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Kinetics of the Reactions of Phenylketene Dimethyl Acetal with Azocarboxylate Esters

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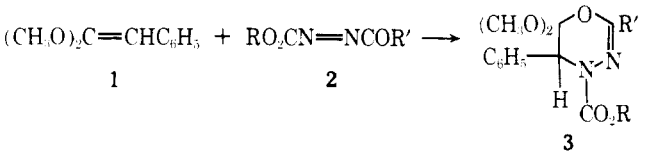
The kinetics of the reaction of phenylketene dimethyl acetal with diethyl azodicarboxylate, dimethyl azodicarboxylate, and ethyl benzoylazocarboxylate to give 5,6-dihydrooxadiazines have been determined. The relative rates in benzene at 40 °C are 1:3.22:29.1. The reactions are accelerated slightly by polar solvents. The relative rates in benzene and acetonitrile are 1:13.4 and 1:3.4 for diethyl azodicarboxylate and ethyl benzoylazocarboxylate, respectively. The enthalpies of activation were highly negative (−36 to −46 cal deg^{-1} mol^{-1}), typical of other $2\pi + 4\pi$ cycloaddition reactions. The question of the involvement of a 1,4-dipolar intermediate vs. a concerted cycloaddition is discussed.

Although there are many reports on the cycloaddition reactions of azocarboxylate esters, there have been only a few kinetic studies. Rodgman and Wright[1] examined the Diels–Alder reactions of dimethyl and diethyl azodicarboxylates with cyclopentadiene. They reported that the rate of reaction with the methyl ester was increased slightly as the solvent was changed from petroleum ether to benzene to dioxane (relative rate, 1:3.3:4.6). Activation parameters calculated from their data on the ethyl esters indicate the normal low enthalpy of activation (11.6 kcal/mol) and highly negative entropy of activation (−33 eu) commonly observed in Diels–Alder reactions. Gustorf and Kim[2] examined the kinetics of the reaction of indene with diethyl azodicarboxylate under the assumption that the product was a 1,2-diazetidine. The product was later shown to be a 5,6-dihydrooxadiazine.[3,4] The reaction was reported to be somewhat faster in polar solvents (relative rate, 1:1.5:5.2:6.2:8.6 in ethyl acetate, benzene, acetic anhydride, acetonitrile, and indene, respectively). The activation parameters were similar to those reported for the reaction with cyclopentadiene, except that the entropy of activation was much more negative ($\Delta H^* = 12.8$ kcal/mol; $\Delta S^* = -44$ eu in indene). Gustorf and co-workers[3] also reported the kinetics of the reaction of diethyl azodicarboxylate with ethyl vinyl ether; in this case the product is a 1,2-diazetidine. Here also, the reaction is accelerated slightly in the more polar solvents (relative rate, 1:1.3:1.7:5.7 in ethyl vinyl ether, ethyl acetate, benzene, acetic anhydride, and acetonitrile). The activation parameters of this $\pi^2 + \pi^2$ reaction were remarkably similar ($\Delta H^* = 11.0$; $\Delta S^* = -46$ in ethyl acetate) to those of the π^2s + π^4s Diels–Alder reaction above. However, in spite of the similarity, a stepwise mechanism was postulated based on a study of secondary isotope effects at the reaction centers.[6,7]

In a study of the reactions of ketene acetals with azocarboxylate esters, it has been shown that the initial products are 5,6-dihydrooxadiazines.[8] In this paper, the kinetics of the reaction of phenylketene dimethyl acetal with dimethyl and diethyl azodicarboxylates and with ethyl benzoylazocarboxylate are reported. The kinetics were monitored by following



a, R = CH_3; R′ = OCH_3
b, R = C_2H_5; R′ = OC_2H_5
c, R = C_2H_5; R′ = C_6H_5

the rate of disappearance of the colored azo compound spectrophotometrically. The reactions were carried out under pseudo-first-order conditions using a 10–40-fold molar excess of phenylketene dimethyl acetal. The first-order plots were linear over 5 half-lives. The rate constants are given in Table I. The second-order rate constants were calculated by dividing k_{obsd} by the phenylketene dimethyl acetal concentration.

