

## 95. Steric Effects on Reaction Rates

Part IX

### Force-Field Parameters for Bridgehead and Rigid Tertiary Carbenium Ions

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Molecular-mechanics calculations for strain of carbenium ions are tested using *Bentley's* unified reactivity scale for bridgehead solvolysis as reference. Excellent correlations are obtained for solvolytic bridgehead reactivity with the calculated steric-energy difference ( $\Delta E_{st}$ ) between substrate (R-H or R-OH) and cation ( $R^+$ ). After adjustment of appropriate force-field parameters, the approach is successfully extended to the rigid, but planar cations derived from structures **15–20**; however, the general set of parameters cannot be applied to highly strained systems such as the cation formed from **17**. With all of the 18 sets of parameters tested, the *2-endo*-norbornyl derivative **16** is adequately correlated, while the *exo* isomer **15** exhibits enhanced reactivity by a factor of *ca.*  $10^2$  to  $10^3$ .

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**Introduction.** – Solvolysis reactions occurring at bridgehead positions are mechanistically simple and homogeneous, since most of the potentially competing pathways are forbidden for structural reasons [1]. Solvolytic reactivity of bridgehead derivatives spans a range of 22 orders of magnitude. It is determined by the strain changes between the substrate RX and the respective carbenium ion  $R^+$ . *Gleicher* and *Schleyer* [2] developed a procedure for calculating these strain changes by molecular mechanics. They then correlated the steric-energy differences between bridgehead molecules and carbenium ions ( $\Delta E_{st}$ ) with the experimental rate constants for solvolysis ( $\log k$ ) within a limited rate range. This range was subsequently extended by *Bingham* and *Schleyer* [3]. For practical reasons, leaving groups of very different reactivity were used, chlorides ( $X = Cl$ ) or bromides ( $X = Br$ ) for the very reactive molecules [4] and *p*-toluenesulfonates ( $X = OTs$ ) or trifluoromethanesulfonates ( $X = OTf$ ) for the less reactive ones. Satisfactory correlations were obtained when  $\Delta E_{st}$  was plotted *vs.*  $\log k$  for solvolysis of series of compounds with identical leaving group. However, the slopes of the correlation lines were significantly different ( $X = Cl$ : 3.12;  $X = Br$ : 2.44;  $X = OTs$ : 1.11;  $X = OTf$ : 0.92) [3].

At that time, no force-fields were available for heteroatoms so that the strain calculations were performed with hydrocarbon models with  $\Delta E_{st}$  referring to  $E_{st}(R^+) - E_{st}(RH)$ . This simplified model is appropriate if no steric interactions occur between the leaving group and the rest of the molecule (*F*-strain). However, the steric requirements of chloride and sulfonate substituents are obviously different, and their omission could lead to systematic errors. Indeed, it was thought that the different slopes for different leaving groups in the strain-reactivity correlations mentioned above were due to *F*-strain [3].

We have recently reexamined the involvement of *F*-strain in bridgehead solvolysis [5] using *Allinger's* [6] MM2 program. The conclusion of our work was that within the series

of bridgehead derivatives, differential  $F$ -strain effects were small in comparison to  $\Delta E_{st}$ . Furthermore, when  $\log k$  for chloride and  $p$ -toluenesulfonate solvolysis was plotted vs.  $\Delta E_{st}$ , correlations of nearly identical slopes were obtained, and it was possible to correlate all of the data by one and the same equation.

The significance of these results is not entirely obvious. On the one hand, the force-field applied to carbenium ions (UNICAT 1) was a trial set of parameters and had not been extensively tested [5]. On the other hand, *Bingham* and *Schleyer* [3] had reported important variations of the  $k_{OTs}/k_{Br}$  rate ratios which are irreconcilable with our results. Fortunately, the leaving-group effect in bridgehead solvolysis has been reexamined experimentally. *Bentley* and *Roberts* [7] reported that for bridgehead derivatives, the rate ratios  $k_{Br}/k_{Cl}$ ,  $k_{OTs}/k_{Br}$ , and  $k_{OTf}/k_{OTs}$  are always constant and solvent-independent. On these grounds, a reactivity scale was established for bridgehead solvolysis, spanning a range of  $10^{22}$ .

