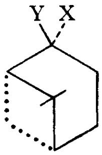
The Solvolysis of Myrtanyl Tosylates: a Comparison of Torsional and Bridging Effects

By J. R. SALMON and D. WHITTAKER*
(*The Robert Robinson Laboratories, University of Liverpool, Liverpool* 7)

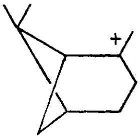
RECENTLY Schleyer[1] has pointed out the importance of torsional effects in favouring *exo*- over *endo*-attack on the 2-norbornyl cation and related systems. In many systems, torsional theory applied to a classical-ion and bridged-ion theory both predict predominance of *exo*- over *endo*-products; we now report results on a system in which torsional theory predicts that the classical ion would give a different product from that predicted on the basis of a non-classical ion.

The solvolyses of the *cis*- (I, X = H, Y = CH_2OTs) and *trans*- (I, X = CH_2OTs, Y = H) myrtanyl toluene-*p*-sulphonates in alkaline methanol are mixed mechanism reactions, a bimolecular reaction proceeding simultaneously with a unimolecular reaction which, by rearrangement, gives rise to the 2-pinanyl cation (II). This ion may subsequently react directly with the solvent, undergo opening of the cyclobutane ring or undergo expansion of the cyclobutane ring to form fenchyl or bornyl derivatives. The last reaction presumably involves either the ion (III) or the ion (IV).

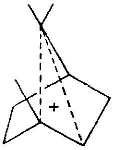
A study of models of (II) suggests that torsional effects would have little influence on the direction of substitution, but (IV) would be expected to give predominantly *exo*-products on the basis of torsional theory.



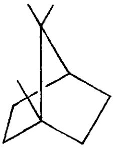
(I)



(II)



(III)



(IV) +

Results of a typical product study are given in the Table. Examination of isobornyl methyl ether under similar chromatographic conditions

TABLE

Products of solvolysis of cis-*myrtanyl toluene*-p-*sulphonate* (0·032M) *in methanol containing* 0·033M-NaOMe *at* 85·0°.

	%
Unknown	0·5
α-Pinene	2
α-Fenchene	5
(Camphene)?	0·5
β-Pinene	18
Limonene	6
α-Fenchyl methyl ether	4
Terpinolene	4
Bornyl methyl ether	2
(*trans*-2-Pinyl methyl ether + unknown)	*ca.* 7
cis-2-Pinyl methyl ether	19
cis-Myrtanyl methyl ether	6
α-Terpinyl methyl ether	28

(Analysis by g.l.c. on a 150 ft. capillary column coated with di-decyl phthalate at 150°. Identities were confirmed by characterisation of samples isolated by preparative scale operation, using a 20 ft. Carbowax 20M column).

showed that the maximum yield of this compound was less than 1% of that of the bornyl isomer.

If we consider the formation of bornyl methyl ether in terms of classical ions, then it must be formed from (IV). Torsional theory, however, predicts that (IV) would give mainly isobornyl methyl ether, and indeed other reactions in which (IV) might be postulated as an intermediate give no trace of bornyl methyl ether.[2] As pointed out previously,[3] (IV) cannot, in different reactions, be the precursor of both bornyl and isobornyl derivatives; torsional theory further shows that this ion is unlikely to give predominantly bornyl derivatives. Clearly, our results cannot be accommodated on the basis of a classical ion in which the direction of substitution is governed by torsional effects. Such difficulties do not arise if (III) is postulated as the precursor of bornyl methyl ether, as the direction of substitution is no longer controlled by steric factors.

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[1] P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 699, 701.

[2] P. Beltramé, C. A. Bunton, A. Dunlop, and D. Whittaker, *J. Chem. Soc.*, 1964, 658; W. Hückel and M. Heinzel, *Tetrahedron Letters*, 1964, 2141.

[3] P. de Mayo, "The Chemistry of Natural Products, Vol. 2, Mono- and Sesqui-terpenoids," Interscience, New York, 1959, p. 154; G. Ourisson, *Proc. Chem. Soc.* 1964, 277.