Registry No.—1, 13049-41-7; **2a**, 2446-84-6; **2b**, 1972-28-7; **2c**, 10465-85-7; α-bromophenylacetaldehyde dimethyl acetal, 14371-25-6.

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Photochemical Reaction of Imidazoles with Unsaturated Nitriles. Chemistry of Encounter Complex and Ion Pair

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The photochemical reactions of various N-unsubstituted (**1a,b**) and N-substituted (**2a–g**) imidazoles with nitriles such as acrylonitrile (AN) and 2-cyanopyridine (CP) were remarkably sensitive to the nature of imidazoles, nitriles, and solvents employed. The N-unsubstituted imidazole, e.g., 2,4,5-triphenylimidazole (**1b**), reacted with AN, giving 2-[2-(2,4,5-triphenyl-2*H*-imidazolyl)]propionitrile (**3b**) both in ethanol and acetonitrile, whereas the N-substituted imidazole, e.g., 1-methyl-2,4,5-triphenylimidazole (**2a**), was led to the [2 + 2] cycloaddition products **4a** and **4a′** in ethanol and 1-methyl-2,4,4-triphenyl-Δ^2-imidazolin-5-one (**5a**) in acetonitrile. On the other hand, **2a** and CP underwent a novel type of regiospecific addition to give 5-cyano-1-methyl-4α-pyridyl-2,4,5-triphenyl-Δ^2-imidazoline (**7a**). Simultaneously **2a** initiated the condensation of CP to yield 2,4′-bipyridine-2′-carbonitrile (**8**) and a terpyridinecarbonitrile **9** by the elimination of hydrogen cyanide. Photolyses of other imidazoles with AN and CP gave similar results. From fluorescence quenching studies, quantum yield measurements, and effects of the solvents and the identity of nitriles on the photoreactions, it is concluded that encounter complexes (or exciplexes) and ion pairs are the key intermediates in these reactions.

Phenomena related to exciplexes have been the subject of much recent investigation. The synthetic utility of ion pairs formed by photosensitized electron transfer from donor to acceptor and mechanistic interest in them has been documented in many papers.[2,3] Acrylonitrile is one of the typical acceptors and its photochemical addition to aromatic substances and alkanones leading to [2 + 2] cycloaddition and/or α-cyanoethylation has been well studied.[4] We now report that the photochemical reaction of imidazoles with nitriles depends strongly on solvents used and the nature of reactants employed and is one of the typical examples which suggest that a variety of photoreactions occur via exciplexes and ion pairs.

Results and Discussion

Photoproducts. Solutions (10^{-2} M) of imidazoles, **1a,b** and **2a–g**, were irradiated by UV light through Pyrex in the presence of a large excess of acrylonitrile (AN) or 2-cyanopyridine (CP). The concentration of CP was adjusted not to absorb an appreciable fraction of the incident light. Products were isolated mainly by chromatographic methods and they are listed in Tables I and II.

Striking features of the photoproducts from the imidazoles and AN are: (1) the N-unsubstituted imidazoles **1a** and **1b** gave α-cyanoethylated products **1c**, **3a**, and **3b** both in ethanol and acetonitrile, and (2) the N-substituted imidazoles **2a**, **2b**, and **2c** gave pairs of [2 + 2] cycloadducts **4a** and **4a′**, **4b** and **4b′**, and **4c** and **4c′** respectively in ethanol, whereas the products obtained from these imidazoles in acetonitrile were Δ^2-imidazolin-5-ones **5a** and **5b** and 1*H*-phenanthro[9,10-*d*]imidazoles **6a–6c**. Since the imidazole **2f** was unreactive toward AN under similar conditions and the reactivity of **1a** was low, the 4,5-diphenyl moiety appears to promote these reactions. *cis*- and *trans*-1,2-dicyanocyclobutanes were isolated in some cases (for **2a–c**) and AN polymers were always formed.

The yield of the imidazolinones **5a** and **5b** was not altered by the addition of a small amount of water to the solvent. Their oxygen atom, however, was found to originate from water which was contained in the solvent. Thus, the formation of **5a** was completely suppressed, when the carefully dried acetonitrile and AN were used. Furthermore, 38.3% ^{18}O-enriched **5a** was obtained by photolysis of **2a** and AN in acetonitrile containing a small amount of 42.0% ^{18}O-enriched water. A control experiment showed that the carbonyl oxygen of the imidazolinone **5a** was not exchanged under the reaction conditions in $H_2{}^{18}O$. These imidazolinones were formed only in the presence of AN with irradiation. Attempts to detect their precursors were unsuccessful.

Photolysis of the N-substituted imidazoles **2a–e** with CP caused apparently unusual modes of reactions, which are (1) the regiospecific addition of CP being accompanied with a cleavage of pyridine–CN bond to the 4–5 double bond of the imidazole to give 5-cyano-4α-pyridyl-Δ^2-imidazolines **7a–e**, (2) the self-condensation of CP to give a bipyridinecarbonitrile **8** and a terpyridinecarbonitrile **9**, and (3) the substitution of hydrogen at C(2) of the imidazole **2e** by the cyano and pyridyl moieties of CP to give imidazoles **2h** and **2i**. Under similar conditions other imidazoles **2f,g** were stable, and the N-unsubstituted imidazole **1b** was transformed slowly to 2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole[5] as the only significant product. Direct as well as sensitized (benzophenone, xanthone,

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Table I. Preparative Photolysis of Imidazoles and Acrylonitrile[a]

imidazole	concn, 10^{-2} M	AN/Im molar ratio	solvent	irrad time, h	products (yields, %)[b,c] cyanoethylation	[2 + 2] cycloadduct	imidazolinone	phenanthroimidazole	conversion of Im, %
2-Ph-**1a**	29.9	17	EtOH	18	**1c** (55), **3a** (33)				4
	15.5	24	MeCN	79	**1c** (55), **3a** (11)				15
2,4,5-$(Ph)_3$-**1b**	1.23	220	EtOH	3.5	**3b** (47)				73
	0.488	420	MeCN	4	**3b** (38)				100
1-Me-2,4,5-$(Ph)_3$-**2a**	2.13	270	EtOH	4		**4a** (61), **4a'** (17)			23[d]
	2.67	220	MeCN	9			**5a** (36)		45[d]
1,2,4,5-$(Ph)_4$-**2b**	0.823	550	EtOH	6		**4b** (28), **4b'** (11)			46[d]
	0.749	290	MeCN	3			**5b** (11)	**6b** (16)	57[d]
1,2-$(Me)_2$-4,5-$(Ph)_2$-**2c**	1.15	190	EtOH	9.5		**4c** (61), **4c'** (5)			64[e]
	1.16	190	MeCN	7				**6c** (26)	51[d]

[a] Abbreviations: Im, imidazole; AN, acrylonitrile; EtOH, ethanol; MeCN, acetonitrile. [b] Yields were calculated based on the consumed imidazoles. [c] In all cases a polymer of AN was formed in a significant amount. [d] A considerable amount of *cis*- and *trans*-1,2-dicyanocyclobutanes was also isolated. [e] 3-Ethoxypropionitrile was also isolated.

Table II. Preparative Photolysis of Imidazoles and 2-Cyanopyridine (CP) in Acetonitrile[a]

imidazole	concn, 10^{-2} M	CP/Im molar ratio	irrad time h	products (yields, %)[b] cyanopyridylimidazoline	pyridine oligomer	substitution	phenanthroimidazole	% conversion Im	% conversion CP
1-Me-2,4,5-$(Ph)_3$-**2a**	0.996	4.2	13	**7a** (50)	**8** (175), **9** (18)		**6a** (20)[c]	96	63
1,2,4,5-$(Ph)_4$-**2b**	0.675	4.9	13	**7b** (9)	**8** (138), **9** (17)		**6b** (62)	90	51
1,2-$(Me)_2$-4,5-$(Ph)_2$-**2c**	1.32	2.5	12	**7c** (55)	**8** (10)			100	46
1-Me-2,4,5-(*p*-Me-$Ph)_3$-**2d**	1.17	5.5	12	**7d** (44)	**8** (210), **9** (18)		**6d** (25)	95	55
1-Me-4,5-$(Ph)_2$-**2e**	1.44	4.8	27	**7e** (7)	**8** (22)	**2h** (9), **2i** (4), **6f** (2)	**6e** (60)	70	21

[a] Abbreviations: Im, imidazole; CP, 2-cyanopyridine. [b] Yields were calculated based on the consumed imidazoles. [c] Hydrogen cyanide was detected by the Mohr method (29% yield).

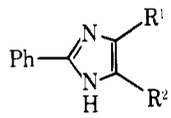
or acetone) irradiation of CP in the absence of the imidazoles did not yield the pyridine oligomers **8** and **9**. In some cases (**2a**, **2b**, and **2d**), **8** was isolated in a yield of more than 100% on the basis of the imidazoles consumed. These results suggest that these imidazoles apparently photosensitized the formation of **8**. AN and CP do not appear to participate in the dehydrocyclization to the phenanthroimidazoles **6**.[5] In fact, **6a** was formed as the only significant product by photolysis of the parent imidazole **2a** without AN or CP in acetonitrile, ethanol, or benzene.

The structures of all new compounds were assigned from their spectral and microanalytical data, except the stereoisomerism of [2 + 2] cycloadducts **4** and cyanopyridylimidazolines **7** and the structural isomerism of **4** and the terpyridine **9**. Chemical reactions of some compounds were studied for the structural confirmation. The pertinent results are illustrated below (see also Experimental Section). The photochemical transformation of the α-cyanoethylated 2*H*-imidazoles **3a** and **3b** to the original imidazoles **1a** and **1b** was probably initiated by an intramolecular hydrogen abstraction with the excited C–N double bond.[6,7] The reaction of **3a** and **3b** with lithium aluminum hydride appears to be a nucleophilic substitution with hydride ion.[6] Although the infrared absorption of the cyano group of the cyanopyridylimidazolines **7a–e** was vanishingly weak, the methanolyses (**7a** → **10a**, **7c** → **10b**, and **7d** → **10c**), the hydolyses (**7a** → **11a** and **7c** → **11b**), and the ^{13}C NMR spectra of **7a** and **7c** established unambiguously the presence of the cyano group.

