Photochemistry of Di(4-pyridyl) Ketone in Isopropyl Alcohol

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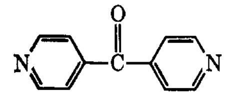
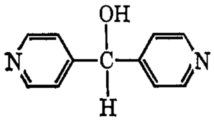
Abstract: The photochemistry of di(4-pyridyl) ketone in isopropyl alcohol solution was studied by consecutive recording of absorption, emission, excitation, nmr, and esr spectra during photolysis and in the following dark period. A number of derivatives of the ketone and its photoreduction product, di(4-pyridyl)methanol, were chemically prepared in order to compare their properties with those of spectroscopically determined intermediates. The kinetics of the dark reaction was used to determine its molecularity and rate constant. The proposed mechanism and the structure of the visible-absorbing intermediate are consistent with observed spectra, isolated photoproducts, and dark-reaction kinetics. In separate experiments the intermediate was mixed with sodium isopropoxide, and the subsequent dark transformations were compared with those in which the ketone itself was photolyzed in the presence of base. Although the structures of the three intermediates in the base reaction were not elucidated, their main spectral features and their sequence in the overall mechanism were clearly determined.

Complexity of dark reactions following irradiation in the photoreduction of benzophenone[2-18] and especially in that of 4,4′-di-*t*-butylbenzophenone[15,19] suggested investigation of another aromatic ketone, di(4-pyridyl) ketone (I). The photochemical transformations of I in isopropyl alcohol were investigated in detail by successive determinations of absorption, emission, excitation, nmr, and esr spectra during irradiation and throughout the subsequent dark period. The reaction kinetics of the intermediate formed on photolysis was determined from uv–visible absorption measurements. Several derivatives of I and of the isolated photoproduct di(4-pyridyl)methanol (II) were synthesized separately. Their properties helped in the characterization of spectroscopically detected intermediates and in the elucidation of the mechanism.



I



II

Results

Consecutive Irradiation. Figure 1 shows gradual changes in the uv absorption spectrum of a degassed 4.0×10^{-4} *M* solution of I in isopropyl alcohol after short exposures to light at 2537 Å. Three clearly defined isosbestic points are observed at 245, 267, and 317 mμ. Progressively upon irradiation an intense red-brown color develops which corresponds to the increase in concentration of a visible-absorbing component with λ_{max} at 438 mμ. The isosbestic points testify to the existence of only two components, I and the colored intermediate (In), throughout our entire irradiation period, which did not exceed 3 min. Concurrent with the disappearance of the main peak of I centered at 282 mμ is the increase not only of the absorption at 438 mμ but also of a shoulder at about 525 mμ and peaks at 257 and 263 mμ.

The same reaction was followed in a sealed quartz nmr tube. Here, 1 ml of a 3% solution of I in isopropyl alcohol was degassed directly in the nmr tube, sealed under vacuum, and irradiated and monitored alternately. The characteristic absorptions of the two equivalent sets of protons of I at δ 7.7 and 8.8 ppm decrease progressively with irradiation and are replaced by new multiplets centered at δ 7.15 and 7.95 ppm. The latter are not those of the hydrol II, which appear as symmetrical doublets at δ 7.1 and 8.1 ppm. Ultimately, either upon long irradiation or following an initial irradiation and long standing, the samples exhibit only absorption of I and its photoproduct II.

Careful examination of the consecutive nmr spectra allowed association of the peaks detected upon initial irradiation at δ 7.15 and 7.95 ppm with the brown-red intermediate In. Actually, the visually observed color intensity paralleled that of these intermediate nmr peaks.

Figure 2 illustrates consecutive changes in the absorption spectrum of a degassed 3.4×10^{-4} *M* solution of I in dilute Me_2CHONa after short exposure to irradiation.

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(1) From work done in partial fulfillment of requirements for the Ph.D. degree at the George Washington University.
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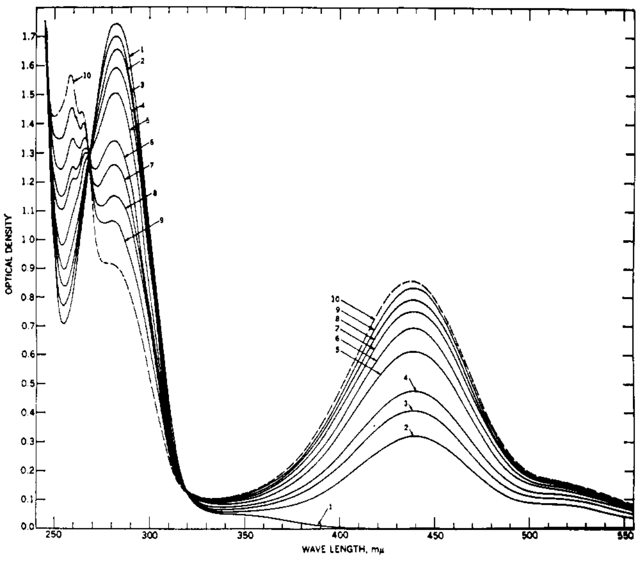


Figure 1. Uv absorption spectrum of a 4.0 × 10^{-4} M solution of I in Me$_2$CHOH in a 1-cm square cell, degassed and sealed, following successive irradiations: (1) before irradiation, (2) after 10 sec of irradiation, (3) after 20 sec, (4) 30 sec, (5) 40 sec, (6) 60 sec, (7) 70 sec, (8) 90 sec, (9) 120 sec, (10) 150 sec.

Again there are three isosbestic points, at 245, 267, and 316 mμ. The absorption band centered at 438 mμ in Figure 1 does not appear in the sample containing isopropoxide. After about 3 min of total irradiation the spectrum was no longer "isosbestic" (Figure 2, curves 8–10).

On addition of 2 drops of concentrated HCl to a dilute solution of I in Me$_2$CHOH, the absorption peaks at 226 and 282 mμ are replaced slowly by two new bands centered at 221 and 259 mμ. After about 10 min, the ketone peak at 282 mμ has virtually vanished. This change corresponds to the quaternization of the pyridyl nitrogen. When such an acidified 10^{-4} M solution is submitted to successive 1-min irradiations, all absorption in the near-uv decreases slowly, mainly because of precipitation of the hydrochloride salt. The only other change was the appearance of an extremely weak broad band at 390 mμ. Throughout 11 min of cumulative irradiation, the concentration of I decreased to less than 20% of the original.

Dark Reaction. Figure 3 displays typical changes in the absorption spectrum of a 4.0 × 10^{-4} M solution of I in Me$_2$CHOH at different intervals in the dark period following an initial 130-sec irradiation. In about 1.5 hr the intense peak at 438 mμ which appeared upon irradiation had virtually vanished.

When an irradiated 4.5 × 10^{-4} M solution of I, which had the characteristic brown color of In, was mixed with concentrated degassed Me$_2$CHONa in isopropyl alcohol, the color vanished with no new significant absorptions appearing in the 280–500-mμ range (Figure 4). Overnight, however, in the dark, a shoulder at 325 mμ developed. Upon additional extensive irradiation, the increased absorption at 325 mμ was supplemented by a new band at 450 mμ and a shoulder at 335 mμ.

Figure 5 shows the changes in the spectrum of a 9.1 × 10^{-4} M degassed solution of I in concentrated sodium isopropoxide upon irradiation and throughout the subsequent dark period. On irradiation two main ab-

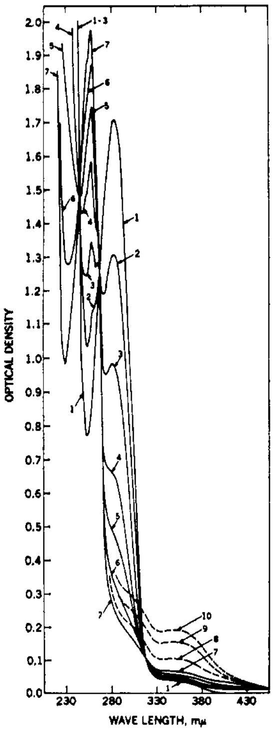


Figure 2. Uv spectrum of a degassed 3.4 × 10^{-4} M solution of I and dilute Me$_2$CHONa in Me$_2$CHOH, following successive irradiations: (1) before irradiation, (2) after 30 sec of irradiation, (3) after 60 sec, (4) 100 sec, (5) 140 sec, (6) 180 sec, (7) 220 sec, (8) 260 sec, (9) 300 sec, (10) 340 sec.

