Importance of Acidity on an Energetically Unfavorable Electron-Transfer Reaction-An Extension of the Rehm-Weller Equation. Photoreaction of Triplet 2,4-Pyridinedicarbonitrile with 2-Propanol

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Abstract: An electron spin resonance study of the radical formed when 2,4-pyridinedicarbonitrile (1) is irradiated in the cavity of an ESR spectrometer has been done and the values of the π -spin populations on the ring atoms were determined from the measured proton and nitrogen couplings. Radicals were generated by in situ photolysis of deaerated solutions of 1. The rate of radical formation was measured in acetonitrile at 33 °C with varying amounts of 2-propanol, water, and hydrochloric acid. Quenching and photosensitization studies show the triplet state of 1 to be the photoreactive state. ΔG_{et} values calculated by the Rehm-Weller equation were found to be endoergic when either the T_1 or the T_2 state of 1 is involved. Evidence is presented which supports a mechanism in which N-H bond formation is coupled to the electron-transfer step, resulting in an excergic process. N-H bond formation becomes the driving force for the reaction.

Electron-transfer reactions of six-membered monoazaaromatic heterocycles have been the subject of a number of investigations over the last 10 years. Much of this work has involved the calculation of the free energy of the electron-transfer step, ΔG_{et} , which was used as a measure of the feasibility of the electron-transfer process. Values of ΔG_{et} were determined from the Rehm-Weller equation² which relates the free energy of the electron transfer to the half-wave oxidation potential of the donor, $E_{1/2}(+)$, the half-wave reduction potential of the acceptor, $E_{1/2}(-)$, the energy of the excited state involved, $E_{0,0}$, and a coulombic attraction term, $e^2/\epsilon a$ (eq 1).

$$\Delta G_{\rm et} = E_{1/2}(+) - E_{1/2}(-) - \Delta E_{0,0} - \frac{e_0^2}{\epsilon a}$$
(1)

As would be expected, reactions that involve electron transfer were generally calculated to be excergic ($\Delta G_{\rm et} < 0$). In some cases, however, electron transfer occurred even though ΔG_{et} was positive. For example, this was found to be the case in a fluorescence quenching study involving alcohols and pyrrolinium salts reported by Mariano et al.3

We have been studying the electron-transfer reactions of 1° and 2° alcohols with excited states of substituted pyridines and quinolines for a number of years. After eq 1 is applied to these systems, it appears that most of them involve an endoergic electron-transfer step. One system that we recently studied is that of 2,4-pyridinedicarbonitrile (1) with 2-propanol. We would now like to report the results of an electron spin resonance study of 1 which we feel offers proof of the importance of proton concentration in a reaction in which $\Delta G_{\rm et} > 0$.

Results and Discussion

An electron spin resonance study of the radical formed when 2,4-pyridinedicarbonitrile (1) is irradiated in the cavity of an ESR spectrometer has been done and the values of the π -spin population on the ring atoms were determined from the measured proton and nitrogen couplings (Table I). Radicals were generated by in situ photolysis of deaerated solutions of 1. The rate of radical formation was measured in acetonitrile at 33 °C with varying amounts of 2-propanol, water, and acid. Hydrochloric acid was

Table I. π -Electron Spin Density Distribution of 2,4-Dicyanopyridinyl Radical 4



position	a, ^{H a}	Pr		
		calcd ^b	exptl	
1N	6.71	0.253	0.175	
1 H	2.54			
2		0.202		
3	1.593	-0.064	0.058	
4		0.270		
5	1.593	0.075	0.058	
6	2.08	0.076	0.075	
7		0.030		
8	2.867	0.076	0.150	
9		0.024		
10	1.054	0.058	0.055	

^a In gauss as determined on the Bruker ER 220D spectrometer. ^b McLachlan MO calculation with $h_{N'} = 1.0$, $k_{CN'} = 2.0$, $k_{CC} = 0.9$ (Rieger, P. H.; Fraenkel, G. K. J. Chem. Phys. **1962** 37, 2795). ^c Determined from proton couplings and the McConnell relation with $Q_{CH}^{H} = -27.7 \text{ G}, Q_{NH}^{H} = -14.5 \text{ (Rakowsky, T. H.; Dohrmann, J. K. Ber.}$ Bunsenges. Phys. Chem. 1975, 79, 18), and $Q_{C'N'}^{N'} = 19.0$ (P. H. Rieger and G. K. Fraenkel).

used, but other acids, such as sulfuric acid, reacted similarly. Though radical formation was observed in acetonitrile with alcohol alone, the rate of radical formation and the steady-state concentration increased when water was added, and a much greater increase was observed when acids was also present. The same complex spectrum was obtained with each combination of solvents.

