of 7-phenyl-7-norbornyl *p*-nitrobenzoate, the rate constant was redetermined to be 2.00×10^{-11} s^{-1} at 25 °C in 70% dioxane. This value gave a better correlation and a ρ of -5.25.

Table I. Corrected Rates of Solvolysis Systems[a]

System	n[b]	ρ[c]	k_H	$-\log (k_H/k_{phenyl})$ Obsd	Calcd	Difference	SD[d]	Ref[e]
Chlorides in 90% Acetone[f]								
Cyclopentyl	5	−4.10	5.02×10^{-13} [g]	10.1586	10.3479	−0.1893	0.1971	3c
7-Norbornyl	4	−5.64	$2.02 - 10^{-21}$ [h]	13.2941	14.2347	−0.9406	0.2712	3c
2-Adamantyl	4	−4.83	1.89×10^{-16} [i]	12.3851	12.1903	0.1948	0.2322	3c
2-Propyl	10	−4.54	2.46×10^{-14} [j]	10.7033	11.4584	−0.7551	0.2183	4
p-Nitrobenzoates in 80% Acetone[k]								
Cyclopentyl	4	−3.82	5.17×10^{-17} [l]	10.7011	9.6412	1.0599	0.1837	18
Cyclopent-3-en-1-yl	4	−3.92	6.25×10^{-18} [m]	11.1062	9.8936	1.2126	0.1885	18
endo-Norbornenyl	3	−4.17	6.54×10^{-20} [n]	10.9666	10.5246	0.4420	0.2005	22
endo-Benzonorbornenyl	3	−4.52	4.77×10^{-21} [o]	10.3089	11.4079	−1.0990	0.2173	27
6-Methoxy-*endo*-benzonorbornenyl	4	−4.05	1.05×10^{-20} [p]	9.9469	10.2217	−0.2748	0.1947	28
6-Methoxy-*exo*-benzonorbornenyl	4	−3.72	8.70×10^{-15} [p]	10.2899	9.3888	0.9011	0.1788	28
3-Nortricyclyl	4	−3.27	1.40×10^{-14} [n,q]	7.4157	8.2531	−0.8374	0.1572	3a
endo-Norbornyl	4	−3.75	2.66×10^{-18} [r]	10.2993	9.4141	0.8852	0.1793	37
exo-Norbornyl	4	−3.83	7.85×10^{-16} [r]	9.9872	9.6665	0.3207	0.1841	37
p-Nitrobenzoates in 70% Dioxane[s]								
7-Norbornyl	6	−5.25	1.01×10^{-24} [t]	13.2967	13.2504	0.0463	0.2524	*u*
7-*anti*-Norbornenyl	3	−2.04	1.44×10^{-13} [t]	4.4711	5.1487	−0.6776	0.0981	*v*

[a] Rate constants at 25 °C. [b] Number of aryl derivatives correlated. [c] ρ value for just aryl derivatives; correlation coefficients for chlorides are 0.999–0.998, for *p*-nitrobenzoates are 1.000–0.999. [d] Standard deviation of calculated $-\log (k_H/k_{phenyl})$. [e] Reference for ρ and k_{phenyl}. [f] Corrected for differences in leaving group and solvent by multiplying the rate of acetolysis by 3.17×10^{-7} (see text). [g] S. Winstein et al., *J. Am. Chem. Soc.*, **74,** 1127 (1952). [h] Reference 10. [i] S. H. Liggero et al., *J. Am. Chem. Soc.*, **92,** 3789 (1970). [j] Reference 13. [k] Corrected for differences in solvent and leaving group by multiplying the acetolysis rate by 3.27×10^{-11}; see ref 11. [l] H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78,** 2735 (1956). [m] S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83,** 3235 (1961). [n] S. Winstein and M. Shatavsky, *J. Am. Chem. Soc.*, **78,** 595 (1956). [o] H. C. Brown and G. L. Tritle, *J. Am. Chem. Soc.*, **90,** 2689 (1968). [p] Calculated from data by D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *J. Am. Chem. Soc.*, **90,** 1901 (1968), in ref 27. [q] Reference 20. [r] R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79,** 3432 (1957). [s] Corrected for differences in leaving group and solvent by multiplying the rate of acetolysis by 1.59×10^{-10} (ref 3b). [t] Reference 10. [u] See text. [v] Calculated from data in ref 3b which react with anchimeric assistance (i.e., the *p*-dimethylaminophenyl and *p*-anisyl derivatives were omitted from the calculations).

The rates of solvolysis of 7-aryl-7-norbornyl *p*-nitrobenzoates in 70% dioxane have been determined over a wide range of reactivity; moreover, the difference between rate constants for a tosylate in acetic acid and a *p*-nitrobenzoate in 70% dioxane was shown experimentally to be 6.3×10^9.[3b] Thus the rate of acetolysis of 7-norbornyl tosylate[10] can be corrected for differences in solvent and leaving group. Henceforth, from a ρ value of −5.25 and the corrected rate of 7-norbornyl tosylate, a γ^+ constant of 2.53 for a hydrogen group is obtained via eq 2.

