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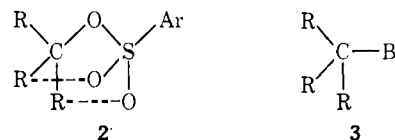
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### A Remarkably Large Solvolytic Rate Enhancement Due to Relief of Ground State Leaving Group Strain<sup>1</sup>

Sir:

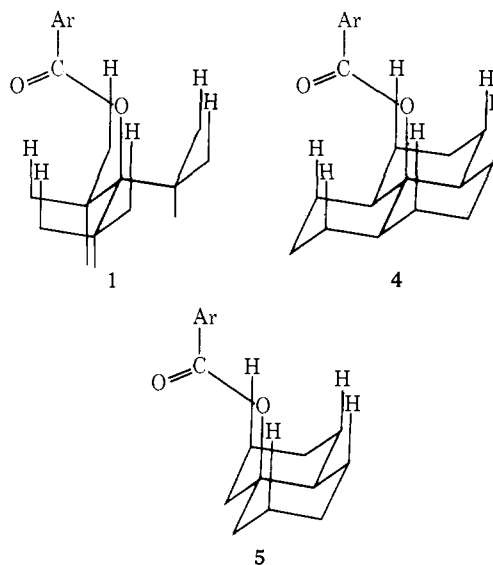
In the past, the significance of ground state steric strain specific to different leaving groups, if considered at all, has often been dismissed as an important contributor to solvolytic rate accelerations.<sup>2-5</sup> Thus, explanations for the large increase in tosylate-bromide ratios in going from primary to tertiary substrates have stressed effects which influence transition state energies;<sup>6</sup> steric effects were discounted.<sup>6a,7</sup> The greatly enhanced solvolytic reactivities of highly branched tertiary *p*-nitrobenzoates, such as tri-*tert*-butylcarbinyl-OPNB (1-OPNB),<sup>9</sup> have been attributed to relief of ground state repulsive nonbonded interaction among the alkyl groups during ionization (B strain).<sup>8,9a</sup> The possibility that rate enhancement by relief of leaving group strain (F strain)<sup>9b</sup> may be quite large apparently has not been appreciated until recently.<sup>3</sup>

In contrast, Schleyer, *et al.*, have pointed out that tertiary tosylates (2) suffer from 1,5-nonbonded interactions not present in the corresponding bromides (3).<sup>4,5</sup> Relief of ground state tosylate strain during ionization may be the major factor contributing to the large OTs-Br ratios in tertiary systems and may be important in secondary substrates as well.<sup>4,5</sup> We now



report unambiguous evidence that relief of similar 1,5- (and 1,6-)nonbonded interactions in congested tertiary *p*-nitrobenzoates can contribute as much as 10<sup>3</sup> to 10<sup>4</sup> acceleration to solvolytic reactivity.

We postulate a remarkably large ground state leaving group effect to explain the 2860-fold solvolytic rate enhancement at 25° of *trans,trans,trans*-perhydro-9b-phenanyl-OPNB (4-OPNB) relative to *trans*-9-decalyl-OPNB (5-OPNB).<sup>1a</sup> 4-OPNB but not 5-OPNB suffers



(1) Based in part on the Ph.D. Theses of (a) W. C. Dickason, Purdue University; *Diss. Abstr.*, 2559-B (1970); (b) R. C. Bingham, Princeton University, 1970; *Diss. Abstr.*, 7178-B (1971).

(2) Exceptions include: (a) effects of the halogen on the rates of solvolysis of tertiary halides (H. C. Brown and A. Stern, *J. Amer. Chem. Soc.*, **72**, 5068 (1950)); (b) effects of the size of leaving group on the direction of bimolecular elimination (H. C. Brown and R. L. Klimisch, *ibid.*, **88**, 1425 (1966); R. A. Bartsch, *J. Org. Chem.*, **35**, 1023 (1970), and references cited therein); (c) relative solvolysis rates of cyclopropyl derivatives (W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 133 (1972), also see ref 3-5).

