175. Steric Effects on Reaction Rates

Part XII

Force-Field Calculations for the Solvolysis of Cyclobutyl and Tricyclyl Derivatives

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Force-field parameters have been developed for the molecular-mechanics calculation of tertiary carbenium ions with tricyclane structure, for tertiary cyclobutyl and cubyl cations. The cyclobutyl parameters are also applicable to tertiary 7-norbornyl cations. Satisfactory plots are obtained for correlation of the rates of solvolysis with the differences in steric energies between carbenium ions and the corresponding bromides.

Introduction. – Bridgehead derivatives constitute a mechanistically homogeneous series in solvolysis reactions. Their solvolytic reactivity has been investigated systematically by *Schleyer* and coworkers [1–3]. The reactions were found to be dominated by strain changes upon change of hybridization of the reacting C-atom from sp^3 to sp^2 in going to the transition state. These strain changes were calculated by molecular mechanics [3], and they were successfully correlated with the experimental rate constants (log k) for solvolysis of bridgehead chlorides, bromides, p-toluenesulfonates, and trifluoromethane sulfonates. The solvolytic reactivity of bridgehead derivatives varies enormously with the structure of the substrate, and it is impossible to measure the rate constants with one and the same leaving group and under identical experimental conditions. For quantitative strain-reactivity correlations, a uniform reactivity scale is a prerequisite. Such a reactivity scale has been set up. *Bentley* and *Roberts* [4] have critically established rate constants for several bridgehead derivatives with different leaving groups. It was found that relative rate constants in the series are almost independent from the leaving group and the solvent, and subsequently to this observation, correction factors for solvent and leaving group changes (chlorides, bromides, p-toluenesulfonates, and trifluoromethane sulfonates) have been proposed. A reactivity scale for standard conditions (TsO leaving group solvolyzing at 70° in 80% aq. EtOH) spanning a rate range of 22 log units was established. Similarly, conversion factors for p-nitrobenzoate solvolysis and for acid-catalyzed dehydration of tertiary alcohols in the bridgehead and non-bridgehead series have been determined by using linear free-energy relationships [5]. The extrapolated rate constants, when taken from different conditions, agree in general within 0.5 log units.

The original strain-reactivity calculations for bridgehead derivatives were carried out with a preliminary force field which was later abandoned. More recently the strain calculations of *Schleyer* have been repeated with a carbenium ion force field similar to his, but incorporated into *Allinger*'s MM2 program [6]. It was found that all of the rate constants established by *Bentley* could be accommodated with the calculated strain changes by means of a single correlation [7]. Tertiary derivatives of general structure, such as acyclic, mono-, and polycyclic compounds fit the same correlation, although the quality of the plot is significantly below that observed for the bridgehead derivatives alone [8].

The calculations with the MM2 force field were, however, incomplete, and the extension to non-bridgehead derivatives was not entirely satisfactory: two structural types of carbenium ions could not be treated with the standard set of parameters, namely tertiary cyclobutyl, and the nortricyclyl and related cations, where the cationic centre carries a cyclopropane ring at the β-position. The case of the cyclobutyl cation is understandable, because MM2 uses special parameters for all cyclobutane derivatives, but at the time it was felt unwarranted to develop a parametrization just for the problematic methylcyclobutyl cation. The lack of parameters for the family of the tricyclyl cations is particularly unfortunate, because some of the tricyclyl derivatives are the least reactive bridgehead compounds solvolyzing with structural retention, and their inclusion in the strain-reactivity plot would enlarge the rate range by *ca.* 4 orders of magnitude.

The extension of the strain calculations to tertiary non-bridgehead compounds revealed an additional deficiency. The 7-methyl-7-norbornyl derivatives exhibited significant deviations from the strain-reactivity plot, the cation being apparently too strained [9]. More detailed inspection of the calculated structures revealed that the force-field calculations attributed an unrealistic bond angle of 110.7° to the cationic centre, while semi-empirical methods (MINDO/3) and *ab initio* calculations (STO-3G) resulted in bond angles of only 98° and 99.5°, respectively [9] [10]. This indicates, that the parametrization is not valid, when large deviations from the ideal bond angles are involved.

This work was initiated with the objective of extension of the force field for carbenium ions to the cases mentioned above and of elimination of the defiency observed in the case of the 7-methyl-7-norbornyl cation.