The irradiations were carried out with a 500-W high-pressure mercury lamp focused on the cavity of the ESR spectrometer. A 0.100 M stock solution of 2,4-pyridinedicarbonitrile in acetonitrile was prepared and used in all subsequent kinetic studies.

The rate of radical disappearance was measured for each run described below by allowing a steady state to be reached, extinguishing the light, and following the signal decay with time. All the rates were found to be essentially the same regardless of acid or alcohol concentration.⁴ The lifetime of the radical was related

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 (2) Rehm, D.; Weller, A. Isr. J. Chem. 1970, 8, 259.

⁽³⁾ Mariano, P. S. Acc. Chem. Res. 1983, 16, 130. For other examples of the effect of pH on the rate of radical formation and disappearance in pyridine systems, please see also: Neta, P.; Patterson, L. K. J. Chem. Phys. 1974, 78, 2211 and references therein.



Figure 1. Plot of 2,4-dicyanopyridinyl radical steady-state level (cm) vs. concentration (in mol/L). (A) The effect of 2-propanol concentration on a 0.09 M solution of 1 in acetonitrile-1.7 M H₂O; (B) the effect of H₂O concentration on a 0.09 M solution of 1 in acetonitrile-1.1 M 2-propanol; (C) the effect of HCl on a 0.09 M solution of 1 in acetonitrile-0.9 M 2 propanol-1.9 M (approximately) H₂O; (D) the effect of benzophenone on a 0.05 M solution of 1 in acetonitrile-1.2 M 2-propanol.

only to the level of the steady state reached and, in some cases, extended to nearly 1 h at 33 °C. In this study we have, therefore, assumed that the steady-state concentration is proportional to the rate of radical formation at t = 0.

The effect of 2-propanol concentration on the steady-state level was examined first when using a solution prepared from 10 mL of stock solution to which 0.33 mL of water was added. To 2.0-mL samples were then added quantities of 2-propanol so that ratios of base to alcohol of 1:0, 1:1, 1:3, 1:5, and 1:10 were obtained. Each sample was deaerated by bubbling nitrogen through the solution for a period of 15 min and carefully transferring samples to capiliary tubes with deaerated pipets. A plot was made of the stationary-state level against alcohol concentration (Figure 1, curve A), which shows a low level of radical formation with increasing 2-propanol concentration. After a 0.91 M 2-propanol concentration was reached, the effect of further addition of alcohol was minimal.

The effect of water was then determined with 2.0-mL samples of a solution prepared from 10.0 mL of stock solution and 0.75 mL of 2-propanol. The molar concentrations of water used were 0.28, 0.82, 1.35, and 1.86. A plot of the steady-state concentration against water molarity (Figure 1, curve B) shows a gradual increase in the steady-state level with increasing water concentration. The levels reached were similar to those found with 2-propanol at equivalent concentrations, as can be seen by comparing curves A and B in Figure 1.

The greatest effect on the rate of radical formation, and therefore on the steady-state level, was observed when the test solution contained acid. For this experiment, a solution was prepared from 20 mL of stock solution, 1.5 mL of 2-propanol, and 0.66 mL water. Two-milliliter samples were prepared from this mixture with acid concentrations ranging from 0.96×10^{-2} to 37×10^{-2} M, while the 2-propanol concentration was maintained at 0.87 ± 0.01 M. The solution with the lowest acid concentration showed an extremely rapid rise in steady-state level which began to decline, gradually at first and then more rapidly, as the concentration of acid was increased (Figure 1, curve C). No ESR signal was observed with solutions that contained hydrochloric acid but no alcohol, confirming that electron transfer was not occurring from the chloride ion. This conclusion is supported by the fact that the same enhancement effect found with hydrochloric acid is also observed with sulfuric acid.

