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.

(43) D. C. Kleinfelter and P. v. R. Schleyer, *J. Amer. Chem Soc.*, **83**, 2329 (1961).

(44) S. Winstein, C. Hansen, and E. Grunwald, *J. Amer. Chem. Soc.*, **70**, 812 (1948).

Acknowledgments.—We wish to thank the National Science Foundation for partial support of this research. We are indebted to Dr. Louis Joris (at the time at Princeton University) for the O–H stretching vibrations in dilute CCl_4 solution.

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

DONALD C. KLEINFELTER,* MELVIN B. WATSKY, AND WILLIAM E. WILDE

Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37916

Received February 13, 1973

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-

(1) J. A. Berson in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963; G. D. Sargent, *Quart. Rev., Chem Soc.*, **20**, 301 (1966); P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1966; H. C. Brown, *Chem. Eng. News*, **45**, 87 (1967).

(2) D. C. Kleinfelter, E. S. Trent, J. E. Mallory, T. E. Dye, and J. H. Long, Jr., *J. Org. Chem.*, **38**, 4127 (1973).

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

(4) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966); H. C. Brown and K. Takeuchi, *J. Amer. Chem. Soc.*, **90**, 2690, 5270 (1968); H. C. Brown and M. H. Rei, *ibid.*, **90**, 6216 (1968); H. C. Brown, P. v. R. Schleyer, R. C. Fort, and W. E. Watts, *ibid.*, **91**, 6848 (1969).

(5) D. C. Kleinfelter, T. E. Dye, J. E. Mallory, and E. S. Trent, *J. Org. Chem.*, **32**, 1734 (1967); D. C. Kleinfelter, *ibid.*, **32**, 3526 (1967).

TABLE I

PRODUCT PERCENTAGES (MOLE PER CENT) OBTAINED FROM THE KINETIC ACETOLYSES

	Hydrocarbons		Alcohols						
Norbornyl tosylate	8	9	2-*n*-Ph 10	3-*x*-Ph 11	7-*s*-Ph 12	3-*n*-Ph 13	7-*a*-Ph 14	5-*n*-Ph 15	5-*x*-Ph 16
3-*n*-Ph-2-*x*[a]	14	6.7	0	0	5.0	23	44	3.6	3.9
3-*n*-Ph-2-*x*[b]	8.0	0	0	0	5.5	27	51	4.5	4.5
3-*n*-Ph-2-*n*[a]	15	18	2.0	0	4.2	24	28	3.6	4.7
3-*x*-Ph-2-*n*[a]	19	2.0	0	1.7	15	15	26	10	11
3-*x*-Ph-2-*n*[c]	33	0	0	1.3	13	13	22	8.7	9.4
7-*a*-Ph-2-*x*[d]	20	6.4	0	0	4.8	21	42	2.2	3.3
7-*s*-Ph-2-*x*[d]	28	0	0	Trace	14	14	30	5.8	7.2
5-*n*-Ph-2-*x*[e]	19	11	0	0	1.5	7.3	15	32	18

[a] Acetolysis was conducted for greater than 10 half-lives at or above the higher (highest) of the temperatures at which the rate data were obtained.[2] Unless otherwise noted the reported percentages are the averages for three different determinations. [b] 110 hr at the reflux temperature of acetic acid. [c] Acetolysis conducted to *ca.* 90% completion. [d] One determination only. [e] One determination only; tosylate was contaminated with *ca.* 20% of the 5-*exo*-phenyl isomer.

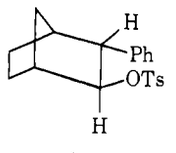
TABLE II

PRODUCT PERCENTAGES (MOLE PER CENT) OBTAINED FROM THE THERMODYNAMIC ACETOLYSES

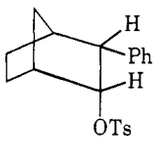
	Hydrocarbons[a]	Alcohols				
Norbornyl tosylate	9 + 17	7-*s*-Ph + 3-*n*-Ph 12 + 13	1-Ph 18	7-*a*-Ph 14	4-Ph + 5-*n*-Ph 19 + 15	5-*x*-Ph 16
3-*n*-Ph-2-*x*[b]	0	26	9.5	49	9	6
3-*n*-Ph-2-*x*[c]	0	4	41	10	36	8
3-*n*-Ph-2-*n*[d]	0	26	22	38	8	6
3-*n*-Ph-2-*n*[c]	3	6.3	34	15	28	14
1-Ph-2-*x*[e]	69 (29) 31	?	67	?	?	0
1-Ph-2-*x*[f]	Trace	8	34	21	32	5

[a] No 8 was found. [b] Acetolysis conducted for 3 hr at 70°. [c] 13 hr at reflux temperature of acetic acid. [d] 17.5 hr at 70°. [e] 0.3 hr at 70°; 4% of alcohols unidentified but assumed (vpc) to be a mixture of all possibilities other than 15 and 16. [f] 16 hr at reflux temperature of acetic acid.

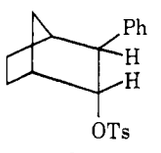
inated with some 5-*exo*-phenyl-2-*exo*-norbornyl tosylate, was acetolyzed. All these product studies were conducted with *at least* 1 mol excess of sodium acetate, *i.e.*, 2 mol of sodium acetate/mol of tosylate, in glacial acetic acid solvent to give the kinetically controlled products. Tosylates **1**, **2**, and 1-phenyl-2-*exo*-norbornyl tosylate (**7**) were also run in acetic acid alone to give the thermodynamically controlled products caused by the accumulation of the *p*-toluenesulfonic acid generated in the acetolyses. The acetolysis of **7** in the presence of sodium acetate has been reported elsewhere.[6]



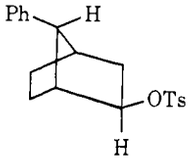
1



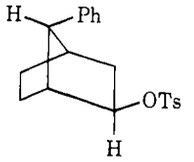
2



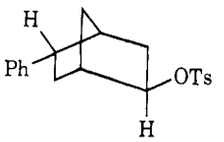
3



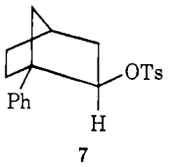
4



5



6

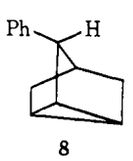


7

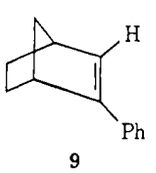
(6) D. C. Kleinfelter, Ph.D. Thesis, Princeton University, 1960, p 301.

