Acidic and Spontaneous Solvolyses of Esters of Bicyclic Alcohols[1]

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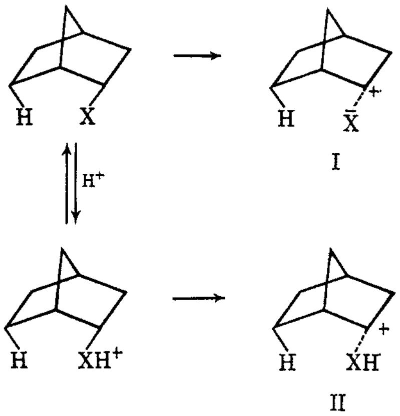
The values of the *exo/endo* rate ratios of *ca.* 10^3 are similar for the acid-catalyzed ($A_{Al}1$) and spontaneous ($B_{Al}1$) solvolyses of esters of camphene hydrate and methylcamphenilol, in aqueous ethanol or dioxane, suggesting that for the *endo* compound, steric hindrance to solvation of the leaving group is not important. The spontaneous solvolyses of camphene hydrate and methylcamphenilyl *p*-nitrobenzoate give predominantly camphene and camphene hydrate or its ether, with small amounts of isoborneol and isobornyl ethyl ether, but solvolysis of isobornyl *p*-nitrobenzoate gives largely isoborneol. The rapid solvolysis of 2-methylisobornyl *p*-nitrobenzoate gives elimination rather than substitution products.

The higher reactivity of *exo*-2-norbornyl compounds over the *endo* compounds in SN1 solvolyses has generally been ascribed to participation of σ electrons in stabilizing the carbonium ionlike transition state for the *exo* compounds; a similar explanation has been given for the prevalence of *exo* products in these reactions.[2,3] Although many workers have noted that steric effects are also important,[2-4] they have generally concluded that the reaction rates and products cannot be explained solely in terms of steric hindrance and acceleration.[2,3] In contrast to the generally accepted views, Brown and his co-workers have argued that σ participation may not be important and have suggested, as a general explanation of the reaction rates and products, that ionization of an *endo* group could be sterically hindered by interference between the leaving group and the *endo* hydrogen atoms on carbons 5 and 6 and that this same effect causes the predominance of *exo* products.[4] Steric hindrance to ionization has been observed with norbornyl derivatives which have 5-*endo*-alkyl substituents.[5]

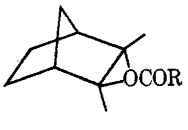
It seemed to us that the concept of steric hindrance to ionization could be tested by examining reactions which had the same initial states, but in which the size of the leaving group in the transition state could be varied. The simplest way of doing this is to compare *exo/endo* rate ratios for spontaneous and acid-catalyzed solvolyses. In the first reaction the leaving group will have considerable anionic character and should therefore be larger by virtue of its solvation, whereas in the second it should carry little charge. If we assume that the transition state has considerable carbonium ion character, we can write I and II as models for the transition states for an *endo* compound (Scheme I).

SCHEME I

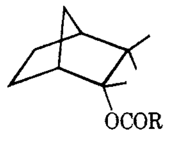


We might therefore expect that in I the interference between the leaving anion and an *endo* hydrogen atom would be greater than that in II between the leaving uncharged group and this atom, particularly in good anion-solvating solvents such as aqueous dioxane and aqueous ethanol. These steric effects upon anion solvation are largely responsible for the differing acid strengths of axially and equatorially substituted cyclohexane carboxylic acids and for the relatively low acidities of sterically congested carboxylic acids.[6]

The available evidence suggested that *exo/endo* rate ratios in acid-catalyzed solvolyses are similar to those found for spontaneous solvolyses,[2,3,7,8] but comparisons of these rate ratios for acid-catalyzed solvolyses of alcohols[7] and carboxylic esters[8] with spontaneous solvolyses of halides[3] or sulfonic esters[2,3] could be misleading; we therefore examined acetates and *p*-nitrobenzoates of camphene hydrate (III) and methylcamphenilol (IV). Our intentions of comparing the rates of ionization of isobornyl and 2-methylisobornyl *p*-nitrobenzoates (V) and (VI) in order to examine the effects of a



III



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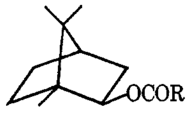
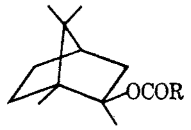


V



VI

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[1] This work was supported in part by grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society. This support is gratefully acknowledged.

