

these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be

obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-1145.

Photoisomerization of 4-Pyridones to 2-Pyridones

Nobuyuki Ishibe*¹ and Jun Masui

Contribution from the Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Kyoto 606, Japan. Received July 27, 1973

Abstract: Irradiation of 1,2,6-trimethyl-3,5-diphenyl-4-pyridone or 1-ethyl-2,6-dimethyl-3,5-diphenyl-4-pyridone with a medium-pressure mercury lamp yielded their isomers, 1,4,6-trimethyl-3,5-diphenyl-2-pyridone or 1-ethyl-4,6-dimethyl-3,5-diphenyl-2-pyridone, respectively. However, photolysis of 1-*n*-propyl-2,6-dimethyl-3,5-diphenyl-4-pyridone or 1-methyl-2,3,5,6-tetraphenyl-4-pyridone produced no reaction. This photoisomerization was shown to proceed *via* the singlet state with moderate quantum efficiency. Mechanistic aspects of the reaction were discussed.

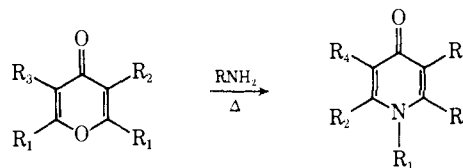
The photochemistry of cyclohexadienones bearing a heteroatom in the ring has been studied extensively.² In most cases the known photoreactions of these compounds are restricted to dimerization and isomerization. In 2-pyridones photodimerization was described about 10 years ago,³⁻⁵ and the [4 + 4] cycloadducts were obtained. The photoisomerization of 1-methyl-2-pyridone to *N*-methyl-2-aza-3-oxabicyclo[2.2.0]hex-5-ene⁶ was accomplished by low-temperature photolysis, and the generality of this photoisomerization of 2-pyridones⁷ was recently established. A kinetic analysis of photoisomerization of 1-methyl-2-pyridone by quenching and sensitization has shown⁸ that the lowest singlet state is involved in the formation of the products. On the other hand, relatively little attention has been given to the photochemical reaction of 4-pyridones. Sugiyama and his group⁹ reported that ultraviolet irradiation of 1,2,6-trimethyl-4-pyridone and 1,2-diphenyl-6-methyl-4-pyridone resulted in recovery of the starting materials.

Formation of the photodimer from 4-pyrones¹⁰ and 4-thiopyrones¹¹ is well known. However, we recently found that introduction of a phenyl group into the C-3 and C-5 positions of 4-pyrene and 4-thiopyrene prevents the formation of the photodimer and that photolysis of

these hindered 4-pyrones¹² and 4-thiopyrones¹³ afforded 2-pyrones and cyclopentadienones, respectively. While the nature of the substituent effect upon photoisomerization of hindered 4-pyrones was not fully understood, it was anticipated that introduction of the phenyl substituent into the C-3 and C-5 positions of 4-pyridones might increase the photoreactivity of 4-pyridones. In this respect 1,2,6-trimethyl-3,5-diphenyl-4-pyridone (**1**), 1-ethyl-2,6-dimethyl-3,5-diphenyl-4-pyridone (**2**), 1-*n*-propyl-2,6-dimethyl-3,5-diphenyl-4-pyridone (**3**), 1-methyl-2,3,5,6-tetraphenyl-4-pyridone (**4**), and 1,2,6-trimethyl-3-phenyl-4-pyridone (**5**) were prepared as the hindered 4-pyridones and their photochemistry was studied. The present paper¹⁴ deals with the photoisomerization of these hindered 4-pyridones to 2-pyridones as well as comparison of the photoreactivity of these compounds with that of hindered 4-pyrones.¹²

Results

Preparative Photochemistry and Product Structure Proof. The synthesis of hindered 4-pyridones (**1-5**) utilized the condensation¹⁵ of the corresponding 4-pyrones (**6-8**) with alkylamines. The structure assigned



- | | |
|---|---|
| 6, R ₁ = Me; R ₂ = R ₃ = Ph | 1, R ₁ = R ₂ = Me; R ₃ = R ₄ = Ph |
| 7, R ₁ = R ₂ = R ₃ = Ph | 2, R ₁ = Et; R ₂ = Me; R ₃ = R ₄ = Ph |
| 8, R ₁ = Me; R ₂ = Ph; R ₃ = H | 3, R ₁ = <i>n</i> -Pr; R ₂ = Me; R ₃ = R ₄ = Ph |
| | 4, R ₁ = Me; R ₂ = R ₃ = R ₄ = Ph |
| | 5, R ₁ = R ₂ = Me; R ₃ = Ph; R ₄ = H |

(12) N. Ishibe, M. Sunami, and M. Odani, *J. Amer. Chem. Soc.*, **95**, 463 (1973); *Chem. Commun.*, 1034 (1971).

(13) N. Ishibe and M. Odani, *Chem. Commun.*, 702 (1971); N. Ishibe, M. Odani, and R. Tanuma, *J. Chem. Soc., Perkin Trans. 1*, 1203 (1972).

(14) For a preliminary description of this work, see N. Ishibe and J. Masui, *J. Amer. Chem. Soc.*, **95**, 3396 (1973).

(15) M. A. F. Elkasche and M. H. Nosseir, *J. Amer. Chem. Soc.*, **82**, 4344 (1960); M. A. F. Elkasche, M. H. Osseir, and A. Abel-Kader, *J. Chem. Soc.*, 4647 (1963).

(1) Author to whom correspondence should be addressed at the Research and Development Laboratory, Dow Chemical Company, Freeport, Texas 77541.

(2) For reviews for the photochemistry of heterocyclic compounds, see P. Beak and W. R. Messer, *Org. Photochem.*, **2**, 117 (1969); S. T. Reid, *Advan. Heterocycl. Chem.*, **11**, 1 (1970).

(3) W. A. Ayer, R. Hayatsu, P. de Mayo, S. T. Reid, and J. B. Stothers, *Tetrahedron Lett.*, 684 (1961).

(4) E. C. Taylor and W. W. Paudler, *J. Amer. Chem. Soc.*, **83**, 4485 (1961); E. C. Taylor and R. O. Kan, *ibid.*, **85**, 776 (1963).

(5) L. A. Paquette and G. Slomb, *J. Amer. Chem. Soc.*, **85**, 765 (1963).

(6) E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, **86**, 950 (1964).

(7) R. C. Deselms and W. R. Scheigh, *Tetrahedron Lett.*, 3563 (1972); H. Furrer, *Chem. Ber.*, **105**, 2780 (1972).

(8) L. J. Sharp and G. S. Hammond, *Mol. Photochem.*, **2**, 225 (1970).

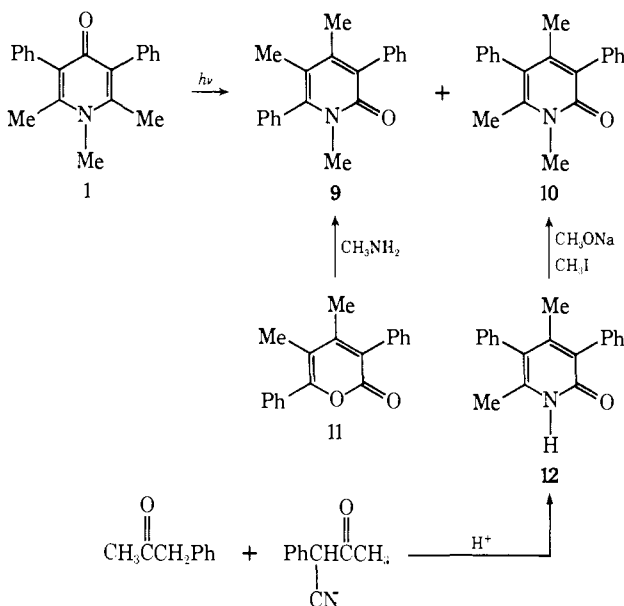
(9) N. Sugiyama, Y. Sato, and C. Kashima, *Bull. Chem. Soc. Jap.*, **43**, 3205 (1970).

