Acetolysis of the 3-Phenyl-, 3-*p*-Anisyl-, and 7-Phenyl-2-norbornyl Tosylates

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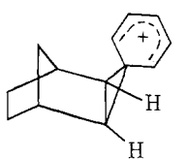
The acetolysis rates of the four 3-phenyl-, the four 3-*p*-anisyl-, and the four 7-phenyl-2-norbornyl tosylates have been determined. It appears that the 3-*endo*-phenyl- and 7-*anti*-phenyl-2-*exo* isomers acetolyze *via* a transition state of approximately equivalent energy relative to tosylate reactant. The 7-*syn*-phenyl-2-*exo* tosylate acetolyzes 33 times as fast as the 3-*exo*-phenyl-2-*exo* compound. That the 3-*endo*-phenyl-2-*endo* isomer reacts faster than its unsubstituted 2-endo parent is attributed to steric acceleration in the former case. The extremely slow rate for the 3-*exo*-phenyl-2-*endo* isomer may be due to steric inhibition to solvation of the developing positive charge in the transition state. The rate retardation in the 3-*exo*-phenyl-2-*exo* compound may result from phenyl π-cloud-developing anion transition-state destabilization. The same effect may be operative in the 1-phenyl-2-*exo* tosylate. Rate increases by the *p*-anisyl group relative to phenyl ranged from 1.1 to 2.7 for the compounds studied.

Our initial interest in the solvolyses of phenyl-substituted norbornyl tosylates stemmed from a desire to assess the geometrical requirement for aryl participation to a phenonium ion intermediate (**1** or **2**) of the



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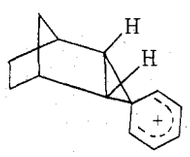

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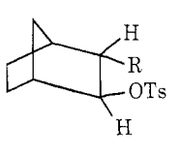
type frequently postulated for solvolyses in acyclic systems.[2] We also anticipated that studies involving fixed geometries with known dihedral angles between aryl and departing tosylate groups might provide insight as to relationships between geometries and the rate-retarding inductive effects of aryl substituents, steric hindrance to ionization, and steric acceleration. In addition, comparison of the rate data from 3-substituted 2-norbornyl tosylates with the related 7-substituted 2-norbornyl derivatives might provide information as to the amount of participation of the C_1–C_6 bond in the transition state for the exo compounds. For example, if the transition state for solvolysis of **3** involves significant σ bond participation with charge delocalization to C-1, then, assuming that the ground states are of identical energy, the inductive effect of the substituent at C-3 should not differ markedly from its effect at C-7 (as in **4**). Conversely, if there is no



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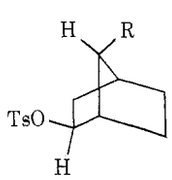

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significant σ participation in the transition states, then the inductive effect of a substituent at C-3 (**3**) on the rate of solvolysis of *exo*-norbornyl tosylate should be similar in magnitude to its effect on the solvolysis rate of *endo*-norbornyl tosylate. Positional responses of the exo/endo rate ratios are generally considered to be one of the most concise methods of analyzing the results in the norbornyl system.[3]

The effects of geminal dimethyl groups at C-3, C-5, C-7,[4] and at C-6[5] on the acetolysis rates of norbornyl tosylates have been reported. Dimethyl substitution at C-3 retards the acetolysis rate of the exo tosylate by a factor of 23 in comparison with its C-7 dimethyl-substituted isomer of Wagner–Meerwein rearrangement. The retardation factor is reduced to 5.8 when the rate data for the C-3 and C-7 dimethyl-substituted endo tosylates are compared. These examples serve to illustrate the involvement of factors other than inductive effects, since inductive effects alone would lead one to an *a priori* expectation of a greater accelerating influence by the more proximate C-3 methyl substituents. While rate and product studies of the effects of chloro and oxygenated substituents at the C-7 position[6] and of methoxy substituents at the C-4, C-5, C-6, and C-7 positions[3] on the acetolyses of 2-norbornyl tosylates have appeared prior and subsequent to our initial communication,[7] the only datum reported on Wagner–Meerwein rearrangement isomers with these substituents is the report that the rate of acetolysis of *cis-exo*-3-chloronorbornyl tosylate is at least 239 times slower than that of 7-*anti*-chloro-2-norbornyl tosylate.[8] This result suggests little generation of positive charge at C-1 in the transition state; *i.e.*, the positive charge is developing largely at C-2, where the rate-retarding inductive effect of the 3-chloro substituent in the former operates maximally and in the latter operates minimally.

Determinations of the acetolysis rates for the four 3-phenyl-2-norbornyl tosylates and the four 7-phenyl-2-norbornyl tosylates should reflect the relative effects of phenyl substituents on the acetolyses of *exo*- and *endo*-norbornyl tosylates. Herein we report the summations of these rate studies along with rate data on

(1) National Aeronautics and Space Administration (NASA) Fellow, 1966–1968.

(2) It would be impractical to list all phenonium ion references. The following references may be considered as representative evaluations of the phenonium ion problem: (a) D. J. Cram, *J. Amer. Chem. Soc.*, **86**, 3767 (1964); (b) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *ibid.*, **87**, 2137 (1965); (c) J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968).

(3) P. v. R. Schleyer, P. J. Stang, and D. J. Raber, *J. Amer. Chem. Soc.*, **92**, 4725 (1970).

(4) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 378 (1965).

(5) P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, **87**, 375 (1965).

(6) (a) P. G. Gassman and J. H. Hornback, *J. Amer. Chem. Soc.*, **91**, 4280 (1969); (b) P. G. Gassman, J. L. Marshall, J. G. Macmillan, and J. H. Hornback, *ibid.*, **91**,, 4282 (1969); (c) P. G. Gassman and J. L. Marshall, *ibid.*, **88**, 2822 (1966); (d) P. G. Gassman and J. L. Marshall, *Tetrahedron Lett.*, 2429, 2433 (1968); (e) P. G. Gassman and J. G. Macmillan, *J. Amer. Chem. Soc.*, **91**, 5527 (1969); P. G. Gassman and J. M. Hornback, *ibid.*, **94**, 7010 (1972).

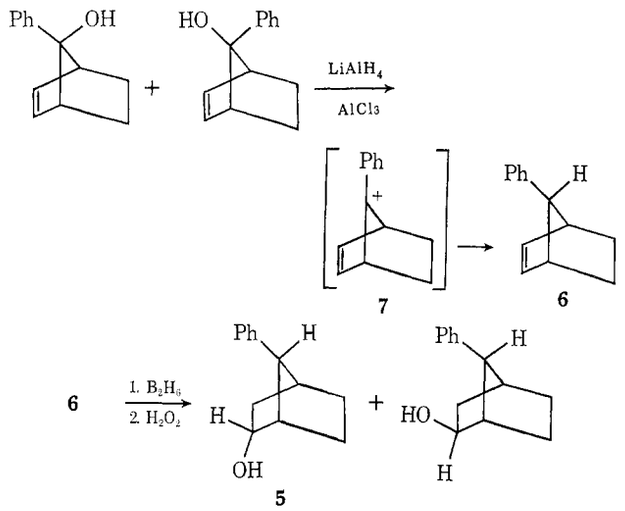
(7) D. C. Kleinfelter, E. S. Trent, J. E. Mallory, and T. E. Dye, *J. Amer. Chem. Soc.*, **88**, 5350 (1966).

