Racemisation and Oxygen Exchange Reactions of the Trimethylnorbornan-2-ols[1]

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The rates of acid-catalysed heterolysis of the C–O bond of borneol (bornan-2,*endo*-ol), isoborneol (bornan-2,*exo*-ol), camphene hydrate (2,3,3-trimethylnorbornan-2,*exo*-ol), and methylcamphenilol (2,3,3-trimethylnorbornan-2,*endo*-ol) have been measured. Camphene hydrate exchanges oxygen in aqueous acid more rapidly than it racemises by a factor of 38, while methyl camphenilol rearranges to a mixture of camphene hydrate and isoborneol, the C–O bond heterolysis being slower than that of camphene hydrate by a factor of $1{\cdot}3 \times 10^3$. Isoborneol both racemises and exchanges oxygen at the same rate, faster than borneol by a factor of $2{\cdot}3 \times 10^5$. The rate ratios for both pairs of alcohols are considered to be electronic as well as steric in origin.

In his comprehensive review of the non-classical ion problem, Sargent[2] draws attention to the relatively unsatisfactory state of knowledge concerning the effects of neighbouring group participation on ionisation at tertiary centres. While participation by σ-bond electrons provides an explanation for acceleration of ionisation of secondary *exo*-norbornyl esters relative to the *endo*-esters, it is less satisfactory in explaining the *exo* : *endo* rate ratio in tertiary systems. The effect of σ-bond electrons should be diminished by competing electron supply from the extra alkyl group,[3] but *exo* : *endo* ratios of 10^3 have been observed. Brown *et al.*[4] have suggested that this is due to retardation of ionisation of tertiary *endo*-derivatives, while Sargent[2] attributes acceleration of ionisation of the *exo*-substituents to steric effects, and Schleyer[5] has suggested that the acceleration results from torsional effects.

Consideration of the problem is handicapped by the variety of leaving groups which need to be used to obtain the necessary rate data; in general, acetolysis of toluene-*p*-sulphonates has been used for secondary systems,[6] while the hydrolysis of t-alkyl *p*-nitrobenzoates has often been studied because the toluene-*p*-sulphonates are very unstable.[2] Chlorides should provide a satisfactory leaving group for both secondary and tertiary systems, but methylcamphenilyl chloride (2,3,3-trimethylnorbornyl 2,*endo*-chloride) has not been prepared though the other three isomeric chlorides (2,3,3-Me_3-2,*exo*-Cl, 1,7,7-Me_3-2,*endo*-Cl, and 1,7,7-Me_3-2,*exo*-Cl) are known.[7,8] All four analogous alcohols are, however, known; we now report rate data on the C–O bond heterolysis of all four in the same solvent system, and compare them with available data on systems in which ionisation is unlikely to be assisted by steric or participation effects.

EXPERIMENTAL

Preparation of Materials.—*Borneol* (*Bornan*-2,endo-*ol*) (I). Commercially available optically active borneol was purified *via* its acid phthalate,[9] and had m.p. 207° (lit.,[10] 208°), $[\alpha]_D^{25}$ $+32{\cdot}9°$ (EtOH, *c* 9·2) (lit.,[10] $+36{\cdot}8°$).

Isoborneol (*Bornan*-2,exo-*ol*) (II). Reduction of camphor {either labelled with ^{18}O by exchange with acidified ^{18}O enriched water in dioxan, or natural optically active material with $[\alpha]_D^{25}$ $-41{\cdot}2°$ (EtOH, *c* 12·6)} with lithium aluminium hydride gave isoborneol containing 14% borneol, which was purified by chromatography on alumina to give isoborneol, m.p. 214° (lit.,[10] 214°), $[\alpha]_D^{25}$ $+31{\cdot}3°$ (EtOH, *c* 2·0) (lit.,[11] $+33{\cdot}9°$). Labelled samples had 1·43 atom % excess of ^{18}O.

