THE NATURE AND TRANSMISSION OF SUBSTITUENT ELECTRICAL EFFECTS IN ALICYCLIC SOLVOLYSIS

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Dedicated to Professor Otto Exner on the occasion of his 75th birthday in recognition of his outstanding contributions to physical organic chemistry and chemometrics.

The correlation of rate constants taken from the literature for 2-*exo*- and 2-*endo*-norbornyl derivatives substituted in positions 1, 4, 5-*exo*, 6-*exo*, 6-*endo*, and 7-*anti* with the triparametric LDR equation and relationships derived from it has been carried out. A delocalized (resonance) electrical effect has been found in all but the 4-substituted derivatives. The resonance effect may be somewhat greater when the leaving group is *exo* than when it is *endo*. Steric effects occur in the 6-*endo*-substituted derivatives. The transition state resembles a classical carbocation rather than the nonclassical norbornyl carbocation. The correlation of solvolysis rate constants for 2- and 3-substituted 1- and 4-*exo*-substituted 2-*exo*-adamantyl derivatives gave no reliable indication that a delocalized electrical effect existed in these systems. A study of solvolysis rate constants for 4-substituted 1-[2.2.2]bicyclooctanyl, 6-*exo*-substituted [2.2.2]bicyclooctan-2-*exo*-yl and 6-*exo*-substituted [2.2.2]bicyclooctan-2-*endo*-yl derivatives showed a delocalized electrical effect only in the latter of these systems. Such an effect was also observed in 4-substituted 2-chloro-2-methylbutane solvolyses. The transmission of electrical effects is by a modified field effect. It is dependent on 1/*n* where *n* is the number of bonds intervening between substituent and reaction site.

Key words: Substituent effects; Steric effects; Modified field effect; Electrical effect transmission; Solvolysis; Norbornanes; Bicyclo[2,2,2]octanes.

In this work we present a study of substituent effects on the solvolyses of substituted alicyclic systems. There is an extensive literature available on both experimental measurements of rate constants for substituted cycloalkane solvolyses and theoretical calculations of the stability of and bonding in cycloalkyl carbocations[1–3]. We have applied correlation analysis to the rate constants for solvolysis of substituted norbornyl (Nbl), adamantyl (Adm), bicyclo[2.2.2]octanyl (Bco), and cyclobutyl (cBu) derivatives in various solvents with various leaving groups in order to determine the composition and the nature of the transmission of electrical effects in these systems. The data sets studied were taken from the literature, they are reported in Appendix. Whenever possible data were correlated with the LDR equation, a triparametric electrical effect model which accounts for substituent effects in all types of systems with electronic demands ranging from directly substituted carbenium ions to directly substituted carbanions[4]. It is written as:

$$Q_X = L\sigma_{lX} + D\sigma_{dX} + R\sigma_{eX} + h \tag{1}$$

$$\eta \equiv R/D \tag{1a}$$

$$P_D \equiv D/(L + D), \tag{1b}$$

where σ_l is the localized electrical effect parameter (it is identical to σ_I); σ_d is the intrinsic delocalized electrical effect parameter; and σ_e is the electronic demand sensitivity electrical effect parameter. η, defined in Eq. (*1a*), is a measure of the electronic demand of the reaction studied. P_D, the percent delocalized effect, defined in Eq. (*1b*), is a measure of the composition of the electrical effect in the reaction studied. When the number of data points available in the set of interest is too small to make the LDR equation statistically reliable the CR equation[5] can be used, it is:

$$Q_X = C\sigma_{CX} + R\sigma_{eX} + h, \tag{2}$$

where σ_C is a composite parameter. It is defined by the relationship:

$$\sigma_{CX} = l\sigma_{lX} + d\sigma_{dX} . \tag{3}$$

The difference between pure and composite parameters is that the former represent a single effect while the latter represent a mixture of two or more. The percent composition of these parameters is given by:

$$P_D = 100d/(l + d). \tag{4}$$

If the constant value of P_D is written as k' then the σ_{CX} parameter for a given value of k' is:

$$\sigma_{CXk'} = \sigma_{lX} + [k'/(100 - k')]\sigma_{dX} . \qquad (5)$$

Writing

$$k^* = k'/(100 - k') \qquad (6)$$

gives

$$\sigma_{CXk'} = \sigma_{lX} + k^*\sigma_{dX} \qquad (7)$$

$$\eta \equiv R/Ck^*. \qquad (7a)$$

η for the CR equation can be calculated from Eq. (*7a*). When steric effects must be accounted for a term in the parameters υ or υ′ is added to the appropriate equation[6–8]. The latter parameter is corrected for the difference in bond length between the substituent–skeletal group bond and the reaction site–skeletal group bond.

The LDRT, CRT, and LDRST equations are

$$Q_X = L\sigma_{lX} + D\sigma_{dX} + R\sigma_{eX} + T\tau + h \qquad (8)$$

$$Q_X = C\sigma_{CX} + R\sigma_{eX} + T\tau + h \qquad (9)$$

and

$$Q_X = L\sigma_{lX} + D\sigma_{dX} + R\sigma_{eX} + S\vartheta + T\tau + h, \qquad (10)$$

where ϑ is either υ′ or υ which are derived from the LDR and CR equations by the inclusion of the term $T\tau$, where τ is the absolute temperature divided by 100 and T its coefficient[5]. They provide another method for obtaining data sets large enough to be statistically significant. The substituent constants used in this work are from our previous work[4,7,8,9–12]. For all of the sets studied the best regression equations are reported, the statistics being given directly beneath the equations.

The reliability of the results obtained for a data set depends on two factors:

1. The ratio of degrees of freedom to number of independent variables, $r_{df/iv}$, given by the number of degrees of freedom, N_{df} divided by the number of independent variables, N_{iv} Best results are obtained in the use of regression analysis when $r_{df/iv} \geq 3$. N_{df} is equal to the number of data points in the set, N_{dp}, less the number of independent variables, N_{iv}, minus one.

2. The range of substituent types in the data set. The optimum data set contains both strong electron donor groups such as OR and NR_2, where R is H or alkyl; and strong electron acceptor groups such as C(O)R, CO_2R, $CONR_2$, CN, and NO_2. Having both strong donor and strong acceptor groups in the data set ensures a wide range of substituent effects. In data sets involving positively charged transition states, the presence of strong donors is particularly important if delocalized (resonance) effects are to be detected. Set designations for data sets that meet both of these requirements are given in bold face, those that meet neither requirement are given in italics.

RESULTS AND DISCUSSION

Norbornyl Systems

1-Substituted 2-*exo*-norbornyl tosylates, **1**, in 80% v/v aqueous EtOH at various temperatures, where X = H, Me, CH_2OAc, CH_2Cl, CH_2OTs, CO_2Me, OAc, Br, Ac, CN, CH_2OH; (set NBL1) gave with the LDRT equation:

$$\log k_X = -8.78(\pm 0.621)\sigma_{lX} - 2.05(\pm 0.538)\sigma_{dX} - 7.84(\pm 3.11)\sigma_{eX} - 39.5(\pm 3.18)\tau_X + 15.3(\pm 1.06) \quad (11)$$

$100R^2$, 90.54; $A100R^2$, 89.36; F, 55.04; S_{est}, 0.234; P_D, 18.9(±5.17); η, 3.82(±1.14); $S°$, 0.339; N_{dp}, 28; N_{df}, 23; N_{iv}, 4; $r_{df/iv}$, 5.75; r_{ld}, 0.104; r_{le}, 0.257; $r_{l\tau}$, 0.896; r_{de}, 0.851; $r_{d\tau}$, 0.109; $r_{e\tau}$, 0.192.

Data at 70 °C (set NBL1A) were correlated with the CR and L equations in order to avoid colinearities giving:

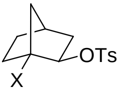
$$\log k_X = -10.8(\pm 0.801)\sigma_{c25X} - 12.6(\pm 5.15)\sigma_{eX} + 3.897(\pm 0.219) \quad (12)$$

$100R^2$, 96.84; $A100R^2$, 96.44; F, 107.2; S_{est}, 0.408; $S°$, 0.212; N_{dp}, 10; N_{df}, 7; N_{iv}, 2; $r_{df/iv}$, 3.50; r_{ce}, 0.535; P_D, 25; η, 3.49(±1.41) and

$$\log k_X = -10.4(\pm 0.869)\sigma_{lX} + 4.32(\pm 0.273) \qquad (13)$$

$100r^2$, 94.75; F, 144.3; S_{est}, 0.493; $S°$, 0.256; N_{dp}, 10; N_{df}; 8, N_{iv}, 1; $r_{df/iv}$, 8.00. The results are in accord with a dependence on σ_d.

1-Substituted norbornyl 2-*exo*-tosylates, **1**, in AcOH at 25 °C, where X = H, Me, Et, Ph, 4-$O_2NC_6H_4$, 4-ClC_6H_4, 4-$MeOC_6H_4$, 4-MeC_6H_4, 3-$MeOC_6H_4$, cHx; (set NBL2) with the LDR equation gave:



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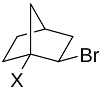

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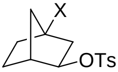

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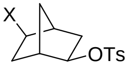

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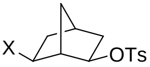

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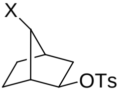

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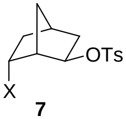

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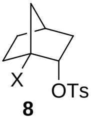

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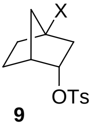

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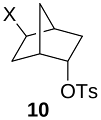

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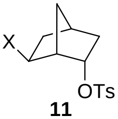

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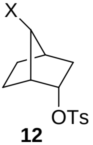

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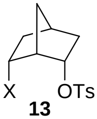

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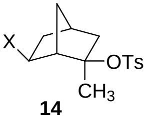

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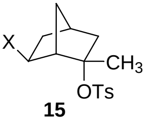

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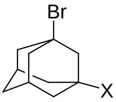

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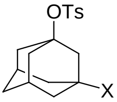

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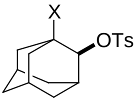

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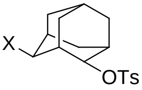

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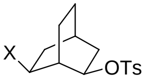

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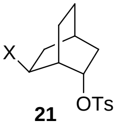

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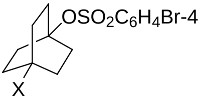

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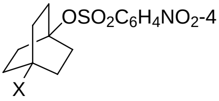

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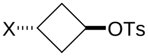

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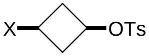

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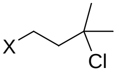

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$$\log k_X = 8.78(\pm 0.674)\sigma_{lX} - 2.09(\pm 0.458)\sigma_{dX} + 1.93(\pm 0.0990) \qquad (14)$$

$100R^2$, 96.61; A$100R^2$, 96.12; F, 85.44; S_{est}, 0.186; $S°$, 0.226; N_{dp}, 9; N_{df}, 6; N_{iv}, 2; $r_{df/iv}$, 3.00; P_D, 19.2(±4.45); r_{ld}, 0.426.

1-Substituted 2-*exo*-norbornyl bromides, **2**, in 80% v/v aqueous EtOH at 25 °C, where X = H, Me, Ph, OAc, NHBz, NH_2, CO_2Me; (set NBR3) gave with the LDR equation:

$$\log k_X = -11.0(\pm 1.81)\sigma_{lX} - 4.44(\pm 1.02)\sigma_{dX} + 1.91(\pm 0.449) \qquad (15)$$

$100R^2$, 92.77; A$100R^2$, 91.32; F, 35.66; S_{est}, 0.679; $S°$, 0.356; N_{dp}, 7; N_{df}, 2; $r_{df/iv}$, 2.00; r_{ld}, 0.095; P_D, 28.8(±7.65); η, 0.

