

A FACILE SYNTHESIS OF BICYCLO (2.1.1) HEXAN - 2 - ONE

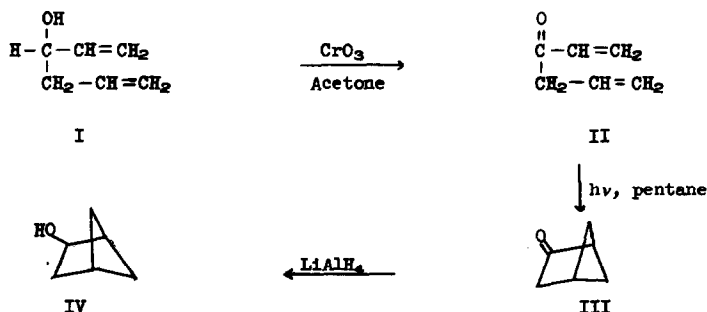
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Widespread progress in the chemistry of bicyclo (2.1.1) hexane derivatives (2) has been handicapped by the lengthy synthetic routes heretofore required. Such routes have involved ring contraction of suitable bicyclo (2.2.1) heptane derivatives and have afforded 5-substituted bicyclo (2.1.1) hexanes. The only previous example of a 2-substituted bicyclo (2.1.1) hexane derivative was prepared by such a photochemical contraction of 5-acetoxycyclo (2.1.1) heptan-2,3-dione, followed by decarboxylation (3).

We wish to report that simple irradiation (4) of the readily available 1,5-hexadien-3-one II provides a facile route to the potentially valuable intermediate bicyclo (2.1.1) hexan-5-one, III. Ketone II, ( $\lambda_{\max}$  212 m $\mu$ ,  $\epsilon$  = 11,000) is an unstable but isolable product (5) of Jones oxidation of the readily available I (6).



Irradiation of crude II in pentane followed by careful fractionation affords III in approximately 30% yield from I. The structure of III (infrared band at  $5.69\mu$ ) was determined by its spectral properties and by hydride reduction to the known IV (3), m.p. 82-83.5° (3). In addition to III two other unidentified cyclopentanones are formed in approximately 10% yield during the irradiation (7).

The formation of III from II is not surprising in view of the known examples of intra-(8) and intermolecular (9) photo chemical additions of enones to olefins. Compound III is an obvious precursor to other small ring systems and suitable modification of II should allow the synthesis of other bicyclo (2.1.1) hexanes.

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#### REFERENCES

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4. Hanovia type L lamp using no filter.
5. Reportedly prepared by I. N. Nazarov and I. I. Zaretetskaya, Bull. Acad. Sci. USSR, Classe Sci. Chim., 200 (1942), C. A. 39, 1619 (1945).
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7. During the course of this work we learned that Prof. P. de Mayo had independently prepared III by an alternant route (see accompanying communication). We are grateful to him for this information, suggestion of simultaneous publication, and for comparison of the samples.
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