(10) For the photodimerization of 4-pyrones, see P. Yates, E. S. Hand, P. Singh, S. K. Roy, and I. W. J. Still, *J. Org. Chem.*, **34**, 4046 (1969), and the references cited therein.

(11) For the photodimerization of 4-thiopyrones, see N. Ishibe and M. Odani, *J. Org. Chem.*, **36**, 4132 (1971), and the references cited therein.

to 4-pyridones rests on their spectral data. Their mass spectra showed an intense peak correspondent with their parent ion and a weak peak due to decarbonylation from the parent ion. The nmr spectra of **1**, **2**, **3**, and **5** exhibited alkyl protons α to the nitrogen atom at δ 3.5–4.0¹⁶ and the equivalent protons of the methyl groups on the C-2 and C-6 positions at δ 2.2–2.3.¹⁷ The *N*-methyl protons of **4** lie over the plane of the phenyl ring on C-2 and C-6 which is not coplanar with the heterocyclic ring, and gives rise to upfield shift (δ 3.05). These spectral data and elemental analyses were in complete agreement with the structures and are given in the Experimental Section.

The photochemical studies were carried out with a medium-pressure mercury lamp in a immersion apparatus using a Vycor filter. Irradiation of **1** in acetonitrile under nitrogen was found to afford one minor product (2.5%), whose structure is assigned as 1,4,5-trimethyl-3,6-diphenyl-2-pyridone (**9**) and one major product (35%), to which we have assigned the structure of 1,4,6-trimethyl-3,5-diphenyl-2-pyridone (**10**). A solution of **1** in methanol was irradiated under similar conditions as above. Conventional isolation procedures afforded **9** (3%) and **10** (30%). The elemental analyses and the mass spectra of these photoproducts (M^+ 289) clearly indicate that they are an isomer of **1**. The infrared spectra of the photoproducts showed strong bands at 1630 cm^{-1} (C=O), suggestive of the conjugated six-membered ring lactam.¹⁸ The mass spectra of the photoproducts showed an intense peak at m/e 261,



whereas the mass spectrum of **1** exhibited a very weak peak at m/e 261 under the same bombardment voltage. A loss of carbon monoxide from the molecular ion is characteristic with 2-pyridone.¹⁹

Chemical confirmation of the structure of the minor photoproduct **9** was obtained by comparison of melting

(16) J. C. N. Ma and E. W. Warnhoff, *Can. J. Chem.*, **43**, 1849 (1965); P. Beak and E. M. Monroe, *J. Org. Chem.*, **34**, 589 (1969).

(17) P. Beak and J. Bonham, *J. Amer. Chem. Soc.*, **87**, 3365 (1965); P. Beak and G. A. Carls, *J. Org. Chem.*, **29**, 2678 (1964).

(18) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen and Co., London, 1968, p 165.

(19) H. Budzikiewicz, C. Djerassi, and D. W. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 359.

point, mixture melting point, ir, and nmr spectra of an authentic sample prepared by the condensation of 3,6-diphenyl-4,5-dimethyl-2-pyrone (**11**)¹² with methylamine according to the established procedures.¹⁵

The mass spectrum of the major photoproduct showed an intense peak at m/e 56.²⁰ This fragment ion appears to be characteristic with 6-methyl-2-pyridones, since 3-, 4-, or 5-methyl-2-pyridones do not show the fragment at m/e 56 in their mass spectra.²¹ This result suggests that a methyl group is at the C-6 position of 2-pyridone. This deduction was supported by the shift of the nmr signals of the C-methyl protons by addition of tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium, $\text{Eu}(\text{fod})_3$.²² Plots of the chemical shifts (δ) from tetramethylsilane for each of the assigned resonances of the methyl protons in 2-pyridones against $[\text{Eu}(\text{fod})_3]/[\text{substrate}]$ ²³ gave linear lines and their slopes are summarized in Table I. The

Table I. Effect of Adding $\text{Eu}(\text{fod})_3$ to a CCl_4 Solution of 2-Pyridones

2-Pyridones	Slopes in plots of δ against $[\text{Eu}(\text{fod})_3]/[\text{substrate}]$		Relative shift induced by $\text{Eu}(\text{fod})_3$			
	C ₃	C ₄	Methyl protons ^a			
	C ₃	C ₄	C ₃	C ₄	C ₅	C ₆
1,3-Dimethyl-2-pyridone	12			8		
1,4-Dimethyl-2-pyridone		1.5		1		
1,5-Dimethyl-2-pyridone			2.8		1.8	
1,6-Dimethyl-2-pyridone				3.0		2.0
9		0.8	1.7		1	2.1
10		0.9		1.5	1.1	1.9

^a The chemical shifts of *N*-methyl protons induced by $\text{Eu}(\text{fod})_3$ were not included.

downfield shifts induced by $\text{Eu}(\text{fod})_3$ were observed in 2-pyridones as expected.²⁴ Comparison of the relative shifts of the methyl protons in the photoproducts with those of 3-methyl-, 4-methyl-, 5-methyl-, and 6-methyl-2-pyridones clearly indicates that a methyl group of the major photoproduct is not at C-3 of 2-pyridone. These results, in addition to the properties of **9**, left structures **10** and **13** as the possible alternatives for consideration. In order to establish the structure of the major photoproduct, both **10** and **13** were independently prepared. 1,5,6-Trimethyl-3,4-diphenyl-2-pyridone (**13**) was prepared by the condensation of 5,6-dimethyl-3,4-diphenyl-2-pyrone with methylamine, which was obtained from the reaction²⁵ of diphenylcyclopropanone with α -methylacetyl pyridinium ylide. Comparison of mixture melting point, ir, and nmr spectra of **13** with those of **10** ruled out **13** as the structure of the major photoproduct. The major photoproduct **10** was identical

(20) The high resolution mass spectrum of **10** indicates that this fragment has the elemental composition of $\text{C}_3\text{H}_6\text{N}$.

(21) R. Lawrence and E. S. Waight, *J. Chem. Soc. B*, 1 (1968).

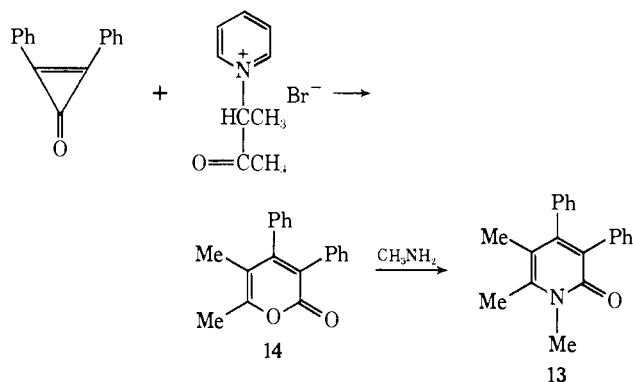
(22) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).

(23) J. K. Sanders, S. W. Hanson, and D. H. Williams, *J. Amer. Chem. Soc.*, **94**, 5325 (1972), and the references cited therein.

