

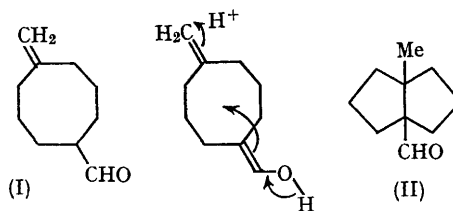
## Formation of a Bicyclo[3,3,0]octane in a Novel Transannular Reaction

By S. H. GRAHAM\* and D. A. JONAS

(Edward Davies Chemical Laboratory, Aberystwyth)

5-METHYLENOCYCLO-OCTANECARBALDEHYDE (I)<sup>1</sup> is isomerised by boiling in water in a nitrogen atmosphere to give a rather unstable aldehyde, m.p. 89–91°,  $\nu_{\max}$  1712  $\text{cm}^{-1}$ ; semicarbazone, m.p. 208°, analysis correct for  $\text{C}_{11}\text{H}_{19}\text{N}_3\text{O}$ . Oxidation of the aldehyde (hydrogen peroxide) gave an acid, m.p. 184°, analysis correct for  $\text{C}_{10}\text{H}_{16}\text{O}_2$ , and  $^1\text{H}$  n.m.r. spectrum including a singlet (3H) at  $\tau$  8.9, and no absorptions due to olefinic protons. Similarly reduction of the aldehyde gave an alcohol, m.p. 119°, for  $\text{C}_{10}\text{H}_{18}\text{O}$ , whose  $^1\text{H}$  n.m.r. spectrum included singlets at  $\tau$  8.97 (3H) and 6.5 (2H) and no lower field signals. The aldehyde is therefore formulated as (II); its production constitutes a novel transannular reaction which is formally the addition of a reactive methylene to

an olefinic bond. This presumably proceeds *via* the enol of (I) and is formulated as being acid-catalysed since acids are common impurities in aldehydes; (II) oxidises very readily and so could not be analysed.



(Received, June 17th, 1968; Com. 785.)

<sup>1</sup> K. H. Baggaley, W. H. Evans, S. H. Graham, D. A. Jonas, and D. H. Jones, *Tetrahedron*, 1968, **24**, 3445.