[2] P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin Inc., New York, N. Y., 1965; G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966), and references cited.

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter IX.

[4] (a) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp 140-158, 174-178; *Chem. Brit.*, 199 (1966), and references cited. (b) For criticism of these views, see S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965), and Special Publication No. 21, The Chemical Society, London, 1967.

[5] H. C. Brown, I. Rothberg, P. v. R. Schleyer, and M. R. Donaldson, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1653 (1966).

[6] H. L. Goering, T. Rubin, and M. S. Newman, *J. Am. Chem. Soc.*, **76**, 787 (1954); G. S. Hammond and D. H. Hoyle, *ibid.*, **77**, 338 (1955); R. D. Stolow, *ibid.*, **81**, 5806 (1959).

[7] C. A. Bunton, K. Khaleeluddin, and D. Whittaker, *Tetrahedron Letters*, 1825 (1963).

[8] H. C. Brown, F. J. Chloupek, and Min-Hon Rei, *J. Am. Chem. Soc.*, **86**, 1247 (1964).

Table I

	Time, min							
	0	28	59	91	138	181	213	∞
Titre	0.072	0.392	0.746	1.023	1.337	1.567	1.723	2.202

1-methyl group in these spontaneous and acid-catalyzed solvolyses were frustrated by the fact that V is solvolyzed with acyl–oxygen fission.

Part of this work, that dealing with the acid hydrolyses of the acetates, has been described briefly elsewhere.[9]

Experimental Section

Materials.—Isoborneol, camphene hydrate, methylcamphenilol, and methylisoborneol were prepared by standard methods.[10] Their purities were checked by gas–liquid partition chromatography using columns packed with Tween or diglycerol on Chromosorb W. A Perkin-Elmer 154 gas chromatograph was generally used. The alcohols were converted into their *p*-nitrobenzoates by treating their sodium or potassium derivatives with the acid chloride,[10] in either benzene or tetrahydrofuran (these solvents were dried by distillation from sodium). The *p*-nitrobenzoates were recrystallized from petroleum ether (bp 80°) to the following constant melting points: camphene hydrate *p*-nitrobenzoate, mp 100° (lit.[8] mp 101°); methylcamphenilyl *p*-nitrobenzoate, mp 141° (lit.[8] mp 144°); 2-methylisobornyl *p*-nitrobenzoate, mp 138°; isobornyl *p*-nitrobenzoate, mp 128° (lit.[10] mp 129°). The acetates were prepared similarly using acetic anhydride and were purified by preparative gas–liquid partition chromatography. The yields of purified acetates were 15–20%, largely because of the difficulty of purifying them, but considerable amounts of side products were formed. The alkoxide in tetrahydrofuran could abstract a proton from acetyl chloride or acetic anhydride, with formation of ketene, and hence resin, and it seems that these alkoxide ions may cause camphene to be eliminated from camphene hydrate *p*-nitrobenzoate; *e.g.*, addition of camphene hydrate *p*-nitrobenzoate to the potassium alkoxide in dry tetrahydrofuran gave an immediate darkening of the solution and after 15 min a pentane extract of it contained camphene, as well as camphene hydrate and unidentified material.

Solvents.—Dioxane was purified as described by Vogel.[11] Absolute ethanol was dried over Linde Molecular Sieve 4A. The mixed solvents were made up by weight so that they corresponded to the volume compositions quoted.

Kinetics.—The hydrolyses of camphene hydrate and methylcamphenilyl acetate were followed by acid–base titration. Stoppered flasks were used for temperatures below 35° and sealed tubes at higher temperatures. Portions of the reaction solution, removed from the flask, or the contents of a sealed tube were titrated against standard sodium hydroxide, under an atmosphere of nitrogen, using phenolphthalein as indicator. This procedure could not be used if the concentration of catalyzing acid was greater than 0.5 *M;* a known amount of more concentrated alkali was then added; and the residual acid then titrated as described above. Perchloric acid was the catalyst in all these experiments.

The solvolyses of the *p*-nitrobenzoates were followed spectrophotometrically. Although the ultraviolet spectra of the acid and the esters are similar, they differ from that of the salt. Therefore aqueous alkali was added to portions of the reaction mixture, taken at various times, so that the net concentration of alkali was 0.001 *M* and the optical densities were measured on a Cary 14 spectrophotometer at 2570, 2600, and 2630 A.