Camphene hydrate (2,3,3-*trimethylnorbornan*-2,exo-*ol*) (IV). Optically active camphene hydrate was prepared by deamination of isobornylamine,[12] and had $[\alpha]_D^{25}$ $-27{\cdot}0°$ (EtOH). The ^{18}O labelled material was prepared by hydrolysis of camphene hydrochloride[13] with ^{18}O enriched water in the absence of acid, and had 0·748 atom % excess of ^{18}O.

Methylcamphenilol (2,3,3-*trimethylnorbornan*-2,endo-*ol*) (III). Reaction of methyl magnesium iodide[14] with commercial camphenilone gave methyl camphenilol, m.p. 117° (lit.,[14] 117°), $[\alpha]_D^{25}$ $+ 4{\cdot}1°$ (EtOH).

Butan-2-ol. A sample of butan-2-ol ($[\alpha]_D^{25}$ $+6{\cdot}9°$) which had been resolved *via* the brucine salt of its hydrogen phthalate, was available from earlier work.[15]

Kinetics.—All kinetic experiments were carried out in dioxan (purified by the method of Vogel[16])–water (3 : 2 v/v). Perchloric acid was used as catalyst throughout, and solutions were made up so that the dioxan : water ratio was kept constant.

Oxygen exchange reactions were followed by removal of samples at intervals, pouring the mixture into water containing a slight excess of alkali and extracting the alcohol with pentane. To measure the ^{18}O content of the alcohol, it was exchanged with carbon dioxide in the presence of

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[9] T. Ikeda and Y. Fujita, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1928, 257.

[10] R. H. Pickard and W. O. Littlebury, *J. Chem. Soc.*, 1907, **91**, 1978.

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[15] C. A. Bunton and D. R. Llewellyn, *J. Chem. Soc.*, 1957, 3402.

[16] A. I. Vogel, ' A Text-Book of Practical Organic Chemistry,' Longmans, London, 1951, 2nd end., p. 175.

phenylenediamine hydrochloride,[17] and the carbon dioxide was analysed by mass spectrometry after purification by g.l.c. using silicone oil E301 as the stationary phase.

Deuterium analyses were carried out by combustion of the alcohol in a conventional microanalysis train, and distillation of the water formed into zinc dust in a sealed tube. The zinc was then heated to convert the water into hydrogen gas. Fresh tubes and zinc were used for each analysis to eliminate memory effects, and the hydrogen gas was analysed by mass spectrometry.

Dehydration reactions were followed by g.l.c. analysis of samples of the mixture removed at intervals. All g.l.c. analyses were carried out on a modified Griffin and George instrument; columns used were a 6 ft 20% Tween-60 on 80—100 mesh Celite, a 6 ft 15% silicone oil E301 on 60—80 mesh Celite, and a 12 ft Diglycerol on 30—60 mesh Celite.

All kinetic runs gave good first-order plots over at least two half-lives. Rate constants were plotted logarithmically against values [18,19] of either $-H_0$ or $-H_R$ and slopes of the straight lines obtained are reported.

The rates of oxygen exchange measured in this way are not necessarily true rates of heterolysis of the alcohols, since we neglect the rate of dehydration. In the case of the secondary alcohols, this may be ignored, since the camphene re-hydrates rapidly to give unlabelled alcohol, but camphene and camphene hydrate form an equilibrium mixture containing roughly equal amounts of each under our reaction conditions. The true rate of C–O bond heterolysis was thus thus obtained by adding to the rate of oxygen exchange a correction for the dehydration.