The results of the kinetic and thermodynamic acetolyses are reported in Tables I and II. The acetolysis products were routinely reduced with $LiAlH_4$ in ether prior to their attempted separation. Hence, in the tables and subsequent discussion the nonhydrocarbon products are referred to as alcohols rather than acetates.

Separation and Identification of Products. Kinetic Conditions.—After reduction with $LiAlH_4$ the products were chromatographed over alumina. Hydrocarbons **8** and **9** eluted simultaneously. An nmr spectrum of this mixture was obtained, and integration of the H-3 proton of **9** at δ 6.21[5] and the benzylic proton of **8** at δ 2.75 allowed the relative percentages to be determined. Integration of the H-1 and H-4 protons of **9** at δ 3.25 and 2.92 confirmed the percentages. These data could also be checked by vpc analysis, since the retention times of **8** and **9** differed slightly.

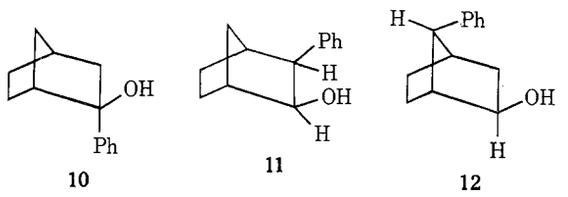


8



9

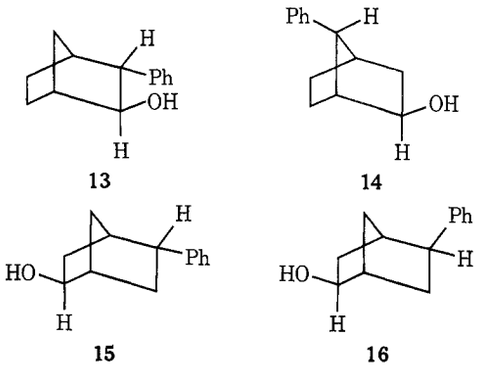
Only in the product study from 3-*endo*-phenyl-2-*endo*-norbornyl tosylate (**2**) was there any tertiary alcohol (**10**) obtained. It was eluted simultaneously with **12**, and, since it had no benzylic or carbinol CH atoms, its percentage in the mixture could be obtained by nmr integration of the phenyl region and the H-2*n* (δ 3.58) and H-7*a* (δ 2.90) protons of **12**.[5] As **10** thermally dehydrated to 1-phenylnortricyclene (**17**) and **9** upon vpc



10 11 12

analysis, a confirmation of the nmr data could be obtained. In only the product study from 3-*exo*-phenyl-2-*endo*-norbornyl tosylate (**3**) was there any 3-*exo*-phenyl-2-*exo*-norbornanol (**11**) obtained. It also eluted simultaneously with **12**. The H-2*n* proton of **12** masked half of the H-2*n* triplet pair of **11** centered at δ 3.87. Twice the unmasked triplet integration divided by the total H-2*n* absorption gave the mole fraction of **11** in the mixture.

In the other product studies the order of eluted alcohols was **12**, 3-*endo*-phenyl-2-*exo*-norbornanol (**13**), 7-*anti*-phenyl-2-*exo*-norbornanol (**14**), and the 5-phenyl-2-norbornanols, 5-*endo*-phenyl-2-*exo*-norbornanol (**15**) and 5-*exo*-phenyl-2-*exo*-norbornanol (**16**). Wherever

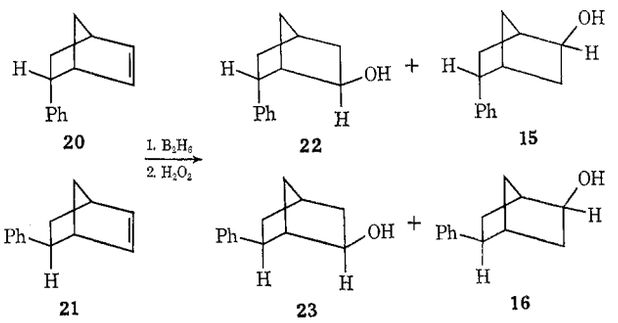


possible, pure compounds were obtained by crystallization or recrystallization of mixtures to minimize the obtaining of product percentages *via* nmr integration. In most cases some **12** could be obtained uncontaminated with **13**, but later mixtures of **12** and **13** could be not be avoided. The benzylic protons of both **12** and **13** absorb at *ca.* δ 2.85. However, the H-1 and H-4 protons of **12** are broad singlets at δ 2.67. Since no protons of **13** absorbed in that region, the percentages of both compounds could be obtained. One-half the δ 2.67 integration divided by the δ 2.85 integration gave the mole ratio of **12** in the mixtures. After small amounts of pure **13** were obtained, mixtures of **13** and **14** were eluted. Integration of the H-3*x* signal of **13** at δ 2.85 and the 7*s* signal of **14** at δ 3.25 gave their relative percentages.

In initial fractions these 3*n* and 7*a* integrations summed to the integration of their H-2*n* absorptions centered at *ca.* δ 3.80. However, with later fractions their sum fell short of the δ 3.80 integration. At the same time a second distinct phenyl singlet appeared at δ 7.09. (The phenyl absorptions for both **13** and **14** coincide as a singlet at δ 7.12.) Somewhat fortuitously, the peak height at δ 7.09 gave a fairly good approximation of the relative per cent of the last two alcohols, **15** and **16**, in these mixtures.

