

# Correlation of Solvolysis Rates of 1-Adamantyl *p*-Toluenesulfonate<sup>1,2</sup>

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**Abstract:** The solvolysis of 1-adamantyl *p*-toluenesulfonate has been studied at several temperatures in 80% ethanol, methanol, ethanol, 2-propanol, and *tert*-butyl alcohol; enthalpies and entropies of activation have been computed. A kinetic study has also been made, at 25.0°, in several other aqueous-organic systems and solvolysis rates have been correlated by the Grunwald-Winstein *mY* equation. One important difference between the solvolysis of tertiary acyclic derivatives and bridgehead derivatives could well be a considerably increased amount of ion-pair return in the latter. For *tert*-butyl alcoholysis, the isolated product is 1-adamantanol, and a control experiment showed 1-adamantyl *tert*-butyl ether to decompose under the experimental conditions. Solvolysis in 80% ethanol at 25.0° leads to 29% 1-adamantyl ethyl ether and 71% 1-adamantanol. A simple route to 1-adamantyl *p*-toluenesulfonate is described and the variations between previously reported melting points are rationalized. Four 1-alkoxyadamantanes have been prepared and characterized.

Previous studies of the solvolytic reactivity of bridgehead derivatives of adamantane have concentrated upon the solvolyses of 1-adamantyl halides,<sup>4-7</sup> 3-substituted 1-adamantyl bromides,<sup>8</sup> and 1-adamantyl *p*-toluenesulfonate<sup>9</sup> in aqueous ethanol, the solvolysis of 1-adamantyl bromide in aqueous dimethyl sulfoxide,<sup>10</sup> and the acetolyses of 1-adamantyl *p*-toluenesulfonate<sup>11,12</sup> and 2-substituted derivatives.<sup>12</sup> Since nucleophilic assistance to ionization and concurrent elimination are both excluded by the bridgehead structure, 1-adamantyl derivatives represent ideal substrates for analysis of substitution reactions in terms of linear free energy relationships, such as the Grunwald-Winstein *mY* equation. Use of the literature data<sup>6</sup> for the solvolysis of 1-adamantyl bromide in aqueous ethanol allows an *m* value of 1.11 to be estimated (Table VI), and a more recent study<sup>9</sup> has led to a corresponding value of 1.08. These values can be compared with reported<sup>5</sup> *m* values, at 25.0°, of 1.13 for both 1-bromobicyclo[2.2.2]octane and 1-bromo-3,3-dimethylbicyclo[2.2.2]octane.<sup>13</sup> Recently, a detailed investigation has been carried out of the relationship between the rates of solvolysis of 1-adamantyl bromide and the *Y* values for a wide range of solvent com-

position.<sup>7,14</sup> A good correlation of the logarithms of the rates with *Y* values, with an *m* value of 1.20, was found for most solvent systems, but significant dispersion was found for aqueous trifluoroethanol and for the previously reported data<sup>10</sup> for aqueous dimethyl sulfoxide. A parallel study with 1-adamantyl *p*-toluenesulfonate is of interest since the *p*-toluenesulfonate group is capable of internal charge dispersal<sup>15,16</sup> and, also, it is more prone to hydrogen-bonded assistance to ionization, and specific solvent effects, than a halide ion leaving group. Further, incorporation of a better leaving group, such as *p*-toluenesulfonate, allows extension to solvents of quite low ionizing power at temperatures close to ambient. An alternate scale of solvent polarities, especially useful for nonhydroxylic solvents, is based upon the anchimerically assisted decomposition or solvolysis rates for *p*-methoxyneophyl *p*-toluenesulfonate.<sup>17</sup> It will be instructive to see whether the solvolysis rates for 1-adamantyl *p*-toluenesulfonate parallel, on a logarithmic scale, the corresponding rates previously reported for *p*-methoxyneophyl *p*-toluenesulfonate.

The preparation of 1-adamantyl *p*-toluenesulfonate has previously been carried out either from 1-adamantanol and the acid chloride in the presence of pyridine<sup>5,11</sup> or by *m*-chloroperbenzoic acid oxidation of the *p*-toluenesulfonate.<sup>12</sup> We found a more convenient technique to be a modification of the silver-ion-assisted substitution reaction which was previously used by Hoffman to give *tert*-butyl *p*-toluenesulfonate from *tert*-butyl bromide.<sup>18</sup>

## Experimental Results

**Solvolyses in Dry Alcohols and 80% Ethanol.** Rates of solvolysis were determined at five temperatures between 5 and 65° for 80% ethanol and the  $\alpha$ -methylated series of alcohols: methanol, ethanol, 2-propanol, and *tert*-butyl alcohol. With the exception of the *tert*-butyl alcohol system, constant first-order rate coefficients

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(3) Petroleum Research Fund Undergraduate Scholar, Summer, 1969. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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(12) B. R. Ree and J. C. Martin, *J. Amer. Chem. Soc.*, **92**, 1660 (1970).

(13) M. Finkelstein, Ph.D. Thesis, Yale University, 1955.

(14) We wish to thank Dr. Schleyer for providing us with preprints of the manuscripts of ref 7 and 21.

(15) H. M. R. Hoffman, *J. Chem. Soc.*, 6753, 6762 (1965).

(16) D. N. Kevill and R. F. Sutthoff, *ibid.*, **B**, 366 (1969).

(17) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Amer. Chem. Soc.*, **83**, 618 (1961).

(18) H. M. R. Hoffman, *J. Chem. Soc.*, 6748 (1965).

were observed throughout each run. With *tert*-butyl alcohol as solvent, the integrated first-order rate coefficients drifted slightly upward as the reaction progressed, and initial values were obtained by extrapolation to zero extent of reaction. For the *tert*-butyl alcohol series, it is these initial values which are reported in Table I, along with values independent of extent of reaction for the other solvent systems. The activation parameters computed from the data of Table I are presented in Table II.

**Table I.** First-Order Rate Coefficients for Solvolysis of 1-Adamantyl *p*-Toluenesulfonate<sup>a</sup>

Temp, °C	$10^6 k_1, \text{sec}^{-1}$				
	80% EtOH <sup>b</sup>	MeOH	EtOH	<i>i</i> -PrOH	<i>tert</i> - BuOH
5.0	328				
15.0	1130	143	11.3		
20.0	2310	265			
25.0	4030	480	44.0	5.98	0.740
35.1	12600	1610	140	22.4	2.64
45.9		5200	543	83.8	8.84
55.0			1380	231	24.4
65.0				671	63.2

<sup>a</sup> With the exception of *tert*-butyl alcohol runs, the standard error for the first-order rate coefficient associated with each run was less than 2% of its value. Owing to the extrapolation to initial values, the corresponding standard errors for *tert*-butyl alcohol runs ranged up to 10%, but were typically less than 5%. <sup>b</sup> Prepared from 4 vol of ethanol and 1 vol of water.