The work of *Bentley* and *Roberts* [7] provides the experimental backup for our calculations. Since their reactivity scale has been developed independently from us, it provides a unique opportunity and at the same time a challenge for testing and/or improving the carbenium-ion force-field. Furthermore, once this reactivity scale can be reproduced by molecular-mechanics calculations, one can go further and examine mechanistically more complicated substrates by comparing their reactivity with the idealized bridgehead behavior.

**Results and Discussion.** – a) *The Bentley-Roberts Reactivity Scale.* *Bentley* and *Roberts* [7] reported rate constants for 19 compounds. One of them, the 1-nortricyclane

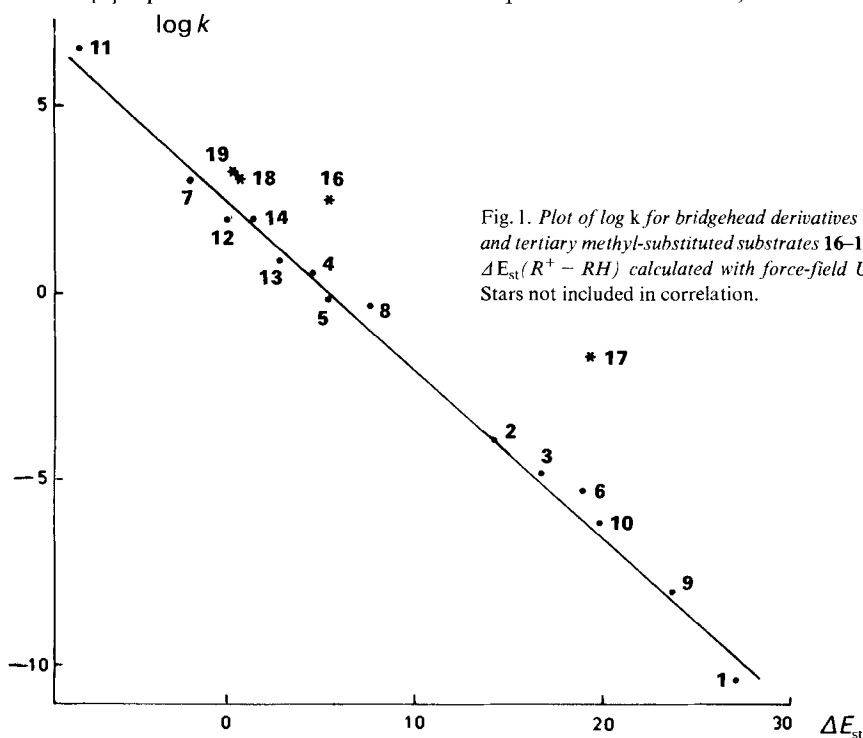


Fig. 1. Plot of  $\log k$  for bridgehead derivatives 1–14 (dots) and tertiary methyl-substituted substrates 16–19 (stars) vs.  $\Delta E_{st}(R^+ - RH)$  calculated with force-field UNICAT 1. Stars not included in correlation.

Table 1. Steric-Energy Difference  $\Delta E_{st}(R^+ - RX)$  and Reactivities ( $\log k$ ) of Tertiary Substrates