(8) H. L. Goering and M. J. Degani, *J. Amer. Chem. Soc.*, **91**, 4506 (1969).

the four 3-*p*-anisyl-2-norbornyl tosylates. In subsequent publications we shall deal with detailed analyses of the acetolysis products[9] and a study of the influence of cyclohexyl substituents on the acetolysis rates.[10]

Synthesis of Compounds.—The preparation and characterization of the four 3-phenyl-2-norbornanols were described previously.[11] The four *p*-anisyl analogs were prepared in a similar fashion. The alcohols 7-*syn*-phenyl-2-*exo*-norbornanol and 7-*anti*-phenyl-2-*exo*-norbornanol were isolated and characterized as products of the acetolyses after reduction with $LiAlH_4$.[12] Reduction with $LiAlH_4$ of 7-*anti*-phenyl-2-norbornanone, prepared by oxidation of the exo alcohol, afforded 7-*anti*-phenyl-2-*endo*-norbornanol.

A convenient route to 7-*syn*-phenyl-2-*endo*-norbornanol (**5**) was not so accessible. As expected by analogy with other syn-7-substituted norbornanones,[13] $LiAlH_4$ reduction of 7-*syn*-phenyl-2-norbornanone gave exclusively attack from the endo direction to re-form the exo alcohol. The key intermediate in the preparation of **5** was 7-*syn*-phenyl-2-norbornene (**6**). Reduction with $LiAlH_4$–$AlCl_3$ by the method of Nystrom and Berger[14] of the mixture of *syn*- and *anti*-phenyl-7-norbornenols formed *via* phenyllithium addition to 7-norbornenone gave only alkene **6**. Evidently the 7-



phenylnorbornenyl cation (**7**) suffers attack by hydride solely from the anti direction, a reaction mode consistent with the necessity for π-bond stabilization of cation **7**.[15] Oxymercuration of **6** gave only the exo alcohol, which was a more convenient preparation than that previously reported.[12] Hydroboration of **6**, on the other hand, gave a *ca.* 3.0:2.0 mixture of exo to endo alcohol, separable by column chromatography. The larger percentage of exo alcohol obtained from hydroboration contrasts with the results from norbornenes with syn methyl substituents[16] in which approximate 1.0:3.5 ratios of exo to endo alcohols were obtained.

Results and Discussion

Rate data for the acetolyses of the eight phenylnorbornyl tosylates and the four *p*-anisyl compounds determined by us are listed in Tables I and II. The data for *exo*- and *endo*-norbornyl tosylates[17] and their 1-phenyl and 1-*p*-anisyl derivatives[18] are included for comparative purposes.

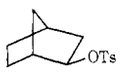
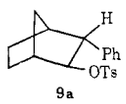
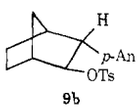
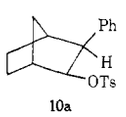
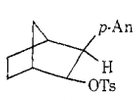
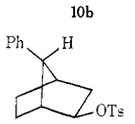
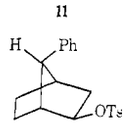
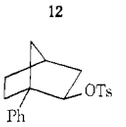
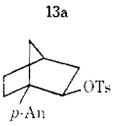
The acetolysis rates for the Wagner–Meerwein rearrangement isomers, 3-*endo*-phenyl- and 7-*anti*-phenyl-2-*exo*-norbornyl tosylates (**9a** and **11**), are practically the same. That isomerization (internal return) of **9a** to **11** competes with acetolysis of **9a** was shown by interrupting its acetolysis after *ca.* 30% reaction and obtaining an equimolar mixture of the two tosylates. A similar experiment starting with pure **11** gave no appreciable amount of **9a**. Since there was a small decrease in rate with progress of time for **9a**, the rate reported was obtained by determinations up through little more than 10% solvolysis and by extrapolation to zero time. One might expect the acetolysis of **9a** to proceed with some steric acceleration resulting from partial relief of unfavorable interactions between an *o*-phenyl hydrogen and the endo-5 hydrogen. Essentially complete isomerization of *endo*-5,6-trimethylene-2-*exo*-norbornyl tosylate to *exo*-5,6-trimethylene-2-*exo*-norbornyl tosylate occurs after about 23% reaction;[19] the acetolysis rate of the former tosylate exceeds the latter by a factor of 3.7, presumably owing to steric acceleration in the former compound. Such steric acceleration does not contribute significantly to the ionization of **9a** relative to that exhibited by the endo trimethylene compound, since steric interactions can be minimized in **9a** by rotation of the benzene ring away from the endo-5 hydrogen.

Thus data analysis of the *endo*-phenyl and *anti*-phenyl isomers, **9a** and **11**, suggests that acetolysis occurs *via* a common intermediate with the two transition states being of approximately equal energy and whose structures lie on the reaction coordinate at positions close to that of the intermediate. The effect of the phenyl on their acetolysis rates is practically the same: *i.e.*, the β-phenyl and γ-phenyl substituent effects are identical. The choice of a suitable model for the rate-retarding inductive effect of phenyl is a difficult one. Winstein, in a number of his publications,[20] has estimated the effect of a β-phenyl substituent to be worth a retardation factor of *ca.* 10. An appropriate monocyclic model with sufficiently remote substituents might be the relative acetolysis rate of *trans*-2-phenylcyclopentyl tosylate *vs.* cyclopentyl tosylate of 0.18.[21] A

(9) D. C. Kleinfelter, M. B. Watsky, and W. E. Wilde, *J. Org. Chem.*, **38**, 4134 (1973).
(10) D. C. Kleinfelter and J. M. Miller, Jr., *J. Org. Chem.*, **38**, 4142 (1973).
(11) D. C. Kleinfelter, T. E. Dye, J. E. Mallory, and E. S. Trent, *J. Org. Chem.*, **32**, 1734 (1967).
(12) D. C. Kleinfelter, *J. Org. Chem.*, **32**, 3526 (1967).
(13) S. Beckmann and R. Mezger, *Chem. Ber.*, **89**, 2738 (1956).
(14) R. F. Nystrom and C. R. A. Berger, *J. Amer. Chem. Soc.*, **80**, 2896 (1958).
(15) P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **92**, 2549 (1970); **91**, 1545 (1969).
(16) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 1990 (1970).
(17) Reference 3 has listed values calculated from data in R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3432 (1957).
(18) D. C. Kleinfelter and P. v. R. Schleyer, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, Abstracts, p 432; D. C. Kleinfelter, *Diss. Abstr.*, **22**, 428 (1961); J. A. Berson in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 182.
(19) K. Takeuchi, T. Oshika, and Y. Koga, *Bull. Chem. Soc. Jap.*, **38**, 1318 (1965).
(20) *Cf.* S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **70**, 821 (1948); S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952).
(21) C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, **91**, 4287 (1969).