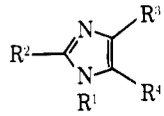
Mechanism. The formation of all the products shown in Tables I and II can be well accommodated by Scheme I in which the photoreactions with 2,4,5-triphenylimidazole (**1b**) and 1-methyl-2,4,5-triphenylimidazole (**2a**) are depicted as a typical case.

The key intermediates proposed are an encounter complex (or exciplex[8]) A and a solvated or dissociated ion pair B. The excited singlet state of the imidazoles ($^1Im^*$) interacts with a nitrile (RCN) to form the complex A (path b), which relaxes via an electron transfer from the imidazole to the nitrile to give B (path c). The complex A between **2a** and AN results in the [2 + 2] cycloadducts **4a** and **4a'** (path d) and the ion pair chemistry of B results in the formation of various final products, i.e., the cyanoethylated 2*H*-imidazole **3b** from **1b** and AN, the imidazolinone **5a** from **2a** and AN, and the cyanopyridylimidazoline **7a** and the pyridine oligomers **8** and **9** from **2a** and CP (paths e–h). The uncomplexed excited imidazoles lead to their own photochemistry to yield the phenanthroimidazole **6a** (path i). In order to prove this scheme, the following series of experiments were done (Tables III–VI).

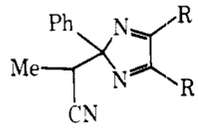
Scheme II is a kinetic expression to represent the gist of Scheme I. The classical energy transfer from the excited imidazole to AN or CP is unlikely in view of their absorption spectra. The value of $k_q\tau$ can be determined from the quenching of the imidazole fluorescence by the nitriles according to the equation



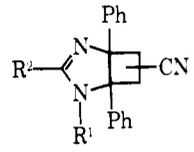
1a, R^1 = H; R^2 = H
b, R^1 = Ph; R^2 = Ph
c, R^1 = H; R^2 = MeCHCN



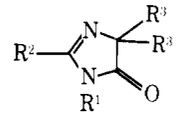
2a, R^1 = Me; R^2 = Ph; R^3 = Ph; R^4 = Ph
b, R^1 = Ph; R^2 = Ph; R^3 = Ph; R^4 = Ph
c, R^1 = Me; R^2 = Me; R^3 = Ph; R^4 = Ph
d, R^1 = Me; R^2 = *p*-MePh; R^3 = *p*-MePh; R^4 = *p*-MePh
e, R^1 = Me; R^2 = H; R^3 = Ph; R^4 = Ph
f, R^1 = Me; R^2 = Ph; R^3 = H; R^4 = H
g, R^1 = Me; R^2 = Ph; R^3 = H; R^4 = Ph
h, R^1 = Me; R^2 = CN; R^3 = Ph; R^4 = Ph
i, R^1 = Me; R^2 = Py(α); R^3 = Ph; R^4 = Ph



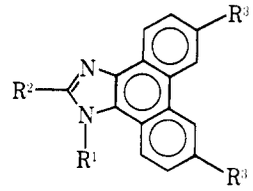
3a, R = H
b, R = Ph



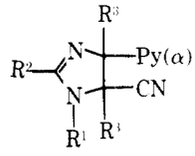
4a and 4a′, R^1 = Me; R^2 = Ph
4b and 4b′, R^1 = R^2 = Ph
4c and 4c′, R^1 = R^2 = Me



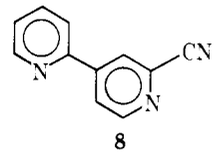
5a, R^1 = Me; R^2 = R^3 = Ph
b, R^1 = R^2 = R^3 = Ph



6a, R^1 = Me; R^2 = Ph; R^3 = H
b, R^1 = R^2 = Ph; R^3 = H
c, R^1 = R^2 = Me; R^3 = H
d, R^1 = Me; R^2 = *p*-MePh; R^3 = Me
e, R^1 = Me; R^2 = R^3 = H
f, R^1 = Me; R^2 = CN; R^3 = H



7a, R^1 = Me; R^2 = R^3 = Ph
b, R^1 = R^2 = R^3 = Ph
c, R^1 = R^2 = Me; R^3 = Ph
d, R^1 = Me; R^2 = R^3 = *p*-MePh
e, R^1 = Me; R^2 = H; R^3 = Ph



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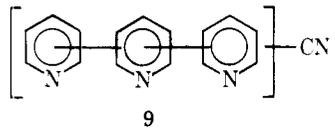
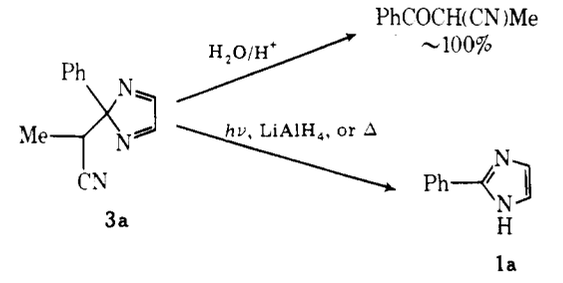


9

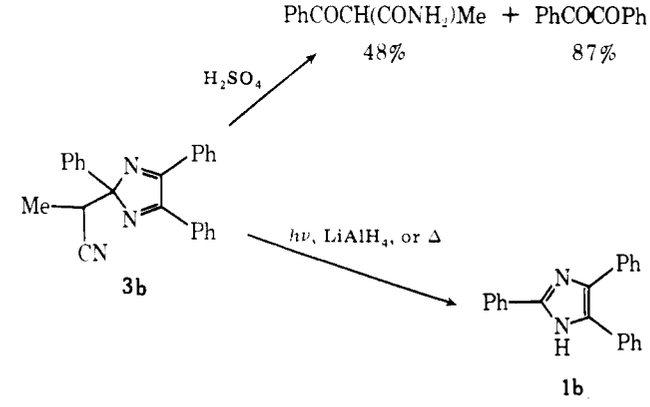
$$I_0/I = 1 + k_q\tau[\mathrm{RCN}] \quad (1)$$

I and I_0 are the quenched and unquenched fluorescence intensities, and k_q and τ are the quenching rate constant and the singlet lifetime of the imidazole in the absence of nitrile, respectively. The value of $k_q\tau$ can also be determined by measuring the quantum yields of products as a function of the nitrile concentration. The equations derived from the steady-state treatment of Scheme II are eq 2 for **3b** and **5a**, eq 3 for **4a** + **4a′**, and eq 4 for **7a**.

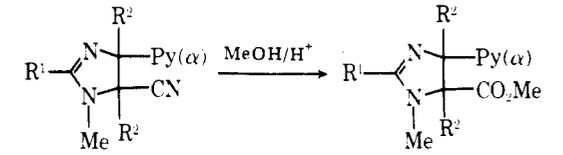
$$\phi(\mathbf{3b})^{-1} \text{ or } \phi(\mathbf{5a})^{-1} = \left(1 + \frac{1}{k_q\tau[\mathrm{AN}]}\right)\left(1 + \frac{k_3 + k_4}{k_2}\right)\left(1 + \frac{k_6}{k_5}\right) \quad (2)$$



3a 1a

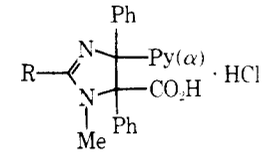


3b 1b



7a, R^1 = R^2 = Ph
c, R^1 = Me; R^2 = Ph
d, R^1 = R^2 = *p*-MePh

10a, R^1 = R^2 = Ph
b, R^1 = Me; R^2 = Ph
c, R^1 = R^2 = *p*-MePh



11a, R = Ph
b, R = Me

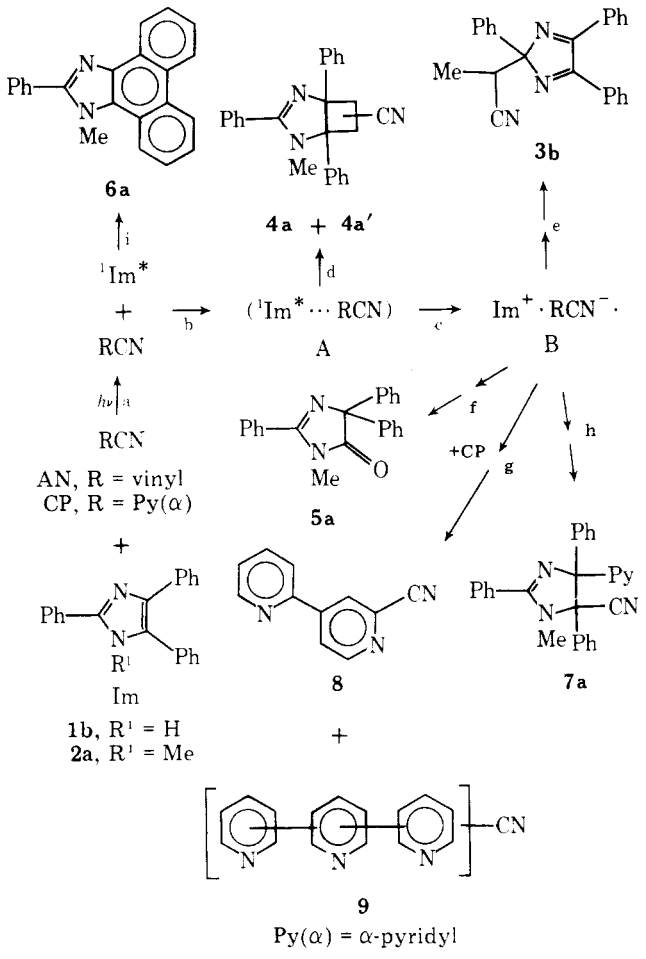
$$\phi(\mathbf{4a} + \mathbf{4a'})^{-1} = \left(1 + \frac{1}{k_q\tau[\mathrm{AN}]}\right)\left(1 + \frac{k_2 + k_4}{k_3}\right) \quad (3)$$

$$\phi(\mathbf{7a})^{-1} = \left(1 + \frac{1}{k_q\tau[\mathrm{CP}]}\right) \times \left(1 + \frac{k_3 + k_4}{k_2}\right)\left(1 + \frac{k_6 + k_7[\mathrm{CP}]}{k_5}\right) \quad (4)$$

Experimentally, plotting of ϕ^{-1} vs. $[\mathrm{RCN}]^{-1}$ gave a linear line in each case, and the value of $k_q\tau$ was calculated from the intercept/slope ratio.[9] As summarized in Table III the values of k_q thus obtained by two different methods agreed fairly well. This fact means that complexation of the excited singlet imidazoles with nitriles is a common process in the photoreaction and the fluorescence quenching, although it is not possible to distinguish between A and B by this level of kinetics.