RESULTS AND DISCUSSION

The rate constants for oxygen exchange, racemisation, and dehydration of camphene hydrate (IV) are given in Table 1. From these data, the activation enthalpy ΔH^* for the reaction is 20 kcal mol^{-1}, and the activation entropy ΔS^* is -5 cal mol^{-1} K^{-1}. Plots of log k against $-H_0$ are linear with slope 1·04. Although this mechanistic criterion for an $A1$ reaction has been frequently criticised,[20] the kinetic form is that expected for acid-catalysed unimolecular fission of the C–O bond.[21]

TABLE 1

Rate constants of acid-catalysed heterolytic reactions of camphene hydrate (IV) in dioxan-water (3 : 2 v/v) containing perchloric acid

Reaction	t/°C	Acid/M	10^4k_1/s^{-1}	H_0
Oxygen exchange	0·0	0·47	0·34	1·36
	0·0	1·18	1·83	0·50
	0·0	1·79	10·9	−0·09
	0·0	2·05	20·0	−0·26
	25·0	0·47	7·94	
Racemisation	25·0	0·50	0·22	
Dehydration	25·0	0·50	0·45	

A study of the reactions of methyl camphenilol (III) in acid showed that it gave neither oxygen exchange nor racemisation, but rearranged to camphene hydrate and isoborneol (II) and was dehydrated to camphene. The overall rate constant for disappearance of methyl camphenilol in dioxan–water (3 : 2 v/v) containing 0·48M-acid at 25°, is $10^6k_1 = 0{\cdot}66$ s^{-1}. Under these conditions, the rate constant for oxygen exchange of camphene hydrate is 794×10^{-6} s^{-1}; correction for dehydration gives the rate constant for acid heterolysis of camphene hydrate as $k_1 = 839 \times 10^{-6}$ s^{-1}, which is faster than that for methyl camphenilol by a factor *ca.* $1{\cdot}3 \times 10^3$.

On prolonged reaction in acid, camphene hydrate rearranges to isoborneol (II) and, under more vigorous conditions, borneol (I). All three alcohols can be dehydrated to camphene, and in dilute acid camphene exists in measureable equilibrium with both (II) and (IV), kinetic factors favouring (IV) and thermodynamic factors (II), as shown by the data in Table 2.

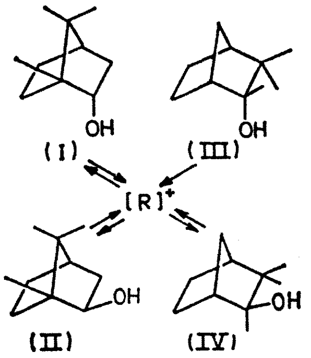
TABLE 2

First-order rate constants for the various steps in the hydration of camphene in aqueous dioxan (3 : 2 v/v) containing 1·46M-perchloric acid at 25·0°

k_1/s^{-1} Camphene $\longrightarrow$ (IV)	1339×10^{-6}
k_1/s^{-1} (IV) $\longrightarrow$ Camphene	1030×10^{-6}
k_1/s^{-1} [Camphene + (IV)] * $\longrightarrow$ (II)	63×10^{-6}
k_1/s^{-1} (II) $\longrightarrow$ [Camphene + (IV)] *	$4{\cdot}3 \times 10^{-6}$

* Equilibrium mixture.

These results may be summarised by the Scheme, in which all four alcohols ionise to a common intermediate R$^+$, whose most rapid reaction is capture by water to give (IV). The next most rapid is loss of optical activity, then capture by water to give (II), and the slowest [22] is capture by water to give (I). The other isomeric alcohol, methyl camphenilol (III) is not formed from R$^+$ in detectable quantities. The Scheme is also consistent with product data on the chloride solvolyses in alkali, where the products are kinetically controlled.[7]



SCHEME

As expected, the secondary alcohols involved in the Scheme react much more slowly than the tertiary. The rate constants for the oxygen exchange and racemisation

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[20] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, 4968, 4973.

[21] J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1917.