TABLE I

KINETIC DATA FOR THE ACETOLYSES OF PHENYL (Ph) AND *p*-ANISYL (*p*-An) SUBSTITUTED 2-*exo*-NORBORNYL TOSYLATES

Exo tosylate	Temp, °C	k_1, sec^{-1}	k_{rel} at 25°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
 8	25.0[a]	2.40×10^{-5}	1.00	22.4	−4.6
 9a	25.0[b]	6.93×10^{-6}	0.289	23.3	−4.0
	30.0	$(1.42 \pm 0.05) \times 10^{-5}$			
	50.0	$(1.35 \pm 0.11) \times 10^{-4}$			
	70.0	$(1.37 \pm 0.03) \times 10^{-3}$			
 9b	25.0	$(1.03 \pm 0.05) \times 10^{-5}$	0.429	22.9	−4.9
	50.0	$(2.23 \pm 0.03) \times 10^{-4}$	(1.49)[c]		
 10a	25.0[b]	1.82×10^{-7}	0.00758	25.5	−3.8
	75.0	$(1.02 \pm 0.05) \times 10^{-4}$			
	95.0	$(7.92 \pm 0.11) \times 10^{-4}$			
 10b	25.0[b]	2.57×10^{-7}	0.0107	24.7	−5.7
	50.0	$(7.05 \pm 0.16) \times 10^{-6}$	(1.41)[c]		
	75.0	$(1.20 \pm 0.04) \times 10^{-4}$			
 11	25.0	$(5.68 \pm 0.13) \times 10^{-6}$	0.237	24.5	−0.2
	50.0	$(1.52 \pm 0.05) \times 10^{-4}$			
 12	25.0	$(6.04 \pm 0.08) \times 10^{-6}$	0.252	23.5	−3.6
	50.0	$(1.41 \pm 0.03) \times 10^{-4}$			
 13a	25.0[d]	9.55×10^{-5}	3.98	22.8	−0.3
 13b	25.0[d]	1.88×10^{-4}	7.83 (1.97)[c]	22.1	−1.6

[a] Reference 17. [b] Extrapolated from higher temperature. Hence, k_1 and k_{rel} are probably reliable to two significant figures. [c] k_{rel} to the Ph analog. [d] Reference 18.

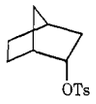
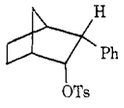
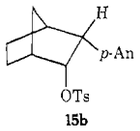
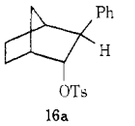
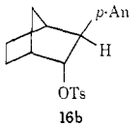
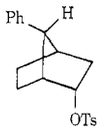
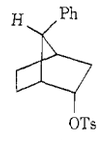
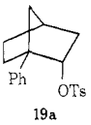
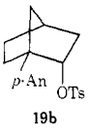
similar, presumably remotely substituted model in a bicyclic system would be 1-phenyl-2-*endo*-norbornyl tosylate (**19a**), whose rate is *ca.* 0.70 times that of *endo*-norbornyl tosylate (**14**).[18] The rate-retarding effects of the phenyl groups in **9a** and **11** of 3.5 and 4.2, respectively, fall within the 1.4–5.5 range for **19a** and the *trans*-2-phenylcyclopentyl system.

The acetolysis rate for the *anti*-phenyl endo tosylate (**17**) relative to its unsubstituted parent (**14**) of 0.29 is approximately equal to the epimeric tosylate (**11**) to exo parent (**8**) ratio of 0.24. In **17** the phenyl is attached γ to the incipient positive charge generated at C-2. If σ participation is involved in **11** with partial positive charge generation at C-1, then one might expect the phenyl to exert a greater rate-retarding inductive effect, since it would be closer to said positive charge than in **17**. Based on such an interpretation, the results would offer dubious evidence for σ participation. Gassman and coworkers[6a] have shown that the rate-retarding effect of an *anti*-chloro substituent on the acetolysis rate of *exo*-norbornyl tosylate ($^1/_{581}$) is only 3.4 times its effect on the acetolysis rate of *endo*-norbornyl tosylate ($^1/_{155}$). The relative effect of phenyl, the rate of **11** *vs.* **8** compared to **17** *vs.* **14**, of only 1.2 is then not surprising when one considers that the chlorine ($\sigma^* = +1.05$) is known to exert a greater inductive effect than phenyl ($\sigma^* = +0.215$). Hence, while the factor of 1.2 is not large, it is in line with the relatively small differences attributed to electron-withdrawing substituents on exo *vs.* endo solvolyses.[6b]

The cis,endo tosylate **15a** undergoes acetolysis at a rate *ca.* 2.4 times that of **14**. This relative rate of 2.4 is presumably due to a combination of steric acceleration and phenyl inductive retardation. From the inductive retardation factor of 0.29 from **9a** one may assign a rate increase for **15a** of 8.1 attributable to steric acceleration. The steric acceleration factor in the 2-phenylcyclopentyl system, the relative rate of *cis- vs. trans*-2-phenylcyclopentyl tosylate, is 4.7. That the effect appears more pronounced in the norbornyl system may stem from the known greater proximity of the cis substituents with dihedral angles of *ca.* 0°. In the

TABLE II

KINETIC DATA FOR THE ACETOLYSES OF PHENYL (Ph) AND *p*-ANISYL (*p*-An) SUBSTITUTED 2-*endo*-NORBORNYL TOSYLATES

Endo tosylate	Temp, °C	k_1, sec^{-1}	k_{rel}, 25°	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu
 14	25.0[a]	8.14×10^{-8}	1.00	26.5	−2.0
 15a	25.0[b]	1.91×10^{-7}	2.35	25.3	−4.5
	50.0	$(5.61 \pm 0.06) \times 10^{-6}$			
	75.0	$(1.10 \pm 0.05) \times 10^{-4}$			
 15b	25.0[b]	2.86 ± 10^{-7}	3.51	26.1	−0.9
	50.0	$(9.37 \pm 0.16) \times 10^{-6}$	(1.49)[c]		
	75.0	$(1.86 \pm 0.04) \times 10^{-4}$			
 16a	25.0[b]	3.19×10^{-10}	0.00392	29.5	−3.0
	80.0	$(8.79 \pm 0.05) \times 10^{-7}$			
	95.0	$(5.51 \pm 0.05) \times 10^{-6}$			
	110.0	$(2.52 \pm 0.03) \times 10^{-5}$			
 16b	25.0[b]	8.50×10^{-10}	0.0104	29.1	−2.5
	75.0	$(1.13 \pm 0.05) \times 10^{-6}$	(2.65)[c]		
	90.0	$(6.72 \pm 0.15) \times 10^{-6}$			
	110.0	$(5.70 \pm 0.06) \times 10^{-5}$			
 17	25.0[b]	2.34×10^{-8}	0.286	26.6	−4.4
	75.0	$(1.68 \pm 0.05) \times 10^{-5}$			
	100.0	$(2.32 \pm 0.08) \times 10^{-4}$			
 18	25.0[b]	2.99×10^{-8}	0.367	25.8	−6.5
	80.0	$(3.90 \pm 0.06) \times 10^{-5}$			
	100.0	$(2.93 \pm 0.08) \times 10^{-4}$			
 19a	25.0[d]	5.66×10^{-8}	0.695	25.0	−7.7
 19b	25.0[d]	6.23×10^{-8}	0.765 (1.10)[c]	25.5	−6.1

[a] Reference 17. [b] Extrapolated from higher temperatures. Hence, k_1 and k_{rel} are probably reliable to two significant figures. [c] k_{rel} to the Ph analog. [d] Reference 18.

