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Neighboring Carbon and Hydrogen. VII. Reactivity of Some Alicyclic and Bicyclic Derivatives[1,2,3]

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In connection with the study of possible driving forces due to participation of carbon or hydrogen, solvolysis rates have been determined for isobornyl, bornyl, *exo*- and *endo*-norbornyl, *neo*menthyl and menthyl halides or arylsulfonates, and, for comparison, cyclohexyl and cyclopentyl arylsulfonates. While the rates of the bornyl, *endo*-norbornyl and menthyl arylsulfonates are virtually identical with that of the cyclohexyl derivative, the rates of the isobornyl, *exo*-norbornyl and *neo*menthyl derivatives exceed those of the corresponding isomeric ones by factors of 2.5×10^5, 350 and 170, respectively. The enhancement of rate in the isobornyl and *exo*-norbornyl cases is considered associated with so-called participation of carbon, the geometry being proper for delocalization of the participating electron pair in the rate-determining ionization. It is possible that so-called participation of hydrogen contributes substantially to enhancement of solvolysis rate of *neo*menthyl derivatives, which tend to have the tertiary hydrogen atom and the leaving group constrained in polar positions and thus *trans* to each other.

In this article we report more of the results of the survey of reactivity in solvolysis which we carried out in connection with the determination of possible driving forces due to participation[4,5] of carbon or hydrogen in the solvolysis process. The reactivities reported are for some alicyclic and bicyclic compounds investigated because of the long-standing evidence in this area for a striking dependence of reactivity on configuration of isomeric molecules.

It has long been known that *cis*-2-alkylsubstituted alicyclic alcohols are dehydrated considerably more rapidly[6] than the *trans* and this difference has sometimes been suggested as an aid to configurational assignments.[7,8] Hückel has been interested for many years in this kind of difference in reactivity,[8] bringing bicyclic pairs of alcohols, such as the isoborneol–borneol pair[6] into the same considerations with the alicyclic pairs such as the neomenthol–menthol[6,8] one by treating the methylene bridge as a substituent. Also, he has extended his consideration to include the relative stabilities of the *p*-toluenesulfonates[8,9,10] of the alcohols in warm methanolic solution.

What we have seen in the relative reactivities of geometric isomers is a possible demonstration of driving forces due to participation of carbon or hydrogen in the solvolysis process. The cyclic compounds, and especially the bicyclic ones, are stereo-electronically instructive and we report in this article the solvolysis rates of isobornyl and bornyl chlorides I and IV (X = Cl), bornyl *p*-toluenesulfonate IV (X = OTs), *exo*- and *endo*-norbornyl *p*-bromobenzenesulfonates II and V (X = OBs) and neomenthyl and menthyl *p*-toluenesulfonates III and VI (X = OTs). For comparison purposes we also report data for cyclopentyl *p*-toluenesulfonate and cyclohexyl *p*-toluenesulfonate and *p*-bromobenzenesulfonate VII (X = OTs or OBs).

The first-order rate constants for the pertinent solvolyses are collected in Table I, which lists also the derived values of the thermodynamic quantities of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, and extrapolated values of certain of the rate constants for comparison purposes. In Table II are shown the rate comparisons isobornyl chloride:bornyl chloride in 80% ethanol, *exo*-norbornylOBs:*endo*-norbornylOBs:cyclohexylOBs in acetic acid, and neomenthylOTs:bornylOTs:menthylOTs:cyclohexylOTs in acetic acid (all at 25°). From these comparisons a combined set of over-all relative reactivities may be derived and this is shown in Table II.

Inspection of the over-all set of relative reactivities shows that, out of the three pairs of geometrically isomeric structures I–VI, one from each pair, namely, the menthyl, *endo*-norbornyl and bornyl isomer, has a solvolysis rate nearly identical (within a factor of 2) with that of cyclohexyl. The other members of the three pairs of isomers show enhanced solvolysis rates, the factors by which the rates exceed that of cyclohexyl being 84 for neomenthyl, 516 for *exo*-norbornyl and 3.5×10^5 for isobornyl. Thus very substantial rate enhancements are involved in certain members of the series I–VI.

