Acetolysis of *exo*-Tricyclo[4,4,1,$1^{2,5}$]dodeca-3,7,9-trien-11-yl Toluene-*p*-sulphonate

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THE formation of *exo*-tricyclo[4,4,1,$1^{2,5}$]dodeca-3,7,9-triene-11-one (I) from tropone and cyclopentadiene, the first example of a thermal (6 + 4) cycloaddition, was recently reported by Cookson and his co-workers[1] and us.[2] We now report the acetolysis of the toluene-*p*-sulphonate of the corresponding alcohol obtained by the lithium aluminium hydride reduction of the ketone.

The toluene-*p*-sulphonate (III), m.p. 138—139·5°,† derived from the alcohol (II),[1,2] has a singlet at 4·75 p.p.m. in its n.m.r. spectrum due to H(12), indicating that the dihedral angles between this hydrogen and the adjacent hydrogens are *ca.* 90°.

When (III) was subjected to acetolysis at 100° for 2 hr., followed by treatment with LiAlH$_4$, two alcohols (IV) and (V) were obtained in 95% and 5% yields, respectively, whereas acetolysis at 110° for 3 hr. followed by LiAlH$_4$ treatment, afforded (IV), (V), and a third alcohol (VI) in 80%, 10%, and 6% yields, respectively.

The alcohol (IV), m.p. 62—66° [acetate (VII), liquid], gave, when dehydrogenated with chloranil, the aromatized alcohol (VIII), m.p. 86—89°, the acetate (IX) of which was found to be identical (v.p.c. and i.r.) with *exo*-benzo[3,4]tricyclo-[3,2,1,$0^{2,7}$]octenyl acetate.[3] Chromic acid oxidation of (VIII) yielded the corresponding ketone (X), m.p. 70·5—71°.

The dehydrogenation of the alcohol (V), {sublimes

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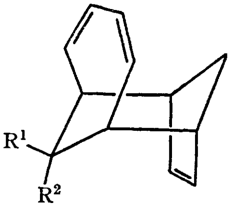
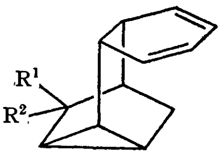
† All new compounds gave satisfactory elemental analyses and u.v., i.r., and n.m.r. spectra.

at 117° [acetate (XI), liquid]}, with chloranil produced the aromatized alcohol (XII), m.p. 110—114°, which, on chromic acid oxidation, yielded the ketone (X). Heating of (IV) and (V) with maleic anhydride yielded the adducts (XIII), m.p. 245—246°, and (XIV), m.p. 189—193°, respectively, and further chromic acid oxidation produced the identical ketone (XV), m.p. 261—262° from both adducts. Therefore, (V) must have the structure shown.

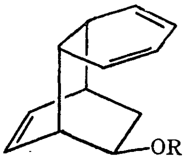
The third alcohol (VI), m.p. 75—76° [acetate (XVI), liquid], with the additional double bond was dehydrogenated to the aromatic alcohol (XVIII), m.p. 96—98°, which was identical with *endo*-benzobicyclo[2,2,2]octadienol.[3]



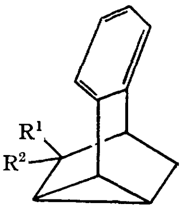
(I) $R^1,R^2=O$
(II) $R^1=H, R^2=OH$
(III) $R^1=H, R^2=OTs$



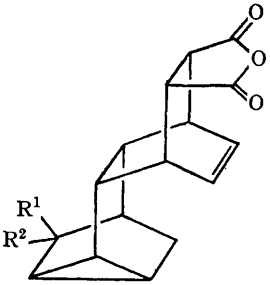
(IV) $R^1=H, \quad R^2=OH$
(V) $R^1=OH, \quad R^2=OH$
(VII) $R^1=H, \quad R^2=OAc$
(XI) $R^1=OAc, R^2=H$



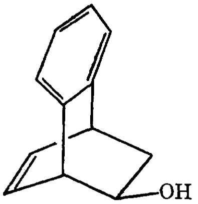
(VI) R=H
(XVI) R=Ac



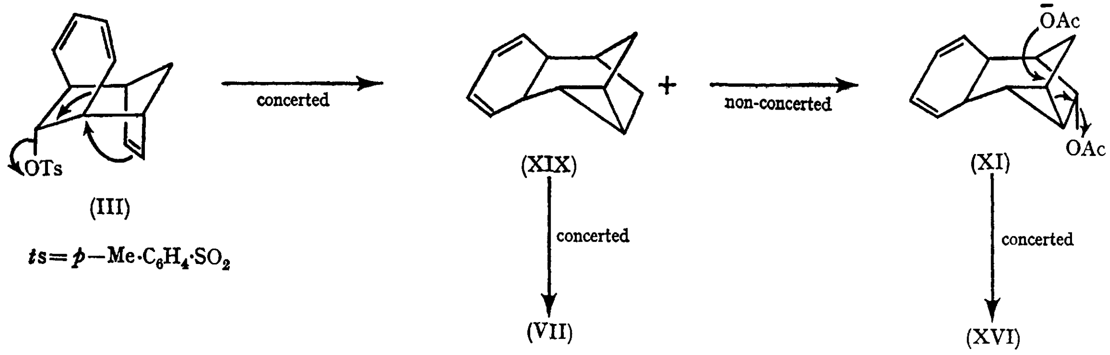
(VII) $R^1=H, \quad R^2=OH$
(IX) $R^1=H, \quad R^2=OAc$
(X) $R^1,R^2=O$
(XII) $R^1=OH, \quad R^2=H$



(XIII) $R^1=H, R^2=OH$
(XIV) $R^1=OH, R^2=H$
(XV) $R^1,R^2=O$



(XVIII)



$ts=p\text{-}Me{\cdot}C_6H_4{\cdot}SO_2$

The formation of (VII) in the acetolysis can be explained by an antiparallel concerted process, while the formation of (XI) and (XVI) indicates some leakage from the concerted process possibly *via* the intermediate cyclopropylcarbinyl ion (XIX) (see the chart below). The latter assumption was supported by the formation of (XI) and (XVI) upon the treatment of (VII) under the solvolytic condition.

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[1] R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Comm.*, 1966, 15.

[2] S. Itô, Y. Fujise, T. Okuda, and Y. Inoue, *Bull. Chem. Soc. Japan*, 1966, **39**, 1951.

[3] H. Tanida, K. Tori, and K. Kitahonoki, *J. Amer. Chem. Soc.*, 1967, **89**, 3212.