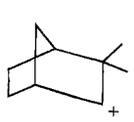
cyclopentyl system the cis substituents are presumably moved further apart with a corresponding smaller effect on the ground-state energy.

The rates of the *syn*-7-phenyl tosylates, **12** and **18**, are only 1.2 and 1.4 times those of their respective *anti*-phenyl isomers, **11** and **17**. This approximate equivalence in rates between the two systems points to the operation of similar effects of the phenyls.

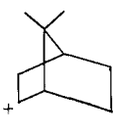
The value of the H–C_2–C_3–H dihedral angle in 3-*exo*-phenyl-2-*endo*-norbornyl tosylate (**16a**) should be near that approximated for **9a**, namely 120°, and no *a priori* effect from the *exo*-3-phenyl other than a rate-retarding inductive one would be anticipated. The observed relative rate of 0.0038 for **16a** when compared with that of **14** is too large a retardation to be ascribed to the inductive factor alone. A retardation factor in the neighborhood of 10^2 must be due to some other cause. An assignment of this factor to some known cause is not intuitively obvious. A tentative hypothesis is that of steric inhibition by phenyl to solvation of the developing positive charge in the transition state for **16a**. Carbonium ions owe a large measure of their inherent stability to stabilization by solvent.[22] Car-

(22) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 315.

bonium ions in the bicyclo[2.2.1]heptyl system are stabilized by solvent preferentially from the exo side. If this solvation were inhibited in the transition state, then the activation energy could be raised sufficiently to account for the rate retardation. *syn*-7-Methyl substituents alter the normal mode of exo approach in additions to norbornanones[13] and in additions to norbornenes involving cyclic processes.[23] The effect of exo 3 substituents has received far less attention. That an *exo*-3-phenyl substituent exerts a smaller steric effect to exo attack than a *syn*-7-phenyl substituent is evidenced by the formation of a 2:1 ratio of endo to exo alcohol from $LiAlH_4$ reduction of 3-*exo*-phenyl-2-norbornanone, which contrasts with the exclusive formation of exo alcohol from 7-*syn*-phenyl-2-norbornanone. Extension of these data to the acetolyses of the endo isomers, **18** and **16a**, fosters the prediction of a slower rate for the *syn*-7-phenyl compound (**18**) if steric inhibition to solvation were involved in the acetolysis of **16a**. The rate ratio for **18** to **16a**, however, is actually 94:1.0. Brown[24] has pointed out the need for caution in extrapolating ketone reduction results to the behavior of carbonium ions in the bicyclo[2.2.1]heptyl system. Although syn substituents may cause ketone reductions to proceed by endo attack, they need not significantly alter the general rule of exo approach of solvent to carbonium ions. If the transition state for solvent approach to a carbonium ion resembles the transition state for tosylate departure, as may be inferred from the familiar Goering–Schwene diagram,[25] then a smaller inhibition to solvation by a syn 7 substituent relative to an exo 3 substituent is not exceptional. The low proportion of acetic acid solvent reaction at the 2 position in the camphenilyl ion (**20**) relative to the aposantenyl ion (**21**), 1:50, has been attributed to steric hindrance in the former ion.[26]



20



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The invocation of steric inhibition to transition state solvation to explain the slow rate for the cis,exo tosylate (**10a**) relative to **8** of 0.0076 is unwarranted. The p orbital being formed in the solvolysis of an exo tosylate would develop beneath the C_1–C_2 bond axis, and solvation difficulties encountered in the transition state for **10a** should not differ appreciably from those of other exo tosylates. In addition, the steric acceleration invoked to explain the rate acceleration of the cis,endo isomer (**15a**) is obviously not operating in the cis,exo isomer (**10a**), although the dihedral angles between the substituents are presumably the same. However, one is forced to conclude that there are increased unfavorable interactions, steric and/or polar, in the transition state for **10a** but not for **15a**.

The slow solvolysis rate of most endo tosylates has been ascribed to steric hindrance to ionization resulting from the necessity for the leaving group to depart in the direction of the endo 6 substituent, H, alkyl, or aryl, as amply demonstrated by Brown and coworkers.[27] The approach of solvent to the developing p orbital in the transition state for the solvolysis of an exo tosylate should also be inhibited by the endo 6 substituent. Counterbalancing this inhibition to solvent coordination is the perfectly aligned C_1–C_6 σ bond which, acting like a solvent nucleophile, stabilizes the developing positive charge by overlapping with the developing p orbital at C-2.[28] This concept implies a bridged, or at least partially bridged, transition state for the departure of most exo tosylates for a secondary norbornyl compound *but* does not require a bridged carbonium ion intermediate. The reaction of solvent with the carbonium ion(s) to give product(s) need not be the microscopic reverse of the generation of the ion(s) from the tosylate. The transition state for the solvent capture may not require carbon bridging.

If for some reason carbon bridging were impeded in the transition state for tosylate departure, then the solvolysis rate might be significantly reduced. Increased steric and/or polar interactions between a phenyl group and leaving tosylate (or other substituent in the molecule) in the transition state could effectively dampen σ participation and retard the rate.[29] The large rate retardation in the cis,exo compound (**10a**) may be due to repulsion between the leaving tosylate anion with its partial negative charge on oxygen and the π cloud of the orientationally restricted phenyl ring. The rigid norbornane skeleton does not possess the conformational mobility of acyclic and simple monocyclic systems like cyclopentane and cyclohexane.[30] Consequently, this rigid three-dimensional structure may provide an ideal system for the investigation of large steric effects. Along with this rigidity one may have preferred orientations of the phenyl ring in the ground state of a reactive species, which may remain so preferred in the transition state. In previous publications[11,12,31] we have demonstrated orientational preferences for exo, endo, 7-syn, and 1-phenyl substituents with and without groups other than H in a cis relationship. This was accomplished *via* compilation of infrared and nmr data for the phenylnorbornanols and nmr data for their *p*-nitrobenzoates and tosylates.

The three exo compounds that exhibited the greatest amount of interaction between the phenyl π cloud and

(23) H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **93**, 7335 (1971); H. C. Brown, J. H. Kawakami, and K.-T. Liu, *ibid.*, **95**, 2209 (1973).

(24) H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966), and subsequent references.

(25) H. L. Goering and H. L. Schewene, *J. Amer. Chem. Soc.*, **87**, 3516 (1965).