**Table II.** Enthalpies ( $\Delta H^\ddagger$ ) and Entropies ( $\Delta S^\ddagger$ ) of Activation for Solvolysis of 1-Adamantyl *p*-Toluenesulfonate<sup>a</sup>

Solvent	$\Delta H^\ddagger, \text{kcal/mol}$	$\Delta S^\ddagger, \text{eu}$
80% ethanol	20.2 ± 0.2	-1.9 ± 0.8
Methanol	20.8 ± 0.3	-4.2 ± 0.9
Ethanol	22.0 ± 0.2	-4.7 ± 0.7
2-Propanol	23.1 ± 0.2	-5.1 ± 0.5
<i>tert</i> -Butyl alcohol	21.7 ± 0.2	-13.8 ± 0.7
Acetic acid <sup>b</sup>	20.6 ± 0.3	-5 ± 1
Acetic acid <sup>c</sup>	20.3 ± 0.5	-4.5 ± 1.7

<sup>a</sup> Errors quoted are standard errors. <sup>b</sup> From ref 11. <sup>c</sup> From ref 12.

Addition of pyridine to *tert*-butyl alcohol solvolyses was found to enhance, rather than reduce, the autocatalysis, and the initial values for the first-order rate coefficient were unchanged (Table III).

**Table III.** Effect of Added Pyridine upon Initial First-Order Rate Coefficients for Solvolysis of 0.052 *M* 1-Adamantyl *p*-Toluenesulfonate in *tert*-Butyl Alcohol at 65.0°

	[C <sub>5</sub> H <sub>5</sub> N], <i>M</i>			
	0.0000	0.0285	0.0570	0.1040
$10^6 k_1^0$	63.2 ± 1.7	65.9 ± 1.7 <sup>b</sup>	60.9 ± 3.8	62.9 ± 3.1
$d^a$	4.0 ± 0.6	8.6 ± 0.8 <sup>b</sup>	13.1 ± 1.4	12.6 ± 1.2

<sup>a</sup> Obtained from *integrated* rate coefficients,  $k_1$ , being related to extent of reaction by  $k_1 = k_1^0 (1 + d[\text{HOTs or C}_5\text{H}_5\text{NHOTs}])$ . <sup>b</sup> Using data obtained up to 50% reaction.

**Solvolysis in Solvents of Varying Ionizing Power.** In addition to the data reported in Table I, a study has been made at 25.0° of the solvolyses in three other aqueous ethanol compositions, two aqueous methanol concentrations, and four each of aqueous acetone and

aqueous dioxane compositions. The rate coefficients, together with the values for the five 25.0° runs from Table I, are reported in Table IV.

**Table IV.** Relationship of 1-Adamantyl *p*-Toluenesulfonate First-Order Solvolytic Rate Coefficients to Solvent Ionizing Power at 25.0°

Solvent <sup>a</sup>	$10^6 k_1, \text{sec}^{-1}$ <sup>b</sup>	<i>Y</i> <sup>c</sup>
80% ethanol	403	0.000
85% ethanol	177	
90% ethanol	68.8	-0.747
95% ethanol	20.7	-1.287
100% ethanol	4.40	-2.033
90% methanol	361	-0.301
95% methanol	144	
100% methanol	48.0	-1.090
80% acetone	46.1	-0.673
85% acetone	16.8	
90% acetone	4.16	-1.856
95% acetone	0.448	-2.76
75% dioxane	70.9	
80% dioxane	20.1	-0.833
85% dioxane	6.87	
90% dioxane	1.57	-2.030
100% 2-propanol	0.598	-2.73
100% <i>tert</i> -butyl alcohol	0.0740	-3.26
100% acetic acid	43.6, <sup>d</sup> 51.5, <sup>e</sup> 58.6 <sup>f</sup>	-1.639

<sup>a</sup> *X*% volume of organic solvent and (100 - *X*)% volume of water. <sup>b</sup> With the exception of the *tert*-butyl alcohol system, the standard error associated with each first-order rate coefficient was less than 2% of its value. <sup>c</sup> Grunwald-Winstein *Y* values from ref 19. <sup>d</sup> From ref 11. <sup>e</sup> From ref 12. <sup>f</sup> From ref 5.

Grunwald-Winstein *Y* values were available from the literature<sup>19</sup> for 13 of the 18 solvent systems studies.

**Effect of Added Salts upon the Ethanolysis.** Added tetraethylammonium *p*-toluenesulfonate, tetraethylammonium chloride, or tetra-*n*-butylammonium perchlorate had no effect upon the directly determined infinity acid titer for runs at 25.0°. True infinity acid titers, after correction for slightly varying weights of 1-adamantyl *p*-toluenesulfonate, were identical with each other and with the value in the absence of added salt. This is significant for the addition of the chloride-containing salt, since it shows that 1-adamantyl carbonium ions are not being trapped by chloride ion to give 1-adamantyl chloride. The chloride is known<sup>5</sup> to solvolyze only extremely slowly at this temperature, even in the much more ionizing 80% ethanol. A rough estimate indicates that at 25.0° the chloride would solvolyze in ethanol about 10<sup>5</sup>-10<sup>6</sup> times slower than the *p*-toluenesulfonate.

The kinetic influences of the two tetraethylammonium salts, the *p*-toluenesulfonate and the chloride, are virtually identical and somewhat less than the influence of equal molarities of tetra-*n*-butylammonium perchlorate (Table V).

**Product Studies.** Previous preparations of 1-adamantyl *p*-toluenesulfonate have shown melting points of 79-83°<sup>11</sup> or 72-75°.<sup>12</sup> Recrystallization from hexane gives two crystalline modifications of melting points 72.5-74.5° and 80.5-81.5°, respectively. Similar polymorphism has previously been observed for *p*-methoxyneophyl *p*-toluenesulfonate.<sup>17</sup>

(19) P. R. Wells, *Chem. Rev.*, 63, 171 (1963).