The relative rates at 40 °C of diethyl azodicarboxylate, dimethyl azodicarboxylate, and ethyl benzoylazocarboxylate, calculated from the data in Table I, are 1:3.22:29.1. The slower rate for the diethyl ester compared with the dimethyl ester is consistent with the Diels–Alder reactions of these compounds with cyclopentadiene, where the relative rates are 1:5.3 in benzene at 23.5 °C.[1] It is also in agreement with the qualitative observation of Firl and Sommer that the dimethyl ester reacts faster than the diethyl ester in its reaction with phenyl vinyl ether; however, in this case the products are mixtures of a 1,2-diazetidine and a 5,6-dihydrooxadiazine in 77:23 and 65:35 ratios for the dimethyl and diethyl esters, respectively.[9]

The increased rate of reaction of ethyl benzoylazocarboxylate over that of the azodicarboxylate esters was not expected, since the reaction of azodibenzoyl with vinyl ethers to give 5,6-dihydrooxadiazines is apparently rather slow.[10] The reaction of ethyl benzoylazocarboxylate with phenylketene dimethyl acetal is regiospecific, giving only **3c**.[8b] Apparently it also reacts with phenyl vinyl ether regiospecifically,[10] although details were not given.

The rates of reaction of both diethyl azodicarboxylate and

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Table I. Kinetics of the Reaction of Azo Esters with Phenylketene Dimethyl Acetal in Benzene

temp, °C	$k_{obsd} \times 10^3$, min^{-1}	$k_2 \times 10^4$, L mol^{-1} s^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}
	Dimethyl Azodicarboxylate			
29.0	2.55	3.00		
40.0	5.09	5.99	11.0 ± 0.5	−38.1 ± 1
50.2	8.84	10.4		
59.4	15.2	17.9		
	Diethyl Azodicarboxylate			
30.0	1.06	1.18		
40.5	1.70	1.89	12.5 ± 1	−36 ± 2
51.0	3.88	4.31		
64.0	9.28	10.3		
40.5	2.13	2.37	in benzene with diphenylamine[a]	
40.5	22.8	25.3	in acetonitrile	
40.5	54.7	60.8	in *tert*-butyl alcohol	
	Ethyl Benzoylazocarboxylate			
22.4	40.2	39.9	6.8 ± 0.5	−46.5 ± 1
30.9	56.7	56.3		
40.8	85.1	84.5		
49.1	114	113		
22.0	135	134	in acetonitrile	

[a] An amount equal to 10% of the weight of the azo compound was used.