The generality and validity of this approach was examined by plotting $\log (k_H/k_{phenyl})$ vs. the ρ values (calculated from the aryl derivatives alone) for a series of tertiary chlorides and *p*-nitrobenzoates. By definition the slope of this line should be made to go through the origin. Rates of secondary tosylates in acetic acid were converted to rates of chlorides in 90% acetone by multiplying the rates of tosylates by a factor of 5.58×10^{-8}. This factor was determined by correcting the factor for converting tosylates in acetic acid to *p*-nitrobenzoates in 70% dioxane (1.59×10^{-10})[3b] to rates of chlorides in 90% acetone by the factor of 2000 which is the difference in rate between 7-phenyl-7-norbornyl *p*-nitrobenzoate in 70% dioxane and 7-phenyl-7-norbornyl chloride in 90% acetone.[3c] Rates of acetolysis for secondary tosylates were converted to rates of *p*-nitrobenzoates in 80% acetone by multiplying the rates of tosylates by a factor of 3.37×10^{-11}.[11]

The corrected rates for a series of secondary substrates (k_H), the observed and calculated values of $-\log (k_H/k_{phenyl})$, and the ρ values of just the aryl derivatives are listed in Table I. The observed $-\log (k_H/k_{phenyl})$ is shown plotted against the ρ values in Figure 1.

In correlating such a diverse assortment of data one might expect some deviation due to the fact that the rate constants were determined in several different laboratories, uncertainties arising from extrapolating the rate constants for unreactive tertiary derivatives from high temperatures to 25 °C, the rates of tosylates are often determined at elevated temperatures and must also be extrapolated to 25 °C, and the corrections for solvent and leaving group may vary from system to system. However, only minor deviations were noted. Indeed the slope was analyzed by regression analysis and found to be 2.52 ± 0.05 with a confidence level of 99.9 (*F* distribution and *t* distribution). Without any restraints the slope is 2.41 ± 0.25 with an intercept of −0.50. (This is represented by the dashed line in Figure 1; confidence level 99.9).

Since this slope should be equal to the γ^+ for hydrogen, this corroborates the determination of γ^+ for hydrogen from the 7-norbornyl system and demonstrates the general applicability of the $\rho\gamma^+$ relationship in correlating the acetolysis of secondary tosylates with their analogous teriary benzylic derivatives.

Rates of tertiary benzylic chlorides reported by Tanida and Tsushima gave excellent correlations with the corresponding secondary tosylates.[12] The $\rho\gamma^+$ treatment of the cyclopentyl, 7-norbornyl, and 2-adamantyl systems gave ρ values of −4.01, −5.30, and −4.89, respectively.

Secondary adamantyl halides and tosylates have been reported to solvolyze without nucleophilic solvent participation; on the other hand, simple secondary aliphatic and cycloaliphatic substrates can experience solvent assistance.[13] The fact that both secondary adamantyl, aliphatic, and cycloaliphatic tosylates can be correlated with their corresponding tertiary benzylic derivatives is suggestive that solvent involvement may be important in certain tertiary benzylic derivatives and varies with the electron demand of the carbonium ion center.[14] Thus the less stable a cationic center the more demand that center will make on the solvent for additional stabilization. Indeed, solvent participation in solvolysis reactions at tertiary carbon atom has been reported.[14]

Neighboring Group Effects. A basic tenet of neighboring

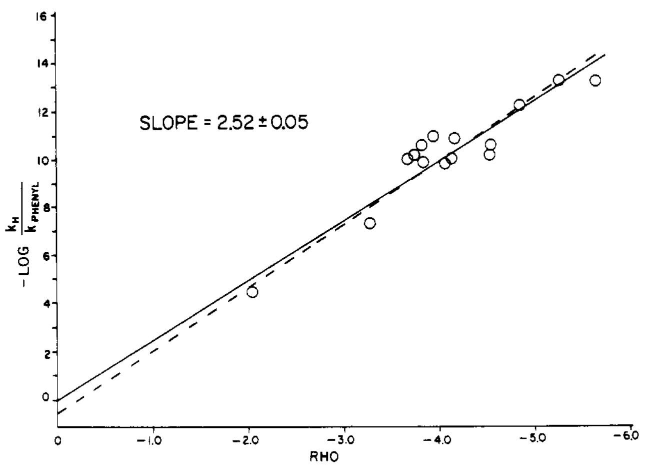


Figure 1. Regression analysis of $-\log (k_H/k_{\text{phenyl}})$ vs. ρ. Dashed line is slope without any restrictions; solid line is slope when intercept is zero.

group effects is that the more stable the carbonium ion center, the less demand that center will make on neighboring groups for additional stabilization through participation.[15] Because the electron demand at the carbonium ion center can be varied by changing the substituent on the aryl group, solvolysis of tertiary benzylic derivatives have been used extensively in the evaluation of neighboring group effects in seccondary substrates. In the past, such an approach has been questioned;[5] however, the $\rho\gamma^+$ relationship has been shown to correlate rates of acetolysis for secondary tosylates with tertiary benzylic derivatives. Henceforth, this technique has been applied in the elucidation of anchimeric assistance by neighboring π and σ bonds.