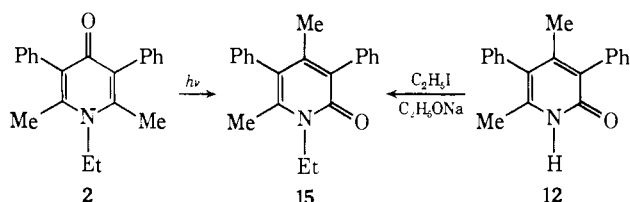
(24) 2-Pyridones might be a bifunctional substrate, of which the nitrogen atom in the ring and the carbonyl oxygen atom can be coordinated by $\text{Eu}(\text{fod})_3$. Separation of the observed shifts into separate contributions due to coordination at each site²³ was not carried out.

(25) For the synthesis of 2-pyridones by the reaction of cyclopropanones with ylides, see T. Eicher, E. v. Angerer, and A. M. Hansen, *Justus Liebigs Ann. Chem.*, **746**, 102 (1971); Y. Hayashi and H. Nozaki, *Tetrahedron*, **27**, 3085 (1971).

(mixture melting point, ir, and nmr spectra) with an authentic sample prepared independently by *N*-methylation of 4,6-dimethyl-3,5-diphenyl-2-pyridone (**12**) obtained by treating α -acetyl benzylcyanide with phenylacetone according to the established procedures.²⁶



When a solution of **2** in acetonitrile was irradiated through a Vycor filter, the sole product formed (31%) was identified as 1-ethyl-4,6-dimethyl-3,5-diphenyl-2-pyridone (**15**). Structure **15** was confirmed by comparison with an authentic sample synthesized in the manner outlined below.



When a dilute solution of **5** in acetonitrile was irradiated through a Vycor filter, the conventional isolation procedures gave only the starting material and a polymeric compound.²⁷ Photolysis of **5** in methanol or *tert*-butyl alcohol did not give the significant quantity of photoproduct. Irradiation of **5** in acetonitrile for shorter periods of time resulted in the recovery of **5** and in the isolation of a polymeric material. It is noteworthy that **5** appears to be photoreactive, whereas 2,6-dimethyl-3-phenyl-4-pyridone is not affected by the prolonged ultraviolet irradiation.¹²

Irradiation of **3** or **4** in acetonitrile with a medium-pressure mercury lamp equipped with a Vycor filter produced no reaction. Prolonged irradiation of **3** or **4** also resulted in the recovery of the starting materials. When photolysis was sensitized by acetophenone, **3** or **4** also recovered unchanged.

Quantum Yield Determinations. The absorption spectra of **1** and **2** in cyclohexane and methanol showed the intense π, π^* band at 275–277 nm and did not exhibit a band corresponding to the n, π^* transition. This was the case in the absorption and phosphorescence spectra of 1-methyl-4-pyridone, while the related compounds such as 4-pyridone and 4-thiopyridone exhibited clearly the n, π^* band in the absorption spectra. Consequently, the π, π^* singlet is considered to be the lowest

(26) J. F. M. Wajon and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **76**, 65 (1957).

(27) Tlc (silica gel) of the reaction mixture showed two weak spots besides the spots corresponding to **5** and a polymeric compound. The isolated quantity (<1 mg) was not enough to identify the structure of photoproducts.

populated state.²⁸ In order to demonstrate conclusively that the π, π^* state of **1** and **2** is the lowest triplet state, we have examined their phosphorescence emission in a rigid glass at 77°K.²⁸ The 0–0 band of **1**^{28, 29} in ethanol glass corresponds to a triplet energy of 71.5 kcal/mol and the radiative lifetime was 1.30 sec. The 0–0 band of **2**^{28, 29} in ethanol glass corresponds to a triplet energy of 72.8 kcal/mol and the lifetime of emission was 1.25 sec. This evidence^{30, 31} indicates that the lowest lying triplet of **1** and **2** is a π, π^* state.

Determination of the quantum yields for the appearance of products from 4-pyridones **1** and **2** was carried out in order to determine the facility of the photorearrangement. Degassed and sealed quartz tubes containing solutions of 4-pyridones and aqueous solutions of potassium ferrioxalate for actinometry³² were irradiated with 253.7-nm light in the rotating photochemical assembly. Reactions were carried out to low conversions to prevent appreciable light absorption by the products, and yields of products were determined by the ultraviolet spectrophotometric method. The results are summarized in Table II.

Table II. Quantum Yields for 2-Pyridone Formation in Direct, Sensitized, and Quenched Irradiations of 4-Pyridones **1** and **2**^a

4-Pyr- idones ^b	Additive	Solvent	Quantum yield ^c
1	None	Methanol	0.21 ^d
1	None	Acetonitrile	0.31 ^d
1	<i>trans</i> -Piperylene (0.5 M)	Methanol	0.21 ^d
1	<i>trans</i> -Piperylene (0.15 M)	Methanol	0.20 ^d
1	<i>trans</i> -Piperylene (0.05 M)	Methanol	0.21 ^d
1	<i>cis</i> -Piperylene (0.5 M)	Methanol	0.19 ^d
1	Acetophenone (0.5 M)	Acetonitrile	0
1	Propiophenone (0.5 M)	Acetonitrile	0
2	None	Methanol	0.25
2	<i>trans</i> -Piperylene (0.5 M)	Methanol	0.24

^a Irradiation conditions are described in Experimental Section. ^b 4-Pyridone concentrations were $3\text{--}7 \times 10^{-3}$ M. ^c Average of 2-pyridone formation from three runs. ^d Quantum yield for appearance of **10**; see ref 33.

Direct runs showed that the photochemical rearrangement of 4-pyridones to 2-pyridones³³ is moderately efficient with quantum yields ranging from 0.21 to 0.31. This magnitude is the same in order as the quantum efficiency of photoisomerization of 4-pyridones to 2-pyridones.¹² As shown in Table II, both *trans*- and *cis*-piperylene did not quench the photoisomerization of

(28) The poor solubility of **1**, **2**, and 1-methyl-4-pyridone in the non-polar solvents precludes measurement of the weak n, π^* absorption band. However, 1-methyl-4-pyridone in ethanol did not show a n, π^* band, whereas 4-pyridone in ethanol showed a clear n, π^* band. These results suggest that the lowest populated state is mainly the π, π^* singlet, although it appears possible that the n, π^* singlet might be populated but not detected since the n, π^* band is possibly buried under the strong π, π^* band. Details of absorption and emission (phosphorescence and fluorescence) spectra of 4-pyridones, 4-thiopyridones, and 4-pyridones will be published in a separate paper.

(29) The clear 0–0 band was not observed as has been observed in the case of 1-methyl-4-pyridone. The band observed as shoulder was assumed to be a 0–0 band. The phosphorescence maxima of **1** and **2** correspond to the triplet energies of 66.5 and 67.5 kcal/mol.

(30) M. Kasha, *Radiat. Res., Suppl.*, **2**, 265 (1969).

(31) H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 6589 (1967).