Effects of solvent polarity on the photoreactions of **2a** with AN and CP and of **1b** with AN are summarized in Tables IV

Scheme I



and V. It can be seen that all the major products, e.g., **3b, 5a, 7a,** and **8,** except **4a** and **4a',** are formed more efficiently in solvents having a higher dielectric constant. This trend implies that these products are formed through an ionic intermediate, i.e., B in Scheme I. The cycloadducts **4a** and **4a'** are mainly formed only in solvents of a medium or low dielectric constant, indicating that the cycloadducts are formed via the excited complex A. It is widely observed that donor–acceptor systems which lead to exciplexes in nonpolar solvents lead, however, in highly polar solvents to the predominant formation of ion pairs through electron transfer, resulting in a change of distribution of final photoproducts.[3]

Products obtained from the photolysis of the imidazole **2a** with CP, AN, methacrylonitrile, crotononitrile, and benzonitrile are summarized in Table VI, together with the reported values of their reduction potential ($E_{1/2}$). The values of $k_q\tau$ determined by the fluorescence quenching of **2a** by the nitriles are also shown in the last column. The values of $E_{1/2}$ were parallel to the values of $k_q\tau$, indicating that a charge-transfer interaction may be responsible for the fluorescence quenching.

Scheme II

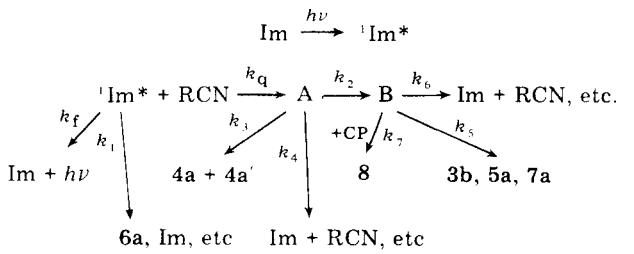


Table III. Values of $k_q\tau$ Determined by Measurements of the Fluorescence Quenching and the Quantum Yields of Product Formation

system	solvent	$k_q\tau$, M^{-1} quenching	$k_q\tau$, M^{-1} product
1b–AN	MeCN	45[a]	36 (**3b**)[d]
2a–AN	MeCN	13[b]	16 (**5a**)[e]
	EtOH	6[b]	*f*
2a–CP	MeCN	19[c]	21 (**7a**)[g]

[a] [**1b**] = 10^{-6} M; [AN] = 0.015–0.15 M. [b] [**2a**] = 10^{-6} M; [AN] = 0.015–0.15 M. [c] [**2a**] = 10^{-6} M; [CP] = 0.03–0.03 M. [d] [**1b**] = 5×10^{-3} M; [AN] = 0.05–2 M. [e] [**2a**] = 5×10^{-3} M; [AN] = 0.05–1 M. [f] Quantum yield measurements for the formation of **4a** + **4a'** failed due to the very efficient polymerization of AN which brought the solution opaque. [g] [**2a**] = 5×10^{-3} M; [CP] = 0.01–0.05 M.

However, the interaction appears very weak in the cases of crotononitrile and benzonitrile, since their values of $k_q\tau$ were negligibly small. This argument was supported by the following facts that while the reactions of CP, AN, and methacrylonitrile with **2a** led to various products, i.e., **4a, 5a, 7a, 8, 9,** and benzil, all of which are most probably formed via A or B, only the phenanthroimidazole **6a** was produced from the reactions of crotononitrile and benzonitrile with **2a**. As mentioned earlier, the formation of **6a** is not concerned with the intermediary formation of A or B.

The free-energy change for the electron transfer from the excited singlet state of the imidazole **2a** to the nitriles in acetonitrile was calculated by the well-known expression[10]

$$\Delta G = E(D/D^+) - E(A^-/A) - E_s - \text{constant} \qquad (5)$$

The polarographic oxidation potential $E(D/D^+)$ and the singlet excitation energy E_s of **2a** were estimated as 1.6[11] and 3.7 V,[12] respectively. The constant term was taken as 0.05 V.[10] The values of ΔG thus calculated were −0.4, −0.2, −0.1, 0.2, and 0.2 V respectively for CP, AN, methacrylonitrile, crotononitrile, and benzonitrile, indicating that the photochemical electron transfer reaction from **2a** to CP, AN, and methacrylonitrile is energetically feasible.

The above mechanistic considerations led us to conclude that the excited complex A and the ion pair B are the key intermediates in these reactions.

The paths f, g, and h in Scheme I can be visualized as Scheme III. There is no doubt that the bipyridine **8** was formed via an electron transfer reaction, since treatment of CP with sodium metal in ether gave a reasonable yield of 8 (10%). Two routes for the self-condensation of CP were considered: (1) one involves the paths g, j, and k on which the imidazole **2a** apparently functions as a sensitizer, and (2) the other involves the paths g, l, m, and n on which **2a** plays a role as an initiator like *N*-ethylcarbazole used in the charge-transfer polymerization of AN.[13] If the former route is true, the quantum yield for the formation of 8 can be represented by eq 6 from the steady-state treatment of Scheme II.

$$\phi(8) = \frac{k_q[CP]}{k_f + k_1 + k_q[CP]} \frac{k_2}{k_2 + k_3 + k_4} \frac{k_7[CP]}{k_5 + k_6 + k_7[CP]} \qquad (6)$$

Thus we can obtain eq 7 by combining eq 4 and 6.

$$\frac{\phi(7a)[CP]}{\phi(8)} = \frac{k_5}{k_7} = \text{constant} \qquad (7)$$

In fact, it was found that the ratio of $\phi(7a)[CP]$ to $\phi(8)$ was roughly constant (Table VII). If the latter route is the case, the ratio should decrease as [CP] increases. Therefore the former route, i.e., paths g, j, and k, appears more probable. The

Table IV. Solvent Effects on the Photoreaction of 2a with Acrylonitrile[a,b]

run no.	solvent dielectric constant	AN/2a molar ratio	product yield, %[c]: [2 + 2] cycloadduct of 4a + 4a'	imidazolinone 5a	phenanthroimidazole 6a	others
1	MeCN, 37.5	220		36		
2		3.6		9	59	
3	AN, 33.0	1070		22		
4	MeOH, 32.6	190	17	9		benzil (17), 12 (12)[d]
5	EtOH, 24.3	270	78			
6	2-PrOH, 18.3	230	74	5	trace	
7	C_6H_6, 2.2	230	48	trace		

[a] 10^{-2} M solution of **2a** was irradiated for 4–11 h. [b] Abbreviations: AN, acrylonitrile; MeCN, acetonitrile; MeOH, methanol; EtOH, ethanol; 2-PrOH, 2-propanol; C_6H_6, benzene. [c] Yields were calculated based on **2a** consumed. In all runs a polymer of AN was formed in a significant amount. *cis*- and *trans*-dicyanocyclobutanes were also always formed except run 4, when 3-methoxypropionitrile was formed. [d] An adduct between one molecule of **2a** and two molecules of AN. It has an α-cyanoethyl group.

Table V. Solvent Effects on the Photoreactions of 1b with Acrylonitrile and 2a with 2-Cyanopyridine

solvent	ϕ_{rel}[a]: cyanoethylated 2*H*-imidazole **3b**	5-cyano-4-pyridylimidazoline **7a**	bipyridinecarbonitrile **8**
MeCN	1	1	1
EtOH	0.41	~0	0.03
2-PrOH		~0	0.11
C_6H_6	0.12	~0	0.03

[a] Relative quantum yields for the formation of products calculated based on the value in acetonitrile. [b] **[1b]** = 3.5×10^{-3} M; [AN] = 0.1 M. [c] **[2a]** = 10^{-2} M; [CP] = 0.04 M.

similar mechanisms may be operative for the formation of *cis*- and *trans*-1,2-dicyanocyclobutanes.

It has been shown that several imidazoles form 1:1 ground-state complexes with a suitable acceptor, such as trinitrophenol.[14] We observed small bathochromic shifts (up to 5 nm) of the absorption spectra of the imidazoles **1a, 1b,** and **2a** with an increasing amount of AN in ethanol or in acetonitrile. Assuming the equilibrium formation of a 1:1 ground-state complex E (eq 8), we estimated[15] the equilibrium constant (K) approximately as 0.1, 0.3, and 0.1 for **1a, 1b,** and **2a,** respectively.

$$\mathrm{Im} + \mathrm{AN} \overset{K}{\rightleftharpoons} \underset{E}{(\mathrm{Im}\cdots\mathrm{AN})} \qquad (8)$$

The effect of formation of E on the fluorescence quenching of the imidazoles **1b** and **2a** by AN seems negligible under the experimental conditions, since the proportion of E to the total amount of the imidazole was calculated to be less than 5% in both cases. The ground-state complex E does not play an important role in the photochemical reaction, either. As summarized in Table VIII, the quantum yields for formation of the cyanoethylated 2*H*-imidazole **3b** and the imidazolinone **5a** changed only a factor of two with respect to AN concentration, while the percentage of E changed as much as 20 times.

