Tetrahedron Letters Vol. 21, pp 2825 - 2826 0040-4039/80/0715-2825$02.00/0
©Pergamon Press Ltd. 1980. Printed in Great Britain

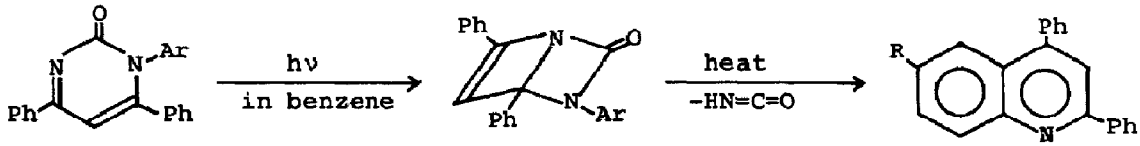
NOVEL SYNTHESIS OF 2,4-DIPHENYLQUINOLINES

Takehiko Nishio*, Katsuhiro Katahira, and Yoshimori Omote

Department of Chemistry, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki, 305, Japan

Summary: 2,4-Diphenylquinolines (3) were quantitatively prepared by heating of 3-aryl-4,6-diphenyl-2-oxo-1,3-diazabicyclo[2,2,0]hex-5-enes (2), which were obtained by photochemical electrocyclization of 1-aryl-4,6-diphenyl-2(1H)-pyrimidin-2-ones (1), in benzene at reflux temperature.

Because of their valuable chemotherapeutic properties, synthesis of quinoline derivatives has been investigated extensively.[1] We wish to report here the novel synthesis of 2,4-diphenylquinolines (3) by thermal reaction of 3-aryl-4,6-diphenyl-2-oxo-1,3-diazabicyclo[2,2,0]hex-5-enes (2), which were obtained by photochemical electrocyclization of 1-aryl-4,6-diphenyl-2(1H)-pyrimidin-2-ones (1). Irradiation of 1,4,6-triphenyl-2(1H)-pyrimidin-2-one (1a) in benzene with a high pressure mercury lamp through a Pyrex filter at room temperature for 15 h gave 3,4,6-triphenyl-2-oxo-1,3-diazabicyclo[2,2,0]hex-5-ene (2a)[2], mp. 95-97°C; ν_{max}^{KBr} 3060, 3030, 1780, 1620, 1590, 1500, 770, and 695 cm^{-1}; $\delta(CDCl_3)$ 6.89(s, 1H), 7.15-7.72(m, 13H), 8.12-8.28(m, 2H), in 50% yield. The compound thus obtained was heated in benzene at reflux temperature for 1 h to give 2,4-diphenylquinoline (3a), mp. 109-111°C (lit.[3] 114°C); ν_{max}^{KBr} 3050, 1590, 1545, 1485, 1405, 770, and 705 cm^{-1}; $\delta(CDCl_3)$ 7.35-7.65(m, 10H), 7.72-7.95(m, 2H), 8.14-8.39(m, 3H), in quantitative yield. 4,6-Diphenylquinoline (3a) was also obtained by direct heating of the photolysate in benzene at reflux temperature without isolation of (2a).[4] The structure of (3a) was identified by direct comparison of its IR and NMR spectra with those of authentic material.[5] Similarly, 2,4-diphenyl-6-methy- (3b) and 2,4-diphenyl-6-methoxyquinoline (3c) were obtained by thermal reaction of 3-p-tolyl-(2b) and 3-p-anisyl-4,6-diphenyl-2-oxo-1,3-diazabicyclo[2,2,0]hex-5-ene (2c), which were produced by photochemical electrocyclization of 1-aryl-4,6-diphenyl-2(1H)-pyrimidin-2-ones (1b-c). The structure of the products (3b-c) was confirmed on the basis of IR and NMR spectra and elemental analyses.



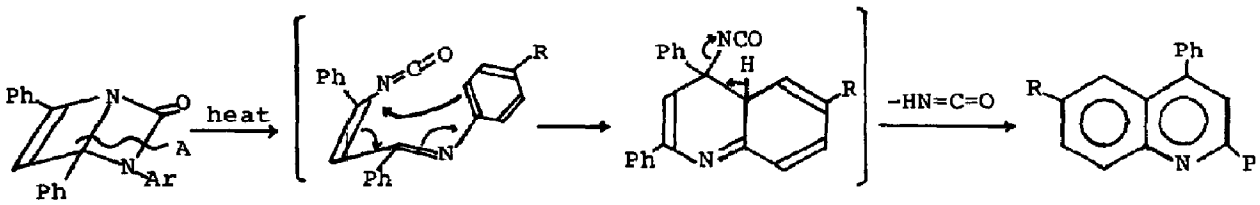
(1) (2) (3)

a; Ar=Ph a; Ar=Ph (50%) a; R=H (quant.)

b; Ar=p-Tolyl b; Ar=p-Tolyl (50%) b; R=Me (quant.)

c; Ar=p-Anisyl c; Ar=p-Anisyl (20%) c; R=MeO (quant.)

The reasonable mechanism for the formation of 2,4-diphenylquinolines (3) by thermal reaction of 3-aryl-4,6-diphenyl-2-oxo-1,3-diazabicyclo[2,2,0]hex-5-enes (2) is proposed in Scheme 1, in which an unstable isocyanate intermediate, forme initially by thermal cleavage of (2) in the direction of A, undergoes the Diels-Alder type electrocyclization, accompanied with a subsequent loss of isocyanic acid, to give the final quinoline (3). Although the isocyanate intermediate (4) could not be trapped with alcohol when (2a) was refluxed in methanol, the formation of isocyanate intermediate (4) was supported by the fact that the IR spectrum of the reaction mixture of (2) in benzene showed an absorption at ca 2250 cm^{-1} due to isocyanate group.



(2) (4) (5) (3)

Scheme 1

References and notes

1) N. Campbell, "Rodd's Chemistry of Carbon Compounds", ed. by E.H. Rodd, Elservier Scientific Publishing Company, Amsterdam. Vol. IVF, p. 231 (1976).

2) Recently, we reported the photochemical electrocyclization of 1,4,6-trisubstituted-2(1H)-pyrimidin-2-ones to 3,4,6-trisubstituted-2-oxo-1,3-diazabicyclo[2,2,0]hex-5-enes: T. Nishio, A. Kato, Y. Omote, and C. Kashima, Tetrahedron Lett., 1978, 1543. T, Nishio, A. Kato, C. Kashima, and Y. Omote, J. Chem. Soc.(Perkin I), 1980, 607.

3) W. Borshe and F. Sinn, Ann., 538, 283 (1939).

4) This reaction means one-pot synthesis of 2,4-diphenylquinolines (3) from 1-aryl-4,6-diphenyl 2(1H)-pyrimidin-2-ones (1).

5) E.A. Fehnel, J. Org. Chem., 31, 2899 (1966).

(Received in Japan 16 April 1980)