In connection with the previous attention given to the relative reactivities of geometrically isomeric alicyclic derivatives, there was a question regarding the nature of the rate-determining process or processes. Thus, the dehydration of the *cis*- and *trans*-2-alkylsubstituted cyclohexanols has sometimes been formulated[11] more along the lines of an E 2 elimination,[12] requiring nucleophilic attack on hydrogen in the rate-determining step as illustrated in VIII for the acid-catalyzed de-

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(3) Taken in part from Ph.D. thesis of Betsy K. Morse, U. C. L. A., 1949.

(4) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, THIS JOURNAL, **74**, 1113 (1952).

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

(6) See G. Vavon and M. Barbier, *Bull. soc. chim.*, **49**, 567 (1931), for semiquantitative studies.

(7) (a) W. Hückel, *et al.*, *Ann.*, **533**, 128 (1937); (b) G. Chiordoglu, *Bull. soc. chim. Belg.*, **60**, 8 (1941).

(8) W. Hückel, O. Neunhoeffer, A. Gercke and E. Frank, *Ann.*, **477**, 99 (1929).

(9) W. Hückel and H. Niggemeyer, *Ber.*, **72B**, 1354 (1939).

(10) W. Hückel, *ibid.*, **77B**, 805 (1944); *C. A.*, **44**, 588 (1950).

(11) *E.g.*, D. H. R. Barton, *Experientia*, **6**, 316 (1950). See, however, a more recent reference to this matter by D. H. R. Barton and W. J. Rosenfelder [*J. Chem. Soc.*, 1048 (1951)].

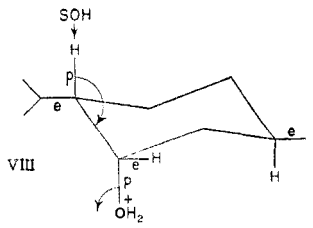
(12) E. D. Hughes, C. K. Ingold, *et al.*, *ibid.*, 2093 (1948).

TABLE I

SUMMARY OF RATE CONSTANTS

Compound	Solvent	Temp., °C.	Concn., *M*	*k*, sec.$^{-1}$	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
CyclopentylOTs	EtOH	50.01	0.024–0.040	$(5.02 \pm 0.06) \times 10^{-5}$		
	AcOH	25.0[a]		1.58×10^{-6}		
	AcOH	50.01	.033–0.039	$(3.84 \pm 0.06) \times 10^{-5}$		
	AcOH	74.58	.028–0.042	$(5.46 \pm 0.06) \times 10^{-4}$	23.7	−6.4
	HCOOH	25.12	.087–0.149	$(7.56 \pm 0.18) \times 10^{-4}$		
	HCOOH	25.0[a]		7.47×10^{-4}		
CyclohexylOTs	AcOH	25.00[a,13,14]		4.88×10^{-8}	27.0[13]	−1.1[13]
	HCOOH	25.12	.081–0.084	$(4.04 \pm 0.07) \times 10^{-5}$		
	HCOOH	25.0[a]		3.98×10^{-5}		
CyclohexylOBs	AcOH	25.0[a,15]		1.71×10^{-7}	26.6	−0.3
	HCOOH	24.40	.083–0.089	$(9.88 \pm 0.40) \times 10^{-5}$		
	HCOOH	25.0[a]		1.07×10^{-4}		
endo-NorbornylOBs	AcOH	49.96	.020	$(8.16 \pm 0.06) \times 10^{-6}$	26.0	−1.5
	AcOH	74.57	.020	$(1.54 \pm 0.02) \times 10^{-4}$		
	AcOH	25.0[a]		2.52×10^{-7}		
	HCOOH	25.02[b]		8.5×10^{-5}		
exo-NorbornylOBs	AcOH	24.96	.020	$(8.79 \pm 0.09) \times 10^{-5}$		
	AcOH	33.73	.020	$(3.04 \pm 0.01) \times 10^{-4}$		
	AcOH	25.0[a]		8.82×10^{-5}		
Bornyl Cl	80% EtOH	74.81	.022	1.50×10^{-7}	28.3	−8.7
	80% EtOH	99.63	.022	2.45×10^{-6}		
	80% EtOH	25.0[a,c]		1.37×10^{-10}		
Isobornyl Cl	80% EtOH	25.00	.0077	$(3.41 \pm 0.014) \times 10^{-5}$	21.8	−5.9
	80% EtOH	49.30	.0077	$(5.97 \pm 0.08) \times 10^{-4}$		
BornylOTs	EtOH	74.96	.03	$(1.29 \pm 0.01) \times 10^{-5}$		
	AcOH	49.90	.028–0.038	$(2.55 \pm 0.03) \times 10^{-6}$	27.3	0.2
	AcOH	74.96	.029–0.034	$(5.87 \pm 0.07) \times 10^{-5}$		
	AcOH	25.0[a]		6.76×10^{-8}		
MenthylOTs	EtOH	74.96	.03–0.04	$(1.34 \pm 0.01) \times 10^{-5}$		
	AcOH	49.90	.03–0.04	$(1.28 \pm 0.02) \times 10^{-6}$	29.9	7.1
	AcOH	74.96	.03–0.05	$(3.97 \pm 0.15) \times 10^{-5}$		
	AcOH	25.0[a]		2.39×10^{-8}		
NeomenthylOTs	EtOH	49.90	.037	$(7.11 \pm 0.07) \times 10^{-5}$		
	AcOH	34.27	.030	$(1.34 \pm 0.01) \times 10^{-5}$	24.6	−0.7
	AcOH	49.90	.030	$(9.9 \pm 0.4) \times 10^{-5}$		
	AcOH	25.0[a]		4.09×10^{-6}		