**Table V.** Effect of Added Salts upon Specific Rates of Solvolysis of 0.052 *M* 1-Adamantyl *p*-Toluenesulfonate in Ethanol at 25.0°<sup>a</sup>

[Salt], <i>M</i>	10 <sup>4</sup> <i>k</i> <sub>1</sub> sec <sup>-1</sup>		
	NEt <sub>4</sub> OTs	NEt <sub>4</sub> Cl	<i>n</i> -Bu <sub>4</sub> NClO <sub>4</sub>
0.0000	4.36	4.36	4.36
0.0127			4.60
0.0186	4.50	4.49	
0.0373	4.62	4.65	
0.0746	4.90	4.86	
0.102			5.42
0.149	4.96	5.11	

<sup>a</sup> Standard error associated with each first-order rate coefficient was less than 1% of its value.

Authentic samples of the ethers expected to result from solvolyses in dry alcohols were prepared by the fast reaction of 1-adamantyl chloride or iodide with silver perchlorate within the appropriate alcohol. The crude products resulting from solvolysis of 1-adamantyl *p*-toluenesulfonate in methanol (25.0°), ethanol (55.0°), and 2-propanol (55.0°) were shown to have pmr spectra identical with those of the previously prepared analytically pure ethers. Also, the spectra possessed the required relative signal integrations for the protons of the 1-adamantyl group and the alkyl group derived from the alcohol. In *tert*-butyl alcohol at 55.0°, even in the presence of a 10% excess of pyridine, the crude product did not contain the sharp *tert*-butyl singlet required for 1-adamantyl *tert*-butyl ether, but rather the spectrum indicated the product to be 1-adamantanol. This was confirmed by comparison of the infrared spectrum with that of an authentic sample.

The reaction product from solvolysis in 80% ethanol at 25.0° gave a pmr spectrum whose integration indicated a mixture of 29% 1-adamantyl ethyl ether and 71% 1-adamantanol. This can be compared with ratios for the corresponding solvolysis of 1-adamantyl bromide, with 40% ether and 60% alcohol at 60°<sup>20</sup> and 51% ether and 49% alcohol at 75°.<sup>21</sup> The percentage of ether was in excellent, but probably fortuitous, agreement with 28.4% reported<sup>22</sup> for an identical solvolysis of *tert*-butyl bromide. For *tert*-butyl bromide, the other products were 14.5% isobutylene and 57.1% *tert*-butyl alcohol.

## Discussion

The acceleration, identical with that produced by the chloride salt, upon adding tetraethylammonium *p*-toluenesulfonate is inconsistent with any appreciable external return. The absence of external return was confirmed by the observation that the infinity titer was unchanged by the presence of chloride ion. If external return did occur, the 1-adamantyl carbonium ion would be trapped by equivalent concentrations of chloride ion with conversion to 1-adamantyl chloride, a stable compound for the duration of the experiment. These results are consistent with the observation<sup>21</sup> of less than 1% 1-adamantyl azide after addition of up to 0.06 *M* sodium azide to the solvolysis of 1-adamantyl bromide in 80% ethanol at 75.0° and with the observation,<sup>20</sup> for the same solvolysis, of an unchanged

(20) J. MacMillan and R. J. Pryce, *J. Chem. Soc. B*, 337 (1970).

(21) J. M. Harris, D. J. Raber, R. E. Hall, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 5729 (1970).

(22) M. Cocivera, Ph.D. Thesis, UCLA, July 1963.

product ratio, at 60°, upon adding 0.1 *M* sodium hydroxide.

While detectable amounts of external return are excluded for these systems, the possibility of internal ion-pair return as a factor contributing toward the kinetic characteristics observed for bridgehead derivatives appears to have been neglected. The higher free energy of a bridgehead carbonium ion relative to an acyclic counterpart, the impossibility of rear-side nucleophilic solvent attack upon the first-formed ion pair, and the impossibility of an elimination reaction upon or within<sup>23</sup> the ion pair will all be factors favoring increased internal return.

One feature, which has been observed for the solvolysis kinetics of bridgehead halides, is an entropy of activation appreciably lower (more negative) than for tertiary acyclic derivatives. A summary has been presented by Schleyer and Nicholas<sup>5</sup> and additional data for 1-adamantyl bromides solvolyses<sup>6,10</sup> and for the solvolyses of 3-substituted-1-adamantyl bromides<sup>8</sup> were presented quite recently. Two alternative explanations have been advanced to explain the reduction in entropy of activation relative to a tertiary acyclic system.<sup>5</sup> One explanation supposes that the absence of rear-side solvation renders front-side solvation more critical, and the total ordering of solvent at the transition state is greater. The other explanation supposes that bridgehead systems are "normal" and the increased rotation of attached groups in flattened acyclic carbonium ions renders these "abnormal." Recently,<sup>16</sup> the similar reductions in entropy of activation observed upon transferring the reactions of *tert*-butyl halides or *tert*-butyl nitrate from a protic to a dipolar aprotic solvent were rationalized in terms of an increase in ion-pair return.

The faster solvolysis of 1-adamantyl *p*-toluenesulfonate relative to 1-adamantyl halides has allowed a study in solvents of lower ionizing power. It can be seen that the entropies of activation, reported in Table II, decrease as the solvent ionizing power is reduced. Indeed, the activation parameters for *tert*-butyl alcohol medium are closely akin to what one would predict for a transfer to an aprotic solvent,<sup>16</sup> with the lower reaction rate, relative to 2-propanol, resulting from a considerable reduction in the entropy of activation and with a partially counterbalancing reduction in the enthalpy of activation. While not uniquely requiring such an explanation, the lowering of the entropy of activation with decrease in the solvent dissociating power would be a direct corollary of assuming appreciable internal ion-pair return within these solvolyses.

At 25.0°, solvolysis was studied in 18 solvent systems and Grunwald-Winstein *Y* values, listed in Table IV, were available from the literature<sup>19</sup> for 13 of these systems. The *m* values calculated using data for four aqueous-organic systems, the four dry alcohols as a system, and the entire 13 solvents of known *Y* value as a system are given in Table VI.

Linear plots were observed for the aqueous ethanol and aqueous acetone systems, but a curved plot is obtained when the four dry alcohols are considered (Figure 1). The curve would intercept the log *k* axis

(23) M. Cocivera and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 1702 (1963).