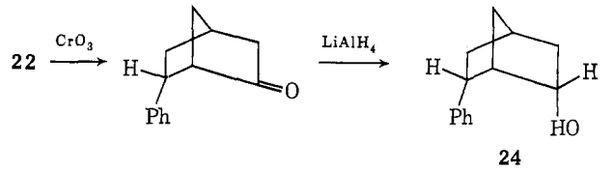
Vapor phase chromatography (vpc) did not afford the desired separation of the isomeric phenylnorbornanols. For example, mixtures of **12**, **13**, **14**, and **15** were eluted as one peak on the chromatogram. Since certain anomeric sugars had been separated successfully by gas chromatography after reaction with hexamethyldisilane (HMDS) and trimethylchlorosilane (TMCS) to form their trimethylsilyl (TMS) ethers,[7] we attempted to extend this application to our compounds. Alcohols **11** and **12** could not be separated as their TMS ethers. However, nmr analysis gave satisfactory percentages for these two isomers when they were eluted together. The TMS ethers of **13**, **14**, and **16** separated cleanly, but the TMS ethers of **14** and **15**, although giving a somewhat unsymmetrical peak on the chromatogram, could not be separated. Fortunately, integration of the isolated downfield H-7*s* signal in **14** gave its percentage, and the percentage of **15** could be obtained from the chromatogram after subtraction of the **14** percentage. Hence, by combined nmr and vpc analyses the per cents of all the acetolysis products were determined. Product percentages from tosylates **1**, **2**, and **3** were obtained three times each, and the deviation between determinations was less than 1.0%.

While compounds **15** and **16** were likely products to have been formed during these solvolyses by analogy with the data from the methylnorbornyl cations,[8] it was necessary to prove their structures. Hydroboration of the Diels–Alder adducts of styrene and cyclopentadiene,[9] a mixture of 5-*endo*-phenyl-2-norbornene (**20**) and 5-*exo*-phenyl-2-norbornene (**21**), gave a mixture of the four alcohols shown below. A vpc analysis of the



TMS ethers of this mixture gave three peaks in the ratio of 44:47:9. The retention time for the 44% peak was identical with that of the TMS derivative of 3-*endo*-phenyl-2-*exo*-norbornanol (**13**) and therefore could not belong to **15** or **16**. Some of the alcohol whose TMS ether corresponded to this 44% peak was isolated by chromatography over alumina. In its nmr spectrum the absorptions at δ 3.05 and δ 3.53 indicate exo benzylic and endo carbinol protons, respectively. The upfield shift of this latter signal relative to the same proton signal in 2-*exo*-norbornanol of δ 3.66[10] suggests some diamagnetic shielding by a proximate phenyl. These data are consistent with the structural assignment of 6-*endo*-phenyl-2-*exo*-norbornanol (**22**). Confirmation of this assignment was accomplished by oxidation of **22** to the ketone, which was reduced with $LiAlH_4$ to the epimeric alcohol, 6-*endo*-phenyl-2-*endo*-norbornanol (**24**). The structural assignment of **24** was proven by analysis of its nmr and ir spectra. In the nmr spectrum the phenyl region was found to be highly split. The

(7) C. C. Sweenley, R. Bentley, M. Makita, and W. W. Wells, *J. Amer. Chem. Soc.*, **85**, 2497 (1963).
(8) J. A. Berson, A. W. McRowe, and R. G. Bergman, *J. Amer. Chem. Soc.*, **89**, 2573 (1967).
(9) K. Alder and H. F. Rickert, *Ber.*, **71**, 373 (1938).
(10) E. W. C. Wong and C. C. Lee, *Can. J. Chem.*, **42**, 1245 (1964).

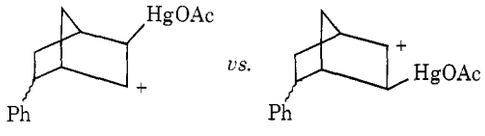


24

only other secondary 2-norbornanol bearing a phenyl substituent which exhibits this type of splitting is 7-*syn*-phenyl-2-*exo*-norbornanol (**12**), whose phenyl and hydroxyl groups are situated in similar proximate positions. The ir spectrum (dilute solution in CCl_4) of **24** showed no free OH absorption but only a bonded peak at 3594 cm^{-1}. From the free peak of 2-*endo*-norbornanol at 3622 cm^{-1} one obtains a $\Delta\nu$ (OH–π) of 28 cm^{-1}, identical with the value found for **12**.

The 47% peak was somewhat unsymmetrical, suggesting the presence of two components. The mixture of 5-phenyl-2-norbornenes is richer in the 5-*endo*-phenyl component (*ca.* 82%), as shown by integration of the benzylic proton signals in the 2-phenylnorbornanes formed by hydrogenation. Hence, the major component of the 47% peak should be 5-*endo*-phenyl-2-*exo*-norbornanol (**15**). The sum of the **15** and **22** percentages should equal the per cent of the norbornene precursor (**20**).

To assist in the remaining structural assignments the alkene mixture was also oxymercurated according to the procedure of Brown.[11] Vpc analysis gave the same three peaks as the hydroboration product mixture but in a distinctly different ratio of 16:73:11. Oxymercuration affords considerably less 6-*endo*-phenyl-2-*exo*-norbornanol (**22**) and thereby less 6-phenyl-2-norbornanols than 5-phenyl-2-norbornanols. This selectivity may be attributed to the electron-withdrawing effect of the phenyl group, which would inhibit positive charge buildup at the more proximate 6 position, as shown below. Traylor[12] has treated 5-*endo*-cyanonorbornene



with mercury acetate and obtained only 5-*endo*-cyano-2-*exo*-norbornyl acetate or its alcohol. The absence of 6-*endo*-cyano-2-*exo* products was explained by the inductive or field effect of the cyano group making the 2 position of the unsymmetrical transition state less susceptible to positive charge accumulation.

