

exothermicity from approximately 2 to 20 kcal/mol depending on the nature of R' and R''.

The proposed mechanism accounts for the more rapid rearrangement of the benzylaminosilanes (R' = Ph) where stabilization of the carbanion relative to the nitrogen anion would occur and the lack of rearrangement of the anilines (R'' = Ph) where stabilization of the nitrogen anion relative to the carbanion should exist. Attempts to investigate the reverse reaction by metalation of the benzyl carbon of compounds such as *N*-trimethylsilyldibenzylamine using excess *tert*-butyllithium or the *n*-butyllithium-tetramethylethylenediamine complex have now been made successfully. More detailed studies of the scope and mechanism of this rearrangement are in progress.

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A. G. Brook,\* J. M. Duff<sup>8</sup>

Lash Miller Chemical Laboratories, The University of Toronto  
Toronto, Ontario, Canada

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### Estimation of Solvolysis Rates of Cyclic Secondary Substrates

Sir:

A major difficulty in the controversy surrounding the importance of anchimeric assistance in the solvolysis of secondary alkyl derivatives<sup>1-5</sup> has been the inability to predict solvolysis rates of cyclic substrates.<sup>6</sup> One method of performing such predictions is by use of a form of the Taft  $\sigma^*$  linear free energy relationship, eq 1.<sup>7-11</sup> For example, solvolysis rates of acyclic deriva-

$$\log k/k_0 = \sigma^* \rho^* \quad (1)$$

tives are correlated by the  $\sigma^*$  treatment, and positive deviation from this correlation has been taken as evidence for anchimeric assistance.<sup>8,9,11</sup> Unfortunately,  $\sigma^*$  constants are not available for cyclic systems and, in certain significant cases, cannot be determined by the usual methods.<sup>7,12</sup>

(1) H. C. Brown, *Accounts, Chem. Res.*, **6**, 377 (1973).

(2) G. D. Sargent in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1972, Chapter 24.

(3) S. Winstein and D. S. Trifan, *J. Amer. Chem. Soc.*, **71**, 2953 (1949); **74**, 1147, 1154 (1952).

(4) S. Winstein, *J. Amer. Chem. Soc.*, **87**, 381 (1965).

(5) G. A. Olah, G. Liang, G. D. Mateescu, and J. L. Riemenschneider, *J. Amer. Chem. Soc.*, **95**, 8698 (1973).

(6) (a) C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964); (b) P. v. R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964); (c) H. C. Brown and J. Muzzio, *ibid.*, **88**, 2811 (1966); (d) H. C. Brown, I. Rothberg, P. v. R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Nat. Acad. Sci. U. S. A.*, **56**, 1653 (1966); (e) actually, the Foote-Schleyer correlation<sup>6a-d</sup> quite accurately predicts acetolysis rates for uncrowded systems in which leaving group-alkyl steric strain is small. It is confusing, however, that both  $k_0$  (e.g., 2-adamantyl) and  $k_s$  (e.g., 2-propyl) substrates lie on the same line. The correlation fails in other solvents.

(7) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., Chapter 13.

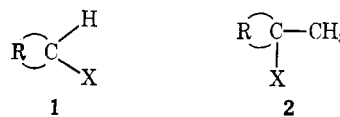
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We have developed a method for prediction of solvolysis rates of secondary cyclic systems (1) which is based on solvolysis rates of the corresponding methyl-substituted tertiary derivatives (2). A linear  $\sigma^*$  plot



is observed for the solvolysis of acyclic tertiary chlorides in 80% aqueous ethanol ( $\rho^* = -3.29$ )<sup>11</sup> and of the *p*-nitrobenzoates in 60% aqueous acetone ( $\rho^* = -2.2$ ).<sup>13</sup> By placing the rates of cyclic tertiary derivatives, 2, on these plots,  $\sigma^*$  values (designated  $\sigma_t^*$ ) can be determined. These  $\sigma_t^*$  values will accurately reflect inductive, hyperconjugative, and steric effects for solvolysis of a secondary cyclic alkyl system if there are no major steric differences between the secondary derivatives and the tertiary models. Substitution of a methyl group onto cyclic (e.g., cyclopentyl) and polycyclic (e.g., 2-norbornyl and 2-adamantyl) systems has been shown to contribute little to ground-state steric strain.<sup>14,15</sup> Exceptions are the medium rings and certain polyalkylated norbornyl derivatives; use of the  $\sigma_t^*$  method for treatment of these complex substrates is deferred.