The following are results obtained on the hydrolysis of methylcamphenilyl acetate (followed titrimetrically) in dioxane–water (60:40 v/v) at 73.4°: [$HClO_4$] = 0.201 *M*, ester ≈0.02 *M*. *Portions (2 cc) of the reaction mixture were added to 3.95 cc of* 0.1 *M* NaOH and the residual acid was titrated with 0.02 *M* NaOH; $10^4k_\psi = 1.18$ sec^{-1} (calculated graphically) (see Table I).

Table II

	Time, min						
	0	65	106	176	227	805	∞
OD_{2570}	0.796	0.729	0.715	0.696	0.678	0.587	0.526
OD_{2600}	0.812	0.748	0.738	0.713	0.706	0.613	0.555
OD_{2630}	0.808	0.750	0.743	0.720	0.717	0.632	0.578

The results given in Table II were obtained on the solvolysis of camphene hydrate *p*-nitrobenzoate, followed spectrophotometrically in initially neutral ethanol–water (80:20 v/v at 55.0°); ester ≈ 1.3 × 10^{-4} *M*. Portions (5 cc) of the reaction mixture were added to 1 cc of 0.1 *M* NaOH; the solution was made up to 10 cc with water; $10^5k_\psi = 2.75$ sec^{-1} (calculated from a plot of log ($\mathrm{OD}_t - \mathrm{OD}_\infty$), where the optical densities were measured at times O, *t*, and ∞ for the various wavelengths.

Products.—The products, after complete reaction, were extracted into pentane and the extract was concentrated under reduced pressure and then dried with Linde Molecular Sieve 4A.[12] The solution was analyzed gas chromatographically using either a 1-ft Apiezon–Chromosorb W column in series with a 6-ft Tween 60–Chromosorb W column at 130° or a 12-ft diglycerol–Chromosorb W column at 100°. The diglycerol column is unsatisfactory for the separation of camphene and tricyclene and because of the low working temperature the retention times were long. Therefore the product composition was determined using the Apiezon and Tween column, except that the relative amount of camphene hydrate and methylcamphenilol was determined using a diglycerol column. Because of the acid-catalyzed equilibriation of products,[7,13] the experiments were done only in slightly alkaline solutions of the *p*-nitrobenzoates.

Our inability to detect the minor products, tricyclene and isobornyl ethyl ether, in some of the experiments does not mean that they were not formed in the reaction, because we used relatively small samples for the analyses in our earlier experiments.

Results

Kinetics.—The rates of hydrolysis of the acetates of camphene hydrate and methylcamphenilol were measured in dioxane–water (60:40 v/v) containing perchloric acid (Table III–V). Added lithium perchlorate speeds the acid hydrolysis of camphene hydrate acetate (Table IV). The rates of solvolysis of the nitrobenzoates

Table III

Acid-Catalyzed Hydrolysis of Camphene Hydrate Acetate[a]

C_{HClO_4}, *M*	10^6k_ψ, sec^{-1}	Log $k_\psi + H_0$
0.099	8.81	0.32
0.099	264[b]	...
0.099	887[c]	...
0.151	12.7	0.22
0.151	383[b]	...
0.151	1070[c]	...
0.229	24.7	0.26
0.253	29.8	0.26
0.253	952[b]	...
0.281	40.8	0.35
0.281	1090[b]	...
0.513	241	0.70
0.799	564	0.66
1.02	941	0.62
1.69	6080	0.78
1.69	6940	0.74

[a] In dioxane–water (60:40 v/v) at 0° unless specified. [b] At 25.0°. [c] At 35.1°.

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(9) C. A. Bunton and D. Whittaker, *Chem. Ind.* (London), 235 (1960).

(10) J. L. Simonsen and L. N. Owen, "The Terpenes," Vol. II, Cambridge University Press, London, 1957, Chapter X.

(11) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1951, p 175.

(12) P. Beltrame, C. A. Bunton, A. Dunlop, and D. Whittaker, *J. Chem. Soc.*, 658 (1964).

(13) M-H. Itei and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 5335 (1966).