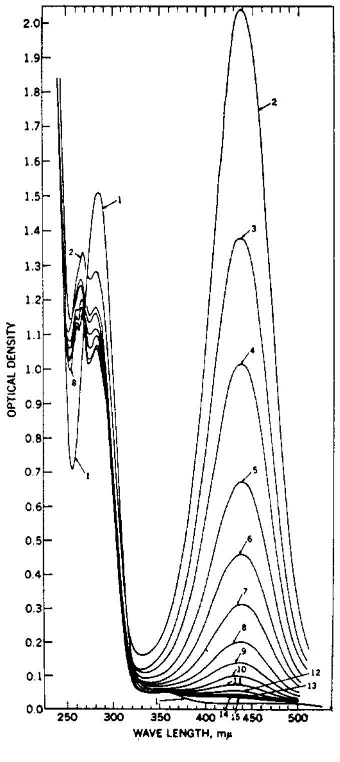


Figure 3. Uv spectrum of a degassed 4.0 × 10^{-4} M solution of I in Me$_2$CHOH, following an initial irradiation: (1) before irradiation, (2) after 130 sec of irradiation, (3) 2 min in the dark after irradiation, (4) 5 min in the dark, (5) 9 min, (6) 13 min, (7) 17 min, (8) 22 min, (9) 27 min, (10) 32 min, (11) 37 min, (12) 44 min, (13) 52 min, (14) 63 min, (15) 77 min.

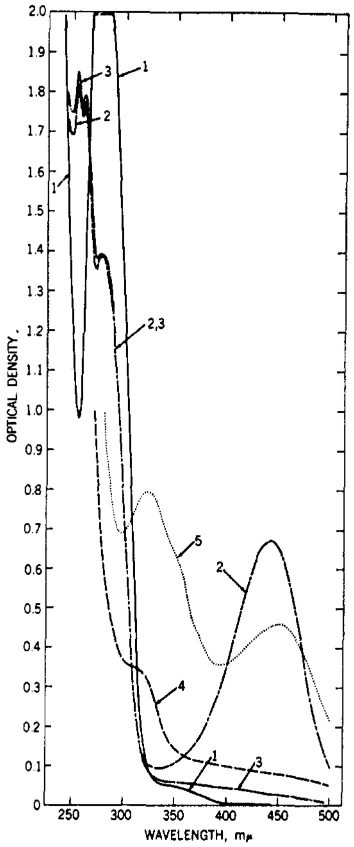


Figure 4. Uv spectrum of a degassed 4.5 × 10^{-4} M solution of I in Me_2CHOH, following initial irradiation and subsequent mixing with Me_2CHONa: (1) before irradiation, (2) after ~2 min of irradiation, (3) immediately after mixing with Me_2CHONa, (4) after 24 hr in dark, (5) following a further 2-hr irradiation.

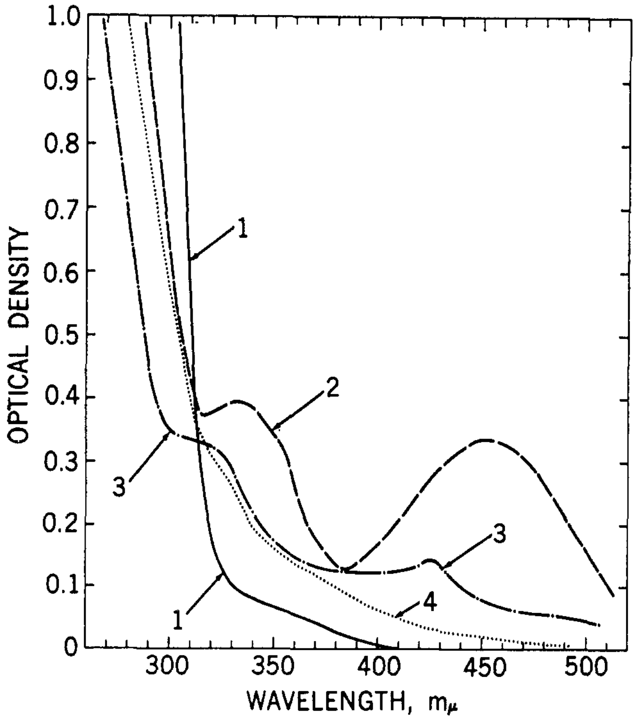


Figure 5. Uv spectrum of a degassed 9.1 × 10^{-4} M solution of I and Me_2CHONa in Me_2CHOH: (1) before irradiation, (2) after 4 min of irradiation, (3) after 6 days in dark and also after 1 month in dark (unchanged), (4) after bubbling O_2 for 30 min and replacing evaporated solvent.

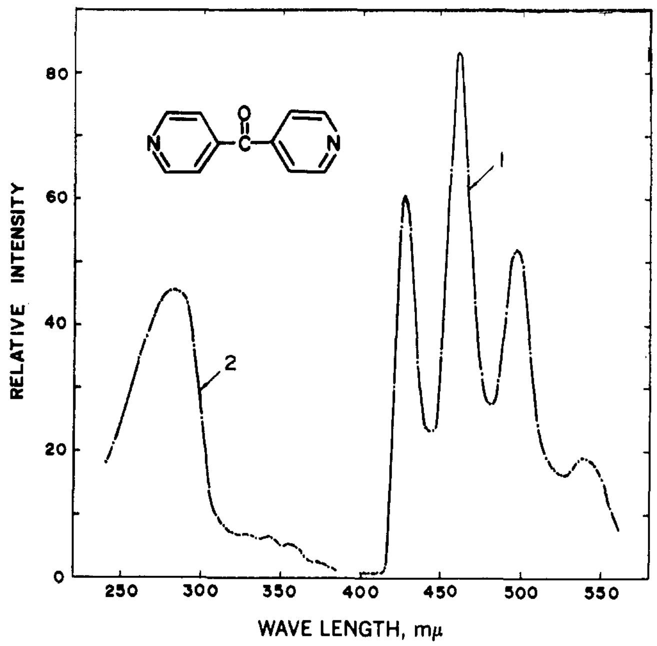


Figure 6. Phosphorescence (1) and excitation (2) spectra of I in isopropyl alcohol glass at 77°K, corrected.

sorption bands appear with λ_{max} at 452 and 335 mμ and a shoulder at 353 mμ. In the dark these peaks decrease slowly over a period of several days to be replaced finally by a broad shoulder at 325 mμ and a visible peak at 430 mμ. The resulting yellow solution emits green fluorescence. The two absorption bands are stable indefinitely in the sealed cell but disappear on exposure to atmospheric oxygen.

Emission and Excitation Spectra. The phosphorescence and phosphorescence–excitation spectra of I shown in Figure 6 closely resemble those of typical aromatic ketones such as benzophenone. That the vibrational structure in both emission and n,π* excitation is characteristic of carbonyl stretching suggests that the lowest triplet is primarily localized in the C–O bond and lies below those of the corresponding n,π* states associated with the pyridyl nitrogens.

When a degassed sample of I in isopropyl alcohol was irradiated briefly at room temperature and frozen immediately, the brown solution, which became red at 77°K, did not exhibit luminescence. Upon further irradiation and moderate periods in the dark at room temperature, the pale yellow solution exhibited a green-yellow fluorescence both in liquid solution and in rigid matrix. This green-yellow emission centered at 470 mμ with excitation maximum at 430 mμ is due to a transitory yellow species formed on photolysis of the hydrol product II. Whenever samples of I were irradiated for extended periods, the green-yellow fluorescence could no longer be detected, the only emission being a very weak long-lived blue phosphorescence characteristic of II (Figures 7 and 8).

Following mixing of I with concentrated Me_2CHONa, the typical ketone phosphorescence at 77°K virtually disappeared without formation of a new luminescence. After 2 min of irradiation at room temperature, these samples exhibited a blue long-lived phosphorescence (Figure 8) and an intense green-yellow fluorescence (Figure 9) which is also easily observable at

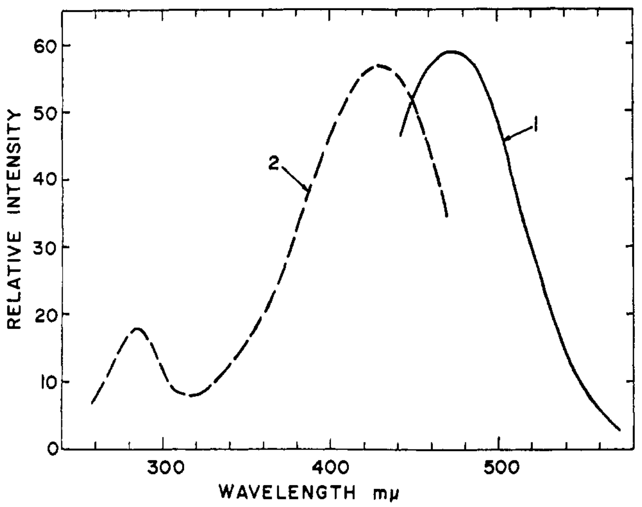


Figure 7. Fluorescence (1) and excitation (2) spectra of the oxygen-sensitive yellow side product formed in low concentration in irradiated solutions of I in Me_2CHOH; this species is actually produced photochemically from hydrol II.