Use of  $\sigma_t^*$  and eq 1 should yield calculated rates for secondary substrates accurate within a factor of 10, with this variation due to temperature and solvent extrapolations and uncertainties in  $\sigma^*$  plots (a factor of 2), and to minor steric variations (a factor of 5). In fact, the average deviation for model substrates is only a factor of 2.

Reaction constants ( $\rho^*$ ) are known for the acetolysis ( $\rho^* = -2.6$ )<sup>10,16</sup> and aqueous ethanolysis ( $\rho^* = -1.92$  in 80% ethanol)<sup>17</sup> of acyclic derivatives. These reactions have been clearly shown<sup>9,16,18-20</sup> to involve nucleophilic solvent assistance (a  $k_s$  process)<sup>18</sup> equivalent to a rate factor of  $10^2$ - $10^4$ . Thus, use of these  $\rho^*$  values yields calculated rates which include assistance of  $10^2$ - $10^4$ .

Comparison of predicted and observed solvolysis rates for several model  $k_s$  substrates<sup>18,20,21</sup> (1-6) shows

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(13) C. F. Wilcox, Jr., and M. E. Mesirov, *J. Amer. Chem. Soc.*, **84**, 2757 (1962).

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Table I. Solvolysis Rates of Cyclic Secondary Tosylates at 25°

R-OTs R =	$\sigma_{\tau}^*$	$-\log k_{\text{obsd}}^a$ (AcOH) [80E]	$-\log k_{\text{calcd}}^a$ (AcOH) [80E]	$\log k_{\text{obsd}} - \log k_{\text{calcd}}$
Cyclopentyl (1)	$-0.48^{b-d}$	(5.78) <sup>e</sup> [3.37] <sup>f</sup>	(5.87) [4.61]	0.09 1.24
Cyclohexyl (2)	$0.10^{b-d}$	(7.32) <sup>e</sup> [6.12] <sup>g</sup>	(7.37) [5.72]	0.05 -0.40
Cycloheptyl (3)	$-0.47^{c,h}$	(5.54) <sup>e</sup>	(5.89)	0.35
Cyclotridecyl (4)	$0.00^{c,h}$	(6.65) <sup>i</sup>	(7.11)	0.45
Cyclopentadecyl (5)	$0.06^{c,h}$	(6.90) <sup>i</sup>	(7.26)	0.36
Cycloheptadecyl (6)	$0.06^{c,h}$	(6.89) <sup>i</sup>	(7.26)	0.37
7-Norbornyl (7)	$1.31^{b,i}$	(13.68) <sup>i</sup> [12.45] <sup>k</sup>	(10.52) [8.04]	-3.16 -4.40
2-Adamantyl (8)	$-0.21^{b,i,l}$	(8.23) <sup>m</sup> [7.62] <sup>m</sup>	(6.56) [5.13]	-1.67 -2.49
7,7-Dimethyl-endo-2-norbornyl (9)	$-0.62^{h,a}$	(7.20) <sup>o</sup>	(5.50)	-1.70
anti-7-Norbornenyl (10)	$-0.45^{b,i}$	(3.43) <sup>p</sup>	(5.94)	2.51
7-Norbornadienyl (11)	$-0.12^{i,a}$	(0.79) <sup>i</sup>	(3.99)	3.81
exo-2-Benzonorbornenyl (12)	$0.14^{i,q}$	(5.60) <sup>r</sup>	(7.47)	1.87
exo-2-Norbornyl (13)	$-0.74^{b,s,t}$	(4.62) <sup>u</sup> [3.64] <sup>v</sup>	(5.19) [4.11]	0.57 0.47
endo-2-Norbornyl (14)	$0.20^{a,t}$	(7.14) <sup>u</sup> [6.40] <sup>v</sup>	(7.63) [5.91]	0.49 -0.49
7,7-Dimethyl-exo-2-norbornyl (15)	$-0.90^{n,a}$	(3.59) <sup>o</sup>	(4.77)	1.18
1-Methyl-exo-2-norbornyl (16)	$-0.86^{a,v}$	(2.91) <sup>p,m</sup>	(4.87)	1.96
6,6-Dimethyl-endo-2-norbornyl (17)	$0.60^{a,w}$	(8.35) <sup>u</sup>	(8.67)	0.32
1-Methyl-endo-2-norbornyl (18)	$0.00^{p,v}$	(7.03) <sup>z,m</sup>	(7.11)	0.08
Cyclobutyl (19)	$0.35^{c,h}$	(5.72) <sup>i</sup>	(8.02)	2.30