Results and Discussion. – Calculations were performed on a total of 50 compounds. The results are summarized in *Table 1*, where the compounds are listed in order of decreasing reactivity. A series of 24 bridgehead or rigid tertiary bridgehead derivatives evenly distributed over the entire rate range was selected, and the steric energy difference $\Delta E_{st}(R^+ - RBr)$ was calculated with the UNICAT 4 carbenium ion force field [7] (*cf. Appendix*) and correlated with the solvolytic reactivity under standard conditions [4] [5] [8] by means of *Eqn. 1*:

$$\log k = -0.394\, \Delta E_{st}\,(R^+ - RBr) + 1.074 \qquad (1)$$
$$\text{with } r = 0.990 \text{ and } \sigma(\log k) = 0.844$$

The rate constants of the tricyclane [11] [12] and cyclobutyl derivatives, which are available from the literature, were extrapolated to 70° (methylcyclobutyl (**30**): [13]; homocubyl (**44**): [14]; cubyl (**42**): [15]) by means of least-square treatment of *Arrhenius* plots, or, if data at only one temperature were available, by means of the *Arrhenius* equation. The leaving group and solvent corrections are given in *Table 2*.

Tricyclyl Derivatives. Calculations with the tricyclyl compounds have been carried out in the past with the *Bingham* force field [11] [12]. Although a satisfactory strain-reactivity

Table 1. *Rate Constants and Strain Calculations for Solvolysis of Tertiary Substrates*

RX[a]	$\mathrm{R^+}$	$E_{\mathrm{st}}(\mathrm{RBr})$[b]	$E_{\mathrm{st}}(\mathrm{R^+})$[b]	$\Delta E_{\mathrm{st}}(\mathrm{R^+ - RBr})$[b]	$\log k_{\mathrm{exp}}$[c]	$\log k_{\mathrm{calc}}$[d]
1*	2-(1,1-Dimethylpropyl)-2-adamantyl	47.66	28.88	−18.78	8.76	9.16
2*	2-(*tert*-Butyl)-2-adamantyl	43.89	25.02	−18.87	8.40	9.19
3*	9-(*tert*-Butyl)-9-bicyclo[3.3.1]nonyl	45.40	26.49	−18.91	8.18	9.21
4	2,3,3-Trimethyl-2-*endo*-norbornyl	59.00	38.88	−20.12	8.11	9.70
5	Tri(*tert*-butyl)methyl	62.37	47.44	−14.93	6.81	7.59
6*	1-Bicyclo[3.3.3]undecyl	43.25	29.27	−13.98	6.44	7.20
7*	2-Neopentyl-2-adamantyl	35.82	23.28	−12.54	4.75	6.62
8	1-(*tert*-Butyl)-1-cyclohexyl	18.84	15.22	−3.62	4.65	2.99
9	2-Methyl-2-bicyclo[2.2.2]octyl	25.34	21.06	−4.28	4.58	3.26
10	2-Methyl-2-*exo*-norbornyl	40.39	32.53	−7.86	4.49	4.71
11*	2-Isobutyl-2-adamantyl	34.46	22.78	−11.68	4.35	6.27
12*	2-Ethyl-2-adamantyl	26.31	20.60	−5.71	3.77	3.84
13	1-Methyl-1-cycloheptyl	15.17	18.39	3.22	3.77	0.20
14	Di(*tert*-Butyl)(methyl)methyl	30.04	21.93	−8.11	3.48	4.81
15	1-Methyl-1-cyclopentyl	13.04	16.08	3.04	3.25	0.28
16*	9-Methyl-9-bicyclo[3.3.1]nonyl	25.37	21.75	−3.62	3.23	2.99
17	(Diethyl)(methyl)methyl	8.55	7.56	−0.99	3.17	1.92
18*	2-Methyl-2-adamantyl	23.79	20.32	−3.47	3.10	2.93
19*	1-Bicyclo[3.3.2]decyl	34.14	28.19	−5.95	3.08	3.94
20	Ethyl(dimethyl)methyl	6.11	5.86	−0.25	2.96	1.62
21	1-Bicyclo[3.1.1]heptyl	42.07	61.99	19.92	2.88[e]	−6.59
22	2-Methyl-2-*endo*-norbornyl	29.14	30.06	0.92	2.49	1.14
23	(*tert*-Butyl)(dimethyl)methyl	12.12	10.20	−1.92	2.45	2.30
24	*tert*-Butyl	3.36	5.32	1.96	2.38	0.72
25	*c*,*c*,*t*-13-Tricyclo[7.3.3.$0^{5,13}$]tridecyl	23.88	21.21	−2.67	2.08	2.60
26	1-Methyl-1-cyclohexyl	9.08	9.67	0.59	2.05	1.27
27*	3-Homoadamantyl	30.91	28.46	−2.45	1.91	2.51
28	7-(*tert*-Butyl)-7-norbornyl	40.71	45.33	4.62	1.83	−0.37
29	1-Tricyclo[3.3.2.$0^{2,8}$]decyl	41.78	41.07	−0.71	1.72[e]	1.80
30	1-Methyl-1-cyclobutyl	31.94	34.05	2.11	1.23[e]	0.66
31	*t*,*t*,*t*-13-Tricyclo[7.3.3.$0^{5,13}$]tridecyl	21.06	18.56	−2.50	0.80	2.53
32*	1-Bicyclo[3.3.1]nonyl	20.08	23.36	3.28	0.51	0.18
33*	6-Protoadamantyl	30.31	36.37	6.06	−0.09	−0.95
34*	1-Bicyclo[3.2.2]nonyl	27.08	30.25	3.17	−0.13	0.22
35*	1-Homoadamantyl	29.44	33.13	3.69	−0.20	0.01
36*	1-Adamantyl	18.24	25.68	7.44	−0.41	−1.51
37	7-Methyl-7-norbornyl	29.18	39.74	10.56	−2.50	−2.78
38*	1-Bicyclo[2.2.2]octyl	20.97	34.91	13.94	−4.00	−4.16
39*	1-Bicyclo[3.2.1]octyl	21.21	37.10	15.89	−5.17	−4.95
40*	1-Noradamantyl	29.10	48.36	19.26	−5.28	−6.32
41*	10-Tricyclo[5.2.1.$0^{4,10}$]decyl	31.54	46.96	15.42	−6.16	−4.76
42	4-Homocubyl	133.24	156.54	23.30	−6.58[e]	−7.97
43*	3-Noradamantyl	31.19	53.68	22.49	−7.28	−7.64
44	1-Cubyl	180.55	201.53	20.98	−7.39[e]	−7.02
45	1-Methyl-4-tricyclo[2.2.2.$0^{2,6}$]octyl	27.08	48.57	21.49	−7.59[e]	−7.23
46*	7-Methyl-3-noradamantyl	32.97	52.83	19.86	−7.96	−6.57
47*	1-Norbornyl	24.76	52.16	27.40	−10.45	−9.64
48*	7,7-Dimethyl-1-norbornyl	30.70	57.11	26.41	−10.49	−9.23
49	4-Tricyclyl	37.21	74.01	36.80	−15.16[e]	−13.46
50	4-Nortricyclyl	32.48	70.21	37.73	−15.99[e]	−13.84