(26) J. A. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 148.

(27) S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 7124 (1968), and references cited therein.

(28) H. C. Brown and coworkers have accumulated a wealth of data supporting the view that tertiary 2-norbornyl derivatives solvolyze *via* nonbridged transition states to classical cation intermediates; *e.g.*, see K. Takeuchi and H. C. Brown, *J. Amer. Chem Soc.*, **90**, 2693 (1968), and prior references. Professor Brown has admitted that the available data do not permit a definitive answer to the question of whether σ participation is present in norbornyl (*i.e.*, secondary norbornyl) itself. The contrast between the lack of bridging in the transition state for the tertiary systems *vs.* the existence of bridging in the transition state for the secondary systems may be resolved by proper assessment of transition state solvation in the two systems. Secondary carbonium ions would require greater stabilization by solvent than the tertiary ions.

(29) One might argue that in the absence of σ participation, *i.e.*, with sole involvement of positive charge generation at C-2, there still could be increased interactions between phenyl and tosylate groups leading to rate retardation. Support of our hypothesis from solvolysis data of the 6-phenyl-2-norbornyl system will be the subject of a future publication.

(30) H. C. Brown and S. Ikegami, *J. Amer. Chem. Soc.*, **90**, 7122 (1968), and ref 24.

(31) D. C. Kleinfelter, *J. Amer. Chem. Soc.*, **89**, 1734 (1967).

O–X substituent (X = H, Ts, and PNB) were the 1-phenyl, *exo*-3-phenyl, and *syn*-7-phenyl derivatives. In the 1-phenyl compounds the preferred phenyl orientation was shown to be that in which the plane of the phenyl ring bisected the 7-bridge protons. In the *exo*-3-phenyl compounds the preferred phenyl orientation is one in which the phenyl plane is orthogonal to the exo C_2–OX bond axis. In 3-*exo*-phenyl-2-*exo*-norbornyl tosylate (**10a**) with the 0° dihedral angle between substituents one might expect to find the greatest destabilization of the transition state owing to interaction between the π cloud and the developing anion. In the *endo*-3-phenyl compounds, however, the preferred phenyl orientation is not that in which the phenyl plane is orthogonal to the endo C_2–OX bond axis. The ir and nmr data reveal considerably less interaction between the π cloud and X substituent. This decreased interaction is a result of the rotation of the phenyl ring away from the unfavorable interaction between an *o*-phenyl hydrogen and the endo-5 hydrogen. Evidently this rotation is sufficient enough to cause some interaction between the phenyl plane and the endo 2 substituent in the ground state which is relieved in its transition state, *viz.*, steric acceleration.

Although the dihedral angle between the 1-phenyl and *exo*-2-tosylate substituents is much larger than 0° (*ca.* 44°), there may still be a fair degree of transition-state destabilization in this system, as revealed by its unexpectedly slow rate of acetolysis[32] in comparison with the 1-alkyl substituted analogs. This interaction in the 1-phenyl compound (**13a**) may lessen the extent of participation by the C_1–C_6 σ bond and consequently the degree of positive charge accumulation at C-1 in its transition state. Where such interaction is not operating, as in the 1-alkyl analogs, σ participation and positive charge development at C-1 are much more evident. The differences between β-alkyl and β-phenyl substituents in stabilizing by resonance a charge-delocalized transition state, as is found in participating systems, have been summarized recently.[33] One would presume that the more the positive charge resides at C-2 in the solvolysis transition state, the greater the ability of phenyl to retard the rate by its inductive effect.

In the *syn*-7-phenyl compounds the preferred phenyl orientation approaches that in which the plane of the benzene ring and the exo C_2 and C_3 substituents are parallel. The C_7–phenyl ring bond bisects the C_2–C_3 bond. If the interaction between the phenyl ring and the 2 substituent is an energetically favorable one, as it presumably is in the OH π bonding case for the alcohol, and as it may be for the *p*-nitrobenzoate and tosylate (a type of weak charge transfer complex between the 7-phenyl and substituent phenyl protons), then the substitutent would orient itself toward the 7-phenyl π cloud. In the tosylate solvolysis, however, the negative charge buildup is on the oxygen directly attached to C-2, and this oxygen with its partial charge may leave in a direction away from the 7-phenyl ring or at least in a manner in which there is no significant transition-state destabilization.

(32) The factor of *ca.* 4.0 for **13a** over **8** is reduced to unity when one considers rates of ionization rather than rates of solvolysis. We wish to thank Professor H. C. Brown for pointing this out to us. Presumably internal return is inoperative in **13a**.

(33) W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 133 (1972).

The four 3-*p*-anisyl-2-norbornyl tosylates were solvolyzed with the purpose of determining whether any directional (dihedral angle) effect operates on the ability of the aryl substituent to transmit its electronic effect to the reaction site. With inclusion of the 1-*p*-anisyl-2-norbornyl tosylates, the compounds and the dihedral angles between the aryl and tosylate substituents are **9b** and **16b**, 120°; **10b** and **15b**, 0°; **13b**, 44°; **19b**, 79°. As can be seen from examination of Tables I and II, the increases in rate afforded by the *p*-anisyl group relative to phenyl range from 1.10 to 2.65. That the minimum effect of the *p*-methoxy substituent is evidenced where the dihedral angle is the closest to 90° (**19b**, ϕ = *ca.* 79°) may be significant. Vicinal coupling constants in the nmr are known to be at a minimum when the dihedral angle is around 90°.[34] Both relative rates with dihedral angles of *ca.* 0° and one of the two with 120° are about the same. The relative rate at 44° for **13b** may be anomalous owing to some partial positive charge buildup at C-1 in the transition state for its acetolysis. The products in this case are derived from the tertiary arylnorbornyl cation.[18] The largest rate increase attributable to the *p*-methoxy substituent of 2.65 is shown by 3-*exo*-*p*-anisyl-2-*endo*-norbornyl tosylate (**16b**), in which the dihedral angle between substituents is *ca.* 120°. Although the ideal dihedral angle for aryl participation of 180° is far from attained in this compound, the fact that the phenyl isomer (**16a**) solvolyzes so slowly may indicate a sufficient driving force for some small degree of aryl participation in **16b**. However, significant aryl participation is unlikely, since *p*-anisyl substituents normally provide far greater rate accelerations relative to phenyl.[35] Attempts to ascribe relative rate differences observed between *p*-anisyl- and phenyl-substituted norbornyl tosylates to differences in dihedral angles would be quite speculative at present.

Experimental Section

Melting points were determined in soft capillary tubes using a Mel-Temp apparatus (Laboratory Devices, Cambridge, Mass.) and are uncorrected. Infrared spectra for the 3-μ region were recorded on a Perkin-Elmer Model 421 grating spectrometer. A Varian A-60 nmr spectrometer, calibrated with tetramethylsilane (δ 0) and chloroform (δ 436.5 Hz), was used for the nmr determinations. Chemical shifts are presumed correct to ±0.01 ppm. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn., and by F. B. Strauss Microanalytical Laboratory, Oxford, England.