TABLE IV

SALT EFFECTS ON THE ACID-CATALYZED HYDROLYSIS OF CAMPHENE HYDRATE ACETATE[a]

C_{HClO_4}, *M*	C_{LiClO_4}, *M*	10^6k_ψ, sec^{-1}
0.229	...	24.7
0.229	0.67	136
0.229	0.97	291
0.229	1.51	902
0.229	2.07	2740
0.229	2.48	3880
0.281	...	40.8
0.281	0.92	276
0.513	...	241
0.513	0.69	842
0.799	...	564
0.799	0.40	1430

[a] At 0° in dioxane–water (60:40 v/v).

TABLE V

ACID-CATALYZED HYDROLYSIS OF METHYLCAMPHENILYL ACETATE[a]

Temp, °C	C_{HClO_4}, *M*	10_6k_ψ, sec^{-1}
35.6	0.161	0.84
35.6	0.201	1.23
44.6	0.161	3.22
55.5	0.101	7.25
55.5	0.201	13.6
73.4	0.080	41.3
73.4	0.101	45.5
73.4	0.161	83.0
73.4	0.189	102
73.4	0.201	118
99.9	0.101	1010

[a] In dioxane–water (60:40 v/v).

TABLE VI

SOLVOLYSIS OF *p*-NITROBENZOATES[a]

Alkyl group	Temp, °C	C_{H^+}, *M*	10^6k_ψ, sec^{-1}
Camphene hydrate	35.6	0	1.70
Camphene hydrate	35.6	0.10	8.62
Camphene hydrate	35.6	0.27	27.4
Camphene hydrate	55.0	0	27.6
Camphene hydrate	55.0	0.10	96.7
Camphene hydrate	55.0	0.27	253
Camphene hydrate	73.0	0	278
Methylcamphenilyl	73.0	0	0.16
Methylcamphenilyl	73.0	0.10	0.66
Methylcamphenilyl	73.0	0.27	1.43
Methylcamphenilyl	100.5	0	4.34
Methylcamphenilyl	100.5	0.10	19.6
Methylcamphenilyl	100.5	0.20	38.3
Isobornyl	74.2	0	0.0018
Isobornyl	74.2	0.10	0.22
Isobornyl	74.2	0.27	0.84
Isobornyl	101.2	0	0.36
Isobornyl	101.2	0.10	2.01
Isobornyl	101.2	0.27	7.83
Methylisobornyl	34.6	0	2.07
Methylisobornyl	34.6	0.10	11.3
Methylisobornyl	34.6	0.27	30.7
Methylisobornyl	55.3	0	36.4
Methylisobornyl	55.3	0.10	107
Methylisobornyl	55.3	0.27	263

[a] In ethanol–water (80:20 v/v).

were measured in both initially neutral and acidic ethanol–water (80:20 v/v) (Table VI). For comparisons of the reactivities of the *p*-nitrobenzoates, we took the rate constant of the acid solvolyses as $k_\psi - k_0$, where k_0 is the rate constant in an initially neutral solution. We compared the reactivities of the acetates using the interpolated rate constants at 0.2 *M* perchloric acid (the contributions of the spontaneous hydrolyses should be relatively small here and neglecting them does not affect our conclusions significantly).

For the hydrolysis of camphene hydrate acetate in dioxane–water (60:40 v/v), plots of log k_ψ against $-H_0$ (Hammett's acidity function[14]) are linear with a slope slightly greater than 1, as can be seen from the slowly but steadily increasing values of log $k_\psi + H_0$ in Table III. These observations confirm our expectation that the hydrolysis is following an $A_{Al}1$ mechanism and added lithium perchlorate speeds the hydrolysis by increasing the protonating power of the acid.[14a]

The entropies of activation of the acid solvolyses of the esters of camphene hydrate, methylcamphenilol, and methylisoborneol (Table VII) are in the range associated with unimolecular acid catalyzed (Al) reactions.[15] However, for isobornyl acetate[16] and *p*-nitrobenzoate (Table VII), the entropies of activation are negative for solvolyses in dilute acid, where these compounds are probably reacting through bimolecular, $A_{Ac}2$, mechanisms.[15,16]