RX	Structure of $R^+$	$\Delta E_{st}(R^+ - RH)$	$\Delta E_{st}(R^+ - ROH)$	$\Delta E_{st}(R^+ - ROH)$	$\log k^a$ (X = OTs, 80% EtOH/70°)
		UNICAT 1	UNICAT 3	UNICAT 4	
1	1-Norbornyl	27.13	30.10	26.77	-10.40
2	1-Bicyclo[2.2.2]octyl	14.24	16.56	13.72	-4.00
3	1-Bicyclo[3.2.1]octyl	16.76			-5.17
4	1-Bicyclo[3.3.1]nonyl	4.50	6.39		0.51
5	1-Bicyclo[3.2.2]nonyl	5.43	5.89		-0.13
6	1-Noradamantyl	18.93			-5.28
7	1-Bicyclo[3.3.2]decyl	-1.97	-2.65	-3.93	3.08
8	1-Adamantyl	7.71	11.31	7.17	-0.40
9	7-Methyl-3-noradamantyl	23.55	24.43	22.45	-7.96
10	10-Tricyclo[5.2.1.0 <sup>4,10</sup> ]decyl	19.39	17.90	18.12	-6.16
11	1-Bicyclo[3.3.3]undecyl	-8.02	-9.55		6.44
12	3-Homoadamantyl	0.15	-		1.97
13	<i>t,t,t</i> -13-Tricyclo[7.3.1.0 <sup>5,13</sup> ]tridecanyl	18.18			0.85
14	<i>c,c,t</i> -13-Tricyclo[7.3.1.0 <sup>5,13</sup> ]tridecanyl	20.68			2.08
15	2-Methyl-2- <i>exo</i> -norbornyl	4.65	4.01	2.56	4.60
16	2-Methyl-2- <i>endo</i> -norbornyl	5.27	4.23	2.78	2.41
17	7-Methyl-7-norbornyl	19.64	16.50		-1.66
18	9-Methyl-9-bicyclo[3.3.1]nonyl	0.56	-0.88	-2.32	3.02
19	2-Methyl-2-adamantyl	0.43	-0.75	-2.37	3.23
20	2,7,7-Trimethyl-2- <i>endo</i> -norbornyl		-0.42		4.00

<sup>a</sup>) Data from [7] and Table 2.

derivative, requires a different type of force-field parameters than the others and was, therefore, not considered in this work. From the remaining series, 14 representative structures RX, *i.e.* 1–14 (see Table 1), were selected. The correlation of  $\log k$  vs.  $\Delta E_{st}(R^+ - RH)$  as calculated by UNICAT 1 [5] is characterized by Eqn. 1 (Fig. 1, Table 1).

$$\log k = -0.45 \Delta E_{st}(R^+ - RH) + 2.49 \quad r = 0.9964 \quad (1)$$

Comparison of this correlation with the previously reported one which is based on rates relative to 1-adamantyl [5] reveals a fit of about the same quality. Similarly, with OH as leaving-group model, the correlation is almost unchanged, except for the intercept (Eqn. 2).

$$\log k = -0.44 \Delta E_{st}(R^+ - ROH) + 1.44 \quad r = 0.9926 \quad (2)$$

The successful correlation of  $\Delta E_{st}$  with Bentley's rate constants should remove the principal objection one could raise against the empirical carbenium-ion force-field. Although straight-line behavior over such a large rate range might not necessarily be expected, it would be difficult to argue against it, once it is observed. At the present time, there appears to be no reason to manipulate the force-field such as to produce a non-linear rate-reactivity plot. However, the question will have to be reconsidered when more experimental data on carbenium-ion stabilities become available.

b) *Extension to Rigid, Methyl-Substituted Tertiary Cations.* The mechanistic homogeneity of bridgehead substrates in solvolysis reactions can be attributed to skeletal rigidity.

Table 2. Calculated Rate Constants ( $\log k_{\text{calc}}$ ) for Solvolysis of Tertiary Substrates for  $X = \text{OTs}$ , 80% EtOH/70°

RX	Structure of $R^+$	$\log k$	Conditions	$\log k_{\text{calc}}$ ( $X = \text{OTs}$ , 80% EtOH/70°)
15	2-Methyl-2- <i>exo</i> -norbornyl	-0.61 <sup>a)</sup>	$X = \text{Cl}$ , 80% EtOH/70°	4.60 <sup>b)</sup>
16	2-Methyl-2- <i>endo</i> -norbornyl	-6.77 <sup>c)</sup>	$X = \text{Cl}$ , EtOH/25°	2.41
17	7-Methyl-7-norbornyl	-11.72 <sup>d)</sup>	$X = \text{Cl}$ , EtOH/25°	-1.66
18	9-Methylbicyclo[3.3.1]nonyl	-6.68 <sup>e)</sup>	$X = \text{NO}_2\text{C}_6\text{H}_4\text{COO}$ , 80% acetone/70°	3.02
19	2-Methyl-2-adamantyl	-1.97 <sup>f)</sup>	$X = \text{Cl}$ , 80% EtOH/70°	3.23
20	2,7,7-Trimethyl-2- <i>endo</i> -norbornyl	-5.70 <sup>g)</sup>	$X = \text{NO}_2\text{C}_6\text{H}_4\text{COO}$ , 80% acetone/70°	4.00

<sup>a)</sup> Ref. [10].