Experimental Section

All melting points are uncorrected. NMR spectra were taken on a Varian T-60 or HA-100 spectrometer. IR, UV, and mass spectra were measured on a JASCO IRA-1 spectrometer, a Shimadzu UV-200 spectrometer, and a Hitachi RMU-6C spectrometer, respectively. The fluorescence spectra were measured on a Shimadzu MPS-50L spectrometer. Column chromatography (CC) and thin-layer chromatography (TLC) were carried out with Mallinckrodt silicic acid (100

Table VI. Products from the Photolysis of 2a with the Varied Nitriles, and the Correlation Among Types of Photoproducts, the Polarographic Reduction Potentials of the Nitriles, and the Values of $k_q\tau$

nitrile[a]	photolysis[b]: nitrile/2a molar ratio	solvent	products (yields, %)[c]		$-E_{1/2}$ V vs. SCE	$k_q\tau$,[m] M^{-1}
CP	4.3	EtOH	**7a** (23), 8 (10)	**6a** (36)	1.8[f]	19
	4.2	MeCN	**7a** (50), 8 (175), **9** (18)	**6a** (20)		
AN	270	EtOH	**4a** + **4a'** (78)[d,e]		2.01[h]	13
	220	MeCN	**5a** (36)[d,e]			
	3.6	MeCN	**5a** (9)	**6a** (59)[d,e]		
methacrylonitrile	180	EtOH	**5a** (<5), benzil (~20)	**6a** (~10)[e]	2.07[i]	0.63
	180	MeCN	**5a** (7)	**6a** (78)		
crotononitrile	200	EtOH		**6a** (80)	2.37[i]	<0.1
	240	MeCN		**6a** (99)		
benzonitrile	32	EtOH		**6a** (75)	2.4[k]	<0.1
	32	MeCN		**6a** (93)		

[a] Abbreviations: CP, 2-cyanopyridine; AN, acrylonitrile. [b] **[2a]** = 10^{-2} M. [c] Calculated based on **2a** consumed. [d] *cis*- and *trans*-dicyanocyclobutanes as the side products. [e] A polymer of the corresponding nitrile was formed. [f] The value estimated by us. The reported value was −2.09 V vs. Ag/AgCl in MeCN.[g] R. O. Loutfy and R. O. Loutfy, *Can. J. Chem.*, **51**, 1169 (1973). See also, J. Volke and V. Skála, *J. Electroanal. Chem.*, **36**, 383 (1972); and A. M. Kardos, P. Valenta, and J. Volke, *ibid.*, **12**, 84 (1966). [h] T. Fueno, K. Asada, K. Morokuma, and J. Furukawa, *J. Polym. Sci.*, **40**, 511 (1959). [i] Chemical Society of Japan, Ed., "Kagaku Binran Kisohen II", Maruzen Tokyo, 1966, pp 1383. [j] H. P. House, L. E. Huber, and M. J. Umen, *J. Am. Chem. Soc.*, **94**, 8471 (1972). [k] The value estimated by us. The reported value was −2.74 V vs. Ag in DMF. [l] P. H. Rieger, I. Bernal, W. H. Reinmuth, and B. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963). [m] Determined by the fluorescence quenching of **2a** in acetonitrile. **[2a]** = 10^{-6} M.

Table VII. Quantum Yields for the Formation of 7a and 8 in Acetonitrile as a Function of CP Concentration[a]

	10^2[CP], M				
	1.03	2.06	3.09	4.13	5.16
$10^4\phi$(**7a**)	2.7	4.2	4.6	6.0	6.9
$10^4\phi$(**8**)	0.9	2.2	2.6	3.2	5.0
$10^2\{\phi$(**7a**)[CP]/ϕ(**8**)$\}$	3.1	3.8	4.6	7.7	7.1

[a] **[2a]** = 6.85×10^{-3} M.

Table VIII. QuantumYields for the Formation of 3b and 5a and the Percentage of the Ground-State Complex with AN E in Acetonitrile as a Function of AN Concentration

	[AN], M				
	0.0503	0.101	0.302	1.01	2.01
$10^4\phi$(**3b**)[a]	6.1	7.3	8.8	9.3	10
E(**1b**–AN), %[c]	1.5	3	8	23	38
$10^4\phi$(**5a**)[b]	3.5	4.8	6.2	7.4	
E(**2a**–AN), %[c]	0.5	1	3	10	

[a] **[1b]** = 3.45×10^{-3} M. [b] **[2a]** = 6.28×10^{-3} M. [c] The proportion of E to the total amount of the imidazole **1b** or **2a**.

mesh) and Merck Kieselgel GF_{254}, respectively. All irradiations were carried out with a 400-W high-pressure mercury lamp surrounded by a Pyrex water-cooling jacket. All the known compounds were identified by direct comparison with an authentic sample (NMR, IR, TLC, GC, and/or mp).

Materials. All solvents,[16] acrylonitrile (AN), methacrylonitrile, and crotononitrile were purified by a simple distillation prior to use. 2-Cyanopyridine (CP) and 2-phenylimidazole (**1a**) were recrystallized from ether and acetonitrile, respectively, before use. The following imidazoles were prepared according to the literature methods, i.e., 2,4,5-triphenyl- (**1b**);[17] 1-methyl-2,4,5-triphenyl- (**2a**);[18] 1,2,4,5-tetraphenyl- (**2b**);[17] 1,2-dimethyl-4,5-diphenyl- (**2c**);[18] 1-methyl-2-phenyl- (**2f**);[19] 1-methyl-4,5-diphenyl- (**2e**);[20] and 1-methyl-2,5-diphenyl- (**2g**)[21] imidazoles. 1-Methyl-2,4,5-tri(*p*-tolyl)imidazole (**2d**) was prepared by methylation[18] of 2,4,5-tri(*p*-tolyl)imidazole[22] (**2d**): colorless crystals from 10:1 MeOH–water; mp 150–151.5 °C; IR (Nujol) 1520, 1495, 825, 820, 735 cm^{-1}; NMR ($CDCl_3$) δ 7.73–6.91 (m, 12, aromatic), 3.44 (s, 3, CH_3N), 2.42 (s, 6, CH_3C), 2.27 (s, 3, CH_3C); UV (EtOH) λ 225 (sh, ϵ 24 000), 286 (21 100) nm. Anal. Calcd for $C_{25}H_{24}N_2$: C, 85.19; H, 6.86; N, 7.95. Found: C, 84.90; H, 6.83; N, 7.68.

Isolation of Photoproducts. A solution of **1b** (1.53 g, 5.17 mmol) in AN (75 mL, 1.14 mol) and EtOH (345 mL) was irradiated under bubbling nitrogen for 3.5 h. The insoluble AN polymers which were formed during the irradiation were filtered off and the filtrate was evaporated under reduced pressure. The residue was chromatographed on 50 g of silica gel. Elution with 1400 mL of C_6H_6 afforded 620 mg of crude α-cyanoethylated 2*H*-imidazole **3b**, which on crystallization from C_6H_6–petroleum ether yielded colorless crystals. Further elution with C_6H_6 (800 mL) afforded a complex mixture (280 mg) which was difficult to separate. The recovered imidazole **1b** (420 mg) was then eluted with $CHCl_3$ (600 mL). Irradiation of other imidazole–nitrile systems was similarly carried out and the photoproducts were separated by CC and/or preparative TLC. Some volatile products were separated by distillation and gas chromatography (Silicone DC 550).

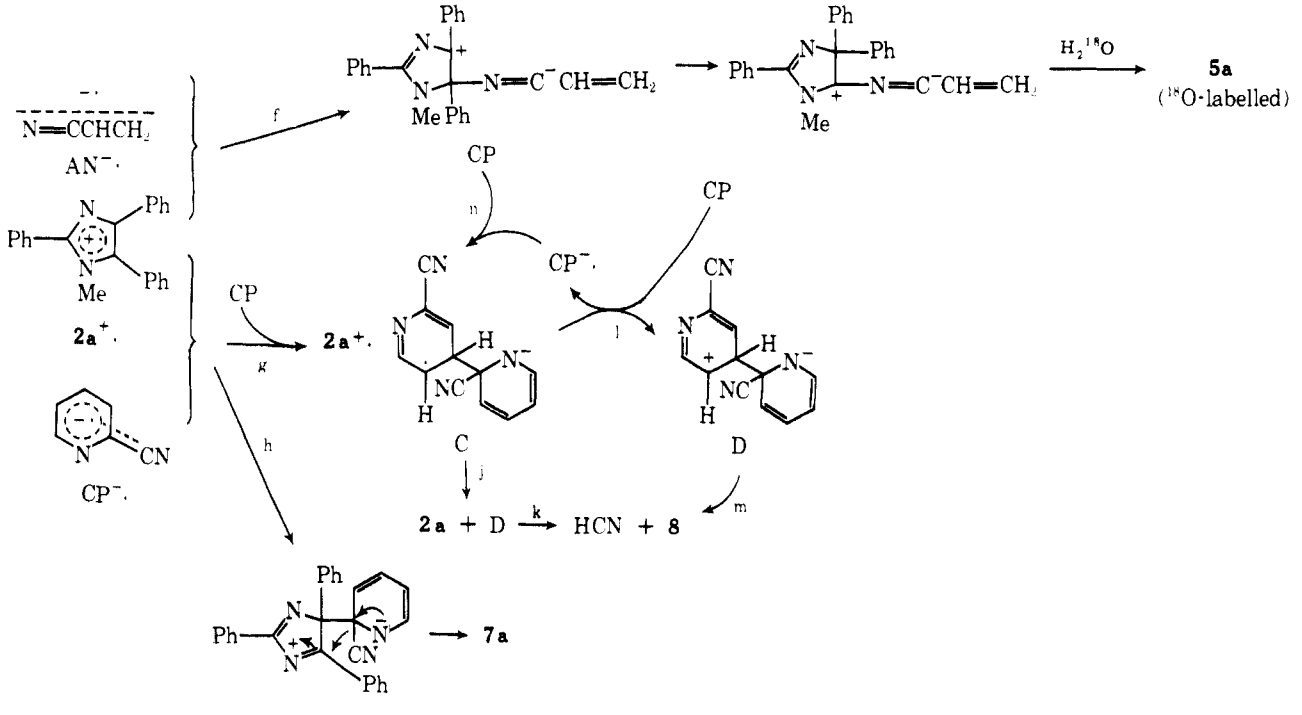
The physical, spectral, and analytical data of new compounds are shown below, including the solvents used for CC and preparative TLC.