1-Substituted 2-*exo*-norbornyl bromides in 20% v/v aqueous EtOH at 25 °C (set *NBL4*), where X = H, Me, Ph, CN, CF_3, CO_2Me, CH_2OH, gave with the CR equation on exclusion of the data point for CH_2OH:

$$\log k_X = -\,11.7(\pm 0.379)\sigma_{c33.3,X} - 5.97(\pm 2.63)\sigma_{eX} + 3.621(\pm 0.184) \qquad (16)$$

$100R^2$, 99.69; A$100R^2$, 99.61; F, 475.1; S_{est}, 0.245; $S°$, 0.0793; N_{dp}, 6; N_{df}, 3; N_{iv}, 2; $r_{df/iv}$, 1.50; r_{ce}, 0.089; P_D, 33.3; η, 1.02(±0.449).

4-Substituted 2-*exo*-norbornyl tosylates, **3**, in 80% v/v aqueous EtOH at various temperatures (set NBL5), where X = H, CH_2OAc, CH_2Cl, CH_2OTs, CO_2Me, OAc, Cl, CN, CH_2OH, gave with the LDRT equation on exclusion of the data point for CH_2OH:

$$\log k_X = -5.08(\pm 0.0767)\sigma_{lX} - 52.1(\pm 0.892)\tau + 18.5(\pm 0.277) \qquad (17)$$

$100R^2$, 99.58; A$100R^2$, 99.56; F, 2 233; S_{est}, 0.0343; $S°$, 0.0700; N_{dp}, 22; N_{df}, 19; N_{iv}, 2; $r_{df/iv}$, 9.30; $r_{l\tau}$, 0.796.

Correlation of the data at 70 °C (set NBL5A) with the LDR equation gave:

$$\log k_X = -5.31(\pm 0.207)\sigma_{lX} + 3.46(\pm 0.0659) \qquad (18)$$

$100R^2$, 98.94; F, 654.4; S_{est}, 0.108; $S°$, 0.117; N_{dp}, 9; N_{df}, 7; N_{iv}, 1; $r_{df/iv}$, 7.00. There is excellent agreement between Eqs (*17*) and (*18*). Substituents at the 4 position do not seem to exert a delocalized effect.

5-*exo*-Substituted 2-*exo*-norbornyl tosylates, **4**, in 80% v/v aqueous EtOH at various temperatures (set NBL6), where X = H, Me, CH_2OH, CH_2OAc, CH_2Br, CH_2OTs, CO_2Me, CH_2OMe, Cl, CN, on correlation with the LDRT equation gave on exclusion of the value for H:

$$\log k_X = -4.27(\pm 0.208)\sigma_{lX} - 1.33(\pm 0.234)\sigma_{dX} - 8.96(\pm 1.44)\sigma_{eX} - 46.7(\pm 2.19)\tau + 16.2(\pm 0.674) \tag{19}$$

$100R^2$, 96.09; A$100R^2$, 95.58; S_{est}, 0.0905; $S°$, 0.219; N_{dp}, 27; N_{df}, 22; N_{iv}, 4; $r_{df/iv}$, 5.50; P_D, 23.8(±4.38); η, 6.74; r_{ld}, 0.311; r_{le}, 0.265; $r_{l\tau}$, 0.867; r_{de}, 0.785; $r_{d\tau}$, 0.225; $r_{e\tau}$, 0.200.

Correlation of the data at 70 °C (set *NBL6A*) with the LDR equation gave:

$$\log k_X = -4.60(\pm 0.207)\sigma_{lX} - 1.26(\pm 0.460)\sigma_{dX} - 8.21(\pm 2.84)\sigma_{eX} + 2.61(\pm 0.126) \tag{20}$$

$100R^2$, 99.12; A$100R^2$, 98.83; F, 187.5; S_{est}, 0.103; $S°$, 0.126; N_{dp}, 9; N_{df}, 5; N_{iv}, 3; $r_{df/iv}$, 1.67; P_D, 21.4(±8.07); η, 6.54; r_{ld}, 0.311; r_{le}, 0.265; r_{de}, 0.785. There is excellent agreement with Eq. (*19*).

6-*exo*-Substituted 2-*exo*-norbornyl tosylates, **5**, in 70% aqueous dioxane at 70 °C (set **NBL7**), where X = H, Me, CH_2Br, CO_2H, CO_2Me, Br, CN, CH_2NH_2, CH_2OH, $CONH_2$, NHAc, SMe, OMe, OH, NH_2, NMe_2, OAc; on correlation with the LDR equation gave:

$$\log k_X = -10.2(\pm 0.859)\sigma_{lX} - 1.67(\pm 0.566)\sigma_{dX} - 7.38(\pm 2.71)\sigma_{eX} + 2.08(\pm 0.288) \tag{21}$$

$100R^2$, 93.34; A$100R^2$, 92.39; F, 60.73; S_{est}, 0.537; $S°$, 0.295; N_{dp}, 17; N_{df}, 13; N_{iv}, 3; $r_{df/iv}$, 4.33; P_D, 14.1(±4.91); η, 4.41; r_{ld}, 0.055; r_{le}, 0.016; r_{de}, 0.555, while in 97% aqueous TFE (set NBL8), where X = H, CH_2OAc, CH_2OTs, CH_2Br, CO_2Me, Br, with the CRT equation the result was

$$\log k_X = -7.69(\pm 1.36)\sigma_{C14.3,X} - 17.0(\pm 3.86)\sigma_{eX} - 17.6(\pm 6.47)\tau + 8.158(\pm 2.179) \tag{22}$$

$100R^2$, 86.20; A$100R^2$, 85.69; F, 20.82; S_{est}, 0.276; $S°$, 0.440; N_{dp}, 14; N_{df}, 10; N_{iv}, 3; $r_{df/iv}$, 3.33; r_{ce}, 0.601; $r_{c\tau}$, 0.937; $r_{e\tau}$, 0.642; P_D, 14.3; η, 13.3(±1.88).

7-*anti*-Substituted-2-*exo*-norbornyl tosylates, **6**, in 80% v/v aqueous EtOH at various temperatures (set NBL9), where X = H, CH_2OAc, CH_2OTs, CH_2Br, CO_2Me, Br, gave with the LDRT equation:

$$\log k_X = -5.04(\pm 0.364)\sigma_{lX} - 0.821(\pm 0.327)\sigma_{dX} - 5.10(\pm 2.90)\sigma_{eX} - 47.6(\pm 3.20)\tau + 17.1(\pm 0.957) \qquad (23)$$

$100R^2$, 95.77; A$100R^2$, 95.07; F, 96.31; S_{est}, 0.124; $S°$, 0.234; N_{dp}, 22; N_{df}, 17; N_{iv}, 4; $r_{df/iv}$, 4.25; r_{ld}, 0.001; r_{le}, 0.262; $r_{l\tau}$, 0.851; r_{de}, 0.805; $r_{d\tau}$, 0.162; $r_{e\tau}$, 0.082; P_D, 14.0(±5.69); η, 6.20(±2.53),
while in 97% aqueous TFE at various temperatures (set *NBL10*), where X = H, Me, CH_2OAc, CH_2Br, CO_2Me, CN, Br, Cl, gave with the CRT equation:

$$\log k_X = -\,6.63(\pm 0.558)\sigma_{c25,X} - 8.97(\pm 3.97)\sigma_{eX} - 40.4(\pm 4.04)\tau + 15.8(\pm 1.27) \qquad (24)$$

$100R^2$, 95.88; A$100R^2$, 94.97; F, 62.09; S_{est}, 0.212; $S°$, 0.249; N_{dp}, 12; N_{df}, 8; N_{iv}, 3; $r_{df/iv}$, 2.67; r_{ce}, 0.583; $r_{c\tau}$, 0.547; $r_{e\tau}$, 0.329; P_D, 25; η, 4.06(±1.75).

6-*endo*-Substituted 2-*exo*-norbornyl tosylates, **7**, in 80% v/v aqueous EtOH at various temperatures (set **NBL11**), where X = H, Me, iPr, *t*-Bu, CH_2NH_2, CH_2Br, NO_2, CO_2Me, OAc, F, Br, CN, OH, OMe; on exclusion of the values for CH_2NH_2, NO_2, CO_2Me, OAc, and OH, gave as the result of correlation with the LDRST equation using the υ' parameters:

$$\log k_X = -\,6.71(\pm 0.537)\sigma_{lX} - 0.790(\pm 0.307)\sigma_{dX} - 2.92(\pm 0.703)\upsilon' - 37.7(\pm 4.62)\tau + 14.6(\pm 1.41) \qquad (25)$$

$100R^2$, 92.53; A$100R^2$, 91.47; F, 61.97; S_{est}, 0.281; $S°$, 0.306; N_{dp}, 25; N_{df}, 20; N_{iv}, 4; $r_{df/iv}$, 5.00; P_D, 10.5(±4.19); η, 0; r_{ld}, 0.190; $r_{l\upsilon'}$, 0.253; $r_{l\tau}$, 0.867; $r_{d\upsilon'}$, 0.042; $r_{d\tau}$, 0.030; $r_{\upsilon'\tau}$, 0.263.

1-Substituted 2-*endo*-norbornyl tosylates, **8**, in 80% v/v aqueous EtOH at various temperatures (set NBL41), where X = H, Me, CH_2OAc, CH_2Cl, CH_2OTs, CO_2Me, Br, gave with the CRT equation:

$$\log k_X = -\,6.16(\pm 0.266)\sigma_{c10,X} - 7.00(\pm 1.20)\sigma_{eX} - 50.8(\pm 3.29)\tau + 15.5(\pm 0.899) \qquad (26)$$

$100R^2$, 97.41; A$100R^2$, 97.08; F, 187.7; S_{est}, 0.103; $S°$, 0.181; N_{dp}, 19; N_{df}, 15; N_{iv}, 3; $r_{df/iv}$, 5.00; r_{ce}, 0.276; $r_{c\tau}$, 0.804; $r_{e\tau}$, 0.168; P_D, 10; η, 10.2(±1.69)
and with the LDRT equation:

$$\log k_X = -6.03(\pm 0.269)\sigma_{lX} - 5.17(\pm 3.41)\tau + 16.0(\pm 0.936) \qquad (27)$$

$100R^2$, 97.06; A$100R^2$, 96.88; F, 263.8; S_{est}, 0.106; $S°$, 0.187; N_{dp}, 19; N_{df}, 16; N_{iv}, 2; $r_{df/iv}$, 8.00; $r_{l\tau}$, 0.808.
There is little to choose between Eqs (*26*) and (*27*).

1-Substituted 2-*endo*-norbornyl tosylates in AcOH at 25 °C (set NBL42), where X = H, OMe, Me, Et, cHx, Ph, C_6H_4Cl-4′, C_6H_4Me-4′, $C_6H_4NO_2$-4′, C_6H_4OMe-4′, gave with the CR equation:

$$\log k_X = -\ 5.69(\pm 0.648)\sigma_{c10,X} - 4.64(\pm 1.96)\sigma_{eX} + 0.827(\pm 0.106) \qquad (28)$$

$100R^2$, 93.07; A$100R^2$, 92.08; F, 40.31; S_{est}, 0.163; $S°$, 0.322; N_{dp}, 9; N_{df}, 6; N_{iv}, 2; $r_{df/iv}$, 3.00; r_{ce}, 0.464; P_D, 10; η, 7.34(±2.99)
and with the LDR equation:

$$\log k_X = -4.59(\pm 0.722)\sigma_{lX} + 1.028(\pm 0.108) \qquad (29)$$

$100r^2$, 85.22; F, 40.38; S_{est}, 0.220; $S°$, 0.436; $100r^2$, 98.94; F, 654.4; S_{est}, 0.108; $S°$, 0.117; N_{dp}, 9; N_{df}, 7; N_{iv}, 1; $r_{df/iv}$, 7.00.
Clearly, results with the CR equation are superior.