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reactions of isoborneol (II), and racemisation of borneol (I) are given in Tables 3 and 4. In both cases, plots of log k against $-H_0$ are curved, the slope increasing with increasing acid concentration, but plots of log k against $-H_R$ are linear with a slope of 0·63 for reaction of (I) and 0·68 for reaction of (II), suggesting unimolecular fission of the protonated alcohol in which the transition state for ionisation lies, in both cases, closer to the carbonium ion than to the protonated alcohol.[23] It is difficult to compare these data with those on the oxygen exchange of camphene hydrate, because the latter reaction is too fast to follow in the region where H_0 and H_R deviate; we note however, that plots of log k against $-H_0$ were curved for the reactions of both borneol and isoborneol, the slope of the latter plot changing from 0·87 to 1·76 as $-H_0$ changed from −0·5 to 1·0.

Table 3

Rate constants of heterolysis of isoborneol in dioxan–water (3 : 2 v/v) containing perchloric acid

[Acid]/M	$10k_1$/s^{-1} at			H_R	H_0
	25·0°	44·6°	75·0°		
0·24		3·14	160		
0·66	0·73	13·5	653	0·70	1·10
1·15	2·27	43·1		−0·27	0·50
1·18	2·73 *			−0·31	0·49
1·58	7·08			−1·10	0·10
2·16	28·4			−2·20	−0·40
2·26	74·8 *			−2·37	−0·47
2·43	139			−2·68	−0·63
2·67	253			−3·11	−0·83
3·36	1220 *			−4·21	−1·39

The rate constants are for racemisation, except those marked with an asterisk, which refer to oxygen exchange.

Table 4

Rate constants of heterolysis of borneol in dioxan–water (3 : 2 v/v) containing perchloric acid

[Acid]/M	10^6k_1/s^{-1} at			H_R	H_0
	75·0°	100·0°	126·1°		
0·62		0·90		0·79	1·14
1·19	0·113	3·81	82·2	−0·36	0·49
1·46		7·72	193	−0·88	0·22
2·35		46·1		−2·54	−0·56
3·13		703		−3·86	−1·20
3·54		1560		−4·46	−1·55

The enthalpies and entropies of activation for both reactions have been calculated from the data. For borneol $\Delta H^* = 36{\cdot}0$ kcal mol^{-1} and $\Delta S^* = +15$ cal mol^{-1} K^{-1}, and for isoborneol $\Delta H^* = 26{\cdot}3$ kcal mol^{-1} and $\Delta S^* = +3$ cal mol^{-1} K^{-1}.

In 0·48M-perchloric acid at 25° the rate ratio $k_{(II)} : k_{(I)} = 2{\cdot}3 \times 10^5$. This ratio is similar to that found for the chloride methanolyses at 25°, for which $k_{exo} : k_{endo} = 1{\cdot}5 \times 10^5$; bornyl chloride methanolysis has $\Delta H^* = 27{\cdot}7$ kcal mol^{-1}, while isobornyl chloride has $\Delta H^* = 24{\cdot}8$ kcal mol^{-1}.

The rate constants for the acid-catalysed heterolysis of borneol and isoborneol were compared with that for the acid catalysed heterolysis of butan-2-ol, since in other systems reactivities of the bicyclic *endo*-isomer and the open chain compound are very similar.[24] The racemisation of butan-2-ol is a unimolecular acid-catalysed reaction in aqueous solvent.[15] The results (Table 5) show that plots of log k against $-H_0$ are linear with a slope of 1·0 in contrast to borneol racemisation, where plots of log k against $-H_R$ are linear.