The major component of the 73% peak is then the TMS ether of 5-*endo*-phenyl-2-*exo*-norbornanol (**15**). If only 16% of **22** forms in the oxymercuration, one must obtain much more than 11% 5-*endo*-phenyl-2-*exo*-norbornanol (**15**) and much less than 11% 6-*exo*-phenyl-2-*exo*-norbornanol (**23**). The only possible assignment to the 11% peak is that of the TMS ether of 5-*exo*-phenyl-2-*exo*-norbornanol (**16**). Consequently, the peak for the TMS ether of **23** is largely masked by the peak for the TMS ether of **15**. It has recently been shown that the TMS ether of pure **23** has a retention time on the low side of the midpeak of these chromatograms, which is the side of the aforementioned peak distortion.[13]

From a mixture of approximately 80% **15** and 20% **16** obtained from chromatography of the alcohols obtained from oxymercuration, a sample of essentially pure **15** was obtained by repeated recrystallizations. Its properties were identical with those of an authentic sample prepared *via* a different route.[14] The TMS ethers of this mixture of alcohols (**15** and **16**) gave chromatograms whose retention times were identical with those of the latter two alcohols of our solvolysis product study. Thus all the products of the kinetic studies were identified and their percentages were obtained.[15]

Discussion of the Kinetic Acetolyses.—Of the multitude of product studies on norbornyl systems recorded in the literature we have chosen to compare our results with those of Gassman and Hornback,[16] who performed rate and product studies with the 7-chloro-2-norbornyl tosylates, with those of Berson and coworkers,[8] who determined product ratios from the 3-methyl-2-norbornyl brosylates, and with those of Collins and Benjamin,[17] who obtained product percentages from the hydrolysis of 3-*endo*-phenyl-3-*exo*-hydroxy-2-*exo*-norbornyl tosylate and its Wagner–Meerwein partner. This allows us to compare our results (phenyl) with a strongly inductive withdrawing substituent (chlorine), a mild electron-releasing group of moderate bulk (methyl), and a phenyl substituent plus a strongly inductive withdrawing group (hydroxyl) on the same carbon atom. Only with the chloro compounds have both rate and product studies been accomplished.

From Table I the Wagner–Meerwein product ratios of **25a** to **26a** were found to be *ca.* 1.0:2.0 except for the acetolysis of 3-*endo*-phenyl-2-*endo*-norbornyl tosylate (**2**), in which case the ratio was *ca.* 1.0:1.2. Of the two carbonium ion intermediates, the 3-*endo*-phenyl-2-norbornyl cation and the 7-*anti*-phenyl-2-norbornyl cation, the former should be less stable owing to the closer proximity of the inductively destabilizing phenyl substituent. In the solvolysis of the chloro- and phenylhydroxy-substituted compounds no product analogous to **25a**, namely **25b** or **25d**, derived from the 3-substituted 2-norbornyl cation was isolated, although a small amount of **25b** may have been present in the unidentified products from the chloro derivatives.[16] In the acetolysis of the methyl-substituted compounds virtually no selectivity existed between the products **25c** and **26c**. The increase in the amount of **25a** formed from acetolysis of the di endo compound (**2**) suggested the involvement of some SN2 displacement competing with unimolecular acetolysis. When **2** was acetolyzed with a 30-mol excess of sodium acetate, the per cent of

(11) H. C. Brown and P. R. Geoghegan, *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

(12) A. Factor and T. G. Traylor, *J. Org. Chem.*, **33**, 2607 (1968).

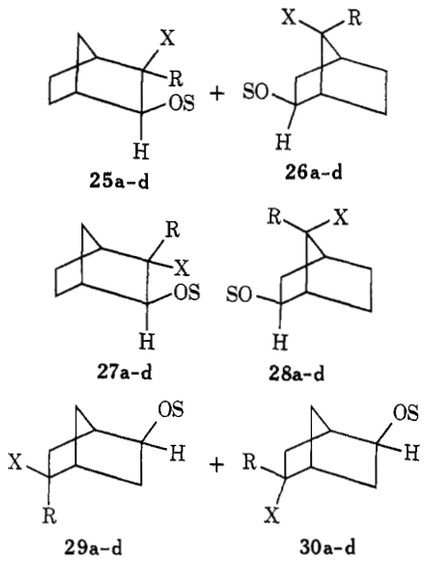
(13) R. A. Ralston, unpublished results.

(14) B. M. Benjamin, Oak Ridge National Laboratories, Oak Ridge, Tenn., kindly furnished us with the properties of his compound (**15**).

(15) The presence of a small amount of 6-*exo*-phenyl-2-*exo*-norbornanol (**23**) is not precluded by these data, since we have recently learned[18] that the acetolysis of the 6-*endo*-phenyl-2-*exo* tosylate under kinetic conditions gives *ca.* ten times as much 6-*exo*-phenyl product as 6-*endo*-phenyl product. The formation of any 6-phenyl products in our solvolysis studies would require a 3,2 exo hydride shift. Since very little such 3,2 shift occurs from a secondary to a tertiary cation in our systems, a secondary–secondary 3,2 shift should be quite unlikely.

(16) P. G. Gassman and J. M. Hornback, *J. Amer. Chem. Soc.*, **91**, 4280 (1969); **94**, 7010 (1972).

(17) C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, **89**, 1652 (1967).



a, X = H; R = Ph; b, X = H; R = Cl;
c, X = H; R = CH_3; d, X = OH; R = Ph.

25a was increased from 24 to 32% and the elimination products were increased from 33 to 41%. Within the elimination products the ratio of 2-phenylnorbornene (**9**) to the phenylnortricyclene (**8**) was increased from 1.2:1.0 to 2.1:1.0. SN2 displacement accounted for 7–8% of the product in the acetolysis of 2-*endo*-norbornyl tosylate.[18]

It was also noted that some 3,2-hydride shift occurred in the acetolysis of **2** to produce 2-*endo*-phenyl-2-*exo*-norbornanol (**10**). Such a production is apparently due to the favorable geometry. The exo-3 hydrogen may concertedly migrate to the 2 position, concomitant with *endo*-2-tosylate departure. The tertiary aryl substituted cation formed by this migration may react with solvent to give tertiary product or lose a proton to produce the olefin **9**. The greater amount of **9** relative to tricyclene (**8**) formed in this acetolysis is presumably due to the operation of this vicinal hydride shift.

