Solvent Effects on the *exo*:*endo* Rate Ratios of Solvolysis of Tetracyclo[8,2,1,$0^{2,9}0^{3,8}$]trideca-3,5,7-trien-11-yl Toluene-*p*-sulphonates

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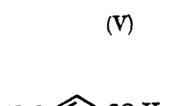
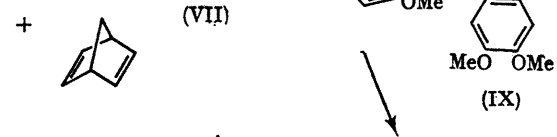
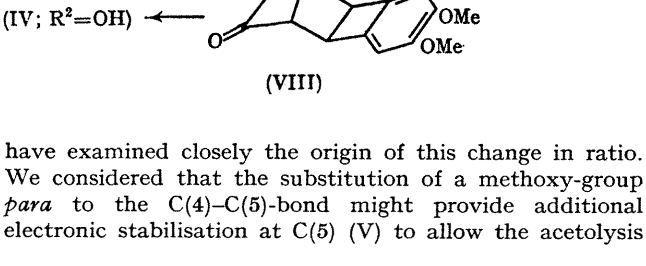
EVIDENCE has been presented that (I) and (II) undergo acetolysis through classical carbonium ions.[1] We have shown that the ratio of the solvolysis rates of (I) and (II) (*exo*:*endo* ratio) is extremely sensitive to the nature of the solvent. Since *exo*:*endo* rate-ratios have been used as a criterion for the non-classical nature of carbonium ions,[2] we have examined closely the origin of this change in ratio. We considered that the substitution of a methoxy-group *para* to the C(4)–C(5)-bond might provide additional electronic stabilisation at C(5) (V) to allow the acetolysis intermediate to have some non-classical character (VI). In the symmetrical dimethoxy-substituted compounds (III) and (IV) the effect of a *para*-methoxy-group in (VI) would be modified to a small extent by a *meta*-methoxy-substituent The solvolyses of (I)—(IV) have been examined in acetic and formic acid.



(I) R^1=OTs, R^2=R^3=H
(II) R^1=H, R^2=OTs, R^3=H
(III) R^1=OTs, R^2=H, R^3=OMe
(IV) R^1=H, R^2=OTs, R^3=OMe



(V) (VI)



(VII) (IX) (VIII)

The dimethoxy-compounds (III) and (IV) corresponding to (I) and (II)[1] were prepared as shown in the scheme. Addition of the benzyne generated from the diazonium salt of 6-aminoveratric acid[3] to a 10 mol. excess of norbornadiene gave (VII) (25%, m.p. 76—77), together with 8% of the 1,3-adduct (IX) (m.p. 89—90°). This preparation further illustrates the utility of the Friedman and Logullo method for the generation of benzynes.[4] Hydroboration followed by oxidation gave (III; R^1 = OH) (m.p. 147—148°). Oxidation of (III; R = OH) in acetone at 0° with Jones reagent gave (VIII) (m.p. 92—93°). Sodium borohydride reduction of (VIII) in methanol gave the *endo*-alcohol (IV; R = OH), m.p. 126—127°.

The comparison of the rate ratio for acetolysis of (I) and (II) (1·37) with that for (III) and (IV) (1·76) indicates that the contribution from (VI) in the solvolysis intermediate is negligible and that (I)—(IV) solvolyse through classical carbonium ions. The similar rate ratio for (III) and (I) compared with (IV) and (II) is probably fortuitous, almost certainly originating in the interaction of the dipole, associated with the aromatic ring, with that of the developing dipole produced at the reaction centre.[5]

For (I) and (II) the *exo*:*endo* rate-ratio changes from 1·37 in acetic acid to 11·4 in formic acid. We consider that this cannot be interpreted in terms of a change from classical to non-classical intermediates from the former to the latter solvent since a similar change in *exo*:*endo* ratio is observed for (III) and (IV). We suggest that the origin of the *exo*:*endo* ratio change with solvent lies in the role played by the solvent in the stabilisation of the transition state of solvolysis of (I)—(IV). Substantial solvation of the transition state occurs in the acetolysis of secondary toluene-*p*-sulphonates. No *endo*-acetate or formate was detected in the solvolysis products of (I)—(IV) providing confirmation of the view[7] that there is substantial hindrance to solvent

Solvolysis of toluene-p-*sulphonates* (I)—(IV)

	$10^7 k$ (sec.$^{-1}$) 75·0°	$10^7 k$ (sec.$^{-1}$) 100·0°	$\Delta H^\ddagger$ (kcal.)	$\Delta S^\ddagger$ (e.u.)	*exo* : *endo* Rate ratio (50°)
(I)–AcOH	79·5[a]	1430[a]	29·1	+1·5	1·37[c]
(II)–AcOH	45·8[a]	683[a]	27·1	−5·2	
(III)–AcOH	148·0	2490	28·4	+0·7	1·76[c]
(IV–AcOH	79·3	1270	27·9	−2·0	
	$10^7 k$ (sec.$^{-1}$) 25·0°	50·0°			
(I)–HCO_2H	257·0	700	24·3	+2·01	11·4
(II–HCO_2H	18·7	585	25·7	+1·63	
(III)–HCO_2H	361·0	8590	23·8	+1·03	9·4
(IV)–HCO_2H	31·7	910	25·2	+0·86	

[a] Ref. 1; [b] rates quoted are the mean of two runs, reproducibility ±2%; [c] extrapolated to 50°.

attack from the *endo*-side in the solvolysis of the *exo*-isomers. This may be reflected in the rates of acetolysis of (I) ($\Delta H^\ddagger$ 29·1 kcal.) and (III) ($\Delta H^\ddagger$ 28·4 kcal.); steric inhibition of solvation is known to decelerate the rate of acetolysis of other compounds.[6] The fact that the acetolysis rates of the *endo*-isomers (II) and (IV), where no solvation problem exists, are slower than (I) and (III), is probably due to steric inhibition to ionisation of the leaving group[7] or torsional effects.[8] In formic acid, however, an S_N1 process is more limiting (or the assistance produced by "backside" solvation of the carbonium ion is less important). Thus the rates of formolysis, compared to acetolysis, of both *exo*-isomers increases by a larger factor than the *endo*-isomers, resulting in the larger *exo* : *endo* rate ratio in formic acid.

We suggest that, for an estimate of the contribution of torsional effects and steric inhibition to ionisation to the solvolysis of the *endo*-isomers of this and similar systems, the *exo* : *endo* ratio obtained from formolysis, rather than acetolysis, should be used.

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‡ Satisfactory analyses and spectral data were obtained for all compounds.

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