<sup>b)</sup> Conversion factor  $1.6 \times 10^5$  [7].

<sup>c)</sup> Calc. from rel. rate of **15**, 25° [11].

<sup>d)</sup> Calc. from extrapolated constants in 80% acetone/25° ( $k = 9.09 \times 10^{-11}\text{s}^{-1}$ ) and rate of 1-adamantyl chloride ( $1.1 \times 10^{-1}\text{s}^{-1}$ ) [12]. Conversion from  $X = \text{OTs}$ , AcOH/70°, gives -2.42 [8].

<sup>e)</sup> Extrapolated from 125°, using  $k(\text{NO}_2\text{C}_6\text{H}_4\text{COO}(t\text{-Bu})) = 2.36 \times 10^{-5}\text{s}^{-1}$  [13].

<sup>f)</sup> From [8].

<sup>g)</sup> Extrapolated from 100° [13], using  $k(\text{NO}_2\text{C}_6\text{H}_4\text{COO}(t\text{-Bu})) = 1.85 \times 10^{-6}\text{s}^{-1}$ .

Backside attack is impossible, and competing elimination pathways (*E2*) are disfavored owing to inappropriate orientation of the developing p orbitals (*anti-Bredt* olefins). In a first step directed towards the generalization of our approach, it is desirable to select structures as close as possible to bridgehead compounds. This requirement is satisfied in the series of compounds **15–20** (see *Table 1* and *2*). The structures are rigid; however, one of the substituents, the  $\text{CH}_3$  group, is not tightened into the polycyclic framework so that the cation may adopt a planar conformation. A mechanistic complication arises owing to the presence of the  $\text{CH}_3$  substituent which allows competitive elimination in the rate-determining step. However, even if all elimination products obtained upon solvolysis of **17** and **19** (51–71 and 7–33%, resp.) [8] [9] are formed by an *E2* pathway, this will influence the rate constants for solvolysis only by a factor of 1–3. This is insignificant in view of the overall reactivity scale.

The rate constants for the non-bridgehead substrates **15–20** were converted to the *Bentley-Roberts* reactivity scale [7] as follows (see *Table 2*): Rate constants of chlorides (80% EtOH/70°) were converted to *p*-toluenesulfonates with the correction factor of  $1.6 \times 10^5$  [7]. Data of chlorides in 100% EtOH/25° were extrapolated to 80% EtOH/70° via the rate constants relative to *t*-BuCl ( $k = 9.70 \times 10^{-8}\text{s}^{-1}$  for EtOH/25° [14] and  $1.51 \times 10^{-3}\text{s}^{-1}$  for 80% EtOH/70°). A similar procedure was adopted for *p*-nitrobenzoate ( $X = \text{NO}_2\text{C}_6\text{H}_4\text{COO}$ ) derivatives. Rate constants relative to  $\text{NO}_2\text{C}_6\text{H}_4\text{COO}(t\text{-Bu})$  in 80% acetone were chosen at temperatures as close as possible to 70° and extrapolated to 70° via  $\text{NO}_2\text{C}_6\text{H}_4\text{COO}(t\text{-Bu})$  ( $k = 5.47 \times 10^{-8}$ , 80% acetone/70°) [10]. A factor of  $5.0 \times 10^9$  was used in order to convert these rates to those of OTs derivatives solvolyzing in 80% EtOH/70°. Values of  $\Delta E_{\text{st}}(R^+ - \text{RH})$  for **16–19** were calculated as for the bridgehead substrates using UNICAT 1 [5] (*Table 1*) and are included in *Fig. 1* (stars). All of the new compounds are more reactive than predicted by the force-field calculations and the most significant deviation occurs with the 7-methyl-7-norbornyl derivative **17**. Before invoking mechanistic arguments for these discrepancies, a reexamination of the force-field parameters for carbenium ions is necessary.