[a] Calculated from data at other temperatures. [b] One preliminary run. [c] Evans and Hamann[16] have very recently reported $\Delta H^{\ddagger} = 30.2$ and $\Delta S^{\ddagger} = -3.4$. These agree with our values within the combined uncertainties. Our extrapolated rate constant at 25° is larger than the value of Evans and Hamann by a factor of 2.



VIII

hydration of neomenthol. On this basis the *cis*-isomer is more rapid because it possesses the tertiary hydrogen atom *trans* to the hydroxyl group. On the other hand, especially for the *p*-toluenesulfonates, Hückel[10] has taken the relative stabilities in alcoholic solvents as reflecting relative rates of ionization to a cationic intermediate. In order to avoid as much as possible the complication from nucleophilic attack on carbon or hydrogens in the rate-determining step, we made most of our measurements of solvolysis rates of arylsulfonates in acetic (or also formic) acid.

While the alcoholysis of neomenthyl *p*-toluenesulfonate may involve nucleophilic attack on hydrogen (or carbon) in the rate-determining step (the alcoholysis rate is nearly as high as that of acetolysis, in contrast to bornyl and menthyl *p*-toluenesulfonates), the rate difference between neomenthyl and menthyl in acetolysis should be much more free of this complication. Further, it is pertinent that the rate difference in formic acid is comparable[17] to that in acetic acid. Also, the substantial enhancement of rate in going from menthyl to neomenthyl is not associated with a closely

(13) S. Winstein and R. Adams, THIS JOURNAL, **70**, 838 (1948).

(14) S. Winstein and A. H. Schlesinger, unpublished work.

(15) S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 821 (1948).

(16) A. G. Evans and S. D. Hamann, *Trans. Faraday Soc.*, **47**, 25 (1951).

(17) J. Schwartz, unpublished work.

TABLE II

RELATIVE RATES AT 25°

	I	II	III	IV	V	VI	VII
X = Cl, 80% EtOH	2.5×10^5	516	84	1	1.47	0.490	1
X = OBs, AcOH							1
X = OTs, AcOH				1.39			1
Over-all rel. rates	3.5×10^5	516	84	1.4	1.5	0.49	1

proportionate increase in the ratio of elimination to substitution associated with solvolysis.[17] All in all, it is clear that the rate differences in Table II reflect relative rates of ionization of the respective materials.

Regarding the reason for the enhanced rate of ionization of the *cis*-2-substituted cyclohexyl and isobornyl derivatives, Hückel has regarded it due to repulsion of the *p*-toluenesulfonate group by the *cis*-alkyl substituent.[8,10] This suggestion amounts to steric facilitation of ionization,[18] focusing attention on only the *cis*-2-alkyl group–*p*-toluenesulfonate group interaction which produces in the original molecule a steric strain which is partially relieved in the transition state. To consider this suggestion it is necessary to inquire into the geometry of the molecules in question.

