

## Flash Vacuum Thermolysis of 5-Substituted-4,4-diphenyl-3-oxa-1-azabicyclo[3.1.0]hexan-2-ones. A New Route to Quinolines.

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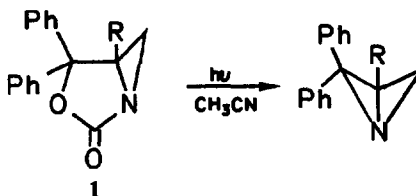
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**Key Words:** Flash vacuum thermolysis; 5-substituted-4,4-diphenyl-3-oxa-1-azabicyclo[3.1.0]hexan-2-ones; Quinolines.

**Abstract:** Thermolysis of bicyclic carbamates produces quinoline derivatives in good yields. A two step reaction is described.

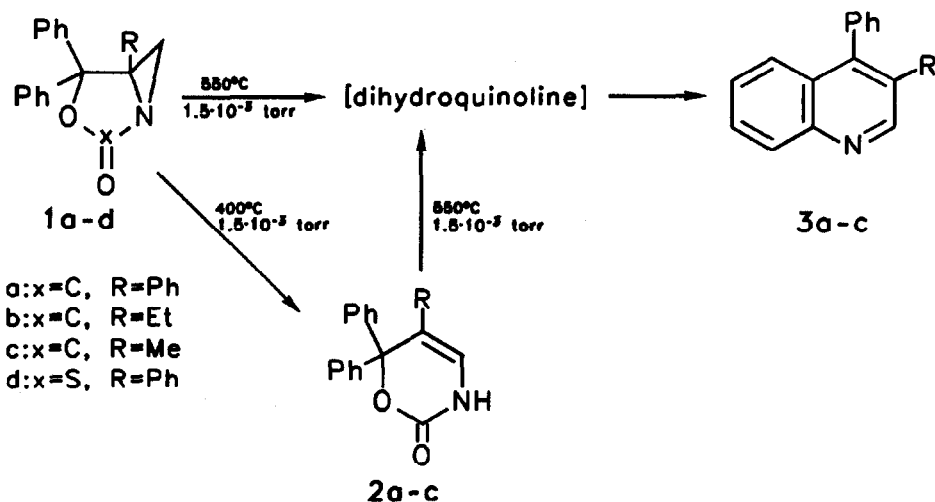
Recently Olsen has described a new method of synthesis of quinoline derivatives by photocyclisation of benzalicycloalkane oximes<sup>1</sup>. We would like to report a new way of synthesis of compounds of this group which was performed using flash vacuum thermolysis of 5,5-diphenyl-3-oxa-1-azabicyclo[3.1.0]hexan-2-one derivatives and 4,5,5-triphenyl-3-oxa-2-thia-1-azabicyclo[3.1.0]hexane 2-oxide.

It is known that photolytic elimination of CO<sub>2</sub> from bicyclic carbamates type 1 leads to azabicyclobutanes<sup>2</sup>.



The purpose of our work was to investigate the rearrangement of these compounds under FVT conditions. We have concluded that thermolysis<sup>3</sup> of compounds 1a-d at 550°C leads in good yields to quinoline derivatives 3a-c<sup>4</sup> (Scheme 1).

If the reaction was carried out in lower temperature i.e. 400°C, the formation of derivatives of 6H-1,3-oxazin-2-one 2a-c and small quantities of 3a-c was observed. These products were too unstable to be isolated and purified. Hence we have registered their IR and <sup>1</sup>H-NMR spectra in crude material only<sup>5</sup>.



Scheme 1.

In the case of 1d, the formation of product type 2 was not observed<sup>6</sup>. The thermolyses of crude 2a-c at 550°C furnished products 3a-c. It let us to state that in the first step, the bridge C-N bond cleaves (stable under photochemical conditions) and CO<sub>2</sub> elimination is the process which needs higher temperature while the SO<sub>2</sub> elimination runs easier. That is the reason why the respective derivative of 6H-1,2,3-oxathiazine 2-oxide was converted directly to quinoline 3a.

It is difficult to discuss the details of the mechanism of the cyclisation intermediate forming after CO<sub>2</sub> elimination. However it seems logical to suggest preliminary formation of dihydroquinolines which spontaneously convert by aromatisation into the stable compound 3.

#### References and Notes.

- Olsen, R.J. *Tetrahedron Lett.* 1991, 32, 5235-5238.
- a) Bartnik, R.; Cebulska, Z.; Laurent, A. *Tetrahedron Lett.* 1983, 24, 4197-4198.  
b) Bartnik, R.; Cebulska, Z.; Laurent, A.; Orłowska, B. *J. Chem. Res.* 1986, (S), 5; (M), 0112-0131.
- The flash thermolysis were carried out in a 30 x 2 cm electrically heated horizontal quartz tube at  $1,5 \cdot 10^{-3}$  torr 1a-d was sublimated in the thermolysis tube (550°C) from a flask held at 120-140°C. The products were collected in a CO<sub>2</sub>-acetone trap.
- A crude product was purified by filtration through the chromatographic column (Al<sub>2</sub>O<sub>3</sub>, light petroleum ether-ether) and by the recrystallization. The compounds we have obtained have identical physical data as in quoted references. 3a, 83% isolated compound, m.p. = 139-141°C (hexan), (Ref. m.p.=140-141°C, Fehnel, E.A.; *J. Heterocycl. Chem.* 1967, 4 (4), 565-570). 3b, 81%, isolated compound m.p. = 96-98°C (light petroleum ether), (Ref. m.p. = 95-97°C (ligroine) Marsili, A. *Ann. Chim.,(Rome)* 1962, 52, 3 - 16, C.A. 57, 2193 i). 3c, 87% isolated compound, m.p. = 86-88°C (light petroleum ether), (Ref. as 3b, m.p.= 84-87°C (ligroine)).
- 2a yellow oil, 87% IR: 3370<sub>NH</sub>, 1790<sub>C=O</sub>, 1655<sub>C=C</sub>. <sup>1</sup>H-NMR: 4.05 (s,1H), 4.65 (s,1H), 7.0 - 7.80 (m,15H). 2b yellow oil, IR: 3410<sub>NH</sub>, 1780<sub>C=O</sub>, 1655<sub>C=C</sub>. <sup>1</sup>H-NMR: 1,0 (t,J=7Hz, 3H), 2.60 (q,J=7Hz, 2H), 4.37 (s, 1H), 4.85 (s,1,1H), 7.0 - 8.0 (m, 10H). 2c yellow oil IR: 3410<sub>NH</sub>, 1770<sub>C=O</sub>, 1655<sub>C=C</sub>. <sup>1</sup>H-NMR: 2.15 (s,3H), 4.20(s,1,1H), 4.48(s,1H), 7.1-7.8(m,10H).
- Thermolysis in 400°C leads to formation of 3a product. In lower temperature we have obtained the mixture of 3a and the starting material.