135878-12-5; **12c**, 135878-15-8; **12d**, 135878-19-2; **12e**, 135878-23-8; **12f**, 135878-25-0; **12g**, 135878-26-1; **13**, 135878-02-3; **18**, 135878-03-4; 18 (phenylseleno derivative), 135878-31-8; **19**, 97400-51-6; **20a**, 61950-54-7; **21a**, 135878-04-5; **22a**, 135878-05-6; **22b**, 135912-60-6; **22c**, 135878-24-9; **23**, 135878-06-7; **27a**, 135878-07-8; **27b**, 135878-13-6; **27c**, 135878-20-5; **28a**, 135878-08-9; **28b**, 135878-14-7; **28c**, 135878-21-6; **31a**, 135878-09-0; **31b**, 135878-16-9; **33a**, 135878-10-3; **33b**, 135878-17-0; **34**, 135878-11-4.

Supplementary Material Available: ^1H and in some cases ^{13}C NMR spectra for all relevant compounds (32 pages). Ordering information is given on any current masthead page.

Phototransposition Chemistry of 1-Methylpyrazole. Deuterium, Methyl, and Fluorine Substitution

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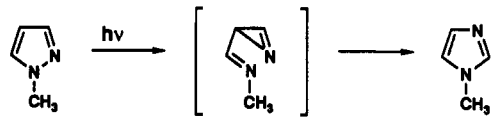
1-Methylpyrazole (1) was observed to undergo photo-ring cleavage to 3-(*N*-methylamino)propenenitrile (17) and phototransposition to 1-methylimidazole (3). Although upon prolonged irradiation 17 is also converted to 3, the efficiency of the 1 → 17 → 3 pathway is low and cannot account for a significant fraction of 3 observed upon short-duration irradiation. Under these conditions, deuterium-labeling studies show that 1 phototransposes to 3 by the P_4, P_6, and P_7 permutation patterns in a ratio of 4.8:6.5:1.0. These scrambling patterns are consistent with mechanisms involving ring contration–ring expansion (P_4) and electrocyclic ring closure followed by one (P_6) or two (P_7) sigmatropic shifts of nitrogen. Methyl and fluorine substitution on the 1-methylpyrazole ring reduces reactivity via the P_6 and P_7 pathways. Thus, 1,5-dimethylpyrazole transposes by these pathways in a ratio of 3.5:1.8:1.0, whereas 5-fluoro-1-methylpyrazole isomerizes only by the P_4 and P_6 pathways in a ratio of 9.7:1.

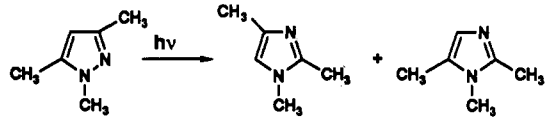
Introduction

The phototransposition chemistry of N-substituted pyrazoles has been of interest[1] since Schmid and co-workers[2] originally reported that 1-methylpyrazole (1) undergoes photoisomerization to *N*-methylimidazole (3). Although



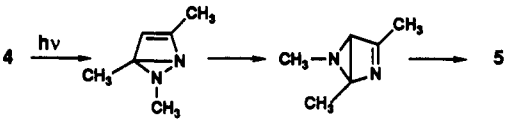
1 2 3

the transposition was rationalized in terms of a ring contraction–ring expansion mechanism,[2] involving the intermediacy of 2-(*N*-methylimino)-2*H*-azirine (2), subsequent studies implicated the operation of other transposition pathways. Thus, Beak and co-workers observed that 1,3,5-trimethylpyrazole (4) phototransposes to 1,2,4-trimethylimidazole (5) and 1,2,5-trimethylimidazole (6).[3]

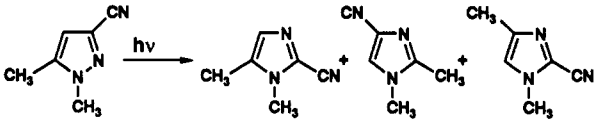


4 5 6

Although 6 results from the 2,3-interchange demanded by the ring contraction–ring expansion mechanism, product 5 cannot be rationalized by this mechanistic pathway. Rather, this product was suggested to arise via a transposition pathway that included initial electrocyclic ring closure, [1,3]-sigmatropic shift of nitrogen, and rearomatization of the resulting 2,5-diazabicyclo[2.1.0]pentene to provide 5.[3]

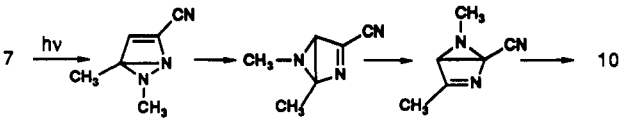


Barltrop, Day, and colleagues later observed that 3-cyano-1,5-dimethylpyrazole (7) undergoes phototransposition to three primary products, 8 and 9, which can be



7 8 9 10

rationalized by the ring contraction–ring expansion mechanism and the one-step nitrogen walk mechanism, respectively, and 10, which cannot arise by either of these transposition pathways but was suggested to arise via a double nitrogen walk mechanism.[4] Such a double walk



had formerly been implicated in the phototransposition chemistry of cyanothiophenes[5] and cyanopyrroles.[6,7] In-

(1) Lablache-Combier, A. *Photochemistry of Hetrocyclic Compounds*; Buchardt, O., Ed.; Wiley: New York, 1976; p 123. Padwa, A. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 501.

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

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

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

(5) Barltrop, J. A.; Day, A. C.; Irving, E. *J. Chem. Soc., Chem. Commun.* **1979**, 881 and 966.

