

CYCLOOCTA-1,5-DIEN-3-ONE AND BICYCLO(4.2.0) OCT-2-EN-4-ONE

AN EXAMPLE OF VALENCE-BOND TAUTOMERISM

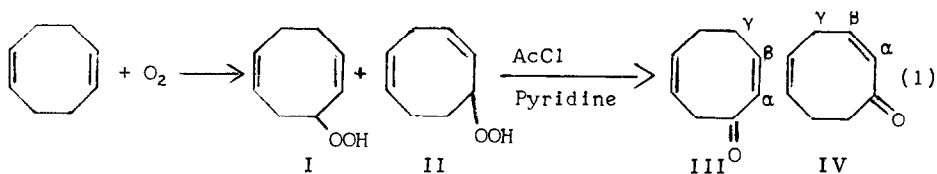
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The autoxidation of cis,cis-1,5-cyclooctadiene proceeds readily in the liquid phase at 60° with the formation of peroxidic products, from which may be isolated, by extraction with 5:1 petroleum ether-benzene solvent, a mixture of hydroperoxides. Catalytic hydrogenation of the mixture yields cyclooctanol as the major product. Although the mixture was not separated, the cyclooctadienyl hydroperoxides I and II are probable constituents on the basis of the NMR spectrum and the absence of appreciable ultraviolet absorption. Dehydration of the hydroperoxide mixture with acetyl chloride/



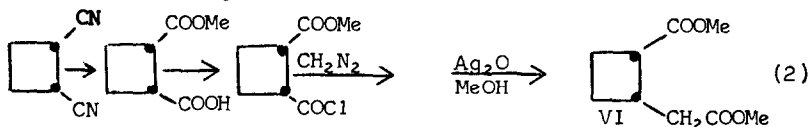
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pyridine gives rise to a mixture of the  $\alpha,8$ -unsaturated ketones, III and IV, b.p.  $64-66^\circ$  at 1.9 mm. (IR ( $\text{CS}_2$ ),  $1682 \text{ cm.}^{-1}$ ; UV (95% ethanol), max 325, 280 and 226  $\mu$ ,  $\epsilon = 6,100$ ). In the olefin region of the NMR spectrum may be discerned two overlapping double triplets due to the  $\beta$ -hydrogen resonances of III and IV. The larger component has for  $H_\beta$ :  $3.55\tau$ ,  $J_{\alpha\beta} = 12 \text{ cps}$ ,  $J_{\beta\gamma} = 7.5 \text{ cps}$ ; and the smaller  $H_\beta$ :  $3.50\tau$ ,  $J_{\alpha\beta} = 12 \text{ cps}$ ,  $J_{\beta\gamma} \sim 7 \text{ cps}$ . In addition to  $H_\alpha$  (overlapping doublets at  $4.10\tau$ ,  $J_{\alpha\beta} \sim 12 \text{ cps}$ ), the remaining NMR spectrum consists of the isolated double bond (multiplet at  $4.25\tau$ ) and the methylene groups at  $6.70$ ,  $7.3$  and  $7.55\tau$ . Hydrogenation of the mixture gives cyclooctanone in good yield. Since all of the spectral data are in accord with an  $\alpha,8$ -unsaturated ketone with an isolated double bond, III and IV are necessary choices and support the assignment of structures I and II to the hydroperoxides. For the reasons outlined below, the major component of the ketone mixture has been allocated structure III.

When the ketone mixture was heated for several hours at  $175-190^\circ$  under nitrogen, a new ketone was obtained. The NMR spectrum of the product showed new resonances at  $3.12$  and  $3.97\tau$  and a marked decrease in the groups centered at  $2.55$ ,  $4.10$  and  $4.25\tau$ . It appeared that the minor component of the original ketone mixture (presumably IV) had remained unchanged but that III had rearranged to another  $\alpha,8$ -unsaturated ketone with

loss of the isolated double bond. Upon hydrogenation, the new ketone mixture absorbed only 1.28 moles of hydrogen per mole, confirming the absence of the isolated double bond in the bulk of the mixture. Gas chromatographic analysis showed two components: cyclooctanone (30%) identified as its 2,4-dinitrophenylhydrazone, m.p. 173.5-177°, mixture m.p. 174-178°; unknown ketone (70%), 2,4 dinitrophenylhydrazone, m.p. 122.2-123.5° (corr.).