**Table VI.** Calculated  $m$  Values for Solvolysis of 1-Adamantyl *p*-Toluenesulfonate at 25.0°

Solvents	No. of points	$m^a$	$\log k_0^a$
80–100% ethanol	4	$0.965 \pm 0.016$	$-2.418 \pm 0.040$
90–100% methanol	2	1.11	-2.11
80–95% acetone	3	$0.960 \pm 0.031$	$-2.663 \pm 0.104$
80–95% dioxane	2	0.93	-2.93
Dry alcohols	4	$1.275 \pm 0.062^b$	$-1.85 \pm 0.30^b$
All <sup>d</sup>	13	$1.098 \pm 0.057$	$-2.366 \pm 0.367$
40–80% ethanol	5	$1.107 \pm 0.018^c$	$-6.373 \pm 0.054^c$

<sup>a</sup>  $\log k = mY + \log k_0$ ; errors quoted are standard errors. <sup>b</sup> Assuming a linear plot; actual plot is curved. <sup>c</sup> Values calculated for 1-adamantyl bromide using rate coefficients from ref 6 and  $Y$  values from ref 19. <sup>d</sup> Excluding acetic acid.

at a more reasonable value than the  $-1.85$  obtained by best fitting of a linear plot and the slope,  $m$  value, is initially of the same order of magnitude as for the other solvent systems but increases appreciably in magnitude as the  $Y$  value becomes more negative.

Recently, rate data became available<sup>6</sup> for the solvolysis of 1-adamantyl bromide in a wide range of ethanol–water compositions and, in combination with  $Y$  values from the literature,<sup>19</sup> a value of  $1.11 \pm 0.02$  can be computed for the  $m$  value at 25.0°. An independent study has led to a value of 1.08 for this system.<sup>9</sup> It has been reported that for dimethyl sulfoxide–water mixtures the ratio of the rate coefficients at 25° in mixtures containing 50% and 20% water, respectively, is 480 for 1-adamantyl bromide and 120 for *tert*-butyl chloride, corresponding to an  $m$  value of 1.29. Previous kinetic studies of bridgehead halides,<sup>13</sup> when adjusted to 25.0°, have also given<sup>5</sup>  $m$  values greater than unity.

Our  $m$  values for solvolyses of 1-adamantyl *p*-toluenesulfonate are typically a little lower than unity and in good agreement with the value of 0.99 reported for aqueous ethanol systems.<sup>9</sup> The possibility of internal charge dispersal within the incipient anion of the transition state should lower the demand for dispersal by solvation<sup>15,16</sup> and, in turn, this should reduce the dependence upon solvent ionizing power. It is of interest in this connection that  $m$  values have been reported<sup>24</sup> as 0.84 for *tert*-butyl nitrate, 0.924 for *tert*-butyl bromide, and (by definition) 1.00 for *tert*-butyl chloride. Lower  $m$  values have also been reported for methyl primary alkyl, secondary alkyl, and benzyl arylsulfonates than for the corresponding halides.<sup>25</sup>

As a general rule the  $m$  values for solvolysis of bridgehead derivatives are somewhat larger in value than the values for corresponding acyclic derivatives. The simplest explanation lies in the application of Hammond's postulate.<sup>26</sup> The higher free energy of bridgehead carbonium ions relative to tertiary acyclic carbonium ions suggests that the transition state for their formation will be situated further along the reaction coordinate, and will show a greater sensitivity to solvent ionizing power. The increase in  $m$  value would also be consistent with increased tendency toward internal ion-pair return.<sup>27</sup> In addition to a dependence

(24) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 1602 (1957).

(25) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(26) G. S. Hammond, *ibid.*, **77**, 334 (1955).

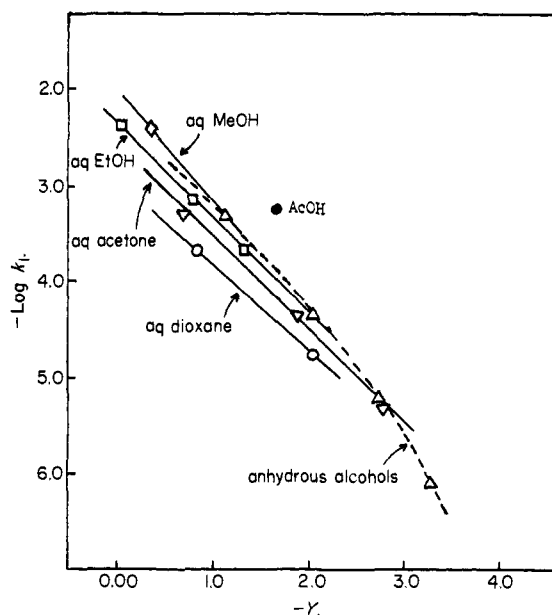


Figure 1. Logarithmic relationship of 1-adamantyl *p*-toluenesulfonate first-order solvolytic rate coefficients ( $k_1$ ,  $\text{sec}^{-1}$ ) to solvent ionizing power.

on ionizing power in forming the ion pair, there would be a further dependence on ionizing (or, more strictly, dissociating) power in determining the ratio of ion-pair return relative to dissociation followed by chemical capture.

The ratio of the rates for identical reactions of *p*-toluenesulfonates and bromides<sup>16</sup> ( $k_{\text{OTs}}/k_{\text{Br}}$ ) is useful in assessing the extent of carbon-leaving-group bond breaking in the transition state. In 80% ethanol at 25.0°, using the value<sup>5,6</sup> for the first-order rate coefficient for solvolysis of 1-adamantyl bromide of  $4.38 \times 10^{-7} \text{ sec}^{-1}$ , a ratio of 9200 is obtained for the two appropriate 1-adamantyl derivatives. This is in excellent agreement with a previously reported<sup>9</sup> value of 9750, surpasses the values<sup>16</sup> for the E1 decomposition of *tert*-butyl derivatives in acetonitrile of 5126 at 0° and 1670 at 50°, but falls short of ratios which have been determined in acetic acid<sup>9</sup> of 200,000 for 1-adamantyl and 16,000 for 2-adamantyl derivatives.