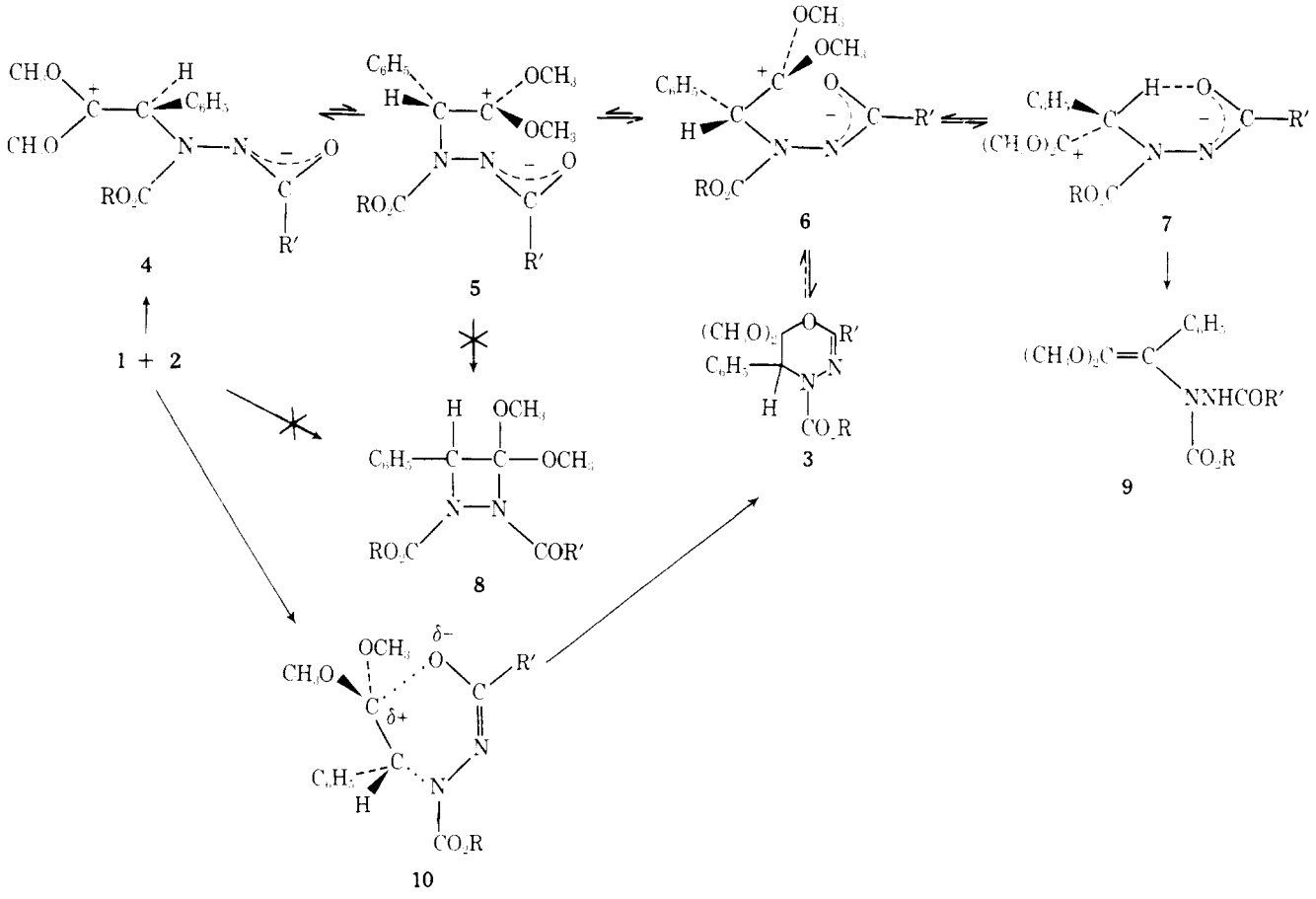
ethyl benzoylazocarboxylate with phenylketene dimethyl acetal were enhanced by changing the solvent from benzene to acetonitrile by factors of 1:13.4 and 1:3.4, respectively. The enhanced rate observed with diethyl azodicarboxylate in *tert*-butyl alcohol may be due to hydrogen bonding of the solvent to the nitrogens of the azo compounds. Rate enhancements of the reaction of dialkyl azodicarboxylate esters with cyclopentadiene by alcohols has been reported.[1] This type of catalysis is sometimes accompanied by a decrease in the apparent order of the reaction. However in *tert*-butyl alcohol the pseudo-first-order plot was linear over at least 5 half-lives.

The addition of the radical inhibitor, diphenylamine, did not decrease the rate of reaction of diethyl azodicarboxylate with phenylketene dimethyl acetal; in fact a small enhancement was observed.

Some of the mechanistic possibilities for these cycloadditions are given in Scheme I. The reaction of ketene acetals with azocarboxylate esters provides an ideal situation for formation of a 1,4-dipolar intermediate. The two alkoxy groups can provide a high degree of stabilization of the positive charge and the amide can provide stabilization of the negative charge as the enolate anion. Let us assume that the 1,4-dipole is formed initially as conformer **4** (or any conformation other than **5–7**). Simple rotation around the C–N bond (least motion) would lead to **5**, the conformation needed for 1,2-diazetidine formation. Examination of models suggests that **5** would be the least stable conformer largely due to the interaction of the groups on the nitrogens. The fact that 1,2-diazetidines are not formed could be explained by assuming that the 1,4-dipole is sufficiently stable that it has time to change to a more stable conformer such as **6** or **7**, leading to **3** or **9**, rather than undergoing ring closure. This idea is consistent with 1,2-diazetidine formation with vinyl ethers,[3,5,6,9,11,12] where the 1,4-dipole would be less stabilized by the single alkoxy group and could undergo kinetic controlled ring closure.