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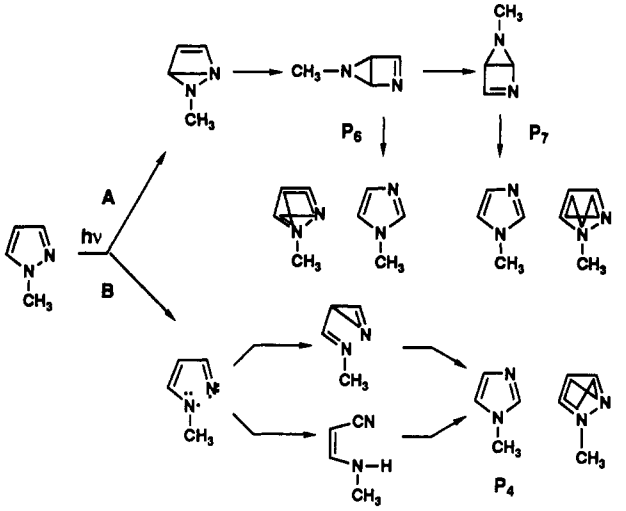
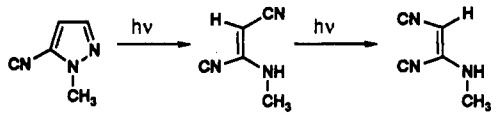
Scheme I



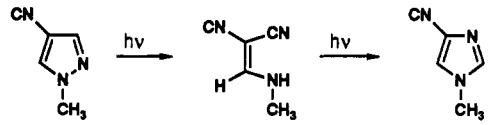
terestingly, in the case of pyrazole 4, it should be noted that the single and double walk mechanisms both lead to 5. Thus, whereas the substitution pattern in 7 allows differentiation of the two walk options, such distinction is impossible in the case of 4.

Finally, Barltrop, Day, and Wakamatsu have also reported that pyrazoles with hydrogen at position 3 also undergo photo-ring cleavage to enaminonitriles.[8] Whereas some enaminonitriles, such as β-(*N*-methylamino)fumaronitrile (12), formed photochemically from 5-cyano-1-



11 12 13

methylpyrazole (11), undergo only $E \rightleftharpoons Z$ photoisomerization (e.g., 12 ⇌ 13),[4] α-cyano-β-(*N*-methylamino)crotononitrile (15), formed from 4-cyano-1-methylpyrazole (14),[4] and a variety of other β-aminoacrylonitriles[9] have been observed to undergo photoconversion to imidazole products. This establishes the pyrazole → enaminonitrile → imidazole as another pyrazole → imidazole transposition pathway.



14 15 16

Scheme I summarizes the various mechanistic pathways implicated in the 1-methylpyrazole → 1-methylimidazole transposition and identifies the permutation pattern associated with each route. As discussed previously by Barltrop and Day, the permutation pattern provides a map of the transposition by determining where each ring atom

Table I

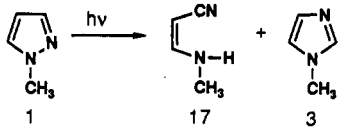
irradiation time (min)	[1], % consumed	[3], % formed	[17], % formed
0	1.65×10^{-2}, 0	0, 0	0, 0
10	1.27×10^{-2}, 23	1.75×10^{-3}, 46.1	8.46×10^{-4}, 22.3
20	1.14×10^{-2}, 31	2.74×10^{-3}, 53.7	12.2×10^{-4}, 23.9
30	1.02×10^{-2}, 38	3.08×10^{-3}, 48.9	15.0×10^{-4}, 23.8

in the product originated in the reactant and thus provides a precise definition of all bond-forming and bond-breaking processes for each phototransposition pathway.[10,11] As the scheme reveals, the scrambling patterns associated with the ring contraction–ring expansion and the enaminonitrile mechanistic pathways are identical and correspond to the P_4 permutation pattern. The scrambling patterns for the single and double step nitrogen walk mechanisms correspond to P_6 and P_7 permutation patterns respectively.

In order to determine the extent to which these various pathways operate in the 1-methylpyrazole → 1-methylimidazole transposition and to evaluate the effects of methyl and fluorine substituents on the operation of the various pathways, we have used the technique of permutation pattern analysis to investigate the phototransposition chemistry of the 1-methylpyrazole–1-methylimidazole heterocyclic system.

Results and Discussion

Solutions of 1-methylpyrazole (1) in acetonitrile were irradiated at ambient temperature with the quartz-filtered light of a 450-W Hg arc.[12] The reactions were monitored by quantitative GLC and by UV absorption spectroscopy. Irradiation of 1 led to the formation of 1-methylimidazole (3) and 3-(*N*-methylamino)propenenitrile (17), identified



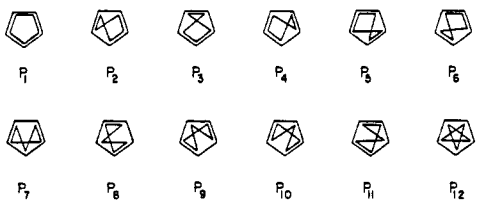
1 17 3

by direct chromatographic and spectroscopic comparison with authentic samples of these compounds synthesized in this laboratory. The results of seven such runs showed that after 30 min of irradiation, 34.1 ± 10.4% of 1 was consumed whereas the absolute yields of 3 and 17 were 70.3 ± 6.0% and 20.6 ± 3.1%, respectively.[13]

(6) Barltrop, J. A.; Day, A. C.; Moxon, P. D.; Ward, R. W. *J. Chem. Soc., Chem. Commun.* **1975**, 786; **1977**, 580.
(7) Barltrop, J. A.; Day, A. C.; Ward, R. W. *J. Chem. Soc., Chem. Commun.* **1978**, 131.
(8) Wakamatsu, S.; Barltrop, J. A.; Day, A. C. *Chem. Lett.* **1982**, 667.
(9) (a) Ferris, J. P.; Orgel, L. E. *J. Chem. Soc., Chem. Commun.* **1966**, *88*, 1074. (b) Ferris, J. P.; Sanchez, R. A.; Orgel, L. E. *J. Mol. Biol.* **1968**, *33*, 693. (c) Ferris, J. P.; Kuder, J. E. *J. Am. Chem. Soc.* **1970**, *92* 2527. (d) Ferris, J. P.; Antonucci, F. R.; Trimmer, R. W. *Ibid.* **1973**, *95*, 919. (e) Ferris, J. P.; Antonucci, F. R. *Ibid.* **1974**, *96*, 2010, 2014. (f) Koch, T. H.; Rodehorst, R. M. *Ibid.* **1974**, *96*, 6707. (g) Ferris, J. P.; Prabhu, K. V.; Strong, R. L.; *Ibid.* **1975**, *97*, 2096. (h) Ferns, J. P.; Trimmer, R. W. *J. Org. Chem.* **1976**, *41*, 13.