2-[2-(2-Phenyl-2*H*-imidazolyl)]propionitrile (3a): colorless crystals from C_6H_6–petroleum ether; mp 76–77 °C; $CHCl_3$ (CC), 15:1 $CHCl_3$–Me_2CO (TLC); IR (Nujol) 2235 (C≡N), 990, 975, 750, 690 cm^{-1}; UV (EtOH) λ 240 (ϵ 1160), 259 (sh, 640), 265 (sh, 590), 269 (sh, 510) nm; NMR ($CDCl_3$) δ 8.30 (d, 1, J = 5.5 Hz, CH=), 8.28 (d, 1, J = 5.5 Hz, CH=), 7.80–7.23 (m, 5, aromatic), 3.47 (quartet, 1, J = 7.5 Hz, $CHCH_3$), 1.34 (d, 3, J = 7.5 Hz, $CHCH_3$). The coupling observed between H-4 and H-5 is because of nonequivalency of them due to the asymmetric α-cyanoethyl group: MS *m/e* (rel intensity) 197 (M^+, 9), 143 ($M^+ - CH_3CHCN$, 100). Anal. Calcd for $C_{12}H_{11}N_3$: C, 73.07; H, 5.62; N, 21.31. Found: C, 73.00; H, 5.61; N, 21.34.

2-[4(or 5)-(2-Phenylimidazolyl)]propionitrile (1c): colorless crystals from 3:1 $CHCl_3$–CCl_4; mp 168.5–169.5 °C; $CHCl_3$ (CC), 10:1 $CHCl_3$–Me_2CO (TLC); IR (Nujol) 2235 (C≡N), 1410, 1145, 790, 710, 690 cm^{-1}; UV (EtOH) λ 270 (ϵ 12 400) nm; NMR ($CDCl_3$) δ 10.16 (s, 1, NH, disappeared on deuteration), 7.97–7.17 (m, 5, aromatic), 7.05 (s, 1, CH=), 3.96 (quartet, 1, J = 7 Hz, $CHCH_3$), 1.63 (d, 3, J = 7 Hz, CH_3); MS *m/e* (rel intensity) 197 (M^+, 76), 182 ($M^+ - CH_3$, 100). Anal. Calcd for $C_{12}H_{11}N_3$: C, 73.07; H, 5.62; N, 21.31. Found: C, 72.81; H, 5.37; N, 21.37.

2-[2-(2,4,5-Triphenyl-2*H*-imidazolyl)]propionitrile (3b): colorless crystals from C_6H_6–petroleum ether; mp 218.5–219 °C; C_6H_6 (CC); IR (Nujol) 2235 (C≡N), 1550, 1490, 1020, 770, 760, 700, 690 cm^{-1};[23] UV (EtOH) λ 266 (ϵ 7500) nm;[23] NMR ($CDCl_3$) δ 8.07–7.23 (m, 15, aromatic), 3.66 (quartet, 1, J = 7.5 Hz, CH), 1.44 (d, 3, J = 7.5 Hz, CH_3). Anal. Calcd for $C_{24}H_{19}N_3$: C, 82.49; H, 5.48; N, 12.03. Found: C, 82.71; H, 5.59; N, 11.79.

Scheme III



2,4-Diazabicylo[3.2.0]hept-2-enes. The possibility of [2 + 4] cycloadduct structure for these compounds was eliminated by their UV spectra. The R_f values of **4a, 4b', and 4c'** were slightly larger than those of **4a', 4b,** and **4c',** respectively.

4a: colorless crystals from C_6H_6–petroleum ether; mp 158–162 °C; $CHCl_3$ (CC), 3:1 C_6H_6–AcOEt (TLC); IR (Nujol) 2230 (C≡N), 1590, 1565, 1500, 1060, 760, 715, 690 cm^{-1}; UV (EtOH) λ 222 (sh, ε 18 300), 266 (2500) nm; NMR ($CDCl_3$) δ 7.97–6.87 (m, 15, aromatic), 4.03–2.84 (m, 3, ABC pattern, J_{AB} = 12 Hz, J_{BC} = 5 Hz, J_{AC} = 10 Hz, CH_2CH), 2.67 (s, 3, CH_3); MS *m/e* (rel intensity) 363 (M^+, 0.1), 310 ($M^+ - CH_2CHCN$, 100). Anal. Calcd for $C_{25}H_{21}N_3$: C, 82.61; H, 5.82; N, 11.56. Found: C, 82.85; H, 5.73; N, 11.42.

4a': colorless crystals from aqueous MeOH; mp 197–200 °C; $CHCl_3$ (CC), 3:1 C_6H_6–AcOEt (TLC); IR (Nujol) 2230 (C≡N), 1590, 1570, 1500, 1065, 765, 710, 695 cm^{-1}; UV (EtOH) λ 222 (sh, ε 16 800), 266 (3000) nm; NMR ($CDCl_3$) δ 7.80–6.77 (m, 15, aromatic), 3.95–3.14 (m, 3, ABC pattern, CH_2CH), 2.60 (s, 3, CH_3); MS *m/e* (rel intensity) 363 (M^+, 0.5), 310 ($M^+ - CH_2CHCN$, 100). Anal. Calcd for $C_{25}H_{21}N_3$: C, 82.61; H, 5.82; N, 11.56. Found: C, 82.21; H, 5.87; N, 11.32.

4b: colorless crystals from C_6H_6–ligroin; mp 214–216 °C; 2:1 C_6H_6–$CHCl_3$ (CC), 50:1 $CHCl_3$–Me_2CO (TLC); IR (Nujol) 2240 (C≡N), 1595, 1570, 1500, 775, 720, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.84–6.56 (m, 20, aromatic), 3.97–2.71 (m, 3, CH_2CH); UV (dioxane) λ 273 (sh, ε 5600), 281 (sh, 4900), 298 (sh, 4200) nm; MS *m/e* (rel intensity) 425 (M^+, 2), 372 ($M^+ - CH_2CHCN$, 100). Calcd for $C_{30}H_{23}N_3$: C, 84.67; H, 5.45; N, 9.88. Found: C, 84.43; H, 5.26; N, 9.84.

4b':[25] IR (Nujol) 2240 (C≡N), 1600, 1570, 1500, 780, 770, 695 cm^{-1}; NMR ($CDCl_3$) δ 7.74–6.44 (m, 20, aromatic), 3.98–2.91 (m, 3, CH_2CH).

4c: colorless crystals from C_6H_6–ether; mp 157–159 °C; $CHCl_3$ (CC), 5:1 $CHCl_3$–Me_2CO (TLC); IR (Nujol) 2240 (C≡N), 1605, 1600, 1580, 770, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.37–6.80 (m, 10 aromatic), 3.91–2.67 (m, 3, CH_2CH), 2.56 (s, 3, NCH_3), 2.22 (s, 3, CCH_3); UV (EtOH) λ 222 (sh, ε 20 600), 255 (sh, 4000) nm; MS *m/e* (rel intensity) 301 (M^+, 0.9), 300 (1.4), 248 ($M^+ - CH_2CHCN$, 51), 165 (100). Anal. Calcd for $C_{20}H_{19}N_3$: C, 79.70; H, 6.35; N, 13.94. Found: C, 79.40; H, 6.60; N, 14.12.

4c':[25] IR (Nujol) 2240 (C≡N), 1600, 1580, 770, 710, 695 cm^{-1}; NMR ($CDCl_3$) δ 7.53–6.74 (m, 10, aromatic), 3.76–3.00 (m, 3, CH_2CH), 2.54 (s, 3, CH_3N), 2.13 (s, 3, CH_3C); UV (EtOH) λ 220 (sh, ε 16 000), 257 (3900) nm.

1-Methyl-2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (6a): colorless crystals from Me_2CO; mp 188–190 °C; $CHCl_3$ (CC), 50:1 $CHCl_3$–Me_2CO (TLC); IR (Nujol) 750, 720, 710, 695 cm^{-1}; NMR ($CDCl_3$) δ 8.92–8.12 (m, 4, aromatic), 7.88–7.33 (m, 9, aromatic), 4.12 (s, 3, CH_3); UV (EtOH) λ 258 (ε 64 200), 285 (18 000), 305 (sh, 16 700), 340 (5100), 356 (5100) nm. Anal. Calcd for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.09. Found: C, 85.84; H, 5.12; N, 9.14.

1,2-Dimethyl-1*H*-phenanthro[9,10-*d*]imidazole (6c): colorless crystals from Me_2CO–petroleum ether; mp 197–201 °C; $CHCl_3$ (CC), 5:1 $CHCl_3$–Me_2CO (TLC); IR (Nujol) 1540, 770, 765, 720 cm^{-1}; NMR ($CDCl_3$) δ 8.77–8.40 (m, 3, aromatic), 8.03–7.20 (m, 5, aromatic), 3.61 (s, 3, CH_3N), 2.37 (s, 3, CH_3C); UV (EtOH) λ 257 (ε 62 000), 282 (10 900), 306 (8500), 340 (1300), 356 (1600) nm. Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.63; H, 6.00; N, 11.13.

2-*p*-Tolyl-1,6,9-trimethyl-1*H*-phenanthro[9,10-*d*]imidazole (6d): colorless crystals from Me_2CO–$CHCl_3$; mp 263–264 °C; C_6H_6 (CC), 50:1 C_6H_6–Me_2CO (TLC); IR (Nujol) 1540, 1180, 830, 805, 730 cm^{-1}; NMR ($CDCl_3$) δ 8.74–8.13 and 7.74–7.20 (m, 10, aromatic), 4.15 (s, 3, CH_3N), 2.61 (s, 6, CH_3C), 2.43 (s, 3, CH_3C); UV (EtOH) λ 255 (sh, ε 46 600), 263 (64 500), 292 (17 700), 309 (13 800), 349 (3900), 366 (4100) nm. Anal. Calcd for $C_{25}H_{22}N_2$: C, 85.68; H, 6.33; N, 7.99. Found: C, 85.68; H, 6.21; N, 7.84.