[a] *: Reference compounds used in *Correlation 1*.

[b] Energies in $\mathrm{kcal \cdot mol^{-1}}$.

[c] Standard conditions: 80% EtOH, 70°, TsO leaving group (data from [8]).

[d] Calculated rate constants from *Eqn. 3*.

[e] Data from *Table 2*.

Table 2. *Calculated Rate Constants* ($\log k_{calc}$) *for Solvolysis of Tricyclyl and Tertiary Cyclobutyl Derivatives*

RX	R^+	$\log k$[a] (70%)	Conditions	$\log k_{calc}$ ($X = TsO$, 80% EtOH, 70°)
21	1-Bicyclo[3.1.1]heptyl	–0.72	$X = Br$, 80% EtOH	2.88[b]
29	1-Tricyclo[3.3.2.0^{2,8}]decyl	5.34$^+$	$X = Cl$, 80% Dioxane	1.72[c]
30	1-Methyl-1-cyclobutyl	–3.98	$X = Cl$, 80% EtOH	1.23[d]
42	4-Homocubyl	–6.39$^+$	$X = Br$, $(CF_3)_2CHOH$	–6.58[e]
44	1-Cubyl	–3.23*	$X = TfO$, MeOH	–7.39[f]
45	1-Methyl-4-tricyclo[2.2.2.0^{2,6}]octyl	–2.28*	$X = TfO$, 60% EtOH	–7.59[g]
49	4-Tricyclyl	–9.84*	$X = TfO$, 60% EtOH	–15.16[g]
50	4-Nortricyclyl	–10.16*	$X = TfO$, 50% EtOH	–15.99[h]

[a] Extrapolated data to 70° by means of least-square treatment of *Arrhenius* plots (*) or by means of *Arrhenius* equation ($^+$).