(3) J. E. Dubois and J. S. Lomas, *Tetrahedron Lett.*, 1791 (1973).

(4) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2538 (1970); (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2542 (1970).

(5) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971).

(6) (a) H. M. R. Hoffmann, *J. Chem. Soc.*, 6753, 6762 (1965); (b) *Tetrahedron Lett.*, 4393 (1967); (c) G. M. Fraser and H. M. R. Hoffmann, *J. Chem. Soc. B*, 265 (1967); (d) H. M. R. Hoffmann and G. M. Fraser, *ibid.*, 425 (1967); (e) R. G. Pearson and J. Songstad, *J. Org. Chem.*, **32**, 2899 (1967); (f) D. D. Roberts and J. G. Traynham, *ibid.*, **32**, 3177 (1967); (g) J. W. S. Trahanovsky and M. P. Doyle, *Chem. Commun.*, 1021 (1967); (h) A. F. Cockerill, *Tetrahedron Lett.*, 4913 (1969); (i) C. H. DePuy and C. A. Bishop, *J. Amer. Chem. Soc.*, **82**, 2532 (1960).

(7) Similarly, M. L. Sinnott and M. C. Whiting, *J. Chem. Soc. B*, 965 (1971), "eliminated" differential steric effects as a contributing factor to erratic tosylate-picrate leaving group ratios.

(8) (a) P. D. Bartlett and M. Stiles, *J. Amer. Chem. Soc.*, **77**, 2806 (1955); (b) P. D. Bartlett and T. T. Tidwell, *ibid.*, **90**, 4421 (1968). This paper does point out that "the more reactive [ester] has the greater steric hindrance around the leaving group," but this observation is not further developed.

(9) (a) H. C. Brown and R. S. Fletcher, *J. Amer. Chem. Soc.*, **71**, 1845 (1949); H. C. Brown, *Science*, **103**, 385 (1946); (b) H. C. Brown, M. D. Taylor, M. Gerstein, and H. Bartholomay, *J. Amer. Chem. Soc.*, **66**, 431 (1944); **69**, 1332 (1947).

from unavoidable repulsive interactions involving (depending on the conformation of the *p*-nitrobenzoate group) the carbonyl oxygen, the carbonyl carbon, and/or the aryl group. These special 1,5- and 1,6-type interactions will not be present in the corresponding chlorides 4-Cl and 5-Cl.

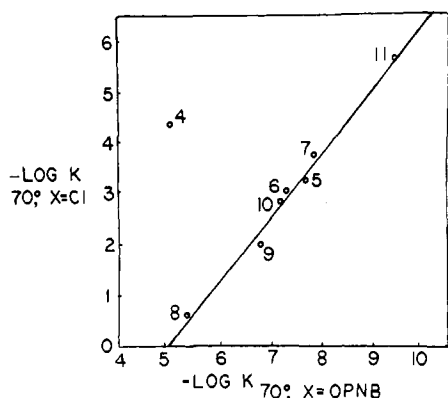
In systems not suffering from such 1,5- and 1,6-nonbonded interactions, quantitative conformational analysis can be used to predict reactivities with reasonable success.<sup>5,10</sup> In the present degree of refinement of this approach, the leaving group is not considered explicitly. The ground state energies are approximated by the parent hydrocarbon and transition state free energies by the carbocation. The difference in these calculated energies,  $\Delta H(\text{calcd})$ , is a reactivity index; for 4,  $\Delta H(\text{calcd})$  is 8.6 kcal/mol. On the basis of eq 1,<sup>5</sup> the

$$-\log k_{\text{Cl}, 80\% \text{EtOH}, 70^\circ} = 0.32\Delta H(\text{calcd}) + 2.15 \quad (1)$$

predicted rate for 4-Cl is  $4.9 \times 10^{-5} \text{ sec}^{-1}$  at 70° in 80% ethanol,<sup>1b</sup> a value which is one-twelfth that found experimentally for 5-Cl (Table I).