In the chair form of cyclohexane, more stable than the boat by *ca.* 5.6 kcal./mole,[19] a substituent may occupy the position of a polar (p) or equatorial (e) hydrogen atom[19,20] (see VIII). The equatorial position tends to be preferred by a substituent, since there is less repulsion energy in this position than in the polar one. For example, in the case of methylcyclohexane, the equatorial conformation is treated by Pitzer and co-workers[19] as 1.8 kcal./mole more stable than the polar one. With more than one substituent, non-bonded interactions tend to be minimized when the most and the largest groups are equatorial. Thus, in the case of *trans*-1,2-dimethylcyclohexane, the (ee) conformation has been treated as 2.7 kcal./mole more stable than the (pp).[19,21] Barton[11] has given an excellent introduction to the use of the above type of conformational analysis in discussing the reactions of alicyclic materials if one bears in mind the relatively small magnitude of the energy quantities which are behind the conformational preferences. These are often small enough that essentially all of a reaction can proceed by way of the less populated conformation if there is an appreciably lower $E^{\ddagger}$ for reaction of this conformation.

From the above discussion, neomenthol, with the 1-Me and 4-*i*-Pr *trans* to each other and the 3-OH and 4-*i*-Pr *cis*, will prefer the conformation shown in III or VIII. The *i*-Pr and Me groups are equatorial and the hydroxyl is polar. Menthol will have the conformation shown in VI, all three substituents being equatorial. Since two adjacent groups on a chair form of cyclohexane ring are equidistant whether they are (ep) as in neomenthol or (ee) as in menthol, the 2-alkyl–OTs interaction to which Hückel[8,10] restricts the discussion, is equally large whether the alkyl group is *cis* or *trans*.

In the case of the bicyclic compounds, I, II, IV and V, the ambiguity of conformation is absent,

(18) (a) H. C. Brown, *Science*, **103**, 385 (1946); (b) H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949); (c) P. D. Bartlett, Paper before 10th National Organic Symposium, Boston, Mass., June, 1947; page 22 of Abstracts.

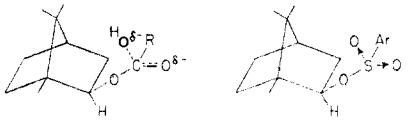
(19) C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

(20) O. Hassel and B. Ottar, *Acta Chem. Scand.*, **1**, 929 (1947).

(21) The situation can be considerably different in the case of adjacent electronegative groups, such as Br, etc., of interest in functional neighboring group participation or 1,2-elimination. Here, other forces are at work to separate two such groups. Thus in the case of *trans*-1,2-dibromocyclohexane, more molecules are (pp) than (ee).[20]

for the strained rigid systems have the 6-ring in a boat form bridged by a methylene group.

Considering steric facilitation of ionization (in a more general sense than Hückel's[8,10]) for both the bicyclic and the menthyl–neomenthyl systems, some impression of the order of magnitude of simple steric facilitation of ionization may be gained from the evidence on steric hindrance to saponification of the corresponding esters. This amounts to using steric strain in the transition state for saponi-

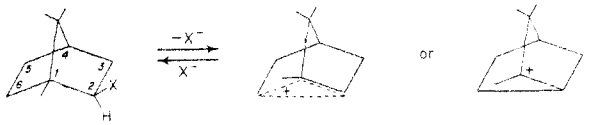


IX X

fication of an ester (IX) as a rough guide to the amount of steric strain in the arylsulfonate (X). The model being used is not really correct in type, but some assistance may be gained in estimating order of magnitude.

In the case of bornyl and isobornyl esters, the factor by which the basic saponification rate of bornyl exceeds isobornyl is 18 for the acid succinate and 24 for the acid phthalate.[22] These small factors lead to the feeling that, while steric facilitation of solvolysis rate may appreciably contribute to the enhancement of rate displayed by isobornyl chloride relative to bornyl chloride, the bulk of the factor, 2.5×10^5 must be accounted for in another manner. Going over to the menthyl–neomenthyl comparison, the basic saponification rate of menthyl acid succinate exceeds that of the neomenthyl ester by a factor[22] of 33. Thus from this it appears possible that steric facilitation of ionization may contribute substantially to the factor of 170 between menthyl and neomenthyl *p*-toluenesulfonate acetolysis rates.