Another ratio which is useful as a mechanistic probe is the ratio of the rates, preferable at 25.0°, in aqueous alcohol and acetic acid of identical  $Y$  value. While we did not make any studies in acetic acid, three previous kinetic studies which have been reported for acetolysis of 1-adamantyl *p*-toluenesulfonate<sup>5,11,12</sup> at 25.0° have an average specific rate of  $5.12 \times 10^{-4} \text{ sec}^{-1}$ . From our linear Grunwald–Winstein plot for aqueous ethanol mixtures, a value for  $k$  of  $-3.99$  can be obtained for the acetic acid  $Y$  value<sup>19</sup> of  $-1.639$ , corresponding to a specific rate of  $1.02 \times 10^{-4} \text{ sec}^{-1}$ . The ratio of rates in aqueous ethanol and acetic acid of identical  $Y$  value is therefore 0.20, in fairly good agreement with a previously reported<sup>9</sup> value of 0.16. By definition, *t*-butyl chloride has a ratio of unity, and the extent to which the ratio rises above unity has been used as a measure of the sensitivity of the reaction to solvent nucleophilicity. If one accepts that there is already essentially complete absence of nucleophilic participation for *tert*-butyl chlo-

(27) S. Winstein, A. Fainberg, and E. Grunwald, *ibid.*, **79**, 4146 (1957).

ride, this ratio of lower than unity requires a different approach toward an explanation. Other values below unity which have previously been reported include<sup>27, 28</sup> 0.4 for 3,3-dimethyl-2-butyl *p*-bromobenzenesulfonate at 70° and 0.7 for 1-bromobicyclo[2.2.2]octane at 100°. Reactions of esters of *p*-toluenesulfonic acid are known to be susceptible to acid catalysis,<sup>17</sup> and the low ratio can be rationalized by assuming acetic acid to exert a stronger electrophilic catalysis for 1-adamantyl *p*-toluenesulfonate than for the standard substrate, *tert*-butyl chloride. In this connection, the corresponding ratios in aqueous ethanol and formic acid of identical *Y* value are 200 for methyl bromide at 50° and 55 for methyl *p*-toluenesulfonate at 75°, and also 20 for isopropyl bromide at 50° and 2 for isopropyl *p*-bromobenzenesulfonate at 70°.<sup>28-30</sup> The dispersion discovered in the Grunwald-Winstein *mY* plots for 1-adamantyl *p*-toluenesulfonate solvolyses in different solvent systems (Figure 1), systems for which 1-adamantyl bromide solvolyses are quite well correlated by a single plot,<sup>7</sup> is probably also a consequence of increased susceptibility to specific electrophilic catalysis.

It has recently been suggested<sup>7</sup> that 1-adamantyl bromide can be considered as a good alternative to *tert*-butyl chloride as a standard for determination of *Y* values. Historically, the solvolysis rates for aren-sulfonate esters in differing solvent systems have correlated rather poorly with *Y* values, and consideration can be given to the possibility of correlating with a new scale based upon 1-adamantyl *p*-toluenesulfonate. It must be noted, however, that solvolysis rates for 1-adamantyl *p*-toluenesulfonate in differing solvent systems correlate quite well with *Y* values in terms of slope (*m* values), and dispersion is lateral in nature. Consequently, substrates such as benzyl *p*-toluenesulfonate which show considerable variation in *m* values (0.394 in alcohols and aqueous ethanol<sup>23</sup> and 0.650 in aqueous acetone<sup>31</sup>) cannot be expected to give a single linear free energy relationship toward 1-adamantyl *p*-toluenesulfonate solvolyses. Further, in aqueous ethanol and acetic acid of identical *Y* value, benzyl *p*-toluenesulfonate shows a rate ratio of 30 in favor of aqueous ethanol, but for 1-adamantyl *p*-toluenesulfonate there is a dramatic reversal, with a ratio of 5 in favor of acetic acid. Apparently, a scale of *Y* values based upon the limiting situation of 1-adamantyl *p*-toluenesulfonate, bond breaking at transition state extensive and nucleophilic assistance absent, will not represent an improvement over the conventional scale for situations where nucleophilic assistance is operative and bond breaking less extensive.

An alternative scale of solvent polarities is based upon the specific rate ( $k_1^{\text{std}}$ ) of anchimerically assisted solvolysis or decomposition of *p*-methoxyneophyl *p*-toluenesulfonate.<sup>17</sup> Data at 25.0° are available for five solvent systems also investigated with 1-adamantyl *p*-toluenesulfonate. Four of these solvent systems (ethanol, 80% ethanol, methanol, and acetic acid) give a good linear free energy correlation:  $\log k_1^{1-\text{AdOTs}} = (2.19 \pm 0.03) \log k_1^{\text{std}} - (8.26 \pm 0.32)$ . In 80% dioxane the solvolysis rate for *p*-methoxyneophyl

*p*-toluenesulfonate is slightly lower than in ethanol, but for 1-adamantyl *p*-toluenesulfonate it is faster by a factor of 4.5. The point for 80% dioxane shows appreciable deviation from the above linear free energy relationship. Aqueous dioxane solvents were found<sup>22</sup> to be similarly anomalous in a logarithmic comparison of neophyl *p*-toluenesulfonate specific solvolysis rates with  $k_1^{\text{std}}$ .

### Experimental Section<sup>32</sup>

**Purification of Solvents.** Methanol, ethanol, and 2-propanol were dried using Bjerrum's method.<sup>34</sup> A 50-ml portion of the alcohol was treated with 5 g of magnesium powder and 5 g of iodine in a dry system. After completion of reaction, 800 ml of the alcohol was added. The mixture was refluxed for several hours and distilled through an 18-in. fractionating column. Titration with Karl Fischer reagent indicated the water content of these alcohols to be less than  $10^{-3}$  *M*.

*tert*-Butyl alcohol was purified by refluxing 500 ml over 20 g of calcium hydride for 2 days and then distilling through an 18-in. fractionating column. Titration with Karl Fischer reagent indicated  $1.5 \times 10^{-3}$  *M* water.

*p*-Dioxane (1 l.) was refluxed overnight with 14 ml of concentrated HCl and 100 ml of water while a stream of nitrogen was bubbled through the solution.<sup>35</sup> After neutralization and drying with KOH pellets, the *p*-dioxane was distilled through an 18-in. fractionating column. Dry *p*-dioxane was obtained by repeated passage through a column of Linde 4A molecular sieves. Titration with Karl Fischer reagent showed  $1.5 \times 10^{-3}$  *M* water.

Acetone (1 l.) was passed through a column of Linde 4A molecular sieves and then distilled from 25 g of molecular sieves.<sup>17</sup>

**1-Adamantyl *p*-Toluenesulfonate.**<sup>14, 12</sup> This compound is extremely moisture sensitive<sup>6</sup> and is best prepared and handled within a drybox. However, batches prepared under less stringent conditions led to rate coefficients, based upon the infinity titer, identical with those from drybox samples.