The Wagner–Meerwein product ratio of **27a** to **28a** was found to be *ca.* 1.0:9.0. Only in the acetolysis of 3-*exo*-phenyl-2-*endo*-norbornyl tosylate (**3**) was any **27a** (**11**) isolated. This product may have been present in the other product studies, but the minute amount, 0.7% or less, was insufficient to allow detection.[19] That the formation of **11** was presumably not *via* any SN2 displacement was substantiated by no greater formation when the acetolysis was conducted in a tenfold excess of sodium acetate. To ascribe this position selectivity of **28a** over **27a** to only the inductive effect of phenyl seems unwarranted in light of the results discussed previously on **25a** and **26a**. The large preference of **28a** over **27a** is apparently due to a larger steric inhibition to solvent approach to the 3-*exo*-phenyl-2-norbornyl cation and the resulting partial attachment in the transition state leading to **27a**. The preference of **28c** over **27c** in the methylnorbornyl system has been shown to be at least 5.6:1.0. In the only acetolysis in which **27c** was isolated the noninvolvement of SN2 displacement was not determined.

No apparent selectivity for **29a** over **30a** was established in our studies except for the acetolysis of the 5-phenyl-2-norbornyl tosylate mixture, which gave a selectivity of 1.8 parts **29a**:1.0 part **30a**. In the other acetolyses a slight preference of **30a** over **29a** was observed. No apparent selectivity was observed in the hydroxyphenyl or the methylnorbornyl systems, although a slight preference of 1.3:1.0 for **29c** over **30c** was obtained in the acetolysis of 5-*endo*-methyl-2-*exo*-norbornyl tosylate. A preference for the 5-*exo*-chloro product (**30b**) apparently existed in the chloronorbornyl acetolyses. In some cases this preference was at least 3:1. Whatever may be causing the preference of one product over another in these product pairs, the difference may be considered to be significant only in the chloronorbornyl studies.

The values listed in Table III are for the ratios of products resulting from a 6,2-hydride shift relative to products resulting from solvent capture of the original cation or its Wagner–Meerwein partner. The values for the hydroxyphenyl, chloro, and methylnorbornyl systems are included where the data are available or calculable. The ratios of 6,2-hydride shift products to initial solvent-captured products are largest for the exo 3-substituted and syn 7-substituted tosylates, the largest ratio being displayed by the phenyl substituted compounds. Also, the smallest ratio for the endo 3- and anti 7-substituted compounds studied is exhibited by the phenyl-substituted compounds. These effects by phenyl strongly support the tenet of steric inhibition by the *exo*-3-phenyl group to solvation of the transition state leading to ionization of the tosylate and steric inhibition to solvent approach in the transition state leading from the intermediate 3-*exo*-phenyl-2-norbornyl cation to acetate product. The greater amount of 7-*anti*-phenyl-2-*exo* product relative to 7-*syn*-phenyl-2-*exo* product, *ca.* 9:1 starting with the *endo*-3-phenyl or *anti*-7-phenyl tosylates and 2:1 from the *exo*-3-phenyl or *syn*-7-phenyl tosylates, indicates appreciable steric inhibition to solvent capture of the 7-*syn*-phenyl-2-norbornyl cation. That the two tosylates, 7-*anti*-phenyl- (**4**) and 7-*syn*-phenyl-2-*exo*-norbornyl tosylate (**5**), acetolyzed at approximately the same rate may be due to the involvement of some steric acceleration in the latter compound. Although participation by methoxyl has been demonstrated in the acetolysis of 7,7-dimethoxy-2-*endo*-norbornyl tosylate,[20] attributing aryl participation to the syn isomer to explain the near identity in rates of the two 7-phenyl-2-*endo*-tosylates seems unwarranted. Finally, it should be noted that, while 3-*endo*-phenyl-2-*exo*-norbornyl tosylate (**1**) suffers internal return to 7-*anti*-phenyl-2-*exo*-norbornyl tosylate (**4**),[1] neither the 3-*exo*-phenyl nor 7-*syn*-phenyl tosylates displayed any internal return. Evidently the steric bulk of the phenyl substituents is such that the tosylate group departs in a direction away from said phenyl substituents so that internal return cannot operate.

As mentioned in our prior publication,[1] a *syn*-7-phenyl substituent exerts a larger steric effect than an *exo*-3-phenyl substituent to $LiAlH_4$ reduction of a

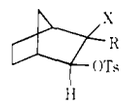
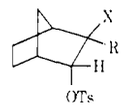
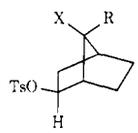
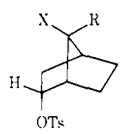
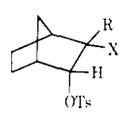
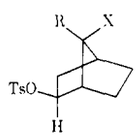
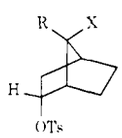
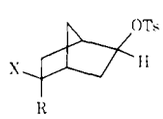
(18) S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, **74**, 1147, 1154 (1952).

(19) Even in the largest scale acetolysis of the other tosylates, *e.g.*, **1** (see Experimental Section), the maximum anticipated amount of **11** would be 70 mg or less.

(20) P. G. Gassman and J. L. Marshall, *Tetrahedron Lett.*, 2429 (1968).

TABLE III

RATIOS OF 6,2-HYDRIDE SHIFT PRODUCT TO INITIAL SOLVENT CAPTURE[a]

Norbornyl tosylate[b]	R = Ph; X = H	R = Cl; X = H	R = Me; X = H	R = Ph; X = OH
	0.19		0.52	0.45
	0.24			
	0.16	0.37		0.43
		0.35		
	3.7		2.0	
	4.0	1.2[c]		
		2.4		
	0.47		0.74	

[a] Hydrocarbon products like **8** and **9** are ignored in these calculations. As a sample calculation the value of 0.19 for the first tosylate (R = Ph; X = H) is obtained by dividing the mole per cent of **25a** and **26a** (67%) into the mole per cent of other products, **27a–30a**. [b] Where R = Me, OTs should be OBs. [c] Goering and Degani report 49.4% anti-chloro and 33.4% syn-chloro products, while Gassman and Hornback[16] report 42 and 49%. If Goering and Degani's data are used, this ratio of 6,2-hydride shift to solvent capture becomes 1.8. These groups are in virtual agreement on the anti-chloro product studies.