If anchimeric assistance is significant in a given system, the rate of reaction must be greater than the rate of solvolysis in the absence of such participation.[16] However, problems can arise in defining an analogous system which solvolyzes without participation.[3a] Such problems can be overcome by the direct comparison of the rate of the secondary derivative with its analogous tertiary benzylic derivatives. Since the more stable tertiary derivatives react with less or no anchimeric assistance, the $\rho\gamma^+$ plot should result in a more quantitative interpretation of anchimeric assistance.

π Participation. In homoallylic systems the mutual interaction between the cationic center and the π electrons can result in large rate enhancements.[17] The exact extent of such π participation is a function of the steric requirements of the system under study. For example, cyclopentyl and Δ^3-cyclopentenyl tosylates give excellent linear correlations with their tertiary benzylic derivatives with ρ values of -4.16 and -4.32, respectively.[18] The absence of any significant π participation is indicated by the linearity and the similar ρ values. These results are in agreement with the report that the degree of puckering in the cyclopentene ring and hence the distance between the π electron cloud of the double bond and the developing cationic center must be crucial in determining the overall effect of π participation.[19]

On the other hand, the introduction of a double bond in 7-norbornyl tosylate greatly increases the rate of solvolysis.[10] The 7-norbornyl and 7-*anti*-norbornenyl tosylates give excellent correlations with their 7-aryl analogues[3b] as shown in Figure 2. The saturated series (used to determine the γ^+ of a hydrogen group) had a ρ of -5.25. For the 7-norbornenyl derivatives, a sharp break in the $\rho\gamma^+$ plot occurs after the *p*-anisyl derivative. For the four compounds (excluding the *p*-anisyl and *p*-dimethylaminophenyl derivatives), ρ was -1.75. The break in the $\rho\gamma^+$ plot and the different ρ values are indicative of anchimeric assistance.

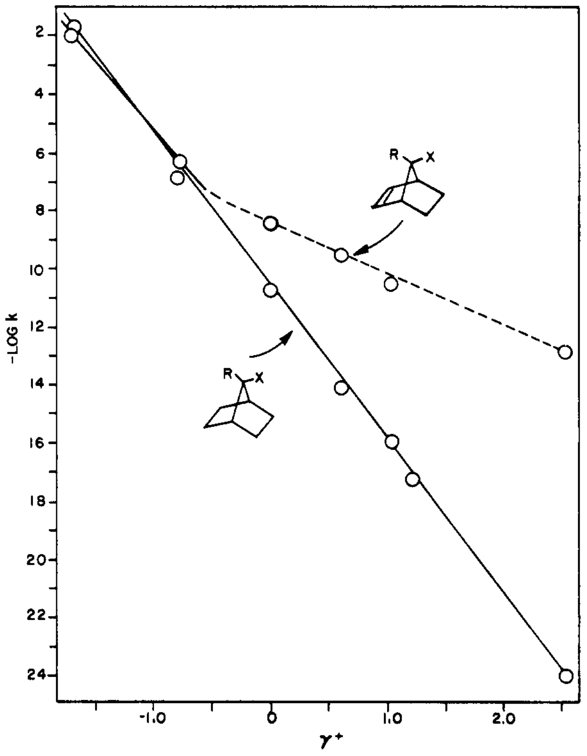


Figure 2. Correlation of tertiary benzylic derivatives of 7-norbornyl and 7-*anti*-norbornenyl *p*-nitrobenzoates with their secondary derivatives (R = aryl or H).