4-Substituted 2-*endo*-norbornyl tosylates, **9**, in 80% aqueous v/v EtOH at various temperatures (set NBL43), where X = H, CH_2OAc, CH_2Cl, CH_2OTs, CO_2Me, OAc, Cl, CN, CH_2OH, gave with the LDRT equation:

$$\log k_X = -3.82(\pm 0.137)\sigma_{lX} - 54.4(\pm 1.87)\tau + 16.6(\pm 0.522) \qquad (30)$$

$100R^2$, 97.95; A$100R^2$, 97.85; F, 454.7; S_{est}, 0.0618; $S°$, 0.154; N_{dp}, 25; N_{df}, 22; N_{iv}, 2; $r_{df/iv}$, 11.0; $r_{l\tau}$, 0.792
and with the LDR equation at 70 °C (set NBL43A) gave:

$$\log k_X = -4.38(\pm 0.225)\sigma_{lX} + 0.912(\pm 0.0716) \qquad (31)$$

$100r^2$, 98.18; F, 378.0; S_{est}, 0.117; $S°$, 0.153; N_{dp}, 9; N_{df}, 7; N_{iv}, 1; $r_{df/iv}$, 7.00.
There is excellent agreement between Eqs (*30*) and (*31*).

5-*exo*-Substituted 2-*endo*-norbornyl tosylates, **10**, in 80% v/v aqueous EtOH at 70 °C (set NBL44A), where X = H, CH_2OH, Me, CH_2OAc, CH_2Br, CH_2OTs, CO_2Me, CH_2OMe, Cl, CN, gave with the CR equation on exclusion of the value for CH_2OH:

$$\log k_X = -\ 2.90(\pm 0.202)\sigma_{c14.3,X} - 3.20(\pm 1.77)\sigma_{eX} + 0.734(\pm 0.0603) \quad (32)$$

$100R^2$, 97.50; A$100R^2$, 97.14; F, 117.0; S_{est}, 0.103; $S°$, 0.194; N_{dp}, 9; N_{df}, 6; N_{iv}, 2; $r_{df/iv}$, 3.00; r_{ce}, 0.458; P_D, 14.3; η, 6.60(±3.63)
and with the LDR equation on exclusion of the value for H as well gave:

$$\log k_X = -2.74(\pm 0.130)\sigma_{lX} + 0.797(\pm 0.0406) \quad (33)$$

$100r^2$, 98.66; F, 442.0; S_{est}, 0.0660; $S°$, 0.134; n, 8.
With the LDRT equation set NBL44 gave:

$$\log k_X = -2.69(\pm 0.160)\sigma_{lX} - 53.6(\pm 3.23)\tau + 16.4(\pm 0.882) \quad (34)$$

$100R^2$, 93.94; A$100R^2$, 93.67; F, 162.8; S_{est}, 0.0972; $S°$, 0.263; N_{dp}, 24; N_{df}, 21; N_{iv}, 2; $r_{df/iv}$, 10.5; $r_{l\tau}$, 0.719
and with the CRT equation on the exclusion of the value for H:

$$\log k_X = -2.66(\pm 0.108)\sigma_{c10,X} - 5.25(\pm 0.693)\sigma_{eX} - 49.0(\pm 1.95)\tau + 15.0(\pm 0.536) \quad (35)$$

$100R^2$, 97.33; A$100R^2$, 97.08; F, 254.9; S_{est}, 0.0682; $S°$, 0.178; N_{dp}, 25; N_{df}, 21; N_{iv}, 3; $r_{df/iv}$, 7.00; r_{ce}, 0.359; $r_{c\tau}$, 0.723; $r_{e\tau}$, 0.297; P_D, 10; η, 17.8(±2.23).
There may be a borderline dependence on the delocalized effect in this set.

6-*exo*-Substituted 2-*endo*-norbornyl tosylates, **11**, in 70% aqueous dioxane at 70 °C (set **NBL45**), where X = H, CH_2OH, Me, OAc, CH_2Br, CH_2NH_2, CO_2H, $CONH_2$, Br, CN, NHAc, SMe, OMe, OH, NH_2, NMe_2, gave with the LDR equation:

$$\log k_X = -4.88(\pm 0.376)\sigma_{lX} - 1.08(\pm 0.272)\sigma_{dX} - 5.14(\pm 1.23)\sigma_{eX} + 1.74(\pm 0.123) \quad (36)$$

$100R^2$, 95.79; A$100R^2$, 95.14; F, 91.06; S_{est}, 0.229; $S°$, 0.237; N_{dp}, 16; N_{df}, 12; N_{iv}, 3; $r_{df/iv}$, 4.00; P_D, 18.1(±4.78); η, 4.77; r_{ld}, 0.116; r_{le}, 0.029; r_{de}, 0.615.

In 97% aqueous TFE at various temperatures (set NBL46), where X = H, Me, CH_2OH, CH_2OAc, CH_2Br, CH_2OTs, CO_2Me, $CONH_2$, OAc, Br, these compounds gave with the LDRT equation:

$$\log k_X = –6.26(\pm 0.194)\sigma_{lX} – 46.6(\pm 2.33)\tau + 15.3(\pm 0.648) \qquad (37)$$

$100R^2$, 97.50; $A100R^2$, 97.41; F, 525.5; S_{est}, 0.112; $S°$, 0.167; N_{dp}, 30; N_{df}, 27; N_{iv}, 2; $r_{df/iv}$, 13.5; $r_{l\tau}$, 0.703.

7-*anti*-Substituted 2-*endo*-norbornyl tosylates, **12**, in 80% v/v aqueous EtOH at various temperatures (set NBL47), where X = H, Me, CH_2OAc, CH_2Br, CO_2Me, CN, Cl, Br, gave with the LDRT equation:

$$\log k_X = –3.51(\pm 0.157)\sigma_{lX} – 1.03(\pm 0.236)\sigma_{dX} –$$

$$3.93(\pm 1.78)\sigma_{eX} – 49.0(\pm 3.03)\tau + 14.99(\pm 0.858) \qquad (38)$$

$100R^2$, 97.08; $A100R^2$, 96.49; F, 1 412; S_{est}, 0.0899; $S°$, 0.194; N_{dp}, 22; N_{df}, 18; N_{iv}, 3; $r_{df/iv}$, 6.00; r_{ld}, 0.001; r_{le}, 0.262; r_{τ}, 0.784; r_{de}, 0.803; $r_{d\tau}$, 0.105; $r_{e\tau}$, 0.227; P_D, 22.7(±5.39); η, 3.81(±1.49)
and in 97% aqueous TFE at various temperatures (set NBL48), where X = H, Me, CH_2Br, CO_2Me, CN, Br, Cl, gave with the LDRT equation:

$$\log k_X = –4.10(\pm 0.386)\sigma_{lX} – 1.02(\pm 0.257)\sigma_{dX} –$$

$$36.2(\pm 5.91)\tau + 12.282(\pm 1.66) \qquad (39)$$

$100R^2$, 89.88; $A100R^2$, 88.53; F, 41.43.; S_{est}, 0.187; $S°$, 0.361; N_{dp}, 18; N_{df}, 14; N_{iv}, 3; $r_{df/iv}$, 4.67; r_{ld}, 0.081; $r_{l\tau}$, 0.131; P_D, 19.9(±5.33); η, 0.

6-*endo*-Substituted 2-*endo*-norbornyl tosylates, **13**, in 80% v/v aqueous EtOH at various temperatures (set NBL49), where X = H, Me, *t*-Bu, F, Br, CN, OH, OMe; on exclusion of the value for OH gave as the result of correlation with the LDRST equation using the υ parameters:

$$\log k = –4.73(\pm 0.597)\sigma_{lX} – 1.61(\pm 0.386)\sigma_{dX} –$$

$$0.556(\pm 0.234)\upsilon – 33.9(\pm 11.3)\tau + 11.0(\pm 3.09) \qquad (40)$$

$100R^2$, 88.52; $A100R^2$, 86.22; F, 26.98; S_{est}, 0.293; $S°$, 0.395; P_D, 25.4(±6.73); η, 0; N_{dp}, 19; N_{df}, 14; N_{iv}, 4; $r_{df/iv}$, 3.50; r_{ld}, 0.517; $r_{l\upsilon}$, 0.216; $r_{l\tau}$, 0.752; $r_{l\upsilon}$, 0.062; $r_{d\tau}$, 0.321; $r_{l\tau}$, 0.228, while on using the υ′ parameters the result is:

$$\log k = -4.51(\pm 0.110)\sigma_{\mathrm{lX}} - 1.87(\pm 0.0851)\sigma_{\mathrm{dX}} - 1.80(\pm 0.565)\sigma_{\mathrm{eX}} -$$

$$3.65(\pm 0.199)\upsilon' - 55.1(\pm 2.74)\tau + 16.99(\pm 0.754) \qquad (41)$$

$100R^2$, 99.50; A$100R^2$, 99.36; F, 515.8; S_{est}, 0.0635; S°, 0.0856; P_{D}, 29.3(±1.48); η, 0.963(±0.299); N_{dp}, 19; N_{df}, 13; N_{iv}, 5; $r_{\mathrm{df/iv}}$, 2.60; r_{ld}, 0.517; r_{le}, 0.280; $r_{\mathrm{l}\upsilon'}$, 0.420; $r_{\mathrm{l}\tau}$, 0.752; r_{de}, 0.067; $r_{\mathrm{d}\upsilon'}$, 0.295; $r_{\mathrm{d}\tau}$, 0.321; $r_{\mathrm{e}\upsilon'}$, 0.329; $r_{\mathrm{e}\tau}$, 0.121; $r_{\upsilon'\tau}$, 0.708.
The best results are obtained with υ′ as the steric parameter. The values of L and D in Eqs (*40*) and (*41*) are in very good agreement. Steric and delocalized electrical effects both make significant contributions in this system.

6-*exo*-Substituted 2-methyl-2-*exo*-norbornyl tosylates, **14**, in 80% v/v aqueous EtOH at various temperatures (set NBL21), where X = H, Me, iPr, CH_2Br, CO_2Me, OAc, CH_2OH, gave with the LDRT equation on exclusion of the value for CH_2OH:

$$\log k_{\mathrm{X}} = -7.54(\pm 0.731)\sigma_{\mathrm{lX}} - 61.0(\pm 5.45)\tau + 20.2(\pm 1.63) \qquad (42)$$

$100R^2$, 89.34; A$100R^2$, 88.67; F, 62.86; S_{est}, 0.179; S°, 0.358; N_{dp}, 18; N_{df}, 15; N_{iv}, 2; $r_{\mathrm{df/iv}}$, 7.50; $r_{\mathrm{l}\tau}$, 0.932,
while with the CRT equation:

$$\log k_{\mathrm{X}} = -6.99(\pm 0.594)\sigma_{\mathrm{c10,X}} - 8.85(\pm 1.48)\sigma_{\mathrm{eX}} -$$

$$55.8(\pm 4.56)\tau + 18.3(\pm 1.37) \qquad (43)$$

$100R^2$, 93.89; A$100R^2$, 93.07; F, 71.69; S_{est}, 0.140; S°, 0.280; N_{dp}, 18; N_{df}, 14; N_{iv}, 3; $r_{\mathrm{df/iv}}$, 4.67; r_{ce}, 0.233; $r_{\mathrm{c}\tau}$, 0.938; $r_{\mathrm{e}\tau}$, 0.272; P_{D}, 10; η, 11.4(±1.65).
Clearly, the CR equation gives best results.