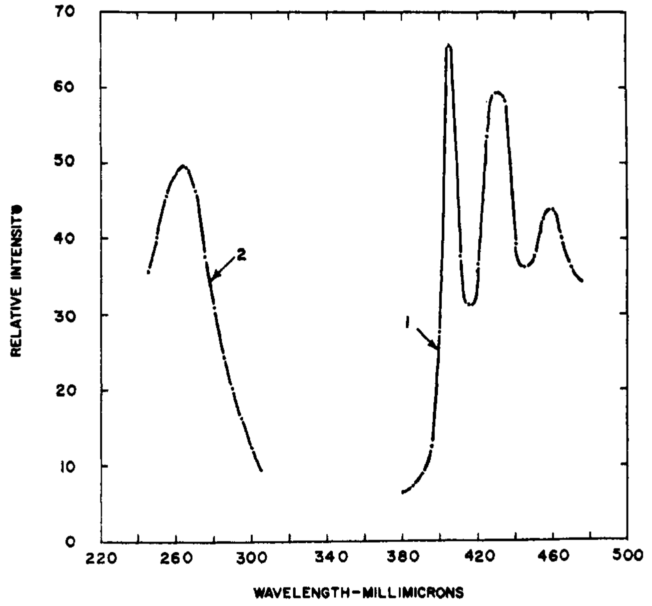


Figure 8. Phosphorescence (1) and excitation (2) spectra of a 10^{-3} *M* solution of I irradiated at room temperature for 2 min in isopropyl alcohol at 77 °K, corrected.

room temperature. The two emissions persisted after extensive irradiation at 25°. The blue solution from nonirradiated I and concentrated Me_2CHONa formed on standing open to air showed only residual ketone phosphorescence; apparently the blue free radical III luminesces neither at 298 °K nor at 77 °K.

The blue ion IV formed from chemically prepared II and concentrated isopropoxide on standing was also nonluminescent; such solutions exhibited only very weak blue phosphorescence with lifetime of several seconds.

A frozen solution of the hydrol monoacetate V showed only very feeble blue-green long-lived phosphorescence similar to that of II.

Esr. On standing open to the air, solutions of I and isopropoxide became blue; these samples gave a strong esr signal. Neither the brown In solution nor the blue

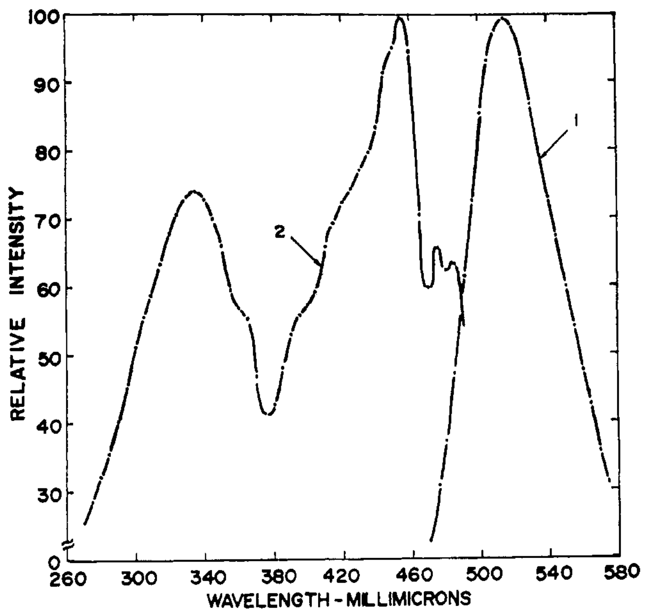
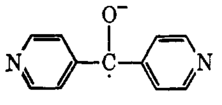
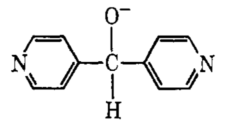


Figure 9. Fluorescence (1) and excitation (2) spectra of irradiated solutions of I and Me_2CHONa, corrected.

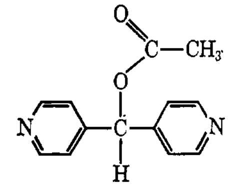
anion IV produced from II and base displayed paramagnetism. Actually, no other solution investigated in the present work gave evidence for free radicals either immediately following irradiation or later during the dark transformations.



III



IV

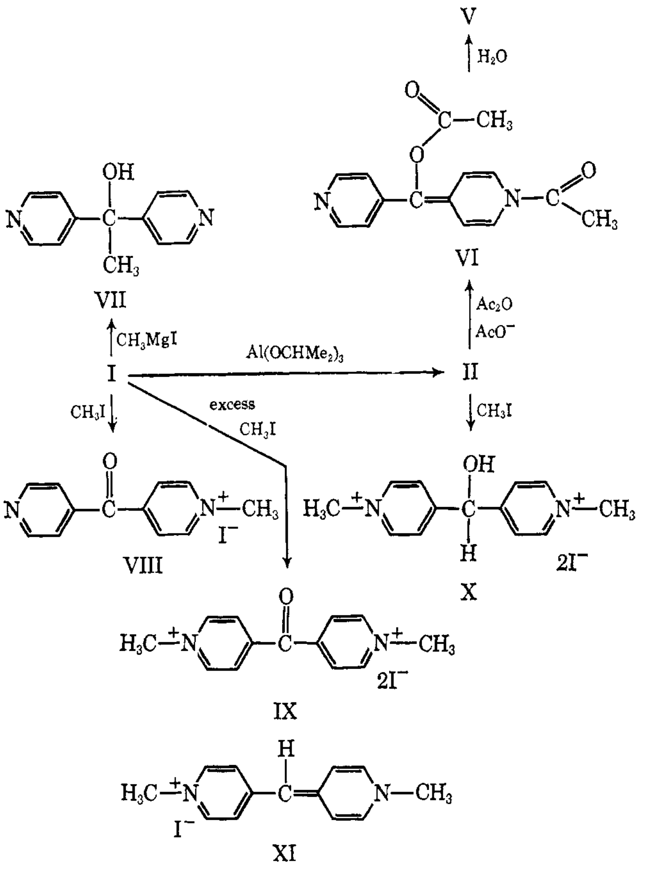


V

Photoproducts. The only product isolated from the photolysis of I in isopropyl alcohol was dipyridylmethanol II. Similarly, the preparative scale irradiation of I in the presence of sodium isopropoxide yielded only hydrol II and blue IV, which proved to have limited stability to air. Except for hydrochloride formation, the photolysis of I in HCl-acidified solutions did not lead to any significant chemical reaction.

During irradiation of I in the absence of oxygen, the solution turns reddish brown at first and changes to persistent light yellow. In the photoreaction in alcoholate solution, the initial blue color becomes green and finally yellow; the green coloration is not due to a separate absorbing species but represents a mixture of the disappearing blue component with its yellow product. A reddish color, developed during photolysis of I in HCl solutions, turned pale yellow on neutralization with NaOH.

Derivatives. Several derivatives of I were prepared chemically in an attempt to establish the identity of the photointermediates and products by comparison of their spectra. Hydrol II was obtained from I by reduction with aluminum isopropoxide. Colorless II was in turn used to prepare blue alcoholate IV, the yellow dimethiodide X, red diacetate VI, and colorless monoacetate V. Colorless dipyridylmethylcarbinol (VII), blue free radical III, yellow methiodide VIII, and orange dimethiodide IX were also obtained from I. In addition, pyridocyanine XI was prepared in solution from 4-benzyl-N-methylpyridinium iodide and base.



Quantum Yield. The photochemical conversion was determined upon completion of the dark reaction by gas chromatographic evaluation of the ratio of I to II. Actinometric measurements on degassed samples gave consistent results in the 0.38–0.42 range.