2-norbornanone. However, as pointed out by Brown,[21] 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 tosylate departure leading to a carbonium ion resembles the transition state for solvent approach to a carbonium ion to give product, then a smaller inhibition to solvation by a syn 7 substituent relative to an exo 3 substituent would not be exceptional. If one were to assume that these latter transition states resembled the products and that the steric interactions were present in the products, then one's tenets could be supported by showing that greater interaction existed between an *exo*-3-phenyl and an exo 2 substituent than between a *syn*-7-phenyl and an exo 2 substituent.

Since the trimethylsilyl group is extremely bulky, it was hoped that the relative rates of formation of the TMS ethers of 7-*syn*-phenyl-2-*exo*-norbornanol *vs.* 3-*exo*-phenyl-2-*exo*-norbornanol might afford an opportunity to assess the degree of steric interaction between the substituents. At room temperature, the alcohols were mixed with a 20-mol excess of the silylating reagents, HMDS and TMCS, in an attempt to produce pseudo-first-order kinetics. Conclusive evidence for the silylation mechanism is lacking, but most authors agree that the rate-determining step is bimolecular involving nucleophilic substitution on silicon.[22] The progress of the reactions was followed by vpc analysis. The alcohols employed were 7-*anti*-phenyl-2-*exo*-norbornanol (**14**) and the 7-*syn*-phenyl (**12**), 3-*exo*-phenyl (**11**), and 1-phenyl (**18**) isomers. In **14**, in which the phenyl and hydroxy substituents are quite remote, the silylation proceeded quite rapidly with approximately 90% completion in 20 min reaction time. The other three isomers silylated slowly enough for sufficient data accumulation. Each reaction seemed to follow first-order kinetics up to a certain point, after which it began to level off. The 7-*syn*-phenyl isomer reacted approximately four times faster than the 3-*exo*-phenyl isomer, thus lending support to our hypothesis that greater interaction exists between an *exo*-3-phenyl and an exo 2 substituent than between a *syn*-7-phenyl and an exo 2 substituent. The 1-phenyl isomer reacted just slightly (1.1:1.0) faster than **11**, demonstrating considerable steric interaction to exist between phenyl and the exo substituent even though the dihedral angle between the substituents is *ca.* 44°.[23]

In order to illustrate further the relative steric interactions between a phenyl and an exo substituent, the methyl signals in the nmr spectra of the acetates of **12**, **11**, and **18** were obtained. These methyl signals were located at δ 1.46, 1.34, and 1.59, respectively. The methyl signal for an acetate in which phenyl is not affecting the chemical shift by a ring current effect is in the neighborhood of δ 2.06 (benzyl acetate) to δ 2.03 (ethyl acetate).[24] Evidently the phenyl group is significantly shielding the acetate methyl group in the three acetates of interest. The greatest interaction is seen in the case of the 3-*exo*-phenyl-2-*exo* acetate. By analogy with the silylation rate data one might expect the phenyl–methyl interaction to be considerably greater in the 1-phenyl isomer than the 7-*syn*-phenyl analog. However, the interaction is actually greater in the 7-*syn*-phenyl compound. One must consider that the methyl protons of the acetate are four bonds removed from C-2 of the norbornane skeleton while the reacting O atom of the alcohol in the silylation reaction is only one bond removed from C-2. Thus, the methyl shielding in the nmr spectra of the acetates should not necessarily reflect the steric effect of the phenyl groups as well as the silylation rate data.

Results of the Thermodynamic Solvolyses.—When

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

(22) A. E. Pierce, "Silylation of Organic Compounds," Pierce Chemical Co., Rockford, Ill., 1968.

(23) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

(24) N. S. Bhacca, D. P. Hollis, L. F. Johnson, E. A. Pier, and J. N. Shoolery, "NMR Spectra Catalog, No. 530," Varian Associates, 1962 and 1963, lithographed by the National Press.

tosylates **1**, **2**, and **7** were acetolyzed in unbuffered acetic acid, in addition to the products observed under kinetic conditions, quantities of 1-phenyl-2-*exo*-norbornanol (**18**) and what is presumed to be 4-phenyl-2-*exo*-norbornanol (**19**) were detected. The percentage of **18** could be obtained from vpc analysis of the alcohol product mixtures, since it had a retention time different from those of the other alcohol products. The TMS ethers of **14**, **15**, and **19** had nearly identical retention times. As mentioned previously, the percentage of **14** could be obtained by integration of the 7-syn-benzylic hydrogen signal in the nmr spectrum. An approximate percentage of **19** could be obtained from vpc analysis of the alcohol products in that its retention time differed from those of the other alcohols except for some small overlap with the peaks of the 7-*syn*- and 3-*endo*-phenyl compounds (**12** and **13**). Distinguishing features in the nmr spectra of **18** and **19** were the absence of any downfield signals due to benzylic protons which are present in all of the other secondary alcohol products.

