

## THERMAL REACTIONS OF 2-AZABICYCLO[3.2.0]HEPTANE-3,4-DIONES

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Thermal reactions of 2-azabicyclo[3.2.0]heptane-3,4-diones containing highly strained four membered ring caused skeletal rearrangements to yield novel heterocycles.

1. A novel epimerization of C<sub>7</sub>-substituents

On treatment with bases such as Et<sub>3</sub>N or DBU in benzene, 7-substituted (1, R<sub>2</sub>=H) and 7,7-disubstituted derivatives (1, R<sub>2</sub>≠H) rapidly epimerized at C<sub>7</sub> to give a thermodynamically more stable isomer (2, R<sub>2</sub>=H) predominantly, then changed into dihydroazatropolones (3).

## 2. Thermolysis of 3-ethoxy-2-azabicyclo[3.2.0]hept-2-en-4-ones

Pyrolysis of 4 or 5 in toluene at 120-200° yielded 2-ethoxy-3,4-dihydropyridines (6) in good yields, formation of which is rationalized by a concerted process of a 1,3-sigmatropic rearrangement followed by cheletropic elimination of CO.

## 3. Thermolysis of 7-vinyl-2-azabicyclo[3.2.0]heptane-3,4-diones and their imidates

The thermal reaction of the 7-vinyl derivatives yielded different products depending on the stereochemistry of vinyl group. The endo isomer, the lactam and its imidate (2 and 5, R<sub>1</sub>=-CH=CH<sub>2</sub>, R<sub>2</sub>=H) afforded a Cope product (7) (3,3-sigmatropic shift) exclusively. On the other hand, the exo isomer (1, R<sub>1</sub>=-CH=CH<sub>2</sub>, R<sub>2</sub>=H) afforded a hydroindole (8) (1,3-shift) and (7, R=H). The exo isomer of the imidate (4, R<sub>1</sub>=-CH=CH<sub>2</sub>, R<sub>2</sub>=H) yielded a dihydropyridine (6, R<sub>1</sub>=-CH=CH<sub>2</sub>, R<sub>2</sub>=H) as a major product.