(32) C. H. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

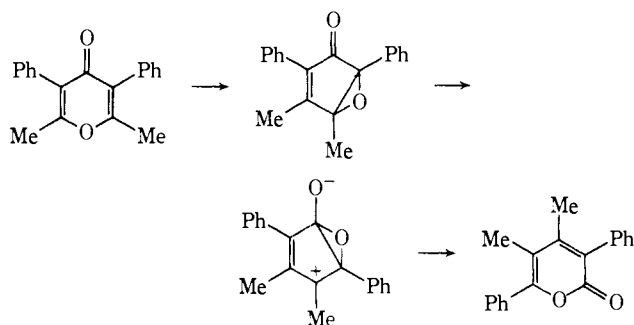
(33) In the preparative photolysis of **1**, both **9** and **10** were formed. Since the quantum yield determination was carried out to low conversions (<2%), the amount of **9** formed was negligible.

4-pyridones to 2-pyridones. Quenching experiments suggest that the singlet state is responsible for this photoisomerization. In order to elucidate further the nature of the excited state responsible for the conversion of **1** to **10**, sensitization experiments were undertaken. In experiments where the sensitizer (acetophenone, $E_T = 74\text{--}76$ kcal/mol and propiophenone, $E_T = 74.6$ kcal/mol) absorbed more than 98% of the incident light and concentrations were adjusted to avoid singlet transfer, the quantum yield was zero. When photolysis of **1** under preparative conditions was sensitized by acetophenone, **1** was also recovered unchanged. Ineffectiveness of both sensitization and quenching clearly indicates that the π, π^* singlet state is responsible for the rearrangement of 4-pyridones **1** and **2**.

Discussion

The acceleration effect of the phenyl group on the photochemical rearrangement of the hindered 4-pyridones to 2-pyridones is reminiscent of similar substituent effects upon the photoisomerization of the hindered 4-pyrones to 2-pyrones¹² and the photoisomerization of the hindered 4-thiopyrones to cyclopentadienones.¹³ However, the predominant path of photorearrangement of hindered 4-pyridones differs from that of corresponding 4-pyrones. Photolysis of **1** or **2** gave **10** or **15**, respectively, as the major product, whereas photolysis of 2,6-dimethyl-3,5-diphenyl-4-pyrene afforded 3,6-diphenyl-4,5-dimethyl-2-pyrone as sole product¹² by the proposed mechanism (Scheme I).

Scheme I



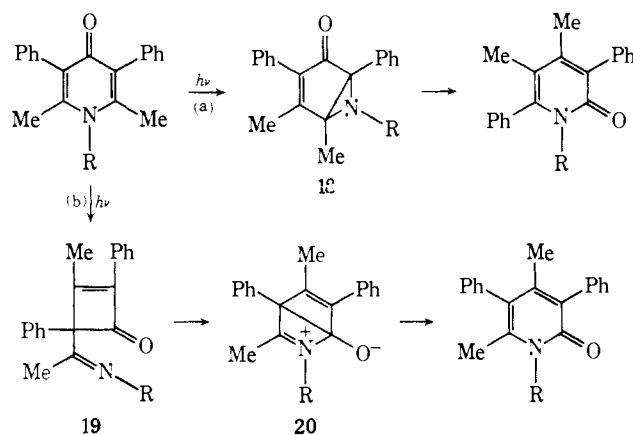
Neither **9** nor **10** is a precursor for each other for the formation of **10** or **9**, independent thermolysis at 180° of **9** or **10** having no effect. Independent irradiation of **9** or **10** through a Vycor filter resulted in recovery of the starting material. These results suggest that the hindered 4-pyridones demonstrate the predominance of a distinctly different mechanism from that of 4-pyrones.

A mechanism to account for the formation of 2-pyridones from 4-pyridones is presented in Scheme II. Photolysis of **1** leads initially to the 6-azabicyclo[3.1.0]hexenone,³⁴ which is converted, in either a photochemical or thermal process, to **9** as a minor product (path a). This photoconversion is analogous to photoisomerization of the hindered 4-pyrones to 2-pyrones¹² as shown in Scheme I, in which the formation of pyrylium 3-oxide³⁵ as an intermediate was detected

(34) The synthetic method of 6-azobicyclo[2.1.0]hexenyl system was recently reported: L. Kaplan, J. W. Pavlik, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **94**, 3283 (1972); A. Mishra, S. N. Rice, and W. Lwowski, *J. Org. Chem.*, **33**, 481 (1968).

(35) For reviews on the photochemical formation of pyrylium 3-oxide derivatives, see E. F. Ullman, *Accounts Chem. Res.*, **1**, 353 (1968); A. Padwa, *Org. Photochem.*, **1**, 92 (1967); N. R. Bertoniere and G. W. Griffin, *ibid.*, **3**, 115 (1973).

Scheme II



indirectly by an ultraviolet spectroscopic method. Since reactions involving the thermal or photochemical ring opening of aziridines to azomethine ylides and their subsequent 1,3-dipolar additions to reactive carbon-carbon multiple bonds are well known,^{36,37} it was anticipated that cleavage of the aziridine ring in the intermediate **18** might form an azomethine ylide. An attempt to trap a transient azomethine ylide with dimethyl acetylenedicarboxylate in the photolysis of **1** was unsuccessful.

For the formation of major products, **10** and **15**, photolysis of **1** or **2** may initially proceed by isomerization to the cyclobutenone derivative **19**, which is then converted to the Dewar isomer **20**³⁸ followed by ring opening of **20** to 2-pyridone (path b). An isolation of vinylcyclobutenone from photolysis of 4-hydroxy-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone was reported.⁴⁰ Baldwin and McDaniel⁴¹ found that photolytic and thermal ring openings of cyclobutenones *via* their valence-isomeric ketene intermediates in methanol give esters. A ketene intermediate was also trapped by phenyl isocyanide.⁴² Photolysis of **1** or **2** in methanol did not give an ester, which was anticipated from nucleophilic attack of methanol to a ketene intermediate, or adduct with methanol, as has been observed in the photoisomerization of pyrroles and furans.⁴³

As mentioned previously, **3** and **4** were not affected by ultraviolet irradiation. Stability of **3** and **4** against light might be explained in terms of the steric effect of the substituents,⁴⁴ since inspection of molecular models suggests that C-N bond cleavage in **3** and **4** would lead to the formation of intermediate **18** or **19** in which there was appreciable steric hindrance. Molecular models also show that there is appreciable steric

(36) E. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, **89**, 1753 (1967); J. H. Hall and R. Huisgen, *Chem. Commun.*, 1187, 1188 (1971).

(37) T. DoMinh and Q. M. Trozzolo, *J. Amer. Chem. Soc.*, **92**, 6997 (1970); A. Padwa and E. Glazer, *ibid.*, **94**, 7788 (1972), and the references cited therein.

(38) Dewar-, primane-, and benzvalene-type intermediates are proposed in the photoreaction of pyridinium cations³⁴ and 3,5-dicarboalkoxy-pyridines.³⁹

(39) T. J. van Bergen and R. M. Kellogg, *J. Amer. Chem. Soc.*, **94**, 8451 (1972), and the references cited therein.

(40) D. A. Plank, J. C. Floyd, and W. H. Starnes, Jr., *Chem. Commun.*, 1003 (1969).

(41) J. E. Baldwin and M. C. McDaniel, *J. Amer. Chem. Soc.*, **90**, 6118 (1968).

(42) N. Obata and T. Takizawa, *Chem. Commun.*, 587 (1971).

(43) H. Hiraoka, *Chem. Commun.*, 1610 (1971).

(44) Comparison of the absorption and emission (fluorescence and phosphorescence) spectra of **3** and **4** with those of **1** and **2**²⁸ did not give distinct evidence to distinguish their photoreactivity.