6-*exo*-Substituted 2-methyl-2-*endo*-norbornyl tosylates, **15**, in 80% v/v aqueous EtOH various temperatures (set NBL61), where X = H, Me, iPr, CH_2Br, CO_2Me, OAc, CH_2OH, gave with the LDRT equation:

$$\log k_{\mathrm{X}} = -3.74(\pm 0.145)\sigma_{\mathrm{lX}} - 62.2(\pm 2.25)\tau + 17.8(\pm 0.591) \qquad (44)$$

$100R^2$, 98.29; A$100R^2$, 98.18; F, 402.3; S_{est}, 0.0558; S°, 0.144; N_{dp}, 17; N_{df}, 14; N_{iv}, 2; $r_{\mathrm{df/iv}}$, 7.00; $r_{\mathrm{l}\tau}$, 0.793.

Adamantyl Systems

3-Substituted 1-adamantyl bromides, **16**, in 80% aqueous dioxane at 100 °C (set ADM1), where X = $C_6H_4NO_2$-4′, CH_2Br, CH_2CO_2Me, CH_2CO_2H, $CH_2C_6H_4NO_2$-4′, CO_2Me, Br, H, gave with the LDR equation:

$$\log k_X = -5.82(\pm 0.610)\sigma_{lX} + 0.986(\pm 0.147) \qquad (45)$$

$100r^2$, 93.83; F, 91.20; S_{est}, 0.234; $S°$, 0.287; N_{dp}, 8; N_{df}, 6; N_{iv}, 1; $r_{df/iv}$, 6.00. In 80% aqueous EtOH at 75.0 °C (set ADM2), where X = H, Me, Et, iPr, *t*-Bu, Ph, CN, CO_2Me, **16** gave with the LDR equation:

$$\log k_X = -6.71(\pm 0.301)\sigma_{lX} + 1.167(\pm 0.0697) \qquad (46)$$

$100r^2$, 98.81; F, 498.3; S_{est}, 0.168; $S°$, 0.126; N_{dp}, 8; N_{df}, 6; N_{iv}, 1; $r_{df/iv}$, 6.00. In 80% v/v aqueous EtOH at various temperatures (set **ADM3**), where X = H, Me, Et, iPr, *t*-Bu, CH_2Br, CH_2OH, CH_2NH_2, $CMe{=}CH_2$, Ph, 4′-$MeOC_6H_4$, 4′-$O_2NC_6H_4$, OMe, OH, SMe, SH, NH_2, NMe_2, Br, CO_2H, $CONH_2$, CN, NO_2, **16** gave on correlation with the LDRT equation on exclusion of the values for OH, NH_2, and NMe_2:

$$\log k_X = -5.41(\pm 0.241)\sigma_{lX} - 44.7(\pm 3.02)\tau + 14.15(\pm 0.840) \qquad (47)$$

$100R^2$, 88.51; A$100R^2$, 88.26; F, 173.3; S_{est}, 0.200; $S°$, 0.350; N_{dp}, 48; N_{df}, 45; N_{iv}, 2; $r_{df/iv}$, 22.5; $r_{l\tau}$, 0.825.

3-Substituted 1-adamantyl tosylates, **17**, in 80% v/v aqueous EtOH at various temperatures (set **ADM4**), where X = H, Me, iPr, NO_2, Cl, CH_2OAc, CH_2OTs, CO_2Me, CN, CH_2OH, OAc, Br, OMe, gave with the LDRT equation on the exclusion of CH_2OH:

$$\log k_X = -5.66(\pm 0.509)\sigma_{lX} - 39.1(\pm 3.71)\tau + 15.6(\pm 1.27) \qquad (48)$$

$100R^2$, 81.54; A$100R^2$, 80.90; F, 61.85; S_{est}, 0.195; $S°$, 0.452; N_{dp}, 31; N_{df}, 28; N_{iv}, 2; $r_{df/iv}$, 14.0; $r_{l\tau}$, 0.792.

1-Substituted 2-adamantyl tosylates, **18**, in 80% v/v aqueous EtOH at 75 °C (set *ADM5*), where X = H, Me, Ph, 4′-MeOPn, 4′-$CF_3C_6H_4$, 4′-O_2NPh, Et, iPr, cPr, *t*-Bu, gave with the LDR equation on exclusion of the value for *t*-Bu:

$$\log k_X = -3.40(\pm 1.66)\sigma_{lX} - 10.2(\pm 2.22)\sigma_{dX} - 0.538(\pm 0.316) \qquad (49)$$

$100R^2$, 88.51; A$100R^2$, 86.59; F, 19.26; S_{est}, 0.353; $S°$, 0.429; N_{dp}, 8; N_{df}, 5; N_{iv}, 2; $r_{df/iv}$, 2.50; P_D, 75.0(±22.4); η, 0; r_{ed}, 0.392.

4-*exo*-Substituted 2-*exo*-adamantyl tosylates, **19**, in 80% v/v aqueous EtOH at various temperatures (set ADM6), where X = H, Me, CH_2Br, CO_2Me, CN, Br, Cl, $CONH_2$, CO_2H, CH_2OMe, CH_2OH, gave with the LDRT equation on the exclusion of CH_2OH:

$$\log k_X = -3.86\ (\pm 0.203)\sigma_{lX} - 51.4\ (\pm 3.09)\tau + 16.7(\pm 0.874) \qquad (50)$$

$100R^2$, 92.37; A$100R^2$, 92.12; F, 181.5; S_{est}, 0.122; $S°$, 0.290; N_{dp}, 33; N_{df}, 30; N_{iv}, 2; $r_{df/iv}$, 15.0; $r_{l\tau}$, 0.827.

Bicyclo[2.2.2]octanyl Systems

6-*exo*-Substituted 2-*exo*-bicyclo[2.2.2]octanyl tosylates, **20**, in 80% v/v aqueous EtOH at 70 °C (set BCO1), where X = H, Me, CH_2OMe, CH_2OAc, CH_2OTs, CO_2Me, CN, CH_2OH, gave with the LDR equation:

$$\log k_X = -5.95(\pm 0.727)\sigma_{lX} + 2.228(\pm 0.187) \qquad (51)$$

$100r^2$, 91.77; F, 66.93; S_{est}, 0.384; $S°$, 0.348; N_{dp}, 8; N_{df}, 6; N_{iv}, 1; $r_{df/iv}$, 6.00, while in 97% w/w aqueous TFE at 70 °C (set BCO2), where X = H, Me, CH_2OMe, CH_2OAc, CH_2OTs, CO_2Me, CN, **20** gave with the LDR equation:

$$\log k_X = -7.95(\pm 0.950)\sigma_{lX} + 3.315(\pm 0.258) \qquad (52)$$

$100r^2$, 93.34; F, 70.03; S_{est}, 0.472; $S°$, 0.305; N_{dp}, 7; N_{df}, 5; N_{iv}, 1; $r_{df/iv}$, 5.00.

6-*exo*-Substituted bicyclo[2.2.2]octan-2-*endo*-yl tosylates, **21**, in 80% v/v aqueous EtOH at 70 °C (set BCO11), where X = H, Me, CH_2OMe, CH_2OAc, CH_2OTs, CO_2Me, CN, CH_2OMe, gave with the CR equation:

$$\log k_X = -5.03(\pm 0.415)\sigma_{c14.3.X} + 2.555(\pm 0.109) \qquad (53)$$

$100r^2$, 96.07; F, 146.8; S_{est}, 0.225; $S°$, 0.229; N_{dp}, 8; N_{df}, 6; N_{iv}, 1; $r_{df/iv}$, 6.00. With the LDR equation on the exclusion of X = CH_2OH:

$$\log k_X = -5.41(\pm 0.452)\sigma_{lX} + 2.644(\pm 0.116) \qquad (54)$$

$100r^2$, 95.98; F, 143.3; S_{est}, 0.227; $S°$, 0.231; N_{dp}, 8; N_{df}, 6; N_{iv}, 1; $r_{df/iv}$, 6.00, while in 97% w/w aqueous TFE at 70 °C (set BCO12) with the CR equation:

$$\log k_X = -7.55(\pm 0.418)\sigma_{c10,X} - 8.89(\pm 3.47)\sigma_{eX} + 3.532(\pm 0.106) \quad (55)$$

$100R^2$, 99.13; A$100R^2$, 98.96; F, 228.4; S_{est}, 0.169; $S°$, 0.123; N_{dp}, 7; N_{df}, 4; N_{iv}, 2; $r_{df/iv}$, 2.00; $r_{c,e}$, 0.632; P_D, 10; η, 10.6(±4.09).

4-Substituted 1-bicyclo[2.2.2]octanyl 4-bromobenzenesulfonates, **22**, in AcOH at 74 °C (set BCO3), where X = H, Me, Et, iPr, *t*-Bu, CO_2Ak, CN, Ph, gave with the LDR equation:

$$\log k_X = -5.84(\pm 0.338)\sigma_{lX} + 0.691(\pm 0.0783) \quad (56)$$

$100r^2$, 98.03; F, 298.5; S_{est}, 0.189; $S°$, 0.162; N_{dp}, 8; N_{df}, 6; N_{iv}, 1; $r_{df/iv}$, 6.00.

4-Substituted 1-bicyclo[2.2.2]octanyl 4-nitrobenzenesulfonates, **23**, in 80% v/v aqueous EtOH at 75 °C (set **BCO4**), where X = H, Me, Et, iPr, *t*-Bu, $MeC{=}CH_2$, Ph, Me_2N, $NHCO_2Et$, OMe, CO_2Et, CN, Br, CO_2NH_2, CO_2Me, gave with the LDR equation:

$$\log k_X = -6.58(\pm 0.301)\sigma_{lX} + 3.412(\pm 0.0968) \quad (57)$$

$100r^2$, 98.07; F, 169.5; S_{est}, 0.202; $S°$, ?; N_{dp}, 14; N_{df}, 12; N_{iv}, 1; $r_{df/iv}$, 12.0.

Cycloalkane Systems

(*E*)-3-Substituted 1-cyclobutyl tosylates, **24**, in 80% aqueous v/v EtOH at 25.8 °C (set CA1), where X = H, Ph, $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$, *t*-Bu, iPr, OEt, Cl, gave with the LDR equation:

$$\log k_X = -7.84(\pm 1.05)\sigma_{lX} + 2.848(\pm 0.218) \quad (58)$$

$100r^2$, 90.33; F, 56.07; S_{est}, 0.456; $S°$, 0.359; N_{dp}, 8; N_{df}, 6; N_{iv}, 1; $r_{df/iv}$, 6.00; r_{ld}, 0.593; r_{le}, 0.012; r_{de}, 0.130.

(*Z*)-3-Substituted 1-cyclobutyl tosylates, **25**, in 80% aqueous v/v EtOH at 25.8 °C (set CA2), where X = H, Ph, $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$, *t*-Bu, iPr, OEt, Cl, gave with the LDR equation:

$$\log k_X = -6.26(\pm 0.849)\sigma_{lx} + 3.257(\pm 0.189) \quad (59)$$

$100r^2$, 91.59; F, 54.66; S_{est}, 0.347; $S°$, 0.343; N_{dp}, 8; N_{df}, 6; N_{iv}, 1; $r_{df/iv}$, 6.00; r_{ld}, 0.530; r_{le}, 0.235; r_{de}, 0.095.