Unless otherwise specified, all ether and ligroin solutions of products were dried over anhydrous sodium sulfate prior to removal of solvent. Ligroin was distilled over potassium permangamate, bp 40–55°.

7-*anti*-Phenyl-2-norbornanone.—To a stirred solution of 7-*anti*-phenyl-2-*exo*-norbornanol (1.46 g, 0.00775 mol), mp 89–90°,[12] in acetone (25 ml) held at 0° was added 8 *N* chromic acid (3.0 ml). Sodium bisulfite was added to consume excess chromic acid, the green chromate sludge was removed by filtration, and the resulting acetone solution of the ketone was dried over anhydrous magnesium sulfate. Evaporation of the acetone left 1.40 g (97.1%) of oily ketone. The 2,4-dinitrophenylhydrazone, prepared in the usual manner,[36] gave mp 224–225° from ethanol–ethyl acetate. *Anal.* Calcd for $C_{19}H_{18}N_4O_4$: C, 62.28; H, 4.95. Found: C, 62.17; H, 4.80.

(34) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(35) For example, see P. v. R. Schleyer and C. J. Lancelot, *J. Amer. Chem. Soc.*, **91**, 4297 (1969), and references cited therein.

(36) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1964, p 247.

7-*anti*-Phenyl-2-*endo*-norbornanol.—Reduction of 7-*anti*-phenyl-2-norbornanone (1.38 g, 0.00741 mol) with lithium aluminum hydride in ether in the standard manner[37] gave the endo alcohol (1.32 g, 95.3%): mp 68.5–69.5° from ligroin (*Anal.* Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.69; H, 8.34.); nmr (CCl_4) δ 7.16 (5 H, s, Ar H's), 4.30 (1 H, t, H-2*x*), 3.50 (1 H, s, exch, CH), 2.88 (1 H, b s, H-7*s*), 2.52 (2 H, m, H-1 and H-4), 2.3–0.8 (6 H, m, remaining H's). The *p*-toluenesulfonate derivative, prepared in the usual manner,[38] gave mp 84–85° from ether. *Anal.* Calcd for $C_{20}H_{22}SO_3$: C, 70.16; H, 6.48. Found: C, 70.21; H, 6.50.

Hydroboration of 7-*syn*-phenylnorbornene (6).—The alkene **6** was prepared from an approximate 50:50 mixture of 7-*syn*-phenyl- and 7-*anti*-phenyl-2-norbornen-7-ols by the method of Nystrom and Berger[14] using lithium aluminum hydride and aluminum chloride in ether solution.[39] Hydroboration of **6** was accomplished by the method of Brown and Zweifel.[40] To a solution of 45 ml of 1.0 *M* sodium borohydride in diglyme and unpurified **6** (25.0 g, 0.147 mol) in 50 ml of diglyme was added dropwise 13 ml of boron trifluoride etherate over a period of 1 hr. After the mixture was stirred for an additional 4 hr, water (10 ml), 3 *N* sodium hydroxide (16 ml), and 30% hydrogen peroxide (16 ml) were added in that order. The mixture was poured into water and extracted with ether, and the ether extracts were washed several times with water to remove the diglyme. After removal of the ether, 24.5 g of an oil remained. Integration of the H-2*x* signal at δ 4.07 in **5** and an H-2*n* signal at δ 3.60 in 7-*syn*-phenyl-2-*exo*-norbornanol gave a 40:60 ratio of alcohol products. Separation of **5** from its exo isomer was attained by chromatography on F-20 alumina with ligroin and ligroin–ether eluents. The exo isomer was largely eluted prior to **5**. The weight of pure **5** plus the weight calculated from the overlapping eluted portions amounted to 40% of the total alcohol collected. Pure **5** had mp 64–65° when recrystallized from ligroin (*Anal.* Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.94; H, 8.58.); nmr (CCl_4) δ 7.15 (5 H, s, Ar H's), 4.07 (1 H, tp, H-2*x*), 3.20 (1 H, s, exch, OH), 3.03 (1 H, b s, H-7*a*), 2.54 (s H, m, H-1 and H-4), 2.3–0.7 (6 H, m, remaining H's). The *p*-toluenesulfonate derivative gave mp 87–88.5° from ether. *Anal.* Calcd for $C_{20}H_{22}SO_3$: C, 70.16; H, 6.48. Found: C, 70.01; H, 6.46.

3-*endo*-*p*-Anisyl-2-*exo*-norbornanol.—The procedure was similar to that employed for the preparation of the phenyl analog[11,41] and for **5** described above. To a mixture of 2-*p*-anisylnorbornene (100 g, 0.500 mol), sodium borohydride (15.7 g, 0.429 mol), and 350 ml of diglyme was added dropwise 64.3 g of boron trifluoride etherate. After the mixture was stirred for 4 hr, 3 *N* sodium hydroxide (107 ml) and 30% hydrogen peroxide (107 ml) were added. The mixture was poured into *ca.* 2 l. of ice water and a white solid precipitated within 15–20 min. Filtration, suction drying, and recrystallization from ligroin gave the desired alcohol (84.6 g, 81.9%): mp 69–70° (*Anal.* Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.14; H, 8.42.); nmr (CCl_4) δ 7.10–6.65 (4 H, AA'BB' system, Ar H's), 3.77 (1 H, largely hidden by OCH_3 signal, H-2*n*), 3.72 (3 H, s, OCH_3), 2.77 (1 H, t, $J_{2n,3x} = J_{3x,4} = 3.5$ Hz, H-3*x*), 2.50 (1 H, s, exch, OH), 2.33 (1 H, m, H-4), 2.12 (1 H, m, H-1), 1.85 (1 H, d m, H-7*s*), 1.5–1.0 (5 H, m, remaining H's); ir (CCl_4, dilute) 3616 cm^{-1} (OH). The *p*-toluenesulfonate gave mp 79–79.5° from ether. *Anal.* Calcd for $C_{21}H_{24}SO_4$: C, 67.73; H, 6.50. Found: C, 67.83; H, 6.70.

2-*endo*-*p*-Anisylnorbornane-2,3-*cis*-*exo*-diol.—To a stirred solution of 2-*p*-anisylnorbornene (30.0 g, 0.150 mol) and chloroform (100 ml) maintained at 5–10° was added slowly a mixture of 30% peracetic acid (77.8 g, 0.301 mol) and sodium acetate (22.9 g). After the yellow reaction mixture was stirred for 12 hr at room temperature, excess sodium bisulfite was added, and the resulting mixture was added to 250 ml of heavily salted (NaCl) water and extracted three times with 200-ml portions of ether. The combined ether extracts were washed once with dilute sodium carbonate and once with water, and then dried. Flash evaporation of the ether and chloroform left 42.0 g of residual orange oil. This orange oil was reduced with lithium aluminum hydride (5.70 g, 0.150 mol) in ether solution in the standard manner.[37] The reaction mixture was refluxed for 12 hr to ensure complete reduction. The ether solution was concentrated to a volume of 85 ml and poured into 250 ml of ligroin to give white, flocculent diol (20.4 g, 58.1%): mp 98–98.5° from ether–ligroin (*Anal.* Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 72.01; H, 7.89.); nmr ($CDCl_3$) δ 7.48–6.80 (4 H, AA'BB' system, Ar H's), 4.10, 3.98 (2 H, s, exch, OH's), 3.98 (1 H, d, $J_{3n,7a} = 1.6$ Hz, H-3*n*), 3.80 (3 H, s, OCH_3), 2.48 (1 H, m, H-1), 2.12 (2 H, m, H-4 and H-7*s*), 1.6–0.9 (5 H, m, remaining H's); ir (CCl_4, dilute) 3606, 3517 cm^{-1} (2 OH's).