A typical procedure is as follows. Hexane was distilled and then dried by passage through Linde 4A molecular sieves. A 2.9-g portion of 1-adamantyl iodide<sup>6, 36</sup> was dissolved in 350 ml of this hexane, within a drybox, and 3.4 g of silver *p*-toluenesulfonate, which had been recrystallized from acetonitrile, was added. After stirring for 24 hr at room temperature in the absence of light, the hexane solution was decanted from the solid residue and evaporated to dryness. A crude yield of 3.5 g (100%), mp 72-79°, was recrystallized from hexane. Two types of crystals were observed to form and, after mechanical separation, melting points were obtained of 72.5-74.5° for square plates and 80.5-81.5° for long square needles. The melting point range of 70-79° typically obtained for bulk samples probably reflects the presence of a mixture of two crystalline forms (lit. mp 72-75°,<sup>12</sup> 78-83°<sup>11</sup>). The analyses reported below are for a sample of melting point range 72.5-79°; ir (KBr-styrofoam) includes 3.43, 3.51, 7.50, 8.48 (sh), 8.58, 9.17, 9.70, 11.18 (br), 12.09, 12.45, 14.03, 15.15  $\mu$ ; pmr  $\tau$  2.22 (d, 2, *J* = 8 Hz), 2.68 (d, 2, *J* = 8 Hz), 7.57 (s, 3, -CH<sub>3</sub>), 7.82 (s, 9), 8.37 (s, 6). Addition of a tared sample to neutral acetone and titration against sodium methoxide in methanol, using resorcinol blue (Lacmoid) as indicator, indicated 0.2% acid initially present and 100.8% acid present after addition of water and complete hydrolysis. Anal. Calcd for C<sub>17</sub>H<sub>22</sub>SO<sub>3</sub>: C, 66.64; H, 7.24; S, 10.46. Found: C, 66.31; H, 7.47; S, 10.42.

**1-Adamantyl Ethyl Ether.**<sup>37</sup> This compound had previously been prepared by the reaction of 1-adamantyl chloride with silver

(32) Melting points were taken in closed capillary tubes. Infrared spectra were obtained on a Beckman IR-8. Pmr spectra<sup>33</sup> were recorded with a Varian A-60A spectrometer system, using chloroform-*d* as solvent. Microanalyses were by the Spang Microanalytical Laboratory, Ann Arbor, Mich. Yields are based upon the 1-adamantyl reactant.

(33) For a discussion of the pmr spectra of several 1-adamantyl derivatives, see R. C. Fort, Jr., and P. von R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965).

(34) H. Lund and J. Bjerrum, *Chem. Ber.*, **64**, 210 (1931).

(35) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1956, p 177.

(36) D. N. Kevill and F. L. Weitl, *J. Org. Chem.*, **35**, 2526 (1970).

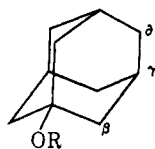
(37) MacMillan and Pryce<sup>20</sup> have recently prepared this compound, by interaction of 1-adamantanol with ethyl iodide in the presence of silver oxide, but no characteristics were reported. References given<sup>20</sup>

(28) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

(29) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948).

(30) S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952).

(31) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

**Table VII.** Chemical Shifts for Adamantyl Protons of 1-Alkoxyadamantanes in  $\text{CDCl}_3$  ( $\tau$ )

Substituent R	$\beta$ -H (6)	$\gamma$ -H (3)	$\delta$ -H (6)	$J_{\beta\gamma}$ , Hz
-H <sup>a</sup>	8.30	7.88	8.39	
-CH <sub>3</sub>	8.27	7.87	8.37	
-CH <sub>2</sub> CH <sub>3</sub> <sup>b</sup>	8.24	7.87	8.37	2.8
-CH(CH <sub>3</sub> ) <sub>2</sub>	8.26	7.88	8.39	2.8
-C(CH <sub>3</sub> ) <sub>3</sub>	8.12	7.93	8.40	2.6

<sup>a</sup> For a commercial (Aldrich) sample. <sup>b</sup> Also,  $\tau$  6.54 (m, 2,  $\text{CH}_2\text{CH}_2$ -), 8.85 (t, 3,  $\text{CH}_3\text{CH}_2$ -).

**Table VIII.** Solvolysis Product Studies

Solvent	Temp, °C	Reaction time, hr	Product weight, <sup>a</sup> g	Identification
Methanol	25.0	76	0.23	1-AdOCH <sub>3</sub>
Ethanol	55.0	26	0.26	1-AdOCH <sub>2</sub> CH <sub>3</sub>
2-Propanol	55.0	31	0.28	1-AdOCH(CH <sub>3</sub> ) <sub>2</sub>
<i>tert</i> -Butyl alcohol <sup>b</sup>	55.0	117	0.22	1-AdOH <sup>c</sup>
80% ethanol	25.0	98	0.23	29% 1-AdOCH <sub>2</sub> CH <sub>3</sub> <sup>d</sup> 71% 1-AdOH

<sup>a</sup> All yields, within experimental error, quantitative. <sup>b</sup> Containing 0.06 *M* pyridine. <sup>c</sup> Spectra identical with those for commercial (Aldrich) sample;  $\nu$  (KBr) 3.05  $\mu$  (-OH). <sup>d</sup> From comparison of integration of signals from ethyl protons with those from 1-adamantyl plus hydroxyl protons.

perchlorate in ethanol,<sup>38</sup> and the spectra recorded in this study were available for comparison purposes. Both 1-adamantyl methyl ether and 1-adamantyl ethyl ether have previously been prepared by the electrolysis of 1-adamantanecarboxylic acid in the appropriate alcohol,<sup>39</sup> but spectral characteristics do not appear to have been reported.

**1-Adamantyl Methyl Ether.** Following the procedure of Kevill and Horvath,<sup>38</sup> 3.95 g of 1-adamantyl chloride was added to a solution of 4.7 g of silver perchlorate in 10 ml of methanol. Immediate evolution of heat and precipitation of silver chloride occurred. Excess silver ion was precipitated by addition of lithium chloride in acetone. The mixture was filtered, the cake washed with methanol, and the filtrate partitioned between water and ether. Evaporation of the ether fraction yielded 3.87 g of liquid residue. A vacuum distillation through a 6-in. fractionating column gave 2.53 g (65%) of colorless viscous liquid, bp 66–68° (3 mm) [lit.<sup>39</sup> bp 90–92° (5 mm)];  $\nu$  (CCl<sub>4</sub>) includes 3.44, 3.51, 6.92, 7.41, 7.68, 9.00, 9.21, 9.52, 11.23  $\mu$ ;  $\nu$  (CDCl<sub>3</sub>)  $\tau$  6.78 (s, 3,  $\text{CH}_3$ -). *Anal.* Calcd for C<sub>11</sub>H<sub>18</sub>O: C, 79.50; H, 10.92. Found: C, 79.44; H, 10.95.