1-Methyl-1*H*-phenanthro[9,10-*d*]imidazole (6e): colorless crystals from ether–Me_2CO; mp 198.5–200.5 °C; $CHCl_3$ (CC), 10:1 $CHCl_3$–Me_2CO (TLC); IR (Nujol) 1530, 750, 720 cm^{-1}; NMR ($CDCl_3$) δ 8.88–7.40 (m, 9, aromatic), 4.16 (s, 3, CH_3); UV (EtOH) λ 225 (ε 14 100), 245 (sh, 40 300), 252 (59 300), 278 (8400), 286 (sh, 6800), 298 (4700), 331 (1000), 347 (1200) nm; MS *m/e* (rel intensity) 232 (M^+, 100), 190 (31). Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.96; H, 4.96; N, 12.06.

2-Cyano-1-methyl-1*H*-phenanthro[9,10-*d*]imidazole (6f): colorless crystals from Me_2CO–ether; mp 244.5–246.5 °C; C_6H_6 (CC), 50:1 $CHCl_3$–Me_2CO (TLC); IR (Nujol) 2230 (C≡N), 760, 720 cm^{-1}; NMR ($CDCl_3$) δ 8.84–7.33 (m, 8, aromatic), 4.36 (s, 3, CH_3); UV (EtOH) λ 223 (sh, ε 19 700), 230 (21 900), 246 (sh, 56 300), 253 (90 700), 258 (sh, 58 800), 277 (sh, 16 500), 296 (15 100), 309 (16 700), 317 (sh, 10 100), 330 (10 600), 346 (13 800) nm; MS *m/e* (rel intensity) 257 (M^+, 100), 190 (33). Anal. Calcd for $C_{17}H_{11}N_3$: C, 79.36; H, 4.31; N, 16.33. Found: C, 79.05; H, 4.03; N, 16.37.

5-Cyano-1-methyl-4-α-pyridyl-2,4,5-triphenyl-Δ²-imidazoline (7a): colorless crystals from ether; mp 188–190 °C; C_6H_6 (CC), $CHCl_3$ (TLC); IR (Nujol) 1620, 1590, 1060, 750, 700 cm^{-1}; NMR ($CDCl_3$) δ 8.80–8.61 (m, 1, α-H of Py), 8.00–6.85 (m, 18, aromatic), 2.73 (s, 3, CH_3); ^{13}C NMR ($CDCl_3$) 32.155 (CH_3), 80.577 and 84.221 (C(4) and C(5) of the imidazoline ring), 118.949 (C≡N), other carbons at 122.486, 123.451, 125.327, 126.988, 127.149, 127.444, 127.765, 128.221, 128.730, 130.472, 133.446, 136.715, 138.886, 147.595, 162.467, 165.923, and 178.652; UV (EtOH) λ 220 (sh, ε 24 600), 260 (7800), 272 (sh, 6000) nm; MS *m/e* (rel intensity)[26] 414 (M^+, 0.5), 270 (100), 167 (62), 139 (23), 118 (11). Anal. Calcd for $C_{28}H_{22}N_4$: C, 81.13; H, 5.35; N, 13.52. Found: C, 81.33; H, 5.34; N, 13.43.

5-Cyano-1-methyl-4-α-pyridyl-2,4,5-tri-*p*-tolyl-Δ²-imidazoline (7d): colorless crystals from ether–Me_2CO; mp 200–201 °C; C_6H_6 (CC), 50:1 C_6H_6–Me_2CO or 80:5:1 $CHCl_3$–petroleum ether–Me_2CO (TLC); IR (Nujol) 1620, 1590, 1525, 1065, 830, 825, 755 cm^{-1}; NMR ($CDCl_3$) δ 8.77–8.62 (m, 1, α-H of Py), 8.02–6.64 (m, 15, aromatic), 2.71 (s, 3, CH_3N), 2.43 (s, 3, CH_3C), 2.27 (s, 3, CH_3C), 2.15 (s, 3, CH_3C); UV (EtOH) λ 228 (ε 28 200), 259 (9300), 265 (sh, 9000), 272 (sh, 7200) nm; MS *m/e* (rel intensity)[26] 456 (M^+, 0.1), 298 (100), 180 (64), 143 (28), 132 (26). Anal. Calcd for $C_{31}H_{28}N_4$: C, 81.54; H, 6.18; N, 12.27. Found: C, 81.26; H, 5.98; N, 12.05.

5-Cyano-1,2-dimethyl-4,5-diphenyl-4-α-pyridyl-Δ²-imidazoline (7c): colorless crystals from Me_2CO–ether; mp 228–230 °C; $CHCl_3$ (CC), 20:1 $CHCl_3$–Me_2CO (TLC); IR (Nujol) 2230 (C≡N, very weak), 1630, 1590, 990, 760, 700 cm^{-1}; NMR ($CDCl_3$) δ 8.80–8.62 (m, 1, α-H or Py), 8.05–6.85 (m, 13, aromatic), 2.75 (s, 3, CH_3N), 2.35 (s, 3, CH_3C); ^{13}C NMR ($CDCl_3$) 15.031 (CH_3C), 30.634 (CH_3N), 79.958 and 83.730 (C(4) and C(5) of the imidazoline ring), 118.768 (C≡N), other carbons at 122.541, 123.341, 127.168, 127.456, 127.799, 128.311, 128.714, 133.341, 136.770, 138.773, 147.630, 162.321, 164.150; UV (EtOH) λ 220 (sh, ε 16 100), 254 (5300), 263 (sh, 4700), 270 (sh, 3200) nm; MS *m/e* (rel intensity)[26] 352 (M^+, 0.1), 208 (100), 167 (31). Anal. Calcd for $C_{23}H_{20}N_4$: C, 78.38; H, 5.72; N, 15.90. Found: C, 78.56; H, 5.59; N, 16.00.

5-Cyano-4,5-diphenyl-1-methyl-4-α-pyridyl-Δ²-imidazoline (7e): colorless crystals from ether; mp 180.5–183 °C; $CHCl_3$ (CC), 10:1 $CHCl_3$–Me_2CO (TLC); IR (Nujol) 2230 (C≡N, very weak), 1620, 1590, 1055, 760, 690 cm^{-1}; NMR ($CDCl_3$) δ 8.84–8.68 (m, 1, α-H of Py), 7.95–6.80 (m, 14, aromatic and NCH=N), 2.84 (s, 3, CH_3); UV (EtOH) λ 252 (ε 5900), 262 (sh, 4500), 268 (sh, 3500) nm; MS *m/e* (rel intensity)[26] 338 (M^+, 0.1), 194 (100), 167 (18). Anal. Calcd for $C_{22}H_{18}N_4$: C, 78.08; H, 5.36; N, 16.56. Found: C, 78.30; H, 5.08; N, 16.70.

5-Cyano-4-α-pyridyl-1,2,4,5-tetraphenyl-Δ²-imidazoline (7b): colorless crystals from aqueous MeOH; mp 94–97 °C; C_6H_6 (CC), 40:1 C_6H_6–Me_2CO (TLC); IR (Nujol) 1595, 1590, 1575, 1495, 760, 750, 690 cm^{-1}; NMR ($CDCl_3$) δ 8.85–8.68 (m, 1, α-H of Py), 7.97–6.84 (m, 23, arom); UV (EtOH) λ 230 (sh, ε 27 700), 255 (sh, 19 200), 298 (sh, 5200) nm; MS *m/e* (rel intensity)[26] 476 (M^+, 0.02), 270 (100), 167 (45). Anal. Calcd for $C_{33}H_{24}N_4$: C, 83.17; H, 5.08; N, 11.76. Found: C, 83.24; H, 4.82; N, 11.48.

2,4'-Bipyridine-2'-carbonitrile (8): colorless crystals from $CHCl_3$–ether; mp 161.5–162 °C; $CHCl_3$ (CC), 50:1 $CHCl_3$–Me_2CO (TLC); IR (Nujol) 2240 (C≡N), 1590, 1000, 785 cm^{-1}; NMR ($CDCl_3$) δ 8.81 (quartet, 1, $H_{6'}$), 8.78 (m, 1, H_6), 8.37 (quartet, 1, $H_{3'}$), 8.13 (quartet, 1, $H_{5'}$), 7.90 (m, 1, H_3), 7.85 (m, 1, H_4), 7.44 (m, 1, H_5), $J_{5'6'}$ = 5.2 Hz, $J_{3'6'}$ = 0.7 Hz, $J_{3'5'}$ = 1.8 Hz, J_{56} = 5 Hz, J_{46} = 3 Hz, J_{36} = 1.5 Hz, J_{45} = 6 Hz, J_{35} = 3 Hz, J_{34} = 8 Hz. The spectrum was analyzed with the aid of decoupling experiments: UV (EtOH) λ 219 (ε 21 100), 249 (10 200), 278 (14 100) nm; MS *m/e* (rel intensity) 181 (M^+, 100), 154 ($M^+ - HCN$, 63), 131 (metastable peak). Anal. Calcd for $C_{11}H_7N_3$: C, 72.91; H, 3.89; N, 23.19. Found: C, 73.04; H, 3.63; N, 23.12.