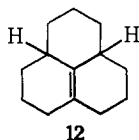
The major discrepancy between this prediction and the experimental *p*-nitrobenzoate data (at 70° in 80% acetone, 4-OPNB/5-OPNB = 466), prompted us to synthesize 4-Cl. This was accomplished from 4-OH by hydrochlorination in pentane in the presence of anhydrous FeCl<sub>3</sub> at -78°. 4-Cl, mp 83.5-84.5°, which had consistent microanalysis and spectra data, gave

(10) J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 4628 (1972), and references cited therein.



**Figure 1.** Correlation of the solvolysis rates of tertiary chlorides in 80% ethanol with the corresponding *p*-nitrobenzoates in 80% acetone at 70° (correlation coefficient = 0.994 omitting 4). The data are summarized in Table I.

only olefin **12** on treatment with KO-*t*-C<sub>4</sub>H<sub>9</sub> in (CH<sub>3</sub>)<sub>2</sub>SO



at 55° for 2 hr or as solvolysis product in 80% ethanol.<sup>11</sup>

The conductometric rate constants for solvolysis of 4-Cl in 80% EtOH were  $5.30 \times 10^{-6} \text{ sec}^{-1}$  at 49.85° and  $7.31 \times 10^{-5} \text{ sec}^{-1}$  at 75.3 (Δ*H*<sup>‡</sup> = 22.4 kcal/mol; Δ*S*<sup>‡</sup> = -13.6 eu). Interpolation gave a rate constant of  $4.36 \times 10^{-5} \text{ sec}^{-1}$  at 70°, a value in excellent agreement with that predicted by eq 1. This confirms the existence of the very large *p*-nitrobenzoate leaving group effect in 4-OPNB.

Figure 1 expresses this leaving group effect graphically. In most systems where 1,5- and 1,6-type non-bonded interactions are absent, *p*-nitrobenzoate rate data are correlated well by eq 2. On the basis of eq 2, 4-OPNB, which deviates markedly, is 2960 times faster than expected. We ascribe this acceleration (amount-

$$-\log k_{\text{Cl}, 80\% \text{ EtOH}, 70^\circ} = -1.24 \log k_{\text{OPNB}, 80\% \text{ acetone}, 70^\circ} - 6.25 \quad (2)$$

ing to 5.4 kcal/mol in free energy) to relief of *p*-nitrobenzoate strain.

This conclusion has important implications for the interpretation of the solvolytic data of highly branched tertiary *p*-nitrobenzoates. As seen in 1-OPNB, (*t*-Bu)<sub>3</sub>COPNB suffers from the same kind of 1,5- and 1,6-interactions as does 4-OPNB. Relief of *p*-nitrobenzoate strain (F strain) should be a significant factor in the acceleration observed (at 70° in 60% (weight) dioxane, 1-OPNB/*t*-Bu-OPNB = 5100).<sup>12</sup> A computer quantitative analysis<sup>13</sup> of such highly congested systems will be presented separately. This analysis shows that little strain is actually relieved during ionization of many but not all highly branched chlorides<sup>14</sup> and

(11) The preparation of the four isomeric perhydro-9*b*-phenalolenols, the chemistry of the perhydrophenalene system, and the solvolytic reactivity of the isomeric *p*-nitrobenzoates will be presented separately.

(12) Calculated from values in ref 9.

(13) Unpublished calculations of D. Khoury, Princeton, University.