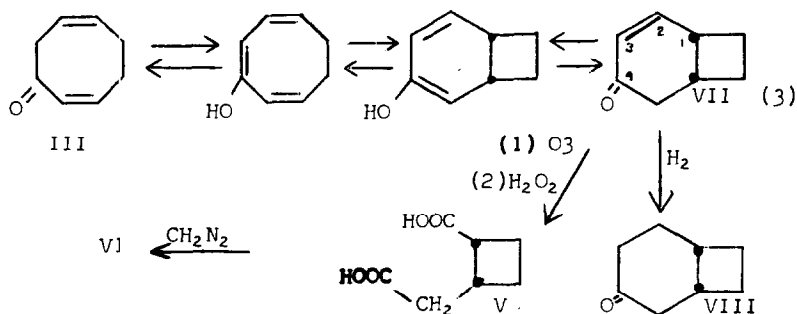
The bicyclic nature of the new ketone was confirmed by ozonolysis and oxidation to *cis*-2-carboxycyclobutylacetic acid (V), m.p. 105-111°. <sup>(1)</sup> Its dimethyl ester (VI) was identical in infrared spectrum and GPC retention time with an authentic sample prepared from *cis*-1,2-dicyanocyclobutane, <sup>(2)</sup> as outlined in equation 2.



Of the possible choices for a bicyclo (4.2.0) octenone which might give rise to V on ozonolysis, VII seemed most reasonable. Hydrogenation would give bicyclo (4.2.0) octan-3-one (VIII) whose dinitrophenylhydrazone has m.p. 122-123°. <sup>(3)</sup> Synthesis of an authentic sample of VIII by the method of Cope and Gleason,<sup>3</sup> confirmed this structure (mixture m.p. of dinitrophenylhydrazones, 121.5-123.2° (corr.) ).

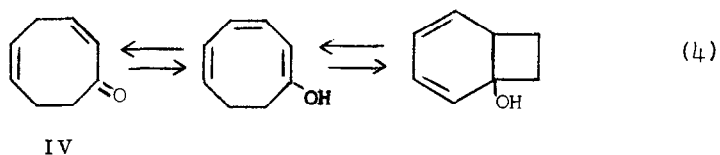
The pattern for the olefinic hydrogen,  $H_2$ , in the NMR spectrum of VII indicates a typical cis olefin coupling  $J_{23} = 10.5$  cps. The  $H_2$  resonance is split further by coupling with two other hydrogens, with  $J \sim 3$  (presumably  $J_{12}$ ) and  $J \sim 1.8$  (coupling with a nonadjacent hydrogen).

Formation of VII may be envisaged as an example of valence-bond tautomerism<sup>(4)</sup> involving the enol form of III (equation 3) in a manner similar to the transformation of 1,3,5-cyclooctadiene to bicyclo(4.2.0)octa-2,4-diene.<sup>(5)</sup> The driving force for the rearrangement  $III \rightarrow VII$  presumably is relief of non-bonded interactions in the eight-membered ring. In this example the equilibrium lies heavily in favor of VII,



as very little III remains in the mixture. In accordance with the suggested equilibrium, some III is still present even after prolonged heating.

A similar transformation for the ketone IV would result in a bicyclic alcohol as shown in equation 4. Apparently, loss of the resonance energy of the conjugated carbonyl system in formation of the bicyclic diene weights this equilibrium in favor of IV. (6)



If it is correct to assume that regeneration of the conjugated carbonyl system is necessary for the bicyclic form to predominate at equilibrium, then the precursor of VII, and the major component of the original ketone mixture, must be III. Therefore, I is the major hydroperoxide from the autoxidation of cis,cis-1,5-cyclooctadiene.

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References

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