TABLE VII

ARRHENIUS PARAMETERS AND *exo/endo* RATE RATIOS

Ester	Reagent	*E*, kcal mole^{-1}	$\Delta S^\ddagger$,[a] eu	k_{exo}/k_{endo}[b]
Camphene hydrate *p*-nitrobenzoate	...	29	+7	1700
Methylcamphenilyl *p*-nitrobenzoate	...	31	−2	
Camphene hydrate *p*-nitrobenzoate	H^+	24	−2	1100[c]
Methylcamphenilyl *p*-nitrobenzoate	H^+	33	+11	
Camphene hydrate acetate	H^+	22	+5	600[d]
Methylcamphenilyl acetate	H^+	27	+2	
Methylisobornyl *p*-nitrobenzoate	...	27	+3	
Methylisobornyl *p*-nitrobenzoate	H^+	21	−10	
Isobornyl *p*-nitrobenzoate	...	29	−13	
Isobornyl *p*-nitrobenzoate	H^+	20	−31	

[a] Calculated for 1 *M* reactants and 25° as standard state. [b] At 73°. [c] With C_{H^+} = 0.27 *M*. [d] Calculated for C_{H^+} = 0.2 *M*.

Products.— The products of solvolysis of the bicyclic esters are given in Table VIII. The major products of solvolysis of camphene hydrate and methylcamphenilyl *p*-nitrobenzoates in neutral or weakly alkaline solution are camphene (VII) and camphene hydrate and its ethyl ether (VIII) (Scheme II). These are the expected major products of a solvolysis in which a carbonium ion intermediate is formed and they are similar to the products of solvolysis of the chlorides.[12] Small amounts of tricyclene (IX) and isoborneol and its ethyl ether (X) are formed. Some methylcamphenilol (XI) was formed during solvolysis of its *p*-nitrobenzoate (IV) possibly by mechanism $B_{Ac}2$, with acyl–oxygen fission,

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[14] (a) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957); (b) C. A. Bunton, J. B. Ley, A. J. Rhind-Tutt, and C. A. Vernon, *J. Chem. Soc.*, 2327 (1957).

[15] L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 1 (1963).

[16] C. A. Bunton, K. Khaleeluddin, and D. Whittaker, *J. Chem. Soc.*, 3290 (1965).

Scheme II

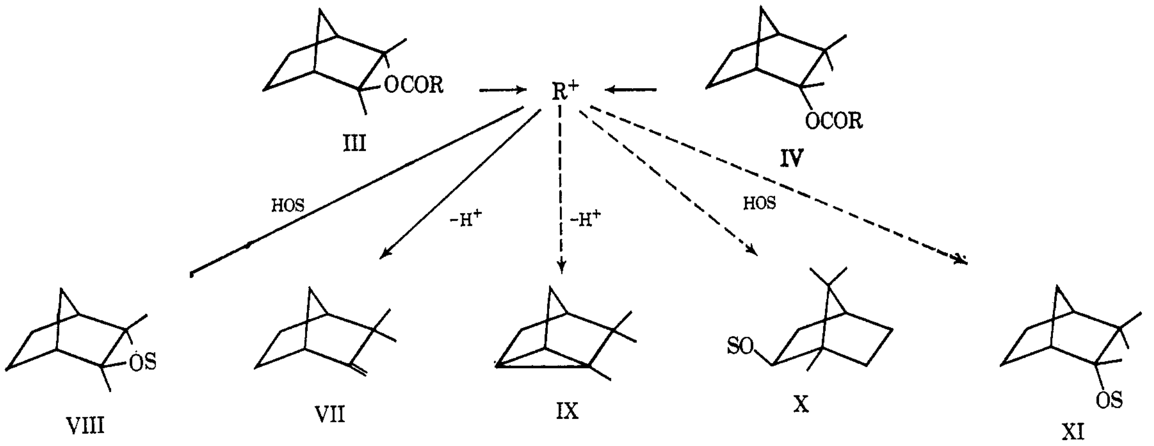


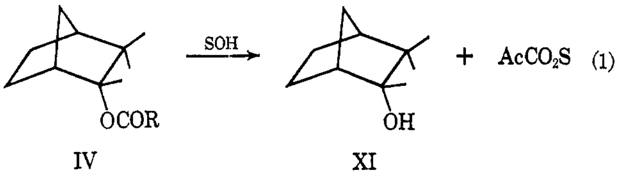
Table VIII

Solvolysis Products of the p-Nitrobenzoates[a]

	Camphene hydrate 55.4°	Camphene hydrate 100°	Methylcamphenilyl 100°
Elimination/substitution	2.3	4.3	2.7
exo-t-ROEt/*exo-t*-ROH	0.32	0.23	0.30
exo-sec-ROH/*exo-t*-ROH	*b*	0.02	0.03
exo-sec-ROEt/*exo-t*-ROEt	*b*	0.04	0.04
endo-t-ROH/*exo-t*-ROH	*b*	Very small[c]	0.1
Tricyclene/camphene	0.02	0.02	0.03

[a] In ethanol-water (80:20 v/v). [b] Sample too small for detection of minor components. [c] The peak was not separated clearly from the larger peak of the *exo*-alcohol.