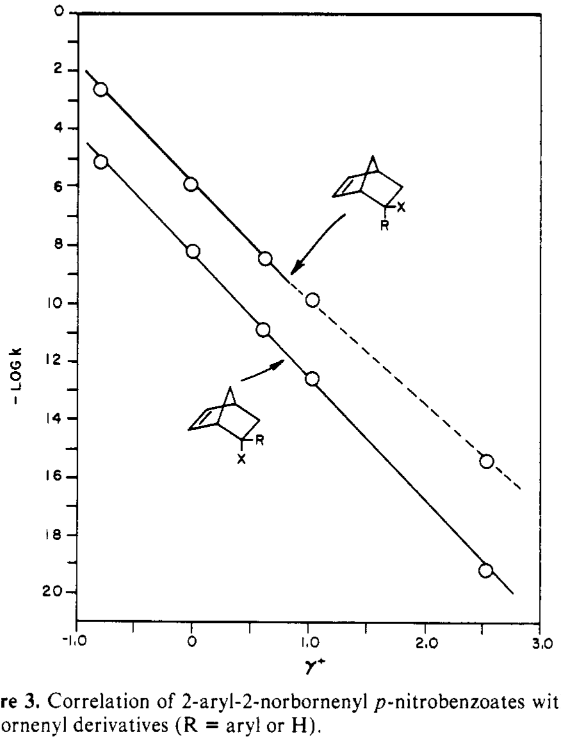


Figure 3. Correlation of 2-aryl-2-norbornenyl *p*-nitrobenzoates with 2-norbornenyl derivatives (R = aryl or H).

In the 2-norbornenyl system exo:endo rate ratios have been used as a criterion for π participation;[20] however, it has been pointed out that the steric environment of the π cloud must contribute to the high exo:endo rate ratio.[21] Correlating the secondary norbornenyl systems with the 2-aryl-2-norbornenyl *p*-nitrobenzoates gives a more quantitative evaluation of the magnitude of π in participation in 2-*exo*-norbornenyl tosylate. For example, the endo derivatives gave an excellent linear correlation (ρ of -4.26); however, in the exo derivatives a break occurs in the $\rho\gamma^+$ plot. As shown in Figure 3, the *p*-anisyl,

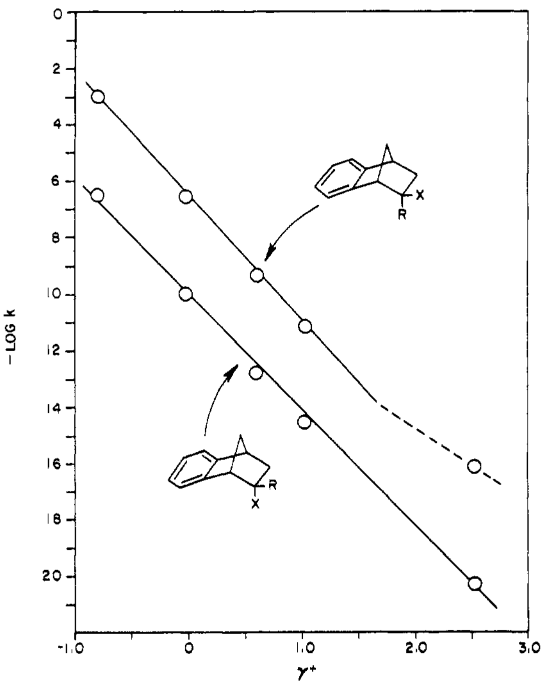
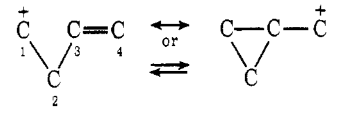


Figure 4. Correlation of 2-aryl-2-benzonorbornenyl *p*-nitrobenzoates with 2-benzonorbornenyl derivatives (R = aryl or H).

phenyl, and *p*-trifluoromethylphenyl derivatives gave a linear $\rho\gamma^+$ plot with a ρ value of -4.21;[22] however, the *m,m'*-bis(trifluoromethyl)phenyl derivative deviates from this slope indicating the onset of π participation.[23] The exact amount of anchimeric assistance can be determined by calculating an unassisted rate for 2-*exo*-norbornenyl tosylate (from the ρ value of the unassisted series,[22] γ^+ for hydrogen, and eq 2) and comparing it with the observed rate. Thus a factor of approximately 18 was attributable to π participation. This value is in line with the reported value of 20.[24]

In a homoallylic cation the electron deficiency should reside on C(1) as well as C(4) (eq 3). A methyl group on C(4) should


(3)

stabilize the carbonium ion and therefore facilitate the delocalization of positive charge into the homoallylic double bond and result in increase π participation.[25] Indeed, the 5-methyl-2-norbornenyl derivatives exhibit enhanced rates for the exo isomers.[26] The differences in ρ values for the exo and endo derivatives (-2.78 and -4.29, respectively) further demonstrate the presence of π participation in the exo isomers.

In the benzonorbornenyl systems, the rate of *endo*-benzonorbornen-2-yl tosylate gave an excellent correlation with the analogous tertiary aryl derivatives;[27] however, with the exo derivatives a break occurs in the $\rho\gamma^+$ plot (Figure 4). The tertiary aryl derivatives gave a linear plot but the *exo*-benzonorbornen-2-yl tosylate deviates from this slope. This denotes π participation, and its magnitude can be determined similar to the determination of π participation for 2-*exo*-norbornenyl tosylate. From the difference between the calculated unassisted rate (1.15×10^{-18} s^{-1}) and the observed rate, factor of 60 is attributable to π participation.