We regard the large factor of 2.5×10^5 between reactivities of isobornyl and bornyl halides in solvolysis to be very largely associated with participation of carbon in the rate-determining ionization. In addition to the rate there is a powerful stereochemical argument in favor of participation. The formation of isobornyl chloride from camphene

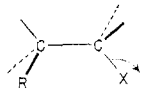


I XI XII

hydrochloride requires a displacement of carbon by chloride ion on C-2 of the camphene-hydro cation XII[23] (or XI).[24] Therefore, at equilibrium, when isobornyl chloride rearranges to camphene hydrochloride, the ionization of isobornyl chloride I must involve displacement of chloride by carbon[25]; in other words, there is participation of carbon in the rate-determining ionization of isobornyl chloride, either XI or XII being produced directly. This same statement may be made for solvolysis type reactions of isobornyl derivatives, which uniformly give rearrangement.[26]

In this system, there is apparently no activation energy for the isobornyl cation → camphene-hydro cation conversion. The atoms C_6, C_1, C_2 and X lie essentially in one plane, with the geometry proper for delocalization of the C_1–C_6 bonding electron pair in the rate-determining ionization; migration of carbon is coupled with the ionization of the C–X linkage.

Solvolysis of bornyl derivatives is instructive, for rearrangement accompanies reactions of bornyl derivatives, the products being essentially the same[10,27] as from isobornyl. However, the configuration of bornyl derivatives is about as unfavorable to participation of carbon in the rate-determining ionization as it is in an open-chain case (XIII) which during ionization is in a rotational position least favorable to participation of R. In the bornyl case, the departing ionizing group is



XIII

leaving the developing *p*-orbital in nearly the direction most unfavorable to participation by the bonding electrons associated with the ring member which later migrates. Thus the migration of carbon in the bornyl case must occur essentially subsequent to ionization.

If ionization of bornyl chloride or bornyl *p*-toluenesulfonate is essentially unassisted by participation of carbon, there is still the question what rate to expect. With alicyclic compounds, ionization rates are affected by the change in so-called angular strain (most important in small rings) and torsional strain[28,29] on going to the transition state. In the case of cyclopentyl compounds, ionization is attended by uneclipsing[28,29] of bonds so ionization rate is enhanced. The cyclohexane ring, in the fully staggered chair form, will, if anything, tend to increase torsional strain in ionization.[28] Thus in 80% ethanol at 25°, with alkyl chlorides there is obtained the following rate sequence[28]

1-methylcyclopentyl, 121 > 1-methylcyclohexyl, 1 < *t*-butyl, 3

The factor between the 5- and 6-ring compounds, *ca.* 120 for the tertiary halides above, could be expected to be less for secondary derivatives, since a methyl group is replaced by hydrogen. (The factor will also depend on the leaving group.)

In the case of the cyclopentyl and cyclohexyl arylsulfonates which are pertinent to the present work the relative reactivities in solvolysis are

(22) G. Vavon, *Bull. soc. chim.*, **49**, 937 (1931).

(23) P. D. Bartlett and I. Pöckel, THIS JOURNAL, **59**, 820 (1937); **60**, 1585 (1938).

(24) T. P. Nevell, E. de Salas and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939).

(25) W. E. Doering, Abstracts of 113th Meeting of the American Chemical Society, Chicago, Ill., April 19 to 23, 1948, p. 41L.

(26) O. Aschan, *Ann.*, **383**, 17 (1911); (b) H. Meerwein and L. Gerard, *ibid.*, **435**, 174 (1924); (c) W. Hückel and F. Nerdel, *ibid.*, **528**, 57 (1937).

(27) (a) W. Hückel, W. Tappe and G. Legutke, *ibid.*, **543**, 191 (1940); (b) W. Hückel and H. Pietrzok, *ibid.*, **543**, 230 (1940); (c) J. Ferns and A. Lapworth, *J. Chem. Soc.*, **101**, 273 (1912).

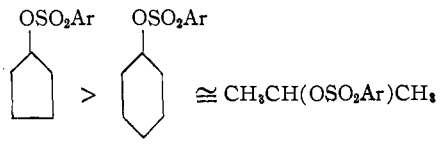
(28) H. C. Brown, R. S. Fletcher and R. B. Johannesen, THIS JOURNAL, **73**, 212 (1951).

(29) P. D. Bartlett, *Bull. soc. chim.*, [5] **18**, 100C (1951).

shown in Table III. The factor between cyclopentyl and cyclohexyl is 38:1 in ethanol at 50°, but this is a poor solvent for assessment of relative reactivities if one wishes to exclude assistance from nucleophilic attack on carbon or hydrogen. In formic acid at 25°, the factor is 19:1 and in acetic acid it is 14–32 at 75–25°, respectively. The reactivity of cyclohexyl *p*-bromobenzenesulfonate is nearly identical with that of the isopropyl ester.