Table III. Preparation of Hindered 4-Pyridones

4-Pyr- idones	4-Pyrones, wt (g)	Amines, wt (g)	Solvent, ml	Product wt, g (%)	Mp, °C	—% (Calcd, Found)—		
						C	H	N
2	6, ^a 1.5	70% aq EtNH ₃ , 30	EtOH, 50	0.6 (35)	242.5–243.5	83.13	6.98	4.62
						82.95	6.92	4.49
3	6, ^a 1.0	<i>n</i> -PrNH ₂ , 15	EtOH, 80	0.3 (26)	231–233	83.29	7.25	4.41
						83.45	7.29	4.53
4	7, ^b 0.5	40% aq MeNH ₂ , 10	MeCN, 50	0.25 (48)	317–318	87.13	5.61	3.39
						87.40	5.85	3.50
5	8, ^c 0.8	40% aq MeNH ₂ , 5	EtOH, 10	0.41 (55)	218–220	78.84	7.09	6.57
						78.61	6.97	6.51

^a Reference 47. ^b P. Yates and J. A. Weisbach, *J. Amer. Chem. Soc.*, **85**, 2943 (1963). ^c R. L. Letsinger and J. D. Jamison, *ibid.*, **83**, 193 (1961).

crowding between the phenyl protons and the *n*-propyl or phenyl protons in the conversion of **19** to **20**.

Unhindered 4-pyridones such as 1,2,6-trimethyl-4-pyridone, 1,2-diphenyl-6-methyl-4-pyridone,⁹ and 1-methyl-2,6-diphenyl-4-pyridone were not affected by ultraviolet irradiation. While we have no adequate explanation on stability of these unhindered 4-pyridones against light, steric crowding of the substituent appears important for the photorearrangement of 4-pyridones.^{44a} Inspection of a molecular model indicates that in the structure of **1–5**, the coplanarity of the phenyl ring with the heterocyclic ring is prevented by the steric repulsion between a phenyl proton and a methyl or phenyl proton. These steric effects are reflected in the hypochromic effect relative to the ultraviolet spectrum of 1-methyl-2,6-diphenyl-4-pyridone. The angle of twist, θ , between the phenyl ring and the heterocyclic ring in the ground state is calculated for these compounds according to the formula $\epsilon/\epsilon^0 = \cos^2 \theta^{45,46}$ and the magnitude is around 35°. The nature of the steric effect on the photochemical reactivity remains attractive to warrant further investigations.

Experimental Section

Melting points were not corrected. Elemental analyses were carried out by Microanalytical Laboratory, Kyoto University, Kyoto, Japan. The infrared spectra were recorded on a JASCO-DS 402G spectrophotometer. The ultraviolet spectra were taken with Hitachi Model 124 or 323 spectrophotometers. The nmr determinations were made on a JEOL PS-100 instrument in CCl₄ or CDCl₃ solvent with chemical shifts, δ , reported in parts per million downfield from internal tetramethylsilane standard. Mass spectra were determined on a Hitachi RMU-6L spectrometer using a direct inlet.

1-Methyl-2,6-diphenyl-4-pyridone was prepared according to the reported method.¹⁵ Solvents were spectrograde for photolysis and reagent grade for column and thin-layer chromatography.

Preparation of Hindered 4-Pyridones. A typical procedure follows with the resulting for the remaining cases tabulated in Table III. A mixture containing 1.5 g of 2,6-dimethyl-3,5-diphenyl-4-pyridone⁴⁷ and 20 g of 40% aqueous methylamine in 100 ml of ethanol was heated in a stainless-steel bomb at 90° for 49 hr. After evaporation of the solvent and methylamine under reduced pressure, the residual solid was recrystallized from benzene to yield 1.05 g (66%) of 1,2,6-trimethyl-3,5-diphenyl-4-pyridone: mp 278.5–279.0°; ir (KBr) 1615, 1525, 1500, 1300, 1100, 755, 705 cm⁻¹; uv (MeOH) 274 nm (ϵ 14,500); nmr (CDCl₃) δ 2.24 (s, 6 H), 3.58 (s, 3 H), 7.1–7.5 (m, 10 H); mass spectrum *m/e* (rel intensity) 290 (14), 289 (M⁺, 80), 288 (100), 274 (4), 273 (6), 260 (11), 115 (20).

(44a) NOTE ADDED IN PROOF. Recently Pavlik found that photorearrangement of 4-pyrones was affected by the solvent polarity. Effect of the solvent polarity upon photorearrangement is an attractive subject of investigation which is in progress in our laboratory. J. W. Pavlik, *J. Amer. Chem. Soc.*, **95**, 7914 (1973).

(45) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

(46) H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1965, p 384.

(47) T. L. Emick and R. L. Letsinger, *Org. Syn.*, **47**, 54 (1967).

Anal. Calcd for C₁₉H₁₉NO: C, 83.01; H, 6.62; N, 4.84. Found: C, 82.91; H, 6.57; N, 4.84.

Spectral Data. 1-Ethyl-2,6-dimethyl-3,5-diphenyl-4-pyridone: ir (KBr) 1620, 1555, 1500, 1450, 1300, 1080, 765, 700 cm⁻¹; uv (MeOH) 275 nm (ϵ 16,600); nmr (CDCl₃) δ 1.40 (t, 3 H, *J* = 6.0 Hz), 2.29 (s, 6 H), 4.02 (q, 2 H, *J* = 5.5 Hz), 7.1–7.4 (m, 10 H); mass spectrum *m/e* (rel intensity) 304 (10), 303 (M⁺ 56), 302 (100), 276 (10), 275 (48), 274 (56), 85 (16).

1-*n*-Propyl-2,6-dimethyl-3,5-diphenyl-4-pyridone: ir (KBr) 1620, 1550, 1500, 1445, 1075, 760, and 710 cm⁻¹; uv (MeOH) 274 nm (ϵ 15,800); nmr (CDCl₃) δ 1.05 (t, 3 H, *J* = 6.0 Hz), 1.7–1.9 (m, 2 H), 2.29 (s, 6 H), 3.8–4.0 (m, 2 H), 7.2–7.5 (m, 10 H).

1-Methyl-2,3,5,6-tetraphenyl-4-pyridone: ir (KBr) 1620, 1600, 1575, 1435, 1300, 1030, 810, 770, 755, 700 cm⁻¹; uv (MeOH) 277 nm (ϵ 13,200); nmr (CDCl₃) δ 3.05 (s, 3 H), 7.0–7.4 (m, 20 H); mass spectrum *m/e* (rel intensity) 414 (12), 413 (M⁺, 53), 412 (100), 396 (9), 385 (5), 118 (20), 77 (30).

1,2,6-Trimethyl-3-phenyl-4-pyridone: ir (KBr) 1625, 1500, 1440, 1350, 1165, 860 cm⁻¹; uv (MeOH) 276 nm (ϵ 15,300); nmr (CDCl₃) δ 2.17 (s, 3 H), 2.37 (s, 3 H), 3.54 (s, 3 H), 6.41 (s, 1 H), 7.2–7.5 (m, 5 H).