Table 3. Calculated Structural Data for Selected Tertiary Cations

		MM2	MINDO/3	STO-3G	4-31G
	C(1)–C(2)	1.485 Å	1.532 Å		1.513 Å
	C(1)–C(5)	1.475 Å	1.480 Å		1.457 Å
	C(2)–C(1)–C(5)	112.6°	114.3°		113.2°
	C(5)–C(1)–C(6)	104.1°	101.0°		102.2°
	D	0.484	0.487		0.489
	C(1)–C(2)	1.481 Å	1.511 Å	1.516 Å	1.478 Å
	C(1)–C(7)	1.475 Å	1.484 Å	1.510 Å	1.486 Å
	C(2)–C(1)–C(6)	116.8°	121.5°	120.1°	120.5°
	D	0.354	0.319	0.388	0.351
	C(1)–C(2)	1.482 Å	1.497 Å	1.502 Å	
	C(2)–C(1)–C(6)	117.1°	117.1°	117.2°	
	D	0.255	0.254	0.253	
	C(1)–C(7)	1.466 Å	1.524 Å	1.525 Å	
	C(7)–C(8)	1.481 Å	1.457 Å	1.501 Å	
	C(1)–C(7)–C(4)	110.7°	98.0°	99.7°	
	D	0.002	0.005	0.009	
	C(1)–C(2)	1.482 Å	1.495 Å	1.496 Å	
	C(2)–C(3)	1.546 Å	1.579 Å	1.591 Å	
	C(2)–C(1)–C(8)	117.3°	116.7°	117.4°	
	D	0.243	0.277	0.243	
	C(1)–C(10)	1.473 Å	1.506 Å	1.498 Å	
	C(1)–C(2)	1.540 Å	1.548 Å	1.568 Å	
	C(1)–C(10)–C(4)	118.6°	117.0°	117.4°	
	D	0.173	0.262	0.246	

We have attempted a re-parametrization using the solvolysis rates of 6 bridgehead (**1**, **2**, **7**, **8**, **9** and **10**) and 4 tertiary methyl-substituted compounds (**16**–**19**) as reference. The parameters in the previously reported force-fields UNICAT 1 [5] and UNICAT 2 [15] were systematically modified, first by changing the balance between those for deformation of the valence-bond angle and the out-of-plane deformation of the cationic center [16]. Later on, small modifications were applied to other terms. The result of the corrections was tested with plots of  $\log k$  vs.  $\Delta E_{\text{st}}(\text{R}^+ - \text{ROH})$  for the test series. Some 18 different sets of parameters were tried; in all of them, **17** presented a major problem. These difficulties can be understood if one compares structural data of carbenium ions obtained by MM2 (UNICAT 3; see below) with data calculated by semi-empirical (MINDO/3) or *ab-initio* methods (STO-3G and 4-31G) [17] (Table 3). In general, there is reasonably good agreement between the various methods, but the structure of the 7-methyl-7-norbornyl cation shows an important discrepancy. The C(1)–C(7)–C(4) bond angle is calculated to be 110.7° with MM2, but MINDO/3 and STO-3G give 98° and 99.7°, respectively. This strong deviation occurs with all MM2 parametrizations tried so far. Apparently, the ion tends to diminish angle strain by opening the valence-bond angle because the corresponding force-constant is too high. Despite of this, the calculations still exaggerate the steric energy of the ion and, as a result, the reactivity of **17** is underestimated since it is based on  $\Delta E_{\text{st}}(\text{R}^+ - \text{ROH})$ . It is interesting to note that similar difficulties have been encountered when Schleyer's carbenium-ion force-field was applied to the 7-methyl-7-norbornyl cation [18]. The applicability of the parametrizations to such

extreme situations is, therefore, questionable and the inclusion of **17** in the test series may lead to distortions. This is indeed observed. A compromise force-field (UNICAT 3) correlates the full set of test compounds according to Eqn. 3:

$$\log k = -0.429 \Delta E_{st}(R^+ - ROH) + 3.15 \quad r = 0.9701 \quad (3)$$

UNICAT 3 was obtained by modification of UNICAT 2 in the following way: The 'ideal' bond angles adjacent to the cationic center were varied according to their substitution pattern [5]. The constant for C-C-C deformation was set to 2.0 and that for out-of-plane deformation to 1.1. Torsional barriers for H-C-C-C were  $V1 = 0.050$ ,  $V2 = 0.300$ , and  $V3 = 0.500$  and for C-C-C-C  $V1 = 0.350$ ,  $V2 = 0.050$ , and  $V3 = 0.40$ . The correlation to which some other structures have been added is shown in Fig. 2. Although **17** is now better treated than with the previous force-fields, UNICAT 3 is not entirely satisfactory, because the bridgehead derivatives start to deviate from the straight line, particularly **8** and **10**.