[b] Conversion factor from $X = Br$: 4×10^3 [4a].

[c] Calc. from rate of 1-Bicyclo[2.2.2]octyl *p*-toluenesulfonate in 80% EtOH ($\log k = -4.00$) [8].

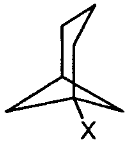
[d] Calc. from rate of *t*-BuCl in 80% EtOH ($\log k = -2.82$); conversion factor from $X = Cl$: 1.6×10^5 [8].

[e] Conversion factor from $X = Br$: 4×10^3 [4a]; correction from $(CF_3)_2CHOH$: $Y_{OTs} = 3.79$ [4b].

[f] Conversion factor from $X = TfO$: 6×10^{-5} [4a]; correction from MeOH: $Y_{TsO} = 1.09$ [4b].

[g] Conversion factor from $X = TfO$: 6×10^{-5} [4a]; conversion factor from EtOH 60%: 12.34 [4b].

[h] Conversion factor from $X = TfO$: 6×10^{-5} [4a]; conversion factor from EtOH 50%: 41.13 [4b].



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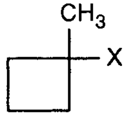

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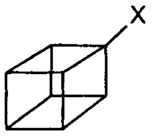

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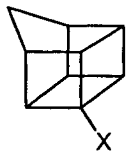

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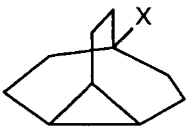

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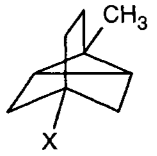

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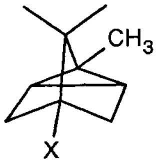

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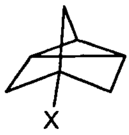

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plot was obtained, the significance of the calculations is questionable, since it was found later that this force field is unreliable for very strained hydrocarbons, such as norbornane and bicyclo[2.2.2]octane [7]. The particular structural feature of the tricyclyl derivatives is the cyclopropane ring which lies approximately on the backside of the cationic centre. In tricyclo[3.3.2.0^{2,8}]decyl derivative **29**-Cl [16], the cyclopropane ring is separated by two CH_2 units from the reactive centre, and the corresponding cation **29**$^+$ can be treated with the normal UNICAT 4 parameters, except for the torsional parameters for the cyclopropane C-atom in γ-position from the cationic centre. These parameters are set to 0.00 for the first- and second-order torsional constants and 0.70 for the third one (see *Table 3*). As *Fig. 1* shows, the compound fits the strain-reactivity plot quite well. This

Table 3. *Force-Field Parameters for Tricyclyl and Tertiary Cyclobutyl Cations*[a])

Angle Bending[b])	Type[c])	Θ_0[d])	k[e])	Torsion[b])	V_1[f])	V_2[f])	V_3[f])
Tricyclyl parameters							
$C(22)-C-C^+$	1	114.5	0.57	$C(22)-C-C-Br$	0.00	−0.41	1.06
$C(22)-C-C^+$	2	115.5	0.57	$C(22)-C-C^+-C$	0.00	0.00	0.70
$C(22)-C-C^+$	3	116.5	0.57	$C(22)-C(22)-C-C^+$	0.00	0.00	0.70
				$C^+-C-C(22)-C$	0.00	0.00	0.70
				$C^+-C-C(22)-H$	0.00	0.00	0.70
Cyclobutyl parameters							
$C-C^+-C$	0	120.0	0.37	$C-C^+-C-C$	0.00	0.00	0.30
$C-C-C^+$	0	109.5	0.27	$C^+-C-C-C$	0.00	0.00	0.37

[a]) When different from the general force-field UNICAT 4.

[b]) Type 22 means a C-atom in a cyclopropane ring.

[c]) Central atom type: 1 ($-CR_2$); 2 ($-CRH$); 3 (CH_2); 0 (general case).

[d]) In deg.

[e]) In mdyn/A.

[f]) In kcal/mol.