The introduction of a 6-methoxy group results in increased π participation in the exo derivatives.[28] Thus, the exo derivatives have substantially lower ρ value (-3.41) than the endo series (-4.04).

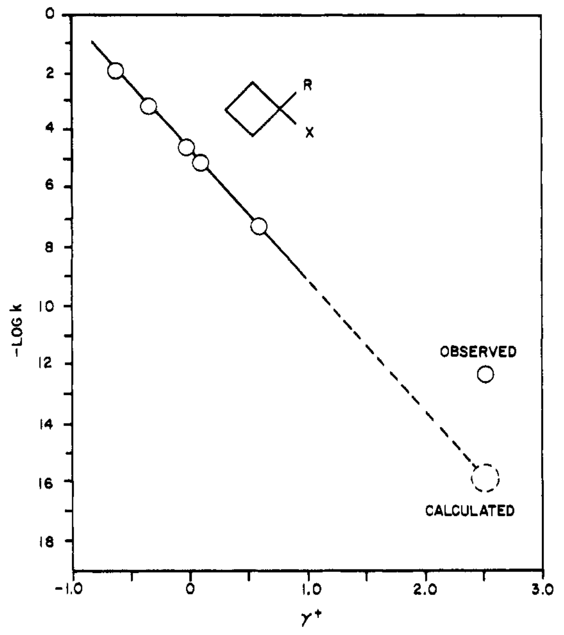
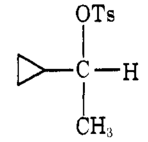
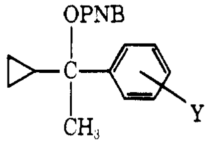


Figure 5. Correlation of 1-aryl-1-cyclobutyl chlorides with 1-cyclobutyl derivative (R = aryl or H).

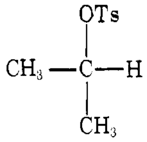
Cyclopropylcarbinyl Systems. The cyclopropyl group is remarkably effective in stabilizing carbonium ions.[29,30] Cyclopropylcarbinyl derivatives undergo rapid rates of solvolysis. Because of this unusual stability the rate of acetolysis of cyclopropylmethylcarbinyl tosylate (**3**) was too rapid to measure. The rates of solvolysis of the 1-aryl-1-cyclopropyl-1-ethyl *p*-nitrobenzoates (**4**) have been determined in 80% acetone.[31]

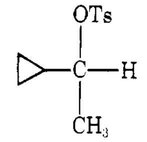

3


4

The rate of **3** can be calculated with the $\rho\gamma^+$ relationship, the ρ value of -2.78 for **4**, the rate of the 1-phenyl derivative, and the γ^+ for hydrogen. After correcting for solvent and leaving group the rate of acetolysis of **3** at 25 °C was 2.83×10^3 s^{-1}.

The magnitude of the rate enhancement by a cyclopropyl group in comparison to a simple secondary system (isopropyl tosylate, **5**) is 8.82×10^5. This is similar to the value of 5×10^5


5

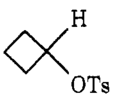

3

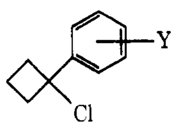
rel rate 1.0 8.82×10^5

previously estimated for a secondary cyclopropylcarbinyl system.[32]

The 3-aryl-3-nortricyclyl *p*-nitrobenzoates and 3-nortricyclyl tosylate gave an excellent $\rho\gamma^+$ plot with a ρ of -3.02.[3a]

Cyclobutyl Cation. The rate of acetolysis of cyclobutyl tosylate (**6**) was reported to be unusually rapid.[33] For example, the 1-aryl-1-cyclobutyl chlorides (**7**) have a ρ value of -4.48;


6


7

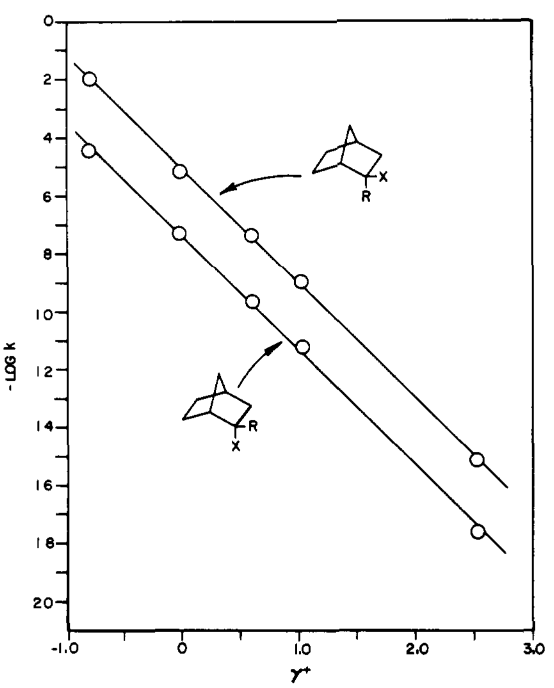


Figure 6. Correlation of 2-aryl-2-norbornyl *p*-nitrobenzoates with 2-norbornyl derivatives (R = aryl or H).