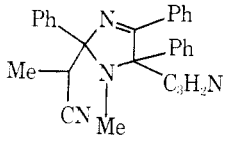
Terpyridine-*x*-carbonitrile (9): light brown crystals from Me_2CO–ether; mp 169–170.5 °C; $CHCl_3$ (CC), 50:1 $CHCl_3$–Me_2CO (TLC); IR (Nujol) 2240 (C≡N), 1590, 855, 780 cm^{-1}; NMR ($CDCl_3$) δ 8.92–7.26 (m); UV (EtOH) λ 225 (ε 24 700), 245 (sh, 21 500), 276 (18 500) nm; MS *m/e* (rel intensity) 258 (M^+, 100), 169 (96). Anal. Calcd for $C_{16}H_{10}N_4$: C, 74.40; H, 3.90; N, 21.70. Found: C, 74.30; H, 3.75; N, 21.46.

2-Cyano-4,5-diphenyl-1-methylimidazole (2h): colorless crystals from ether; mp 144.5–147 °C; C_6H_6 (CC), 50:1 $CHCl_3$–Me_2CO (TLC); IR (Nujol) 2230 (C≡N), 760, 700, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.56–7.00 (m, 10, aromatic), 3.56 (s, 3, CH_3); UV (EtOH) λ 271 (ε 21 300) nm; MS *m/e* (rel intensity) 259 (M^+, 100), 258 (65), 243 (42), 89 (40), 77 (48). Anal. Calcd for $C_{17}H_{13}N_3$: C, 78.74; H, 5.05; N, 16.21. Found: C, 79.03; H, 4.80; N, 16.43.

4,5-Diphenyl-1-methyl-2-α-pyridylimidazole (2i): colorless crystals from ether; mp 126–128 °C; $CHCl_3$ (CC), 10:1 $CHCl_3$–Me_2CO (TLC); IR (Nujol) 1590, 790, 690 cm^{-1}; NMR ($CDCl_3$) δ 8.67–8.49 (m, 1, α-H of Py), 8.44–8.23 (m, 1, Py), 7.90–6.86 (m, 12, aromatic), 3.89 (s, 3, CH_3); UV (EtOH) λ 235 (sh, ε 13 200), 305 (20 600) nm; MS *m/e*

(rel intensity) 311 (81), 310 (100). Anal. Calcd for $C_{21}H_{17}N_3$: C, 81.00; H, 5.50; N, 13.50. Found: C, 81.07; H, 5.30; N, 13.53.

12: colorless crystals from ether; mp 194–197 °C; C_6H_6 (CC), 5:1 $CHCl_3$–C_6H_6 (TLC); IR (Nujol) 2240 (C≡N), 1620, 1615, 1295, 1230, 770, 705, 695, 685 cm^{-1}; NMR ($CDCl_3$) δ 7.97–7.12 (m, 17), 3.77 (quartet, 1, J = 7 Hz, $CHCH_3$), 2.22 (s, 3, CH_3N), 1.48 (d, 3, J = 7 Hz, CH_3CH); UV (EtOH) λ 253 (ε 15 000), 285 (sh, 3300) nm; MS m/e (rel intensity) 416 (M^+, 0.05), 336 (91), 310 ($M^+ - 2AN$, 37), 233 (336–PhCN, 100). Anal. Calcd for $C_{28}H_{24}N_4$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.80; H, 5.78; N, 13.53. Hydrolysis of **12** (24 mg, 0.058 mmol) with 6% HCl (0.8 mL, 1.3 mmol) in ethanol (3 mL) at reflux for 4 h gave 2-benzoylpropionitrile (71%) and benzil (33%). From these data, **12** is believed to have a structure of Δ^3-imidazoline.



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Chemical Reactions of Photoproducts. Hydrolysis of 3a. A solution of **3a** (92 mg, 0.466 mmol) in EtOH (1 mL) was heated with 6% HCl (3 mL, 5.1 mmol) under reflux for 4 h. The mixture was extracted with ether to give essentially pure 2-benzoylpropionitrile (82 mg, ~100% yield).

Hydrolysis of 3b. A mixture of **3b** (316 mg, 0.905 mmol) and 75% H_2SO_4 (974 mg, 7.5 mmol) was heated at 100 °C for 1 h. The reaction mixture was treated with water (10 mL) and extracted with ether. The ethereal extracts were separated by preparative TLC ($CHCl_3$) to yield 166 mg (87%) of benzil and 76 mg (48%) of 2-benzoylpropionamide.

Photolysis of 3a. A Pyrex tube containing a solution of **3a** (140 mg) in EtOH (40 mL) was purged with nitrogen, closed with a glass stopper, and then irradiated externally for 14 h. The photolysate was separated by preparative TLC (15:1 $CHCl_3$–Me_2CO) to give 22 mg (64%) of **1a** and 93 mg of recovered **3a.**

Photolysis of 3b. A Pyrex tube containing a solution of **3b** (62 mg) in MeCN (25 mL) was similarly irradiated to afford 24 mg (47%) of **1b** and 2 mg of recovered **3b.**

Reaction of 3a with $LiAlH_4$. A solution of **3a** (52 mg, 0.264 mmol) in absolute ether (5 mL) was heated with 10 mg (0.264 mmol) of $LiAlH_4$ under reflux for 2.5 h. The mixture was treated with water (1 mL) then with 5% NaOH and extracted with ether. The ethereal extracts were separated by preparative TLC (5:1 $CHCl_3$–Me_2CO) to afford 17 mg (47%) of **1a.**

Reaction of 3b with $LiAlH_4$. A mixture of **3b** (513 mg, 1.47 mmol) and $LiAlH_4$ (100 mg, 2.65 mmol) in THF (40 mL) was similarly treated to give 353 mg (82%) of **1b.**

Thermolysis of 3a. **3a** partly decomposed on GC (1 m column of Silicone DC 550 operated at 200 °C, 2 atm/cm^2 He as a carrier gas). A solution of **3a** (41 mg) in cumene (5 mL) was heated under reflux for 36 h. Almost all **3a** (80%) was recovered unchanged. The only product isolated was bicumyl.

Thermolysis of 3b. A solution of **3b** (31 mg) in cumen (5 mL) was heated under reflux for 12 h. The reaction mixture was separated by preparative TLC (50:1 $CHCl_3$–Me_2CO) to afford 5 mg (~100%) of **1b** and 25 mg of recovered **3b.**

Thermolysis of 4a. A solution of **4a** (16 mg) in cumene (2 mL) was similarly treated to give 11 mg (69%) of **2a** and a trace of **4a.**

$LiAlH_4$ Reduction of 5a. A mixture of **5a** (129 mg, 0.396 mmol) and $LiAlH_4$ (12 mg, 0.32 mmol) in absolute ether (20 mL) was heated under reflux for 3 h. The reaction mixture was treated with water (2 mL), filtered to remove some insoluble solid, and evaporated. The residue was separated by preparative TLC (20:1 $CHCl_3$–MeOH) to give 63 mg of recovered **5a** and 25 mg (38%) of 5-hydroxyl-1-methyl-2,4,4-triphenyl-Δ^2-imidazoline, which was crystallized from Me_2CO–MeOH to give colorless crystals: mp > 195 °C dec; IR (Nujol) 1595, 1570, 1120, 1065, 705, 690 cm^{-1}; UV (EtOH) λ 222 (ε 7100), 260 (sh, 1800) nm; NMR (1:1 $CDCl_3$–CD_3OD) δ 7.77–7.16 (m, 15, aromatic), 5.73 (s, 1, CH–O), 4.57 (s, 1, disappeared on deuteration, OH), 2.97 (s, 3, CH_3); MS m/e (rel intensity)[26] 328 (M^+, 3), 310 ($M^+ - H_2O$, 100), 269 (40). Anal. Calcd for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53. Found: C, 80.07; H, 6.13; N, 8.27.

Methanolysis of 7a. A solution containing **7a** (104 mg, 0.251 mmol) and 35% HCl (0.5 mL, 4.9 mmol) in MeOH (5 mL) and C_6H_6 (3 mL) was heated at 52–57 °C for 5.5 h. The reaction mixture was neutralized to pH 8 with 5% NaOH and extracted with ether. The ethereal extracts were separated with preparative TLC (50:1 $CHCl_3$–Me_2CO) to afford 29 mg of recovered **7a** and 54 mg (67%) of 5-carbomethoxy-1-methyl-4-α-pyridyl-2,4,5-triphenyl-Δ^2-imidazoline (**10a**) which on crystallization from EtOH–petroleum ether afforded colorless crystals: mp 209.5–211 °C; IR (Nujol) 1735 (C=O), 1625, 1590, 1215, 1195, 1060, 1025, 785, 760, 750, 705, 690 cm^{-1}; NMR ($CDCl_3$) δ 8.70–8.51 (m, 1, α-H of Py), 7.87–6.76 (m, 18, aromatic), 3.46 (s, 3, OCH_3), 2.68 (s, 3, NCH_3); UV (EtOH) λ 220 (sh, ε 17 000), 263 (4800) nm; MS m/e (rel intensity)[26] 447 (M^+, 0.1), 388 ($M^+ - CO_2H_3$, 2.5), 270 (100), 167 (45), 139 (16), 118 (53). Anal. Calcd for $C_{29}H_{25}N_3O_2$: C, 77.83; H, 5.63; N, 9.39. Found: C, 77.57; H, 5.39; N, 9.25.

Methanolyses of 7d and 7c were similarly carried out to afford a 64% yield of 5-carbomethoxy-1-methy-4-α-pyridyl-2,4,5-tri-p-tolyl-Δ^2-imidazoline (**10c**) and a 49% yield of 5-carbomethoxy-1,2-dimethyl-4,5-diphenyl-4-α-pyridyl-Δ^2-imidazoline (**10b**), respectively.

10c: colorless crystals from EtOH–ligroin; mp 202–205 °C; IR (Nujol) 1740 (C=O), 1630, 1590, 1215, 1180, 1065, 1035, 830, 750 cm^{-1}; NMR ($CDCl_3$) δ 8.60–8.44 (m, 1, α-H of Py), 7.70–6.53 (m, 15, aromatic), 3.42 (s, 3, OCH_3), 2.66 (s, 3, NCH_3), 2.41 (s, 3, CCH_3), 2.17 (s, 3, CCH_3), 2.08 (s, 3, CCH_3); UV (EtOH) λ 222 (sh, ε 21 700), 265 (6100) nm; MS m/e (rel intensity)[26] 489 (M^+, 0.05), 430 ($M^+ - CO_2Me$, 6.5), 298 (100), 180 (61), 132 (85). Anal. Calcd for $C_{32}H_{31}N_3O_2$: C, 78.50; H, 6.38; N, 8.58. Found: C, 78.28; H, 6.45; N, 8.34.

