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OXYGEN EXCHANGE OF SOME BICYCLIC ALCOHOLS

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In acid, camphene hydrate (I) exchanges its oxygen atom with water much faster than it decomposes to camphene and isoborneol (III); c.f. ref.1 for similar behaviour of the chloride. But its epimer, methyl camphenilol (II), decomposes to (I) and camphene, and thence to (III), without exchanging its oxygen atom. Under more drastic conditions (I) and (II) are thermodynamically unstable with respect to (III); isoborneol (III) then exchanges its oxygen atom, and racemises, at the same rates in acid. Under still more drastic conditions its epimer, borneol (IV), racemises, and exchanges its oxygen atom, and also is decomposed. The rates of the acid catalysed C-O heterolysis of (I)-(IV) are therefore given by the net rates of oxygen exchange (or racemisation) and chemical decomposition and can be compared with the known rates of heterolyses of open chain alcohols.

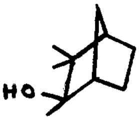
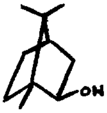
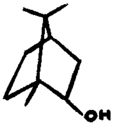
These rate constants of heterolysis, extrapolated where necessary to common experimental conditions, are tabulated. Because much of the reactivity differences are in the activation energies the relative rates are very sensitive to temperature, in particular, borneol, s-butanol and t-butanol, would be relatively less unreactive if the rates were compared at a higher temperature.

The rate constant for oxygen exchange of t-butanol has been measured in water[2]. Assuming that the relative rates of heterolysis of t-butanol in water and aqueous dioxan will be the same as for s-butanol, (Table 1 and ref. 3), from the rate constant for heterolysis of t-butanol in unit activity sulphuric acid at 55°, $10^5k = 13{\cdot}3$ sec^{-1}, we estimate that in dioxan-water 60:40 v/v containing 0·47 M perchloric acid $10^8k \approx 2$ sec^{-1}, and $k_I/k_{tBuOH} \approx 2 \times 10^4$; and $k_{II}/k_{tBuOH} \approx 30$. Therefore camphene hydrate (I) is very much more reactive than t-butanol, and methyl camphenilol (II) is slightly more reactive.

TABLE 1

Rate constants for heterolysis of bicyclic alcohols

At 25°, $[HClO_4]$ = 0·48 M, dioxan-water 60:40 v/v

	 I	 II	 III	 IV	■-BuOH
$10^6 k(sec^{-1})$	794	0.66	0.46	2×10^{-6}	4×10^{-6}
Rel. rate	1	0.8×10^{-3}	0.6×10^{-3}	3×10^{-9}	5×10^{-9}
E kcal. $mole^{-1}$	20	-	27	36	35

Similar reactivity differences are observed for solvolysis of the chlorides excepting that of (II) , and both electronic[4] and steric[5] effects have been proposed to account for these differences. Participation of sigma electrons at the rear of the reaction centre should stabilise the transition states for the exo-isomers, (I) and (III), but not affect those for the endo-isomers (II) and (IV), and the effect should be, and is, greatest when the participating centre is tertiary, and the reaction centre secondary, as in (III), rather than the converse as in (I). The similarity of the rates of heterolysis of the endo-and open chain compounds, particularly in the secondary series, accords with the expected absence of participation in these systems.

Steric factors must also be present, and may operate in two ways. They may destabilise, (i) the initial state, i.e., provide steric acceleration[5], or (ii) the transition state, i.e., provide internal steric hindrance to C-O bond stretching.[6]

Steric acceleration should assist heterolysis of (I) and (II), because eclipsing strain in the initial state is relieved in the transition state, and (I) and (II) are thermodynamically unstable with respect to (III). Similarly (III) is thermodynamically unstable with respect to (IV)[7]. The possible importance of factor (ii), internal steric hindrance to ionisation, is more difficult to assess: it is suggested that endo-hydrogen atoms should hinder bond breaking in compounds similar to (II) and (IV)[6]. On this view the endo-isomers are regarded as unreactive compounds, instead of having normal reactivities, and conversely the exo-isomers are then not necessarily regarded as especially reactive.

However it seems to be impossible to accommodate all the results for these alcohols, or their chlorides, solely in terms of steric effects, and direct substituent effects at the reaction centre. If interference to the departure of the leaving group is all important in (II), then the gem-dimethyl groups should hinder solvolysis of (III), which is much more reactive than (IV) or s-butanol: the chlorides behave similarly[4]. Therefore although steric hindrance to heterolysis may be signigicant in (II) and (IV) and steric acceleration in (I), (II) and (III), these effects are not all important and electronic participation (synartesis or anchimerism) cannot be ignored. The relative importance of the two factors will vary from one system to another, but if participation introduces non-classical character into the carbonium ion derived from (III), or the transition state which precedes it, there should also be some non-classical character in the transition state for the heterolysis of of (I) or its chloride.

Participation of sigma-electrons should also control the stereochemistry of addition to the carbonium ion, e.g. addition of water occurs preferentially from the exo-direction, although the gem-dimethyl groups should block that approach[8]. Therefore steric factors alone cannot explain the stereochemistry of the reaction.

It is assumed that these differences in reactivity are not caused by large differences in the basicities of the oxygen atoms in the transition states. The positive charge on the carbonium ion is largely developed in the transition states for heterolyses of secondary and tertiary alcohols[9], and therefore the basicities of the oxygen atoms should not depend markedly upon the nature of the alconol.

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