Formation of Hydroazulenes by Solvolytic Rearrangement of 9-Methyldecalin-1-toluene-*p*-sulphonates[1]

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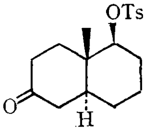
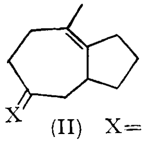
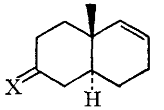
THE bicyclic hydroazulenic sesquiterpenoids have long eluded synthesis, owing to a dearth of methods for the efficient construction of the bicyclo[5,3,0]-decane skeleton which will allow the stereospecific inclusion of various functional side-chains. One solution was recently demonstrated by Marshall and Partridge in their elegant total synthesis of bulnesol.[2] We now report that hydroazulenes can be produced in good yield by the solvolytic rearrangement of 9-methyldecalin-1-toluene-*p*-sulphonates (tosylates).



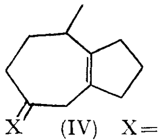
(I)



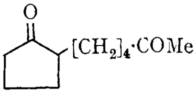
(II) X=O
(V) X=H_2



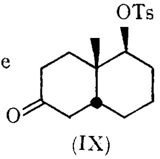
(III) X=O
(VI) X=H_2



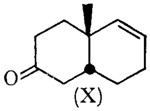
(IV) X=O
(VII) X=H_2



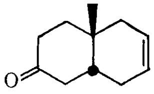
(VIII)



(IX)



(X)



(XI)

When the *trans*-fused keto-tosylate (I) (m.p. 136—137°, prepared by esterification of the known alcohol[3]) is refluxed in anhydrous acetic acid containing two equivalents of potassium acetate, there is produced a mixture of the isomeric C_{11} ketones (II) [78%, 2,4-dinitrophenylhydrazone (DNP) m.p. 154—155°], (III) (10%), and (IV) (5%), along with several minor products. Octalone (III) (m.p. 54—55°) is also obtained when (I) is treated with lithium chloride in refluxing dimethylacetamide. Wolff–Kishner reduction of the solvolysis mixture gave a mixture of bicyclic $C_{11}H_{18}$ isomers containing (V), (VI), and (VII) in a ratio of 78 : 10 : 5. Ozonolysis of this mixture gave mainly dione (VIII) [ν_{max} 1736, 1712 cm.$^{-1}$; τ 7·93 (CH_3CO)], thus verifying the structure of the major solvolysis product. Treatment of this mixture with naphthalene-2-sulphonic acid in acetic acid caused the (V) : (VI) : (VII) ratio to change from 78 : 10 : 5 to 24 : 13 : 51, thus indicating that (VII) and hence (IV), is also a hydroazulene. Since the n.m.r. spectrum of the equilibrated mixture shows increased saturated methyl resonance, but not increased vinyl resonance, (VII) and (IV) must have the indicated structures.

Solvolysis of the corresponding *cis*-fused keto-tosylate (IX)[4] under identical conditions gave (II) (9%), (X) (74%) and (XI) (13%). Compound (X) (2,4-DNP m.p. 103—104°) was identified by comparison with an authentic sample.[4] Compound (XI) (2,4-DNP m.p. 156—157·5°) undergoes catalytic hydrogenation to afford the known *cis*-10-methyl-2-decalone.[5]

The fact that (I) affords much more hydroazulene upon solvolysis than (IX) is probably a conformational consequence. The rigid structure of (I) requires the tosylate group to occupy an equatorial position and assures an anti-coplanar disposition of the C(9)–C(10) bond and the tosylate group. Thus, migration can occur concomitantly with ionization. In (IX), the molecule may adopt the non-steroid conformation, in which the tosylate group is axial. However, this conformation places the tosylate group and the C(9)–C(10) bond in a gauche arrangement and precludes synchronous ionization–migration.

The rearrangement of (I) to (II) suggests that such reactions will prove useful in the synthesis of guiazulenic sesquiterpenoids, since requisite stereochemistry at various positions on the hydroazulene nucleus can easily be controlled before the rearrangement step, while the rigid *trans*-decalin system is still intact.

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[1] Previous paper: C. H. Heathcock and T. R. Kelly, *Chem. Comm.*, 1968, 267.

[2] J. A. Marshall and J. J. Partridge, *J. Amer. Chem. Soc.*, 1968, **90**, 1090.

[3] C. B. C. Boyce and J. S. Whitehurst, *J. Chem. Soc.*, 1960, 2680.

[4] C. H. Heathcock, R. A. Badger, and J. W. Patterson, jun., *J. Amer. Chem. Soc.*, 1967, **89**, 4133.

[5] W. G. Dauben, J. B. Rogers, and E. J. Blanz, *J. Amer. Chem. Soc.*, 1954, **76**, 6384.