Photochemistry of Phenyl-Substituted 1-Methylpyrazoles

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Direct irradiation of 1-methyl-4-phenylpyrazole (**2**) in methanol results in regiospecific phototransposition to 1-methyl-4-phenylimidazole (**4**) and in photocleavage to (*E*)/(*Z*)-3-(*N*-methylamino)-2-phenylpropenenitrile (**5**) and (*E*)/(*Z*)-2-(*N*-methylamino)-1-phenylethenyl isocyanide (**6**). Deuterium labeling confirms that the phototransposition occurs *via* the P_4 permutation pathway. Separate experiments show that **5** and **6** undergo (*Z*) → (*E*) isomerization and photocyclization to imidazole **4**. Quantum yields for these reactions show that the sequence **2** → **6** → **4** is a major pathway for the P_4 phototransposition of **2** → **4**. Isocyanides were also detected as intermediates in the P_4 phototransposition of a variety of other pyrazoles confirming the generality of this pathway in pyrazole photochemistry. Direct irradiation of 1-methyl-5-phenylpyrazole (**3**) resulted in the formation of 1-methyl-5-phenylimidazole (**7**), 1-methyl-2-phenylimidazole (**8**), and 1-methyl-4-phenylimidazole (**4**). Deuterium labeling revealed that these products were formed by P_4, P_6, and P_7 permutation pathways, respectively. (*E*)/(*Z*)-3-(*N*-methylamino)-3-phenylpropenenitrile (**9**) and (*E*)/(*Z*)-2-(*N*-methylamino)-2-phenylethenyl isocyanide (**10**) photocleavage products were also formed in this reaction. Irradiation of **3** in furan solvent did not result in phototransposition but led to the formation of *endo* and *exo* adducts formed by Diels−Alder reaction of furan with 4-phenyl-5-methyl-1,5-diazabicyclo[2.1.0]pent-2-ene. This constitutes the first direct evidence for the formation of a 1,5-diazabicyclo[2.1.0]hex-2-ene from photolysis of a pyrazole and is consistent with the electrocyclic ring closure−heteroatom migration mechanism suggested for the P_6 and P_7 phototranspositions.

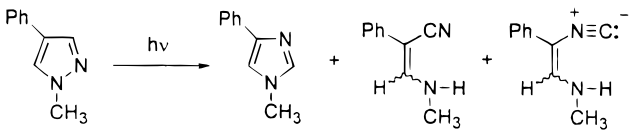
Introduction

1-Methylpyrazoles undergo phototransposition to 1-methylimidazoles and photocleavage to *N*-methylenamino nitriles.[1−5] Permutation pattern analysis[6,7] revealed that the phototransposition occurs by the P_6, P_7, and/or the P_4 permutation pathways and thus by up to three different mechanistic routes. Replacement of the 1-methyl group with phenyl substantially alters the regiochemistry of the phototransposition. Thus, 1-phenylpyrazoles transpose regiospecifically to 1-phenylimidazoles *via* the P_4 pathway.[8] In this report we present the results of our study of the photochemistry of 1-methylpyrazoles substituted with phenyl at the carbon atoms of the pyrazole ring rather than at nitrogen. These studies provide information regarding the nature of intermediates on the phototransposition pathways.

Results and Discussion

1-Methyl-3-phenylpyrazole (**1**) does not undergo transposition even after prolonged photolysis in methanol solvent. Thus, after irradiation of a solution of **1** in methanol (3.0 mL, 2.0×10^{-2} M) for 42 h, 42% of **1** was consumed, but no volatile products could be detected by gas−liquid chromatographic (GLC) analysis.

In contrast, we have recently shown that 1-methyl-4-phenylpyrazole (**2**) undergoes phototransposition to 1-methyl-4-phenylimidazole (**4**) and photocleavage resulting in the formation of (*E*)/(*Z*)-3-(*N*-methylamino)-2-phenylpropenenitrile (**5**) and (*E*)/(*Z*)-2-(*N*-methylamino)-1-phenylethenyl isocyanide (**6**).[9] The permutation pattern



2 **4** ***(E) I(Z)*-5** ***(E) I(Z)*-6**

for the phototransposition of **2** to **4** was determined by studying the phototransposition of 5-deuterio-1-methyl-4-phenylpyrazole (**2**-5-d_1), which was synthesized by exchange of the C-5 proton by treatment of **2** with butyllithium followed by quenching of the lithium reagent with D_2O. The mass spectrum of the resulting product exhibited a molecular ion at *m/e* 159, indicating complete deuteration of **2**. In addition, the ^{1}H NMR spectrum of the deuterated product exhibited a one-proton singlet at δ 7.80 for the C-3 proton of **2** but showed no signal at δ 7.60 where the C-5 proton of **2** is known to absorb. This confirms that the product is 5-deuterio-1-methyl-4-phenylpyrazole (**2**-5-d_1).

Irradiation of a solution of **2**-5-d_1 in methanol (20 mL, 2.0×10^{-2} M) for 3 h followed by preparative layer chromatography led to the isolation of the phototransposition product. The mass spectrum of this material

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

(1) Tiefenthaler, H.; Dörscheln, W.; Göeth, H.; Schmid, H. *Helv. Chim. Acta* **1967**, *50*, 2244.

(2) (a) Beak, P.; Miesel, J. L.; Messer, W. R. *Tetrahedron Lett.* **1967**, 5315. (b) Beak, P.; Messer, W. R. *Tetrahedron* **1969**, *25*, 3287.

(3) Barltrop, J. A.; Day, A. C.; Mack, A. G.; Shahrisa, A.; Wakamatsu, S. *J. Chem. Soc., Chem. Commun.* **1981**, 604.

(4) Wakamatsu, S.; Barltrop, J. A.; Day, A. C. *Chem. Lett.* **1982**, 667.

(5) Pavlik, J. W.; Kurzweil, E. M. *J. Org. Chem.*, **1991**, *56*, 6313.

(6) For a discussion of permutation pattern analysis in aromatic phototransposition chemistry and its application to the analysis of the phototransposition reactions of five-membered heteroaromatics, see: Barltrop, J. A.; Day, A. C. *J. Chem. Soc., Chem. Commun.* **1975**, 177. Barltrop, J. A.; Day, A. C.; Moxon, P. D.; Ward, R. W. *J. Chem. Soc., Chem. Commun.* **1975**, 786.

(7) For five-membered heterocycles containing two heteroatoms there are 12 different ways of transposing the five ring atoms resulting in 12 permutation patterns identified P_1−P_{12}. For a table showing these permutation patterns see ref 5.

(8) Pavlik, J. W.; Connors, R. E.; Burns, D. S.; Kurzweil, E. M. *J. Am. Chem. Soc.* **1993**, *115*, 7645.

(9) Pavlik, J. W.; Kebede, N.; Bird, N. P.; Day, A. C.; Barltrop, J. A. *J. Org. Chem.* **1995**, *60*, 8138

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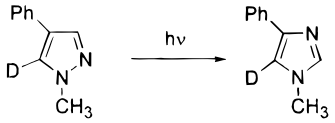
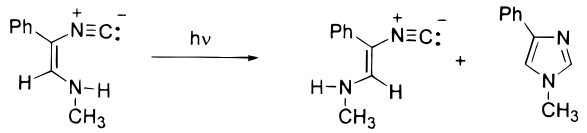
exhibited a base peak at *m/e* 159 showing that the deuterium label had not been lost during the reaction and isolation. The ^{1}H NMR spectrum exhibited a one-proton singlet at δ 7.71 for the C-2 proton of **4** but no signal at δ 7.15 where the C-5 proton of 1-methyl-4-phenylimidazole is known to absorb. This shows that 5-deuterio-1-methyl-4-phenylpyrazole (**2**-5-d_1) has undergone phototransposition to 5-deuterio-1-methyl-4-phenylimidazole (**4**-5-d_1) and confirms that the transposition has occurred *via* the P_4 permutation pathway.



2-5d$_1$ **4-5d$_1$**

Monitoring the photoreaction of 1-methyl-4-phenylpyrazole (**2**) as a function of irradiation time revealed the continuous consumption of **2** and the formation of imidazole **4** and nitrile **5**. During the 3 h of irradiation, however, ^{1}H NMR analysis showed that the concentration of isocyanide **6** reached a maximum after approximately 1 h and then decreased upon further irradiation. Indeed, when the reaction was discontinued after 1 h of irradiation, UV-absorption and ^{1}H NMR analysis showed that 21% of **2** had been consumed, while **4**, **5**, and **6** had been formed in yields of 17%, 12%, and 68%, respectively.

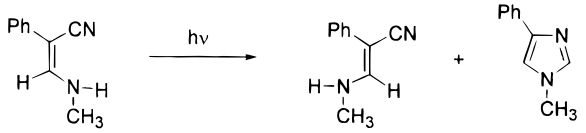
The formation and subsequent consumption of **6** suggested that the isocyanide might be an intermediate in the conversion of **2** to **4** and/or **5**. This possibility was explored by monitoring the direct irradiation of purified (*Z*)-**6**. A solution of (*Z*)-**6** in methanol (3.0 mL, 1.44 $\times$ 10^{-2} M) was irradiated for 5 min. UV and ^{1}H NMR spectroscopic analysis of the resulting solution showed a 24% consumption of (*Z*)-**6**. In addition to the doublet at δ 3.10 due to residual (*Z*)-**6**, the ^{1}H NMR spectrum showed a second doublet at δ 2.86 due to the formation of (*E*)-**6** in 51% yield and a singlet at δ 3.70, confirming the formation of imidazole **4** in 28% yield. These results



(Z)-**6** *(E)*-**6** **4**

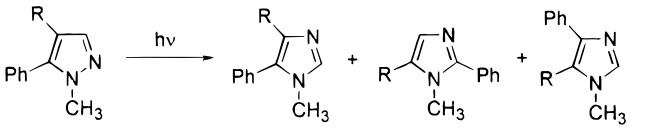
clearly show that isocyanide (*Z*)-**6** undergoes (*Z*) $\rightarrow$ (*E*) isomerization and photocyclization to imidazole **4**. In addition, cyclization of (*Z*)-**6** to **4** was also observed when the former was heated to 80 °C. No evidence, however, could be detected for the photochemical or thermal isomerization of isocyanide **6** to enaminonitrile **5**.