For comparison purposes we have also examined the solvolyses of 4-substituted 2-chloro-2-methylbutanes, **26**, in 80% v/v aqueous EtOH at 60.00 °C (set **AC1**), where X = H, Me, Et, iPr, *t*-Bu, NO_2, MeS, Me_2N, OMe, CO_2Et, CN, Cl, CH_2Cl, gave with the LDR equation:

$$\log k_X = -3.39(\pm 0.149)\sigma_{lX} - 0.472(\pm 0.161)\sigma_{dX} - 0.699(\pm 0.656)\sigma_{eX} - 2.826(0.0524) \qquad (60)$$

$100R^2$, 98.07; A$100R^2$, ?; F, 227.5; S_{est}, 0.110; $S°$, 0.137; N_{dp}, 13; N_{df}, 9; N_{iv}, 3; $r_{df/iv}$, 3.00; r_{ld}, 0.154; r_{le}, 0.066; r_{de}, 0.511; P_D, 13.9 (±?); η, 0.

Delocalized Electrical Effects

Norbornyl systems. Delocalized (resonance) electrical effects occur at the 1, 5, 6, and 7 positions of the incipient 2-norbornyl carbocation in the *exo*-Lg series and probably in the *endo*-Lg series as well. *Exo* systems have larger *L* and *D* values (in magnitude) than do *endo* systems. There is no detectable delocalized electrical effect of substituents in the data sets for 4-substituted 2-*exo*-norbornyl tosylates, 4-substituted 2-*endo*-norbornyl tosylates, and 6-*exo*-substituted 2-*endo*-2-methylnorbornyl tosylates. This may well be due to the lack of strong electron donor groups in these sets.

Adamantyl systems. There is no detectable delocalized effect in 3-substituted 1-adamantyl tosylates and bromides and in 4-*exo*-substituted 2-*exo*-adamantyl tosylates. There is possible delocalization in 1-substituted 2-adamantyl tosylates.

Bicyclo[2.2.2]octyl systems. There is no detectable delocalized effect in 4-substituted 1-bicyclo[2.2.2]octanyl 4-bromobenzenesulfonates and 4-nitrobenzenesulfonates or in 6-*exo*-substituted 2-*exo*-bicyclo[2.2.2]octanyl tosylates. There may be delocalization in 6-*exo*-substituted 2-*endo*-bicyclo- [2.2.2]octanyl tosylates.

Cyclobutyl systems. There is no detectable delocalized effect in (*E*)-3-substituted 1-cyclobutyl and (*Z*)-3-substituted 1-cyclobutyl tosylates.

Acyclic systems. There is a significant delocalized effect in 4-substituted 2-chloro-2-methylbutanes.

Values of the composition of the electrical effect, P_D, and the electronic demand, η, with their standard errors are given for all the data sets studied in Table I. P_D is much less than that normally encountered in carbocation forming reactions in which the substituent is either directly bonded to positive carbon or conjugated with it. η values tend to be large indicating considerable electronic demand. *L* values seem to be a function of the distance between X and C^2. If this is the case then they behave like other molecular ionization (Mi) reactions.

L as a Function of *n*

We have shown that the dependence of substituent localized electrical effect transmission is best represented by a modified field effect model in which *L*, the coefficient of σ_1, is a function of r^{-m} where *r* is the distance between the substituent X and the closest atom of the reaction site Y as long as the angle θ formed by *r* and the XG bond (G is the skeletal group to which X and Y are bonded) is less than 45° (refs[13,14]). We have also shown that *n*, the number of bonds between X and Y, is a suitable measure of *r* and that *m* depends on the type of reaction. In order to compare solvolysis reactions previously discussed with those considered in this work we have correlated *L* values for the substituted 2-*exo*-norbornyl and 2-*endo*-norbornyl derivatives with the equations:

$$-L = \frac{a_1}{n^2} + a_2 \log k_{\mathrm{H}} + a_3 n_{\mathrm{Br}} + a_0 \qquad (61)$$

$$-L = \frac{a_1}{n} + a_2 \log k_{\mathrm{H}} + a_3 n_{\mathrm{Br}} + a_0 \qquad (62)$$

$$\log(-L) = a_1 \log n + a_2 \log k_{\mathrm{H}} + a_3 n_{\mathrm{Br}} + a_0 \,. \qquad (63)$$

In addition to the terms in *n* which account for the dependence of the *L* values on distance, log k_{H} was used to parameterize the reaction conditions and as the leaving group Lg was either OTs or Br, it was accounted for by the variable n_{Br} which takes the value 1 when Lg is Br and 0 when it is not. The results of the correlations for the 2-*exo* derivatives are:

$$-L = 26.1(\pm 4.27)/n^2 + 1.86(\pm 0.884)n_{\mathrm{Br}} + 2.97(\pm 0.684) \qquad (64)$$

$100R^2$, 90.40; A$100R^2$, 89.43; *F*, 42.35; S_{est}, 0.926; *S*°, 0.39; *n*, 12.

$$-L = 19.3(\pm 2.96)/n + 1.91(\pm 0.831)n_{\mathrm{Br}} - 0.225(\pm 1.10) \qquad (65)$$

$100R^2$, 89.30; A$100R^2$, 88.23; *F*, 37.57; S_{est}, 0.977; *S*°, 0.378; *n*, 12.

TABLE I
Values of n, P_D, and η

Set	G	n	i	j	Lg	Solvent	T, °C	P_D	S_{PD}	η	Sη
NBL1	Nbl	2	1	2x	OTs	80% AE	var	18.9	5.17	3.82	1.14
NBL1A	“	2	1	2x	OTs	“	70	25		3.49	1.41
NBL2	“	2	1	2x	OTs	AcOH	25	19.2	4.45	0	
NBL3	“	2	1	2x	Br	80% AE	25	28.8	7.65	0	
NBL4	“	2	1	2x	Br	20% AE	25	33.3		1.02	0.449
NBL5	“	3	4	2x	OTs	80% AE	var	0			
NBL5A	“	3	4	2x	“	“	70	0			
NBL6	“	4	5x	2x	“	“	var	23.8	4.38	6.74	Ind
NBL6A	“	4	5x	2x	“	“	70	21.4	8.07	6.54	Ind
NBL7	“	3	6x	2x	“	70% AD	70	14.1	4.91	4.41	0.630
NBL8	“	3	6x	2x	“	97% ATFE	var	14.3		13.3	1.88
NBL9	“	3	7a	“	“	80% AE	“	14.0	5.69	6.20	2.53
NBL10	“	3	7a	2x	“	97% ATFE	“	25		4.06	1.75
NBL11	“	3	6x	2x	“	“	“	19.9	5.33	0	
NBL21	“	3	6x	2x	“	80% AE	“	10		11.4	1.65
NBL41	“		1	2n	OTs	80% AE	“	10		10.2	1.69
NBL42	“		1	2n	“	AcOH	25	10		7.34	2.99
NBL43	“		4	2n	“	80% AE	70	0			
NBL43A	“		4	2n	“	80% AE	70	0			
NBL44	“		5x	2n	“	“	var	10		17.8	2.23
NBL44A	“		5x	2n	“	“	70	0			
NBL45	“		6x	2n	“	70% AD	“	18.1	4.78	4.77	
NBL46	“		6x	2n	“	97% ATFE	var	0			
NBL47	“		7a	2n	“	80% AE	“	22.7	5.39	3.81	1.99
NBL48	“		6n	2n	“	97% ATFE	“	19.9	5.53	0	
NBL49	“		6n	2n	“		“	25.4	6.78		
NBL61	“		6x	2n	“	80% AE	“	0			
CA1	cBu		(*E*)-3	1	“		25.8	0			
CA2	“		(*Z*)-3	1	“		“	0			

TABLE I
(*Continued*)

Set	G	*n*	*i*	*j*	Lg	Solvent	*T*, °C	P_D	S_{PD}	η	*S*η
ADM1	Adm	3	3	1	Br	80% AD	100	0	–	–	–
ADM2	“	3	3	1	“	80% AE	25.8	0	–	–	–
ADM3	“	3	3	1	“	“	var	0	–	–	–
ADM4	“	3	3	1	OTs	“	var	0	–	–	–
ADM5	“	2	1	2	“	80% AE	75	75.0	22.4	0	–
ADM6	“	3	4x	2x	“	“	var	0	–	–	–
BCO1	Bco	3	6x	2x	“	“	70	0	–	–	–
BCO2	“	3	6x	2x	“	97% ATFE	70	0	–	–	–
BCO3	“	4	4	1	OBs	AcOH	74	0	–	–	–
BCO4	“	4	4	1	ONs	80% AE	75	0	–	–	–
BOC11	“	3	6x	2n	OTs	80% AE	70	14.3	–	0	–
BOC12	“	3	6x	2x	“	97% ATFE	70	10	–	10.6	4.09
AC1	$(CH_2)_2CMe_2$	3	4	2	Cl	80% AE	60	13.9		0	

Abbreviations: G, skeletal group; *n*, number of bonds between X and the atom to which the leaving group is bonded; *i*, location of X; *j*, location of Lg; Lg, leaving group; AE, aqueous ethanol; AD, aqueous dioxane; ATFE, aqueous 1,1,1-trifluoroethanol; OTs, tosylate; OBs, 4-bromobenzenesulfonate; ONs, 4-nitrobenzenesulfonate; x, *exo*; n, *endo*; a, *anti*; var, various temperatures.
Sets 21 and 61 have a Me group in the 2 position. Sets in boldface are highly reliable.

$$\log(-L) = -1.15(\pm 0.148)\log n + 0.0978(\pm 0.0447)\, n_{Br} + 1.30(\pm 0.0681) \qquad (66)$$

$100R^2$, 92.28; A$100R^2$, 91.51; F, 53.79; S_{est}, 0.0503; $S°$, 0.321; n, 12.

These results show excellent agreement with those obtained previously for the solvolysis of XGCHLgMe, where Lg is Cl or $OC_6H_4NO_2$-4, and of $XGCMe_2Cl^{14}$.

Similarly for the 2-*endo* derivatives

$$-L = 15.4(\pm 2.57)/n^2 + 2.21(\pm 0.377) \qquad (67)$$

$100r^2$, 83.73; F, 36.02; S_{est}, 0.511; $S°$, 0.457; n, 9.

$$-L = 12.1(\pm 1.77)/n - 0.0355(\pm 0.640) \qquad (68)$$

$100r^2$, 87.09; F, 47.21; S_{est}, 0.455; $S°$, 0.407; n, 9.

$$\log(-L) = -1.07(\pm 0.157) \log n - 1.11(\pm 0.0747) \qquad (69)$$

$100r^2$, 86.96; F, 46.68; S_{est}, 0.0476; $S°$, 0.409; n, 9.
Again the results are in agreement with those obtained for other solvolysis reactions. It must be noted that in the correlation with Eqs (*61*)–(*63*) it is assumed that most of the positive charge on carbon in the transition state is located at position 2.

D as a Function of *n*

We have also reported that, when P_D is approximately constant D, the coefficient of σ_d is a function of n^{-m}. Correlating D values for 2-*exo*-norbornyl derivatives, for which the mean value of P_D for those data sets in which a delocalized effect was found is 21.5(±6.03), with equations of the same type as Eqs (*61*)–(*63*) gives:

$$-D = 7.22(\pm 2.98)/n^2 + 2.59(\pm 0.610)n_{Br} + 0754(\pm 0.490) \qquad (70)$$

$100R^2$, 85.16; A$100R^2$, 83.51; F, 22.96; S_{est}, 0.674; $S°$, 0.452; n, 11.

$$-D = 5.54(\pm 2.33)/n + 2.61(\pm 0.612)n_{Br} - 0.237(\pm 0.893) \qquad (71)$$

$100R^2$, 84.88; A$100R^2$, 83.20; F, 22.46; S_{est}, 0.680; $S°$, 0.456; n, 11.