In an effort to determine whether or not salification of the pyridine base occurs in these acid solutions, an attempt was made to prepare the hydrochloride salt. This was not successful.

Furthermore, an NMR spectrum of a solution of 2,4-pyridinedicarbonitrile in acetonitrile- d_3 , 2-propanol- d_8 , and DCl showed no significant change with acid-to-base ratios of 20:1. It can be assumed, then, that the two cyano groups decrease the basicity of the pyridine ring to a level below detectable limits. This conclusion was supported by cyclic voltammetry experiments of 1 in acetonitrile, which showed that the half-wave reduction potential gradually shifted to less negative values with the addition of small quantities of 2-propanol or acid and became more irreversible. This shift to more positive potential is predictable by the Nernst equation on the basis of protonation of the reduced species, the radical anion of 1.

Excitation and emission spectra of 1 were taken in 2-methyltetrahydrofuran and in ethanol at 77 K. Fluorescence was not observed in either solvent; however, excitation spectra showed a maximum at 298 nm in the furan and at 290 nm in ethanol. In the less polar tetrahydrofuran, phosphorescence occurs at 429 nm and is shifted to 450 nm in ethanol with an increase in intensity of approximately 3-fold.⁵ The absorption spectrum showed a maximum at 281 nm and was not significantly affected by solvent.

In order to determine the photon dependence of the radicalforming process, we undertook an ESR study in which 0.1 M solutions of 1 were irradiated in the cavity of the spectrometer by using a 100-W xenon-mercury lamp. The concentration of radicals was plotted as a function of time t using four different light intensities, and ν_0 in the equation $\nu_0 = kI^n$ was determined at t = 0. A plot of log v_0 vs. log I gave a straight line with n =1.03 (r = 0.98). From this value of *n*, it may be concluded that the formation of the 2,4-dicyanopyridinyl radical by direct excitation proceeds by a monophotonic process.⁶

The involvement of the triplet state of 1 in radical formation is demonstrated by the nearly complete quenching that occurs with piperylene and the photosensitization that occurs with benzophenone (Figure 1, curve D). In an attempt to detect a solvent-separated radical ion pair, a CIDNP study was done with a solution of 1 in acetonitrile, 2-propanol- d_8 , and D_2O . No signal was observed, indicating that either the radical ion pair did not form or that its concentration was below detectable limits.⁷

Regarding the mechanism of the radical-forming process, three paths were considered in an attempt to explain our results. These included (a) electron transfer to the triplet state of 1 followed by N-H bond formation, (b) N-H bond formation in the excited state followed by electron transfer, and (c) simultaneous electron transfer and N-H bond formation. The essential difference between these routes is the relative timing of the electron transfer and protonation steps.

If one assumes that the T_1 state is the one most likely involved in this process, then path a may be ruled out on the basis of the highly positive ΔG_{et} that would result from this state. According to the Rehm-Weller equation, the driving force for electron transfer would be the energy of the triplet state. ΔG_{et} for a reaction involving T_1 , assuming an encounter distance of 7 Å in this polar medium ($\epsilon_{20} \approx 37$) and a triplet energy which should be no greater than 71 kcal/mol, was calculated to be +28 kcal/mol.⁸ This highly endoergic reaction from the T₁ state, clearly, would no be feasible. In the past, we have observed biphotonic electron-transfer reactions of nitrogen heterocyclic bases in an upper triplet state with ground-state alcohols.⁹ In the case of 1, the reaction has been found to be monophotonic. However, even though radical formation most likely occurs through the T_1 state, the photo-

⁽⁴⁾ There is some indication that at the higher acid concentrations, the rate of radical disappearance increases by a factor of approximately 1.5 as determined by measuring the rate of disappearance with the light off as a function of acid concentration.

⁽⁵⁾ In acetonitrile, there is a weak fluorescence band at 327 nm that shifted toward the blue and disappeared when alcohol was added. Due to a poor glass, the noise level was too high for confirmation.

⁽⁶⁾ Castellano, A.; Catteau, J. P.; Lablache-Combier, L. Tetrahedron 1975, 31, 2255 and references therein.

⁽⁷⁾ A similar experiment with triethylamine gave some indication of radical formation.