Table 5

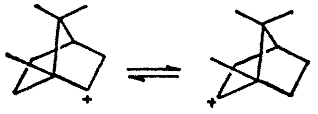
Rate constants of racemisation of butan-2-ol in dioxan–water (3 : 2 v/v) containing perchloric acid

[Acid]/M	10^6k_1/s^{-1} at		H_0
	100·9°	59·8°	
0·74	3·42		0·98
1·40	12·6		0·28
1·50	19·2		0·19
1·93	46·4		−0·20
2·32	99·2	0·32	−0·52
2·76	259	0·69	−0·89
3·25	589	2·16	−1·30
3·46	1752	4·36	−1·47
4·09		12·0	−2·01

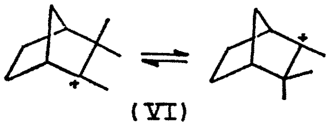
In 0·48M-acid at 25·0°, the rate of racemisation of butan-2-ol is twice that of borneol, but as the racemisaton of butan-2-ol in aqueous dioxan probably involves predominant inversion, as it does in water, the rates of heterolysis are almost identical. From the data in Table 5, the racemisation of butan-2-ol has $\Delta H^* = 34{\cdot}3$ kcal mol^{-1}, and $\Delta S^* = +11$ cal mol^{-1} K^{-1}.

Our observations are consistent with the assumption that borneol is not abnormally unreactive, although effects due to bond angle strain, non-bonding interactions, and torsional strain complicate rate comparisons. We suggest, however, that the effect of torsional strain on reactivities of bornyl derivatives is small, since the rates of ionisation of bornyl and *endo*-norbornyl derivatives are similar.[6-8,25]

It has been pointed out [26] that racemisation proceeding through the common ion R^+ produced by ionisation of (I), (II), and (IV) may take place either by a [6,2] hydride shift, shown in the hypothetical classical ions (V) or by a [3,2] methyl shift, shown in the hypothetical classical ions (VI). Similar mechanisms can be written for similar reactions involving non-classical ions.



(V)



(VI)

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[23] R. H. Boyd in 'Solute-Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Dekker, New York, 1969.

[24] P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1964, **86**, 1854.

[25] J. D. Roberts and W. Bennett, *J. Amer. Chem. Soc.*, 1954, **76**, 4623.

[26] J. D. Roberts and J. A. Yancey *J. Amer. Chem. Soc.*, 1953, **75**, 3165.

To distinguish between the two mechanisms, either of which could explain the racemisation of isoborneol, we repeated this reaction in a solvent in which the water had been replaced by deuterium oxide (4 : 1 v/v dioxan–D_2O was used, to increase solubility of the alcohol). We would expect equilibration with camphene to result in labelling of the C-1 methyl group with deuterium, and any methyl shift would then place deuterium in the *gem*-dimethyl group.

Isoborneol recovered after 10 half-lives of the racemisation reaction had a deuterium content of 14·5 atom %, compared with the calculated value of 16·7 atom % if one methyl group had all its hydrogen replaced by deuterium. The n.m.r. spectrum of the product showed all the deuterium to be on the C-1 methyl group. Clearly, racemisation takes place entirely by hydride shift, as was observed in experiments on camphene.[27] After 1500 half-lives of the racemisation, however, 45·6 atom % deuterium were incorporated which almost completely removed all methyl signals from the n.m.r. spectrum, showing the methyl shift to have taken place, but more slowly than the hydride shift.

The rates of ionisation of the four alcohols (I)—(IV) to give the ion R^+ are compared in Table 6, and the rates of ionisation of butan-2-ol and the rate of ionisation of t-butanol calculated from published data [28] are compared.

TABLE 6

Rate constants for the heterolysis of trimethylnorbornan-2-ols and comparable acyclic alcohols at 25° in dioxan–water (3 : 2 v/v) containing 0·48M-$HClO_4$

	(I)	(II)	Butan-2-ol	(III)	(IV)	t-Butanol
$10^6/k_1$ s^{-1}	2 $\times 10^{-6}$	0·46	4 $\times 10^{-6}$	0·66	839	0·02
Relative rate	1	2·3 $\times 10^5$	2	3·3 $\times 10^5$ 33	4·2 $\times 10^8$ 4·2 10^4	10^4 1
ΔH^*/kcal mol^{-1}	36	26	34		20	