Irradiation of 1,2,6-Trimethyl-3,5-diphenyl-4-pyridone. A solution containing 1.0 g of 1,2,6-trimethyl-3,5-diphenyl-4-pyridone in 600 ml of acetonitrile was irradiated under nitrogen at 28° for 9 hr using a 500-W Ushio medium-pressure mercury lamp equipped with a Vycor filter. Removal of the solvent *in vacuo* left a yellow solid, which was chromatographed on silica gel with chloroform-ether (4:1) as eluent. The 500-ml collection afforded a colorless solid, which, after recrystallization from ligroin-benzene gave 0.025 g (2.5%) of 1,4,5-trimethyl-3,6-diphenyl-2-pyridone: mp 203.0–203.5°; ir (KBr) 1625, 1600, 1580, 1280, 1015, 790, 750, 700 cm⁻¹; uv (MeOH) 316 nm (ϵ 12,800); nmr (CCl₄) δ 1.72 (s, 3 H), 1.97 (s, 3 H), 3.10 (s, 3 H), 7.1–7.5 (m, 10 H); mass spectrum *m/e* (rel intensity) 289 (M⁺, 98), 288 (100), 261 (26), 260 (31), 115 (36), 105 (20), 77 (72), 51 (28).

Anal. Calcd for C₂₆H₁₉NO: C, 83.01; H, 6.62; N, 4.84. Found: C, 83.20; H, 6.33; N, 4.78.

The next 500-ml fraction furnished a solid, which, after recrystallization from ligroin-benzene, gave 0.35 g (35%) of 1,4,6-trimethyl-diphenyl-2-pyridone: mp 179.5–181.0°; ir (KBr) 1625, 1585, 1530, 1495, 1445, 1430, 1305, 1100, 955, 785, 775, 750, 700 cm⁻¹; uv (MeOH) 316 nm (ϵ 10,200); nmr (CCl₄) δ 1.62 (s, 3 H), 2.06 (s, 3 H), 3.51 (s, 3 H), 7.1–7.4 (m, 10 H); mass spectrum *m/e* (rel intensity) 289 (M⁺, 78), 288 (100), 261 (44), 260 (39), 115 (27), 77 (39), 56 (37).

Anal. Calcd for C₂₆H₁₉NO: C, 83.01; H, 6.62; N, 4.84. Found: C, 83.14; H, 6.45; N, 4.63.

Irradiation of 0.8 g of 1,2,6-trimethyl-3,5-diphenyl-4-pyridone in 600 ml of methanol was conducted under nitrogen at 28° for 8 hr using a 300-W Taika medium-pressure mercury lamp equipped with a Vycor filter. A similar work-up of the reaction mixture as mentioned above gave 0.024 g (3%) of 1,4,5-trimethyl-3,6-diphenyl-2-pyridone and 0.24 g (30%) of 1,4,6-trimethyl-3,5-diphenyl-2-pyridone.

Irradiation of 1-Ethyl-2,6-dimethyl-3,5-diphenyl-4-pyridone. A solution of 0.4 g of 1-ethyl-2,6-dimethyl-3,5-diphenyl-4-pyridone in 500 ml of acetonitrile was irradiated under nitrogen with a 500-W medium-pressure mercury lamp using a Vycor filter at 29° for 5 hr. The solvent was removed under reduced pressure and the residual solid was chromatographed on silica gel with chloroform-ether (7:1) as eluent. The 400-ml collection gave a solid, which, after recrystallization from petroleum ether-benzene, gave 0.124 g (31%) of 1-ethyl-4,6-dimethyl-3,5-diphenyl-2-pyridone: mp 159.5–

160.5°; ir (KBr) 1635, 1585, 1535, 1450, 1310, 1105, 755, 705 cm⁻¹; uv (MeOH) 316 nm (ϵ 9620); nmr (CCl₄) δ 1.32 (t, 3 H, $J = 6.0$ Hz), 1.61 (s, 3 H), 2.11 (s, 3 H), 4.16 (q, 2 H, $J = 5.5$ Hz), 7.1–7.5 Hz (m, 10 H); mass spectrum m/e (rel intensity) 303 (M⁺, 99), 302 (71), 275 (50), 274 (100), 246 (12), 230 (10), 203 (14), 202 (17), 189 (11), 115 (12), 77 (10).

Anal. Calcd for C₂₁H₂₁NO: C, 83.13; H, 6.98; N, 4.62. Found: C, 83.06; H, 7.01; N, 4.49.

Irradiation of 1-*n*-Propyl-2,6-dimethyl-3,5-diphenyl-4-pyridone or 1-Methyl-2,3,5,6-tetraphenyl-4-pyridone or 1-Methyl-2,6-diphenyl-4-pyridone. A solution of 4-pyridone (0.2–0.3 g) in acetonitrile or methanol (350 ml) was irradiated under nitrogen for 10–14 hr using a Ushio 500-W medium-pressure mercury lamp equipped with a Vycor filter. The solution was concentrated to 10 ml and the reaction mixture showed only one spot on tlc (silica gel), the R_f value being the same as that of the starting material. The recovery of the starting material was nearly 100%.

Irradiation of 1,2,6-Trimethyl-3-phenyl-4-pyridone. A solution of 0.1 g of 1,2,6-trimethyl-3-phenyl-4-pyridone in 350 ml of acetonitrile was irradiated under nitrogen for 9 hr using a 500-W Ushio medium-pressure mercury lamp equipped with a Vycor filter. Column chromatography of the reaction mixture on silica gel with chloroform did not afford isolable quantity of photoproduct but gave only the starting material (0.01 g) and a polymeric compound.

Photolysis of 0.3 g of 1,2,6-trimethyl-3-phenyl-4-pyridone in 350 ml of methanol or *tert*-butyl alcohol under similar conditions as mentioned above failed to isolate a significant quantity of photoproduct.

1,4,5-Trimethyl-3,6-diphenyl-2-pyridone. A suspension of 0.54 g of 4,5-dimethyl-3,6-diphenyl-2-pyridone and 10 g of 40% aqueous methylamine in 20 ml of ethanol was heated in a sealed tube at 80° for 72 hr. After evaporation of the solvent and methylamine *in vacuo*, chromatography of the residual solid on silica gel with chloroform–ether (4:1) as eluent gave 0.17 g (30%) of 1,4,5-trimethyl-3,6-diphenyl-2-pyridone, mp 202.5–204.0°. Its ir, uv, and nmr spectra were consistent with those of the product **9** obtained by photolysis of 1,2,6-trimethyl-3,5-diphenyl-4-pyridone.

Anal. Calcd for C₂₀H₁₉NO: C, 83.01; H, 6.62; N, 4.84. Found: C, 82.91; H, 6.64; N, 4.71.

1,4,6-Trimethyl-3,5-diphenyl-2-pyridone. To a solution containing 0.6 g of 4,6-dimethyl-3,5-diphenyl-2-pyridone and 0.05 g of sodium methylate in 10 ml of methanol was added dropwise 0.2 g of methyl iodide at 5°. The reaction mixture was refluxed gently for 1 hr and poured into cold water. The mixture was extracted with chloroform, washed with water, and dried over anhydrous sodium sulfate. After evaporation of the solvent, chromatography of the residual solid on silica gel with chloroform–ether (4:1) gave a solid, which, after recrystallization from petroleum ether–benzene, afforded 0.17 g (27%) of 1,4,6-trimethyl-3,5-diphenyl-2-pyridone, mp 182.0–182.5°. Its ir, uv, and nmr spectra were consistent with those of **10** obtained by photolysis of 1,2,6-trimethyl-3,5-diphenyl-4-pyridone.

Anal. Calcd for C₂₀H₁₉NO: C, 83.01; H, 6.62; N, 4.84. Found: C, 82.95; H, 6.44; N, 4.86.