⁽⁸⁾ $E_{1/2}(-)$ for 1 was measured to be -1.38 V against SCE in acetonitrile. $E_{1/2}(+)$ for 2-propanol was estimated to be 3.0 V by using the equation $E_{1/2}(+) = 0.89$ (I.P.) - 6.04 with I.P. = 10.15 V (Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. J. Org. Chem. 1972, 37, 916.

⁽⁹⁾ Caronna, T.; Morrocchi, S.; Vittimberga, B. M. J. Org. Chem. 1981, 46, 34.

Scheme I



physical characteristics of the excited states of 1 are such that it may be possible to populate the T₂ state directly from the S₁ state through intersystem crossing as described below.¹⁰ From our emission studies, it may be concluded that the T₁ state is π,π^* , while the S₁ state is n,π^* . The T₂ state would most likely be n,π^* and the S₂ state π,π^* . If the S₁(n,π^*) state lies very near the S₂(π,π^*) state, the two states could mix by vibronic coupling. The degree of enhanced phosphorescence would then be determined by the level of mixing of the two states, as well as $\Delta E_{S_1-T_1}$. When alcohol is added, the S₁(n,π^*) state could take on a high degree of π,π^* character through mixing, resulting in a decrease in the efficiency of intersystem crossing to the T₁(π,π^*) level. If, however, ΔE between S₁(π,π^*) and T₂(n,π^*) is small, an efficient crossover to T₂ would occur, resulting in an increase in phosphorescence, as was observed. The observation that the absorption maximum is not affected by solvent but that phosphorescence increases with those same solvents supports this hypothesis.

Reactions directly from T_2 would be unlikely by path a due to the expected short lifetime of this state and positive $\Delta G_{\rm et}$ that would result from such reactions. The energy of the S_1 state was calculated to be 94 kcal/mol from absorption and excitation data. The highest energy for T_2 would most likely not exceed 93 kcal, resulting in a $\Delta G_{\rm et}$ of +6.5 kcal/mol for reactions involving this state. Furthermore, reactions of either triplet state would result in a radical ion pair with a triplet spin state, which would most likely lead to radical formation without hydrogen ion dependence.

Path b requires that the basicity of the reactive triplet state be greater than that of the ground state and that an electron transfer to the conjugate acid of 1 be energetically feasible. No data are available on the basicity of the triplet state of 1; it is, however, unlikely that the $T_1 \pi, \pi^*$ state is significantly more basic than the ground state because of the strong polarizing effect of the cyano groups. But even if N-H bond formation were to occur by this mechanism, the electron transfer would still be endoergic from T_1 . If one assumes that $E_{1/2}(-) = 0.9$ V for the conjugate acid of 1, a potential which would be approximately half a volt more positive than that of the unprotonated base, then the expected $\Delta G_{\rm et}$ value would be +16 kcal/mol from T_1 . The T_2 state is most likely n, π^* and would not be expected to be more basic than the ground state.

The mechanism that we feel best explains our results is c (Scheme I). We have no evidence for the formation of an exciplex, but it seems reasonable to assume that a collision complex is involved. If the complex has a relatively shallow well, the photophysical characteristics of the heterocycle should be little affected. On direct irradiation, the initially formed singlet of 1 undergoes intersystem crossing to a triplet state which could be a T_2 state initially but would rapidly undergo internal conversion

(10) For a discussion of this phenomenon see: Turro, N. J. Modern Molecular Photochemistry; Benjamin/Cummings: Menlo Park, CA, 1978; p 380. to T_1 . This triplet collides with an alcohol molecule, yielding the complex. Because of the unfavorable energetics, charge transfer does not occur at this point. The lifetime of this complex should be approximately $10^{-9}-10^{-10}$ s. Since the formation of radicals depends on the availability of protons, we propose that nitrogen protonation occurs during the lifetime of the complex and becomes part of the electron-transfer step and that no transfer occurs without proton involvement. If an N-H bond energy of 90 kcal/mol¹¹ is included in the ΔG_{et} calculation by eq 1, then the electron transfer becomes exoergic to the extent of approximately 83 kcal/mol if T_2 is involved and 62 kcal/mol if T_1 is involved. Apparently by this mechanism, the reaction is energetically feasible from either state. Furthermore, the sensitivity of the steady-state level to low concentrations of added acid (10:1, base/acid) indicates that the acid may be acting as a catalyst. This is explainable on the basis that for every proton removed from the solution in the electron-transfer process, a proton would be returned to the solution by the reacting alcohol molecules, thereby maintaining the proton concentration at a constant level (Scheme I).