3-*endo*-*p*-Anisyl-2-norbornanone.—A mixture of 2-*endo*-*p*-anisylnorbornane-2,3-*cis*,*exo*-diol (50.3 g, 0.215 mol) and 70% perchloric acid (500 ml) was stirred at room temperature until all the diol had dissolved (*ca.* 1 hr). The resulting light brown solution was poured into 750 ml of ice water and was allowed to stand for 1 hr until crystallization was complete. The solid was filtered, dissolved in ether, and washed with aqueous sodium carbonate. Evaporation of the ether afforded an oil which crystallized upon addition of ligroin. Recrystallization from ligroin gave the ketone (39.6 g, 85.5%): mp 63.5–64.5° (*Anal.* Calcd for $C_{14}H_{16}O_2$: C, 77.55; H, 6.41. Found: C, 77.75; H, 6.46.); nmr (CCl_4) δ 7.15–6.70 (4 H, AA'BB' system, Ar H's), 3.71 (3 H, s, OCH_3), 3.30 (1 H, d, $J_{3x,4} = 4.4$ Hz, H-3*x*), 2.75, 2.60 (2 H, m, H-4 and H-1), 2.0–1.2 (6 H, m, remaining H's). The 2,4-dinitrophenylhydrazone gave mp 181–182° from ethanol–ethyl acetate. *Anal.* Calcd for $C_{20}H_{20}O_5N_4$: C, 60.60; H, 5.09. Found: C, 60.70; H, 5.22.

The ketone could also be prepared by reaction of the diol with concentrated sulfuric acid at 0°, but the yields were much less (max 50.0%, average *ca.* 25%), presumably owing to sulfonation of the aryl ring.

3-*endo*-*p*-Anisyl-2-*endo*-norbornanol.—Reduction of 3-*endo*-*p*-anisyl-2-norbornanone (3.85 g, 0.0178 mol) with lithium aluminum hydride in ether in the standard manner[37] gave the endo alcohol (3.90 g, 100%): mp 51.0–52.0° from ligroin (*Anal.* Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 831. Found: C, 77.14; H, 8.42.); nmr (CCl_4) δ 7.20–6.65 (4 H, AA'BB' system, Ar H's), 4.16 (1 H, d p, $J_{2x,3x} = 9.8$, $J_{2x,1} = 4.4$ Hz, H-2*x*), 2.91 (1 H, d p, $J_{2x,3x} = 9.8$, $J_{3x,4} = 3.8$ Hz, H-3*x*), 2.30 (2 H, m, H-1 and H-4), 1.90 (1 H, s, exch, OH), 2.0–1.1 (6 H, m, remaining H's); ir (CCl_4, dilute) 3609 cm^{-1} (OH). The *p*-toluenesulfonate gave mp 90.0–91.0 from ether. *Anal.* Calcd for $C_{21}H_{24}SO_4$: C, 67.73; H, 6.50. Found: C, 67.70; H, 6.45.

3-*exo*-*p*-Anisyl-2-*endo*-norbornanol.—A solution of 3-*endo*-*p*-anisyl-2-norbornanone (50.3 g, 0.234 mol), ethylene glycol (1200 ml) and potassium hydroxide (51.0 g, 0.910 mol) was refluxed for 12 hr and then worked up according to the procedure reported[42] for the phenyl analog. Distillation gave a clear oil (32.8 g, 65.0%), bp 120–140° (0.25 mm), which was shown by nmr integration to be *ca.* 61% 3-*exo*-*p*-anisyl-2-*endo*-norbornanol, 31% 3-*endo*-*p*-anisyl-2-*endo*-norbornanol, and 8% 3-*exo*-*p*-anisyl-2-*exo*-norbornanol. Chromatography over F-20 alumina with ligroin–ether eluent gave 12.2 g of a mixture of cis alcohols which could not be separated, and a second portion, 19.6 g of 3-*exo*-*p*-anisyl-2-*endo*-norbornanol: mp 64–65° from ether–ligroin (*Anal.* Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.80; H, 8.10.); nmr (CCl_4) δ 7.15–6.60 (4 H, AA'BB' system, Ar H's), 3.98 (1 H, t, $J_{1,2x} = J_{2x,3n} = 4.1$ Hz, H-2*x*), 2.90 (1 H, s, exch, OH), 2.20 (3 H, m, H-3*n*, H-1, and H-4), 2.1–1.1 (6 H, remaining H's); ir (CCl_4, dilute) 3622 cm^{-1} (OH). The *p*-toluenesulfonate gave mp 99.5–100.5 from ether. *Anal.* Calcd for $C_{21}H_{24}SO_4$: C, 67.73; H, 6.50. Found: C, 67.64; H, 6.51.

3-*exo*-*p*-Anisyl-2-norbornanone.—The procedure employed was similar to that used for the preparation of 7-*anti*-phenyl-2-norbornanone from the alcohol. From 3-*exo*-*p*-anisyl-2-*endo*-norbornanol (8.12 g, 0.0376 mole) and 8 *N* chromic acid (7.0 ml) in 25 ml of acetone there was obtained the desired ketone (4.60 g, 56.2%): mp 68–69° from ether–ligroin (*Anal.* Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.67; H, 7.66.); nmr (CCl_4) δ 7.20–6.65 (4 H, AA'BB' system, Ar H's), 3.70 (3 H, s, OCH_3), 2.91 (1 H, d, $J_{3n,7a} = 3.1$ Hz, H-3*n*), 2.78, 2.52 (2 H, m, H-4 and H-1), 2.1–1.2 (6 H, m, remaining H's). The 2,4-dinitrophenylhydrazone melted over a 20° range after repeated recrystallization from ethanol–ethyl acetate. By analogy

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(38) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 1180.

(39) The characterization of **6**, its spectral properties, and those of other hydrocarbon by-products from this and analogous reactions will be the subject of a future publication.

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(41) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *J. Amer. Chem. Soc.*, **86**, 4913 (1964).

(42) D. C. Kleinfelter, *J. Org. Chem.*, **32**, 840 (1967).

with the phenyl analog[43] it was assumed that a mixture of 2,4-dinitrophenylhydrazones of the *exo*-*p*-anisyl and *endo*-*p*-anisyl ketones was formed.