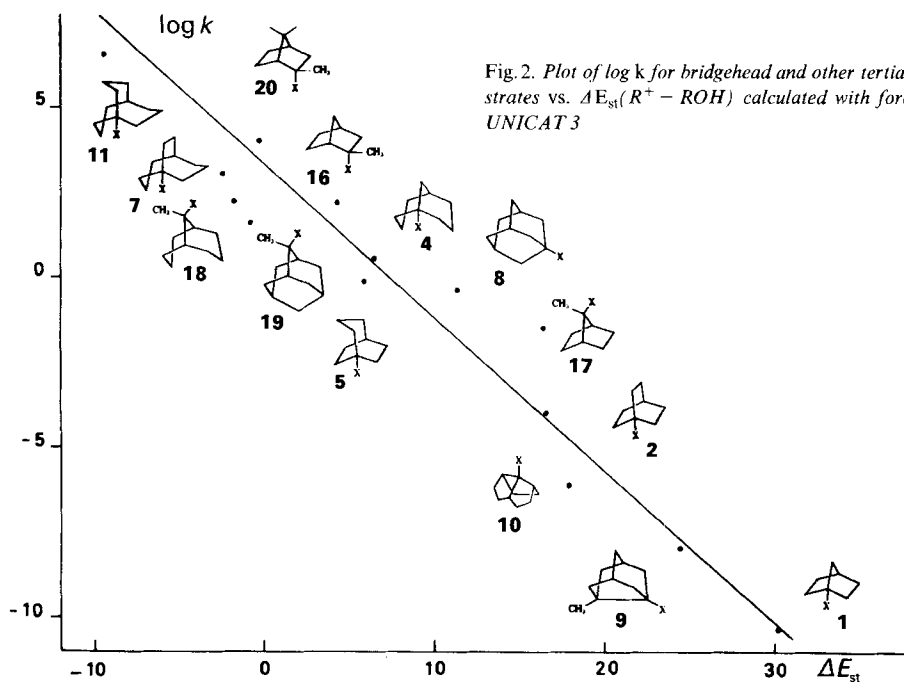
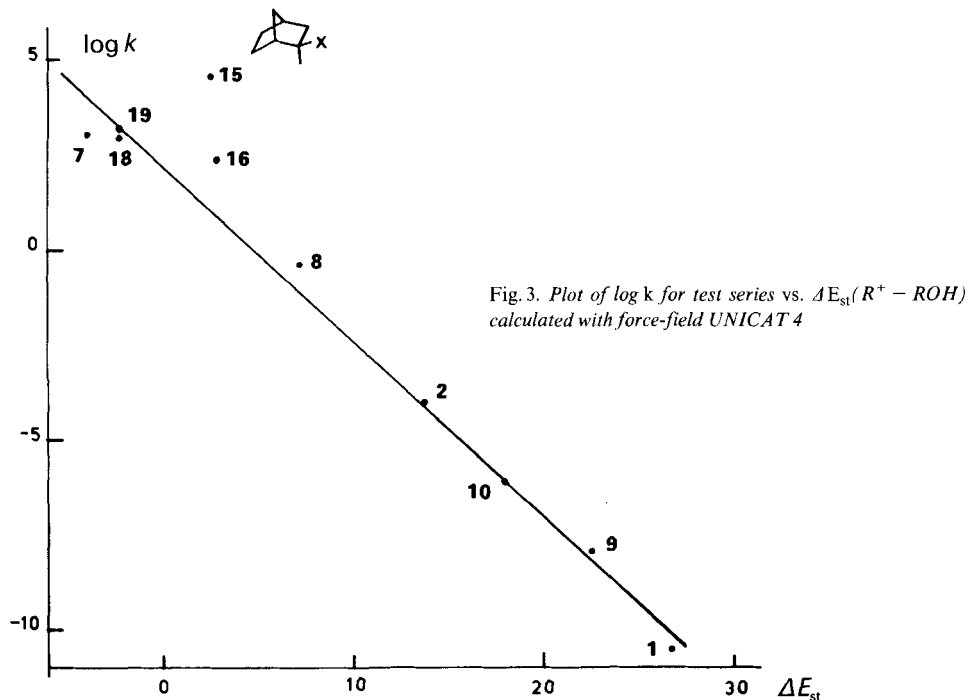