Each point of the steady-state curves in Figure 1 is proportional to the rate of radical formation at t = 0 for the particular composition involved. In turn, each of these rates is proportional to the concentration of available protons. In the case of water and 2-propanol, the concentration of protons is low, and this is manifested in a small increase in the rate of radical formation at t = 0 with each increase in water or alcohol concentration. This results, respectively, in a correspondingly small increase in the steady-state level. Abstraction of the α -hydrogen of the alcohol by the excited base can be ruled out on the grounds that curves B and C were determined with essentially the same concentration of 2-propanol and base. In the event that radical formation involved hydrogen abstraction, it would be reasonable to expect that the same steady-state levels should eventually be reached in every case (exclusively of D) shown in Figure 1.

Our results have shown that the driving force for this reaction is the energy associated with the formation of the N-H bond. Whether or not an electron transfer occurs depends on the availability of protons. The proton may be supplied by alcohol or water, both of which are weakly ionized, or by mineral acid.

We have examined the products from the photoreaction of 1 in aqueous 2-propanol and found that the principal product is 2-pyridinecarbonitrile, formed as the result of the decyanation of the 4-position of 1. A complete account of this work will be submitted for publication soon.

Experimental Section

Materials. All solvents used in this study were analytical grade. The acetonitrile was obtained from the Carlo Erba Co. or Aldrich Chemical Co. (HPLC grade), the 2-propanol from E. Merck and Co., and the 37% hydrochloric acid from the Mallinckrodt Chemical Co. The 2,4-pyridinedicarbonitrile was obtained from the ICN Nutritional Biochemicals Co. and melted at $89-89.5 \,^{\circ}\text{C}$ (lit.¹² $88-91 \,^{\circ}\text{C}$). This was checked by HPLC and used without further purification.

ESR Spectrometry. All ESR spectra were taken on either a Varian E104 or a Bruker ER 220D spectrometer. The radical of 2,4-pyridinedicarbonitrile was generated in situ by irradiation of solutions of the base in the cavity of an ESR instrument. The solutions were prepared from a 0.100 M stock solution of 1 in acetonitrile and varying amounts of water, 2-propanol, and hydrochloric acid. Each solution was deaerated by nitrogen bubbling for at least 15 min and then transferred to a Pyrex capillary melting point tube with a deaerated pipet. The tubes were filled to a level well above the region of the cavity and then centered in the cavity. Irradiation was carried out with a 500-W high-pressure mercury lamp which had the same orientation with respect to the sample for each run and focused on the sample. Each kinetic run was made with measurements taken every 15 s. The relative steady-state radical concentrations were taken as the relative heights from the base line of the steady-state levels in centimeters of chart paper and appear in Figure 1. Each point in Figure 1 is an average of at least two runs. No correction was made for any change in concentration of 1 as a result of dilution during sample preparation, since the change was small and would not

⁽¹¹⁾ See: Inbar, S.; Linschitz, H.; Cohen, S. G. J. Am. Chem. Soc. 1981, 103, 1048 and references therein.

⁽¹²⁾ Feeley, W. E.; Beavers, E. M. J. Am. Chem. Soc. 1959, 81, 4004.

change the shape or relative positions of the curves in Figure 1 to any significant extent.

Effect of Each Solvent Component on the Rate of Radical Formation. 2-Propanol. To 10 mL of stock solution was added 0.33 mL of water. To 2-mL samples of this solution were added quantities of 2-propanol so that ratios of base to alcohol of 1:1 (0.015 mL of 2-propanol), 1:3 (0.045 mL), 1:5 (0.09 mL), and 1:10 (0.15 mL) were obtained. The results appear as curve A in Figure 1. The concentration of 1 varied between 0.097 and 0.090 M in this series.

 H_2O . The effect of water concentration was determined with 10 mL of stock solution to which 0.75 mL of 2-propanol was added. Twomilliliter samples were taken and water added to each so that the molar concentrations of water were 0, 0.28 (0.01 mL of H₂O), 0.82 (0.03 mL), 1.35 (0.05 mL), and 1.86 (0.07 mL). The concentration of 1 varied between 0.093 and 0.090 over this range. The results are shown in Figure 1, curve B.