The direct irradiation of enaminonitrile **5** was also investigated. When a solution of **5** in methanol (97% *Z*, 3.0 mL, 2.0 $\times$ 10^{-2} M) was irradiated for 20 min, ^{1}H NMR analysis of the residue showed that 39% of (*Z*)-**5** had been consumed and that an almost quantitative yield of (*E*)-**5** had been formed. A very small singlet could also be discerned at δ 3.76 due to the formation of a trace quantity of imidazole **4**.[10] Irradiation of the solution for 3.0 h under the same conditions resulted in the consumption of 42% of (*Z*)-**5** and the formation of (*E*)-**5** and imidazole **4** in yields of 36% and 33%, respectively.



(Z)-**5** *(E)*-**5** **4**

Unlike 1-methyl-4-phenylpyrazole (**2**), 1-methyl-5-phenylpyrazole (**3**) did not undergo regiospecific phototransposition. When a solution of **3** in methanol (3.0 mL, 2.0 $\times$ 10^{-2} M) was irradiated for 3.0 h, GLC analysis showed the consumption of 76% of **3** and the formation of three volatile products that were identified as 1-methyl-5-phenylimidazole (**7**), 1-methyl-2-phenylimidazole (**8**), and 1-methyl-4-phenylimidazole (**4**) in yields of 30, 29, and 31%, respectively. These photoproducts were identified by direct comparison of their chromatographic and spectroscopic properties with those of authentic samples of these compounds synthesized in this laboratory.



3 (R = H) **7** **8** **4**

3-4d$_1$ (R = D) **7-4d$_1$** **8-5d$_1$** **4-5d$_1$**

The permutation patterns for these products were confirmed by studying the phototransposition chemistry of 4-deuterio-1-methyl-5-phenylpyrazole (**3**-4-d_1) prepared by the acid-catalyzed deuterium exchange of **3**. Deuterium incorporation was confirmed by the mass spectrum, which exhibited a molecular ion at *m/e* 159. Furthermore, the ^{1}H NMR spectrum exhibited a one proton singlet at δ 7.53 for the C-3 proton but no signal for the C-4 proton at δ 6.33.

A solution of **3**-4-d_1 in methanol (50 mL, 2.0 $\times$ 10^{-2} M) was irradiated for 1.5 h. ^{1}H NMR analysis of the individual phototransposition products, separated by preparative-layer chromatography, showed that H-3 of the reactant had transposed to position 2 in 1-methyl-5-phenylimidazole (**7**-4-d_1), to position 4 in 1-methyl-2-phenylimidazole (**8**-5-d_1), and to position 2 in 1-methyl-4-phenylimidazole (**4**-5-d_1) confirming that the transpositions had occurred *via* the P_4, P_6, and P_7 permutation pathways.

The photoreaction of **3** was also monitored by ^{1}H NMR spectroscopy after shorter irradiation times. Thus, after irradiation of a solution of **3** in methanol (3.0 mL, 2.0 $\times$ 10^{-2} M) for 8 min, the ^{1}H NMR spectrum of the residue showed the appearance of three singlets at δ 3.62, 3.56 and 3.60 due to the formation of the P_4, P_6, and P_7 *N*-methylimidazoles **7**, **8**, and **4**. In addition, the spec-

(10) For additional examples of the photocyclization of enamino nitriles see: (a) Ferris, J. P.; Kuder, J. E.; Cantalano, A. W. *Science* **1969**, *1966*, 765. (b) Ferris, J. P.; Kuder, J. E.; *J. Am. Chem. Soc.* **1970**, *92*, 2527. (c) Koch, T. H.; Rodehorst, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 6707. (d) Ferris, J. P.; Trimmer, R. W. *J. Org. Chem.* **1976**, *41*, 19. (e) Ferris, J. P.; Narang, R. S.; Newton, T. A.; Rao, V. R. *J. Org. Chem.* **1979**, *44*, 1273.

Table 1. Quantum Yields for Pyrazoles 1−3

reactant	ϕ(consumption)	$\phi(P_4)$	ϕ(isocyanide)	ϕ(cyanide)	$\phi(P_6)$	$\phi(P_7)$
1	0					
2	0.22 ± 0.01	0.037 ± 0.002	0.11 ± 0.01	0.0080 ± 0.001		
3	0.041 ± 0.003	0.0080 ± 0.0001	$<10^{-3}$	$<10^{-3}$	0.014 ± 0.001	0.022 ± 0.007

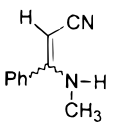
Table 2. Quantum Yields for Nitrile and Isocyanide Photolysis

reactant	ϕ(consumption)	ϕ(*E*-isomer)	$\phi(P_4$ imidazole)
(*Z*-**5**	0.26 ± 0.01	0.26 ± 0.01	$<10^{-3}$
(*Z*)-**6**	0.42 ± 0.01	0.22 ± 0.01	0.12 ± 0.01

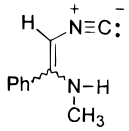
Table 3. Spectroscopic Data

compd	abs, λ (nm)	log ϵ	fl(0,0) kcal/mol	ph(0,0) kcal/mol	ϕ_f	ϕ_p	τ_f (ns)	τ_p (s)
1	248.3	4.20	104.4	73.9	0.36	0.19	13.10	7.67
2	249.7	4.24	104.8	77.3	0.31	0.47	7.47	8.17
3	238.0	4.24	103.7	72.9	0.30	0.37	4.68	8.75

trum also revealed one pair of doublets (J = 5.3 Hz) at δ 2.73 and 2.84 and a second pair at δ 2.78 (J = 4.9 Hz) and 3.28 (J = 3.5 Hz). Although the compounds responsible for these signals were not isolated, the first pair of doublets was assigned to the *E* and *Z* isomers of 3-(*N*-methylamino)-3-phenylpropenenitrile (**9**) by comparison with the ^{1}H NMR spectrum of (*E*)-**9** synthesized in this laboratory. The second pair of doublets is consistent with the *E*- and *Z*-isomers of isocyanide **10**. As expected from



(E)/(Z)-**9**



(E)/(Z)-**10**

these assignments, after 20 min of irradiation the doublets due to the (*E*)- and (*Z*)-nitrile **9** continued to grow in intensity while those assigned to isocyanide **10** were substantially diminished.

Quantum Yields. The quantum yields for reactant consumption and product formation from irradiation of phenyl-substituted 1-methylpyrazoles **1**−**3** and enaminonitrile **5** were determined in triplicate using 1,3-dimethyluracil[11] as the actinometer while the quantum yields for the reaction of isocyanide **6** were determined using 1,3-cycloheptadiene[11] as the actinometer and are tabulated in Table 1 and 2.

Sensitized Irradiations. Sensitized irradiations of phenyl-substituted pyrazoles **1**−**3** (E_T = 72.9−77.3 kcal/mol based on the 0,0 band of phosphorescence) were carried out in acetone (E_T = 79−82 kcal/mol).[12] All of these phenyl-substituted pyrazoles were found to be unreactive as triplets.

Spectroscopic Properties. Pyrazoles **1**−**3** exhibit structureless absorption spectra in methanol solvent with absorption maxima (Table 3) ranging from 238 to 250 nm with extinction coefficients consistent with $\pi \rightarrow \pi^*$ transitions. **1**−**3** exhibit both fluorescence and phosphorescence in methanol/ethanol. At 77 K, discernible 0,0 bands in the fluorescence spectra are at approximately 104 kcal/mol while the 0,0 bands in the phosphorescence indicate that the triplet states are located at 73−77 kcal/mol. The quantum yields of fluorescence at room temperature and phosphorescence at 77 K are shown in Table 3 and reveal that the unreactive 3-phenyl isomer **1** has a fluorescence-to-phosphorescence ratio of 2.6, whereas the more reactive 4- and 5-phenylisomers **2** and **3** have larger proportions of phosphorescence with fluorescence-to-phosphorescence ratios of only 0.8. The measured fluorescence and phosphorescence lifetimes at room temperature and at 77 K, respectively, are also shown in Table 3.[13] The 5-phenyl isomer **3** was observed to exhibit double fluorescence decay with lifetimes of 2.82 and 7.14 ns. This may be due to emission from conformations with different angles of twist between the phenyl and pyrazole rings. The forced single-exponential decay gave a lifetime of 4.68 ns, which is the value shown in Table 3. These lifetimes of S_1 and T_1 states and the energy gaps are consistent with π,π^* configurations. The values of the radiative rate constants for fluorescence and the rate constants for the formation of various products have been calculated from $k_f = \phi_f/\tau_f$ and $k_r = \phi_{product}/\tau_f$ and are shown in Table 4.

Generality of Isocyanide Pathway. These results reveal the operation of two different photocleavage−photocyclization pathways for the P_4 transposition. The quantum yields for geometrical isomerization and photocyclization of enaminonitrile (*Z*)-**5** given in Tables 1 and 2 confirm our earlier suggestion that at short irradiation times this pathway cannot account for a significant portion of the P_4 imidazole formed.[5] In contrast, the quantum yields for the same reactions of (*Z*)-**6** show that even at short irradiation times transposition *via* an isocyanide intermediate can account for formation of a significant fraction of the imidazole product.