1-Ethyl-4,6-dimethyl-3,5-diphenyl-2-pyridone. To a solution containing 0.1 g of 4,6-dimethyl-3,5-diphenyl-2-pyridone²⁶ and 0.01 g of sodium ethylate in 10 ml of ethanol was added dropwise 0.05 g of ethyl iodide at 5°. Similar work-up as before gave 0.018 g (16%) of 1-ethyl-4,6-dimethyl-3,5-diphenyl-2-pyridone, mp 159–160°. Its ir, uv, and nmr spectra were consistent with those of **15** obtained by photolysis of 1-ethyl-2,6-dimethyl-3,5-diphenyl-4-pyridone.

Anal. Calcd for C₂₁H₂₁NO: C, 83.13; H, 6.98; N, 4.62. Found: C, 83.05; H, 7.05; N, 4.51.

5,6-Dimethyl-3,4-diphenyl-2-pyridone. A solution containing 1.1 g of α -methylacetylpyridinium bromide (mp 120–126°) prepared from the reaction of α -bromoethyl methyl ketone with pyridine in benzene,⁴⁸ 1.0 g of diphenylcyclopropanone, and 0.75 g of diisopropylethylamine in 30 ml of benzene was stirred at room temperature for 16 hr. After removal of the solvent *in vacuo*, the residual solid was chromatographed on silica gel and eluted with chloroform. After evaporation of the solvent under reduced pressure, the residual solid was recrystallized from methanol to yield 0.2 g (15%) of 5,6-dimethyl-3,4-diphenyl-2-pyridone: mp 169–171°; ir (KBr) 1705, 1620, 1530, 1445, 1320, 950, 760, 705 cm⁻¹; nmr (CDCl₃) δ 1.73 (s, 3 H), 2.35 (s, 3 H), 5.9–7.3 (m, 10 H); mass spec-

trum m/e (rel intensity)⁴⁹ 277 (10), 276 (M⁺, 46), 249 (20), 248 (100), 205 (52), 77 (17), 43 (21).

Anal. Calcd for C₁₉H₁₆O₂: C, 82.58; H, 5.84; O, 11.58. Found: C, 82.54; H, 6.54; O, 11.57.

1,5,6-Trimethyl-3,4-diphenyl-2-pyridone. A suspension containing 0.2 g of 5,6-dimethyl-3,4-diphenyl-2-pyridone and 3.4 g of 40% aqueous methylamine in 10 ml of ethanol was heated in a sealed tube at 80° for 30 hr. After removal of the solvent and methylamine *in vacuo*, chromatography on silica gel with chloroform–ether (4:1) as eluent gave a colorless solid. Recrystallization from petroleum ether–benzene afforded 0.02 g (10%) of 1,5,6-trimethyl-3,4-diphenyl-2-pyridone: mp 174–175°; mixture mp (with 1,4,6-trimethyl-3,5-diphenyl-2-pyridone) 130–148°; ir (KBr) 1630, 1575, 1525, 1445, 1420, 1385, 1020, 795, 705 cm⁻¹; nmr (CCl₄) δ 1.82 (s, 3 H), 2.43 (s, 3 H), 3.68 (s, 3 H), 6.9–7.3 (m, 10 H).

Anal. Calcd for C₂₀H₁₉NO: C, 83.01; H, 6.62; N, 4.84. Found: C, 82.78; H, 6.50; N, 4.90.

Sensitized Irradiation of 1,2,6-Trimethyl-3,5-diphenyl-4-pyridone. A solution containing 0.6 g of 1,2,6-trimethyl-3,5-diphenyl-4-pyridone and 25 g of acetophenone in 800 ml of acetonitrile was irradiated with a 500-W Ushio medium-pressure mercury lamp using a Pyrex filter. After 36 hr of irradiation, chromatography on silica gel afforded only acetophenone and the 4-pyridone, and the recovery of the latter was nearly 100%.

Thermolysis of 1,4,5-Trimethyl-3,6-diphenyl-2-pyridone and 1,4,6-Trimethyl-3,5-diphenyl-2-pyridone. A solution containing 0.05 g of 1,4,5-trimethyl-3,6-diphenyl-2-pyridone or 1,4,6-trimethyl-3,5-diphenyl-2-pyridone in 5 ml of mesitylene was heated in a seal tube at 180° for 14 hr. In each case, no new spot on tlc was observed and the recovery of the starting material was nearly 100%.

Photolysis of 1,4,5-Trimethyl-3,6-diphenyl-2-pyridone and 1,4,6-Trimethyl-3,5-diphenyl-2-pyridone. A solution containing 0.15 g of 1,4,5-trimethyl-3,6-diphenyl-2-pyridone or 1,4,6-trimethyl-3,5-diphenyl-2-pyridone in 180 ml of acetonitrile was irradiated under nitrogen for 72 hr using a 100-W medium-pressure mercury lamp equipped with a quartz filter. After concentration of the reaction mixture to 5 ml, no new spot was observed in both cases and the recovery was nearly 100%.

Irradiation of 1,2,6-Trimethyl-3,5-diphenyl-4-pyridone in the Presence of Dimethyl Acetylenedicarboxylate. A solution containing 0.1 g of 1,2,6-trimethyl-3,5-diphenyl-4-pyridone and 0.09 g of dimethyl acetylenedicarboxylate in 180 ml of acetonitrile was irradiated under nitrogen for 72 hr using a 100-W medium-pressure mercury lamp equipped with a quartz filter. Chromatography on silica gel gave both of the starting materials in nearly 100% recovery.

Quantum Yield Determinations. Dilute solutions of 1,2,6-trimethyl-3,5-diphenyl-4-pyridone or 1-ethyl-2,6-dimethyl-3,5-diphenyl-4-pyridone in acetonitrile or methanol (*ca.* 0.003–0.007 M) in quartz test tubes were irradiated in a merry-go-round apparatus used in conjunction with a Rayonet Model RPR-100 photochemical reactor (Southern New England Ultraviolet Co.) containing four 253.7-nm lamps. The samples in photolysis tubes were degassed using three freeze–thaw cycles using a pump. 10⁻² mm, before being sealed off. These samples were irradiated to less than 2% conversion simultaneously with a potassium ferrioxalate actinometer.³² After irradiation, the concentrations of the photoproduct were determined by quantitative ultraviolet spectroscopy at 315 nm for **10** and at 316 nm for **15**. The absorption due to the starting material was corrected to determine the degree of reaction.

Lanthanide-Induced Shifts in Proton Nuclear Magnetic Resonance Spectra of 2-Pyridones. Methyl-2-pyridones were prepared by diazotization of the corresponding aminopycolines, followed to

(49) The mass spectrum exhibited an intense peak at m/e 205, formed by the elimination of the acetyl radical from the fragment, [M – CO]⁺ at m/e 248. This strongly indicates the presence of the methyl group at C-6 of 2-pyridone. Confirmation was obtained from the Diels–Alder reaction of this 2-pyridone with benzene, generated from diphenyliodonium-2-carboxylate,⁵⁰ which gave 1,2-dimethyl-3,4-diphenyl-naphthalene. A mixture of 0.14 g of 5,6-dimethyl-3,4-diphenyl-2-pyridone and 0.225 g of diphenyliodonium-2-carboxylate in 3 ml of diethylbenzene was heated with a microburner until the reaction mixture turned to an amber solution. After diethylbenzene was carefully distilled off, 10 ml of 95% ethanol was added to the residual oil and refluxed for 1 hr. Upon standing the solution at 0°, a colorless solid was separated, which on recrystallization from ethanol afforded 0.07 g (45%) of 1,2-dimethyl-3,4-diphenyl-naphthalene: mp 151–152°; nmr (CCl₄) δ 2.20 (s, 3 H), 2.73 (s, 3 H), 6.9–7.5 (m, 14 H).