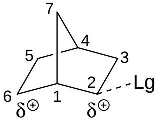
$$\log(-D) = -1.03(\pm 0.417) \log n + 0.335(\pm 0.126)n_{Br} + 0.683(\pm 0.192) \qquad (72)$$

$100R^2$, 75.96; A$100R^2$, 73.28; F, 12.64; S_{est}, 0.142; $S°$, 0.575; n, 11.

The results are in reasonable agreement with those for the transmission of the localized effect. There is no significant difference between the fit in Eqs (*70*) and (*71*) but Eq. (*72*) is significant and gives *m* equal to –1.

L as a Function of the Transition State Charge Distribution

The distance *r* between X^i and C^2 is given approximately by *n*, the number of bonds separating them. *i* is the number of the C atom to which X is bonded. The closer the substituent is to a major charge the smaller the value of *L* will be. We can predict the sequence of *L* values from this. Thus, for the classical carbocationic transition state, **27**, the predicted order of *L* is $L^1 \approx L^3 > L^4 \approx L^6 \approx L^7 > L^5$, the observed orders with *exo*-Lg are $L^1 \approx L^6 > L^4 \approx L^7 > L^5$, and with *endo*-Lg are $L^1 > L^6 \approx L^4 \approx L^7 > L^5$.



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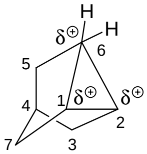

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For the norbornyl nonclassical carbocationic transition state, **28**, the predicted order is $L^1 \approx L^6 > L^3 \approx L^5 \approx L^7 > L^4$ while the observed order with *exo*-Lg is $L^1 \approx L^6 > L^4 \approx L^7 > L^5$, and for *endo*-Lg is $L^1 > L^6 \approx L^4 \approx L^7 > L^5$. It is clear that the classical carbocationic transition state is in better agreement with the observed order of *L* values than is the nonclassical carbocationic transition state. There is no question at this time that the thermodynamically stable structure of the norbornyl carbocation is nonclassical[15]. We can only account for the substituent effects in terms of a kinetically preferred classical transition state forming an ion that is rapidly converted to the stable nonclassical structure.

Delocalized Effects in Saturated Systems

Substituents bonded to sp^3 hybridized carbon atoms have long been known to exhibit delocalized effects. It is this that accounts for the significant delocalized electron donor effect of alkyl groups bonded to sp^2 hybridized carbon. Correlation of the dipole moments of MeX and *t*-BuX shows a significant dependence on the delocalized effect[16]. The localized and delocalized effects combine to produce a charge on X which is then transmitted by a modified field effect to the carbon atom to which the leaving group is bonded. As expected, P_D values are much less when the substituent is bonded to sp^3 carbon than when it is bonded to sp^2 carbon.

CONCLUSION

Detectable delocalized (resonance) electrical effects occur in saturated systems when the electronic demand of the reaction site is large enough. The electrical effect is transmitted by a modified field effect, its dependence on distance being a function of n^{-m} where n is a measure of the distance between the substituent and reaction site.

Solvolysis of 2-norbornyl derivatives according to our results involves a classical carbocationic transition state in the rate-determining step, the product undergoes rapid change to the stable nonclassical carbocation which then undergoes rapid reaction to form products. The transition state is further along the reaction coordinate in the *exo* series than it is in the *endo* series.

APPENDIX

Data Sets Used in the Correlations

NBL1. 1-Substituted 2-*exo*-norbornyl tosylates in 80% v/v aqueous EtOH at various temperatures[17]. X, 10^5 k_1, T (°C): H, 2 620, 70.00; Me, 16.1, 0.36; 61.5, 10.03; 217, 20.15; CH$_2$OH, 11.9, –0.51; 47.0, 9.16; 207, 20.57; CH$_2$OAc, 13.6, 30.08; 46.7, 40.04; 143, 50.06; CH$_2$Cl, 31.1, 40.25; 93.7, 50.10; 273, 60.05; CH$_2$OTs, 19.6, 49.99; 59.3, 60.00; 186, 69.99; CO$_2$Me, 13.0, 80.34; 34.1, 90.10; 85.9, 100.00; Ac, 16.0, 60.00; 46.0, 70.00; 128, 80.33; OAc, 7.32, 69.81; 7.45, 70.02; 328, 109.98; CN, 1.27, 119.75; 3.16, 129.84; 7.83, 139.96.

NBL1A. 1-Substituted 2-*exo*-norbornyl tosylates in 80% v/v aqueous EtOH at 70 °C (ref.[17]). X, 10^5 k_1: H, 2 620; Me, 41 300; CH$_2$OH, 43 200; CH$_2$OAc, 1 150; CH$_2$Cl, 738; CH$_2$OTs, 183; CO$_2$Me, 4.39; Ac, 16.0; OAc, 7.45; Br, 0.380; CN, 0.00584.

NBL2. 1-Substituted 2-*exo*-norbornyl tosylates in AcOH at 25 °C (ref.[18]). X, 10^5 k_1: H, 2.40; OMe, 2.98; Me, 125; Et, 187; Ph, 9.55; 4; –O$_2$NC$_6$H$_4$, 0.780; 4′-ClC$_6$H$_4$, 6.68; 4′-MeC$_6$H$_4$, 15.8; 4′-MeOC$_6$H$_4$, 18.8; 6′-MeOC$_6$H$_4$, 9.66; cHx, 3.51.

NBL3. 1-Substituted 2-*exo*-norbornyl bromides in 80% v/v aqueous EtOH at 25 °C (ref.[19]). X, 10^7 k_1: H, 11; OAc, 0.023; CO$_2$Me, 0.0054; NHBz, 12; NH$_2$, 510; Me, 1 850; Ph, 33.

NBL4. 1-Substituted 2-*exo*-norbornyl bromides in 20% v/v aqueous EtOH at 25 °C (ref.[20]). X, 10^6 k_1: H, 3 100; CO$_2$Me, 0.194; CN, 0.000665; CH$_2$OH, 6.19; CF$_3$, 0.0125; Me, 96 000; Ph, 36 000.

NBL5. 4-Substituted 2-*exo*-norbornyl tosylates in 80% v/v aqueous EtOH at various temperatures[21]. X, 10^5 k_1, T (°C): H, 2 620, 70.00; CH$_2$OH, 56.2, 40.01; 175, 50.02; 484, 60.03; CH$_2$OAc, 50.1, 50.11; 142, 59.97; 382, 69.99; CH$_2$Cl, 40.8, 50.01; 116, 59.97; 298, 69.67; CH$_2$OTs, 19.9, 50.69; 57.0, 60.31; 150, 69.98; CO$_2$Me, 21.5, 61.04; 55.6, 69.95; 145, 79.95;

OAc, 23.6, 70.13; 65.3, 80.08; 166, 90.04; CN, 21.0, 90.03; 53.2, 100.17; 123, 110.17; Cl, 26.4, 79.99; 68.4, 90.06; 162, 99.92.

NBL5A. 4-Substituted 2-*exo*-norbornyl tosylates in 80% v/v aqueous EtOH at 70 °C (ref.[21]). X, 10^5 k_1: H, 2 620; $\mathrm{CH_2OH}$, 1 300; $\mathrm{CH_2OAc}$, 383; $\mathrm{CH_2Cl}$, 309; $\mathrm{CH_2OTs}$, 151; $\mathrm{CO_2Me}$, 55.0; OAc, 23.4; Cl, 9.88; CN, 2.97.

NBL6. 5-*exo*-Substituted 2-*exo*-norbornyl tosylates in 80% v/v aqueous EtOH at various temperatures[21]. X, 10^5 k_1, T (°C): H, 2 620, 70.00; Me, 63.1, 40.22; 477, 51.10; 4 750, 90.09; $\mathrm{CH_2OH}$, 49.9, 49.81; 146, 59.44; 413, 70.00; $\mathrm{CH_2OAc}$, 16.5, 51.38; 389, 59.44; 121, 70.00; $\mathrm{CH_2OTs}$, 45.0, 70.00; 125, 79.93; 317, 90.12; $\mathrm{CO_2Me}$, 35.8, 70.00; 101, 79.93; 259, 90.12; CN, 31.8, 100.02; 75.6, 110.02; 166, 120.01; Cl, 52.5, 90.09; 123, 99.68; 283, 109.97; $\mathrm{CH_2OMe}$, 97.9, 59.44; 280, 70.00; 722, 79.92; $\mathrm{CH_2Br}$, 91.9, 70.00; 240, 79.93; 572, 90.12.

NBL6A. 5-*exo*-Substituted 2-*exo*-norbornyl tosylates in 80% v/v aqueous EtOH at 70 °C (ref.[21]). X, 10^5 k_1: H, 2 620; $\mathrm{CH_2OH}$, 413; $\mathrm{CH_2OAc}$, 121; Me, 1 190; $\mathrm{CH_2OTs}$, 45.0; $\mathrm{CO_2Me}$, 35.8; Cl, 7.92; CN, 1.87; $\mathrm{CH_2OMe}$, 280; $\mathrm{CH_2Br}$, 91.9.

NBL7. 6-*exo*-Substituted 2-*exo*-norbornyl tosylates in 70% v/v aqueous dioxane at 70.0 °C (ref.[22]). X, 10^4 k_1: H, 358; Me, 109; $\mathrm{CH_2Br}$, 1.06; $\mathrm{CO_2H}$, 0.0597; $\mathrm{CO_2Me}$, 0.0633; Br, 0.00151; CN, 0.00123; $\mathrm{CH_2NH_2}$, 88.4; $\mathrm{CH_2OH}$, 59.7; $\mathrm{CONH_2}$, 0.756; NHAc, 2.21; SMe, 3.34; OMe, 2.88; OH, 6.05; $\mathrm{NH_2}$, 225; $\mathrm{NMe_2}$, 1450; OAc, 0.00814.

NBL8. 6-*exo*-Substituted 2-*exo*-norbornyl tosylates in 97% w/w aqueous 1,1,1-trifluoroethanol at various temperatures[23]. X, 10^5 k_1, T (°C): H, 54.2, 5.00; 172, 15.00; 492, 25.00; $\mathrm{CH_2OAc}$, 44.5, 59.92; 119, 70.05; 298, 80.20; $\mathrm{CH_2Br}$, 71.4, 70.00; $\mathrm{CH_2OTs}$, 13.3, 70.00; $\mathrm{CO_2Me}$, 55.4, 99.90; 130, 109.90; 285, 120.00; Br, 4.14, 110.00; 6.46, 115.07; 10.0, 120.10.

NBL9. 7-*anti*-Substituted 2-*exo*-norbornyl tosylates in 80% v/v aqueous EtOH + 1.1 equivalent $\mathrm{Et_3N}$ at various temperatures[24]. X, 10^5 k_1, T (°C): H, 3 580, 70.00; Me, 55.1, 30.05; 184, 40.04; 512, 50.06; $\mathrm{CH_2OAc}$, 40.8, 49.55; 121, 59.72; 331, 69.95; $\mathrm{CH_2Br}$, 126, 64.93; 319, 75.08; 754, 85.15; Cl, 106, 90.17; 249, 99.75; 565, 109.80; $\mathrm{CO_2Me}$, 11.6, 49.55; 34.6, 59.76; 94.4, 69.94; CN, 37.8, 99.40; 87.2, 109.48; 201, 119.84; Br, 83.4, 89.86; 186, 99.40; 401, 109.48.