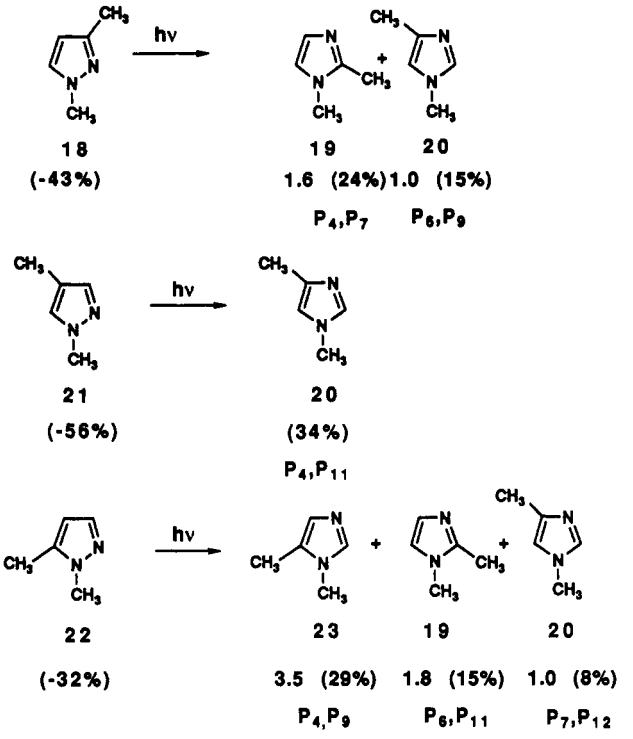
(10) For a discussion of permutation pattern analysis in aromatic phototransposition reactions in five-membered heteroaromatics, see: Barltrop, J. A.; Day, A. C. *J. Chem. Soc., Chem. Commun.* **1975**, 177 and refs 6 and 7.
(11) For five-membered heterocycles containing two heteroatoms there are 12 different ways of transposing the five ring atoms resulting in the 12 permutation patterns shown below.

PERMUTATION PATTERNS IN FIVE-MEMBERED RINGS



In this symbolism, the outer pentagon represents the original connections between the atoms of the ring and the internal pattern shows the order in which the ring atoms are connected in the transposed product.
(12) *N*-Methylpyrazole exhibits $\pi \rightarrow \pi^*$ absorption at 218 nm, whereas the dimethylpyrazoles shown in Scheme II absorb at 221, 226, and 217 nm, respectively. Thus, it was necessary to employ the unfiltered emission from the Hg arc light source.

Scheme II



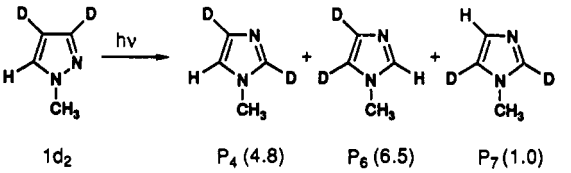
The formation of 3 and 17 were also monitored as a function of irradiation time. Table I shows the continuous consumption of 1 and the formation of 3 and 17. Continued analysis after prolonged irradiation of this solution showed that the concentration of 17 begins to decrease while the concentration of 3 continues to slowly increase, suggesting that 3 is being formed from 17. This possibility was explored by monitoring the direct irradiation of 17. Thus, when a solution of 17 (1.0×10^{-2} M in acetonitrile, 86% cis, 14% trans) was irradiated for 30 min under identical conditions, less than 2% of 17 was consumed and 1-methylimidazole (3) was detected by GLC analysis. This shows that although 17 can be converted to 3, this reaction is not as efficient as the formation of 3 upon excitation of 1. Indeed, after 20 min of irradiation, no reaction of 17 other than cis → trans isomerization could be detected. Accordingly, upon short-duration irradiation of 1, when the concentration of 17 in solution is much less than 1.0×10^{-2} M and is therefore absorbing very little light, the 1-methylimidazole (3) formed must not arise via the enaminonitrile route.

Permutation pattern analysis of the conversion of 1-methylpyrazole (1) to 1-methylimidazole (3) by the remaining mechanistic pathways (Scheme I) reveals that only C-5 of the reactant transposes to a unique position in the product. Thus, conversion of 1-methylpyrazole (1) to 1-methylimidazole (3) via the P_4, P_6, or P_7 pathways is accompanied by the transposition of C-5 of the reactant to ring positions 5, 2, or 4 in the product.

In order to study the transposition process with minimum substituent perturbation, we have synthesized and studied the phototransposition chemistry of 3,4-dideuterio-1-methylpyrazole ($1d_2$). This compound was synthesized from 3-bromo-1-methylpyrazole with essentially complete deuteration at C-3 and with 84% deuteration at C-4 according to the procedure presented in the experimental section.

(13) All yields in this paper are percent yields determined by quantitative GLC and based on the number of moles of reactant consumed.