Since the observed products of the reactions of ketene acetals with azodicarboxylate esters are mixtures of **3** and **9**, closure of the 1,4-dipole to the six-membered ring and intra-

Scheme I



molecular hydrogen transfer would both have to be faster than 1,2-diazetidine formation. Further, it has been shown in the case of **3a** and **3b** that the 5,6-dihydrooxadiazine structure is formed initially, but it opens back up over a period of time to give **9** via irreversible proton transfer. It should be emphasized that the opening of **3** and conversion to **9** may be unique to the 6,6-dialkoxy-5,6-dihydrooxadiazine system, since the oxadiazine derived from azodicarboxylate esters and phenyl vinyl ether does not open up over a period of 3 weeks at 40 °C.[8] At the same time, products analogous to **9** are apparently not formed.

It is not necessary to postulate initial formation of a 1,4-dipole to account for the products. The oxadiazine **3** could just as well be formed via the normal concerted Diels–Alder reaction, followed by ring opening to give the 1,4-dipole, which undergoes irreversible proton transfer to **9**. This raises the general question as to whether any of the substitution products of type **9** are formed from an initially formed 1,4-dipole, or whether these arise only by decomposition of oxadiazines (or 1,2-diazetidines). If 1,4-dipolar intermediates are claimed to be involved in a cycloaddition, and substitution products such as **9** are missing, the claim should be suspect.

If one assumes that the transition state in the $\pi^2s + \pi^4s$ reaction is somewhat polar as depicted in structure **10**, one can account for the small acceleration of the reaction by polar solvents. This point should not be overemphasized, however, since the magnitudes of the solvent effects given in Table I are not a whole lot larger than that for the reaction of azocarboxylate esters with cyclopentadiene,[1] where the transition state would be symmetric, or with indene,[3] where the transition state would not be expected to be very polar. Contrary to claims in the literature,[3,13] the formation of a 1,4-dipole should be accompanied by a large solvent effect if formation of the 1,4-dipole is rate determining, i.e.

$$1 + 2 \xrightarrow{\text{slow}} 4 \xrightarrow{\text{fast}} 3 \qquad (1)$$

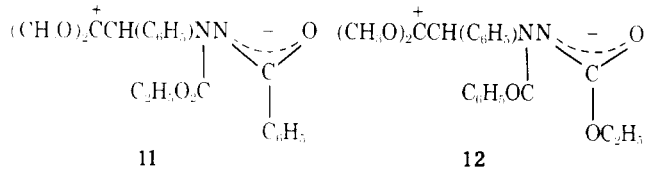
On the other hand if formation of the 1,4-dipole is an equilibrium process and product formation is rate determining, polar solvents should favor formation of the dipole, but disfavor formation of **3**.

$$1 + 2 \overset{\text{fast}}{\rightleftharpoons} 4 \xrightarrow{\text{slow}} 3 \qquad (2)$$

In this situation, the concentration of the 1,4-dipole would have to increase to an appreciable concentration during the reaction. Since the detection of **4** has not been possible, this does not seem like a very good explanation of the small solvent effect.

Either the rate-determining formation of a 1,4-dipole **4** (eq 1) or the concerted path via the polar transition state **10** can explain the acceleration of the rate as the alkoxy group of the azodicarboxylate ester is changed from ethoxy to methoxy in line with the increase in the inductive effect of the groups.

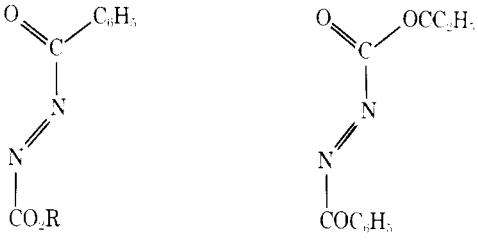
The mechanism must explain both the increased rate of reaction with ethyl benzoylazocarboxylate as compared to diethyl azodicarboxylate and also the regiospecificity of the reaction. In the dipolar mechanism, the two possible 1,4-dipoles would be **11** and **12**.



