

of the *trans* isomer. The previously reported synthesis involved the esterification of *trans*-4-cyclohexene-1,2-dicarboxylic acid.<sup>24</sup>

*trans*-Bicyclo[4.3.0]non-3-ene-8-carboxamide. *trans*-Diethyl  $\Delta^4$ -tetrahydrophthalate was reduced to the known diol,<sup>24</sup> which was converted to ditosylates 4 (Scheme I) (50% yield, based on diol, after one crystallization from methanol, m.p. 91–93°; lit.<sup>24</sup> m.p. 94–95.5°). Diethyl-*trans*-bicyclo[4.3.0]non-3-ene-8,8-diethyl dicarboxylate was prepared from the ditosylate, hydrolyzed to the dicarboxylic acid, and decarboxylated to *trans*-bicyclo[4.3.0]non-3-ene-8-carboxylic acid (5) by the previously employed methods.<sup>24</sup> The monocarboxylic acid (3.5 g.) was refluxed with 17 ml. of thionyl chloride for 20 min., and the mixture was added dropwise to ice-cooled, concentrated ammonium hydroxide. Attempted crystallization from water gave an oil which solidified (1.85 g., 54%), m.p. 140–160°. Crystallization from a more dilute solution in water gave an analytical sample of *trans*-bicyclo[4.3.0]non-3-ene-8-carboxamide, m.p. 170–171°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>15</sub>NO: C, 72.69; H, 9.15. Found: C, 72.55; H, 8.96.

(24) D. C. Ayres and R. A. Raphael, *J. Chem. Soc.*, 1779 (1958).

8-Cyano-*trans*-bicyclo[4.3.0]non-3-ene (6). A previously recommended method for amide dehydration was used.<sup>25</sup> Benzenesulfonyl chloride (1.94 g., 0.011 mole) was added to a stirred mixture of crude *trans*-bicyclo[4.3.0]non-3-ene-8-carboxamide (1.85 g., 0.011 mole) at such a rate that the temperature did not exceed 70°. The reaction was strongly exothermic, following an induction period. The resulting slurry was stirred with ether. The ether layer was washed with 4 ml. of 6 *N* hydrochloric acid and water. The dried ether layer gave 1.0 g. of product, b.p. 80–85° (0.9 mm.), which appeared to be contaminated with the amide starting material (infrared absorption at 1650 cm.<sup>-1</sup>). Redistillation through a microspinning-band column gave 0.16 g. of 8-cyano-*trans*-bicyclo[4.3.0]non-3-ene (6) (Scheme I), b.p. 52–58° (0.6 mm.).

*Anal.* Calcd. for C<sub>10</sub>H<sub>13</sub>N: C, 81.58; H, 8.90. Found: C, 81.12; H, 8.91.

The same compound has been prepared by a different method and reported in a preliminary communication without experimental details.<sup>26</sup>

(25) C. R. Stephens, E. J. Bianco, and F. J. Pilgrim, *J. Am. Chem. Soc.*, 77, 1701 (1955).

(26) H. B. Henbest and B. Nicholls, *Proc. Chem. Soc.*, 225 (1958).

## Solvents of Low Nucleophilicity. VII. Solvolysis of Unbranched Secondary Alkyl Tosylates in Acetic, Formic, and Trifluoroacetic Acids<sup>1</sup>

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*Rates of solvolysis of secondary propyl, butyl, pentyl, hexyl, and heptyl tosylates in formic and trifluoroacetic acids were determined and compared with reported rates in acetic acid. An unusually high sensitivity to electron release by alkyl groups is found for the solvolyses in trifluoroacetic acid. Values of  $\rho_f$  were -15.7, -7.79, and -5.72 for reactions in trifluoroacetic, formic, and acetic acids, respectively.*

A remarkably large portion of the organic chemical literature currently deals with secondary tosylate solvolyses. Not surprisingly, relatively little attention has been given to comparison of unbranched secondary aliphatic tosylates. The rewards to be gained in this somewhat restricted area are exemplified by Pritzkow and Schoppler's study of the rates of acetolysis of heptyl and octyl tosylates (among others).<sup>3</sup> 2-Heptyl tosylate and 2-octyl tosylate solvolyzed at almost identical rates ( $k = 4.81$  and  $4.64$ , respectively), while the four other secondary tosylates in the heptyl and octyl series constituted a faster reacting group having

rate constants which varied only from 9.22 to 10.14. The average 2.05-fold rate increase in the second group of compounds, compared to the first, was attributed to the stronger electron release of the larger alkyl groups compared to that of methyl groups. Logarithms of the acetolysis rates of the tosylates, R<sub>1</sub>R<sub>2</sub>CHOTs, were well correlated with the sum of the  $\sigma^*$ -values of R<sub>1</sub> and R<sub>2</sub>, but the  $\rho^*$  value (-2.58) was different from that (-3.49) found by Streitwieser in an earlier correlation which encompassed tosylates having strong electron-attracting substituents.<sup>4</sup>