Although isocyanides have been spectroscopically detected as intermediates in the analogous P_4 isoxazole-to-oxazole phototransposition,[14] this is the first example of the involvement of an isocyanide in the P_4 pyrazole-to-imidazole reaction. Furthermore, the chemical and quantum yields observed show that the photocleavage-photocyclization pathway *via* an isocyanide intermediate constitutes a major P_4 transposition pathway.

To determine the generality of this pathway, the photoreactions of a variety of *N*-substituted pyrazoles were reinvestigated. After irradiation of a solution of 1-methylpyrazole (**11**) in acetonitrile (3.0 mL, 2.0 × 10^{-2} M) for 5 min, ^{1}H NMR analysis of the crude reaction mixture showed the appearance of the *N*-methyl singlet at δ 3.68 due to the formation of 1-methylimidazole (**12**) and to a pair of doublets at δ 2.71 (J = 5.1 Hz) and 2.97 (J = 4.9 Hz) due to the *N*-methyl groups of (*E*)- and (*Z*)-enaminonitriles **13**. In addition to these previously reported products,[5] the ^{1}H NMR spectrum also showed a second pair of doublets at δ 2.59 (J = 5.1 Hz) and 2.89 (J = 5.0 Hz) that decreased in intensities upon more prolonged irradiation times consistent with the formation and subsequent consumption of isocyanides (*E*)-**14** and (*Z*)-**14**. In addition, the solution had the characteristic penetrating odor associated with an isocyanide. Simi-

(11) Numao, N.; Hamada, T.; Yonemitsu, O. *Tetrahedron Lett.* **1977**, 1661.

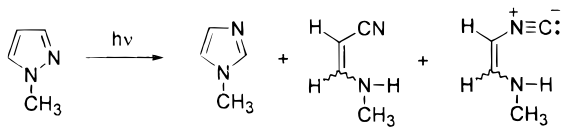
(12) Schmidt, M. W.; Lee, E. K. C. *J. Am. Chem. Soc.* **1970**, *92*, 3579.

(13) Fluorescence lifetimes were measured by Dr. A. M. Halpern, Department of Chemistry, Indiana State University.

(14) (a) Ferris, J. P.; Antonucci, F. R. *J. Am. Chem. Soc.* **1974**, *96*, 2014. (b) Ferris, J. P.; Trimmer, R. W. *J. Org. Chem.* **1976**, *41*, 13.

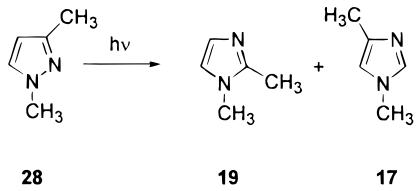
Table 4. Rate Constants

compd	10^{-6} k_f (s^{-1})	$10^{-6}k_r(P_4)$ (s^{-1})	10^{-6} k_r(isocyanide) (s^{-1})	10^{-6} k_r(cyanide) (s^{-1})	$10^{-6}k_r(P_6)$ (s^{-1})	$10^{-6}k_r(P_7)$ (s^{-1})
1	27.48					
2	41.50	4.04	15.73	0.87		
3	64.10	1.83	<0.2	<0.2	3.24	5.04

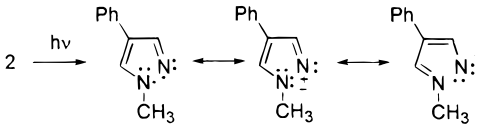


larly, in addition to *N*-methylimidazoles **17** or **17**−**19**, ^{1}H NMR examination of the crude reaction mixtures obtained after irradiation of 1,4-dimethylpyrazole (**15**) or 1,5-dimethylpyrazole (**16**) showed pairs of doublets (J = 5.0 Hz) at δ 2.81 and 2.92 or at δ 2.69 and 2.95 due to the *N*-methyl groups of the (*E*)- and (*Z*)-enamino nitriles **20** or **22** and a second pair of doublets (J = 5.0 Hz) at δ 2.78 and 2.88 or at δ 2.58 and 2.86, indicating the presence of the (*E*)- and (*Z*)-isocyanides **21** or **23**. 4-Methyl-1-phenylpyrazole (**24**) reacted similarly. After 15 min of irradiation of a solution of **24** in acetonitrile (3.0 mL, 2.0 × 10^{-2} M), ^{1}H NMR analysis of the crude reaction mixture showed two pairs of doublets at δ 1.82 (J = 1.3 Hz) and 1.87 (J = 1.8 Hz) due to the allylic α methyl group coupling with the β-proton of the enaminonitriles (*E*)- and (*Z*)-**26** and a second pair of doublets of lesser intensity at δ 1.59 (J = 1.3 Hz) and 1.66 (J = 1.4 Hz) suggesting the presence of isocyanides (*E*)- and (*Z*)-**27**.

Interestingly, IR examination of this residue showed absorption bands at 2195 cm^{-1} due to the nitrile functional group and at 2103 cm^{-1} confirming the presence of an isocyanide. Furthermore, whereas the band at 2195 cm^{-1} increased after irradiation for 30 min, the band at 2103 cm^{-1} due to the isocyanide was substantially decreased in intensity, consistent with the transient nature of the isocyanide. Finally, although 1,3-dimethylpyrazole (**28**) is known to transpose to 1,2-dimethylimidazole (**19**) and 1,4-dimethylimidazole (**17**) *via* the P_4 and P_6 pathways,[5] ^{1}H NMR analysis of the crude reaction mixtures obtained from irradiation of an acetonitrile solution of **28** (30 mL, 2 × 10^{-2} M) showed the clean conversion of the reactant pyrazole **28** to the imidazole products **19** and **17** without the formation of either enaminonitrile or isocyanide intermediates.



Mechanistic Discussion. The photochemistry of pyrazoles has been suggested to involve a competition between electrocyclic ring closure leading to P_6 and P_7 transpositions and cleavage of the N−N bond resulting in the formation of the precursor of the P_4 transposition product.[5] 1-Methyl-4-phenylpyrazole (**2**) transposes regiospecifically *via* the latter pathway. Thus, excitation of **2** is suggested to result in cleavage of the N−N bond resulting in the formation of a species that can be viewed as diradical **2a** or zwitterion **2b**, which are resonance forms of β-iminovinyl nitrene **2c**.

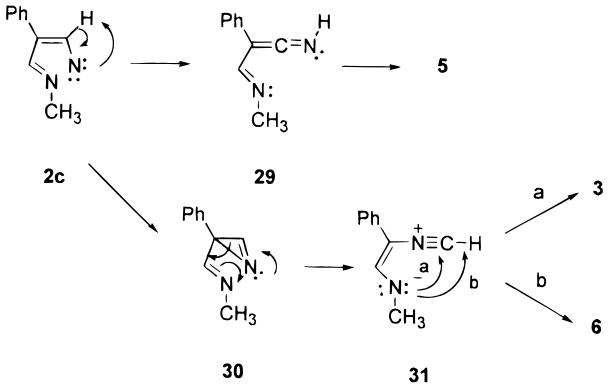


AM1 calculations are consistent with cleavage of the N_1−N_2 bond upon photochemical excitation of **2**. These calculations reveal that the N_1−N_2 bond length increases from 1.35 Å in the ground state of **2** to 4.75 Å in the energy-minimized excited singlet state of **2**. This corresponds to a change in the N_1−N_2 bond order from 1.13 to ∼0 indicating that cleavage of the N_1−N_2 bond is essentially complete by the time the molecule reaches the relaxed excited single state. These same calculations, however, also indicate that excitation is also accompanied by substantial breaking of the C_3−C_4 bond and an increase in the N_2−C_3 bond order, suggesting that H−C_3−N_2 is being expelled from the molecule.[15] These calculations also suggest that in the relaxed excited singlet state the departing H−C≡N molecule is almost perpendicular to the plane of the N_1−C_5−C_4 portion of the molecule, indicating substantial twisting in the S_1 state. These calculations, however, describe reactions

(15) It is interesting to note that loss of HCN is a major fragmentation pathway in the mass spectrum of **2**.

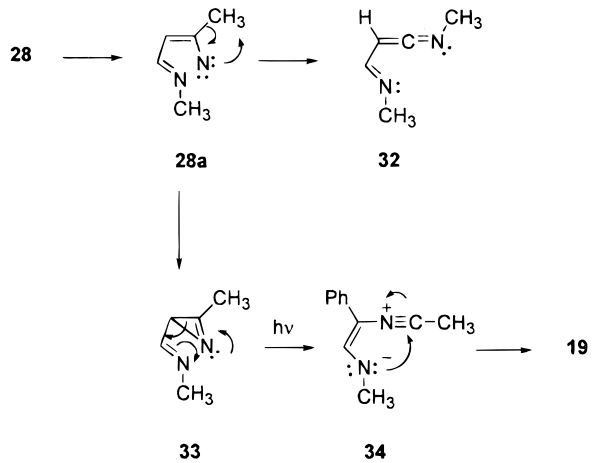
occurring in the gas phase and may not accurately reflect bonding changes upon excitation in solution.