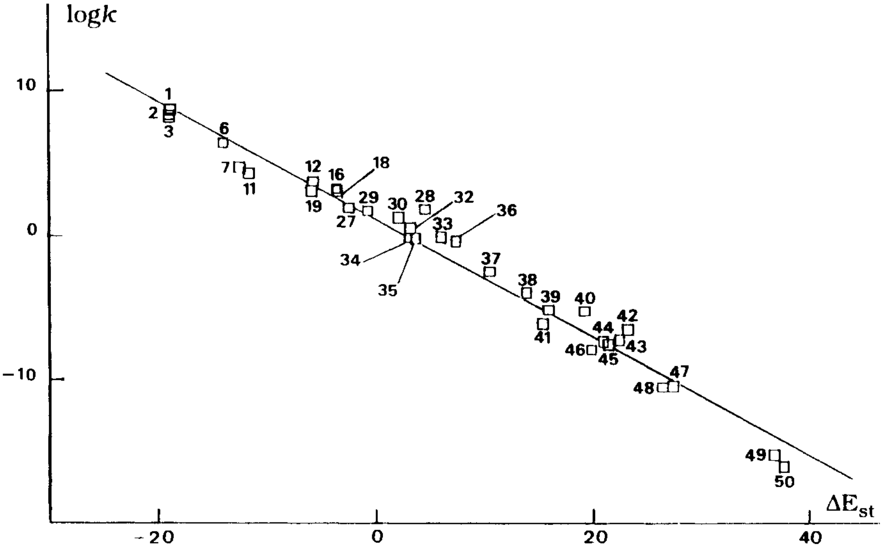

Fig. 1. *Plot of* log k *for solvolysis of bridgehead derivatives including nortricyclyl, cyclobutyl, and 7-norbornyl compounds* vs. $\Delta E_{st}(R^+ - RBr)$

suggests that the cyclopropane ring exerts no electronic effect on the transition state for solvolysis, and it is, therefore, justified to assume no such effect also for all other members of the tricyclyl series. The cyclopropane ring of 1-methyl-4-tricyclo[2.2.2.$0^{2,6}$]octyl (**45**-OTf) has two C-atoms separated only by one CH_2 group from the reacting centre, and the same situation occurs three times in the 4-tricyclyl derivatives **49**-OTf and **50**-OTf (this particular structural feature is not covered by the UNICAT 4 parameters). The experimental heats of formation of nortricyclane compounds are well reproduced by MM2 by means of special parameters to account for the C-atoms bonded to a cyclopropane [17], for which the ideal bond angle is slightly increased. This increment is used by analogy for the carbenium ions. An additional correction is needed to account for the fact that the ideal bond angles α to a carbenium-ion centre vary throughout the series of the bridgehead cations according to the substitution pattern of the α-C-atom, and this correction must also be applied to the tricyclyl structures. Finally, torsional parameters for a cyclopropane C-atom in β-position to the cationic centre must be introduced. The full set of parameters is summarized in *Table 3*. *Fig. 1* shows the regression line defined by the bridgehead derivatives with the norticyclane family (and the cyclobutyl cations) added. The fit is satisfactory, considering that some of the rate constants were extrapolated from very high temperature down to 70°.

Tertiary Cyclobutyl Cations. The treatment of cyclobutyl cations by molecular-mechanics calculations is more problematic. The secondary ion is a rapidly equilibrating set of three degenerate nonclassical bicyclobutonium ions and three degenerate cyclopropylcarbinyl cations [18]. The structure of the 1-methylcyclobutyl cation is not definitely established, but the ion is nonplanar and possibly in equilibrium with a minor species [19]. This suggests that the tertiary ion should be nonclassical. In contrast, the fact that 1-methylcyclobutyl chloride solvolyzes at a *ca.* 5 times lower rate that 1-methylcyclohexyl chloride indicates a classical structure for the ion, and this was used in support of the *I*-strain hypothesis [13]. Clearly, if the ion is nonclassical, then the use of molecular-mechanics calculations may be questionable.

We have modified, by trial and error, the UNICAT 4 force field to accomodate cyclobutyl cations by reducing the force-constants for $C{-}C^{+}{-}C$ and $C{-}C{-}C^{+}$ angle bending (*Table 3*), while the out-of-plane deformation remained unchanged. Using the previously reported increments [19], (including 1 inductive correction for α-substituents), the gas-phase enthalpy of formation of the ion is calculated to 193.5 kcal/mol, while the experimental value is 193.0 [21]. With the same parametrization, the rate of solvolysis can be accomodated with the strain-reactivity correlation (*Fig. 1*). It should be noted, however, that the force constant used in these calculations for the bond-angle deformation of the cationic centre is extremely low. This undoubtedly expresses the fact that the parameters compensate some nonclassical stabilisation of the carbenium ion.