Since a knowledge of secondary tosylate solvolysis rates in trifluoroacetic acid was needed in connection with our studies of long-range inductive effects,<sup>5</sup> we undertook, with some reluctance the measurement of rates for all of the unbranched propyl, butyl, pentyl, hexyl, and heptyl compounds. In addition, the solvolysis rates in formic acid were obtained. These rate studies, with the acetic acid solvolysis studies from the literature, constitute a continuation of our program of comparing the properties of the weakly nucleophilic

(1) Supported in part by National Science Foundation Grant G-20904.

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(3) W. Pritzkow and K. H. Schoppler, *Chem. Ber.*, 95, 834 (1962).

(4) A. Streitwieser, *J. Am. Chem. Soc.*, 78, 4935 (1956).

(5) (a) P. E. Peterson and C. Casey, *Tetrahedron Letters*, 1569 (1963); (b) P. E. Peterson and G. Allen, *J. Am. Chem. Soc.*, 85, 3608 (1963); (c) P. E. Peterson and E. Tao, *ibid.*, 86, 4503 (1964).

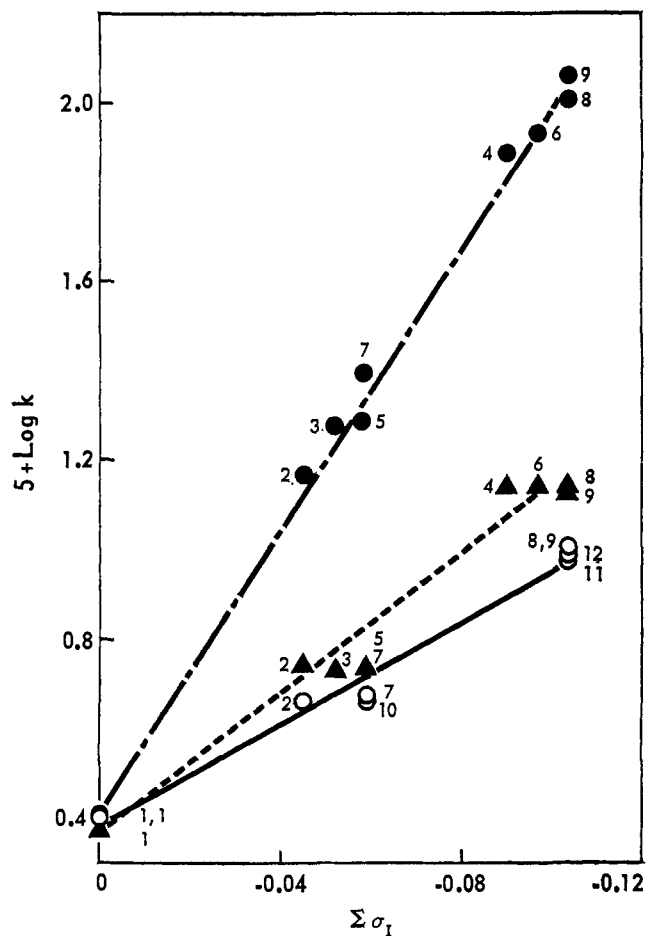


Figure 1. Hammett-Taft plot of solvolysis of tosylates in acetic acid. Identification of tosylates: 1, 2-propyl; 2, 2-butyl; 3, 2-pentyl; 4, 3-pentyl; 5, 2-hexyl; 6, 3-hexyl; 7, 2-heptyl; 8, 3-heptyl; 9, 4-heptyl; 10, 2-octyl; 11, 3-octyl; 12, 4-octyl. Identification of solvent: acetic acid (O, —); formic acid (▲, ---); trifluoroacetic acid (●, ———).

solvents, acetic acid, formic acid, and trifluoroacetic acid. A modification of the recently reported ultraviolet spectroscopic method of Swain and Morgan<sup>6</sup> was found to be the first generally useful method for measurement of tosylate solvolysis rates in trifluoroacetic acid.

