Bredt's Rule. A Derivative of Bicyclo[4,2,1]non-1(8)-ene

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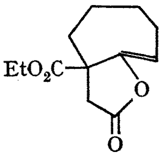
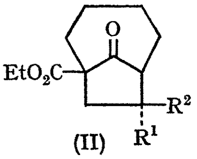
Summary The bicyclo[4,2,1]nonanols (II; R^1 = H, R^2 = OH; R^1 = OH, R^2 = H) are obtained by reduction of the lactone (I) with lithium hydrido-t-butoxyaluminate, and dehydrochlorination of the chloride (II; R^1 = H, R^2 = Cl) with collidine affords the bridgehead olefin (V).

REDUCTION of the enol lactone (I) with lithium hydrido-t-butoxyaluminate afforded a mixture from which the epimeric alcohols (II; R^1 = H, R^2 = OH, and R^1 = OH, R^2 = H) were isolated by chromatography on silica gel; the main individual component of the mixture was the *endo*-alcohol (II; R^1 = OH, R^2 = H). Oxidation of either epimer with Jones' reagent[1] gave the diketone (II; R^1, R^2 = O). This route to bridged bicyclic ketones has been used previously with δ-enol lactones[2] but not, so far as we are aware, with γ-lactones. Treatment of the tosylates of the two alcohols with sodium ethoxide in ethanol led to ring-fission products, but with boiling collidine smooth elimination of toluene sulphonic acid took place with formation of the olefin (III). Its n.m.r. spectrum showed an AB quartet, due to two olefinic protons, at τ 3·87, the low-field doublet of which was further split by coupling with the bridgehead hydrogen (J_{AB} 6·8 Hz., J_{AX} 2·4 Hz.). The structure was confirmed by reduction with palladium and hydrogen to the dihydro-compound (IV; R = CO_2Et) and by conversion into the known bicyclononanone (IV; R = Me).[3]

From the reaction of the tosylate (II; R^1 = OTos, R^2 = H) with collidine we obtained a small yield of another product, besides the olefin (III), which we believe to be the bridgehead olefin (V), although the available evidence does not entirely preclude a structure in which the double bond is at the bridgehead position in the seven-membered ring. The same compound was formed in 40% yield as a colourless unstable liquid, b.p. 104° (air bath temp./0·25 mm.), by dehydrochlorination with collidine of the chloride obtained from the major alcohol (II; $R^1 = OH$, $R^2 = H$) with phosphoryl chloride in pyridine. The structure assigned to this compound is supported by its elemental analysis† and molecular weight (m/e 208), i.r. (ν_{max} 1740, 1715, 1610 cm.$^{-1}$) and u.v. [λ_{max} 241 (ϵ 3908), 310 (208) nm.] spectra, by the n.m.r. spectrum, which shows the presence of a single olefinic proton (finely split doublet, τ 3·25), and by its rapid quantitative hydrogenation over palladium to the bicyclononanone (IV; $R = CO_2Et$). Inspection of models reveals that the double bond and the ketonic carbonyl group in (V) cannot be coplanar, accounting for the low intensity of the short wavelength u.v. absorption band.

According to the well known Bredt's rule[4] a double bond can only be accommodated at the bridgehead position of a bicyclo compound if the rings are larger than a certain minimum size. It has been thought until recently that the necessary condition for an isolable compound was that the sum of the bridging carbon atoms (the "S" number) should be greater than or equal to 9, but the present finding, together with the recent syntheses of bicyclo[3,3,1]non-1-ene,[5] suggests that the practical limit of Bredt's rule may in fact be $S \geqslant 7$. It should be noted, however, that the bicyclo[4,2,1]nonane system is evidently unable to accommodate a double bond between C-1 and C-9, for bicyclo[4,2,1]nonan-9-one could not be brominated in the position α- to the carbonyl group and did not exchange hydrogen for deuterium when treated with alkaline deuterium oxide.[6]


(I)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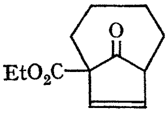
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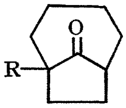
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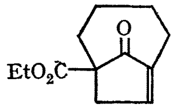
(V)

Added in proof. A synthesis of the parent bicyclo-[4,2,1]non-1(8)-ene has recently been reported.[7]

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† All compounds referred to give satisfactory analytical and spectral data.

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