Properties of Derivatives of Tricyclo[6,*n*,0,0^{2,7}]tri-2,4,6-enes. Abnormal Reaction of Toluene-*p*-sulphonic Acid with 8,12-Dimethyl- and 8-Methyl-tricyclo[6,4,0,0^{2,7}]tri-2,4,6-en-1-ols. Synthesis of Some *anti*-2,7-Benzobicyclo[3,2,1]octene Derivatives

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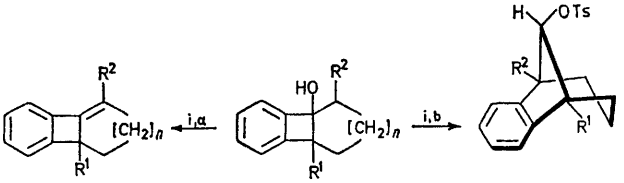
Summary Structure (**3a**) has been assigned to a compound obtained in 85% yield, by the action of the toluene-*p*-sulphonic acid on 8,12-dimethyltricyclo[6,4,0,0^{2,7}]tri-2,4,6-en-1-ol (**1c**); the synthesis of some derivatives of *anti*-2,7-benzobicyclo[3,2,1]octen-12-ol is reported.

We have shown previously[1] that the action of toluene-*p*-sulphonic acid on the alcohols (**1a**) and (**1b**) leads to the hydrocarbons (**2a**) and (**2b**) respectively (Scheme 1). We report here quite different and unexpected behaviour of the alcohols (**1c**) and (**1d**).[2]

Treatment of alcohol (**1c**) under the conditions given in Scheme 1 leads to the tosylate (**3a**), m.p. 108—109.† The i.r., n.m.r. [δ (CCl_4): 0·85—2·0 (m, 6H), 1·11 (s, 6H), 2·45 (s, 3H), 4·35 (s, 1H), and 6·87—7·98 (m, 8H) p.p.m.] and u.v.



(2) (1) (3)

a; $R^1 = R^2 = H$, $n = 2$
b; $R^1 = R^2 = H$, $n = 3$

a; $R^1 = R^2 = H$, $n = 2$
b; $R^1 = R^2 = H$, $n = 3$
c; $R^1 = R^2 = Me$, $n = 2$
d; $R^1 = Me$, $R^2 = H$, $n = 2$

a; $R^1 = R^2 = Me$ (85%)
b; $R^1 = Me$, $R^2 = H$ (75%)

Scheme 1

i; *p*-$MeC_6H_4{\cdot}SO_3H$, *in benzene*, a, 2 h *reflux*, b, 3 h *reflux*

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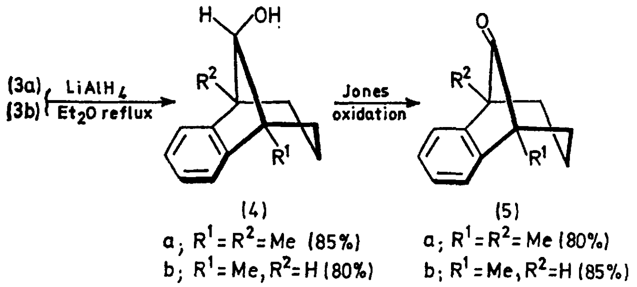
† Satisfactory analytical data were obtained for all products.



Scheme 2

spectra [$\lambda_{max.}$ (EtOH) 272 (log ϵ 3·22), 264 (3·26), and 260 (3·15) nm] are consistent not only with the given structure, but also with a compound containing a benzocyclobutene skeleton.[1,3] The structure was proved decisively by X-ray diffraction. Such a result shows the unusual reactivity of (**3a**) towards toluene-*p*-sulphonic acid.

Similarly, (**3b**) is obtained as a solid, m.p. 80°, from (**1d**). The latter differs from (**1a**) only in the nature of R^1, showing clearly the important role played by this substituent on the course of the reaction. The structure of (**3b**) was determined by comparison of its i.r., n.m.r., and u.v. spectra with those of (**3a**), and by comparison of the spectral data for (**4b**), m.p. 90°, and (**5b**), m.p. 30°, with those of (**4a**), m.p. 85—86°, and (**5a**), m.p. 50°, respectively. (**4a**) and (**5a**) were obtained from (**3a**)‡ by the methods shown *in* Scheme 2.

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‡ Spin-decoupling of the n.m.r. spectrum of (**4b**) indicated that the hydroxy-group was *anti* with respect to the benzene ring.

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[2] The synthesis of (**1c**) and (**1d**) has been reported; P. Caubère, G. Guillaumet and M. S. Mourad, *Tetrahedron*, 1972, **28**, 95.
[3] P. G. Gassman and H. P. Benecke, *Tetrahedron Letters*, 1969, 1089 (and related references); L. Bill and G. Descotes, *Bull. Soc. chim. France*, 1971, 2617.