Before considering the relative reactivities of the alcohols, it is important to distinguish between ionisation to give an ion pair and dissociation of the ion pair to give chemically distinct products; in only a few cases have these steps been separated for norbornyl compounds. Ion pairing should be relatively unimportant in our acid-catalysed reactions. For dissociation of an ion pair, the ions have to penetrate a solvent shell, but for oxygen exchange of an alcohol the departing water molecule merely has to equilibrate with the solvent by entering the solvent shell. This process should be very rapid,[29] *e.g.* the dissociation of water molecules from the inner co-ordination sphere of a large cation such as Rb^+ or Cs^+ has a rate constant of *ca.* 10^9 s^{-1}.

Since our data have been obtained by acid-catalysed heterolysis of the C–O bond of a series of alcohols, it might appear that differences in the basicities of the alcohol could be a major factor in determining their reactivities. Under our conditions, only a small amount of the substrate is protonated, *i.e.* the initial state is the solvated proton and the alcohol, ROH. Since the reaction rate depends only on the free energy difference between the initial and transition states, then in the reaction (1) in which the transition state has most of the

$$\mathrm{ROH} + \mathrm{H}^+ \longrightarrow [\mathrm{R}^+\cdots\mathrm{OH}_2] \longrightarrow \text{products} \qquad (1)$$

positive charge on the organic portion of the ion, the free energy of activation does not depend in any direct way upon the free energy of protonation of the alcohol. This situation would be different if the substrate was fully protonated or if there was considerable positive charge on the leaving group in the transition state.

From the data in Table 6, it is clear that isoborneol reacts faster than borneol by a factor of 2·3 × 10^5, which is attributed in part to acceleration of ionisation by participation of the 1,6-bond electrons, and in part to differences in the ground-state energies of the alcohols. Bornyl compounds are more stable than isobornyl compounds,[30] and therefore part of the enhanced reactivity of isoborneol and its chloride [31] is an initial state effect, showing that interactions between the *exo*-chloride or hydroxy-groups and the C-7 and C-1 methyl groups are more important than interaction between *endo*-substituents and the C-1 methyl group and C-6 hydrogen atom. The tertiary alcohols show a smaller acceleration, and the factor of 1·3 × 10^3 agrees well with that of 8·9 × 10^2 for the solvolysis of the *p*-nitrobenzoates of the 2-methylnorbornan-2-ols [32] and factors of 6 × 10^2 to 1·7 × 10^3 for the acid-catalysed and spontaneous solvolyses of the esters [4,33] of (III) and (IV). This rate difference has been attributed by some authors wholly to steric effects. However, methylcamphenilol was never observed in equilibrium with camphene hydrate and isoborneol in dilute acid * and therefore the heterolysis of methylcamphenilol must be sterically accelerated relative to that of the more reactive camphene hydrate. In this system, it appears that the instability derives from repulsions between an *endo*-methyl substituent on C-2 and the hydrogen atoms on C-1 and C-6 being greater than those of an *exo*-hydroxy-group on C-2 and the hydrogens on C-1 and C-7.

Brown *et al.*[4] suggested that the rate of reaction of camphene hydrate and other *exo*-derivatives was normal and that of methyl camphenilol and other *endo*-derivatives was reduced by non-bonded steric effects. This is

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* At 25·0° in dilute acidic aqueous dioxan the equilibrium mixture of alcohols contained *ca.* 5% of camphene hydrate. *ca.* 1% Of methyl camphenilol could have been detected with the equipment used.

[27] W. R. Vaughan, C. T. Goetschel, M. H. Goodrow, and C. L. Warren, *J. Amer. Chem. Soc.*, 1963, **85**, 2282.

[28] I. Dostrovsky and F. S. Klein, *J. Chem. Soc.*, 1955, 791.

[29] E. F. Caldin in 'Fast Reactions in Solution,' Blackwell Scientific Publications, Oxford, 1964, p. 277.