### Results and Discussion

Rate data are reported in Table I, and Hammett-Taft plots for the rates in acetic, formic, and trifluoroacetic acids are shown in Figure 1. The same scale is employed in all plots. The high  $\rho_{\text{R}}$ -value for the reaction in trifluoroacetic acid ( $-15.7$ ), commands immediate attention, upon comparison with the lower values in formic and acetic acid ( $-7.79$  and  $-5.72$ , respectively), although a high value was anticipated from earlier rate studies involving only the hexyl tosylates.<sup>7</sup> Caution should be observed in comparing the  $\rho_{\text{R}}$ -value for reaction in acetic acid with the other two values, since the acetic acid rates were measured at a higher temperature ( $70$  instead of  $25^\circ$ ). The  $\rho$ -values might exhibit somewhat more than the usual temperature dependence in these hydrogen-bonding solvents.

(6) C. G. Swain and C. Morgan, *J. Org. Chem.*, **29**, 2097 (1964).

(7) P. E. Peterson and C. Casey, *ibid.*, **29**, 2325 (1964).

Table I. Rates of Solvolysis of Secondary Alkyl Tosylates

Tosylate	$k \times 10^5, \text{sec.}^{-1}$		
	Trifluoroacetic acid <sup>a</sup>	Formic acid <sup>b</sup>	Acetic acid <sup>c</sup>
2-Propyl	2.49	2.38	2.551
2-Butyl	14.6	5.50	4.792
2-Pentyl	19.0	5.35	
3-Pentyl	76.8	14.08	
2-Hexyl	19.2	5.43	
3-Hexyl	86.6	13.8	
2-Heptyl	24.9	5.47	4.808
3-Heptyl	103	13.8	10.14
4-Heptyl	115	13.2	10.14
2-Octyl			4.639
3-Octyl			9.22
4-Octyl			9.66

<sup>a</sup> At  $25^\circ$ ,  $0.05 M$  tosylate,  $0.125 M \text{NaO}_2\text{CCF}_3$ . <sup>b</sup> At  $25^\circ$ ,  $0.1 M$  tosylate. <sup>c</sup> At  $70 \pm 0.5^\circ$ ,  $0.2 M$  tosylate, no  $\text{NaOAc}$ . Data from ref. 3.

It is tempting to attribute this high  $\rho$ -value to the low nucleophilicity of trifluoroacetic acid. That is, in the absence of effective solvation of the cationic transition state by solvent molecules, electron supply from within the reacting tosylate molecule might become unusually important. However Taft has stated that "it is not yet possible generally to predict even crudely the value of  $\rho$  from a theoretical or empirical consideration of the nature of the reaction and the experimental conditions."<sup>8</sup>

An illustration of the difficulty of predicting the magnitude of  $\rho$ -values in carbonium ion reactions is presented by secondary tosylate solvolyses in acetic acid ( $\rho^* = -3.49$ ) and tertiary halide solvolyses in  $80\%$  ethanol ( $\rho^* = -3.20$ ).<sup>9</sup> Although the transition state for formation of a tertiary carbonium ion (latter reaction) might at first be thought to involve much less sensitivity to electron demand within the molecule, the  $\rho^*$  value is almost as large in absolute magnitude as that for the former reaction, in which a secondary ion is formed. Accordingly our own results are probably best presented in terms of an empirical correlation. Within the series of acids studied, a low bond-forming tendency (nucleophilicity) of the oxygen atoms in the solvent is accompanied by a high  $\rho$ -value for tosylate solvolyses.<sup>10</sup> Interestingly, the solvent nucleophilicity also appears to determine the "rearranging power" of the solvents.<sup>11</sup> Accordingly a determination of  $\rho$  for tosylate solvolyses in an unknown solvent may permit a qualitative prediction of the extent of rearrangement expected for various carbonium ion reactions in the same solvent.

The solvolysis of tosylates in trifluoroacetic acid is more sensitive to variation of the substituents than are the reactions used originally to determine  $\sigma^*$ . Accordingly it is tempting to examine the data for the possibility of constructing a better set of values. At present, however, such detailed interpretation should probably be deferred until more experience is gained

(8) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 572.

(9) Ref. 8, p. 608. Comparison of  $\rho_1$  and  $\rho^*$  values is made by the relationship  $\rho^* = 0.45\rho_1$ .

(10) It is assumed that the possible temperature dependence of  $\rho$ , previously mentioned, does not affect the relative order of the  $\rho_1$  values.