3-*exo*-*p*-Anisyl-2-*exo*-norbornanol.—Reduction of 3-*exo*-*p*-anisyl-2-norbornanone (4.60 g, 0.0213 mol) with lithium aluminum hydride in ether in the standard manner[37] gave a mixture of 3-*exo*-*p*-anisyl-2-*endo*-norbornanol and 3-*exo*-*p*-anisyl-2-*exo*-norbornanol (4.40 g, 94.8%), in an approximate 2:1 ratio (nmr integration). The di exo alcohol was eluted first with 5% ether–95% ligroin. This alcohol gave mp 51.0–51.5° from ligroin (*Anal.* Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.22; H, 8.50.); nmr (CCl_4) δ 7.12–6.85 (4 H, AA'BB' system, Ar H's), 3.76 (1 H, largely hidden by OCH_3 signal, H-2*n*), 3.70 (3 H, s, OCH_3), 2.73 (1 H, d m, $J_{2n,3n}$ = 6.9 Hz, H-3*n*), 2.33, 2.21 (2 H, m, H-4 and H-1), 1.97 (1 H, d m, $J_{7s,7a}$ = *ca.* 10 Hz), 0.80 (1 H, b s, exch, OH), 1.7–0.9 (5 H, m, remaining H's); ir (CCl_4, dilute) 3582 cm^{-1} (OH). The *p*-toluenesulfonate gave mp 83–84° from ether. *Anal.* Calcd for $C_{21}H_{24}SO_4$: C, 67.73; H, 6.50. Found: C, 67.58, H, 6.59.

Kinetic Procedures.—Anhydrous acetic acid was prepared by distillation from acetic anhydride. Substrate concentrations for titrimetric kinetics were generally 0.015–0.030 *M* except for **9a** and **9b**, which were also acetolyzed at concentrations of *ca.* 0.10 *M* to obtain kinetics *via* extrapolation. This change in concentration did not affect the rate constants obtained. The method of Winstein[44] was employed for the titrimetric tosylate acetolyses. Bromthymol Blue and Crystal Violet were used as indicators. All tosylates displayed good first-order kinetics. Eight titrimetric points were usually taken per kinetic run and most acetolyses were followed to 70% reaction or greater.

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Registry No.—**5**, 41770-08-5; *exo*-**5**, 14181-14-7; **6**, 29266-12-4; **8**, 959-42-2; **9a**, 10561-82-7; **9b**, 41770-13-2; **10a**, 10472-63-6; **10b**, 41770-15-4; **11**, 14181-18-1; **12**, 14181-15-8; **13a**, 14182-95-7; **13b**, 41770-19-8; **14**, 840-90-4; **15a**, 10472-58-9; **15b**, 41770-22-3; **16a**, 10561-85-0; **16b**, 41770-24-5; **17**, 41770-25-6; **18**, 41770-26-7; **19a**, 14182-98-0; **19b**, 41770-28-9; 7-*anti*-phenyl-2-norbornanone, 41770-29-0; 7-*anti*-phenyl-2-norbornanone 2,4-dinitrophenylhydrazone, 41770-30-3; 7-*anti*-phenyl-2-*exo*-norbornanol, 14181-16-9; 7-*anti*-phenyl-2-*endo*-norbornanol, 41770-32-5; 3-*endo*-*p*-anisyl-2-*exo*-norbornanol, 41770-33-6; 2-*p*-anisylnorbornene, 24920-37-4; 2-*endo*-*p*-anisylnorbornane-2,3-*cis*-*exo*-diol, 10381-57-4; 3-*endo*-*p*-anisyl-2-norbornanone, 10381-58-5; 3-*endo*-*p*-anisyl-2-norbornanone 2,4-dinitrophenylhydrazone, 41770-37-0; 3-*endo*-*p*-anisyl-2-*endo*-norbornanol, 10381-60-9; 3-*exo*-*p*-anisyl-2-*endo*-norbornanol, 41770-39-2; 3-*exo*-*p*-anisyl-2-norbornanone, 41770-40-5; 3-*exo*-*p*-anisyl-2-*exo*-norbornanol, 41770-41-6.

Acetolysis Products from Some Phenylnorbornyl Tosylates

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Kinetic product analyses were obtained for 3-*endo*-phenyl-2-*exo*-, 3-*endo*-phenyl-2-*endo*-, 3-*exo*-phenyl-2-*endo*-, 7-*anti*-phenyl-2-*exo*-, 7-*syn*-phenyl-2-*exo*-, and a mixture of 5-*endo*-phenyl-2-*exo*- and 5-*exo*-phenyl-2-*exo*-norbornyl tosylates. Thermodynamic product analyses were obtained for 3-*endo*-phenyl-2-*exo*-, 3-*endo*-phenyl-2-*endo*-, and 1-phenyl-2-*exo*-norbornyl tosylates. The results from the kinetic analyses were compared with those obtained from the 7-chloro-, 3-methyl-, and 3-*endo*-phenyl-3-*exo*-hydroxy-2-norbornyl tosylates. The preference of 7-*syn*-phenyl-2-*exo* product over 3-*exo*-phenyl-2-*exo* product is attributed to steric inhibition to solvent approach to the 3-*exo*-phenyl-2-norbornyl cation. Under thermodynamic conditions amounts of 1-phenyl-2-*exo* and 4-phenyl-2-*exo* products were detected. With sufficient reaction time the products formed under thermodynamic conditions approach the same equilibrium mixture.

Carbonium ions generated in the norbornyl system have been extensively studied.[1] In any significant investigation involving solvolysis rate determinations one must also consider the products of the solvolyses. In a previous paper[2] we have reported upon the acetolysis rates for the four 3-phenyl-2-norbornyl tosylates, their *p*-anisyl analogs, and the four 7-phenyl-2-norbornyl tosylates in order to determine the relative effects of the aryl substituents on the acetolysis rates. In this paper we report upon the acetolysis products obtained from a number of these phenylnorbornyl tosylates.

If the effect of an aryl group on the energy of the transition state leading from starting tosylate to the carbonium ion intermediate is similar in magnitude to the energy of the transition state leading from said intermediate to a solvolysis product, as has been represented[3] and supported[4] by Goering and Schewene diagrams, then there should be some correlation between the acetolysis rates and product distributions. Since the endo transition state energies for both the tosylate departure and solvent capture are considered to be so high relative to their exo counterparts, no endo products should be obtained.

The tosylates for which acetolysis products were determined are 3-*endo*-phenyl-2-*exo*-norbornyl tosylate (**1**), 3-*endo*-phenyl-2-*endo*-norbornyl tosylate (**2**), 3-*exo*-phenyl-2-*endo*-norbornyl tosylate (**3**), 7-*anti*-phenyl-2-*exo*-norbornyl tosylate (**4**), and 7-*syn*-phenyl-2-*exo*-norbornyl tosylate (**5**). The preparation and characterization of these tosylates and their alcohol precursors have been described previously.[5] In addition, 5-*endo*-phenyl-2-*exo*-norbornyl tosylate (**6**), contam-

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