(14) For example, V. J. Shiner, Jr., and G. F. Meier, *J. Org. Chem.*, **31**, 137 (1966), showed that the more reactive chloride obtained from di-*tert*-butylmethylcarbinol (P. D. Bartlett and M. S. Swain, *J. Amer. Chem. Soc.*, **77**, 2801 (1955)) was not di-*tert*-butylmethylcarbinyl

**Table I.** Comparison of Solvolysis Rates of Chlorides in 80% Ethanol with the Corresponding *p*-Nitrobenzoates in 80% Acetone at 70°

Compound	<i>k</i> <sub>(Cl)</sub> , sec <sup>-1</sup> (80% ethanol, 70°)	<i>k</i> <sub>(OPNB)</sub> , sec <sup>-1</sup> (80% acetone, 70°)
<b>4</b>	$4.36 \times 10^{-5}$ <sup>a</sup>	$8.35 \times 10^{-8}$ <sup>a</sup>
2-Methyl-2- <i>exo</i> -norbornyl ( <b>8</b> )	$2.42 \times 10^{-1}$ <sup>b</sup>	$3.75 \times 10^{-6}$ <sup>c</sup>
2-Methyl-2-adamantyl ( <b>9</b> )	$1.05 \times 10^{-2}$ <sup>d</sup>	$1.32 \times 10^{-7}$ <sup>e</sup>
<i>tert</i> -Butyl ( <b>10</b> )	$1.51 \times 10^{-3}$ <sup>f</sup>	$5.47 \times 10^{-8}$ <sup>g</sup>
<b>6</b>	$7.63 \times 10^{-4}$ <sup>h</sup>	$3.99 \times 10^{-8}$ <sup>g</sup>
<b>5</b>	$5.68 \times 10^{-4}$ <sup>i</sup>	$1.79 \times 10^{-8}$ <sup>g</sup>
<b>7</b>	$1.95 \times 10^{-4}$ <sup>h</sup>	$1.18 \times 10^{-8}$ <sup>a</sup>
1-Adamantyl ( <b>11</b> )	$2.45 \times 10^{-6}$ <sup>j</sup>	$3.05 \times 10^{-10}$ <sup>a</sup>

<sup>a</sup> This work. <sup>b</sup> K. L. Servis, S. Borcic, and D. E. Sunko, *Tetrahedron*, **24**, 1247 (1968). <sup>c</sup> S. Ikegami, D. L. Vander-Jagt, and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 7124 (1968). <sup>d</sup> J. M. Harris, unpublished results, Δ*H*<sup>‡</sup> = 22.3 kcal/mol and Δ*S*<sup>‡</sup> = -2.9 eu. <sup>e</sup> Reference 10. <sup>f</sup> A. H. Farnberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956). <sup>g</sup> H. C. Brown and W. C. Dickason, *ibid.*, **91**, 1226 (1969). <sup>h</sup> Reference 5. <sup>i</sup> A. F. Boschung, M. Geisel, and C. A. Grob, *Tetrahedron Lett.*, 5169 (1968); K. B. Becker, A. F. Boschung, M. Geisel, and C. A. Grob, *Helv. Chim. Acta*, **56**, 2747 (1973). <sup>j</sup> P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 2700 (1961).

alcohols.<sup>3</sup> Whenever possible, solvolytic reactivity studies should employ chloride or similar leaving groups as opposed to esters in order to minimize F-strain effects.

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chloride (18.4 times more reactive than *tert*-butyl chloride) but rather was triptyldimethylcarbinyl chloride (89,000 times more reactive than *tert*-butyl chloride). Our calculations<sup>13</sup> are in agreement with these results.

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### Evidence against Appreciable Hidden Return in Solvolyses of Simple Secondary Substrates

Sir:

A new mechanism for anchimeric assistance has been postulated recently;<sup>1-3</sup> acceleration due to neighboring

(1) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 6031 (1969).

(2) (a) V. J. Shiner, Jr., and W. Dowd, *J. Amer. Chem. Soc.*, **91**, 6528 (1969); (b) V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *ibid.*, 7748 (1969).

(3) (a) W. M. Schubert and P. H. LeFevre, *J. Amer. Chem. Soc.*, **91**, 7746 (1969); **94**, 1639 (1972); (b) W. M. Schubert and W. L. Henson, *ibid.*, **93**, 6299 (1971).