The same set of parameters also accommodates the solvolytic reactivity of the cubyl and 4-homocubyl derivatives **42** and **44**, respectively. The *Bingham* force field predicts cubyl trifluoromethanesulfonate to be completely inert ($k < 10^{-12}$ s^{-1} at 250°) [3], while the experimental rate constant, extrapolated to standard conditions, is *ca.* 1000 times higher than that of the 1-norbornyl derivative. Various hypotheses have been advanced in order to explain the unexpectedly high solvolytic reactivity of cubane derivatives [14] [15], but the final explanation of the phenomenon is still open to debate. The stability of the cubyl cation in the gas phase is not yet known, but *ab initio* calculations at the MP2 level, by inclusion of electron correlation [22], place the heterolytic bond-dissociation energy of cubane 7.3 kcal/mol below that of norbornane. MM2 calculates the ionization of bromocubane 11.1 kcal/mol below that of 1-bromonorbornane. Irrespective of the origin of the nonclassical stabilization of the cyclobutyl and cubyl cations, it appears justified to view the latter as a superposition of cyclobutyl cations, and no additional stabilization appears to be present in **42**$^{+}$ and **44**$^{+}$.

The parameters developed for the 1-methylcyclobutyl cation also reproduce the rate of solvolysis of tertiary 7-norbornyl derivatives. Contrary to MM3, MM2 has no provision for substituents at a five-membered ring, and the program rejects the special cyclobutane parameters, if the calculated structure is a cyclopentane. To circumvent this problem, a special cationic centre was created with the parameters of the cyclobutyl cation and used for the tertiary 7-norbornyl cations. With these parameters, MM2 calculates the gas-phase enthalpy of formation of the 7-methyl-7-norbornyl cation to 183.4 kcal/mol. The experimental value, determined from the gas-phase basicity [23] of 7-methylene norbornane and the enthalpy of formation of the latter [24], is 179.9 (preliminary value). The discrepancy between experiment and calculations does not lead to notable deviations in the strain-reactivity correlation (*Fig. 1*), and this suggests, that it might be attributable to the inductive corrections which are used in order to convert the calculated steric energies to enthalpies of formation of cations. The correlation combining the bridgehead with the nortricyclyl and cyclobutyl derivatives (*Fig. 1*) is of the form

$$\log k = -0.408\, \Delta E_{st}(\mathrm{R}^+ - \mathrm{RBr}) + 1.220 \qquad (2)$$

$$\text{with } r = 0.988 \text{ and } \sigma(\log k) = 1.022$$

There is, however, one compound that does not fit this correlation. 1-Bromobicyclo[3.1.1]heptane (**21**) solvolyzes *ca.* 10^9 times faster than predicted on the grounds of the strain calculations. It has been proposed that the high solvolytic reactivity of this compound should be attributable to through-space stabilization in the 1-bicyclo[3.1.1]heptyl cation [25]. This hypothesis is based on the observation that introduction of a 5-(methoxycarbonyl) group in **21** decreases the reaction rate by a factor of 6.5×10^5. In comparable systems, such as 3-substituted adamantyl bromide the rate effect of the COOR group is only 120 [25], and in cubane, the methoxycarbonyl substituent at C(4) retards the rate by a factor of *ca.* 100 [14]. At the present stage of development, the force-field calculations do not take in consideration such electronic effects, and on these grounds, the deviation of **21** from the strain-reactivity plot is explicable. On the other hand, the deviation is unexpectedly large, and we cannot rule out the possibility that it might be partially due to an inadequate parametrization. It is indeed difficult to understand, why much stronger bridging should occur in the 1-bicyclo[3.1.1]heptyl cation than in the 1-methylcyclobutyl cation. Attempts to adjust the parameters for the cyclobutyl cations to reproduce also the properties of the bicyclo[3.1.1]heptyl system were, however, unsuccessful.