In addition to recyclizing to the pyrazole reactant, rearrangement of β-imino vinyl nitrene **2c** to nitrile **5**, either by direct transfer of hydrogen from C-3 of the original pyrazole to nitrogen, or possibly by way of ketene imine **29**, is an expected pathway for a terminal vinyl nitrene.[16] Alternatively, **2c** would also be expected to undergo intramolecular cyclization to yield iminoazirine **30**,[17] a plausible precursor of nitrile **5**, isocyanide **6**, and imidazole **3**. Although azirines unsubstituted at C-2 are generally not thermally stable, one such azirine has been found to rearrange photochemically to both a nitrile and an isocyanide.[18] Although it is plausible that nitrile formation may involve the vinyl nitrene formed by C−N bond fission, azirines are also known to undergo photochemical ring opening of the C−C bond, which in the present case would yield nitrile ylide **31**, a likely precursor of imidazole **3** and isocyanide **6**. Indeed, a number

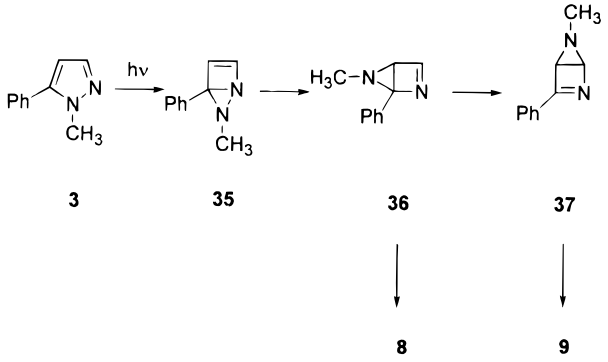


of β-acyl nitrile ylides and one example of a β-imino nitrile ylide have been generated by irradiation of acyl or iminoazirines and shown to cyclize to oxazoles or to an imidazole.[19,20] In these cases, the azirines were substituted with a phenyl group at C-2, and thus isocyanides and nitriles were not possible products.

Similarly, 1,3-dimethylpyrazole (**28**) would undergo photocleavage to vinyl nitrene **28a**, which could rearrange to an unstable *N*-methylketene imine **32** or undergo ring closure to azirine **33** which bears a C-2 methyl substituent. Photochemical ring opening of **33** would yield nitrile ylide **34**, which could cyclize to 1,2-dimethylimidazole **19** but could not yield as isocyanide. This is consistent with our observation that **28** transposes to **19** without the formation of nitrile or isocyanide photocleavage products.



In addition to phototransposition *via* the P_4 pathway and photocleavage to nitriles and isocyanides, reactions that are mechanistically analogous to those already discussed for 1-methyl-4-phenylpyrazole (**2**), the 5-phenyl isomer **3** also phototransposes *via* the P_6 and P_7 pathways. These pathways have previously been rationalized by assuming that photocleavage of the N−N bond, the initial step on the P_4 reaction pathway, competes with electrocyclic ring closure, which would yield 1,5-diazabicyclopentene **35**, which can undergo one or two consecutive 1,3-sigmatropic shifts of nitrogen.[5] Rearomatization of the isomeric 2,5-diazabicyclopentene intermediates **36** and **37** would thus provide the P_6 and P_7 imidazoles **8** and **9**. Although the electrocyclic ring closure-heteroatom



migration mechanism adequately rationalizes formation of the P_6 and P_7 imidazole products, and although similar bicyclic intermediates have been chemically trapped in the analogous phototransposition reactions of cyanopyrroles,[21] no evidence for such intermediates in pyrazole photochemistry has been presented.

AM1 calculations, however, are consistent with electrocyclic ring closure in the first excited state of **3**. These calculations thus reveal that upon relaxation the excited singlet molecule begins to undergo disrotatory ring deformation with N_1 moving out of the plane by 14.4°. In addition, excitation is also accompanied by decreases in the N_2-C_3 and C_4-C_5 bond orders and an increase in the C_3-C_4 bond order. These calculations thus suggest that the geometry and bond orders of the S_1 relaxed pyrazole **3** are approaching the structure of 1,5-diazabicyclo[2.1.0] intermediate **35** and are consistent with electrocyclic ring closure. These predicted changes are quite different from those suggested for 4-phenylpyrazole **2**, which was not predicted to undergo disrotatory deformation and which indeed was not observed to react by the electroyclic ring closure−heteroatom migration pathway.

In an attempt to trap such a bicyclic intermediate, the photochemistry of 1-methyl-5-phenylpyrazole (**3**) was also studied in furan solvent. Under these conditions pho-

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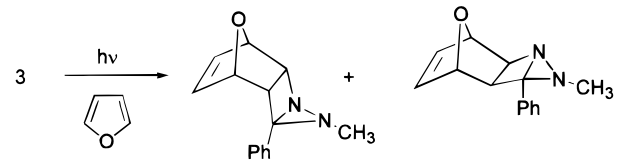
totransposition was not observed. Instead, irradiation led to the formation of a thermally labile oil that was identified as a mixture of the *endo* and *exo*-pyrazole−furan [4 + 2] adducts **38** and **39**. Thus, the ^{13}C NMR



38 **39**

spectrum shows two sets of signals characteristic of *endo* and *exo* isomers of an unsymmetrically substituted 7-oxabicyclo[2.2.1]hept-2-ene ring system.[22,23] The more intense set of signals was assigned to the endo isomer **38** since this was presumed to be the major product. Thus, the spectrum exhibits signals for the nonequivalent vinyl carbons at δ 147.4 and 137.4 for the major isomer and at δ 149.6 and 135.7 for the minor isomer. Similarly, signals for the two nonequivalent C-1 and C-4 carbons of the major isomer were observed at δ 103.5 and 80.0 and at δ 102.3 and 79.4 for the minor isomer. In this case, the upfield signals at δ 80.0 and 79.4 were assigned to the bridgehead carbon on the same side of the molecule as the phenyl ring. Inspection of molecular models indicates that this carbon would indeed be in the shielding zone of the phenyl ring. The spectrum also shows two sets of signals for the nonequivalent C-1 and C-2 carbon atoms at δ 62.1 and 56.5 for the major isomer and at δ 63.0 and 55.3 for the minor isomer. Finally, in addition to signals for the phenyl and quarternary benzyl carbons in the δ 126−128 region, signals at δ 37.5 and 36.7 due to the *N*-methyl carbons of the major and minor isomer were also present.

The structures of these adducts are consistent with furan trapping of a photochemically generated 1,5-diazabicyclopentene intermediate **35**. Indeed, heating of adducts **38** and **39** at 100 °C resulted only in the formation of the original pyrazole, 1-methyl-5-phenylpyrazole (**3**). Neither imidazole **8** nor **9** could be detected by ^{1}H NMR or GLC analysis. This indicates that [4 + 2] trapping of the initially formed 1,5-diazabicyclopentene **35** is faster than 1,3-sigmatropic shift of nitrogen. It also indicates that 1,5-diazabicyclopentene **35**, generated on the ground state by the retro-Diels−Alder reaction of **38** and **39**, aromatizes to pyrazole **3** rather than undergoing sigmatropic shift of nitrogen to a 2,5-diazabicyclic species. This is consistent with our previous suggestion that the first sigmatropic shift of nitrogen in the pyrazole → imidazole transposition occurs on the S_1 surface and that internal conversion to the ground-state 1,5-diazabicyclopentene results only in its return to the starting pyrazole.[24]

It is of interest to understand how changing the position of the phenyl substituent on the pyrazole ring alters the manner in which the excitation energy is partitioned in the three isomeric phenyl-substituted 1-methylpyrazoles.

For 1-methyl-5-phenylpyrazole (**3**), the excited singlet state partitions between fluorescence, $\phi_f = 0.30$, intersystem crossing, $\phi_T = 0.68$, and reaction, $\phi_r = 0.041$. Thus, only 4% of the excitation energy results in chemical reaction, and essentially all of this is channeled into the electrocyclic ring closure−heteroatom migration pathway. This is consistent with the predictions of AM1 calculations, which show that energy minimization of the excited state of **3** is accompanied by disrotatory ring deformation with N_1 moving out of the plane by 14.4°.

When the location of the phenyl ring is changed to position 4 of the pyrazole ring, several significant changes are observed. First, the rates of fluorescence and intersystem crossing both decrease. In contrast, the rate of photochemical reactivity is enhanced by a factor of 3.4. Taken together, these kinetic changes result in a decrease in the quantum yield of triplet formation from 0.68 for **3** to 0.40 for **2** and in an increase in the quantum yield for fluorescence from 0.28 to 0.38. The largest change, however, is the increase in the quantum yield for reaction from 0.041 for **3** to 0.22 for **2**. Furthermore, this reactivity is now completely channeled into the P_4 reaction pathway. Thus, the total P_4 rate constant changes from less than 2.23×10^6 s^{-1} for **3** to 20.6×10^6 s^{-1} for **2**. This rate enhancement is presumably due to the effect that the C-4 phenyl group has on breaking the N−N bond due to stabilization of the initially formed diradical **2a** or zwitterion **2b**, which is possible when the phenyl ring is located at the 4 position but is not possible when it is on position 5 on the pyrazole ring. This effect is also supported by calculations that predict that the N−N bond is essentially broken in the energy-minimized excited singlet state of 1-methyl-4-phenylpyrazole (**2**) but is intact in the corresponding excited singlet state of 1-methyl-5-phenylpyrazole (**3**).

Neither the recorded nor the calculated electronic spectra provide an obvious reason for the lack of reactivity of 1-methyl-3-phenylpyrazole (**1**). Placing the phenyl group at ring position 3 is again accompanied by decreases in the rate constants for both fluorescence and intersystem crossing. In the absence of photochemical reactivity, these changes account for the increased lifetime of the singlet state. This isomer is also the most luminescent of the three isomers with 68% of the absorbed light returned as fluorescence and phosphorescence. The relatively low quantum yield for phosphorescence of 0.19 for this isomer, as compared to 0.47 and 0.37 for **2** and **3**, is not due to a low triplet yield but rather to a relatively low quantum efficiency for phosphorescence of 0.37. It is also interesting to note that AM1 calculations predict that photochemical excitation of **1** is not accompanied by either disrotatory deformation, as in the case of **3**, or by breaking of the N−N bond, as in the case of **2**. This is consistent with its lack of reactivity. Furthermore, it is relevant to point out that a similar trend in reactivity has also been observed with phenylisothiazoles and phenylisoxazoles. Thus, current work in our laboratory has shown that 3-phenylisothiazole and 3-phenylisoxazole are also substantially less reactive than their 4- and 5-phenyl isomers.