NBL10. 7-*anti*-Substituted 2-*exo*-norbornyl tosylates in 97% w/w aqueous 1,1,1-trifluoroethanol at various temperatures[23]. X, 10^5 k_1, T (°C): H, 28 000, 70.00; Me, 57.1, 0.00; 904, 25.55; 2 100, 34.95; $\mathrm{CH_2OAc}$, 1 240, 70.00; $\mathrm{CH_2Br}$, 800, 70.00; $\mathrm{CO_2Me}$, 307, 70.00; CN, 23.8, 99.98; 77.0, 115.08; 112, 120.04; Br, 51.4, 70.00; Cl, 61.1, 70.00.

NBL11. 6-*endo*-Substituted 2-*exo*-norbornyl tosylates in 80% v/v aqueous EtOH at various temperatures[25]. X, 10^5 k_1, T (°C): H, 3 580, 70.00; Me, 205, 60.00; 547, 69.75; 1 390, 79.78; iPr, 14.1, 39.40; 50.6, 50.35; 152, 60.00; *t*-Bu, 55.6, 60.50; 149, 39.00; 504, 223; $\mathrm{CH_2Br}$, 153, 89.70; 330, 99.00; 721, 109.40; F, 3.51, 110.22; 8.17, 119.31; 20.3, 129.38; Br, 3.45, 119.97; 8.32, 130.00; 19.0, 139.75; CN, 1.07, 120.00; 2.57, 130.00; 6.65, 139.50; $\mathrm{CO_2Me}$, 30.2, 60.20; 81.2, 69.80; 203, 79.20; OAc, 15.4, 80.32; 39.4, 90.17; 92.3, 99.95; $\mathrm{CH_2NH_2}$, 60.2, –20.00; 173, –10.13; 499, 0.07; OH, 23.8, 49.78; 72.0, 59.59; 202, 70.15; OMe, 8.93, 59.91; 27.6, 70.01; 79.5, 80.17; $\mathrm{NO_2}$, 8.40, 100.00; 20.1, 110.00; 45.2, 120.00.

NBL21. 6-*exo*-Substituted 2-*exo*-2-methylnorbornyl tosylates in 80% v/v aqueous EtOH at various temperatures[26]. X, 10^5 k_1, T (°C): H, 16.8, 49.90; 53.1, 59.97; 153, 69.97; 2 700, 100.00; Me, 21.0, 49.97; 72.3, 60.02; 219,69.89; 4 770, 100.00; iPr, 32.9, 49.88; 111, 60.32; 337, 70.28; 6 350, 100.00; $\mathrm{CH_2Br}$, 26.4, 79.97; 80.0, 89.98; 215, 99.68; 223, 100.00; $\mathrm{CO_2Me}$, 39.8, 100.00; 104, 109.75; 246, 119.75; 628, 129.80; OAc, 5.75, 99.85; 5.86, 100.00; 98.1, 120.21; 118, 129.64; $\mathrm{CH_2OH}$, 37.5, 60.02; 120, 69.98; 364, 80.00; 2 780, 100.00.

NBL41. 1-Substituted 2-*endo*-norbornyl tosylates in 80% v/v aqueous EtOH at various temperatures[17]. X, 10^5 k_1, T (°C): H, 8.42, 70.00; Me, 27.7, 79.88; 72.8, 89.94; 183, 100.00; CH_2OAc, 13.6, 99.98; 33.9, 109.78; 83.0, 100.00; CH_2Cl, 8.42, 99.86; 21.2, 109.94; 51.0, 119.90; CH_2OTs, 9.90, 109.91; 24.1, 119.97; 57.1, 130.04; CO_2Me, 4.89, 110.08; 10.2, 118.63; 26.4, 129.89; Br, 1.21, 124.47; 1.85, 129.81; 2.84, 135.04.

NBL41A. 1-Substituted 2-*endo*-norbornyl tosylates in 80% v/v aqueous EtOH at 70 °C (ref.[17]). X, 10^5 k_1: H, 8.42; Me, 10.1; CH_2OAc, 0.604; CH_2Cl, 0.391; CH_2OTs, 0.168; CO_2Me, 0.0891; Br, 0.00484.

NBL42. 1-Substituted 2-*endo*-norbornyl tosylates in AcOH at 25 °C (ref.[18]). X, 10^8 k_1: H, 8.14; OMe, 0.482; Me, 9.46; Et, 9.20; Ph, 5.66; 4′-$O_2NC_6H_4$, 0.418; 4′-ClC_6H_4, 1.89; 4′-MeC_6H_4, 5.40; 4′-$MeOC_6H_4$, 6.22; 6′-$MeoC_6H_4$, 4.89; cHx, 73.2.

NBL43. 4-Substituted 2-*endo*-norbornyl tosylates in 80% v/v aqueous EtOH at various temperatures[21]. X, 10^5 k_1, T (°C): H, 8.42. 70.00; CH_2OH, 13.2, 79.98; 35.6, 90.05; 90.2, 99.94; CH_2OAc, 4.50, 80.20; 11.9, 90.04; 31.4, 100.06; CH_2Cl, 9.09, 90.11; 22.9, 100.06; 55.7, 110.13; CH_2OTs, 12.3, 99.98; 30.3, 109.97; 72.4, 120.02; CO_2Me, 19.1, 109.95; 46.0, 120.05; 107, 130.07; OAc, 8.97, 110.03; 21.7, 120.05; 107, 130.01; CN, 4.30, 119.92; 6.71, 125.03; 10.1, 129.97; Cl, 3.91, 109.97; 9.27, 120.03; 21.2, 130.61.

NBL43A. 4-Substituted 2-*endo*-norbornyl tosylates in 80% v/v aqueous EtOH at 70 °C (ref.[21]). X, 10^5 k_1: H, 8.42; CH_2OH, 4.64; CH_2OAc, 1.51; CH_2Cl, 1.99; CH_2OTs, 0.592; CO_2Me, 0.345; OAc, 0.156; CN, 0.0299; Cl, 0.0750.

NBL44. 5-*exo*-Substituted 2-*endo*-norbornyl tosylates in 80% v/v aqueous EtOH at various temperatures[21]. X, 10^5 k_1, T (°C): H, 8.42. 70.00; Me, 17.7, 80.28; 49.1, 90.39; 111, 99.93; CH_2OH, 35.4, 89.86; 88.9, 99.92; 202, 109.97; CH_2OAc, 16.2, 88.89; 39.7, 99.28; 96.4, 109.41; CH_2OTs, 7.95, 89.90; 17.3, 99.29; 42.3, 440.46; CO_2Me, 18.4, 99.30; 45.4, 109.55; 108, 119.67; CN, 7.89, 109.33; 18.7, 119.54; 43.0, 129.75; Cl, 10.7, 109.92; 24.1, 119.87; 49.2, 129.00; CH_2OMe, 27.7, 90.02; 63.9, 99.32; 152, 109.52; CH_2Br, 28.9, 100.55; 65.5, 109.96; 145, 120.05.

NBL44A. 5-*exo*-Substituted 2-*endo*-norbornyl tosylates in 80% v/v aqueous EtOH at 70 °C (ref.[21]). X, 10^5 k_1: H, 8.42; CH_2OH, 5.22; CH_2OAc, 2.15; CH_2OTs, 1.30; CH_2OMe, 3.98; CH_2Br, 1.63; CO_2Me, 1.01; Me, 6.36; CN, 0.172; Cl, 0.304.

NBL45. 6-*exo*-Substituted 2-*endo*-norbornyl tosylates in 70% v/v aqueous dioxan at 70.0 °C (ref.[22]). X, 10^6 k_1: H, 84.2; Me, 60.2; CH_2Br, 6.75; CO_2Me, 0.0633; CO_2H, 0.0597; Br, 0.406; CN, 0.140; CH_2NH_2, 37.3; CH_2OH, 43.9; $CONH_2$, 7.12; NHAc, 10.7; SMe, 20.9; OMe, 42.9; OH, 100; NH_2, 255; NMe_2, 62.5; OAc, 1.21.

NBL46. 6-*exo*-Substituted 2-*endo*-norbornyl tosylates in 97% w/w aqueous 1,1,1-trifluoroethanol at various temperatures[23]. X, 10^5 k_1, T (°C): H, 5.71, 68.86; 149, 79.86; 334, 90.00; Me, 21.5, 59.82; 150, 79.92; CH_2OH, 17.2, 70.00; 172, 100.01; 388, 110.17; 674, 120.07; CH_2OAc, 47.7, 100.14; 113, 110.17; 251, 120.21; CH_2Br, 27.5, 100.17; 64.6, 110.10; 141, 120.13; CH_2OTs, 15.9, 100.13; 38.1, 110.19; 87.8, 120.21; CO_2,Me, 6.24, 100.14; 15.4, 110.15; 37.2, 120.18; $CONH_2$, 15.6, 99.97; 37.1, 110.00; 86.1, 120.05; OAc, 4.32, 110.00; 6.63, 115.10; 9.77, 120.11; Br, 1.57, 110.15; 2.38, 115.20; 3.53, 120.13.

NBL46A. 6-*exo*-Substituted 2-*endo*-norbornyl tosylates in 97% w/w aqueous 1,1,1-trifluoroethanol at 70 °C (ref.[23]). X, 10^5 k_1: H, 6.34; Me, 59.3; CH_2OH, 17.2; CH_2OAc, 2.77; CH_2Br, 1.65; CH_2OTs, 0.850; CO_2Me, 0.289; $CONH_2$, 0.840; OAc, 0.108; Br, 0.373.

NBL47. 7-*anti*-Substituted 2-*endo*-norbornyl tosylates in 80% v/v aqueous EtOH + 1.1 equivalent Et_3N at various temperatures[24]. X, 10^5 k_1, T (°C): H, 8.42, 70.00; Me, 28.4, 79.87; 74.0, 90.01; 173, 99.29; CH_2OAc, 8.66, 69.69; 20.8, 98.89; 49.9, 109.05; CH_2Br, 15.5, 99.44;

38.7, 109.62; 92.2, 119.73; CO_2Me, 5.87, 99.47; 15.0, 109.58; 36.3, 119.57; CN, 1.84, 109.52; 4.38, 119.57; 10.3, 129.88; Br, 7.20, 109.52; 17.3, 119.65; 39.4, 129.70.

NBL48. 7-*anti*-Substituted 2-*endo*-norbornyl tosylates in 97% w/w aqueous 1,1,1-trifluoroethanol at various temperatures[23]. X, 10^5 k_1, T (°C): H, 63.4, 70.00; Me, 109, 70.00; CH_2Br, 3.10, 70.00; 29.8, 94.98; 69.3, 105.07; 150, 115.09; Cl, 7.74, 100.00; 18.4, 110.02; 45.4, 120.50; CO_2Me, 11.9, 100.03; 29.1, 110.20; 45.8, 115.08; 72.7, 120.10; CN, 2.20, 115.08; 2.96, 120.23; 5.98, 130.12; Br, 6.17, 100.03; 23.3, 115.09; 34.2, 120.04.

NBL49. 6-*endo*-Substituted 2-*endo*-norbornyl tosylates in 80% v/v aqueous EtOH at various temperatures[25]. X, 10^5 k_1, T (°C): H, 24.1, 79.12; 59.6, 89.77; 142, 119.86; Me, 23.9, 99.80; 60.0, 110.00; 139, 119.86; *t*-Bu, 39.9, 100.00; 93.9, 110.00, 223, 120.00; F, 4.98, 125.31; 7.28, 130.33; 106, 135.33; Br, 0.831, 125.00; 1.79, 135.00; 2.92, 139.60; CN, 0.599, 140.00; OH, 14.5, 54.81; 42.6, 64.77; 123, 74.86; OMe, 9.75, 99.91; 24.7, 109.47; 58.4, 120.05.

