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THE COMPARISON BETWEEN OXIDATION AND ACETOLYSIS RATES IN RIGID SYSTEMS

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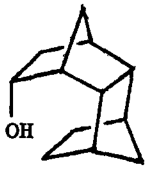
The recent work of Rothberg[1] on the comparison of the rates of oxidation of I and II and the solvolytic rates of their corresponding p-toluene-sulphonates prompts us to report our studies on the rates of oxidation of III - VI.[2]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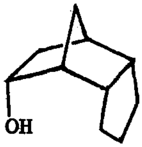
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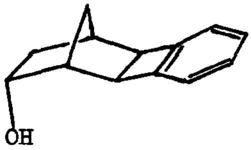
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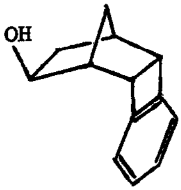
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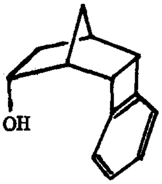
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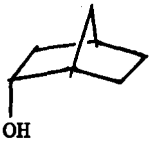
VII


VIII

The high rate of oxidation (Table 1) of VI indicates the greater steric interactions between the hydroxyl group and the endo-5,6- substituent compared to that between the endo-6-hydrogen and the hydroxyl group of both IV and endo-norborneol (VII). The rate determining step in the chromic acid oxidation of secondary alcohols is the decomposition of the intermediate chromate ester. Steric effects have been shown to cause marked rate accelerations[3] and are thought to be due to the relief of non-bonded interactions present in the ground state. Thus, the transition state for the reaction resembles the carbonyl product.[4]

TABLE 1

Rates of Chromic Acid Oxidation of Alcohols at 33.0°C in 40% Aqueous Acetic Acid[a]

Compound		$k_2 \times 10^3$ l mole^{-1}sec^{-1}	Relative Rate
VIII	Exo OH	3.52	1.0
VII	endo OH	23.2	6.6
III	exo Bz - exo OH	2.60	0.74
IV	exo Bz - endo OH	18.5	5.3
V	endo Bz - exo OH	4.27	1.2
VI	endo Bz - endo OH	228	65

a) Concentrations were 1.76×10^{-3}M in chromic acid and 1.80×10^{-3}M in alcohol.

A comparison of the rate of oxidation of III and V with that for exo-norborneol (VIII) confirms the view that inductive effects are small in these reactions.[5] The oxidation rate of V is seen to be somewhat greater than III; this may be due either to the non-bonded interactions between the endo-5,6-substituent and the endo-2 hydrogen, or to the small but different polar environment of the hydroxyl group in the starting alcohols.

Table 2 compares the relätive rates of oxidation of the alcohols and the acetolysis rates of the corresponding p-toluenesulphonates. We allow a factor of 10 for the inductive deceleration and other factors associated with the benzene ring in III - VI so that a direct comparison can be made to the relative rates of acetolysis of I and II. The carbonyl frequency of the ketones IV, VI, I and II are almost identical so that hybridisation or angle strain differences[6] cannot explain the different rates of acetolysis. It is obvious that no quantitative correlation exists between the rates of oxidation and solvolysis although a qualitative comparison proves extremely enlightening in respect of the transition states of the solvolysis reactions.

TABLE 2

	Compound	Rel. Rates of Acetolysis	Rel. Rates of Oxidation	Ketone Frequency (cm.$^{-1}$)
VII	endo OH	1.0	1.0	1751
IV	exo Bz - endo OH	0.90*	0.80	1746
VI	endo Bz - endo OH	.022*	9.8	1742.5
II		0.10[a]	68[a]	1743[a]
I		22[a]	206[a]	1743[a]

* corrected for inductive effects

[a] Ref. 1

Rothberg postulates[1] that the rate of acetolysis of I is increased over VII due to the possibility that, in the ionisation, a path other than perpendicular to the resulting carbonium ion would be followed, resulting from the large ground state strain. A study of Dreiding models indicates that non-bonded interactions would decrease at a very early stage of ionisation. VI, however, although possessing only a fraction of the ground state strain of I, solvolyses much slower than VII since steric strain increases as the transition state is formed. Evidently the situation with II is somewhere between that of I and VI, where although the interactions in the ground state are much greater in II than in VI, non-bonded interactions are greater in the transition state of acetolysis of VI than in II.

Our observations, together with those of Rothberg, indicate that there can exist a spectrum of situations where compounds with similar ground state interactions will solvolyse at an accelerated or decelerated rate compared to a model system. Thus, measurement of the rates of oxidation of alcohols is not necessarily a useful guide in predicting the rates of solvolysis of the corresponding p-toluenesulphonates.

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