Conclusion

Chemical and quantum yields show that the photocleavage−photocyclization pathway *via* an isocyanide intermediate is a major route for the P_4 phototransposition of 4-phenyl-1-methylpyrazole (**2**). Furthermore, it has been shown that this pathway is general to a variety of other pyrazoles that bear hydrogen at the C-3 ring position.

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These results also show that a 1,5-diazabicyclo[2.1.0]hex-2-ene intermediate can be trapped by photolysis of 5-phenyl-1-methylpyrazole (**3**) in furan solvent. This constitutes the first direct evidence for the intermediacy of a 1,5-diazabicyclo[2.1.0]hex-2-ene in the P_6 and P_7 pyrazole-to-imidazole phototransposition.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were recorded at 200 and 50.3 MHz on a Bruker FT-NMR system. ^{1}H and ^{13}C chemical shifts were measured relative to internal Me_4Si and $CHCl_3$, respectively. Infrared spectra were recorded on a PE-1620 FT spectrometer. GLC was performed on a PE-9000 FID instrument equipped with 15 m × 3 μm 50% methylphenylsilicon phase capillary column. Mass spectra were recorded with an HP 5970B mass-selective detector interfaced to an HP 5880 capillary gas chromatograph. Ultraviolet absorption spectra were recorded on a Hitachi U-2000 spectrometer. Luminescence spectra were recorded on a PE-LS 50 spectrometer. Flash column chromatography was carried out on silica gel, 40 μm average particle size (J. T. Baker, Inc.). Preparative-layer chromatography was carried out on 20 × 20 cm glass plates coated with 2 mm of Kieselgel 60 F_{254} (Merck).

Syntheses of Reactants and Products. Compounds previously described in the literature were prepared as follows: 3-(*N*-methylamino)-2-phenylpropenenitrile (**5**, 97.1% *Z*) by condensation of phenylformylacetonitrile with *N*-methylformamide;[25,26] 3-(*N*-methylamino)-3-phenylpropenenitrile (**9**, 93.9% *E*) by methylation of 3-amino-3-phenylpropenenitrile with methylamine hydrochloride;[27,28] 4-phenyl-1-H-imidazole in three steps from acetophenone;[29] 1-methylpyrazole (**11**) by methylation of pyrazole using trimethyl phosphate;[30] 1,3- and 1,5-dimethylpyrazole (**28**) and (**16**) as a mixture by condensation of methylhydrazine with 4,4-dimethoxy-2-butanone and each isomer purified to greater than 99.6% purity by repeated spinning-band distillation;[31] 1,4-dimethylpyrazole (**15**) by condensation of 1,1,3,3-tetraethoxy-2-methylpropane[32] and methylhydrazine dihydrogen sulfate;[33] 1,4-and 1,5-dimethylimidazole (**17**), and (**18**) as a mixture by methylation of 4-methylimidazole using methyl iodide,[34] separated by reduced-pressure spinning band distillation.

1-Methyl-3-phenylpyrazole (1). A solution of phenyl 3-chlorovinyl ketone[35] (20.3 g, 121.9 mmol) in diethyl ether (200 mL) was kept in an ice bath, and *N*-methylhydrazine (24.0 mL, 451.0 mmol) was added dropwise over 1 h with continuous stirring. The mixture was refluxed for 3 h and cooled in an ice bath. Saturated $NaHCO_3$ (80 mL) was added dropwise and the organic phase separated. The aqueous layer was extracted with CH_2Cl_2 (4 × 50 mL), and the combined organic phase was dried ($MgSO_4$) and concentrated by rotary evaporation to afford a crude product (19.6 g, 89.4% yield) that was analyzed by GLC and found to contain two major components in a 3.4:5.5 ratio. A portion of the crude product (6.0 g) was subjected to silica gel (150 g) flash column chromatography. The column (18 cm long × 8 cm diameter) was eluted with CH_2Cl_2 (500 mL) and CH_2Cl_2:EtOAc (95:5, 300 mL). Fractions of about 10 mL were collected, and fractions 67−89 were concentrated to yield 1-methyl-3-phenylpyrazole (1) as a white solid: mp 54−55 °C (lit.[36] mp 56 °C); 1.4 g (9.1 mmol, 24%); ^{1}H NMR ($CDCl_3$) δ 3.89 (s, 3H), 6.52 (d, J = 2.3 Hz, 1H), 7.31−7.38 (m, 4H), 7.77 (d, J = 2.2 Hz, 1H), 7.80 (m, 1H);[37] ^{13}C NMR ($CDCl_3$) δ 39.0, 102.8, 125.4, 125.5, 127.5, 128.6, 131.3;[38] IR (KBr) 3112, 2936, 1704, 1603, 1503, 1451, 1353, 1306, 1232, 1147, 1080, 1030, 948, 918, 763 cm^{-1}; UV (CH_3CN) λ_{max} (log ϵ) 253 (4.24); MS *m/e* 158 (100), 157 (30), 130 (13), 117 (9), 103, (5), 89 (8), 77 (21), 55 (13), 51 (11), 42 (17).

1-Methyl-4-phenylpyrazole (2). Methylhydrazine (8.0 g, 173.6 mmol) was added dropwise to a mechanicallly stirred solution of 3-chloro-2-phenylpropenal[39] (8.4 g, 50.5 mmol) in ether (25 mL) maintained under a N_2 atmosphere at ∼0 °C. The resulting mixture was heated at reflux for 3 h, cooled in an ice bath, and treated by dropwise addition of aqueous saturated $NaHCO_3$ (80 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 50 mL) and the combined organic phase dried ($MgSO_4$) and concentated by rotary evaporation. The resulting yellow solid (8.8 g) was subjected to silica gel (300 g) flash column chromatography. The column (36.0 × 5.5 cm) was eluted with CH_2Cl_2, and 16 fractions (100−150 mL) were collected. Fractions 9−15 afforded 1-methyl-4-phenylpyrazole (**2**) as a white solid, 4.2 g (46.2% isolated yield). Sublimation (110−112.5 °C, 0.2 Torr) gave **2** as a white crystalline solid: mp 100−101 °C (lit.[40] mp 101−103 °C); ^{1}H NMR ($CDCl_3$) δ 4.00 (s, 3H), 7.43−7.22 (m, 5H), 7.60 (s, 1H), 7.80 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 39.1, 133.0, 125.5, 126.3, 126.9, 128.8, 136.7;[38] IR (KBr) 3035, 1604, 1560, 1451, 1415, 1363, 1324, 1213, 1195, 1075, 991, 955, 905, 849, 812, 754 cm^{-1}; UV λ_{max} (CH_3CN) (log ϵ) 254 (4.12); MS *m/e* 158 (100) 143 (1), 130 (20), 117 (15), 116 (20), 103 (7), 77 (7), 63 (19), 42 (24), 38 (12).

5-Deuterio-1-methyl-4-phenylpyrazole (2-5-d_1). To a solution of **2** (0.32 g, 2.03 mmol) in freshly dried THF (10 mL) at −77 °C was added *n*-BuLi (2.5 mL, 4.0 mmol), and the mixture stirred for 30 min.[41] The temperature of the solution was brought to 0 °C, and D_2O (0.1 mL, 5.0 mmol) was added. After further stirring for 30 min, the solution was brought to room temperature and stirred for 8 h. To the mixture was added water (4.0 mL) and the organic layer separated. The aqueous layer was extracted with CH_2Cl_2 (4 × 25 mL), and the combined organic phase was washed with brine (5 mL) followed by water (10 mL). The organic phase was dried ($MgSO_4$), and the solvent was removed by rotary evaporation to yield 5-deuterio-1-methyl-4-phenylpyrazole (**2**-5-d_1) as a white solid: mp 90−92 °C; 0.27 g (1.70 mmol, 83.7% with 83.2% D-incorporation); ^{1}H NMR ($CDCl_3$) δ 4.00 (s, 3H), 7.43−7.22 (m, 5H), 7.80 (s, 1H); MS *m/e* 159 (100), 158 (34), 131 (17), 118 (14), 117 (25), 104 (6), 103 (11), 77 (8), 43 (25), 39 (11).

1-Methyl-5-phenylpyrazole (3). Methylhydrazine (22.5 g, 489.1 mmol) was added dropwise to a mechanically stirred solution of 3-chloro-3-phenylpropenal[42] (23.0 g, 138.1 mmol) in ether (125 mL) maintained under a N_2 atmosphere at ∼0 °C. The resulting mixture was heated at reflux for 3 h, cooled in an ice bath, and neutralized with saturated $NaHCO_3$. The resulting solution was extracted with CH_2Cl_2 (4 × 50 mL), dried ($MgSO_4$), and concentrated to afford a red liquid (23.0 g) that contained **3** and **1** in a 6.6:2.8 ratio. A portion of the crude product (19.0 g) was subjected to steam distillation, and the distillate (1 L) was extracted with ether (4 × 100 mL). The etheral extract was dried (Na_2SO_4) and concentrated to give an oily residue (10.2 g). A portion (2.0 g) of this was subjected to silica gel (100 g) flash column chromatography. The column (14.0 cm long × 5.5 cm diameter) was eluted with

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dichloromethane:ethyl acetate (95:5), and fractions of 8−10 mL were collected. Fractions 22−35 provided 1-methyl-5-phenylpyrazole (**3**) as a colorless oil: bp 90−95 °C (1.5 Torr) (lit.[43] bp 105 °C (1.0 Torr)) 557.0 mg (3.5 mmol, 27.9%); ^{1}H NMR ($CDCl_3$) δ 4.00 (s, 3H), 6.33 (d, J = 1.6 Hz, 1H), 7.45 (s, 5H), 7.53 (d, J = 1.6 Hz, 1H); ^{13}C NMR δ 37.3, 105.8, 128.3, 128.5, 128.6, 130.0, 139.0, 143.3;[43] IR (KBr) 3100, 3059, 1606, 1576, 1542, 1484, 1472, 1440, 1275, 1228, 1179, 979, 783 cm^{-1}; UV (CH_3CN) λ_{max} (log ϵ) 245 (4.03); MS *m/e* 158 (100), 130 (24), 115 (19), 110 (22), 91 (14), 77 (20), 63 (18), 51 (18), 50 (17).

