BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3596—3597 (1969)

Photoisomerization of 1,2-Diphenyl-6-methyl-2,3-dihydro-4-pyridone

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(Received May 30, 1969)

There have been many papers about the photochemical isomerization and dimerization of 2-cyclohexenones.[1] Yates reported that 2,6-dimethyl-2,3-dihydro-4-pyrone was dimerized by light.[2] Recently we have found a method of synthesizing 2,3-dihydro-4-pyridones from *β*-diketones and Schiff bases.[3] As an analogy with cyclohexenone and 2,3-dihydropyrone, the photochemistry of 2,3-dihydro-4-pyridone is of interest.

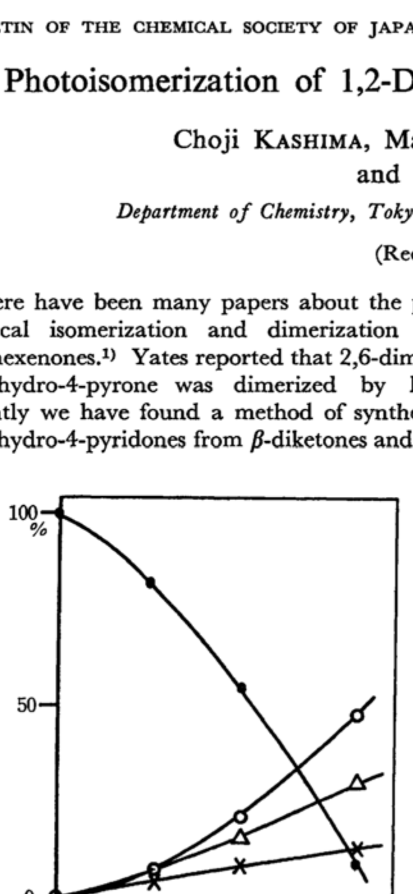

Fig. 1. The change of I and the production of II, III and IV with time.
—●— I, —○— II, —△— III, -✳- IV

A solution of 1,2-diphenyl-6-methyl-2,3-dihydro-4-pyridone (I) in benzene or methanol was irradiated with a high-pressure mercury lamp through a Pyrex filter. No apparent change was observed after irradiation for a week. However, by the irradiation of a methanol solution of I with a low-pressure mercury lamp through a Vycor filter, three products (II, III, and IV) were obtained. Figure 1 shows the change in I and in the production of II, III, and IV with the time.

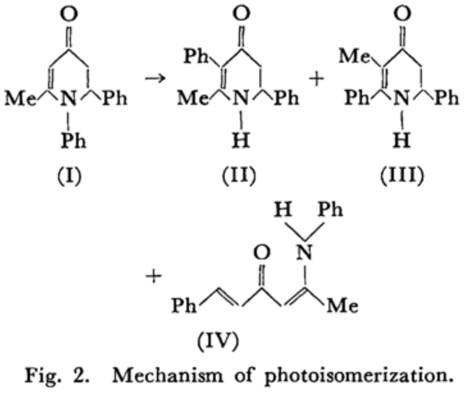

Fig. 2. Mechanism of photoisomerization.

After irradiation for 100 hr, the products were separated. The structures of the products were deduced by means of the spectral data listed in Table 1. The IR and UV spectra showed the re-

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1) S. N. Ege and P. Yates, *Can. J. Chem.*, **45**, 2933 (1967); W. G. Dauben, G. W. Shaffer and N. D. Vietmeyer, *J. Org. Chem.*, **33**, 4060 (1968); H. E. Zimmerman, R. D. Rieke and J. R. Scheffer, *J. Am. Chem. Soc.*, **89**, 2033 (1967); H. E. Zimmerman and K. G. Hancock, *ibid.*, **90**, 3749 (1968).

2) P. Yates and D. J. Macgregor, *Tetrahedron Letters*, **1969**, 453.

3) N. Sugiyama, M. Yamamoto and C. Kashima, This Bulletin, **42**, 1357 (1969).

TABLE 1.