3,4-Dideuterio-1-methylpyrazole ($1d_2$) was irradiated until GLC analysis showed that slightly less than 10% of $1d_2$ had been converted. This low conversion assured that transposition via the enaminonitrile pathway is trivial and that 1-methylimidazole → 1-methylimidazole secondary phototransposition is also insignificant. The unconverted $1d_2$ and the resulting dideuterio-1-methylimidazole were each collected by preparative GLC. ^{1}H NMR analysis of the recovered $1d_2$ showed no scrambling of the C-5 proton. ^{1}H NMR analysis of the isolated dideuterated 1-methylimidazole $3d_2$ in DMSO-d_6 revealed signals of almost equal area at δ 7.08 and 7.54, due to protons at C-5 and C-2 of the 1-methylimidazole ring, and a signal of much smaller area at δ 6.86 due to the C-4 ring proton. These results clearly show that the C-5 proton of $1d_2$ has transposed with approximately equal frequency to ring positions 5 and 2 of the 1-methylimidazole product—signaling almost equal operation of the P_4 and P_6 pathways—whereas to a lesser extent the C-5 proton has transposed to ring position 4, revealing that a smaller amount of 1-methylimidazole arises via the P_7 pathway. More quantitatively, these results show that 3,4-dideuterio-1-methylpyrazole ($1d_2$) undergoes phototransposition via the P_4, P_6, and P_7 pathways in a ratio of 4.8:6.5:1.0

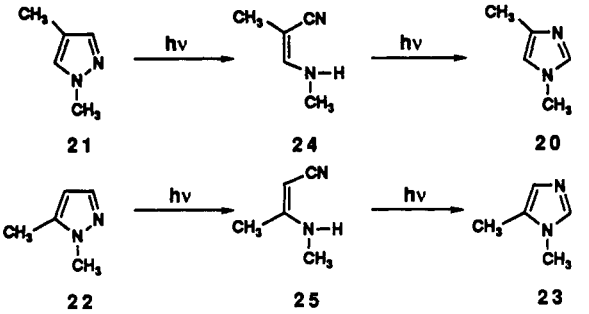


Methyl Substitution. In order to study the effects of ring methyl substitution on the phototransposition chemistry, we have also investigated the phototransposition chemistry of 1-methylpyrazoles in which the various ring carbon atoms are systematically labeled with a second methyl group. Each isomer, 2.0×10^{-2} M in acetonitrile, was irradiated under nitrogen at ambient temperature, and product formation was monitored as a function of irradiation time using quantitative capillary GLC under conditions that allowed clean separation of all dimethylpyrazole reactants and possible dimethylimidazole products.

Scheme II shows the primary products actually formed upon direct excitation of each dimethylpyrazole in acetonitrile solution. In this scheme the numbers in parentheses represent the absolute quantity of reactant consumed or the percent yield of product formed[13] after 20 min of irradiation while the numbers before the parentheses represent product ratios. Thus, 1,3-dimethylpyrazole (18) transposed to a mixture of 1,2-dimethylimidazole (19) and 1,4-dimethylimidazole (20) in a ratio of 1.6 to 1. Both products were detected after 5 min of irradiation. Although further irradiation was accompanied by a continued increase in the quantity of each product, the ratio remained essentially constant at 1.6 to 1. This concentration vs irradiation time profile confirmed that both 19 and 20 are primary phototransposition products. Throughout the first 10 min of irradiation of 1,4-dimethylpyrazole (21), the only product detected was 1,4-dimethylimidazole (20). Although more prolonged photolysis was accompanied by the formation of 1,2-dimethylimidazole (19), the concentration vs irradiation time profile indicated that 19 was formed from 20 in a secondary phototransposition process. As required by this interpretation, direct irradiation of an acetonitrile solution of 20 was accompanied by its photoconversion to 19.[14] Finally, upon irradiation, 1,5-di-

methylpyrazole (22) transposed to a mixture of 1,5-dimethylimidazole (23), 1,2-dimethylimidazole (19), and 1,4-dimethylimidazole (20) in a ratio of 3.5:1.8:1.0. All three products were detected after 5 min of irradiation, and their concentration vs irradiation time profile confirmed that all are primary products. These results show that these dimethylpyrazoles undergo only pyrazole → imidazole phototranspositions. Although the GLC analysis could have detected dimethylpyrazole products, none were observed.

In addition to phototransposition, after 30 min of irradiation, dimethylpyrazoles 21 and 22 were also observed to undergo photo-ring cleavage to yield 2-methyl-3-(*N*-methylamino)propenenitrile (24) and 3-(*N*-methylamino)butenenitrile (25), respectively. The yield of 24



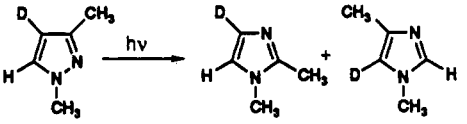
21 24 20

22 25 23

remained essentially constant at approximately 3% throughout the 30-min irradiation time, suggesting that 24 was being photochemically consumed at an efficient rate. This was experimentally confirmed. Five minutes of irradiation of a 1.25×10^{-2} M solution of 24 in acetonitrile was accompanied by the consumption of 45% of the starting β-aminopropenenitrile. Despite its efficient reactivity, the yield of 1,4-dimethylimidazole (20) was only ~2%, again indicating that the pyrazole → enaminonitrile → imidazole route is not a major pathway in this transposition. The yield of 25 reached a maximum of 22.0 ± 4.6% after 15 min of irradiation of 22. During that same irradiation time the yields of 23, 19, and 20 were 36.5 ± 3.1%, 18.7 ± 2.3%, and 11.0 ± 4.0%, respectively. This accounts for 88% of the mass in this reaction. Irradiation of a 1.0×10^{-2} M solution of β-aminoacrylonitrile 25 was accompanied by inefficient formation of 1,5-dimethylimidazole (23). Thus, 23 could not be detected until after 30 min of irradiation when approximately 16% of 25 had been consumed and 23 was formed in 20% yield.

Permutation Pattern Analysis. Considering the positions of the labeled ring atoms, the major or only phototransposition product obtained in each of these reactions was formed by either P_4 or P_7, P_4 or P_{11}, or P_4 or P_9 permutation patterns, respectively. The simplest inference is that these products are P_4 permutation pattern products since this pattern is common to all cases. Similar reasoning suggests that 1,4-dimethylimidazole (20) and 1,2-dimethylimidazole (19) are P_6 products from 18 and 22, respectively. Finally, it seems likely that 1,4-dimethylimidazole (20) is formed from 22 via a P_7 permutation process. This analysis shows that these dimethylpyrazoles undergo pyrazole → imidazole transpositions by up to three distinct permutation patterns—P_4, P_6, and P_7—and hence by up to three distinct transposition mechanisms.