4-Deuterio-1-methyl-5-phenylpyrazole (3-4-d_1). 1-Methyl-5-phenylpyrazole (**3**) (0.832 g, 5.27 mmol) was dissolved in 70% D_2SO_4 in D_2O (2.0 mL, 14.3 mmol) and kept at 70−74 °C for 3.5 days while the H−D exchange was monitored using ^{1}H NMR spectroscopy. After neutralization by dropwise addition of saturated $NaHCO_3$, the resulting mixture was extracted with dichloromethane (4 × 50 mL). The organic extract was dried ($MgSO_4$) and concentrated to give a light yellow oily product (0.824 g) that was distilled to give 4-deuterio-1-methyl-5-phenylpyrazole (**3**-4-d_1) as colorless oil: bp 70 °C (0.40 Torr); 0.735 g (4.74 mmol, 88.4% yield); ^{1}H NMR ($CDCl_3$) δ 4.00 (s, 3H), 7.50 (m, 5H), 7.53 (s, 1H); MS *m/e* 159 (100), 131 (20), 130 (9), 116 (15), 104 (17), 103 (3), 91 (15), 77 (22), 51 (19).

1-Methyl-2-phenylimidazole (8). Dimethyl sulfate (2.7 g, 21.4 mmol) was added dropwise to 2-phenyl-1*H*-imidazole (2.0 g, 13.9 mmol). A vigorous reaction set in after 10 min at room temperature. The resulting mixture was heated over a steam bath for 30 min, and the residue was made alkaline with concentrated ammonia (5 mL) and extracted with dichloromethane (3 × 25 mL). The organic extract was dried ($MgSO_4$) and concentrated to give a brown oily residue (1.7 g). Distillation gave a colorless oil: bp (Kugelrohr oven temp) 70−100 °C (0.2 Torr) (lit.[44] bp 175 °C (15 Torr)). The distillate (1.5 g) was subjected to flash column chromatography over silica gel (110 g) that was washed with hexane:triethylamine (5:1) prior to sample application. The column (15 cm long × 5.0 cm diameter) was eluted with dichloromethane, and 40 fractions of 10 mL were collected. Concentration of fractions 15−24 afforded **8** as a light yellow oil: 0.41 g (2.59 mmol, 18.6% yield); ^{1}H NMR ($CDCl_3$) δ 3.56, (s, 3H), 6.90 (s, 1H), 7.10 (s, 1H), 7.20−7.80 (m, 5H); UV (MeOH) λ_{max} (log ϵ) 257 (4.08); MS *m/e* 158 (75), 157 (100), 130 (8), 116 (12), 104 (12), 103 (10), 90 (6) 89 (14), 77 (15), 54.1 (17), 51 (15). Concentration of fractions 28−40 gave unreacted 2-phenyl-1*H*-imidazole: 1.01 g (50.5%).

1-Methyl-4- and 1-Methyl-5-phenylimidazole (4 and 7). Dimethyl sulfate (1.9 g, 14.8 mmol) was added to 4-phenyl-1*H*-imidazole[29] (2.0 g, 13.9 mmol) at room temperature. After the solid dissolved, the light brown liquid was heated over a steam bath for 30 min and left overnight at room temperature. The mixture (3.0 g) was dissolved in H_2O (5.0 mL) and made alkaline by the addition of aqueous saturated $NaHCO_3$. This was extracted with dichloromethane (3 × 25 mL), and the combined organic phase was dried ($MgSO_4$) and concentrated. The residual oil (2.1 g) was subjected to silica gel (100 g washed with hexane:triethylamine, 5:1) flash column chromatography. The column (14.0 cm long × 5.5 cm diameter) was eluted with dichloromethane (350 mL), and 47 fractions (6−10 mL) were collected. Fractions 35−39 were combined and concentrated to give 1-methyl-4-phenylimidazole (**4**) (25.4 mg), while fractions 40−43 were combined and concentrated to give a mixture of 1-methyl-5-phenylimidazole (**7**) and 1-methyl-4-phenylimidazole (**4**) (320.0 mg). This mixture was subjected to preparative layer chromatography (silica gel washed with hexane: triethylamine, 5:1) and eluted with dichloromethane:methanol (9:1) to give three bands. Band 1 (lowest R_f) gave unreacted 4-phenyl-1*H*-imidazole; band 2 (intermediate R_f) gave 1-methyl-5-phenylimidazole (**7**) as a white solid (32.0 mg); band 3 (highest R_f) contained 1-methyl-4-phenylimidazole (**4**) (101.0 mg), which was recrystallized from ether to give a pale yellow crystalline solid, 58.1 mg (0.37 mmol 2.5% yield). The total yield of **4** was 73.5 mg (0.46 mmol, 3.1% yield) obtained as a light yellow solid: mp 108−110 °C (lit.[45] mp 110−111 °C); ^{1}H NMR ($CDCl_3$) δ 3.60 (s, 3H), 7.10 (s, 1H) 7.2−7.5 (m, 4H), 7.7 (s, 1H), 7.8 (s, 1H); UV (MeOH) λ_{max} (log ϵ) 256 (4.08); MS *m/e* 158 (100), 157 (12), 131 (6), 130 (12), 117 (16), 116 (38), 89 (28), 77 (7), 63 (18), 51 (9). 1-Methyl-5-phenylimidazole (**7**) was obtained as a white solid: mp 94.5−96.0 °C (lit.[45] mp 96−97 °C); ^{1}H NMR ($CDCl_3$) δ 3.62 (s, H), 7.39 (m, 5H), 7.50 (s, 1H); UV (MeOH) λ_{max} (log ϵ) 251 (4.11); MS *m/e* 158 (100), 157 (46), 131 (5), 130 (25), 115 (15), 104 (6), 89 (15), 77 (21), 63 (18), 51 (18).

Irradiation and Analysis Procedures. To monitor photoreactions on an analytical scale, 3.0 mL of a solution of the appropriate reactant in methanol or acetonitrile was placed in a quartz tube (7 mm i.d. × 15 cm long), sealed with a rubber septum, and purged with nitrogen for 2−5 min prior to irradiation. In the case of phenyl-substituted pyrazoles the solutions were irradiated at 254 nm in a Rayonet photochemical reactor with 16 low-pressure Hg lamps. Pyrazole without a phenyl substituent was irradiated using a 450-W high-pressure Hg lamp in a water-cooled quartz immersion well. Preparative-scale reactions were carried out by irradiating 50 mL of a nitrogen-purged solution of the appropriate reactant in a quartz tube (2.2 cm i.d. × 20 cm long).

The formation of phototransposition products was monitored by GLC analysis at 180 °C without concentrating the solutions. The retentions of the products at 180 °C are given relative to the appropriate starting compound. Quantitative GLC analysis of reactant consumption and product formation was accomplished using calibration curves constructed for **4**, **7**, and **8** by plotting the detector response *vs* 10 standards of known concentration. Correlation coefficients ranged from 0.989 to 1.000. The formation of photocleavage products were monitored by UV absorption spectroscopy of the diluted solution (1:500) and ^{1}H NMR spectroscopy of the residue obtained by concentrating the irradiated solution to dryness.

1-Methyl-3-phenylpyrazole (1). A solution of **1** (3.0 mL, 2.0 × 10^{-2} M) in methanol was irradiated for total of 42 h. After 11.25 h and 42 h of irradiation GLC analysis showed that 21% and 46% of **1** had been consumed but that no volatile products were formed.

1-Methyl-4-phenylpyrazole (2). A solution of **2** (50 mL, 2.0 × 10^{-2} M) in methanol was irradiated for 1 h. The resulting solution was concentrated, and the residue (0.156 g, 98.7% recovery) was subjected to silica gel (60 g) flash chromatography. The column (25 cm long × 2.2 cm diameter) was eluted with dichloromethane (200 mL) followed by dichloromethane:ethyl acetate (9:1, 300 mL), and 10 mL fractions were collected. Fraction 7 was concentrated to give (*Z*)-2-(*N*-methylamino)-1-phenylethenyl isocyanide (**6**) as a white solid: mp 97.5−98.0 °C; 0.018 g (1.14 × 10^{-4} mol, 17.8% yield); ^{1}H NMR ($CDCl_3$) δ 3.1 (d, J = 4.5 Hz, 3H), 4.2 (br s, 1H), 6.8 (d, J = 12.6 Hz, 1H), 7.1−7.3 (m, 5H); ^{13}C NMR δ ($CDCl_3$) 34.4, 121.4, 125.3, 128.9, 132.0, 137.2; IR (NaCl window) 3319, 2105 (−N≡C), 1650, 748, 638 cm^{-1}; UV λ_{max} (CH_3OH) nm (log ϵ) 225 (3.98), 263 (3.86), 298 (4.15), 313 (4.14); MS *m/e* 158.2 (100), 157.2 (11.2), 131.1 (7.9), 130.1 (10.2), 117.2 (18.1), 116.0 (35.4), 103.0 (6.4), 89.1 (27.1), 63.1 (15.3), 51.1 (10.0). Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.75; H, 6.38; N, 17.71. Found: C: 75.76, H: 6.26, N: 17.73.

