7-Oxatricyclo[4,3,0,$0^{5,8}$]nonane and *exo*-Bicyclo[3,2,1]octan-8-ol *via* an Intramolecular Paterno–Büchi Reaction

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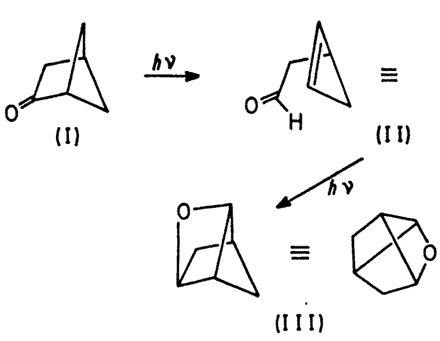
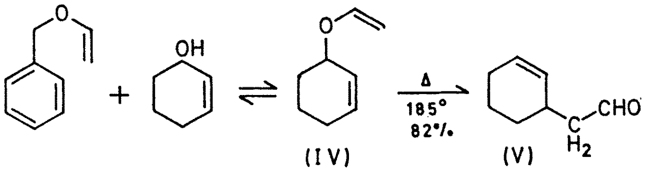
Summary U.v. irradiation of Δ^2-cyclohexenylacetaldehyde in degassed pentane solution gives 7-oxatricyclo[4,3,0,$0^{5,8}$]-nonane, which is converted by refluxing ethereal lithium aluminium hydride into *exo*-bicyclo[3,2,1]octan-8-ol.

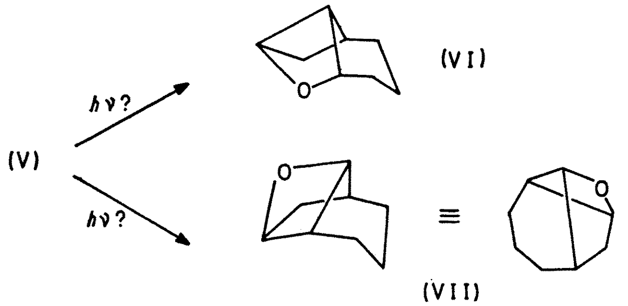
IT was recently reported[1] from this laboratory that the irradiation of bicyclo[2,1,1]hexan-2-one (I) gave Δ^2-cyclobutenylacetaldehyde (II) as the only volatile primary product, and that upon continued irradiation (II) underwent an intramolecular Paterno–Büchi reaction[2] to give a tricyclic oxetan (III).



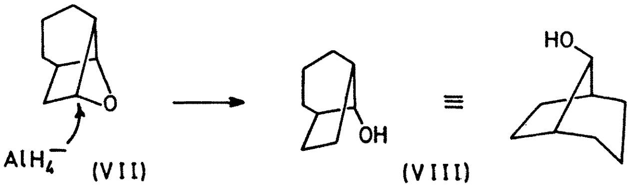
As part of a study of the possible utility of the photocyclization of aldehydic cyclo-olefins to give bridged ring systems, we have investigated the course of the irradiation of Δ^2-cyclohexenylacetaldehyde (V). Although available by alternative routes,[3] the aldehyde (V) was most conveniently obtained by the thermal rearrangement of Δ^2-cyclohexenyl vinyl ether (IV) as shown below. A 50% yield of (IV) was realized by fractional distillation of a mixture of benzyl vinyl ether, cyclohex-2-enol, and mercuric acetate.



Using a 450w Hanovia lamp fitted with a Vycor filter, a dilute solution of (V) in degassed pentane was irradiated to give 40% of a colourless solid, m.p. 68°. The mass spectrum† and an elemental analysis demonstrated that the molecular formula of the product was $C_8H_{12}O$. The i.r. spectrum suggested that the product was an oxetan. It was not possible on the basis of the n.m.r. spectrum to choose between the two possible oxetan structures corresponding to the two addition orientations shown below.



That the photoproduct was 7-oxatricyclo[4,3,0,$0^{5,8}$]-nonane (VII) was demonstrated by the fact that it was converted (68%) in refluxing ethereal lithium aluminium hydride into a $C_8H_{14}O$ alcohol, m.p. 192—193°, in excellent agreement with the value (192°) reported[4] for *exo*-bicyclo-[3,2,1]octan-8-ol (VIII). The exclusive formation of (VIII) during the reductive cleavage is more easily understood when (VII) is drawn in such a way as to emphasize the presence of an oxabicyclo[2,1,1]hexane nucleus and its subsequent attack at the less hindered bridgehead position. This convenient photochemical entrée into the bicyclo-[3,2,1]octane series from readily available starting materials provides an attractive alternative to existing techniques.[4,5]



A.T.H. was a National Institutes of Health Trainee, 1967—69. We acknowledge partial support of this work by a grant from the N.I.H.

(*Received, August* 25*th,* 1969; *Com.* 1305.)

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† Mass spectra were obtained through the good offices of the Cornell High Resolution Mass Spectrometer Facility.

[1] J. Meinwald and R. A. Chapman, *J. Amer. Chem. Soc.*, 1968, **90**, 3218.

[2] For example, see N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, 1968, **90**, 6863.

[3] C. W. Whitehead, J. T. Traverso, H. R. Sullivan, and F. J. Marshall, *J. Org. Chem.*, 1961, **26**, 2814.

[4] R. B. Woodward and C. S. Foote, *Tetrahedron*, 1964, **20**, 687.

[5] For a leading reference, see N. A. LeBel and R. J. Maxwell, *J. Amer. Chem. Soc.*, 1969, **91**, 2307.