however, the $\rho\gamma^+$ plot of **6** and **7** is nonlinear and is indicative of anchimeric assistance in **6** (Figure 5).[34]

The amount of anchimeric assistance in **6** has been difficult to estimate because of the lack of a suitable reference compound which solvolyzes without assistance.[15] The tertiary derivatives, **7**, react without anchimeric assistance[35] and can be used to obtain an unassisted rate. Henceforth, from the $\rho\gamma^+$ relationship, the ρ value of **7**, and the group constant for a secondary tosylate, and unassisted rate constant of $1.27 \times 10^{-16}\ s^{-1}$ was obtained. Therefore from the values of the calculated unassisted rate and the actual rate, a rate enhancement of 5840 can be attributed to anchimeric assistance.

Norbornyl System. The $\rho\gamma^+$ relationship is useful in elucidating both π and σ participation. Rate enhancements as low as 18 can be assigned to anchimeric assistance. It is of prime importance to apply the $\rho\gamma^+$ treatment to the 2-norbornyl system. The norbornyl system has been the center of controversy for over 10 years.[5c,36] The 2-aryl-2-norbornyl derivatives are reported to solvolyze without assistance.[37] Both the exo and endo 2-norbornyl systems reveal excellent $\rho\gamma^+$ correlations between the tertiary aryl and the secondary derivatives (Figure 6).

The linearity and similar ρ values of −3.95 and −3.98 for the exo and endo derivatives corroborate Brown's conclusion that σ participation is not a major factor in the solvolysis of 2-*exo*-norbornyl derivatives.[36] Furthermore, the observed −log (k_H/k_{phenyl}) for both the 2-norbornyl systems is greater, not less than the calculated values as should be the case if participation were important.

In order to totally address this problem one must also consider internal return. The acetolysis of 2-*exo*-norbornyl *p*-bromobenzenesulfonate was shown to react with internal return ($k_\alpha/k_t = 4.6$).[38] The polarimetric exo:endo rate ratio was 1600. Thus it was stated that the polarimetric rate provides a better estimate of anchimeric assistance.[39] In the $\rho\gamma^+$ relationship one might ask if polarimetric rates of **1** should be compared with the titrimetric rates of **2**; moreover, are polarimetric rates a better criteria for anchimeric assistance.

Tertiary *p*-nitrobenzoates and chlorides have been reported to react with internal return.[40] For example, in a study of the titrimetric and polarimetric rates of methanolysis of optically active 1,2-dimethyl-2-*exo*-norbornyl chloride, internal return was observed and a k_α/k_t of 2.3 was noted.[40a] However, optically active products were obtained which indicated that a bridged symmetrical intermediate must be absent. Therefore, these workers concluded that the reaction proceeded through a classical carbonium ion. Thus, *internal return is not synonymous with anchimeric assistance.* Moreover, since tertiary systems can react with internal return, it would be unwise to attempt to correlate polarimetric rates with titrimetric rates without first evaluating the importance of internal return in **2** as well as **1**.

Conclusions

A linear free-energy relationship has been developed which permits the direct correlation of the rates of acetolysis of secondary tosylates with their corresponding tertiary benzylic derivatives. This relationship was shown to be generally applicable to a large number of systems. Thus results from various research groups over the past 20 years can now be compared under a unified theory. Furthermore, in the study of neighboring group effects, a better understanding and a more quantitative interpretation of anchimeric assistance can now be obtained.

Experimental Section

The preparation of 7-phenyl-7-norborneol was carried out by the addition of phenylmagnesium bromide to 7-norbornone, mp 50–51 °C (lit. mp 49–50 °C).[41] The *p*-nitrobenzoate was prepared from the lithium alkoxide and *p*-nitrobenzoyl chloride, mp 128–129 °C (lit. mp 127.5–128.5 °C).[41] Rates of solvolysis were determined in 70% dioxane (v/v) as described in the literature.[3b] The kinetic data were: $k^{150\ °C} = 1.06 \times 10^{-4}\ s^{-1}$, $k^{125\ °C} = 1.04 \times 10^{-5}\ s^{-1}$, $\Delta H^{\ddagger} = 30.5$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -5.2$ eu.

Acknowledgment. The author wishes to thank Professor C. Walling of the University of Utah for his helpful suggestions about the means for a valid demonstration of the statistical significance of the data in this manuscript.

References and Notes

(1) Presented in part at the 170th National Meeting of the American Chemical Society, Chicago, Ill., August 1975, ORGN 87.