In assigning these permutation patterns to the transposition products shown in Table I, it should be noted that, although P_4 and P_7 permutations have completely different bond-breaking–bond-forming requirements, in the case of 1,3-dimethylpyrazole (18), both pathways lead coincidentally to 1,2-dimethylimidazole (19) and the processes are therefore not distinguishable by product identification. This ambiguity was removed by studying the phototransposition chemistry of 1,3-dimethylpyrazole-*4-d* ($18d_1$). This reactant, 2×10^{-2} M in acetonitrile, was irradiated until GLC analysis showed 10% conversion of the starting pyrazole $18d_1$ in order to avoid secondary phototranspositions. The resulting dimethylimidazole products were first separated from unconverted $18d_1$ by column chromatography on silica gel, and the dimethylimidazole products were collected as a mixture by preparative GLC. ^{1}H NMR analysis of unconverted $18d_1$ showed no deuterium scrambling in the reactant, again confirming the absence of pyrazole → pyrazole transpositions. ^{1}H NMR analysis of the mixture of dimethylimidazole products $19d_1$ and $20d_1$ showed only two ring protons at δ 6.96 and 7.38. This confirms that the C-5 proton of $18d_1$ has transposed to position 5 in $19d_1$ and to position 2 in $20d_1$, as demanded by the P_4 and P_6 permutations, respectively. The absence of a signal at δ 6.68 shows that none of the C-5 proton of $18d_1$ has transposed to ring position 4 in $19d_1$ as would be required by operation of the P_7 permutation pathway. Accordingly, within the limits of the ^{1}H NMR analytical method, $18d_1$ has transposed only by the P_4 and P_6 pathways.

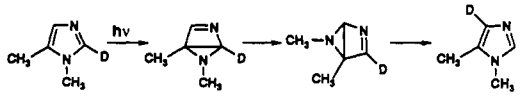


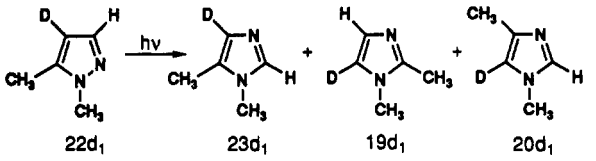
$18d_1$ $19d_1$ $20d_1$

Permutation pattern analysis does show that the P_4, P_6, and P_7 pathways can be unambiguously distinguished in the case of 1,5-dimethylpyrazole (22) since the three pathways lead to different products, viz., 23, 19, and 20. These permutation patterns were confirmed for the latter reaction by monitoring the photochemistry of 1,5-dimethylpyrazole-*4-d* ($22d_1$). After 10% photoconversion of $22d_1$, the unconverted reactant was separated from the imidazole products by silica gel column chromatography and $23d_1$ and the mixture of $19d_1$ and $20d_1$ were each collected by preparative GLC. ^{1}H NMR analysis of $23d_1$ in DMSO-d_6 showed a single ring proton absorbing at δ 7.45 as expected for the C-2 proton in $23d_1$. This confirms that the C-3 proton of $22d_1$ has transposed to position 2 in $23d_1$ as required by the P_4 permutation pathway. Furthermore, ^{1}H NMR analysis of the mixture of $19d_1$ and $20d_1$ in DMSO-d_6 revealed ring protons at δ 6.68 and 7.38. This clearly confirms that the C-3 proton in $22d_1$ has transposed to position 4 in $19d_1$ and to position 2 in $20d_1$ as demanded by the P_6 and P_7 permutation pathways, respectively.

Fluorine Substitution. The effect of fluorine substitution on the phototransposition chemistry of 1-methylpyrazole has also been studied. Scheme III shows the primary products formed upon direct irradiation of 1.0 × 10^{-2} M solutions of each isomeric fluoro-1-methyl-

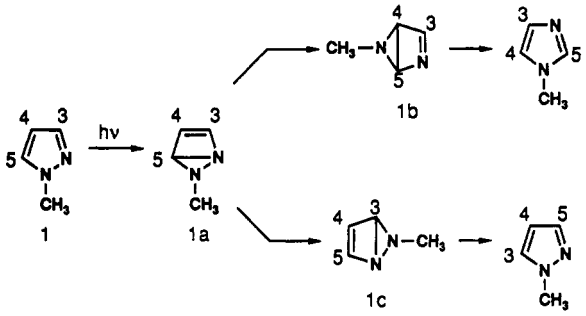
(14) Irradiation of 1,2- or 1,4-dimethylimidazole led to a photoequilibrium mixture of both compounds. Although irradiation of 1,5-dimethylimidazole did not lead to the formation of any new phototransposition product, irradiation of 2-deuterio-1,5-dimethylimidazole was accompanied by scrambling of the deuterium between positions 2 and 4. These results are consistent with a 1-methylimidazole → 1-methylimidazole phototransposition via a P_6 permutation process involving initial electrocyclic ring closure, 1,3-sigmatropic shift of nitrogen, and rearomatization to the transposed imidazole.





pyrazole in acetonitrile. Thus, 3-fluoro-1-methylpyrazole (**26**) and 4-fluoro-1-methylpyrazole (**27**) were each observed to phototranspose to a single primary product, 2-fluoro-1-methylimidazole (**29**) and 4-fluoro-1-methylimidazole (**30**), respectively. Photolysis of 5-fluoro-1-methylpyrazole (**28**) was accompanied by formation of two phototransposition products, 5-fluoro-1-methylimidazole (**31**) and 2-fluoro-1-methylimidazole (**29**) in a ratio of 9.1:1.0. Both products were detected by GLC after 5 min of irradiation, and the concentration vs irradiation time profile confirms that they are both primary products. The photocleavage reaction was not investigated in these cases.