Crystallization of **10b** failed. It was a white solid: mp 35–50 °C; IR (film) 1740 (C=O), 1640, 1595, 1230, 1210, 755, 695 cm^{-1}; NMR ($CDCl_3$) δ 8.65–8.49 (m, 1, α-H of Py), 7.64–6.77 (m, 13, aromatic), 3.44 (s, 3, OCH_3), 2.74 (s, 3, NCH_3), 2.29 (s, 3, CCH_3); MS m/e (rel intensity)[26] 385 (M^+, 0.1), 208 (100), 167 (21), 118 (8). Anal. Calcd for $C_{24}H_{23}N_3O_2$: C, 74.78; H, 6.01; N, 10.90. Found: C, 73.43; H, 6.26; N, 9.94.

Hydrolysis of 7a. A solution containing **7a** (285 mg, 0.688 mmol) in 4% HCl (15 mL, 16.9 mmol) was heated at 75–78 °C for 6 h. Colorless crystals which appeared gradually in the course of the reaction were collected by filtration. The crystals weighed 265 mg (82%) and were pure 5-carboxy-1-methyl-4-α-pyridyl-2,4,5-triphenyl-Δ^2-imidazoline hydrochloride (**11a**): mp > 194 °C dec; IR (Nujol) 2760–2230 (NH^+), 1725 (C=O), 1605, 1595, 1565, 1210, 1190, 1170, 805, 750, 720, 710, 700 cm^{-1}; NMR (CD_3OD) δ 8.71–8.54 (m, 1, α-H of Py), 8.19–6.77 (m, 18, aromatic), 4.89 (s, 2, disappeared on deuteration, OH and NH^+), 3.19 (s, 3, CH_3); UV (EtOH) λ 232 (sh, ε 17 300), 265 (sh, 9700) nm; MS m/e (rel intensity)[26] 311 (73), 270 (100), 167 (87), 118 (93). Anal. Calcd for $C_{28}H_{24}N_3O_2Cl$: C, 71.56; H, 5.15; N, 8.94; Cl, 7.54. Found: C, 71.74; H, 5.32; N, 8.87; Cl, 7.79.

Hydrolysis of 7c was similarly carried out to afford an 83% yield of 5-carboxy-1,2-dimethyl-4,5-diphenyl-4-α-pyridyl-Δ^2-imidazoline hydrochloride (**11b**): colorless crystals; mp > 215 °C dec; IR (Nujol) 3120–2220 (NH^+ and COOH), 1750 (C=O), 1590, 1170, 790, 690 cm^{-1}; NMR (CD_3OC) δ 8.75–8.56 (m, 1, α-H of Py), 8.06–6.85 (m, 13, aromatic), 4.91 (s, 2, disappeared on deuteration, OH and NH), 3.22 (s, 3, NCH_3), 2.69 (s, 3, CCH_3); UV (EtOH) λ 239 (ε 10 200), 258 (sh, 77 000), 264 (sh, 7000), 271 (sh, 4900) nm. Anal. Calcd for $C_{23}H_{22}N_3O_2Cl$: C, 67.72; H, 5.44; N, 10.30; Cl, 8.69. Found: C, 67.44; H, 5.30; N, 10.33; Cl, 8.96.

Esterification of 11a. A solution of **11a** (27 mg) in MeOH (10 mL) saturated with HCl gas was heated at 50–55 °C for 50 h. The reaction mixture was neutralized with 10% NaOH to pH 8. A white precipitate formed was found to be pure **10a** (62% yield).

Esterification of 11b was similarly carried out. Essentially pure **10b** was obtained in a yield of 62% by extraction with ether.

Oxygen-18 Incorporation Experiment. A solution of 125 mg of **2a** and 40 μL of $H_2{}^{18}O$ (Prochem, 42.0 atm %) in carefully dried MeCN (15 mL) and AN (5 mL) was charged in a Pyrex tube, purged with nitrogen, closed with a glass stopper, and then irradiated externally for 13 h. The photolysate was filtered to remove the AN polymer and evaporated to remove the solvent. The residue was separated with preparative TLC (5:1 $CHCl_3$–C_6H_6) to afford, in addition to the recovered **2a** (48 mg), 12 mg (15%) of ^{18}O-enriched **5a,** which was crystallized from petroleum ether–$CHCl_3$ to give colorless crystals, mp 171.5–173 °C (lit. mp of unlabeled **5a**[18] 165 °C). It was assayed mass spectroscopically (M^+, $M^+ + 2$) to contain 38.3% ^{18}O in the carbonyl oxygen. Simultaneously, the mass spectra of the authentic **5a** and of **5a** which was similarly treated with $H_2{}^{18}O$ were taken. Even a slight evidence for the increase of ^{18}O content in the latter sample could not be found.

Reaction of CP with Na. To a solution of CP (327 mg, 3.15 mmol) in ether (30 mL) was added 150 mg (6.5 mmol) of sodium metal at room temperature. The mixture was stirred overnight and 15 mL of water was added then extracted with ether. The ethereal extracts were separated by preparative TLC (17:1 $CHCl_3$–Me_2CO) to give 15 mg (10% yield) of **8** and 75 mg (50% yield) of α-picolinamide in addition to 200 mg of the recovered CP.

Fluorescence Quenching. The fluorescence intensities for solutions of **1b** and **2a** containing varied amounts of the nitriles (AN, CP,

MN, and CN) were measured at room temperature on a Shimadzu MPS-50L. The irradiations were done at 290 nm except the CP case, where it was at 330 nm. The intensity ratios I_0/I were calculated at wavelengths of the maximal emission (**1b:** 384 nm in EtOH, 386 nm in MeCN; **2a:** 382 nm in EtOH, 385 nm in MeCN). No special care was taken for deaeration of solutions.

Quantum Yield Measurements. Quantum yields for the formation of **3b, 5a, 7a,** and 8 were measured on a merry-go-round apparatus at 20 °C: Sample solutions were purged with nitrogen before irradiation. The intensities of light filtered through potassium chromate–potassium carbonate solution were measured by ferrioxalate actinometry[28] ($I_0^i = 6.7 \times 10^{17}$ quanta/s). The products were assayed by a Shimadzu CS-900 TLC Scanner. The error limit of the quantitative TLC was estimated as ±50%. Benzil and benzophenone were used as the internal standard for **3b** and for **5a, 7a,** and 8, respectively. The solvent systems were 3:1 $CHCl_3$–C_6H_6 for **3b,** 2.5:1 $CHCl_3$–C_6H_6 for **5a,** and 30:1 C_6H_6–Me_2CO for **7a** and 8. The irradiations were stopped at less than 10% conversion.

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Registry No.—**1a,** 670-96-2; **1b,** 484-47-9; **1c,** 52910-09-5; **2a,** 22397-44-0; **2b,** 13730-10-4; **2c,** 16340-59-3; **2d,** 67921-77-1; **2e,** 50609-88-6; **2f,** 3475-07-8; **2g,** 15994-89-5; **2h,** 67921-78-2; **2i,** 67921-79-3; **3a,** 52910-10-8; **3b,** 52910-11-9; **4a,** 52910-12-0; **4a′,** 52910-13-1; **4b,** 67921-80-6; **4b′,** 67921-81-7; **4c,** 67921-82-8; **4c′,** 67921-83-9; **5a,** 24133-91-3; **5b,** 58469-45-7; **6a,** 58484-95-0; **6b,** 16408-28-9; **6c,** 67921-84-0; **6d,** 67921-85-1; **6e,** 50609-89-7; **6f,** 67921-86-2; **7a,** 67921-87-3; **7b,** 67921-88-4; **7c,** 67921-89-5; **7d,** 67921-90-8; **7e,** 67921-91-9; **8,** 67921-92-0; **9,** 67988-41-4; **10a,** 67921-93-1; **10b,** 67921-94-2; **10c,** 67921-95-3; **11a,** 67951-66-0; **11b,** 67921-96-4; 12, 67921-97-5; AN, 107-13-1; CP, 100-70-9; methacrylonitrile, 126-98-7; crotononitrile, 4786-20-3; 5-hydroxy-1-methyl-2,4,4-triphenyl-Δ^2-imidazoline, 67921-98-6.

References and Notes

(1) Photoinduced Reactions 102.
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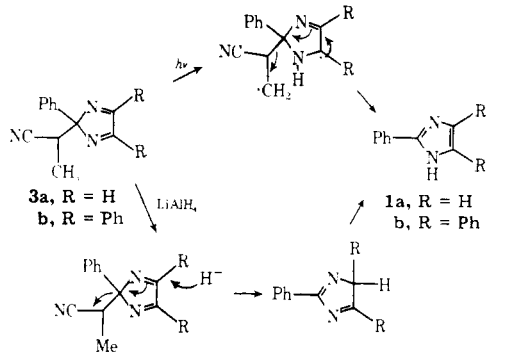

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(8) However, we have no direct evidence for the formation of the exciplex such as exciplex fluorescence.
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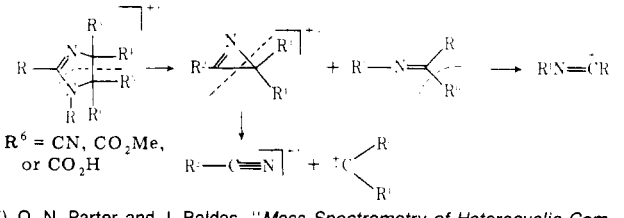
(25) We were unsuccessful in obtaining an analytically pure sample of these compounds.
(26) The mass spectra of Δ^2-imidazolines **7a–e, 10a,b,** and **11a,b** were reasonably interpreted by the following fragmentation pattern.[27]



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