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

(3) (a) For example, see H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **97,** 1927 (1975), and references cited therein; (b) P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, **92,** 2549 (1970); (c) H. Tanida and T. Tsushima, *ibid.*, **92,** 3397 (1970); (d) H. Tanida and H. Matsumura, *ibid.*, **95,** 1586 (1973).

(4) H. C. Brown and Y. Okamoto, *J. Org. Chem.*, **22,** 485 (1957).

(5) (a) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *J. Am. Chem. Soc.*, **90,** 1901 (1968); (b) H. Tanida, *Acc. Chem. Res.*, **1,** 239 (1968); (c) G. D. Sargent in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1972, Chapter 24; (d) G. A. Olah, *Acc. Chem. Res.*, **9,** 41 (1976).

(6) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **96,** 265 (1974).

(7) Because of the availability of data for acetolysis of secondary tosylates, rates of acetolysis should be extrapolated to the corresponding solvent and leaving group for the analogous tertiary benzylic derivative. Moreover, it should be noted that for an accurate comparison, one cannot determine the rate of a simple secondary chloride or *p*-nitrobenzoate in an aqueous solvent because this can result in S_N2 behavior or ester hydrolysis. Because rate constants for the tertiary derivatives were determined titrimetrically, only titrimetric rates of acetolysis were used in this study.

(8) For example, see R. Taylor, *J. Chem. Soc.*, 4881 (1962); P. J. Brignell, P. E. Jones, and A. R. Katritzky, *J. Chem. Soc. B*, 117 (1970), and references cited therein.

(9) This is a logical choice since this system has been studied extensively and has the largest rate spread carried out for a solvolysis reaction; ref 3b.

(10) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77,** 4183 (1955).

(11) Rates of tosylates in acetic acid were converted to rates of *p*-nitrobenzoates in 80% acetone by multiplying the rates of the tosylates by a factor of 3.27×10^{-11}. This factor was determined by correcting the factor for converting tosylates in acetic acid to *p*-nitrobenzoates in 70% dioxane (1.59×10^{-10}; ref 3b) to rates of *p*-nitrobenzoates in 80% acetone by the factor of 0.206. See A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78,** 2770 (1956).

(12) The cyclohexyl series gave a less than excellent correlation. This could be the result of differences in the position of the leaving group (axial or equitorial) in going from the 2 to 3° system, steric hindrance to resonance

in the tertiary system due to the conformation of the aryl ring [for example, see N. L. Allinger and M. T. Tribble, *Tetrahedron Lett.*, 3259 (1971)], or some other factor.

(13) D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 5977 (1970); J. K. Fry, C. L. 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); J. M. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2542 (1970).

(14) (a) F. G. Bordwell, P. F. Wiley, and T. G. Mecca, *J. Am. Chem. Soc.*, **97**, 132 (1975); (b) A. Miotti and A. Fava, *ibid.*, **88**, 4274 (1966).

(15) S. Winstein, B. K. Morse, E. Grunwald, K. C. Shreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952).

(16) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Am. Chem. Soc.*, **75**, 147 (1953).

(17) For a review, see P. R. Story and B. C. Clark in "Carbonium Ions" (ref 5c), Chapter 23.

(18) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **97**, 7454 (1975).

(19) (a) P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963); (b) B. A. Hess, Jr., *J. Am. Chem. Soc.*, **93**, 1000 (1971).

(20) S. Winstein, H. Walborsky, and K. C. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950).

(21) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **94**, 7920 (1972).

(22) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 2398 (1973).

(23) H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **97**, 7442 (1975).

(24) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **94**, 5899 (1972).

(25) (a) H. C. Brown, E. N. Peters, and M. Ravindranathan, *J. Am. Chem. Soc.*, **97**, 2900 (1975); (b) R. A. Sneen, *ibid.*, **80**, 3982 (1958); (c) P. G. Gassman and D. S. Patton, *ibid.*, **91**, 2160 (1969).

(26) H. C. Brown, E. N. Peters, and M. Ravindranathan, *J. Am. Chem. Soc.*, **97**, 7449 (1975).

(27) H. C. Brown, S. Ikegami, and K.-T. Liu, *J. Am. Chem. Soc.*, **91**, 5909 (1969).

(28) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **91**, 5911 (1969).

(29) H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **95**, 2400 (1973).

(30) For recent reviews, see (a) H. G. Richey, Jr., in "Carbonium Ions" (ref 5c), Chapter 25; (b) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, *ibid.*, Chapter 26.

(31) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 2397 (1973).

(32) (a) J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.*, **90**, 4303 (1968); (b) E. C. Friedrich, M. A. Saleh, and S. Winstein, *J. Org. Chem.*, **38**, 860 (1973).

(33) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 3542 (1951); R. H. Mazur et al., *ibid.*, **81**, 4390 (1959).

(34) Data for **6** taken from H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78**, 2735 (1956), and corrected for difference in solvent and leaving group (i.e., 7.42 $\times 10^{-13}$ s^{-1}).