TABLE III

RELATIVE REACTIVITIES OF CYCLOPENTYL, CYCLOHEXYL AND ISOPROPYL ARYLSULFONATES



EtOH, 50°	38	1[14]	
AcOH, 75°	14	1[30]	
50°	21	1[13,14]	
25°	32	1	1.4[5]
HCOOH, 25°	19	1	0.57[5]

With respect to $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of activation cyclopentyl *p*-toluenesulfonate has a lower $\Delta H^{\ddagger}$ by 3.3 kcal./mole and a lower $\Delta S^{\ddagger}$ by *ca.* 5 e.u. than the cyclohexyl ester; the $\Delta S^{\ddagger}$ for cyclopentyl is essentially identical with that for isopropyl. This situation is similar to that for the tertiary chlorides in 80% ethanol[28,31] where the 5-ring compound has a $\Delta S^{\ddagger}$ *ca.* 4.2 e.u. smaller and a $\Delta H^{\ddagger}$ 4.1 kcal./mole smaller than the 6-ring compound and the $\Delta S^{\ddagger}$ for the 5-ring compound is essentially equal to that for *t*-butyl chloride.

Going back to the bornyl case, it might be expected to show at least some of the rate enhancement of cyclopentyl due to uneclipsing of bonds during ionization. On the other hand, such features as angular strain and steric hindrance to solvation could be rate-retarding. That the rate of bornyl *p*-toluenesulfonate would turn out to be so closely identical with that of the cyclohexyl ester could not be predicted, but with a total factor of only *ca.* 20 between cyclopentyl and cyclohexyl, this result is not difficult to accommodate. It is interesting that bornyl *p*-toluenesulfonate is nearly identical with cyclohexyl not only in rate but in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Table I). The factor of 2.5×10^5 between isobornyl and bornyl is nearly exactly due to a difference in $\Delta H^{\ddagger}$, judging by the data with the chlorides (Table I).

The driving force associated with participation of carbon in isobornyl ionization is very much larger than in analogous open-chain cases,[4,5] but, except for one analogy, we are not yet prepared to discuss this difference in adequate thermochemical or thermodynamic terms. The analogy which helps to rationalize the greater driving force due to carbon participation in the bicyclic system is the one between the ring formation attending the change from an olefin to a cyclopropane and the development of ring character in the transition state for ionization which proceeds with participation of carbon.[4] The available evidence shows that in bicyclic compounds it is easier to close an additional ring than in open-chain cases. Thus, for example, the ΔH is more positive for the conversion of propylene to cyclopropane than for the conversion of camphene to tricyclene.[32] Also, ring compounds have a smaller entropy than analogous open-chain cases,[33] so entropy effects from this cause will tend to oppose ring formation. However, the more rigid the case (for example, a bicyclic one), the smaller, it would appear, would be the entropy loss associated with formation of still an additional ring.

The 1-Me group in isobornyl derivatives (I) must assist[4] the ionization and the data for the *exo*- and *endo*-norbornyl *p*-bromobenzenesulfonates (II and V) supply evidence on the extent to which a driving force remains when the 1-Me group is removed. The rate in acetic or formic acid solvents (Tables I and II) and the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in acetic acid (Table I) for *endo*-norbornyl *p*-bromobenzenesulfonate V are nearly identical with those for cyclohexyl, as in the bornyl case. The *exo*-norbornyl ester II exceeds the *endo*-isomer in rate by a factor of 350, suggesting that *ca.* half the driving force[4] displayed in isobornyl remains in the simpler norbornyl system; again, the bicyclic system differs from analogous open-chain cases. A stereochemical study of this system is reported elsewhere.[34] The *exo*-norbornyl *p*-bromobenzenesulfonate solvolyses so rapidly in acetic acid that a large enough temperature range has not yet been studied to obtain $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ reliably. The indication from the rates at 24.96 and 33.73° (Table I) is that some of the rate increase from *endo*- to *exo*-norbornyl may be due to a change in $\Delta S^{\ddagger}$.