[30] H. Meerwein and K. van Emster, *Ber.*, 1922, **55**, 2506.

[31] C. A. Bunton and D. Whittaker, *Chem. and Ind.*, 1960, 235.

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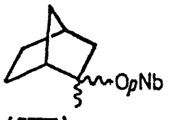
[33] C. A. Bunton, C. O'Connor, and D. Whittaker, *J. Org. Chem.*, 1967, **32**, 2812.

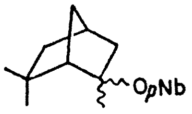
not consistent with the observed rate of reaction of t-butanol relative to (III) and (IV), although an open chain compound may be an unsatisfactory model for reactions of corresponding cyclic compounds. We note, however, that the rates of solvolysis of methylcamphenilyl and *endo*-norbornyl compounds are similar respectively to those of t-butyl and isopropyl or s-butyl compounds. Ascribing the $k_{exo} : k_{endo}$ values for tertiary systems wholly to steric hindrance to departure of the leaving group [4] also makes it difficult to understand the similarity of rate ratios for the acid catalysed and spontaneous hydrolysis [33] of the esters of (III) and (IV), and of the acid heterolysis of the tertiary alcohols.

Sargent [2] suggested that tertiary *exo*-2-norbornyl derivatives may be accelerated by interaction between the *endo*-substituent on C-2 and the *endo*-hydrogen atom on C-6, this interaction being released by ionisation of the *exo*-substituent on C-2. Brown *et al.*[34] have elegantly provided evidence for methyl–methyl interactions in similar positions by measuring the rates of solvolysis of *p*-nitrobenzoates (*p*Nb) (VIII)—(IX) in aqueous 80% acetone at 25°. Clearly, methyl–methyl interactions of this type can have large effects on rate differences.



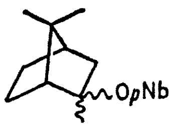
(VII)

k_{exo}:k_{endo} 855



(VIII)

3·63 × 10⁶



(IX)

6·1

However, the main effect of the extra methyl groups is on only one member of the *exo–endo* pair, and these effects are similar, as is shown by the rate comparisons [k_1 (VIII, *exo*) : k_1 (VII, *exo*) = 7·3 × 10²; k_1 (IX, *endo*) : k_1 (VII, *endo*) = 5·7 × 10²].[34] The similarity of these rate ratios suggests that the 6,6-dimethyl group has an effect on the rate of ionisation of the *endo*-ester of (VII) roughly similar to that of the 7,7-dimethyl group on the rate of ionisation of the *exo*-ester of (VII). Consequently, we should expect that the effects of the hydrogen atom on C-6 in (VII) will have roughly the same non-bonded steric effect on the rate of solvolysis of the *endo*-ester as the hydrogen atom on C-7 has on the rate of solvolysis of the *exo*-ester. We can, therefore, neglect any effects of the interaction between the *endo*-substituent on C-2 and the *endo*-hydrogen atom on C-6 when considering the *exo* : *endo* rate ratio in (VII).

Further support for the theory that these effects are small has been obtained by introducing 6,6-dimethyl groups into *exo*-norbornyl bromobenzenesulphonate,[35] which actually decreases the rate of ionisation of the *exo*-substituent on C-2.

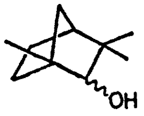
The largest remaining unconsidered non-bonding interaction of substituents on C-2 in (III) and (IV) is with the methyl groups on C-3. Huckel and Kern's [36] data on the ethanolysis of the toluene-*p*-sulphonates of the fenchols (at 50°) and isofenchols (at 40°) (Table 7) suggest that these are small for secondary compounds.

