

Synthesis and Reductive Ring Cleavage of
N-Carbethoxy-8-azatricyclo[4.3.0.0^{7,9}]nonane.

Paolo A. Tardella and Lucio Pellacani

Istituto di Chimica Organica dell'Università, 00185 Roma, Italy.

Received January 6, 1975

Sir:

We know only two examples of 5-azabicyclo[2.1.0]-pentane ring systems (1). The synthetic and theoretical interest in such heterocycles and our involvement in the study of ethyl azidoformate decomposition in bicyclo[4.n.0]alkanes (2), prompted us to investigate the reaction between *cis*-bicyclo[4.2.0]oct-7-ene (I) (3) and ethyl azidoformate (II).

The first step to be expected was the 1,3-dipolar addition of II in consequence of ring strain, as verified in norbornene (4) (5) (6) in norbornadiene (6) (7) and in highly strained olefins, although in the latter case only rearranged products were isolated (8).

After standing 9 or 27 days at room temperature, the mixture of 20 mmoles of I and 20 mmoles of II in 6.5 ml. of *n*-pentane was recovered nearly unchanged; the only product was a tar.

However irradiation of 20 mmoles of II and 71 mmoles of I in 18 ml. of *n*-pentane in a quartz vessel at room temperature for 5 hours using an OSRAM 125 watt high pressure lamp, gave (ca. 30% based on ethyl azidoformate) the products III to VII.

The nitrene addition product, *N*-carbethoxy-8-azatricyclo[4.3.0.0^{7,9}]nonane (III), was the main component (67%), and was purified by repeated column chromatography (silica gel, benzene:ethyl acetate = 9:1).

The structure of III was deduced by spectral data (*m/e* 195(M⁺), 166(M⁺-Et), 152(M⁺-C₃H₇), 122(M⁺-EtOCO), 80 (base peak); ir (carbon tetrachloride): 1725 cm⁻¹; nmr (carbon tetrachloride): δ 1.30 (3H, t), 2.90 (2H, m), 4.13 (2H, q)).

The stereochemistry is presumed *anti* on the basis of the coupling constant observed for 2.90 δ signal (*J* ca. 1 cps).

Its reduction under mild conditions (Pd/C 10%, 1 atmosphere, room temperature) furnished *cis*-*N*-carbethoxy-8-azabicyclo[4.3.0]nonane (VIII), identified by spectral data (ir, nmr, ms) and by glc comparison with an authentic specimen prepared from the corresponding amine (9).

The observed reductive ring fission seems peculiar for this system and parallels more the behaviour of bicyclo[2.1.0]pentane (10) than that of other polycyclic aziridines (11).

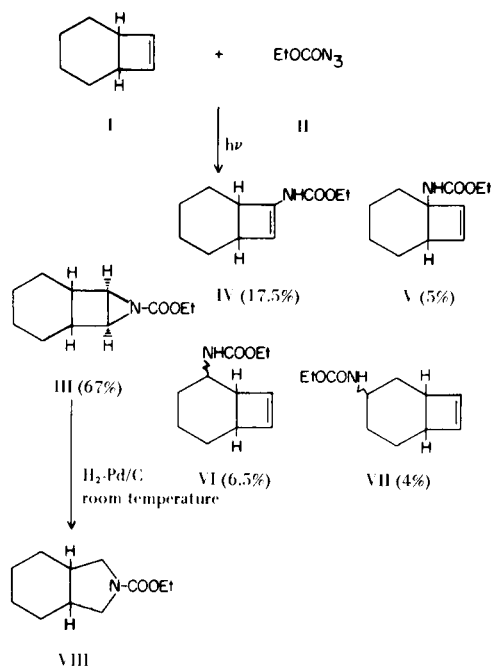
The nitrene insertion products IV to VII were not separated and were identified by glc comparison on a capillary column of their corresponding saturated carbamates with authentic samples (2).

Acknowledgment.

We thank C. N. R. (Roma) for financial support and Mr. Paolo Valle for experimental assistance.

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