HETEROCYCLES, Vol 19, No 1, 1982

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

Takehiro Sano and Yoshie Horiguchi
Showa College of Pharmaceutical Sciences,
Setagaya, Tokyo 154, Japan
Yoshisuke Tsuda
Faculty of Pharmaceutical Sciences, Kanazawa University,
Kanazawa 920, Japan

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_7-substituents

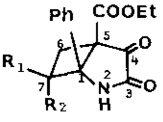
On treatment with bases such as Et_3N or DBU in benzene, 7-substituted (1, R_2=H) and 7,7-disubstituted derivatives (1, $R_2 \neq H$) rapidly epimerized at C_7 to give a thermodynamically more stable isomer (2, R_2=H) predominantly, then changed into dihydroazatropolones (3).

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

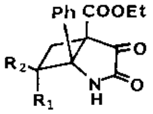
Pyrolysis of 4 or 5 in toluene at 120-200° yielded 2-ethoxy-3,4-dihydropyridines (6) in good yields, formation of which is rationalized by a concerted process of a 1,3-sigmatropic rearrangement followed by cheletropic elimination of CO.

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

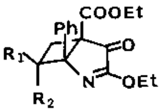
The thermal reaction of the 7-vinyl derivatives yielded different products depending on the stereochemistry of vinyl group. The endo isomer, the lactam and its imidate (2 and 5, R_1=-CH=CH$_2$, R_2=H) afforded a Cope product (7)(3,3-sigmatropic shift) exclusively. On the other hand, the exo isomer (1, R_1=-CH=CH$_2$, R_2=H) afforded a hydroindole (8)(1,3-shift) and (7, R=H). The exo isomer of the imidate (4, R_1=-CH=CH$_2$, R_2=H) yielded a dihydropyridine (6, R_1=-CH=CH$_2$, R_2=H) as a major product.



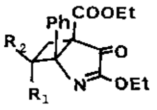
1



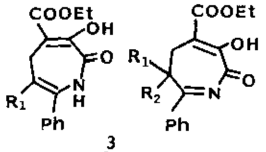
2



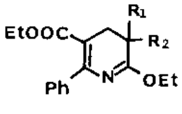
4



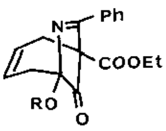
5



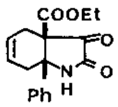
3



6



7



8