TABLE 7

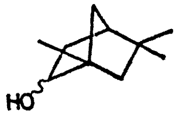
Ethanolysis of fenchyl (at 50°) and isofenchyl (at 40°) toluene-*p*-sulphonates

	Fenchyl	Isofenchyl
$10^6k_1(exo)/s^{-1}$	319	414
$10^6k_1(endo)/s^{-1}$	0·085	0·15
$k_{exo} : k_{endo}$	3·7 × 10³	2·8 × 10³

This type of interaction has a larger effect on the rates of ionisation of tertiary than secondary compounds, as shown by the rates of solvolysis of the *p*-nitrobenzoates in Table 8, measured in aqueous 60% dioxan at 50°. (These conclusions are based on overall rates of solvolysis, and assume that internal return is unimportant.)



Fenchols

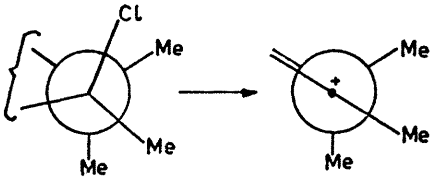


Isofenchols

TABLE 8

p-Nitrobenzoate	VII (*exo*)	VII (*endo*)	(IV-*p*NB)	(III-*p*NB)
$10^6k_1/s^{-1}$	1·96	0·0237	16·5	0·0278
$k_{exo} : k_{endo}$	82·7		594	

However, rate enhancement by 3,3-dimethyl groups is not particularly large even in tertiary systems. In both secondary and tertiary systems these interactions can be relieved by twisting the ring, which in the tertiary system would make the conformation of the initial state of the *exo*-isomer more favourable to ionisation, and hence have the opposite effect on the *endo*-isomer. These torsional effects, illustrated by the Newman projections (X) and (XI) along the C-2–C-3 bond of camphene hydrochloride, have been discussed by Schleyer.[4]



(X) (XI)

exo-tertiary chloride

The above arguments eliminate steric effects as the unique source of the high *exo* : *endo* rate ratio in the camphene hydrate–methylcamphenilyl systems, suggesting that electronic effects must assist the ionisation of the tertiary *exo*-isomer. The problems in interpreting electronic effects wholly in terms of σ-bond participation have been noted by many workers, and it has been pointed out that in particular this explanation cannot be applied in terms of the simple valence bond theory to the

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[34] H. C. Brown and S. Ikegami, *J. Amer. Chem. Soc.*, 1968, **90**, 7122; S. Ikegami, D. L. V. Jagt, and H. C. Brown, *ibid.*, p. 7124.

[35] P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, 1965, **87**, 375.

[36] W. Huckel and H.-J. Kern, *Annalen*, 1965, **687**, 40.

ionisation of *exo*-tertiary compounds.[3] Experimental support for this view has been provided[37] by recent studies of the bromination of substituted norbornenes, in which the orientation of the π orbital permits σ-bond delocalisation to stabilise the transition state for *exo*-approach of the electrophile, though not for *endo*-approach. Consequently, the initial approach of a reagent of moderate steric requirements is controlled by electronic effects. However, bromination of the 2-phenylnorbornenes, in which the electronic effects of the phenyl substituent should be more important than σ-bond delocalisation is subject to steric approach control. In our tertiary system, we cannot, then, consider the observed *exo* : *endo* rate ratio entirely in terms of σ-bond delocalisation.

As pointed out by Jensen,[38] C–C bond hyperconjugation provides a satisfactory alternative explanation for an electronic stabilisation of the transition state for ionisation of either a secondary or a tertiary *exo*-norbornyl system. The vast range of the *exo* : *endo* rate ratios of substituted norbornyl compounds must then result from summation of a number of effects, both steric and electronic, rather than from one dominant effect.

Our evidence is consistent with the assumption that C–C bond hyperconjugation is a major source of electronic stabilisation of a forming cationic centre provided that the geometry of the system is favourable.

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[2/193 *Received, 31st January,* 1972]

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[38] F. R. Jensen and B. E. Smart. *J. Amer. Chem. Soc.*, 1969, **91**, 5688.