Fractions 10−18 were concentrated to give a mixture of (*E*)- and (*Z*)-3-(*N*-methylamino)-2-phenylpropenenitrile (**5**),[26,27] 0.009 g (5.70 × 10^{-5} mol, 8.9% yield).

Fractions 26−33 were concentrated to give unreacted 1-methyl-4-phenylpyrazole (**2**), 0.057 g (3.6 × 10^{-4} mol, 36.5% recovery). Fraction 34 was concentrated to give 1-methyl-4-phenylimidazole (**4**),[45] 0.011 g (6.96 × 10^{-5} mol, 10.9% yield).

5-Deuterio-1-methyl-4-phenylpyrazole (2-5-d_1). A solution of **2**-5-d_1 (20.0 mL, 2.0 × 10^{-2} M) in methanol was placed in a quartz tube (2.2 cm i.d. × 12 cm long), sealed with a septum, and purged continuously with nitrogen while being irradiated for 3.0 h. The resulting solution was concentrated to dryness, and the residue (0.053 g, 85% recovery) was subjected to preparative layer chromatography (silica gel,

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acetonitrile). The band at $R_f = 0.12$ gave 5-deuterio-1-methyl-4-phenylimidazole (**4**-5-d_1) as a white solid: mp 107−110 °C; 0.020 g (1.26×10^{-4} mol, 32%); ^{1}H NMR ($CDCl_3$) δ 3.60 (s, 3H), 7.2−7.5 (m, 4H), 7.75 (s, 1H), 7.81 (s, 1H); MS *m/e* 159 (100), 158 (24), 131 (14), 118 (16), 117 (42), 104 (6), 90 (18), 89 (18), 63 (19), 51 (11).

(*Z*)-2-(*N*-Methylamino)-1-phenylethenyl Isocyanide (6). A solution of **6** (3.0 mL, 1.44×10^{-2} M in CH_3OH) was irradiated for 5 min. Analysis by UV absorption spectroscopy before and after irradiation after 1:500 dilution showed the optical density at 300 nm decreased from 0.431 to 0.382, showing that 24% of **6** was consumed. The resulting solution was concentrated to dryness, and the residue (0.005 g, 3.16×10^{-5} mol, 73.5% recovery) was analyzed by ^{1}H NMR. The spectrum showed signals for the *N*-methyl group of the *E* and *Z* isomers of **6** at δ 3.02 (d, $J = 4.5$ Hz) and 2.85 (d, $J = 4.5$ Hz), respectively, and a singlet at δ 3.68 due to the *N*-methyl group of **4**.

(*Z*)/(*E*)-3-(*N*-Methylamino)-2-phenylpropenenitrile (5). A solution of **5** (97% *Z*, 3.0 mL, 2.0×10^{-2} M) in methanol was irradiated for 20 min. The resulting solution was concentrated to dryness, and the residue (0.007 g, 74% recovery) was analyzed by ^{1}H NMR. The spectrum ($CDCl_3$) showed a singlet of very low intensity at δ 3.60 due to the *N*-methyl group of **4** and two doublets at δ 3.11 and 2.97 ($J = 5.1$ Hz) for the *N*-methyl groups of the *Z* and *E* isomers of **5**, respectively. Integration indicated that the *Z*:*E* ratio has changed to 58.1:41.9 (39% consumption of (*Z*)-**5**.

1-Methyl-5-phenylpyrazole (3). A solution of **3** (3.0 mL, 2.0×10^{-2} M) in methanol was irradiated for 2.0 h. GLC analysis of the irradiated solution showed 76% consumption of **3** (retention time of 2.70 min) and the formation of 1-methyl-2-phenylimidazole (**8**) (30%), 1-methyl-5-phenylimidazole (**7**) (31%), and 1-methyl-4-phenylimidazole (**4**) (29%) with relative retentions of 2.13, 4.04, and 2.53, respectively.

Three solutions of **3** (3.0 mL, 2.0×10^{-2} M) in methanol were each irradiated for 8, 15, or 20 min. In each case the resulting solution was concentrated to dryness, and the residue was analyzed by ^{1}H NMR spectroscopy. In addition to signals due to imidazoles **4**, **7**, and **8**, the ^{1}H NMR spectra showed signals at δ 2.73 (d, $J = 5.32$ Hz), 2.78 (d, $J = 4.90$ Hz), 2.84 (d, $J = 5.30$ Hz), and 3.28 (d, $J = 3.50$ Hz) due to the *N*-methyl groups of (*E*)-3-(*N*-methylamino)-3-phenylpropenenitrile (**9*E***), (*E*)-2-(*N*-methylamino)-2-phenylethenyl isocyanide (**10*E***), (*Z*)-3-(*N*-methylamino)-3-phenylpropenenitrile (**9*Z***), and (*Z*)-2-(*N*-Methylamino)-2-phenylethenyl isocyanide (**10*Z***).

4-Deuterio-1-methyl-5-phenylpyrazole (3-4-d_1). A solution of **3**-4-d_1 (50.0 mL, 2.1×10^{-2} M) in methanol was irradiated for 1.5 h. The resulting solution was concentrated to dryness to yield the crude product (0.163 g, 99% recovery). A portion (0.092 g) of this residue was subjected to preparative layer chromatography (silica gel, acetonitrile). The bands at $R_f = 0.40$ gave 5-deuterio-1-methyl-4-phenylimidazole (**4**-5-d_1) (0.026 g, 1.64×10^{-4} mol, 28% yield): ^{1}H NMR ($CDCl_3$) δ 3.60 (s, 3H), 7.2−7.5 (m, 4H), 7.7 (s, 1H), 7.8 (s, 1H); MS *m/e* 159 (100), 158 (19), 131 (12), 130 (4), 118 (18), 117 (40), 104 (5), 90 (28), 89 (15), 77 (8), 63 (16), 51 (9).

The band at $R_f = 0.22$ gave 5-deuterio-1-methyl-2-phenylimidazole (**8**-5-d_1) 0.013 g (8.2×10^{-5} mol, 14% yield); ^{1}H NMR ($CDCl_3$) δ 3.65 (s, 3H), 7.10 (s, 1H), 7.2−7.8 (m, 5H); MS *m/e* 159 (84), 158 (100), 131 (6), 116 (10), 104 (13), 103 (8), 90 (7), 89 (8), 77 (14), 55 (16), 51 (15). The band at $R_f = 0.07$ gave 4-deuterio-1-methyl-5-phenylimidazole (**7**-4-d_1): 0.009 g (5.7×10^{-5} mol, 10% yield); ^{1}H NMR ($CDCl_3$ + a drop of (TFA)) δ 3.90 (s, 3H), 7.40 (s, 2H), 7.60 (s, 3H), 8.82 (s, 1H) MS *m/e* 159 (100), 158 (62), 131 (20), 118 (22), 117 (18), 116 (14), 104 (18), 103 (26), 91 (17), 90 (23), 89 (23), 77 (30), 63 (21), 56 (20), 55 (14), 51 (24). The band at $R_f = 0.60$ gave unreacted 4-deuterio-1-methyl-5-phenylpyrazole (**3**-4-d_1) 0.026 g (1.64×10^{-4} mol, 28% recovery).

1-Methyl-5-phenylpyrazole (3) in Furan. A solution of **3** (50 mL, 2.0×10^{-2} M) in furan was irradiated for 1.0 h. The resulting solution was concentrated to dryness, and the residue (0.186 g) was subjected to preparative layer chromatography (silica gel, acetonitrile). The band at $R_f = 0.70$ gave unreacted 1-methyl-5-phenylpyrazole (**3**), 0.041 g (2.6×10^{-4} mol, 26% recovery). The band at $R_f = 0.75$ gave 0.105 g of a pale yellow oil that was subjected to a second preparative layer chromatography (silica gel, acetonitrile). The band at $R_f = 0.75$ gave a mixture of adducts **38** and **39** as an almost colorless oil: 0.083 g (3.7×10^{-4} mol, 50.0% yield); ^{1}H NMR ($CDCl_3$) major adduct δ 2.48, (s, 3H), 4.01 (m, 1H), 4.13 (m, 1H), 4.94 (dd, 1H, $J = 3.30$, 6.75 Hz), 5.01 (dd, 1H, $J = 2.80$, 2.80 Hz), 6.85 (dd, 1H, $J = 1.57$, 2.82 Hz), minor adduct δ 2.78, (s, 3H), 4.13 (m, 1H), 4.26 (m, 1H), 5.17 (dd, 1H, $J = 8.67$, 6.46 Hz), 5.22 (dd, 1H, $J = 2.94$, 2.94 Hz), 6.45 (dd, 1H, $J = 1.74$, 2.77 Hz), 6.57 (d, 1H, $J = 2.19$). In addition, both adducts exhibited overlapping multiplites for the phenyl protons from δ 7.18−7.42: ^{13}C NMR ($CDCl_3$) major adduct δ 37.5, 56.5, 62.1, 80.0, 103.5, 137.4, 147.4; minor adduct δ 36.7, 55.3, 63.0, 79.4, 102.3, 135.7, 149.6. In addition, both adducts exhibited overlapping signals for the phenyl and benzyl carbons from δ 126.7−128.6: IR (neat) 3058, 3027, 2954, 2924, 2867, 2792, 1724, 1604, 1464, 1493, 1447, 1276, 1308, 1138, 1049, 940, 862, 755, 700, 641 cm^{-1}.