**1-Adamantyl Isopropyl Ether.** A slurry of 3.0 g of 1-adamantyl iodide in 10 ml of 2-propanol was combined, at ice-bath temperature, with a solution of 2.4 g of silver perchlorate in 10 ml of 2-propanol. To this well-mixed slurry were added a few milliliters of pyridine and 1.0 g of sodium iodide. The mixture was filtered through a Büchner funnel and the cake washed well with benzene. The total filtrate was successively washed with 0.05 *M* HCl and water, followed by drying over anhydrous MgSO<sub>4</sub>. Evaporation under reduced pressure gave 1.84 g (83%) of a colorless liquid, mp 18.5–19.5°;  $\nu$  (hexane) includes 7.82, 8.58, 9.09, 9.27, and 10.07  $\mu$ ;  $\nu$  (CDCl<sub>3</sub>)  $\tau$  6.07 (m, 1,  $J = 6.0$  Hz,  $-\text{CH}(\text{CH}_3)_2$ ), 8.92 (d, 6,  $J = 6.0$

for 1-adamantyl ethyl ether (actually a 1934 paper not 1954) and for 1-adamantanol both appear to be irrelevant

(38) D. N. Kevill and Sr. V. M. Horvath, Abstracts, 5th Caribbean Chemical Symposium, Barbados, B. W. I., Jan 1969, pp 28–29. The characterization is as follows: mp 15–15.5° [lit.<sup>39</sup> bp 110–111° (14 mm)];  $\nu$  (CCl<sub>4</sub>) includes 3.44, 3.51, 6.52, 8.01, 9.01, 9.22, 10.29  $\mu$ ;  $\nu$  (CDCl<sub>3</sub>)  $\tau$  6.61 (m, 2,  $J = 6.9$  Hz,  $\text{CH}_3\text{CH}_2$ -), 7.87 (s, 3,  $\gamma$ -H), 8.29 (d, 6,  $\beta$ -H), 8.37 (m, 3,  $\delta$ -H), 8.92 (t, 3,  $J = 6.9$  Hz,  $\text{CH}_3\text{CH}_2$ -).

(39) F. N. Stepanov, V. F. Baklan, and S. S. Guts, *Sin. Prir. Soedin., Ikh Analogov Fragmentov*, 1965, 95 (1965); *Chem. Abstr.*, 65, 627b (1966).

Hz,  $-\text{CH}(\text{CH}_3)_2$ ). *Anal.* Calcd for C<sub>13</sub>H<sub>22</sub>O: C, 80.35; H, 11.41. Found: C, 80.08; H, 11.21.

**1-Adamantyl *tert*-Butyl Ether.** To a solution of 2.0 g of 1-adamantyl iodide in 10 ml of *tert*-butyl alcohol containing 2 g of pyridine was added a solution of 2.0 g of silver perchlorate in 5 ml of *tert*-butyl alcohol. Heat and a silver iodide precipitate were immediately generated. After addition of 1.0 g of sodium iodide and stirring, the solution was filtered through a Büchner funnel. The cake was washed with benzene and the total filtrate was then treated with successive portions of water until the smell of pyridine was absent from the aqueous extracts. The organic layer was dried over anhydrous MgSO<sub>4</sub> and evaporated under reduced pressure to leave 1.27 g (80%) of a white solid, mp 49–52°. Recrystallization from methanol at 0° gave 1.17 g (75%); mp 54–55.5°;  $\nu$  (hexane) includes 8.20, 8.48, 9.10, 9.28, 10.11, 11.75, 14.90  $\mu$ ;  $\nu$  (CDCl<sub>3</sub>)  $\tau$  8.72 (s, 9,  $(\text{CH}_3)_3\text{C}$ -). *Anal.* Calcd for C<sub>14</sub>H<sub>24</sub>O: C, 80.73; H, 11.61. Found: C, 80.83; H, 11.92. Attempts to prepare this *t*-butyl ether by the same procedures as the corresponding methyl, ethyl, and isopropyl ethers resulted only in the isolation of high yields of 1-adamantanol.

**Table IX**

A. Temp, 35.1°; 2-ml Aliquots; [C <sub>10</sub> H <sub>15</sub> OTs], 0.0521 <i>M</i> ; Solvent, 100% Ethanol; Titrers, ml of 0.0105 <i>M</i> Methanolic NaOMe						
Time, sec	0	255	654	1287	2146	3369
Titer	0.83	1.14	1.63	2.36	3.20	4.25
10 <sup>6</sup> k <sub>1</sub> , sec <sup>-1</sup>		1.36	1.41	1.43	1.41	1.40
Time, sec	4985	7142	9921	13128	∞	
Titer	5.34	6.49	7.70	8.46	9.92	
10 <sup>6</sup> k <sub>1</sub> , sec <sup>-1</sup>	1.38	1.37	1.42	1.39		
B. Temp, 25.0°; 2-ml Aliquots; [C <sub>10</sub> H <sub>15</sub> OTs], 0.0256 <i>M</i> ; Solvent, 95% Acetone; Titrers, ml of 0.00519 <i>M</i> Methanolic NaOMe						
Time, sec	0	2742	14412	36375	96798	
Titer	0.29	0.40	0.86	1.68	3.56	
10 <sup>6</sup> k <sub>1</sub> , sec <sup>-1</sup>		4.22	4.26	4.33	4.33	
Time, sec	110532	167631	198567	255012	∞	
Titer	3.95	5.28	5.94	6.78	9.84	
10 <sup>6</sup> k <sub>1</sub> , sec <sup>-1</sup>	4.35	4.41	4.50	4.46		
C. Temp, 25.0°; 2-ml Aliquots; [C <sub>10</sub> H <sub>15</sub> OTs], 0.0522 <i>M</i> ; Solvent, 100% Ethanol Containing 0.149 <i>M</i> $\text{NET}_4\text{Cl}$ ; Titrers, ml of 0.01046 <i>M</i> Methanolic NaOMe						
Time, sec	0	1491	2724	4749	6588	12874
Titer	0.29	1.00	1.52	2.34	3.05	4.88
10 <sup>6</sup> k <sub>1</sub> , sec <sup>-1</sup>		5.10	4.99	5.29	5.09	4.99
Time, sec	18312	23139	29523	38124	48009	∞
Titer	6.10	6.92	7.82	8.62	9.12	9.97
10 <sup>6</sup> k <sub>1</sub> , sec <sup>-1</sup>	5.00	4.98	5.13	5.17	5.05	
D. Temp, 65.0°; 2-ml Aliquots; [C <sub>10</sub> H <sub>15</sub> OTs], 0.0522 <i>M</i> ; Solvent, 100% <i>tert</i> -Butyl Alcohol Containing 0.104 <i>M</i> Pyridine; Titrers, ml of 0.01037 <i>M</i> Methanolic NaOMe						
Time, sec	0	525	1126	2491	3925	5605
Titer	0.03	0.35	0.77	1.64	2.60	3.59
10 <sup>6</sup> k <sub>1</sub> , sec <sup>-1</sup>		6.15	6.78	7.10	7.52	7.85
Time, sec	7605	9604	12043	15052	17700	∞
Titer	4.62	5.61	6.64	7.65	8.20	10.07
10 <sup>6</sup> k <sub>1</sub> , sec <sup>-1</sup>	7.95	8.45	8.90	9.42	9.85	

<sup>a</sup> True infinity titer, determined after time interval equivalent to 20 half-lives.