Deuterium labeling studies presented earlier show that 1-methylpyrazole (**1**) undergoes phototransposition predominantly (~60%) by the nitrogen walk pathway. In this process the initially formed 1,5-diazabicyclo[2.1.0]pentene (**1a**) could plausibly undergo nitrogen walk in the opposite



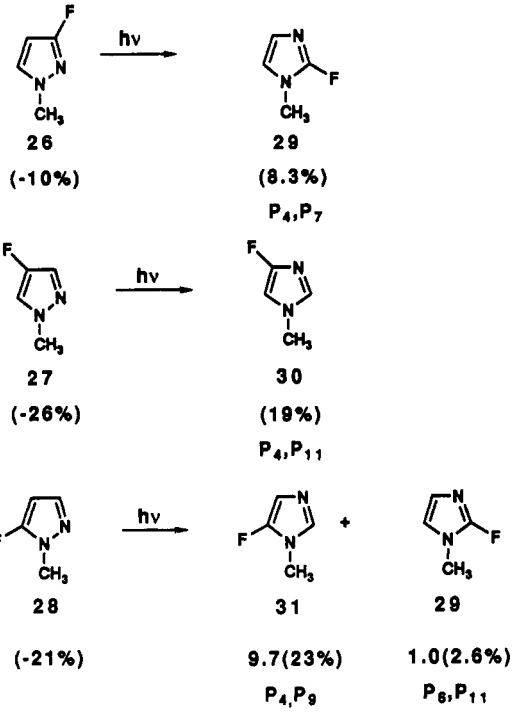
direction to yield **1c** and, after rearomatization, 1-methylpyrazole with $C_5 \rightleftharpoons C_3$ scrambling. No such scrambling of the C-5 proton could be detected by ^1H NMR analysis of unconverted $\mathbf{1d_2}$. This confirms the absence of pyrazole → pyrazole phototranspositions and indicates that nitrogen walk to form 2,5-diazabicyclo-[2.1.0]pentene **1b** is much faster than nitrogen walk in the opposite direction.

The data in Schemes II and III show that methyl and fluorine ring substitution enhances the P_4 process relative to the P_6 and P_7 walk pathways. Thus, although 1,5-dimethylpyrazole (**22**) transposes to P_4, P_6, and P_7 products, the total P_6 and P_7 walk pathways constitute only 40% of the total transposition process. In the case of 1,3-dimethylpyrazole (**18**), although the walk mechanism constitutes 45% of the total transposition, this reaction is restricted to the one-step P_6 process. The relative decrease in the walk process is even more pronounced with fluorine substitution. Thus, only 10% of the 5-fluoro-1-methylpyrazole (**28**) transposition occurs via the P_6 pathway. Finally, 3-fluoro-1-methylpyrazole (**26**) and both 4-methyl- and 4-fluoro-substituted 1-methylpyrazoles (**21**) and (**27**) transpose only to P_4 permutation pattern products.

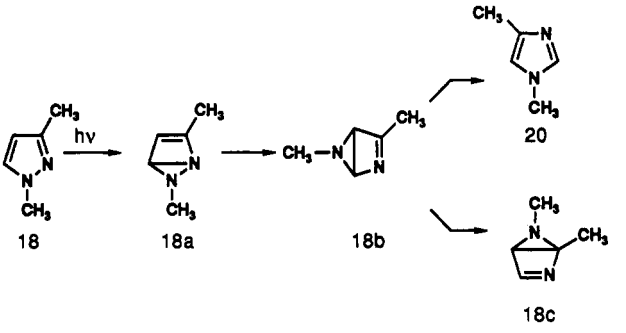
The extent to which the nitrogen walk mechanism operates may be controlled by the position of the methyl group in the intermediate diazabicyclopentene. In all isomers it would be expected that the first nitrogen walk would be favorable since a 2,5-diazabicyclo[2.1.0]pentene should be substantially more stable than the initially formed 1,5-diazabicyclo[2.1.0]pentene.

In the case of 1,3-dimethylpyrazole (**18**), the second nitrogen walk (**18b** → **18c**) would not be expected to occur since it would result in the conversion of **18b**, stabilized

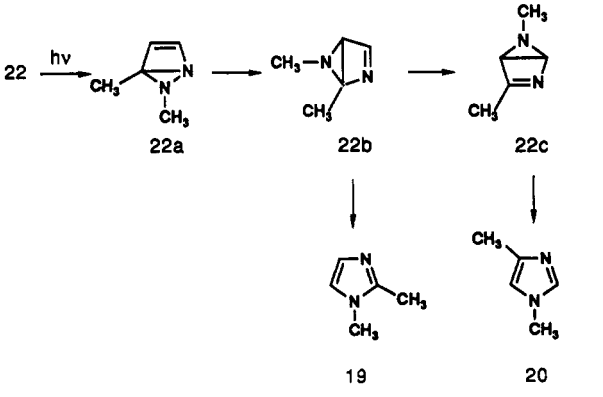
Scheme III



by methyl substitution at the polar C–N double bond, to a less stable isomer **18c** with the methyl substituent at the bridgehead position. Aromatization of **18b** to **20**, the observed product, would be expected to occur faster than the second nitrogen walk to yield **18c**. Absence of a P_7 product in this reaction is consistent with this reasoning.

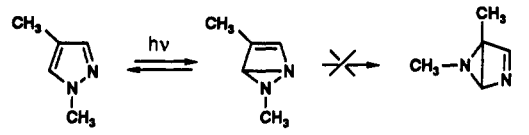


In the case of 1,5-dimethylpyrazole (**22**), in addition to the first nitrogen walk converting **22a** to **22b**, the second [1,3]-shift would also be favorable since it would lead to **22c**, the more stable isomer. Thus, in addition to aromatization of **22b** to the observed P_6 product **19**, aromatization of **22c** would provide **20**, the observed P_7 product.