Acyclic and Monocyclic Derivatives. In previous communications, we have reported calculations for acyclic and monocyclic tertiary derivatives. It was found that $\Delta E_{st}(\mathrm{R}^+ - \mathrm{ROH})$ correlated with log *k* in the same way as for the bridgehead derivatives, although there was considerably more scatter in the plot, and the compounds appeared slightly accelerated with respect to the rigid polycyclic systems [7]. These calculations have now been repeated using the Br substituent as leaving-group model, and the results are shown in *Fig. 2*. The correlation relating 49 compounds (**21** excluded) is given by *Eqn. 3*:

$$\log k = -0.407\, \Delta E_{st}(\mathrm{R}^+ - \mathrm{RBr}) + 1.514 \qquad (3)$$

$$\text{with } r = 0.977 \text{ and } \sigma(\log k) = 1.290.$$

We attribute *ca.* 50% of the standard deviation on log *k* to uncertainties in the rate constants owing to the various extrapolations in establishing the reactivity scale, and the other 50% to the calculations and nonuniform mechanisms of solvolysis. There is some improvement in comparison to previous calculations, where OH was used as leaving-group model. In particular, the tri(*tert*-butyl)methyl cation ($\mathbf{5}^+$) which deviated badly, is

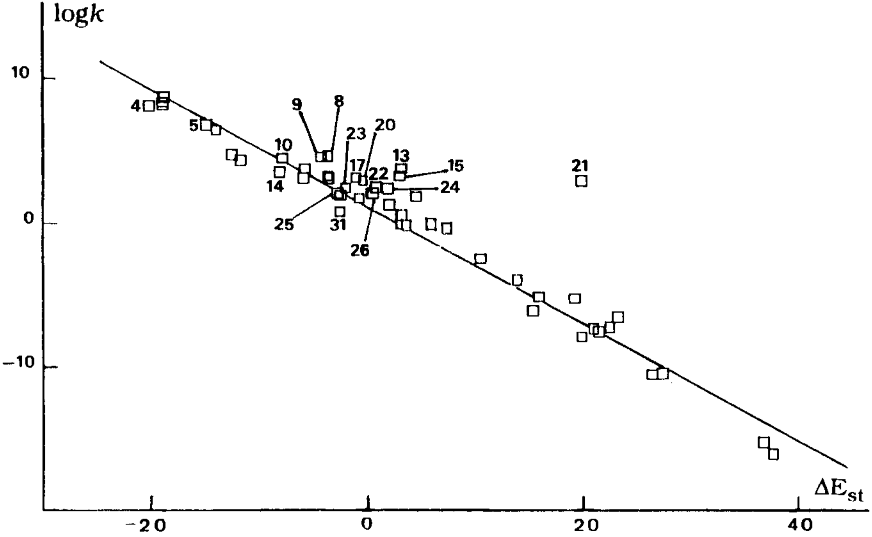

Fig. 2. *Plot of log* k *for solvolysis of 49 tertiary derivatives* vs. $\Delta E_{st}(R^+ - RBr)$. Data from *Table 1.*

now quite well-behaved. This raises some disturbing questions concerning the reliability of the alcohol force field, which we have used in previous work [26], and which will have to be re-examined.

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Appendix

Table 4. *Force-Field Parameters for Tertiary Carbenium Ions* (UNICAT 4)

Stetching vibration	r^{o}[a])	k[b])
$C^+–C$	1.483	7.40
$C^+–H$	1.084	7.40

Angle Bending	Type[d])	Θ^{o}[e])	k[b])
$C–C^+–H$	0	120.0	2.00
$C–C^+–C$	0	120.0	2.00
$C–C–C^+$	1	109.5	0.57
$C–C–C^+$	2	110.5	0.57
$C–C–C^+$	3	111.5	0.57
$C^+–C–H$	1	109.5	0.57
$C^+–C–H$	2	110.2	0.57
$C^+–C–H$	3	111.0	0.57

Torsion	V_1[c])	V_2	V_3
$C^+–C–C–H$	0.00	0.00	0.70
$C^+–C–C–C$	0.00	0.00	0.70
$C–C^+–C–H$	0.00	0.00	0.70
$C–C^+–C–H$	0.00	0.00	0.70
$C–C^+–C–H$	0.00	0.00	0.70
$C–C^+–C–H$	0.00	0.00	0.70

Out of Plane bending	k[b])
	0.90

Van der Waals	r^*[a])	ε[c])
	1.900	0.044

[a]) In Å. [b]) In mdyn/Å. [c]) In kcal·mol^{-1}. [d]) Central atom type: 1 ($-CR_2-$); 2 ($-CRH-$); 3 ($-CH_2-$); 0 (General case). [e]) In deg.

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