11 **12**

The dipole **11** would be expected to be more stable than **12** because of the greater stabilization of the enolate ion in **11**. This would account for the regiospecificity. Also the formation of the more stable anion would account for the rate enhancement.

If the reaction proceeds through a concerted Diels–Alder reaction, the above stabilization effects would also apply if the transition state is relatively polar as indicated in structure **10**; except in this case, the stabilizing effect of the anion should be much reduced. Also, in this case, the ketene acetal is donating electrons from its HOMO to the LUMO of the azo-



13 **14**

compound. The substitution of a benzoyl group for a carboalkoxy group lowers the LUMO of the azo compound,[8b] making it a better electrophile, i.e., the diene **13** is more electrophilic than diene **14** and hence the rate enhancement.

In summary, either the 1,4-dipolar mechanism or the concerted $\pi^2s + \pi^4s$ mechanism can explain the observations with the exception of the solvent effect. The small solvent effect is consistent with the concerted $\pi^2s + \pi^4s$ mechanism, but it can be accommodated by the 1,4-dipolar mechanism only if dipole formation is fast compared to ring closure. Since this seems unlikely in this case, the authors view the reaction as a normal concerted Diels–Alder reaction. Further, if this is the case, it seems most unlikely that the reaction of vinyl ethers with azocarboxylate esters to give 5,6-dihydrooxadiazines involves a 1,4-dipole[2,3,5,6,9-12] either.

Experimental Section

Ethyl benzoylazocarboxylate was prepared from the hydrazine[14] by oxidation with chlorine following the Rabjohn procedure.[15] Dimethyl azodicarboxylate was prepared in the same manner. Diethyl azodicarboxylate was purchased from Aldrich Chemical Co. All of the azo compounds were carefully distilled before use. Phenylketene dimethyl acetal was prepared from α-bromophenylacetaldehyde dimethyl acetal,[16] using an adoption of the procedure of McElvain and Beyerstedt.[17] It was distilled immediately before use. To avoid polymerization of the phenylketene dimethyl acetal all glassware was washed with base and water and thoroughly dried before use. The benzene used as solvent was spectral grade, dried over sodium for several days.

Phenylketene Dimethyl Acetal. Potassium (6.50 g, 0.210 g-atom) was refluxed in 112 g of anhydrous *tert*-butyl alcohol until the potassium had dissolved. To this solution was added 39.1 g (0.160 mol) of α-bromophenylacetaldehyde dimethyl acetal[16] dropwise with stirring. The excess *tert*-butyl alcohol was distilled off through a 30-cm Vigreux column. The residue was fractionated on a spinning band column under reduced pressure to give 19.4 g (74.1%): bp 81–83 °C (1 mm) (lit.[18] bp 124–6 °C (14 mm)); IR (neat) 1650 cm^{-1}; NMR ($CDCl_3$) δ 3.54 (s, 3 H), 3.62 (s, 3 H), and 4.50 (s, 1 H).

Kinetic Measurements. The kinetics of the reactions were followed by monitoring the disappearance of the visible absorption of the azo compound at λ_{max} in benzene:diethyl azodicarboxylate, 402 nm; dimethyl azodicarboxylate, 403.5 nm, and ethyl benzoylazocarboxylate, 430 nm. A Unicam SP. 800 spectrophotometer equipped with a variable temperature cell holder was used for the measurements. The reactions were carried out under pseudo-first-order conditions, using a large excess of phenylketene dimethyl acetal (0.25–1.2 mol/L). The plot of ln *A* vs. time was linear over at least 5 half-lives. The observed rate constants were calculated using a least-squares computer program. Enthalpies of activation were calculated from a plot of $\ln k_{obsd}/T$ vs. $1/T$. The second-order rate constants, k_2, were calculated from the slope of a plot of k_{obsd} vs. phenylketene dimethyl acetal concentration. The entropies of activation were calculated at the temperature given in Table I.

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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