Thermolysis of Adducts 38 and 39. Adducts **38** and **39** (0.015 g, 6.63×10^{-5} mol) were dissolved in DMSO-d_6. ^{1}H NMR analysis indicated only **38** and **39** with no 1-methyl-5-phenylpyrazole (**3**) present in the solution. The resulting solution was heated at 100 °C for 25 min. ^{1}H NMR analysis showed the decomposition of **38** and **39** and the formation of **3**. Similarly, GLC analysis of **38** and **39** at 180 °C showed only the presence of **3**.

1-Methylpyrazole (11). Three solutions of **11** (3.0 mL, 2.4×10^{-2} M) in acetonitrile were each irradiated for 5, 10, or 15 min. The resulting solutions were concentrated to dryness, and each residue was analyzed by ^{1}H NMR spectroscopy. The spectra ($CDCl_3$) showed a decrease in the signals at δ 3.70 (s, 3H), 6.22 (dd, $J = 2.24$, 1.49 Hz, 1H), 7.34 (d, $J = 2.24$ Hz, 1H),7.48 (d, $J = 1.49$ Hz, 1H) due to the consumption of 1-methylpyrazole (**11**), a continuous increase in the signals at δ 3.68 (s, 3H), 6.84 (s, 1H), 7.00 (s, 1H), 7.41 (s, 1H); at δ 2.59 (d, $J = 5.05$ Hz, 3H), 3.72 (d, 13.67 Hz, 1H), 6.52 (dd, $J = 12.88$, 8.89 Hz, 1H); and at δ 2.71 (d, $J = 5.12$ Hz, 3H) 3.91 (d, $J = 8.57$ Hz, 1H), 7.05 (dd, $J = 13.67$, 8.57 Hz, 1H) due to the continuous formation of 1-methylimidazole (**12**), (*E*)-3-(*N*-methylamino)propenenitrile (**13*E***), and (*Z*)-3-(*N*-methylamino)propenenitrile (**13*Z***), respectively, and an increase and subsequent decrease in the signals at δ 2.89 (d, $J = 4.96$ Hz, 3H) and δ 2.97 (d, $J = 4.92$ Hz, 3H) due to the *N*-methyl group of (*E*)-2-(*N*-methylamino)ethenyl isocyanide (**14*E***) and (*Z*)-2-(*N*-methylamino)ethenyl isocyanide (**14*Z***), respectively.

1,4-Dimethylpyrazole (15). Five solutions of **15** (3.0 mL, 2.1×10^{-2} M) in acetonitrile were each irradiated for 5, 10, 15, 30, or 60 min. The resulting solutions were concentrated to dryness, and each residue was analyzed by ^{1}H NMR. The spectra ($CDCl_3$) showed a decrease in the signals at δ 2.03 (s, 3H) and 3.83 (s, 3H) due to the consumption of 1,4-dimethylpyrazole (**15**), a continuous increase in the signals at δ 2.17 (s, 3H), 3.60 (s, 3H), at δ 2.80 (d, $J = 5.39$ Hz), and at δ 2.92 (d, $J = 5.06$ Hz) due to the continuous formation of 1,4-dimethylimidazole (**17**), (*E*)-2-methyl-3-(*N*-methylamino)propenenitrile (**20*E***), and (*Z*)-2-methyl-3-(*N*-methylamino)propenenitrile (**20*Z***), respectively, and an increase and subsequent decrease in signals at δ 2.78 (d, $J = 5.28$ Hz) and at δ 2.88 (d, $J = 5.39$ Hz) due to the formation and subsequent consumption of (*E*)-1-methyl-2-(*N*-methylamino)ethenyl isocyanide (**21*E***) and (*Z*)1-methyl-2-(*N*-methylamino)ethenyl isocyanide (**21*Z***).

1,5-Dimethylpyrazole (16). Four solutions of **16** (3.0 mL, 2.1×10^{-2} M) in acetonitrile were irradiated for 10, 15, 30, and 60 min, respectively. The resulting solutions were concentrated to dryness, and each residue was analyzed by ^{1}H NMR. The spectra ($CDCl_3$) showed a decrease in the signals at δ 2.24 (s, 3H) and 3.76 (s, 3H) due to the consumption of 1,5-dimethylpyrazole (**16**), a continuous increase in the signals at δ 2.35 (s, 3H), 3.54 (s, 3H), at δ 2.10 (s, 3H), 3.60 (s, 3H), at δ 2.17 (s, 3H), 3.50 (s, 3H), at δ 2.68 (d, $J = 5.76$ Hz, 3H), and at δ 2.94 (d, $J = 5.26$ Hz, 3H) due to the continuous formation of 1,2-dimethylimidazole (**19**), 1,4-dimethylimidazole (**17**), 1,5-dimethylimidazole (**18**), (*E*)-3-methyl-3-(*N*-methylamino)propenenitrile(**22*E***) and (*Z*)-3-methyl-3-(*N*-methylamino)propenenitrile(**22*Z***), and an increase and subsequent decrease in the

signals at δ 2.57 (d, $J = 4.20$ Hz, 3H) and δ 2.85 (d, $J = 5.32$ Hz, 3H) due to the formation and subsequent consumption of (*E*)-2-methyl-2-(*N*-methylamino)-ethenyl isocyanide (**23*E***) and (*Z*)-2-methyl-2-(*N*-methylamino)ethenyl isocyanide (**23*Z***).

4-Methyl-1-phenylpyrazole (24). Five solutions of **24** (3.0 mL, 2.1×10^{-2} M) in methanol were irradiated for 5, 10, 15, 30, and 60 min, respectively. The resulting solutions were concentrated to dryness, and each residue was analyzed by ^{1}H NMR and IR spectroscopy. The ^{1}H NMR spectra ($CDCl_3$) showed a gradual decrease in the signal at δ 2.16 (s, 3H) due to the consumption of 4-methyl-1-phenylpyrazole (**24**), a continuous increase in the signals at δ 2.30 (s, 3H), at δ 1.59 (d, $J = 1.26$ Hz, 3H), and at δ 1.66 (d, $J = 1.40$ Hz, 3H) due to the continuous formation of 4-methyl-1-phenylimidazole (**25**), (*E*)-2-methyl-3-(*N*-phenylamino)propenenitrile (**26*E***), and (*Z*)-2-methyl-3-(*N*-phenylamino)propenenitrile (**26*Z***), and an increase and subsequent decrease in the signals at δ 1.82 (d, $J = 1.40$ Hz, 3H) and d 1.87 (d, $J = 1.33$ Hz, 3H) due to the formation of (*E*)-1-methyl-2-(*N*-phenylamino)ethenylisocyanide (**27*E***) and (*Z*)-1-methyl-2-(*N*-phenylamino)ethenylisocyanide (**27*Z***). The IR spectra showed a continuous increase in an absorption signal at 2195 cm^{-1} ($-C\equiv N$) and an increase and subsequent decrease in an absorption signal at 2103 cm^{-1} ($-N^+\equiv C:^-$).

1,3-Dimethylpyrazole (28). Three solutions of **28** (3.0 mL, 2.3×10^{-2} M) in acetonitrile were irradiated for 5, 10, and 15 min, respectively. The resulting solutions were concentrated to dryness, and each residue was analyzed by ^{1}H NMR. The spectra ($CDCl_3$) showed a decrease in signals at δ 2.26 (s, 3H) and 3.80 (s, 3H) due to the consumption of 1,3-dimethylpyrazole (**28**) and a continuous increase in the signals at δ 2.20 (s, 3H), 3.54 (s, 3H) and at δ 2.17 (s, 3H), 3.60 (s, 3H) due to the formation of 1,2-dimethylimidazole (**19**) and 1,4-dimethylimidazole (**17**), respectively.

Quantum Yield of Reactions. Quantum yields of reactions were determined in triplicate by simultaneously irradiating solutions (3.0 mL each) of the reactants and the actinometer in Rayonet a reactor. The consumption of the reactant and the formation of products were monitored using GLC, UV absorption, and ^{1}H NMR spectroscopy. 1,3-Dimethyluracil[11] was used as the actinometer for 1-methyl-4-phenylpyrazole (**2**) and 1-methyl-5-phenylpyrazole (**3**). Cyclohepta-1,3-diene[11] was used as the actinometer for 2-(*N*-methylamino)-1-phenylethenylisocyanide (**6**). The quantum yield of reaction for the reaction of 3-(*N*-methylamino)-2-phenylpropenenitrile (**5**) was measured relative to the reaction of (**2**).

Sensitization. Solutions of 1-methyl-4-phenylpyrazole (**2**) and 1-methyl-5-phenylpyrazole (**3**) in methanol (3.0 mL, 1.0×10^{-2} M) and in acetone (3.0 mL, 1.2×10^{-2} M) were placed in Pyrex tubes, sealed with rubber septa, purged with nitrogen for 10 min, and irradiated in a Rayonet reactor equipped with 16 300 nm lamps. The solutions were monitored as a function of irradiation time by GLC.

Luminescence Spectra, Energies, and Lifetime of Excited States. Fluorescence and phosphorescence spectra were recorded at room temperature and at 77 K, respectively, in methanol:ethanol (1:1) using solutions with optical densities less than 0.25 at 250 nm. Excitation and emission wavelengths were set at 250 and 310 nm for fluorescence and at 250 and 435 nm for phosphorescence. Quantum yields of fluorescence were determined relative to *p*-xylene.[46] Decay constants and lifetimes for triplet states were obtained from plots of natural logarithm of the phosphorescence decay versus time.

Method of Calculation. All AM1[47] calculations were performed using the MOPAC[48] program with standard parameters. In general, structures obtained from PC-MODEL[49] were the starting points for AM1 optimizations using standard minimization techniques and internal coordinates.

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