Although little 3,2-hydride shift occurred in the kinetic acetolyses, such is obviously not the case under thermodynamic conditions. Evidently sufficient driving force is operating to produce the tertiary 2-phenylnorbornyl cation under these conditions. The tertiary acetate formed from this ion should be quite labile in the acetic acid–*p*-toluenesulfonic acid medium and would reionize and then rearrange to the 1-phenyl-2-*exo*-norbornyl cation, which would afford the more stable secondary acetate. The nearly exclusive product from the buffered acetolysis of **7** is 2-phenylnorbornene (**9**). This contrasts with the changeover to 1-phenyl-2-*exo*-norbornyl acetate under thermodynamic conditions. Given sufficient reaction time even the 1-phenyl-2-*exo*-acetate will react to give a mixture of secondary acetates of 6,2, 3,2, and Wagner–Meerwein rearrangements. In fact it appears that all tosylates studied approach the same equilibrium mixture of acetates with sufficient reaction time. Of the alcohol products obtained from heating **7** at 70° in acetic acid for 20 min, 94% was **18**. Refluxing **7** for 16 hr in acetic acid reduced the amount of **18** to 34% and gave *ca.* 27% of **19**. Acetolysis of **1** at 70° for 3 hr gave *ca.* 13% of **18** and **19**, while refluxing **1** in acetic acid for 13 hr increased the percentages of these products to nearly 70%. The amount of **13** and **14** produced under these conditions decreased from *ca.* 75% in the former case to *ca.* 14% in the latter. Similar accumulation of 1- and 4-substituted products was obtained in the methylnorbornyl systems studied under the thermodynamic conditions.[8]

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. A Varian Aerograph A90-P3 gas chromatograph equipped with a 6 ft $\times$ 0.25 in. 20% SE-30 Chromosorb W column was used for gas chromatographic determinations of product mixtures. A Varian A600-D flame ionization detector gas chromatograph equipped with a 5 ft $\times$ 0.125 in. 3% SE-30 Chromosorb W column was used in studying the rates of formation of some of the trimethylsilyl (TMS) ethers. In all chromatographic work the column temperature was *ca.* 190° with a helium flow rate of 75 ml/min. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

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 and had bp 40–55°.

Acetolyses (kinetic) were carried out under the conditions given in Table I. The tosylates were dissolved in the acetic acid (reagent, 99.9%) containing the sodium acetate; the initial concentrations of tosylate and sodium acetate were *ca.* 0.2 *M* in substrate and 1.0 *M* in base except for two acetolyses, those of **1** and **3** (not reported in Table I), in which the base concentration was much greater (see text). After acetolyses were judged to be complete the reaction solutions were cooled and poured into a large volume (1 l. or more) of ice water. The oily product mixtures were extracted with ligroin and with ether; the combined extracts were washed with aqueous sodium carbonate and dried, and the solvent was removed by flash evaporation. The oily residues were dissolved in anhydrous ether and reduced with lithium aluminum hydride in the standard manner.[25] After removal of the ether solvent, ligroin was added and the ligroin solution was refrigerated for several days. The white solid of 7-*anti*-phenyl-2-*exo*-norbornanol (plus small amounts of 3-*endo*-phenyl-2-*exo*-norbornanol) that formed in most instances was filtered, analyzed by vpc and nmr, and weighed. The filtrates were chromatographed over F-20 alumina using ligroin and ligroin–ether mixtures as eluents. Analyses of these chromatographs are discussed in the text. The material balances (moles of reactants, moles of products, percentage yields) are listed in Table IV.

TABLE IV

YIELD DATA FOR KINETIC ACETOLYSES

Norbornyl tosylate	Moles of reactant	Reaction time, hr	Moles of product	Yield, %
1	0.0731	12.5	0.0644	88.1
	0.0731	13.0	0.0632	85.2
	0.0141	110	0.0125	89.5
2	0.0731	13.0	0.0519	71.0
	0.0585	13.0	0.0467	29.8
3	0.0518	110	0.0451	87.1
	0.0535	110	0.0460	86.0
	0.3515	110	0.0455	87.5
	0.0608	8.5	0.0498	81.2
4	0.0206	10.0	0.0187	91.0
5	0.0224	10.0	0.0201	89.7
6	0.0291	10.0	0.0271	93.1

Acetolyses (thermodynamic) were carried out under the conditions given in Table II. The initial concentrations of tosylate were *ca.* 0.2 *M* in substrate. The product work-up was accomplished in the same manner as that described for the kinetic acetolyses. The material balances are listed in Table V.

TABLE V

YIELD DATA FOR THERMODYNAMIC ACETOLYSES

Norbornyl tosylate	Moles of reactant	Reaction time, hr temp, °C	Moles of product	Yield, %
1	0.0400	13 (reflux)	0.0320	80.0
	0.0145	3 (70)	0.0115	79.5
2	0.0155	13 (reflux)	0.0123	79.9
	0.0150	17.5 (70)	0.0119	79.8
7	0.0249	16 (reflux)	0.0210	84.0
	0.0160	0.3 (70)	0.0135	84.5

5-*endo*-Phenyl- and 5-*exo*-Phenyl-2-norbornenes (20 and 21).—The reaction was carried out in a manner similar to that reported,[9] but with the following modifications. A mixture of dicyclopentadiene (132 g, 1.00 mol), styrene (104 g, 1.00 mol), and hydroquinone (4.0 g) was heated at 140–150° for 4 hr, then cooled, and the hydroquinone was removed by filtration. The remaining solution was distilled *in vacuo* to give a clear, colorless liquid (87.5 g, 51.5%), bp 80–85° (1 mm) [lit.[9] bp 121–125° (11

(25) W. G. Brown, *Org. React.*, **6**, 469 (1951).

mm)]. A small sample (*ca.* 2.0 g) of this product was hydrogenated with PtO_2 catalyst in a Paar bomb. Integration of the benzylic protons at δ 3.13 and 2.65 in the two phenylnorbornanes produced gave a percentage of **20**:**21** of **82**:**18**. The relative percentages of **20**:**21** varied somewhat with reflux time and temperature.