The neomenthyl–menthyl case needs more study, but the present results in solvents such as acetic or formic acid are consistent with some assistance to ionization of neomenthyl from so-called hydrogen participation. The tertiary hydrogen atom on C_4 in neomenthyl *p*-toluenesulfonate (III) is constrained in the polar (p) position, perfectly *trans* to the OTs group, also constrained in a polar (p) position. This situation is more favorable to hydrogen participation, although the usual question[4] where hyperconjugation leaves off and participation begins, is present here. It is significant that especially with neomenthyl derivatives, one begins to encounter rearrangements, as in the reaction of neomenthol and phosphorus pentachloride[35] or of neomenthylamine with nitrous acid.[27a] In such reactions we have the complication of several possible mechanisms. An indication of the prominence of the role assumed by the tertiary hydrogen atom on C_4 in the chain of events from neomenthyl *p*-toluenesulfonate (III) to products in solvolysis-elimination comes from a product study[17] which is not yet complete and will be reported elsewhere. For example, while menthyl *p*-toluenesulfonate yields a mixture of Δ^2- and Δ^3-

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menthenes, with the latter somewhat predominant (a typical so-called Saytzeff result[12]) in ethanol,[27a] acetic acid[17] or formic acid[17] solvents, the olefin from neomenthyl *p*-toluenesulfonate contains none, or at least negligible amounts, of the Δ^2-isomer.[17] One can begin to recognize that it will be possible for participation to determine the stereochemistry and products of elimination of the type labeled E1 by Hughes, Ingold and co-workers.[12]

The thermodynamic quantities of activation for acetolysis of neomenthyl and menthyl *p*-toluenesulfonates are given in Table I but, for a fuller understanding of them, there are required more data on alicyclic cases, some which constrain the ionizing group to the polar or equatorial positions. For neomenthyl *p*-toluenesulfonate, the $\Delta S^{\ddagger}$ is indistinguishable from that for cyclohexyl, the rate enhancement over that for cyclohexyl being due to a decreased $\Delta H^{\ddagger}$. For menthyl *p*-toluenesulfonate, the near equality of the rate with that for cyclohexyl comes from compensating effects on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The value of $\Delta H^{\ddagger}$ for menthyl is higher, but $\Delta S^{\ddagger}$ is also higher.

The neomenthyl–menthyl system is analogous to others where qualitative or semiquantitative evidence exists for an enhanced reactivity for the isomer with the tertiary hydrogen *trans* to the OH or OTs group. For instance, the *p*-toluenesulfonate of *cis*-α-decalol, m.p. 93°, is very reactive.[8,10] It turns out that the rough relative dehydration rates of Vavon[6] parallel the relative acetolysis rates of the arylsulfonates in Table II. This not only gives some indication of what is going on in the dehydrations, but it furnishes us some rough relative ionization rates. Thus it appears that the factor between reactivities of the *cis*- and *trans*-2-methylcyclohexanol in dehydration (and therefore presumably in solvolysis of the *p*-toluenesulfonates) is at least as large as for neomenthol–menthol.

Experimental Part

Cyclopentyl *p*-Toluenesulfonate.—Cyclopentanol, b.p. 139.0–139.2°, prepared by reduction of cyclopentanone with lithium aluminum hydride, was converted to the *p*-toluenesulfonate, m.p. 27–28°, in the usual manner.

Anal. Calcd. for $C_{12}H_{16}SO_3$: C, 59.97; H, 6.71. Found: C, 59.91; H, 6.61.

Cyclohexyl Arylsulfonates.—The samples of cyclohexyl *p*-toluenesulfonate and *p*-bromobenzenesulfonate were prepared similarly to those previously reported.[15]

Bornyl Chloride.—This material, m.p. 126–127°, was prepared by addition of hydrogen chloride to redistilled pinene,[36] b.p. 154–156°, in chloroform. After water and potassium carbonate was added to the reaction mixture, the bornyl chloride was obtained by steam distillation and recrystallized from ethanol.

Isobornyl Chloride.—This material, m.p. 160–162°, was prepared from borneol with phosphorus pentachloride and ferric chloride by the method of Hückel and Pietrzok,[37] and recrystallized from ethanol by solution at room temperature and cooling.

Bornyl *p*-Toluenesulfonate.—This material, m.p. 81–82° (reported[27b] m.p. 80.5°), was prepared in 63% yield from recrystallized borneol, m.p. 208–211°, by the conventional method in anhydrous pyridine, allowing a reaction time of one week in the cold room.

Anal. Calcd. for $C_{17}H_{24}SO_3$: C, 66.20; H, 7.84. Found: C, 66.12; H, 8.12.