Photolysis in Isopropyl Alcohol

Mechanism. All spectroscopic observations and the identity of the photoproduct are consistent with the following photoreduction mechanism.

$$\mathrm{Py_2CO\ (S_0)} \xrightarrow{h\nu} \mathrm{Py_2CO\ (S^*)} \xrightarrow{\mathrm{ISC}} \mathrm{Py_2CO\ (^3n,\pi^*)} \qquad (1)$$

$$\mathrm{Py_2CO\ (^3n,\pi^*)} + \mathrm{Me_2CHOH} \longrightarrow \mathrm{Py_2\dot{C}OH} + \mathrm{Me_2\dot{C}OH} \qquad (2)$$

$$\mathrm{Py_2\dot{C}OH} + \mathrm{Me_2\dot{C}OH} \longrightarrow \mathrm{In} \qquad (3)$$

$$\mathrm{In} \xrightarrow{k_D} \mathrm{Py_2CHOH} + \mathrm{Me_2CO} \qquad (4)$$

Following absorption in the singlet manifold of I, the primary photoprocess (1) leads, after efficient intersystem crossing, to formation to the lowest triplet state, which is the n,π* triplet associated with the carbonyl chromophore. The identity of this state as the lowest triplet and reactive state is suggested not only by the phosphorescence spectrum of I, which exhibits characteristic C=O vibrational progression, but also by the fact that heterocyclic nitrogen n,π* and π,π* triplets are not usually capable of hydrogen abstraction, step 2. This second step is required by the overall process and is confirmed by the weak esr signal obtained from frozen samples of I in $\mathrm{Me_2CHOH}$ which have been irradiated extensively at 77°K. Apparently the formation of the red-brown intermediate In is the result of a fast recombination of the dipyridylketyl and dimethylketyl free radicals in the solvent cage, step 3.

The only reasonable alternate possibility for the buildup of a colored intermediate with the properties exhibited by In is recombination of two dipyridylketyl free radicals, analogous to the formation of "isobenzopinacol" proposed by Schenck, *et al.*,[10] for the intermediate in the photoreduction of benzophenone. Presumably, this isobenzopinacol underwent subsequent rearrangement to final product, benzopinacol. However, we consider this alternative less probable than the one in step 3. First, we found no evidence of tetrapyridyl glycol. Second, the dimerization of two dipyridylketyls would require additional diffusion. And, finally, this process does not explain satisfactorily the fate of the dimethylketyl free radicals. That tetramethyl glycol is not formed during photolysis of I in $\mathrm{Me_2CHOH}$ was clearly established by gas chromatography, since no peak at the proper retention time could be detected from the final reaction mixture. An attack of the $\mathrm{Me_2\dot{C}OH}$ on I with formation of $\mathrm{Py_2\dot{C}OH}$ + $\mathrm{Me_2CO}$ and subsequent dimerization of the two dipyridylketyls seems improbable because if the dimethylketyls diffuse out of the solvent cage, they certainly would also dimerize to pinacol and because such mechanistic routes in the analogous photoreduction of benzophenones were ruled out by the kinetics of the dark reaction.[18, 19]

The final step of the above scheme, dark reaction 4, was followed spectrophotometrically by monitoring the decrease in the band centered at 437 mμ (Figure 3). This reaction is unimolecular, as shown by the fact that the reaction proceeds to completion regardless of the extent of I → In initial photoconversion and by the linearity of the kinetic plot. It is not surprising that the product-formation step contrasts with the bimolecular dark reaction of benzophenones, since the end products are also different.

Identity of In. There seems to be no direct way of determining the structure of the colored intermediate In, since it is too unstable and too sensitive to oxidation to isolate and since trapping experiments with active dienes have failed.[20] It remains then to show a plausible structure which is compatible with all observed properties, namely, intense visible absorption, nonluminescence in $\mathrm{Me_2CHOH}$ at both 77°K and 298°K, thermochromicity, sensitivity to oxidation, fast (ionic-like) reaction with sodium isopropoxide, diamagnetism, unimolecular kinetics of the dark reaction, and compatibility with products—dipyridylmethanol and acetone.

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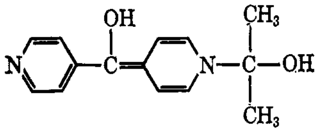
(20) Solutions (100 ml) of 0.5 g of I in isopropyl alcohol were freeze–pump–thaw degassed in a large quartz flask provided with a side reservoir in which the trapping agent was simultaneously degassed. After flame sealing, the ketone solution was irradiated until highly colored and then mixed with the coreactant—freshly cracked cyclopentadiene—or various cyclones. No Diels–Alder adduct was isolated and apparently the progress of the dark reaction, step 4, was unaffected by the presence of the diene.

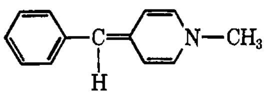
We propose structure XII for In.



XII

In addition to the mechanistic criteria used above, the structure taken for In was based on comparison with spectral properties of a number of derivatives of both ketone I and its photoproduct II (see Table I). The properties listed in Table I tend not only to suggest XII but also to eliminate a number of alternatives.

An intense absorption in the visible without evidence of paramagnetism implies extended conjugation. It is difficult to envision a structure in which the conjugation embraces both pyridyl rings without the quinoid–enol–enolate configuration. Like the quinoid compound diacetate VI and benzylidine derivative XIII, In absorbs intensely in the visible and does not luminesce.

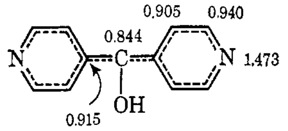


XIII

Both the ionic-like reaction with base and the sensitivity to air oxidation are compatible with an enol configuration.

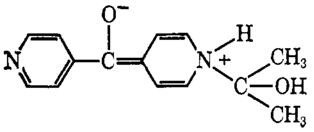
The transitory nmr absorption between 7 and 8 ppm attributed to the intermediate resembles that of the diacetate VI in acetic anhydride.

Coupling of the $Me_2\dot{C}OH$ radical in the 4 position of $Py_2\dot{C}OH$ seems reasonable in view of similar *para* attacks on triphenylmethyl[21] and on benzophenone,[22] as well as the reaction between cumyl and *t*-butyl,[23] all of which form quinoid adducts. In addition, a Hückel calculation of $Py_2\dot{C}OH$ (XIV) (13 π electrons) gives the electron densities shown in XIV.[24] Since the $Me_2\dot{C}OH$ radical is expected to behave as an electrophilic moiety,[23,25] it seems natural for coupling with its cage partner $Py_2\dot{C}OH$ to occur in the 4 position, where the electron density is significantly higher than on any carbon atom. Furthermore, N-coupling is favored by the higher time-averaged probability of finding the unpaired electron of $Py_2\dot{C}OH$ on the heteroatom compared to that of the 4 position of the analogous carbocyclic diphenylketyls formed in the photoreduction of benzophenones.

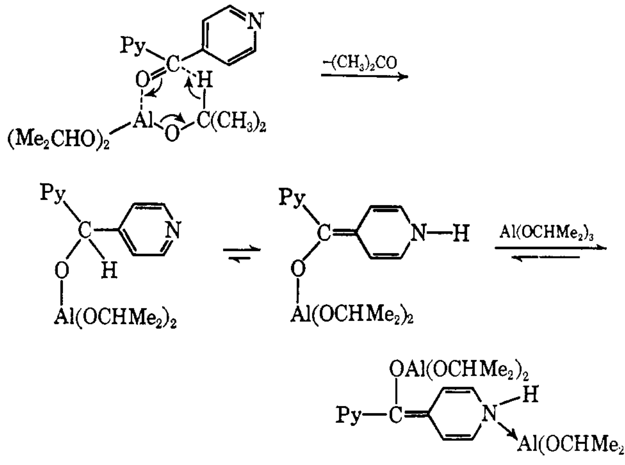


XIV

The thermochromicity of In (brown at 298°K with λ_{max} 437 mμ and red at 77°K with λ_{max} ~550 mμ) could be explained in a natural way by the temperature dependence of the tautomerism. Zwitterion structures such as XV have been documented for pyridones and other pyridine derivatives in neutral solution.[26–29] Prototropism from the neutral to the dipolar species is known to take place *via* the solvent.[30] The identification of the red species of In at low temperature agrees with the structures of the two red derivatives listed in Table I, namely, the diacetate VI (λ_{max} 547 mμ) and the reduction complex obtained from excess aluminum isopropoxide and I (λ_{max} 565 mμ). This latter complex, like the diacetate VI and zwitterion XV, is presumably enol–quinoid structure XVI. The bathochromic shift observed on cooling brown In would be predicted by elementary theoretical treatment of the two tautomers XII and XV. Since the absorption band in the visible is intense ($\epsilon > 10^4$), it can be attributed only to a $\pi \rightarrow \pi^*$ or an intramolecular charge-transfer (CT) transition. A Hückel calculation[24] on the zwitterion XV (13 π electrons) predicts $\Delta E = 0.58\beta_{CC}$ for the lowest $\pi \rightarrow \pi^*$ transition; whereas, for enol XII, $\Delta E = 0.76\beta_{CC}$ or $\Delta E = 0.74\beta_{CC}$, depending on whether the nitrogen in the quinoid ring is included in the delocalization (13 π electrons) or not (12 π electrons). Thus, the red shift is consistent with the expected absorption maxima of the assumed structures for In. If these bands are due to a CT transition, the shift would be difficult to predict but would be consistent with that reported for a merocyanine dye in which again the quinoid structure absorbed at shorter wavelengths than the corresponding zwitterion.[31]