Hydroboration of 20 and 21 and Isolation of 6-*endo*-Phenyl-2-*exo*-norbornanol (22).—The procedure employed was that of Brown and Zweifel[26] as applied to that reported for the hydroboration of 7-*syn*-phenylnorbornene.[2] From a mixture of **20** and **21** (18.7 g, 0.111 mol), sodium borohydride (4.20 g, 0.111 mol), and 17.0 g of boron trifluoride etherate, there was obtained after treatment with 3 *N* sodium hydroxide and 30% hydrogen peroxide and subsequent work-up a clear, oily alcohol mixture (17.1 g, 82.2%). Attempted distillation of this oil *in vacuo* resulted in decomposition. The analysis of the product composition is discussed in the text. The alcohol mixture (9.44 g, 0.0500 mol) was dissolved in 90:10 ligroin–ether and chromatographed over F-20 alumina. **22** was eluted with 75:25 ligroin–ether. One recrystallization from ligroin gave pure **22** (2.88 g, 30.4%): mp 65–66° (*Anal.* Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.74; H, 8.53.); nmr (CCl_4) δ 7.12 (5 H, s, Ph H's), 3.53 (1 H, m, H-2*n*) 3.05 (1 H, m, H-6*x*), 2.65 (1 H, s, b, exch, OH) 2.24 (2 H, m, H-1 and H-4), 1.9–1.1 (6 H, m, remaining H's).

6-*endo*-Phenyl-2-*endo*-norbornanol (24).—From **22** (1.00 g, 0.00532 mol) and 8 *N* chromic acid (3 ml) in 10 ml of acetone there was obtained the ketone, 6-*endo*-phenyl-2-norbornanone (0.71 g, 71%). This oily ketone was reduced with lithium aluminum hydride in the standard manner.[26] After removal of the ether solvent there was obtained **24** (0.525 g, 73% based on ketone): mp 49.5–51° from ligroin (*Anal.* Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.86; H, 8.59.); nmr (CCl_4) δ 7.3–7.0 (5 H, m, Ph H's), 4.05 (1 H, m, H-2*x*), 3.33 (1 H, m, H-6*x*), 2.67 (1 H, m, H-1), 2.25 (1 H, m, H-4), 0.80 (1 H, s, exch, OH), 2.15–0.70 (6 H, m, remaining H's); ir (CCl_4, dilute) 3594 cm^{-1} (OH).

Oxymercuration of 20 and 21 and Isolation of 5-*endo*-Phenyl-2-*exo*-norbornanol (15).—The procedure employed was similar to that of Brown and Geoghegan.[11] To a stirred solution of mercuric acetate (19.0 g, 0.0596 mol) in water (50 ml) and tetrahydrofuran (50 ml) were added **20** and **21** (8.50 g, 0.0500 mol). The reaction mixture immediately turned deep yellow; after 100 sec the color faded, but stirring was continued for another 400 sec. To the cloudy white mixture was added 3.0 *N* sodium hydroxide (50 ml) and a solution (50 ml) of 0.5 *M* sodium borohydride in 3.0 *N* sodium hydroxide. After 5 min of stirring, the mixture was extracted with three 50-ml portions of ether. The ether extracts were washed four times with water to remove the tetrahydrofuran. The dried ether solution was treated with lithium aluminum hydride (1.00 g) in the standard manner[26] to reduce the acetate that had formed. After removal of the ether solvent, 8.65 g of colorless oil remained. Vpc analysis revealed 5.0% unreacted **20** and **21**. The yield of alcohol products was 8.2 g (87%). The analysis of the product composition is discussed in the text. The reaction products (8.60 g) were dissolved in 25 ml of ligroin and chromatographed over F-20 alumina. The unreacted **20** and **21** were eluted quickly with ligroin. A small amount of **22** was eluted with 75:25 ligroin–ether. The desired alcohol (**15**) and 5-*exo*-phenyl-2-*exo*-norbornanol (**16**) were eluted simultaneously with 70:30 ligroin–ether. From this mixture there was obtained 0.41 g of **15** after crystallization from ligroin in a Dry Ice–acetone bath, vacuum sublimation, and recrystallization from ligroin. The solid gave mp 55–57° (compared to mp 60–61° for that of Benjamin[14]); the nmr spectrum in CCl_4 solution superimposed on the spectrum provided by Benjamin. The H-2*n* and H-5*x* signals (multiplets) absorb at δ 3.63 and 3.02, respectively. The mixture of **15** and **16** [with perhaps a trace of 6-*exo*-phenyl-2-*exo*-norbornanol (**23**)] was converted to the tosylate mixture, an oil, in the usual manner. This oil was used for the acetolysis product study.

Preparation of the TMS Derivatives.—The method of preparation was similar to that of Sweenley and coworkers.[7] Alcohol (or alcohol mixture, *ca.* 40 mg) and 0.1 ml of CCl_4 were placed in a small screw top vial. To this solution were added a 0.1 ml of HMDS and 0.05 ml of TMCS. The mixture was heated for 5–10 min over a steam bath to ensure complete reaction.

To measure the rates of TMS ether formation, 10.0 mg (5.32×10^{-5} mol) of alcohol was dissolved in 0.10 ml of CCl_4. To this solution were added 0.200 ml (0.210 g, 0.00124 mol) of HMS and 0.100 ml (0.128 g, 0.00117 mol) of TMCS. The densities of HMDS and TMCS as determined with the use of a Mettler 1-911 Gram-Atic balance were found to be 1.05 and 1.27 g/ml, respectively. The amount of TMS ether derivative formed and the amount of alcohol unreacted were obtained by vpc analysis. The rate constants for TMS ether formation were obtained by plotting ln [TMS ether] *vs.* time and by calculation.

Registry No.—**1**, 10561-82-7; **2**, 10472-58-9; **3**, 10561-85-0; **4**, 14181-18-1; **5**, 14181-15-8; **6**, 41914-80-1; **7**, 14182-95-7; **8**, 41894-48-8; **9**, 4237-08-5; **10**, 17989-93-4; **11**, 10472-45-4; **12**, 14181-14-7; **13**, 944-56-9; **14**, 14181-16-9; **15**, 41914-87-8; **16**, 41914-88-9; **17**, 4601-86-9; **18**, 14182-93-5; **19**, 41919-90-3; **20**, 41914-91-4; **21**, 26280-24-0; **22**, 41914-92-5; **24**, 41914-93-6.

(26) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 2544 (1961).