***l*-Menthyl *p*-Toluenesulfonate.**—*l*-Menthol, recrystallized from pet. ether, m.p. 44–46.5°, was converted to *p*-toluenesulfonate, m.p. 93.5–94° (reported[38] m.p. 96°), in 80% yield when the pyridine solution of the reagents was left one week in the cold room.

***d*-Neomenthyl *p*-Toluenesulfonate.**—*d*-Neomenthol, b.p. 81.5–83.5° (6 mm.), obtained by saponification of Eastman Kodak Co. *d*-neomenthyl acetate was converted in low yield by the usual method to *p*-toluenesulfonate, m.p. 65–65.5° (reported[39] m.p. 63°).

Anal. Calcd. for $C_{17}H_{26}SO_3$: C, 65.77; H, 8.44. Found: C, 65.88; H, 8.54.

***endo*-Norbornyl *p*-Bromobenzenesulfonate.**—Pure *endo*-norbornyl alcohol[34] (7.44 g.), m.p. 152.0–153.0°, was dissolved in 52 ml. of anhydrous pyridine to which was then added 17.9 g. (5% excess) of purified *p*-bromobenzenesulfonyl chloride with cooling. After two days in the cold room there was obtained 21.33 g. (97.2%) of material, m.p., after recrystallization from chloroform–pet. ether, 60.0–61.7°, equivalent wt. in solvolysis, 333.7 (calcd. 331.2).

Anal. Calcd. for $C_{13}H_{15}O_3SBr$: C, 47.14; H, 4.57. Found: C, 47.12; H, 4.74.

***exo*-Norbornyl *p*-Bromobenzenesulfonate.**—From 7.01 g. of *exo*-norbornyl alcohol,[34] m.p. 127.8–128.5°, there was obtained 12.89 g. (62.3%) of *p*-bromobenzenesulfonate, m.p. 55.7–57.0° on recrystallization from petroleum ether, equivalent wt. in solvolysis 336.6 (calcd. 331.2). A similar preparation starting with 10.0 g. of *exo*-norbornyl alcohol yielded 27.14 g. (92.0%) of crude *exo*-norbornyl *p*-bromobenzenesulfonate.

Anal. Calcd. for $C_{13}H_{15}O_3SBr$: C, 47.14; H, 4.57. Found: C, 46.68; H, 4.63.

TABLE IV

SOLVOLYSIS OF BORNYL CHLORIDE IN 80% EtOH AT 99.63°

t (hours)	(H^+) $10^3\ M$	(RCl) $10^3\ M$	$10^6\ k$ (sec.$^{-1}$)
0.00	0.00	21.52	(2.4)
22.40	3.54	17.98	2.23
47.87	6.22	15.30	1.98
74.85	8.41	13.11	1.84
142.85	12.30	9.22	1.65

TABLE V

SOLVOLYSIS OF ISOBORNYL CHLORIDE IN 80% EtOH AT 25.00°

t (min.)	(H^+) $10^3\ M$	(RCl) $10^3\ M$	$10^4\ k$ (sec.$^{-1}$)
	0.00	7.69	
0	0.43[a]	7.26	
88	1.52	6.17	0.308
138	2.23	5.46	.344
200	2.89	4.80	.345
270	3.61	4.08	.356
377	4.42	3.27	.353
		Mean	.341 ± 0.014

[a] Observed 4 minutes after preparation of solution.

Kinetic Measurements.—Solvolysis kinetics were measured by our previous methods.[4,5,15] In the solvolyses of the *p*-toluenesulfonates or *p*-bromobenzenesulfonates, no unusual features were noted in the kinetic behavior.

The solvolysis of bornyl and isobornyl chlorides in 80% ethanol require slight comment. The rate of bornyl chloride was very low, temperatures of 75 and 100° being necessary, and the rate constants tended to drift downward as illustrated in Table IV for a run at 99.63°. The initial rate constants were estimated by extrapolation and these are the ones listed in Table I. The derived values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, also given in Table I, are thus subject to more than the usual uncertainty. In the case of isobornyl chloride the solvolysis in 80% ethanol, illustrated in Table V, showed good first order behavior except for a small amount of early fast reaction ascribed to a slight contamination with camphene hydrochloride.

LOS ANGELES, CALIFORNIA RECEIVED AUGUST 20, 1951

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