(11) See ref. 5b for a discussion of several known examples.

with the newly developed ultraviolet method for determination of rates.

It may also be mentioned that our tosylate solvolysis rates would be expected to reflect any steric interactions in the tosylates which could be relieved in the transition state for reaction. The previous instances of strong inductive effects involving carbonium ion reactions in trifluoroacetic acid<sup>5</sup> suggest, however, that our rate results reflect inductive electron release by alkyl groups. In view of the recently discovered instances of apparent electron-attracting properties of alkyl groups,<sup>12</sup> it is particularly interesting that our own studies have resulted in a new extreme example of electron release by alkyl groups.<sup>13</sup>

### Experimental Section

**Solvents and Tosylates.** Trifluoroacetic acid (Allied Chemical Corp.) and 98% formic acid (Eastman) were distilled through a 3-ft., helix-packed column. Middle cuts were used for solvolyses.<sup>14</sup> Except as noted below, tosylates were prepared from commercially available alcohols as previously described.<sup>15</sup> 2-Hep-  
tanol was prepared since gas chromatography of commercial alcohol (K & K Laboratories) showed a major amount of a second component. 3-Pentanol was prepared from ethyl magnesium bromide and propionaldehyde. Commercial 3-pentanol (K & K Laboratories) contained approximately 30% of 2-pentanol.

**Formolyses.** Rates of solvolysis of 0.1 *M* solutions of tosylate in anhydrous formic acid were determined at 25.0 ± 0.05° (as measured with a Bureau of Standards calibrated thermometer) by the titrimetric method described in the literature.<sup>16</sup>

**Trifluoroacetolyses.** Rates of solvolysis of 0.05 *M* solutions of tosylate were determined at 25.0 ± 0.05° by a modification of an ultraviolet spectroscopic method which was recently reported. The required

(12) For references see H. D. Holtz and L. M. Stock, *J. Am. Chem. Soc.*, **86**, 5188 (1964).

(13) Examples of strong electron release by alkyl groups involving gas phase ionization potentials of radicals, hydrocarbons, amines, etc., are cited by A. Streitwieser in "Progress in Physical Organic Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, pp. 1-30.

(14) P. D. Bartlett, C. E. Dills, and H. G. Richey, *J. Am. Chem. Soc.*, **82**, 5414 (1960), have recommended distillation of 98% formic acid as a method for the preparation of the anhydrous acid.

(15) H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

(16) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

amount of tosylate was weighed in a volumetric flask and diluted to 10 ml. with trifluoroacetic acid, 0.125 *M* in sodium trifluoroacetate, which had been previously brought to 25°. One-milliliter aliquots were withdrawn at appropriate intervals and quenched in somewhat less than 50 ml. of 95% ethanol in a volumetric flask. Additional 95% ethanol was added to bring the volume to 50 ml., and the absorbance was measured at the sharp maximum near the 273.3 m $\mu$ , using a Beckman DU spectrophotometer.

First-order rate constants (*k*) were determined from plots of log (*A* - *A*<sub>∞</sub>) vs. time according to the formula  $k = 2.303 \log [\Delta(A - A_{\infty})]/\Delta t$  where *A* is the absorbance, *A*<sub>∞</sub> is the absorbance after 7 or more half-lives, and *t* is the time. Results of a typical rate determination are given in Table II.

**Table II.** Absorbance of Quenched Solutions from Solvolysis of 3-Pentyl Tosylate in Trifluoroacetic Acid

Time, sec.	Absorbance, 273.2 m $\mu$
0	0.371 <sup>a</sup>
65	0.354
300	0.313
673	0.262
960	0.235
1260	0.207
1800	0.171
7200	0.096 <sup>b</sup>

<sup>a</sup> Estimated value obtained by extrapolation of rate plot to time = 0. <sup>b</sup> "Infinity" absorbance.

The quenched solutions were shown to be stable for short periods (10 min.), although a detectable decrease in absorbance occurred upon longer standing (60 min.). Spectra of quenched solutions recorded on a Bausch and Lomb Spectronic 505 spectrometer showed absorbance which increased with decreasing wave length in the range 280 to 250 m $\mu$ , with sharp maxima at 272, 266, and 261 m $\mu$ . Absorbances at each of these maxima decreased by similar amounts with increasing per cent solvolysis. The maximum at 272 m $\mu$  (273.2 on the DU) was used in measuring rates, since it was well separated from the opaque region due to absorption by trifluoroacetic acid at wave lengths shorter than 250 m $\mu$ .