Synthesis of *trans*-Cyclo-oct-1-en-3-ol by Hydrolysis of *exo*-8-Bromobicyclo[5,1,0]octane

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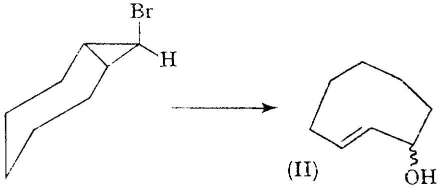
RECENT interest in *trans*-cyclo-octene has been primarily concerned with methods of synthesis[1] and with its resolution and racemisation.[2] Few studies have been reported on derivatives of this system, apart from a preparation of *trans*-cyclo-oct-2-en-1-one in solution,[3] and a scrutiny of the photochemical formation and pyrolysis of *trans-cis*-cyclo-octa-1,3-diene.[4]

Monosubstituted *trans*-cyclo-octenes are potentially of interest as examples of an unusual form of diastereoisomerism possessing one plane of chirality, the *trans*-cyclo-octene part, and one centre of chirality, the asymmetric carbon atom. In addition, if such *trans*-cyclo-oct-1-en-3-yl derivatives could be prepared they might be expected to be chemically interesting as examples of highly strained olefins possessing adjacent functionality. We report here a synthesis of *trans*-cyclo-oct-1-en-3-ol and a preliminary examination of its chemistry.

8,8-Dibromobicyclo[5,1,0]octane[5] was reduced using "dimsyl sodium" in dimethyl sulphoxide[6] to give *exo*-8-bromobicyclo[5,1,0]octane (I). Silver ion-catalysed hydrolysis of the latter in aqueous dioxan at 100° gave *cis*-cyclo-oct-1-en-3-ol in high yield; however, in the absence of silver ion, hydrolysis in aqueous dioxan (1 : 2 by volume) for 28 hr. under reflux gave *trans*-cyclo-oct-1-en-3-ol (II; 60%) contaminated with $< 0.5\%$ of the *cis*-isomer. The uncatalysed hydrolysis is therefore a highly stereospecific concerted process which conforms to the stereochemical rules suggested for the solvolysis of cyclopropyl halides and tosylates,[7] despite the high strain expected for the allylic cation in this case. Apparently the silver ion promotes the isomerisation of *trans*- to *cis*-cyclo-oct-1-en-3-ol, since a control experiment showed that the *trans*-alcohol could be converted into the *cis*-isomer by heating with silver nitrate in aqueous dioxan.



(I) (II)

Spectral data for the alcohol (II) were entirely consistent with the structure assigned. The infrared spectrum showed bands at 820, 935, and 985 cm.$^{-1}$ closely analogous to a related series of bands in *trans*-cyclo-octene; the n.m.r. spectrum showed absorption notably at τ 4·3—4·5 (2H), C-1–H and C-2–H and at 5·74, multiplet (1H) C-3–H*; and the mass spectrum was very similar to that of *cis*-cyclo-oct-1-en-3-ol.

trans-Cyclo-oct-1-en-3-ol is relatively stable, thus it can be distilled, b.p. 92°/10 mm., and it survives treatment with 5% sulphuric acid in aqueous acetone under reflux. Hydrogenation of (II) in ethyl acetate over palladium–carbon gave cyclo-octanol and cyclo-octanone (2 : 1). When heated under reflux with palladium–carbon in ethanol a mixture of *cis*-cyclo-oct-1-en-4-ol, *cis*-cyclo-oct-1-en-3-ol, and cyclo-octanone (70 : 25 : 5) was obtained.

We are currently investigating other reactions of this alcohol, particularly those which might lead to a definition of the configuration at C-3.

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* In particular the possibility of a transannular reaction having occurred in the preparation of (II) leading to a non-allylic alcohol was excluded by a spin decoupling experiment (kindly performed by Mrs. E. Richards) whereby irradiation of the vinyl protons resulted in collapse of the C-3–H multiplet to a quartet (X part of an ABX system).

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