Fig. 2. Plot of  $\log k$  for bridgehead and other tertiary substrates vs.  $\Delta E_{st}(R^+ - ROH)$  calculated with force-field UNICAT 3

If **17** is excluded from the test series, the correlations improve significantly, but the best fit is obtained with still another force-field (UNICAT 4). The latter was derived from UNICAT 1 by decreasing the C-C-C and C-C-H parameters from 2.28 to 2.00. The parameter for out-of-plane bending of the cation was increased from 0.80 to 0.90. The correlation for the remaining 9 compounds of the test series with UNICAT 4 is given by Eqn. 4 (Fig. 3).

$$\log k = -0.457 \Delta E_{st}(R^+ - ROH) + 2.27 \quad r = 0.9916 \quad (4)$$



The standard deviation is 0.74 in  $\log k$ . For comparison, the other force-fields have the following correlation coefficients ( $r$ ) and standard deviations ( $s$ ) for the reduced test series: UNICAT 1:  $r = 0.9899$ ,  $s = 0.81$ ; UNICAT 2:  $r = 0.9630$ ,  $s = 1.53$ ; UNICAT 3:  $r = 0.9836$ ,  $s = 1.03$ . Thus, once **17** is excluded from the series, only minor variations occur. Although the parametrization UNICAT 4 leads to the best fit for this particular set of compounds, other force-fields may prove superior for general use. We intend to examine this question in the context of the solvolysis of flexible tertiary substrates.

c) *Solvolysis of 2-Methyl-2-exo- and -endo-norbornyl Derivatives.* The observation that the tertiary 2-methyl-2-*exo*-norbornyl derivatives **15** solvolyze faster than the *endo* isomers **16** [19] is part of the still ongoing controversy on the nature of the secondary 2-norbornyl cation [20]. *Grob* and *Waldner* [21] have provided evidence that differential bridging accounts for the observed *exo/endo* rate ratio, and most authors agree with the hypothesis that the *exo* transition state should be stabilized, although much less than the *exo* transition state of the secondary derivatives [22]. At the present stage of development, the force-field approach can only describe classical ions. No provision is made for bridging. If bridging occurs, the calculated energy of the ion comes out too high. This is indeed observed for the 2-methyl-2-norbornyl cation. UNICAT 4 together with the increments given in [23] leads to  $\Delta H_f = 173.1$  kcal/mol, while the experimental value is 171.3 [24]. As a consequence, the *exo* isomer **15** falls out of the strain-reactivity correlation by 2–3 log units (*Fig. 3*) not only with UNICAT 4, but with all of the parametrizations tested in this work. In contrast, the *endo* isomer **16** behaves normally in the strain-reactivity correlations. This is consistent with the postulated [21] absence of bridging in the *endo* transition state. The calculations reveal no evidence for leaving-group

hindrance in the case of **16**, but this question will need further investigation by expansion of the set of reference compounds.

**Conclusions.** – The present work shows that the rates of solvolysis of bridgehead substrates with halide and *p*-toluenesulfonate leaving groups can be expressed by strain changes between substrate and the intermediate cation, as calculated by molecular mechanics. The correlation can be extended to rigid methyl-substituted tertiary substrates after adjustment of the force-field parameters; however, the result is less satisfactory than for bridgehead substrates alone. Very strained polycyclic methyl-substituted (planar) cations should be treated with a different set of parameters. The calculations suggest that the 2-methyl-2-*endo*-norbornyl derivatives behave normally, *i.e.* without leaving-group hindrance, while the *exo* isomer is accelerated. However, these results must await confirmation by comparison with other structures.

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