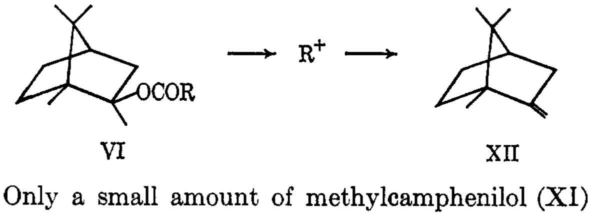
arising from attack of the small amount of alkali in the sodium carbonate (eq 1). Very little methylcamphenilol was formed in the solvolysis of camphene hydrate p-nitrobenzoate.



(1)

Isobornyl p-nitrobenzoate behaves quite differently in that isoborneol (formed by fission of the acyl–oxygen bond) rather than camphene hydrate (formed from a carbonium ion) is the major substitution product in weakly alkaline solution; therefore for this ester the rate of ionization must be slower than its rate of solvolysis and it was not studied in detail.

The solvolysis of t-methylbornyl p-nitrobenzoate (VI) gave olefin, presumably 1-methyl-α-fenchene (XII) (eq 2).



(2)

Only a small amount of methylcamphenilol (XI) is formed during the solvolysis of camphene hydrate p-nitrobenzoate (Table VIII) and its glpc peak was not clearly separated from the large peak of camphene hydrate, although the peaks were separated when more methylcamphenilol was present, as in the reaction of methylcamphenilyl p-nitrobenzoate (Table VIII).

Discussion

In the following discussion we shall assume that for esters of the bicyclic tertiary alcohols, the rates of solvolyses in these polar hydroxylic solvents are the rates of carbonium ion formation, but that solvolysis is faster than carbonium ion formation for isobornyl p-nitrobenzoate because of the incursion of acyl–oxygen fission. It is unlikely that internal return is important in these polar hydroxylic solvents,[17,18] but, if it did occur, its effect would be to make the observed rates of the *exo* compounds less than the rates of ionization, whereas the intermediate formed from the *endo* compounds would return to the more reactive *exo* compounds, which would then decompose very rapidly.

Our values for k_{exo}/k_{endo} for the spontaneous solvolyses of camphene hydrate and methylcamphenilyl p-nitrobenzoate in aqueous ethanol are larger than those for these esters in initially neutral aqueous dioxane[8] where $k_{exo}/k_{endo} = 593$ at 50°, but they are close to the ratio of *ca.* 10^3 found for the acid-catalyzed reactions of the esters (Table VII) and the alcohols.[7] It may be that there is some incursion of acyl–oxygen fission during the hydrolysis of methylcamphenilyl p-nitrobenzoate in aqueous dioxane. The values of k_{exo}/k_{endo} for both the spontaneous and acid-catalyzed solvolyses of the esters of camphene hydrate and methylcamphenilol are *ca.* 10^3 but decrease with increasing temperature.

The formation of isobornyl alcohol and ether as minor products is entirely understandable if it is assumed that ionization of the camphene hydro- and methylcamphenilylcarboxylic esters and isobornyl chloride generate a common carbonium ion, whose structure would be very similar to that of a hypothetical tertiary cation.[2a,19a] If classical carbonium ions are in equilibrium with each other, we must assume that attack of solvent upon the ions is slower than equilibration.[4b,19b]

The similarity of these *exo*/*endo* rate ratios for these spontaneous and acid-catalyzed solvolyses of camphene hydrate and methylcamphenilol is hard to understand if steric hindrance to ionization of an *endo* isomer is the

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[17] S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147, 1154 (1952); S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *ibid.*, **76**, 2597 (1954); S. Winstein, J. S. Gall, S. Smith, and H. Hojo, *ibid.*, **82**, 1010 (1960).