XV



XVI

In Absorption. The absorption spectrum of the brown intermediate shown in Figure 10 was calculated

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[24] We used $\alpha_N = \alpha_C + 1.5\beta_{CC}$, $\alpha_{C3} = \alpha_C + 0.3\beta_{CC}$, and $\beta_{CN} = \beta_{CC}$, suggested, for example, in A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, New York, N. Y., 1961, Chapter 5.

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[27] R. Adams and V. V. Jones, *J. Amer. Chem. Soc.*, **69**, 1803 (1947).

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[29] S. A. Harris, *ibid.*, **63**, 3363 (1941).

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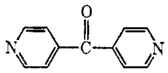
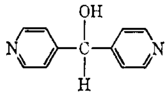
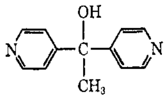
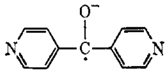
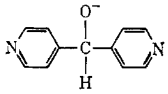
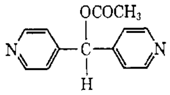
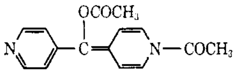
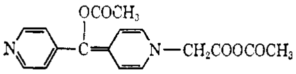
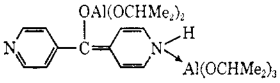
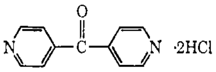
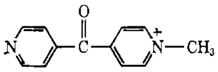
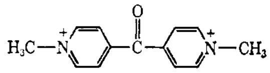
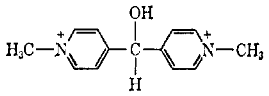
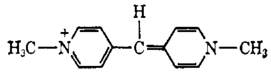
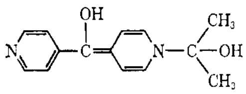
Table I. Properties of Derivatives and Intermediates.

Compound	Visible–uv absorption λ_{max}, mμ (ϵ)	Comments
	228 (14,600) 280 (4180)	Colorless, blue phosphorescence, λ_{max} 425, 460, 495, and 530 mμ (carbonyl vibrational progression)
	257 (5400) 252 (sh) (5070) 263 (sh) (4060)	Colorless, long-lived weak blue phosphorescence, λ_{max} 405, 432, and 460 mμ
	258 (4200) 251 (sh) (3810) 263 (sh) (3120)	Colorless, colorless in acetic anhydride
	672	Deep blue, paramagnetic species formed from I in concentrated isopropoxide in air, air sensitive
	685	Blue, diamagnetic anion from hydrol II and concentrated isopropoxide, air sensitive
	256 (5300) 265 (sh) (5000)	Colorless, no fluorescence or phosphorescence
	547 (10,800) 520 (sh) (6020)	Blood red, not isolated, no fluorescence at room temperature
	543 500 (sh)	Blood red, not isolated, obtained on photolysis of I in acetic anhydride, assumed structure analogous to In
	565 525 (sh)	Purple-red, not isolated, product from aluminum isopropoxide reduction of I before hydrolysis, assumed structure
	221 259	Colorless
 I$^-$	227 (31,500) 258 (8690) 387 (20)	Yellow
 2I$^-$	440 (sh)	Brick red
 2I$^-$	226 (32,500) 258 (7500) 536 (2420)	Yellow-orange, red-purple solution in Me$_2$SO
 I$^-$	502.5 (29,000)	Yellow-brown
 (In)	447 (10,300) 260 (4300)	Red-brown, proposed structure for In, not isolated, thermochromic: red at 77°K, nonluminescent
In$_1$	452 335	Low extinction coefficient, 280–500 mμ, formed in basic solution upon irradiation of I, air sensitive
In$_2$	353	Colorless, photoproduct of hydrol II
In$_3$	430 325	Yellow, photostable, green fluorescence, λ_{max} = 512 mμ, air sensitive

from curves 1 and 2 in Figure 3 by the expression $\epsilon_{In} = (a - \epsilon_{Py_2CO}[Py_2CO])/([Py_2CO]_0 - [Py_2CO])$, where ϵ is the molar extinction coefficient, a is the absorbance of the solution, and the subscript zero refers to the initial concentration. [Py$_2$CO] was estimated from the decrease in the peak near 280 mμ where the extinction coefficient

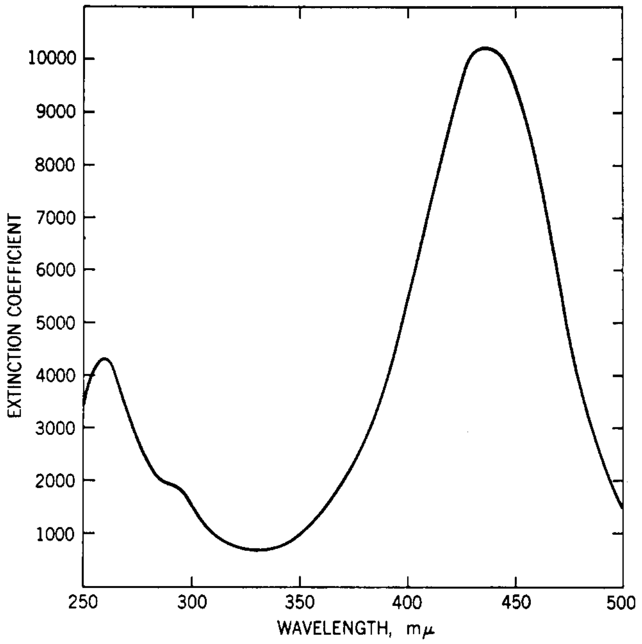


Figure 10. Calculated extinction coefficients for intermediate In.

of In is less than half that of I. The expression used for calculation of ϵ_{In} is easily derived for a two-component mixture such as that formed upon irradiation. Since the extent of photolysis in Figure 3 was kept well within the isosbestic range, the existence of additional species is precluded.

Kinetics. Changes in the uv-visible absorption of a 4.0×10^{-4} *M* solution of I in $\mathrm{Me_2CHOH}$, irradiated to 50% conversion, were followed throughout the subsequent dark period. Since only In absorbs at 447 mμ, it is easy to determine its concentration at different times from the curves in Figure 3. The only rate expression agreeing with experimentally observed decrease in In concentration was $-d[\mathrm{In}]/dt = k_{\mathrm{D}}[\mathrm{In}]$, or its integrated form $\ln ([\mathrm{In}]_0/[\mathrm{In}]) = k_{\mathrm{D}}t$, where $t = 0$ is the time immediately after irradiation. The semilog plot of [In] *vs.* *t*, shown in Figure 11, gives an almost perfect straight line with slope $k_{\mathrm{D}} = 9.5 \times 10^{-2}$ sec^{-1}. The unimolecularity of this reaction contrasts with the second-order dark reaction of benzophenones and was used to confirm the product formation above (see Mechanism).