Hydrochloric Acid. The effect of hydrochloric acid was examined by first preparing a solution composed of 20 mL of stock solution, 1.5 mL of 2-propanol, and 0.66 mL of water. Two-milliliter samples were prepared with acid concentrations of 0.96×10^{-2} , 1.94×10^{-2} , 4.75×10^{-2} , 9.38×10^{-2} , 18.2×10^{-2} , 26.5×10^{-2} , and 37.1×10^{-2} M. The 2propanol concentration was maintained at 0.87 ± 0.01 M, while the concentration of 1 varied between 0.090 and 0.087 M.

Piperylene. The effect of piperylene was determined with a 9.2×10^{-2} M solution of 2,4-pyridinedicarbonitrile in a solution composed of 30.8 mL of acetonitrile, 2.30 mL of 2-propanol, and 1.0 mL of water. Three solutions were prepared which contained 1.0×10^{-2} , 2.0×10^{-2} , and 9.9 \times 10⁻² M concentrations of piperylene. Samples were then run as described above. The highest concentration of piperylene which contained a 1:1 molar ratio of base to quencher showed essentially complete quenching of radical formation. Even the solution containing the lowest concentration of piperylene showed over 80% quenching.

Benzophenone. The effect of benzophenone was determined with a 0.047 M solution of 1 in 13/1 acetonitrile/2-propanol. Samples were prepared by taking 2-mL portions and adding aliquots of a 0.27 M solution of benzophenone in the same solvent. The molar ratio of 1/benzophenone in each sample is as follows: 0.047:0.0041, 0.045:0.0080, 0.045:0.012, and 0.041:0.036. The results appear as curve D in Figure

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Observation by ESR of an Acrylate Radical Conformationally Locked by Complexation with SnCl₄

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Abstract: The variation of conformational and electronic structures of 3,3-dimethyl-1-methoxy-1-(methoxycarbonyl)butyl radical by complexation with SnCl₄ was studied in chlorobenzene at various temperatures (5-130 °C) by means of ESR spectroscopy. The addition of equimolar amounts of SnCl₄ to the dimer reduced the standard enthalpy (ΔH°) and entropy (ΔS°) for the dimer = radical equilibrium from 41.4 to 12.1 kcal/mol and from 49.2 to -6.7 cal/mol·deg at 25 °C, respectively. The ESR spectrum at 23 °C indicated a twisted conformation of the radical and trigonal bipyramid structure of SnCl₄ by complexation. These results were also supported by the ESR study on a deuterated compound.

Selectivity and rate are often influenced by the addition of a metal salt in reactions involving carbon-centered free radicals. Not only rate acceleration but also an increase in regioselectivity, higher regulation of polymer sequencies, and high retention of configuration have already been reported for metal-assisted Diels-Alder reactions¹ and radical polymerizations² as well as the formation of Grignard reagents.³ These reactions have been explored as to mechanism as well as application, and the intermediacy of a complexed radical with restricted rotation has been assumed in certain cases. But as yet, little direct evidence has been obtained. In this paper we wish to report a twisted conformation for 2 coordinated with SnCl₄ in which SnCl₄ has a trigonal bipyramid structure.

2

Experimental Section

1

Materials. A mixture of methyl 2-methoxyacrylate⁴ (3.00 g, 25.9 mmol) and 2,2'-azobis[2-methylpropane] (5.50 g, 38.7 mmol) in benzene (7.00 mL) was irradiated with a 100-W high-pressure mercury lamp for 1 day at ambient temperature. After removal of benzene, the mixture was diluted with methanol (10.0 mL) and cooled to 0 °C to afford a colorless solid. Recrystallization of the solid from methanol gave white needles (1.80 g, 40% yield based on methyl 2-methoxyacrylate) of 1. Furthermore, liquid product (1.75 g, 39%) of 1 was also isolated from the residue by thin-layer chromatography. The needles and the liquid were assigned to the racemic and meso forms of 1, respectively, on the

⁽¹³⁾ When a CuSO₄ filter solution is used and most of the light is absorbed by benzophenone, the pyridinyl radical is observed immediately.

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