NBR61. 6-*exo*-Substituted 2-*endo*-2-methyl norbornyl tosylates in 80% v/v aqueous EtOH at various temperatures[26]. X, 10^5 k_1, T (°C): H, 16.8, 49.90; 53.1, 59.97; 153, 69.97; Me, 21.0, 49.97; 72.3, 60.02; 219, 69.89; iPr, 32.9, 49.88; 111, 60.32; 337, 70.28; CH_2Br, 15.9, 119.91; 37.8, 129.63; 99.2, 140.12; CO_2Me, 6.74, 119.85; 18.7, 130.04; 50.3, 140.22; OAc, 9.12, 129.65; 23.9, 139.91; CH_2OH, 28.7, 109.94; 74.8, 120.00; 174, 129.54.

ADM1. 3-Substituted 1-adamantyl bromides in 80% aqueous dioxane at 100 °C (ref.[27]). X, 10^5 k_1: 4′-$O_2NC_6H_4$, 0.389; CH_2Br, 0.464; CH_2CO_2Me, 2.19; CH_2CO_2H, 2.17; $CH_2C_6H_4NO_2$-4′, 1.43; CO_2Me, 0.218; Br, 0.013; H, 10.7.

ADM2. 3-Substituted 1-adamantyl bromides in 80% aqueous EtOH at 75.0 °C (ref.[28]). X, 10^5 k_1: H, 13.8; Me, 9.76; Et, 13.4; iPr, 19.3; *t*-Bu, 29.0; Ph, 2.39; CN, 0.00241; CO_2Me, 0.115.

ADM3. 3-Substituted 1-adamantyl bromides in 80% aqueous EtOH at various temperatures[29]. X, 10^5 k_1, T (°C): H, 7.16, 70.00; Me, 5.31, 70.00; Et, 7.28, 70.00; iPr, 10.9, 70.00; *t*-Bu, 16.6, 70.00; 45.8, 80.00; 116, 90.00; CH_2Br, 13.4, 110.0; 31.1, 120.0; 63.3, 130.0; CO_2H, 11.1, 120.0; 27.4, 130.0; 58.7, 140.0; Br, 5.57, 140.0; 12.0, 150.0; 24.3, 160.0; CN, 1.17, 135.0; 5.08, 155.0; NO_2, 0.556, 150.0; 4.13, 180.0; $CMe{=}CH_2$, 18.4, 90.0; 49.1, 100.0; 109, 110.0; Ph, 28.8, 100.0; 67.3, 110.0; 157, 120.0; SMe, 5.04, 100.0; 11.8, 110.0; 26.4, 120.0; OMe, 0.974, 70.0; OH, 3.37, 70.0; 25.1, 90.0; 65.1, 100.0; CH_2NH_2, 34.6, 90.0; 86.5, 100.0; 199, 110.0; $CONH_2$, 8.17, 110.0; 19.4, 120.0; 44.0, 130.0; CH_2OH, 31.1, 90.0; 78.4, 100.0; 183, 110.0; NH_2, 267, 70.0; NMe_2, 8 500; SH, 4.52, 110.0; 9.43, 120.0; 18.9, 130.0; 4′-HOC_6H_4, 23.2, 90.0; 57.8, 100.0; 136, 110.0; 4′-$MeOC_6H_4$, 16.8, 90.0; 39.9, 100.0; 93.3, 110.0; 4′-$H_2NC_6H_4$, 12.4, 80.0; 32.0, 90.0; 80.2, 100.0; 4′-$Me_2NC_6H_4$, 13.9, 80.0; 36.5, 90.0; 89.5, 100.0; 4′-$O_2NC_6H_4$, 14.5, 110.0; 34.2, 120.0; 76.1, 130.0.

ADM4. 3-Substituted 1-adamantyl tosylates in 80% aqueous EtOH at various temperatures[30]. X, 10^5 k_1, T (°C): H, 63.0, 9.45; 232, 20.00; 756, 30.00; Me, 50.3, 9.50; 187, 19.95; 592, 30.00; iPr, 27.4, 0.00; 109, 9.98; 386, 20.05; CH_2OAc, 36.6, 30.06; 116, 40.05; 323, 50.13; CH_2OTs, 29.9, 40.07; 91.9, 50.12; 255, 60.00; CH_2OH, 29.0, 10.00; 109, 20.00; 376, 30.00; CO_2Me, 31.2, 50.00; 92.1, 59.85; 260, 70.00; OAc, 35.3, 60.03; 99.4, 70.00; 261, 80.00; Cl, 6.04, 80.13; 151, 90.27; 334, 99.60; Br, 16.0, 70.00; CN, 44.2, 89.95; 104, 100.00; 229, 109.72; NO_2, 24.7, 100.05; 57.2, 110.13; 131, 120.28; OMe, 23.6, 20.00; 84.5, 30.00; 276, 40.00.

ADM5. 3-Substituted 1-adamantyl tosylates in 80% aqueous EtOH at 75.0 °C (ref.[31]). X, 10^4 k_1: H, 0.192; Me, 4.10; Ph, 1.64; 4′-$MeOC_6H_4$, 2.70; 4′-$CF_3C_6H_4$, 0.186; 4′-$O_2NC_6H_4$, 0.0790; Et, 12.3; iPr, 28.6; cPr, 8.32; *t*-Bu, 506.

ADM6. 4-*exo*-Substituted 2-*exo*-adamantyl tosylates in 80% aqueous v/v EtOH at various temperatures[32]. X, 10^5 k_1, T (°C): H, 46.8, 70.00; 138, 80.02; 375, 60.02; Me, 56.7, 70.00;

165, 80.00; 444, 90.00; CH_2OH, 22.7, 70.00; 66.8, 80.00; 188, 90.00; CH_2OMe, 35.0, 80.00; 97.8, 90.00; 265, 100.00; CH_2OAc, 12.6, 80.00; 37.5, 90.00; 98.4, 100.00; CH_2Br, 30.0, 90.00; 80.1, 100.00; 207, 110.00; CO_2H, 39.4, 100.00; 106, 110.01; 260, 119.92; CO_2Me, 39.4, 100.00; 72.8, 110.00; 177, 120.00; $CONH_2$, 31.0, 90.00; 85.5, 100.03; 203, 109.40; Cl, 28.6, 110.05; 72.9, 120.16; 169, 129.40; Br, 7.74, 100.30; 21.4, 110.74; 52.6, 120.60; CN, 1.49, 100.00; 12.5, 110.00; 30.3, 120.00; 73.5, 130.00.

BCO1. 6-*exo*-Substituted 2-*exo*-bicyclo[2.2.2]octanyl tosylates in 80% v/v aqueous EtOH at 70 °C (ref.[33]). X, 10^5 k_1: H, 370; Me, 223; CH_2OMe, 35.8; CH_2OAc, 7.91; CH_2OTs, 2.31; CO_2Me, 1.58; CN, 0.144; CH_2OH, 85.2.

BCO2. 6-*exo*-Substituted 2-*exo*-bicyclo[2.2.2]octanyl tosylates in 97% w/w aqueous 1,1,1-trifluoroethanol at 70 °C (ref.[33]). X, 10^5 k_1: H, 6 100; Me, 5 150; CH_2OMe, 248; CH_2OAc, 43.8; CH_2OTs, 7.83; CO_2Me, 4.65; CN, 0.168.

BCO3. 4-Substituted 1-bicyclo[2.2.2]octanyl brosylates in AcOH at 74 °C (ref.[28]). X, 10^5 k_1: H, 11.3; Me, 3.38; Et, 4.04; iPr, 4.75; *t*-Bu, 6.24; Ph, 0.874; CO_2Ac, 0.0789; CN, 0.0025.

BCO4. 4-Substituted 1-bicyclo[2.2.2]octanyl 4'-nitrobenzenesulfonates in 80% v/v aqueous EtOH at 75.00 °C (ref.[33]). X, 10^6 k_1: H, 4 620; Me, 4 790; Et, 1 300; iPr, 1 530; *t*-Bu, 1 850; $MeC{=}CH_2$, 487; Ph, 277; Me_2N, 74.0; $NHCO_2Et$, 18.0; OMe, 10.2; CO_2Et, 13.7; CN, 0.547; Br, 2.18; CO_2NH_2, 35.6; CO_2Me, 12.6.

BCO11. 6-*exo*-Substituted 2-*endo*-bicyclo[2.2.2]octanyl tosylates in 80% v/v aqueous EtOH at 70 °C (ref.[33]). X, 10^5 k_1: H, 370; Me, 418; CH_2OMe, 153; CH_2OAc, 43.2; CH_2OTs, 14.0; CO_2Me, 8.46; CN, 0.400; CH_2OH, 293.

BCO12. 6-*exo*-Substituted 2-*endo*-bicyclo[2.2.2]octanyl tosylates in 97% w/w aqueous 1,1,1-trifluoroethanol at 70 °C (ref.[33]). X, 10^5 k_1: H, 6 100; Me, 9 230; CH_2OMe, 1 270; CH_2OAc, 261; CH_2OTs, 74.7; CO_2Me, 44.5; CN, 0.477.

CA1. (*E*)-3-Substituted 1-cyclobutyl tosylates in 80% v/v aqueous EtOH at 25.8 °C (ref.[35]). X, 10^3 k_{rel}: H, 1; Ph, 200; 4-MeC_6H_4, 333; 4-ClC_6H_4, 90.9; *t*-Bu, 143; iPr, 333; OEt, 5.26; Cl, 0.0667.

CA2. (*Z*)-3-Substituted 1-cyclobutyl tosylates in 80% v/v aqueous EtOH at 25.8 °C (ref.[35]). X, 10^5 k_1: H, 1; Ph, 267; 4-MeC_6H_4, 400; 4-ClC_6H_4, 130; *t*-Bu, 800; iPr, 6 250; OEt, 43.5; Cl, 2.00.

AC1. 4-Substituted 2-chloro-2-methylbutanes in 80% v/v aqueous EtOH at various temperatures[36]. X, 10^5 k_1, T (°C): H, 10.4, 40.13; 30.5, 49.86; 86.9, 59.57; Me, 35.6, 52.05; 152, 66.00; 262, 71.90; Et, 8.75, 40.00; 52.5, 56.25; 251, 71.75; iPr, 47.2, 56.00; 337, 76.00; *t*-Bu, 21.2, 50.00; 60.8, 60.00; 164, 70.00; CH_2NMe_2, 18.7, 50.00; 54.5, 60.00; 157, 70.01; CH_2Cl, 21.4, 59.94; 52.6, 69.95; 118, 79.77; CH_2OH, 34.7, 50.10; 94.9, 59.94; 252, 70.00; CO_2Et, 23.2, 69.97; 61.8, 79.97; 153, 90.02; CO_2H, 35.0, 69.87; 86.2, 79.93; 202, 89.95; Cl, 6.18, 70.01; 16.6, 79.97; 41.5, 90.00; CN, 37.7, 100.07; 86.5, 110.00; 182, 119.55; NMe_2, 35.7, 56.00; 304, 76.00; NO_2, 0.242, 60.00; 7.84, 90.37; 20.2, 99.80; 56.2, 110.15; SMe, 7.55, 56.00; 21.7, 66.00; 58.8, 76.00; OMe, 10.4, 56.00; 30.5, 66.00; 85.7, 76.00; OH, 16.4, 52.05; 48.6, 62.00; 141, 71.90.

AC1A. 4-Substituted 2-chloro-2-methylbutanes in 80% v/v aqueous EtOH at 60.00 °C (ref.[36]). X, 10^6 k_1: H, 902; Me, 820; Et, 779; iPr, 712; *t*-Bu, 608; NO_2, 2.42; MeS, 116; Me_2N, 559; OMe, 161; CO_2Et, 84.1; CN, 8.38; Cl, 22.0; CH_2Cl, 216.

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