(35) For example, ^{1}H NMR data are consistent with classicial 1-phenylcyclobutyl cation; see G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Am. Chem. Soc.*, **94**, 146 (1972).

(36) H. C. Brown, *Acc. Chem. Res.*, **6**, 377 (1973); (b) H. C. Brown and E. N. Peters, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 132 (1974).

(37) H. C. Brown, M. Ravindranathan, K. Takeuchi, and E. N. Peters, *J. Am. Chem. Soc.*, **97**, 2899 (1975).

(38) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1154 (1952).

(39) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Am. Chem. Soc.*, **87**, 376 (1965).

(40) (a) H. L. Goering and J. V. Clevenger, *J. Am. Chem. Soc.*, **94**, 1010 (1972); (b) H. L. Goering and K. Humski, *ibid.*, **90**, 6213 (1968). (c) For benzhydryl *p*-nitrobenzoates, see H. L. Goering and H. Hopf, *ibid.*, **93**, 1224 (1971).

(41) A. Fentiman, Jr., Ph.D. Thesis, The Ohio State University, 1969.

Vinylic Cations from Solvolysis. 24.[1] Degenerate β-Aryl Rearrangements during the Solvolysis of 1,2-Dianisyl-2-phenylvinyl Bromides and Trianisylvinyl Bromide. Free Vinyl Cations as Intermediates

Yoram Houminer, Etta Noy, and Zvi Rappoport*

Contribution from the Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel. *Received December 31, 1975*

Abstract: The degenerate β-phenyl rearrangement in the 1,2-dianisyl-2-phenylvinyl cation (**8**) and the β-anisyl rearrangement in the trianisylvinyl cation (**13**) were studied by using the precursor bromides labeled by β-$CD_3OC_6H_4$ groups. In AcOH, Me_3CCOOH, or aqueous EtOH, **8** does not rearrange at all or only to a small extent, while 53 ± 6% of β-phenyl rearrangement was found in TFE. Ion **13** shows 11.5, 35, 0, and 100% β-anisyl rearrangement in 60% EtOH, AcOH, Me_3CCOOH, and TFE, respectively, and it can be captured by Br^- before rearrangement in AcOH and TFE. It is suggested that the rearrangement proceeds via free open vinyl cations, whose selectivity is not due to a rapid migration of the β-aryl group between a pair of degenerate vinyl cations. The direction and extent of rearrangement in phenyl- and anisyl-substituted triarylvinyl cations are determined by the better charge dispersal ability of the anisyl group, either in the ground or transition state. Low nucleophilicity and high dissociation power of the solvent favor the rearrangement, making TFE the best medium for these reactions. Relative rate constants for reactions of triarylvinyl cations (capture by Br^- (k_{Br}), capture by the solvent (k_{SOH}), β-phenyl migration ($k_{r(Ph)}$), and β-anisyl migration ($k_{r(An)}$)) were evaluated. E.g., k_{Br} (1 M $[Br^-]$):$k_{r(An)}$:k_{SOH} = 78:25:1 for **13** in TFE, and k_{Br} (1 M $[Br^-]$):k_{SOH}:$k_{r(Ph)}$ = 21:1:<0.01 for **8** in AcOH. The possible use of degenerate rearrangements for obtaining the heterolysis rate in nonsolvolytic media and the effect of the α substituent on the nature of the cationic intermediate are discussed. The limitations of the mass spectral and the NMR analyses in studying the degenerate rearrangements are scrutinized.

The cationoid intermediates formed in the solvolysis of triarylvinyl halides or sulfonates participate in a variety of processes, such as capture by the leaving group,[2,3] the solvent,[2,3] or other nucleophiles,[2,3,4] and rearrangement of a β-aryl group across the double bond.[5]

$$\mathrm{Ar^3Ar^2C{=}C(X)Ar^1 \xrightarrow{-X^-} Ar^3Ar^2C{=}C^+{-}Ar^1}$$
$$\mathrm{\rightleftharpoons Ar^3{-}{}^+C{=}CAr^1Ar^2 + Ar^2{-}{}^+C{=}CAr^1Ar^3 \qquad (1)}$$

The extent of the rearrangement and the stereochemistry of its products depend on several factors: the relative stability and the capture vs. rearrangement rates of the rearranged and unrearranged ions; and the nature of the cationoid intermediate, whether it is bridged[6] or open.[5]

Substituent and solvent effects on the β-aryl rearrangement across the double bond will be better understood if a series of closely related reactions are compared. Triarylvinyl systems substituted by all the possible combinations of phenyl and anisyl groups provide such a series as shown in Scheme I (eq 2-9).[7] The precursors are four α-phenyl- and four α-anisyl-substituted systems, where each subseries includes a pair of geometrical isomers. Two compounds are di-β-phenyl and two compounds are di-β-anisyl substituted, and the other four are