Reaction with Isopropoxide

Reactions of the initial ketone I, its photointermediate In, and the product II with sodium isopropoxide were of interest in view of the complexity of the analogous reactions in benzophenones.[19] In addition, they were expected to contribute toward elucidation of both the identity of In and the overall mechanism in neutral solution.[32]

Anion Radical of I. The deep blue solutions ($\lambda_{\max}$ 672 mμ) formed upon slow diffusion of atmospheric oxygen into concentrated $\mathrm{Me_2CHONa}$ solutions of I gave an esr spectrum indistinguishable from that reported for the free radical obtained on electrochemical reduction of I in acetonitrile.[33] The anion free radical III is stable for several days in undisturbed solution but its blue color disappears on brief shaking with air. A similar but fainter color ($\lambda_{\max}$ 685 mμ) developed slowly in concentrated isopropoxide solutions of dipyridylmethanol (II). This visible absorption probably corresponds to alkoxide ion IV, since the solutions did not display paramagnetism. It should be pointed out that small amounts of free radical III were formed during degassing of samples of I in base as indicated by the blue tint and the weak visible absorption band at 672 mμ. However, the concentrations of III were so small as not to interfere with subsequent measurements upon photolysis and in the dark.

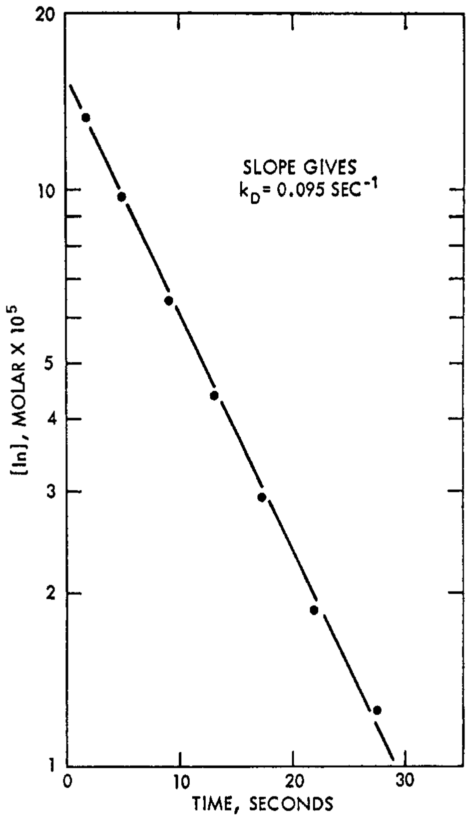


Figure 11. Kinetics of the dark reaction.

Photolysis in Dilute Base. Changes in the uv-visible absorption spectrum of repeatedly irradiated dilute samples of I indicate the presence of only unreacted I ($\lambda_{\max}$ 282 mμ) and its photoproduct II ($\lambda_{\max}$ 258 mμ) throughout the isosbestic range (Figure 2, curves 2–7). On prolonged irradiation, however, another photointermediate, designated $\mathrm{In_2}$ (see below), absorbing in a band centered at 353 mμ, is formed (curves 8–10). The band decreases slowly in the dark and disappears in about 1–2 days. We observed that $\mathrm{In_2}$ builds up only when the concentration of hydrol II has increased significantly and only in the presence of light. Additional experiments in which degassed hydrol II in isopropoxide solution was exposed to 254-mμ exciting light proved that $\mathrm{In_2}$ is indeed a photoproduct of II in basic solution. It is interesting to note that this photolysis takes place with a high quantum yield and generates spectroscopically detectable intermediates of moderate lifetime, whose further dark reactions can be studied by monitoring their absorption and emission. Detailed results will be reported elsewhere. Nonetheless, since $\mathrm{In_2}$ was formed only as a minor side product in most

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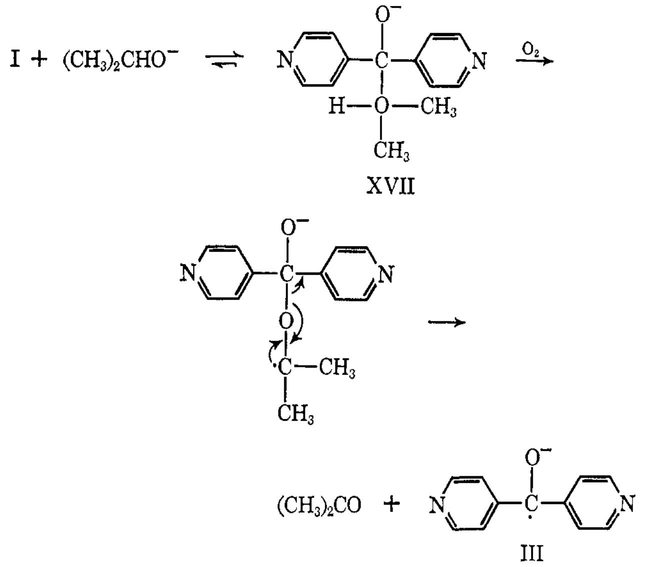
(32) Besides, fooling around with all those colored solutions was fun.
(33) J. C. M. Henning, *J. Chem. Phys.*, **44**, 2139 (1966).

photoreactions of the ketone I, its presence did not interfere with the major transformations.

Reaction in Concentrated Base. On mixing a solution of I with concentrated Me$_2$CHONa an equilibrium is established, probably I $\rightleftharpoons$ XVII. Depending on the alkoxide concentration, the equilibrium may be almost totally displaced toward formation of XVII. This is shown not only by the decrease in the $\pi \rightarrow \pi^*$ band at 282 mμ with concomitant increase in absorption in the 245–270-mμ region of the uv spectrum but especially by the virtually complete disappearance of the characteristic carbonyl phosphorescence in degassed solution at 77°K. Another equilibrium, I + (CH$_3$)$_2$CHO$^-$ $\rightleftharpoons$ IV + (CH$_3$)$_2$CO, cannot be ruled out. However, this alternative, requiring hydride ion abstraction, seems less likely than the alkoxide addition given above. This is supported by the fact that no blue coloration, expected for IV, appeared on mixing I and isopropoxide in the absence of oxygen and that no acetone phosphorescence was detected in deaerated frozen samples.



XVII

III

Photolysis in Concentrated Base. All spectroscopic observations and product isolation from irradiation of isopropoxide solutions of I agree with the following mechanism.

$$\begin{tikzcd} \mathrm{I} + (\mathrm{CH_3})_2\mathrm{CHO}^- \arrow[r, "h\nu"] \arrow[d, shift left] & \mathrm{In}_1\ (+\ \mathrm{In}_2) \\ \mathrm{XVII} \arrow[u, shift left] & \end{tikzcd} \qquad (5)$$

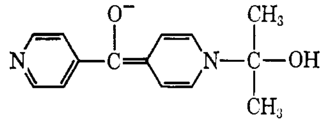
$$\mathrm{In}_1 \xrightarrow[\text{(days)}]{\text{dark}} \mathrm{In}_3 \qquad (6)$$

The absorption bands at 335 and 452 mμ which appeared on irradiation are attributed to species labeled In$_1$, whereas the barely discernible shoulder at 353 mμ is most probably caused by the formation of small amounts of In$_2$. In the dark the two peaks associated with In$_1$ are replaced over a period of several days with two other main bands at 325 and 430 mμ, which are attributed to a final photoproduct In$_3$. This species is stable indefinitely both in the dark and upon further extensive irradiation. It is also responsible for the intense blue-green fluorescence shown in Figure 9. That the two peaks at 325 and 430 mμ belong to the fluorescent In$_3$ is proven by the excitation spectrum, which, despite all inaccuracies introduced by sample geometry and correction factors, strongly resembles the absorption spectrum. The yellow color disappears rapidly upon admission of air into the sample cell. Therefore, In$_3$, like In$_1$, is oxygen sensitive.

For samples in which the solutions of I and the base have been carefully degassed separately and mixed only after a portion of I was converted photolytically to the brown-red In (Figure 4), the visible absorption band at 437 mμ disappeared instantaneously on mixing, with the formation of a weakly absorbing species in the 280–500-mμ region, presumably In$_1$. On standing in the dark overnight the characteristic absorption of In$_3$ began to appear. On prolonged irradiation of these samples, the presence of In$_3$ was clearly shown by its absorption and fluorescence.

That the fast initial reaction of In with base does not involve either the unreacted ketone I present or the small amounts of product hydrol II is demonstrated by the equal absorption of curves 2 and 3 in Figure 4 at 282 (ketone) and 257, 263 mμ (dipyridylmethanol).