[18] J. A. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

[19] (a) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p 62; (b) C. A. Bunton and C. O'Connor, *Chem. Ind.* (London), 1182 (1965).

major factor in determining relative reactivities. On the other hand, σ participation could occur in both the acid-catalyzed and spontaneous solvolyses of the *exo* isomers, although we would expect it to be less important in these systems where a secondary alkyl group would be interacting at a tertiary carbonium center than in systems in which both centers are secondary; initial state steric effects should affect both sets of solvolyses and are known to be small for these compounds.[8]

The similarity of the rates of ionization of camphene hydrate and methylisobornyl p-nitrobenzoates (III) and (VI), Table VI, shows that the rate enhancements due to relief of eclipsing strain and to secondary participation at a tertiary carbonium ion center in III approximately balance those due to relief of steric strains between the leaving group and the 1- and 7-methyl groups[9] and to tertiary participation at a tertiary carbonium ion center in VI. (Brown and his coworkers have presented rate data for solvolyses of 1,2-dimethylnorbornyl derivatives which show that participation must be less important in the ionization of 1,2-dimethylnorbornyl compounds than in the corresponding 1-methyl compounds, which they consider to exclude participation in the 1,2-dimethylnorbornyl system.[4a,20])

Recently it has been pointed out that torsional effects in bicyclo[2.2.1] compounds should favor *exo* over *endo* attack upon a carbonium ion and *exo* over *endo* departure, although the magnitude of these effects is not yet known. These torsional effects could be of major importance in determining *exo/endo* rate ratios and the stereochemistry of carbonium ion capture in these tertiary systems.[21]

If steric hindrance to ionization, or its equivalent, which is steric hindrance to solvation of the leaving group, is all important, we would expect to find systematic variations in the *exo/endo* rate ratios with changes in the nature of the leaving group and in the ability of the solvent to solvate it. Even though the solvents range from acetic acid to aqueous ethanol, and these ratios apply to both spontaneous and acid-catalyzed solvolyses, *exo/endo* rate ratios of 10^2 to 10^3 are generally observed.[7,8,18]

Our observation of similar *exo/endo* rate ratios irrespective of the formal charge upon the leaving group is consistent with all the other evidence. For example, similar *exo/endo* rate ratios are observed for the spontaneous acetolysis of the norbornyl tosylates and the acid-catalyzed acetate exchange.[22] Similarly borohydride ion and neutral molecules such as methanol and acetic acid behave similarly with respect to the preferred positions of attack upon 2-apobornyl,[23] 2-methoxynorbornyl, and 2-methoxybornyl[24] cations.[25] Despite large differences in the nature of the solvents and reagent, the general pattern of preferred loss and attack from the *exo* direction persists in these reactions involving norbornyl cations, even when the bulky 7-substituents are present.

Registry No.—III, R = p-$NO_2C_6H_4$, 13421-46-0; III, R = CH_3, 13389-75-8; IV, R = p-$NO_2C_6H_4$, 13389-76-9; IV, R = CH_3, 13389-77-0; V, R = p-$NO_2C_6H_4$, 13389-78-1; VI, R = p-$NO_2C_6H_4$, 13389-79-2.

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[25] We are grateful to the referees for pointing out these analogies between solvolyses and carbonium ion capture.

Homogeneous Oxidations of Alcohols with Palladium(II) Salts

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Primary and secondary alcohols are smoothly oxidized to the corresponding acetals and ketones by palladium(II) salts under mild conditions, typically 70–120°. This reaction, which becomes catalytic in the presence of oxygen and a reoxidant compound, is retarded by the chloride ion and by more than small amounts of water. Some oxidations are characterized by a secondary ester forming reaction. Tertiary alcohols do not react under these conditions.

The heterogeneous oxidation of alcohols to carbonyl compounds, catalyzed by noble metal compounds, has been known at least since Strecker's oxidation of cinnamyl alcohol to cinnamaldehyde with PtO and oxygen.[2] More recent heterogeneous alcohol oxidations with platinum and palladium are discussed by Ioffe[3] and by Heyns and Paulsen.[4] The capacity of dissolved palladium(II) salts to effect similar oxidations was strongly implied by Berzelius' observation that upon reflux of a wet ethanolic solution of potassium palladium chloride most of the palladium became reduced.[5] A recent short study by Moiseev's group indicates that these reactions, when carried out in mostly (95–98%) aqueous systems, are sluggish even at reflux.[6] The tendency of substantially anhydrous alcohols to reduce palladium(II) under much milder conditions has been noted as an undesired side reaction,[7] and the closely analogous reduction by alcohols of rhodium(III) to

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