(40) Chemical shifts of adamantyl protons are reported in Table VII.

**Acid-Catalyzed Decomposition of 1-Adamantyl *tert*-Butyl Ether.** A 0.112-g sample of 1-adamantyl *tert*-butyl ether was allowed to stand for 53 hr at 25.0° within 10 ml of *tert*-butyl alcohol containing 0.05 *M* HCl. Evaporation to dryness gave 0.082 g (100%) of white solid whose pmr and ir spectra indicated it to be 1-adamantanol.

**Product Studies.** A 0.43-g portion of 1-adamantyl *p*-toluenesulfonate was solvolyzed in 25 ml of the appropriate solvent. After completion of reaction, the solution was partitioned between water and hexane. The hexane fraction was dried over anhydrous MgSO<sub>4</sub> and evaporated to dryness to give the solvolysis product, which was identified by comparison of ir and pmr spectra with those of appropriate authentic samples. The data are summarized in Table VIII.

**Kinetic Procedures.** At suitable time intervals, 2-ml aliquots were removed from 25 ml of bulk solution. For runs in dry alcohols, 25 ml of temperature-equilibrated solvent was added to slightly in excess of 0.4 g of 1-adamantyl *p*-toluenesulfonate. For runs in aqueous organic solvents, all prepared on a volume-to-volume basis, the rate at which the substrate passed into solution was frequently low compared to the reaction rate and, therefore, the substrate was dissolved in the organic phase and an appropriate volume of water added immediately prior to the start of the kinetic run. Also, for some runs carried out in aqueous-organic solvents, the concentration of 1-adamantyl *p*-toluenesulfonate was halved.

Aliquots were quenched by drowning in 20 ml of acetone, neutral to resorcinol blue (Lacmoid) indicator, and cooled within a solid CO<sub>2</sub>-acetone or ice-salt bath, and the acid which had developed was titrated against a standardized solution of sodium methoxide in methanol. For runs in the presence of pyridine or quaternary ammonium salts, the appropriate concentration of additive was introduced into the solvent prior to its addition to the substrate. Infinity titers were estimated by removing aliquots into 10 ml of 60% ethanol, allowing them to stand for several hours prior to addition of 20 ml of acetone and titration as indicated above. For each run, a mean value of two infinity determinations was taken. For several of the faster kinetic runs, true infinity titers were also obtained by direct addition to neutral acetone and these closely agreed with the infinity titers estimated by the above technique.

With the exception of the *tert*-butyl alcohol runs, first-order rate coefficients were obtained from a statistical computation of the slope of a plot of  $\log [(titer)_{t=\infty} - (titer)_{t=}]$  against time. For the *tert*-butyl alcohol runs, integrated rate coefficients were determined on a point-by-point basis, as in example D of Table IX, and an initial value was obtained by statistical extrapolation of a plot of these coefficients against extent of reaction to zero extent of reaction. In the four illustrative runs which appear in Table IX, the first-order rate coefficients reported for each point are the integrated first-order rate coefficients with respect to 1-adamantyl *p*-toluenesulfonate.

## Electronic Structures of Low-Spin, Square-Pyramidal Complexes of Nickel(II)

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**Abstract:** Detailed electronic spectral measurements at 300 and 77°K have been carried out on square-pyramidal complexes of the type [Ni(diars)<sub>2</sub>X]<sup>2+</sup> (diars = *o*-phenylenebisdimethylarsine; X = Cl, Br, I, CNS, CN, thiourea, NO<sub>2</sub>, As). Assignment of the ligand-field bands leads to a d-level ordering  $xy < xz, yz < z^2 \ll x^2 - y^2$ . Central to this interpretation is identification of the main absorption band as the symmetry-allowed <sup>1</sup>A<sub>1</sub> → <sup>1</sup>E ( $xz, yz \rightarrow x^2 - y^2$ ) transition. The assignment was facilitated by the low-temperature measurements, and by comparison with electronic spectral results on the four-coordinate [Ni(diars)<sub>2</sub>]<sup>2+</sup> complex. Comparison of the ligand-field spectra for [Ni(diars)<sub>2</sub>X]<sup>2+</sup> (X = Cl, Br, I) with those for analogous trigonal-bipyramidal complexes shows large differences. At low temperatures, there are three bands in the square-pyramidal cases, whereas two bands are resolved in the trigonal bipyramids. These results and other electronic spectral criteria are presented which provide a means of distinguishing between the square-pyramidal and trigonal-bipyramidal geometries in the d<sup>8</sup> low-spin electronic configuration. The charge-transfer region of the spectra of the four- and five-coordinate complexes is complicated by intraligand diarsine absorption.

It has been known for some time that the bisdiarsine complexes of M(II) (M = Ni, Pd, Pt) readily form adducts of higher coordination number with various simple ligands (X).<sup>3,4</sup> The pioneering work of Nyholm on the transition metal complexes of diarsine included conductivity and spectrophotometric evidence which indicated that these adducts are five coordinate in solution. Since that time, additional evidence has been provided by Peloso and coworkers, who were able to determine formation constants and thermodynamic parameters for a wide range of the [M(diars)<sub>2</sub>X]<sup>2+</sup> (M = Ni(II), Pd(II), Pt(II)) species.<sup>5</sup> The suggestion that

these five-coordinate complexes are square pyramidal<sup>4</sup> has received strong support from the determination of the crystal and molecular structure of the once very puzzling compound<sup>6</sup> now known<sup>7</sup> to be [Ni(diars)-(triars)](ClO<sub>4</sub>)<sub>2</sub>. The complex ion is composed of a nearly regular square pyramid of As atoms about the central nickel atom. Although a significant number of low-spin d<sup>8</sup> square-pyramidal structures have been determined by X-ray methods,<sup>8-12</sup> and some electronic

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