Identity of In$_1$ and In$_3$. In view of the enol structure XII proposed for In it seems reasonable to assume enolate configuration XVIII for the intermediate formed on irradiation of ketone I in base. Its visible absorption, diamagnetism, air sensitivity, and fast (ionic-like) production from In tend to substantiate this structure. In addition, one can easily visualize natural pathways for conversion of XVIII to isolated photoproduct II. However, since the chemistry of pyridine derivatives, in which tautomerism is possible, is exceedingly complex, the evidence for the proposed structure of In$_1$ remains tentative. For the same reason and the fact that there is no resemblance between the spectra of In$_3$ and of derivatives of I and II, we refrain from speculating on the structure of In$_3$. Aside from its identity for which additional analytical work is required, the absorption and emission spectra of the intermediates, as well as the consecutive steps in the overall mechanism, are clearly defined.



XVIII

Experimental Section

Di(4-pyridyl) ketone was prepared by a procedure similar to that of Wibaut and Heeringa,[34] modified for consistently improved yields. Spectrograde isopropyl alcohol (Fisher) was used without further purification. Sodium isopropoxide solutions were freshly prepared from metallic sodium and the alcohol. Solutions of I were degassed by repeated freeze–pump–thaw cycles in 1-cm absorption cells provided with side reservoirs and flame-sealed under vacuum.[19] Irradiations were carried out with a 9-W shortwave hand lamp, Model UVS-11 (Ultraviolet Products), for all spectroscopic work. Preparative-scale runs were made under nitrogen with a Hanovia 450-W Hg-arc lamp with a Corex-sleeve filter. For actinometric measurements, a Bausch and Lomb high-intensity monochromater, Model 5, was used in conjunction with the high-pressure Hg source. The ferrioxalate actinometer of Hatchard and Parker[35] was employed to monitor light intensities. The conversions in these measurements were evaluated by gas chromatography

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[34] J. P. Wibaut and L. G. Heeringa, *Rec. Trav. Chim. Pays-Bas*, **74**, 1003 (1955).

[35] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. Ser. A*, **235**, 518 (1956).

after completion of the dark reaction. Uv-visible absorption spectra were recorded on the Cary 14RI spectrophotometer in double-beam mode. Since the dark reaction following irradiation of I was fast compared with that of benzophenone and its alkyl derivatives, the changes in the absorption spectra in the dark were monitored more frequently and with shorter scan time. For determination of emission and excitation spectra, the samples were degassed in sealable quartz tubes which could be lowered into the cold-finger dewar of the Aminco-Bowman spectrophotofluorimeter. Nmr spectra were recorded on a Hitachi Perkin-Elmer nmr spectrometer, Model R-20, with internal Me_4Si standard. Mass spectra were run on a Perkin-Elmer 270GC mass spectrograph, and infrared spectra were taken on a Perkin-Elmer 221 infrared spectrometer.

Di(4-pyridyl) Ketone (I). To freshly prepared *n*-butyllithium (20.4 g, 0.32 mol) in 200 ml of anhydrous ether cooled to −75° was added dropwise 51 g (0.32 mol) of 4-bromopyridine in 200 ml of anhydrous ether at temperatures no higher than −40°, and the brownish suspension was stirred for an additional 15 min at −75°. To the resulting mixture, 33.3 g (0.32 mol) of 4-cyanopyridine in 400 ml of dry tetrahydrofuran was added dropwise over a 30–40-min period. The orange-red mixture was stirred for another 30–40 min at −75°, after which the temperature was gradually allowed to rise to −20°. Following hydrolysis with 300 ml of water, the ether layer was extracted with five 60-ml portions of 10% H_2SO_4. The combined water layer and acid extracts were heated to remove residual ether, decolorized with activated charcoal, made basic with a potassium hydroxide solution, extracted with ten 50-ml portions of chloroform, dried over magnesium sulfate, and evaporated. The orange-white residue gave white crystals, mp 141–141.5°, upon recrystallization from 85% ligroin–15% pyridine: yield, 19.6 g (34%); uv (Me_2CO) λ_{max}, mμ (ϵ), 228 (42,000), 280 (12,000); ir ν (CCl_4) 1667 cm^{-1} (C=O); nmr (CS_2) δ 8.75 (4 H, complex doublet, 2,2′,6,6′ pyridyl H's), 7.50 ppm (4 H, complex doublet, 3,3′,5,5′ pyridyl H's).

Anal. Calcd for $C_{11}H_8N_2O$: C, 71.69; H, 4.40; mol wt, 184. Found: C, 71.79; H, 4.62; mol wt, 196.

Photolysis of I. I (0.2 g, 1.1 mmol) in 15 ml of isopropyl alcohol was irradiated in a quartz cell for 2 hr while oxygen-free nitrogen was bubbled through the solution. The solid residue obtained upon vacuum removal of solvent was stirred mechanically with 25 ml of ether and the remaining solid recrystallized from *p*-dioxane at low temperature, yielding 80% colorless crystals. Melting point, ir spectrum, nmr spectrum, and elemental analysis agree with those of chemically prepared II.

When 0.2 g of I in 15 ml of concentrated Me_2CHONa solution was irradiated similarly for 2 hr, the blue residue obtained on solvent removal turned yellow on exposure to air. Addition of 5 ml of water separated a small amount of di(4-pyridyl)methanol (II). The water extract was neutralized with dilute HCl and evaporated under vacuum. Column chromatography of the residue on silica gel eluted with isopropyl alcohol yielded only the hydrol II and unreacted I. The conversion was 70%.

A mixture of 0.2 g (4.1 mmol) of I, 15 ml of isopropyl alcohol, and 0.1 ml of concentrated hydrochloric acid was irradiated for 2 hr. During photolysis a red color developed and a small amount of precipitate formed, which was found to be the hydrochloride of I. Following solvent evaporation, the reddish residue was dissolved in water, neutralized with dilute NaOH, and evaporated to dryness. Column chromatography on silica gel (Me_2CHOH) resulted in 85% recovery of I.

Di(4-pyridyl)methanol (II). To a solution of 3.0 g (16 mmol) of I in 100 ml of hot Me_2CHOH was added 50 ml of 1 *M* freshly prepared aluminum isopropoxide. On heating, the stirred mixture became first pink, then deep red. Several hours later, after no acetone was detected in the distillate, the solvent was removed in a rotary evaporator. The purple-blue residue was then hydrolyzed and suction filtered. Evaporation of the filtrate gave 1.4 g (7.5 mmol) of II, and an additional 0.5 g (2.7 mmol) was obtained by Soxhlet extraction of the white solid from hydrolysis: white needles (benzene), mp 184–186°; uv λ_{max}, mμ (ϵ), 258 (5400); ir ν (KBr) 3040 (C–OH), 2824 cm^{-1} (O–C–H); nmr (Me_2SO-d_6) δ 8.45 (4 H, complex doublet, 2,2′,6,6′ pyridyl H's), 7.32 (4 H, complex doublet, 3,3′,5,5′ pyridyl H's), 5.68 (1 H, doublet, OH), 6.29 ppm (1 H, doublet, CH).

Anal. Calcd for $C_{11}H_{10}N_2O$: C, 70.92; H, 5.42; mol wt, 186.1. Found: C, 70.65; H, 5.56; mol wt, 186.

I and II with Isopropoxide. When crystals of either I or II were covered with a concentrated sodium isopropoxide solution, a blue coloration developed slowly starting at the solution–crystal interface and proceeding toward the surface of the solution. On shaking in air, the blue color disappeared immediately but was regenerated on standing. This process could be repeated several times before the blue color failed to redevelop. Whereas ketone I requires traces of oxygen to turn blue, hydrol II does not. The esr spectrum of dilute blue solution of I in base was recorded on a Varian Model 4500 epr spectrometer.

Hydrol Monoacetate V. Upon treatment of 1.0 g (5.4 mmol) of II with 1.0 g (12.1 mmol) of sodium acetate in 25 ml of acetic anhydride a red solution formed immediately. The mixture was allowed to stand overnight with stirring and was hydrolyzed by addition of 100 ml of water with gentle warming. The resulting yellowish solution was then neutralized with sodium carbonate and extracted several times with chloroform. The total $CHCl_3$ extract (400 ml) was dried over magnesium sulfate, filtered, and vacuum evaporated. Orange crystals formed from the oil upon addition of *n*-heptane were recrystallized from an ethanol–heptane mixture to yield 0.3 g (1.3 mmol, 24%) of colorless crystals: mp 82–83°; uv λ_{max}, mμ (ϵ), 256 (5300); ir ν (KBr) 1735 (C=O), 1235 cm^{-1} (C—O—C); nmr (CCl_4) δ 8.45 (4 H, complex doublet, 2,2′,6,6′ pyridyl H's), 7.08 (4 H, complex doublet, 3,3′,5,5′ pyridyl H's), 6.65 (1 H, singlet, O—C—H), 2.13 ppm (3 H, singlet, $COCH_3$).

Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.42; H, 5.26; mol wt, 228. Found: C, 68.40; H, 5.58; mol wt, 225 (osmometer).

Diacetate VI. The diacetate was prepared only in solution by dissolving either hydrol II or monoacetate V in acetic anhydride to form a blood red solution. Attempts to isolate VI were unsuccessful: uv (Ac_2O) λ_{max}, mμ (ϵ), 547 (10,800); nmr (Ac_2O, scan below 5.0 ppm only) δ 8.10 (4 H, broad singlet), 7.00 (4 H, doublet), 6.32 ppm (1 H, singlet). Structure VI must be regarded as incompletely defined, since the quaternization of the remaining nitrogen with acetate has not yet been ruled out.

2,2-Di-4-pyridylethanol (VII). CH_3I (7 ml) was added slowly to a suspension of 3.64 g (0.15 g-atom) of Mg in 100 ml of anhydrous ether with cooling to maintain gentle reflux. After 4 hr of additional reflux, 1.84 g (10.0 mmol) of I in 300 ml of tetrahydrofuran was added and the reddish mixture refluxed for another hour. The solution was hydrolyzed with saturated NH_4Cl solution and the aqueous layer was repeatedly extracted with a total of 300 ml $CHCl_3$. The combined ether and chloroform extracts were dried over $MgSO_4$ and evaporated to dryness at room temperature. The residue was extracted with hot benzene, from which VII crystallized: yield 0.6 g (3 mmol, 33%); mp 174–175°; mol wt, 200 (mass spectroscopy) (calcd, 200); uv (Me_2CHOH), λ_{max}, mμ (ϵ), 258 (4200); ir ν (KBr) 3210 cm^{-1} (OH); nmr (Me_2SO-d_6) δ 8.35 (4 H, doublet 2,2′,6,6′ pyridyl H's), 7.31 (4 H, complex doublet, 3,3′,5,5′ pyridyl H's), 6.09 (1 H, singlet, OH), 2.80 ppm (3 H, singlet, CH_3).

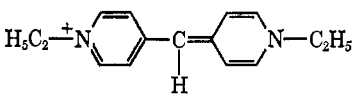
Di(4-pyridyl) Ketone Monomethiodide (VIII). To a suspension of 0.4 g (2.2 mmol) of I in 5 ml of methyl ethyl ketone was added 1.5 ml of CH_3I. The reddish solution was warmed gently for 0.5 hr. The brown-red crystals which formed were filtered and washed with $CHCl_3$: yield 0.4 g (1.2 mmol, 55%); mp 175–177° dec; uv (H_2O) λ_{max} (ϵ) 258 (8690), 227 (31,500), 387 (br) (20); ir ν (KBr) 1680 cm^{-1} (C=O); nmr (Me_2SO-d_6) δ 9.00 (2 H, doublet, 2,6 pyridinium H's), 8.65 (2 H, complex doublet, 3,5 pyridinium H's), 8.15 (2 H, doublet, 2′,6′ pyridyl H's), 7.50 (2 H, complex doublet, 3′,5′ pyridyl H's), 4.30 ppm (3 H, singlet, N—CH_3).

Anal. Calcd for $C_{12}H_{11}N_2OI$: C, 44.17; H, 3.37. Found: C, 43.87; H, 3.16.

Di(4-pyridyl) Ketone Dimethiodide (IX). I (0.5 g, 2.7 mmol) in 100 ml of methyl ethyl ketone was added dropwise into a refluxing solution of 30 ml of CH_3I in 50 ml of methyl ethyl ketone. After 3–4 hr of refluxing, orange-red crystals separated from the reddish solution. Additional crystals were obtained on evaporation of the solution. The red-orange crystals were washed with acetone and dried: yield 1.5 g (1.1 mmol, 41%); mp 246–248°; ir ν (KBr) 1694 cm^{-1} (C=O); nmr (Me_2SO-d_6) δ 9.30 (4 H, doublet, 2,2′,6,6′ pyridinium H's), 8.35 (4 H, doublet, 3,3′,5,5′ pyridinium H's), 4.50 ppm (6 H, singlet, N–CH_3).

Di(4-pyridyl)methanol Dimethiodide (X). In 50 ml of hot methyl ethyl ketone was dissolved I (0.3 g, 1.6 mmol). Excess CH_3I (10 ml) in 10 ml of methyl ethyl ketone was added dropwise, in a nitrogen atmosphere. Upon refluxing the pinkish solution overnight, yellow-orange crystals appeared. These were filtered and washed with methyl ethyl ketone: yield 0.5 g (1.1 mmol, 69%); mp 199–200° dec, black; uv (H_2O) λ_{max} (ϵ) 258 (7500), 226 (32,500), 536 (2420, in Me_2SO); ir ν (KBr) 3170 cm^{-1} (OH); nmr (Me_2SO-d_6) δ 9.00 (4 H, doublet, 2,2′,6,6′ pyridinium H's), 8.25 (4 H, doublet, 3,3′,5,5′ pyridinium H's), 6.52 (1 H, singlet, O–C–H), 4.35 ppm (6 H, singlet, N–CH_3), OH proton missing because of ionization.

Pyridocyanine XI. 4-Benzylpyridine methiodide was prepared by the method of Koenigs, *et al.*[36] This methiodide (3 g) was treated with 25 ml of concentrated aqueous NaOH in the presence of ether. On shaking, the ether layer became orange-red. A portion of the ether extract was examined for visible absorption. The identity of pyridocyanines XI and XIX was established by Sprague and Brooker,[37] and their properties are included in Table I.


XIX

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Structure and Conformational Analysis of Coordination Complexes. The αα Isomer of Chlorotetraethylenepentaminecobalt(III)

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Abstract: A procedure for the quantitative conformational analysis of metal complexes is elaborated and applied to the αα isomer of the chlorotetraencobalt(III) ion (tetraen = 1,4,7,10,13-pentaazatridecane). The crystal structure of this ion as the chloride perchlorate salt was determined. The unit cell is monoclinic, space group $P2_1/c$, with a = 9.85 (1), b = 13.80 (1), c = 13.91 (1) Å, and β = 119.3 (1)°. The central secondary nitrogen of the ligand is coordinated *trans* to the chloro group. The remaining nitrogen atoms coordinate so that the ligand is attached to three octahedral faces which share a common vertex at the central secondary nitrogen. The complex ion has an approximate mirror symmetry which is destroyed in detail by an unexpected envelope conformation of a chelate ring having a primary nitrogen atom. Energy minimization calculations have shown that this is not the lowest energy conformation to be expected in the gas phase, and close contacts in the crystal confirm that it is due to crystal packing. Where these particular contacts are absent, the computed geometry agrees with that observed to within several standard deviations. The lattice chloride ion forms three hydrogen bonds to hydrogen atoms of both primary amino groups and the central secondary amino group of the same cation. This trigonal interaction has been postulated for anion to complex ion pairs in solution, but has not been previously detected in the solid state.

By consideration of a few nonbonded interactions, Corey and Bailar[1] were able to predict that metal complexes with flexible rings were able to adopt preferred conformations. These studies yielded an energy difference between conformations, but since they assumed a rigid structure they are unable to predict detailed molecular geometry. Considerable success has recently been obtained with more complete force fields in organic[2-4] and polymer[5] molecules using efficient energy search and minimization techniques. These studies have demonstrated the value of the quantitative approach for hydrocarbon, heterocyclic, and biopolymer molecules in the reliable prediction of their molecular geometry, thermodynamic properties, and vibrational spectra.

One of these procedures[3] has been applied to the molecular structures of three isomeric cobalt complexes of 1,4,7,10,13-pentaazatridecane (tetraethylenepentamine ≡ tetraen) of the type $[Co(tetraen)Cl]^{2+}$. It was hoped that the very unusual conformational features of these complexes could be traced to an intra- or intermolecular source and that accurate "gas state" geometries and energy differences could be calculated for these kinds of compounds. The results of a less general quantitative procedure for carbon- and nitrogen-substituted ethylenediamine complexes of the type $Co(NH_3)_4en$ have recently appeared.[6] In this procedure the strain energy of the complex is explored as a function of selected and independent geometric variables one at a time. A partial energy surface of the molecule is found from which the minima are deduced. The results described below were obtained by minimization of the strain energy allowing the atomic Cartesian coordinates to vary simultaneously. This method

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