<sup>a</sup> AcOH = acetic acid; 80E = 80% (v/v) aqueous ethanol; conversion factors for solvent and leaving group change are those commonly used, references 11 and 19a. <sup>b</sup> Average value from tertiary chloride and *p*-nitrobenzoate. <sup>c</sup> H. C. Brown and M. Borkowski *J. Amer. Chem. Soc.*, **74**, 1894 (1952). <sup>d</sup> H. C. Brown and W. J. Hammar, *ibid.*, **89**, 6378 (1967). <sup>e</sup> S. Winstein, *et al.*, *ibid.*, **74**, 1127 (1952). <sup>f</sup> J. M. Harris, unpublished results. <sup>g</sup> P. v. R. Schleyer, *et al.*, unpublished results. <sup>h</sup>  $\sigma_{\tau}^*$  from tertiary chloride. <sup>i</sup> H. C. Brown and G. Ham, *J. Amer. Chem. Soc.*, **78**, 2735 (1956). <sup>j</sup> Reference 22a. <sup>k</sup> P. v. R. Schleyer, *et al.*, *J. Amer. Chem. Soc.*, **91**, 5386 (1969). <sup>l</sup> Reference 14. <sup>m</sup> Reference 2. <sup>n</sup> H. C. Brown and S. Ikegami, *J. Amer. Chem. Soc.*, **90**, 7122 (1968). <sup>o</sup> S. Winstein, *et al.*, *ibid.*, **87**, 378 (1965). <sup>p</sup> Reference 11. <sup>q</sup>  $\sigma_{\tau}^*$  from tertiary *p*-nitrobenzoate. <sup>r</sup> H. C. Brown and G. L. Trittle, *J. Amer. Chem. Soc.*, **88**, 1320 (1966). <sup>s</sup> K. L. Servis, *et al.*, *Tetrahedron*, **24**, 1247 (1968). <sup>t</sup> H. C. Brown, *et al.*, *J. Amer. Chem. Soc.*, **86**, 1248 (1964). <sup>u</sup> P. v. R. Schleyer, *et al.*, *ibid.*, **87**, 375 (1965). <sup>v</sup> H. C. Brown and M. H. Rei, *ibid.*, **86**, 5004 (1964). <sup>w</sup> H. C. Brown, *et al.*, *ibid.*, **90**, 7122 (1968).

excellent agreement (Table I). Compounds 7-9 are indicated<sup>1,18,22</sup> to react without nucleophilic or neighboring group assistance (a  $k_c$  process),<sup>18</sup> and, as expected, the predicted rates containing  $10^2$ - $10^4$  assistance are too large by this amount. The validity of the  $\sigma_{\tau}^*$  derivation is also corroborated by examination of known<sup>22,23</sup> anchimerically assisted ( $k_A$ )<sup>18</sup> substrates 10-12; observed rates are equal to or greater than the predicted assisted rates.

The following generality results: those compounds with rates equal to or greater than predicted are assisted ( $k_s$  or  $k_A$ ) and those reacting slower than predicted are unassisted. *exo*-2-Norbornyl (13) provides an important<sup>1-6</sup> illustration. Olah, *et al.*,<sup>5</sup> have convincingly shown that the norbornyl cation is non-classical. The question arises as to the extent to which the transition state for the solvolysis of 13 resembles the cation intermediate;<sup>5</sup> can participation lag behind ionization?<sup>1,4</sup> Our results dispel this possibility; the agreement of observed and predicted rates shows that solvolysis of this compound is assisted and that  $\sigma$  participation must be concerted with ionization. Interestingly, the solvolysis of *endo*-2-norbornyl (14) is also indicated to be normal; that is, its rate is consistent with a  $k_c$  process.<sup>2,3</sup> Similar predictions obtain for the other norbornyl derivatives 15-18. Finally, the

acetolysis rate for cyclobutyl (19) tosylate (100 times faster than predicted) is only consistent with the strong  $\sigma$  participation others have proposed for this reaction.<sup>24</sup>

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(24) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, ref 2, Chapter 26.

J. Milton Harris,\* Samuel P. McManus\*

Department of Chemistry, The University of Alabama in Huntsville  
Huntsville, Alabama 35807

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### <sup>13</sup>C-<sup>13</sup>C Coupling Constants in a Series of <sup>13</sup>C-Enriched Amino Acids

Sir:

While <sup>13</sup>C nmr has become an increasingly popular tool in the study of peptides, none of the studies published to date has concerned <sup>13</sup>C coupling constants. This is predominantly because of the poor sensitivity and low natural abundance of the <sup>13</sup>C nucleus. Use of <sup>13</sup>C-enriched materials reduces these problems very greatly, opening new opportunities for <sup>13</sup>C nmr studies of peptide structure and conformation. A number of studies in systems other than peptides have appeared,<sup>1</sup>

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