	I	II	III	IV
λ_{max}^{EtOH} nm (ε)	240 (2180)		243 (4500)	232 (11700)
	327 (10400)	343 (14300)	347 (9500)	297 (12600)
				383 (29100)
ν cm^{-1}	1630	1635	1635	1640
	1600	1600	1600	1580
	1550	1540	1540	
τ^{CDCl_3}	8.13	8.32	8.02	7.94
	7.09	7.02	7.07	
		6.60	6.62	−3.17
	5.08	5.13	5.18	
	4.81			4.80
				3.50
				2.58
	2.6—3.2	2.6—3.2	2.6—3.2	2.5—3.2

lation of the 2,3-dihydro-4-pyridone structures in II and III. In the NMR spectra of II and III, the signals of the ABX pattern at τ 7.1 and 5.1, which are assignable to the 2-methine proton and the 3-methylene protons, were observed. Though the olefinic proton signal at τ 4.81 was not found, new singlet signals were observed at τ 5.13 and 5.18 which were changed by deuterium exchange. These results suggest that II is 2,5-diphenyl-6-methyl-2,3-dihydro-4-(1H)-pyridone and that III is 2,6-diphenyl-5-methyl-2,3-dihydro-4-pyridone.

However, IV did not show the characteristic absorption bands of 1,3-dihydro-4-(1H)-pyridone in the IR and UV spectra. In the NMR spectrum of IV, the singlet of one olefinic proton and a pair of doublets of two olefinic protons were observed at τ 4.80, 3.50, and 2.58. The singlet at τ −3.17, which disappeared upon the deuterium exchange, was assigned to the NH proton signal. These facts and the elemental analyses indicated that the structure of IV was 5-anilino-1-phenyl-1,4-hexadien-3-one. This was further confirmed by the fact that IV was identical with the condensation product of 2-anilino-2-penten-4-one and benzaldehyde after it had been treated with sulfuric acid.

Experimental

Materials. 1,2-Diphenyl-6-methyl-2,3-dihydro-4-pyridone (I) was synthesized from acetylacetone and benzylideneaniline in liquid ammonia;[3] mp 85°C. The spectral data are shown in Table 1.

Irradiation. Through the Vycor filter, a solution of 500 mg of I in 5 m*l* of methanol was irradiated by a high-pressure mercury lamp (450 W), and the reaction products were detected. However the photoproduct was not detected from a methanol or benzene solution of I through a Pyrex filter in a week. By the irradiation of a solution of 200 mg of I in 10 m*l* of methanol with a low-pressure mercury lamp (80 W) through a Vycor filter, I was isomerized to II, III, and IV. The change was monitored with the NMR spectrometer shown in Fig. 1.

Products II, III, and IV. After the irradiation of a solution of 300 mg of I in 10 m*l* of methanol for 100 hr, the colorless crystals which formed were filtered out and washed with cold methanol; mp 257°C.

Found: C, 82.00; H, 6.49; N, 5.27%. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32%.

The filtrate was concentrated under reduced pressure, and the residue was passed through a silica-gel (Merck 7734) column with a benzene - ethyl acetate (2 : 1 v/v) mixture. A yellow fraction and a pale yellow fraction were collected separately. The former fraction contained IV, and the latter contained III, showing R_f 0.85 and 0.44 on silica-gel (Wako-gel B-5) thin-layer chromatography with a benzene - ethyl acetate (2 : 1 v/v) mixture. The spectral data of II, III, and IV are summarized in Table 1.

5-Anilino-1-phenyl-1,4-hexadiene-3-one (IV). To 200 m*l* of liquid ammonia containing 2.1 g of potassium amide there were added 3 g of 2-anilino-2-penten-4-one at −33°C. After the mixture had been stirred one hour, 2 m*l* of benzaldehyde was added and stirring was continued for 2 hr. After the removal of the solvent at room temperature, the residue was acidified with concentrated hydrochloric acid. The product was extracted with chloroform, and the organic layer was washed with aqueous ammonia and then with water. The solvent was evaporated, and the residue was dissolved in 20 m*l* of concentrated sulfuric acid at room temperature. After 20 min, the solution was poured onto crashed ice and extracted with chloroform. The organic layer was washed with an aqueous sodium bicarbonate and with water, and then dried over calcium chloride. After the removal of the solvent, the residue was passed through a silica-gel (Merck 7734) column. The yellow fraction was collected, and the slovent evaporated. The residue was recrystallized from *n*-hexane, mp 101°C, which was identified with the above its R_f value of 0.44.

Found: C, 81.89; H, 6.72; N, 5.41%. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32%.