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PHOTOISOMERIZATION OF ENDO- AND EXO-TRICYCLO$[3.2.1.0^{2,4}]$OCTENE-6

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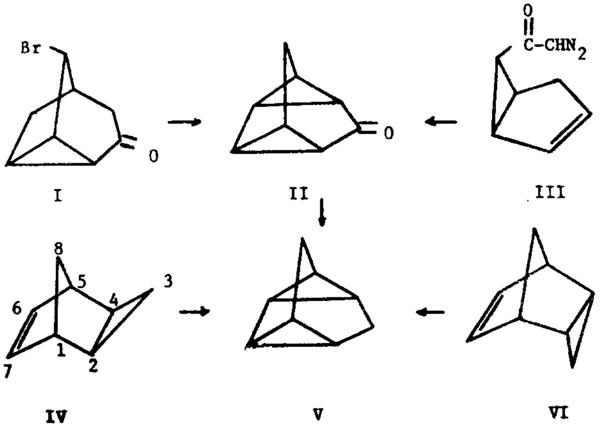
Syntheses of tetracyclo$[3.3.0.0^{2,8}0^{4,6}]$octan-3-one (II) by dehydrobromination of I (1) and by intramolecular carbenoid addition to the double bond resulting from photolytic and copper catalyzed decomposition of diazomethyl ketone III(2) have recently been reported. A third logical synthetic route to this ring system would be through valence isomerization of <u>exo</u>- or <u>endo</u>-tricyclo$[3.2.1.0^{2,4}]$octene-6 (IV → V or VI → V). The



recent communication by Prinzbach, Eberbach and von Veh (3) reporting the successful photoisomerizations of the *anti*-3,6,7-tricarbomethoxy and *anti*-3,6,7 tricarboxylic acid derivatives of IV and the unsuccessful photoisomerization of the parent hydrocarbon (IV) prompts us to report some complementary experiments.

Irradiation of an ether solution of *exo*-bicyclo[3.2.1.0^{2,4}]octene-6 (IV) (4) using unfiltered light from a 450 watt Hanovia high pressure mercury lamp resulted in a 29% yield of tetracyclo[3.3.0.0^{2,8}0^{4,6}]octane (V) (*Anal*. Calcd. for C_8H_{10}: C, 90.50; H, 9.50; Found: C, 90.50; H, 9.26; mol. wt. 106, mass spectrum). No unsaturation is evident in the infrared or n.m.r. spectra. Strong bands at 3020 and 800 cm.$^{-1}$ in the infrared suggest a structural element similar to nortricyclene (5), and overlapping multiplets centered at 8.34 and 8.70 τ in the n.m.r. spectrum are consistent with a structure closely related to quadricyclene (6). Final structural confirmation was obtained by Wolff-Kishner reduction of tetracyclic ketone II. The hydrocarbon prepared by this method and by photoisomerization of IV were identical as demonstrated by n.m.r. and infrared spectral comparison.

The successful photoisomerization of IV aroused our interest in the susceptibility of the *endo*- isomer to similar isomerization. In particular, it seemed feasible to probe the possibility of stereochemical control (7). In comparing structures IV and VI one notes the bent transannular bond (C-2 - C-4) of the cyclopropane ring in IV is on the *endo* side of the norbornene ring and points toward the π-orbital, while the analogous bond in VI is on the *exo* side of the ring and points away from the π-orbital and thus seems to be in a much less favorable position for orbital interaction. Apparently, however, these differences in spatial arrangement are not critical, since irradiation of *endo*-tricyclo[3.2.1.0^{2,4}]-

octene-6 (VI) (8), using reaction conditions identical to those used with IV, resulted in a 15% yield of V. The ratio of yields of tetracyclic V produced from IV to that produced from VI is not large but is in the anticipated direction. In addition, the stereochemical differences between IV and VI are not reflected in the ultraviolet spectra which are nearly identical (IV, λ_{max} 192 mμ, log ε 3.95; VI, λ_{max} 192 mμ, log ε 4.00) and quite similar to norbornene (λ_{max} 195 mμ, log ε 3.73) (9).

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