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ACETOLYSIS OF CIS- AND TRANS-9-t-BUTYLSPIRO[4,5]DEC-6-YL p-TOLUENESULPHONATE

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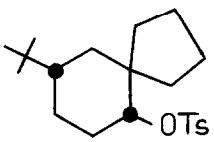
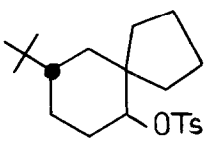
As an extension of our interest in solvolytic routes to the 9-decalyl cation,[1] we have investigated the acetolysis of cis- and trans-9-t-butylspiro[4,5]dec-6-yl p-toluenesulphonate (I) and (II), respectively.[2] We wish to report that the reactions of the two esters are noteworthy for their complete stereospecificity in generating the isomeric 2-t-butyl-9-decalyl cations (III) and (IV). The acetolysis of (II) also provides a definite example of a cyclohexyl derivative which solvolyses via a boat conformation of the six-membered ring.[5]



I



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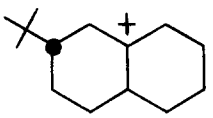

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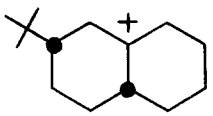
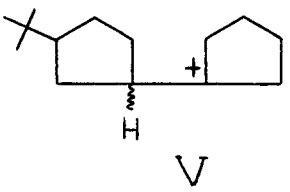


IV

That the esters (I) and (II) undergo acetolysis with anchimeric assistance is clearly evident from kinetic studies.[6] Particularly relevant is the fact that the cis-ester in acetic acid containing sodium acetate at 25° is 360 times more reactive than cis-4-t-butyl-2,2-dimethylcyclohexyl p-toluenesulphonate while the trans-ester (II) is 24 times more reactive than trans-4-t-butyl-2,2-dimethylcyclohexyl p-toluenesulphonate.[7]

The products[8,9] formed from the compounds (I) and (II), and which are shown in Table I,

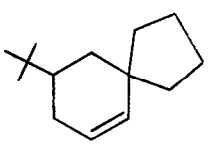


V

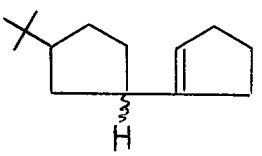
prove that the cis-ester undergoes ring expansion to give exclusively trans-2-t-butyl-9-decalyl cation (III) while the trans-ester undergoes both ring-expansion and ring-contraction to give cis-2-t-butyl-9-decalyl cation (IV) (but none of (III)) and 1-(3'-t-butylcyclopentyl)cyclopentyl cation (V)[10], respectively.

TABLE I: Products from acetolysis of (I) and (II)

Substrate	Product (% Yield)								
	(VI)	(VII)	(VIII)	(IX)	(X)	(XI)	(XII)	(XIII)	Acetates
(I)	0.4	0	0	2.9	11.6	0	0	78.9	6.2
(II)	0.7	4.1	3.6	0	0	21.7	0.9	66.1	2.9

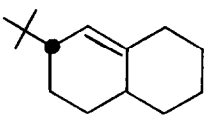


VI

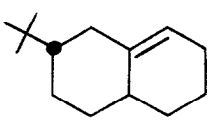


VII

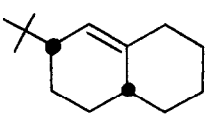
VIII



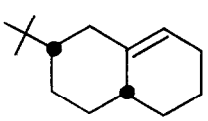
IX



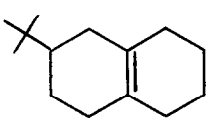
X



XI

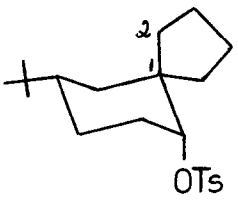


XII

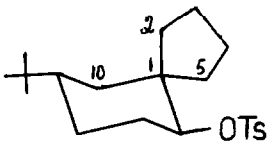


XIII

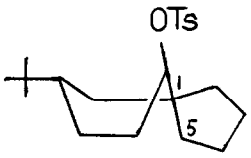
In the most stable conformation (XIV) of the ester (I), the C_1-C_2 bond of the cyclopentyl ring and the axially disposed leaving group are anti-periplanar to each other. This factor ("the sp^3 alignment factor"[11]), combined with relief of ring strain, is responsible for the cis-ester yielding exclusively the trans cation (III) in an ionisation which is very considerably anchimerically assisted.



XIV



XV



XVI

The products formed from trans-9-t-butylspiro[4,5]dec-6-yl p-toluenesulphonate (II) show that the ester must react via two different conformations. In the most stable chair conformation (XV), the C_1-C_{10} bond and the leaving group have the ideal anti-periplanar arrangement; ring contraction thus takes place to give the cation (V). The ring-expansion process is most reasonably explained by invoking the involvement of the boat conformation (XVI) in which the C_1-C_5 bond and the leaving group are anti-periplanar to each other thus allowing concerted ionisation and rearrangement to occur to give the cis cation (IV) to the exclusion of its isomer (III).

Acknowledgements

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2. After the commencement of this work, a very much less thorough study of the acetolysis of compounds (I) and (II) was reported.[3] In particular, the involvement of the cations (III) and (IV) could not be determined since the olefins (IX) - (XII) and the acetates mentioned in ref. 8 were apparently not available. For comments about the earlier study, see Capon.[4]
3. H. Christol, A.P. Krapcho, R.C.H. Peters, and C. Arnal, Tetrahedron Lett; 2799 (1969).
4. B. Capon in "Organic Reaction Mechanisms" (Ed. B. Capon and C.W. Rees) (Interscience) 1969, p.16.

5. The possible involvement of non-chair conformers in the solvolysis of cyclohexyl derivatives has been extensively investigated; see J.E. Nordlander and T.J. McCrary, J.Amer.Chem.Soc., 94, 5133 (1972) and references therein.
6. The rates of acetolysis for (I) and (II) obtained by us are essentially identical with those reported earlier.[3]
7. J-C. Richer and P. Belanger, Canad.J.Chem., 47, 3281 (1969).
8. The olefins (VI) - (XIII) have been synthesised by unambiguous routes and have been characterised by microanalytical and spectral data. The acetates formed from the ester (I) were 3α-t-butyl-1,3,4,5,6,7,8,8aα-octahydro-4aβ(2H)-naphthalenyl acetate (4.4%), 3α-t-butyl-1,3,4,5,6,7,8,8aα-octahydro-4aα(2H)-naphthalenyl acetate (1.7%) and an unknown acetate (0.1%). The ester (II) gave 3α-t-butyl-1,3,4,5,6,7,8,8aβ-octahydro-4aβ(2H)-naphthalenyl acetate (2.9%) as the sole acetate.
9. Analysis of the mixtures of products was achieved by gas-liquid chromatography. A capillary column (Apiezon L, 100 m by 0.5 mm) was the only one (of a large number tested) which gave a satisfactory separation of the olefins (VI - XIII).
10. A distinction between the two isomers of (V) could not be made when it was found that the two isomers of the olefin (VII) could not be separated by g.l.c. It would be predicted that the trans isomer of cation (V) would have been formed from (II).
11. A. Nickon and R.C. Weglein, J.Amer.Chem.Soc., 97, 1271 (1975).