Anal. Calcd for C₂₄H₂₂: C, 93.48; H, 6.52. Found: C, 93.23; H, 6.49.

(50) L. F. Fieser and M. J. Haddadin, *Org. Syn.*, **46**, 107 (1966).

(48) F. Krohnke, *Chem. Ber.*, **68**, 1177 (1935).

alkylation with dimethyl sulfate, analogous to previously reported syntheses⁵¹ and was fully characterized by spectral properties (uv, ir, and nmr). These compounds were stored over P₄O₁₀ *in vacuo*. The lanthanide-shift reagent used in this study was europium(III) tris-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, which was stored over P₄O₁₀ *in vacuo*. Tetramethylsilane was used as an internal reference for all measurements. The solvent employed for all samples was molecular-sieve dried CCl₄.

The runs were performed in the following manner. The concen-

(51) R. Adams and A. W. Schrecker, *J. Amer. Chem. Soc.*, **71**, 1186 (1949); J. E. Eldridge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961).

tration of the substrate was kept constant and only the lanthanide shift reagent concentration varied. The initial sample was prepared in a clean, oven-dried nmr tube by first putting in 0.3 g of Eu(fod)₃ and the appropriate amount of substrate, so that after the addition of CCl₄ and TMS, the concentration of the substrate was at the desired value. Since the correctness of the substrate concentration is crucial, a solution approximately 0.5 M in substrate was added to the tube (its exact amount determined gravimetrically) rather than the pure substrate. Successive samples were then prepared by adding aliquots of a substrate stock solution (usually 0.15 M in CCl₄ with 4% TMS) of the same concentration of substrate as in the initial sample.

The Photochemistry of 3-Alkylidenecyclohexanones. The Role of Olefin Geometrical Isomerization in the Triplet-State Reactivity of β,γ -Unsaturated Ketones¹

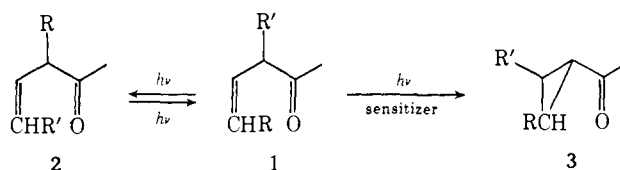
Kenneth G. Hancock* and Ronald O. Grider

Contribution from the Department of Chemistry, University of California at Davis, Davis, California 95616. Received July 31, 1973

Abstract: The photochemical reactions of 3-methylene-2,2,5,5-tetramethylcyclohexanone (**4**), 3-ethylidene-2,2,5,5-tetramethylcyclohexanone (**5**), and their photoproducts have been investigated. Direct irradiation of **4** produces a singlet-state 50:50 photoequilibrium of **4** and 3,3-dimethyl-5-isopropylidenecyclohexanone (**9**). Direct irradiation of (*Z*)-3-ethylidene-2,2,5,5-tetramethylcyclohexanone (**5-(Z)**) produces a 68:32 singlet-state photoequilibrium of (*E*)-3-ethylidene-2,2,5,5-tetramethylcyclohexanone (**5-(E)**) and 3-isopropylidene-2,5,5-trimethylcyclohexanone (**14**). Quantum yields were 0.13, 0.18, 0.20, and 0.30 for reactions **4** → **9**, **9** → **4**, **5** → **14**, and **14** → **5**, respectively. No direct singlet-state isomerization of **5-(Z)** to **5-(E)** was observed. The stereospecificity of the **14** → **5-(E)** isomerization is discussed in terms of intimate diradical and/or concerted mechanisms for the 1,3-acyl shifts. The triplet state of **4** is unreactive although it was shown to accept triplet energy from acetophenone. Photosensitization of **5-(Z)** causes isomerization to a triplet-state 1:4 photoequilibrium of **5-(Z)** and **5-(E)**, with a zero-conversion quantum yield of 0.53. The $\pi-\pi^*$ configuration of the triplet state was demonstrated by phosphorescence. The contrast between the triplet reactivity of **5** and isostructural units in steroids is discussed in terms of the relative energetics of cis-trans isomerization *vs.* the 1,2-acyl shift.

A particularly intricate structure-reactivity relationship apparently characterizes the photochemistry of β,γ -unsaturated ketones.^{4,5} From the welter of diverse reactions that have been reported, the dominant pattern to emerge has been that of a general reaction dichotomy separating singlet-state and triplet-state processes. In this generalization singlet excited states of β,γ -unsaturated ketones most typically undergo a reversible photochemical 1,3-acyl shift to isomeric β,γ -unsaturated ketones (**1** ⇌ **2**). In contrast, triplet excited states generated by photosensitization typically rearrange *via* a 1,2-acyl shift to cyclopropyl ketones (**1** → **3**, the oxa-di- π -methane rearrangement).^{6,7}

There are for both singlets and triplets, however, a



number of photoreactions which are more or less competitive with the 1,3- and 1,2-acyl shifts, depending on subtle structural features of the β,γ -unsaturated ketones in ways which are currently more enigmatic.^{4,5} For example, although mechanistic details of these processes are only now emerging, both decarbonylation^{8,9} and γ -hydrogen abstraction^{5,10,11} are competitors to the singlet-state 1,3-acyl shift. Triplet-state β,γ -unsat-

(1) Portions of this work have appeared in preliminary communications.^{2,3}

(2) K. G. Hancock and R. O. Grider, *Tetrahedron Lett.*, 4281 (1971).

(3) K. G. Hancock and R. O. Grider, *Tetrahedron Lett.*, 1367 (1972).

(4) In the absence of a detailed review, a recent compendium of references to the varied photochemical reactions of β,γ -unsaturated ketones is given by K. N. Houk, D. J. Northington, and R. E. Duke, Jr., *J. Amer. Chem. Soc.*, **94**, 6233 (1972).

(5) P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, **94**, 9252 (1972).

(6) W. G. Dauben, M. S. Kellogg, J. I. Seeman, and W. A. Spitzer, *J. Amer. Chem. Soc.*, **92**, 1786 (1970).

(7) (a) R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, **93**, 3957 (1971); R. S. Givens and W. F. Oettle, *ibid.*, **93**, 3963 (1971).

(8) (a) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966); (b) D. I. Schuster, F.-T. Lee, A. Padwa, and P. G. Gassman, *ibid.*, **30**, 2262 (1965); (c) N. C. Yang and D. M. Thap, *Tetrahedron Lett.*, 3671 (1966).

(9) Note, however, that P. S. Engel and H. Ziffer [*Tetrahedron Lett.*, 5181 (1969)] report quenching of decarbonylation in bicyclo[4.3.0]non-1(6)-en-8-one by piperylene.

(10) J. C. Dalton and H.-F. Chan, *J. Amer. Chem. Soc.*, **95**, 4085 (1973).

(11) Other examples include: (a) ref 8c; (b) E. F. Kiefer and D. A. Carlson, *Tetrahedron Lett.*, 1617 (1967); (c) T. Matsui, A. Komatsu, and T. Moroe, *Bull. Chem. Soc. Jap.*, **40**, 2204 (1967); (d) R. C. Cookson, J. Hudec, G. E. Usher, and A. Szabo, *Tetrahedron*, **24**, 4353 (1968); (e) R. C. Cookson and N. R. Rogers, *J. Chem. Soc., Chem. Commun.*, 809 (1972).