Although these arguments rationalize product formation in the case of **18** and **22**, the logic cannot be extended to the case of 1,4-dimethylpyrazole (**21**). Whereas we would

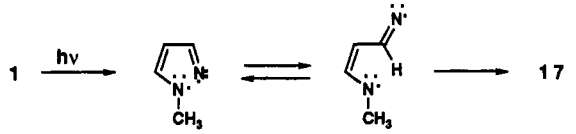
again anticipate the first nitrogen walk of **21a** to **21b** to be favorable, no P_6 imidazole resulting from the aromatization of **21b** was detected. Thus, either **21** does not



21 **21a** **21b**

undergo electrocyclic ring closure, or **21a** undergoes rearomatization back to **21** faster than [1,3]-sigmatropic rearrangement. Although these arguments qualitatively rationalize some of the observed results, a more thorough understanding of the energetics of the ground- and excited-state surfaces must await the more quantitative description of the reaction coordinate presented in the accompanying paper.[15]

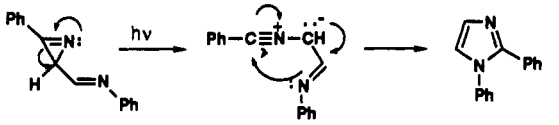
The mechanistic interpretation shown in Scheme I requires that electrocyclic ring closure is in competition with photochemical cleavage of the N–N bond resulting in acyclic species **1d**. Two pathways are envisioned for this



1d **1d'**

species. First, in the presence of a hydrogen at C-3 of the 1-methylpyrazole ring, H-atom transfer from C-3 to N-1 would yield the observed enaminonitrile **17**. Although these products can be isolated, continued irradiation results in their inefficient conversion to 1-methylimidazole (**3**) via a P_4 permutation process, possibly by way of an iminoazetine, as originally suggested by Ferris and Kuder[9c] to rationalize the photoconversion of β-aminocrotononitrile to 4-methylimidazole or by way of an azirine intermediate as suggested by Bigot and Roux on the basis of theoretical studies.[16] The enaminonitrile → imidazole conversion is inefficient, however, and cannot account for a significant fraction of the 1-methylpyrazole → 1-methylimidazole P_4 transposition process.

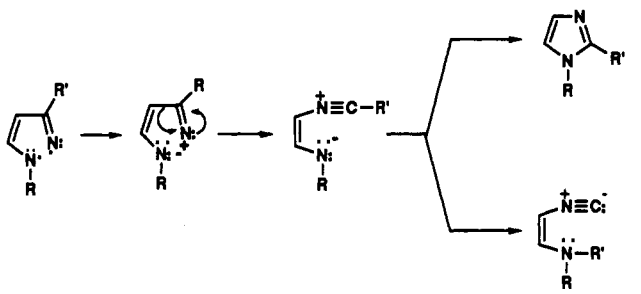
Schmidt and co-workers originally suggested that diradical species **1d** cyclizes to 2-(*N*-methylimino)-2*H*-azirine (**2**), which undergoes subsequent ring expansion to the imidazole product.[2] Preliminary computational studies, conducted in these laboratories, agree with this suggestion and indicate that the conversion of biradical **1d** to iminoazirine **2** is a particularly facile gound-state process.[17] These studies reveal that rotation around the C_3–C_4 bond leads to ring closure to **2** before reaching confirmation 1d', the geometry required for H-transfer and enaminonitrile formation. Although previous workers have demonstrated the involvement of acylazirines in the analogous isoxazole → oxazole P_4 phototransposition,[18] iminoazirines have not been detected in the pyrazole → imidazole phototransposition. 3-Phenyl-2-(*N*-phenylimino)-2*H*-azirine (**32**) has



32 **33** **34**

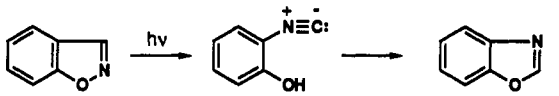
been independently synthesized, however, and shown to undergo photorearrangement to 1,2-diphenylimidazole (**34**) as the exclusive product,[19] presumably via the nitrile ylide intermediate **33**.[20] These results lend support to the ring contraction–ring expansion mechanism and the intermediacy of a 2*H*-azirine species. Failure to detect these intermediates may be due to their high degree of thermal reactivity in the absence of suitable stabilizing substituents.

It is plausible that azirine formation is in competition with a 1,2-shift of C-4 from carbon to nitrogen[21] followed by cyclization to yield 1-methylimidazole (R = CH_3, R' = H) or by proton transfer to yield isonitrile **35**. Isonitrile



35

37 has been detected as an intermediate in the photoconversion of indoxazene (**36**) to benzoxazole (**38**).[9e] Although such an intermediate has not been detected in the pyrazole → imidazole transposition reaction, isonitrile **35** could undergo thermal or photochemical conversion to imidazole **3**, or could be the precursor of the observed enaminonitrile.[22]



36 **37** **38**

It is interesting to note that azirine formation and subsequent electrocyclic ring opening leads to the same species obtained by the 1,2-shift pathway. Thus, the net effect of azirine formation and ring opening is a shift of the C-4 ring carbon from C-3 to N-2. The transition state for the 1,2-shift pathway would have considerable azirine character. Accordingly, whether the azirine is an isolable intermediate or whether it is a reactive species on the transposition reaction coordinate may depend on the presence or absence of structural features that stabilize the azirine.

(15) See: Connors, R. E.; Pavlik, J. W.; Burns, D. S.; Kurzweil, E., next paper in this journal.

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Conclusion

These results show that 1-methylpyrazole (1) undergoes phototransposition to 1-methylimidazole by four distinct mechanistic pathways. Ring methyl and fluorine substitution can substantially alter the extent to which each pathway operates. Thus, substitution at ring position 4 restricts the phototransposition to the P_4 process while substitution at ring position 3 by methyl or fluorine substantially or totally favors the P_4 pathway. Finally, 5-substituted 1-methylpyrazoles are the least perturbed and continue to react by the P_4 and by the P_6 and/or the P_7 walk processes. Additional experimental and computational studies directed toward understanding the mechanistic aspects of the pyrazole → imidazole transposition are currently in progress in our laboratory.

Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra were recorded at 200 and 52.3 MHz on a Bruker FT-NMR system. ^1H and ^{13}C chemical shifts were measured relative to internal Me_4Si and $CHCl_3$, respectively. Infrared spectra were recorded on a PE-683 or a PE-1720 FT spectrometer. GLC was performed on a PE-8500 FID instrument equipped with a 30 m × 0.25 mm i.d. fused silica column coated with 0.25 μ Supelcowax 10 bonded phase (Column A) or on a PE-3920 FID instrument using a 6 ft × $^1/_8$ in. column packed with 2% OV-225 on Chromosorb G (Column B) or a 6 ft × $^1/_4$ in. column packed with 2% Carbowax 20M-TPA on Chromosorb G (Column C) for preparative scale work. Mass spectra were recorded using an HP 5970B mass selective detector interfaced to an HP 5880 capillary gas chromatograph. Elemental analyses were determined by Desert Analytics, Tucson, AZ.

Preparation of Starting Materials and Products. Compounds previously described in the literature were prepared as follows: 1-methylpyrazole (1) by methylation of pyrazole using trimethylphosphate;[23] 1,3- and 1,5-dimethylpyrazole (18) and (22) as a mixture by the condensation of methylhydrazine with 4,4-dimethoxy-2-butanone and each isomer purified to greater than 99.6% purity by repeated spinning-band distillation;[24] 1,4-dimethylpyrazole (21) by condensation of 1,1,3,3-tetraethoxy-2-methylpropane[25] and methylhydrazine dihydrogen sulfate;[26] 1,4- and 1,5-dimethylimidazole (20) and (23) as a mixture by methylation of 4-methylimidazole using methyl iodide,[27] separated by reduced-pressure spinning-band distillation and each isomer purified by preparative GLC at 180 °C; 3-fluoro-1-methylpyrazole (26) from 3-amino-1-methylpyrazole;[28,29] 4-fluoro-1-methylpyrazole (27) from 4-nitro-1-methylpyrazole;[29,30] 3(5)-fluoropyrazole[31] from 3(5)-aminopyrazole[32] and selectively methylated using dimethylsulfate[29] to provide 5-fluoro-1-methylpyrazole (28); 2-fluoro-1-methylimidazole (29)[33] from 2-amino-1-methylimidazole hydrochloride;[34] 4-fluoro-1-methylimidazole (30)[35] from 4-nitro-1-methylimidazole;[36] 5-fluoro-1-methylimidazole (31) from 4-(5)-fluoroimidazole;[35,37] 3-(methylamino)propenenitrile (17) from 3-ethoxyacrylonitrile and methylamine;[38] 2-methyl-3-(methylamino)propenenitrile (24) from 3-ethoxy-2-methylpropenenitrile and methylamine;[38,39] 3-(methylamino)-2-butenenitrile (25) from 3-aminocrotononitrile and methylamine hydrochloride.[40]

3,4-Dideuterio-1-methylpyrazole ($1d_2$). 3-Amino-1-methylpyrazole (21.0 g, 0.216 mol) was dissolved in 150 mL of 48% HBr at 0 °C with stirring. Sodium nitrite (15.0 g, 0.217 mol) in 15 mL of water was added dropwise to the stirred solution over a period of 1 h while the temperature was maintained at −5 to 0 °C until the white precipitate dissolved and a positive starch–iodide test was obtained. While the solution of the diazonium ion was maintained at 0 °C, it was added slowly in small portions to a solution of freshly prepared Cu_2Br_2 (from 135 g, 0.554 mol of $CuSO_4 \cdot 5H_2O$) in 180 mL of 48% HBr also maintained at 0 °C. The resulting solution was allowed to stir at 0 °C for 3 h and then allowed to warm to room temperature and neutralized to pH 7 with sodium bicarbonate. The resulting solid was collected by suction filtration, extracted (Sohxlet) with CH_2Cl_2 for 24 h, and concentrated. Distillation provided 3-bromo-1-methylpyrazole as a colorless liquid [bp 54–56 °C (1.5 Torr)]: yield 15.3 g (0.0951 mol, 44.0%); IR (neat) 3143, 3119, 2944, 1510, 1360, 1334, 1284, 1169, 1070, 1035, 955, 754 cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$) δ 3.85 (s, 3 H), 6.13 (d, 1 H, J = 2.0 Hz), 7.26 (d, 1 H, J = 2.0 Hz); ^{13}C NMR (52.3 MHz; $CDCl_3$) δ 39.3, 108.3, 124.9, 131.8; MS m/e 161.95 (100), 160.95 (27), 159.95 (95), 158.95 (24), 81.05 (36), 80.05 (27), 79.05 (13), 54.05 (33), 53.05 (16), 52.05 (32), 51.05 (18). Anal. Calcd for $C_4H_5N_2Br$: C, 29.84; H, 3.13; N, 17.40; Br, 49.63. Found: C, 29.83; H, 3.10; N, 17.43; Br, 49.47.

3-Bromo-1-methylpyrazole (0.96 g, 6.0 mmol) in anhydrous diethyl ether was stirred at −100 °C (ethanol–liquid N_2 bath) under a N_2 atmosphere, and t-BuLi (1.7 M in pentane, 4.0 mL, 6.8 mmol) was added dropwise over 5 min. After being stirred at −100 °C for 1 h, CH_3OD (1.0 mL) was added, the resulting solution was allowed to warm to room temperature, and the suspension filtered. The filtrates from 20 such reactions were combined and concentrated by distillation. Distillation (Kugelröhr) of the residual oil gave 3-deuterio-1-methylpyrazole: oven temperature 110 °C, atm pressure, (lit.[23] bp 127 °C at atm pressure); 2.6 g (0.031 mol, 26% yield); ^1H NMR (200 MHz, $CDCl_3$) δ 3.90 (s, 3 H), 6.22 (d, 1 H, J = 1.7 Hz), 7.35 (d, 1 H, J = 1.7 Hz); MS m/e 83.2 (100), 82.2 (50), 55.1 (36), 54.1 (41), 53.1 (13), 52.1 (15), 42.1 (37).

3-Deuterio-1-methylpyrazole (2.6 g, 0.031 mol) in D_2SO_4 (5.0 mL, 70% in D_2O) was maintained at 75 °C while protected from atmospheric moisture. After 10 days ^1H NMR analysis indicated 82% deuteration at C-4. The resulting solution was added dropwise to a rapidly stirred suspension of $NaHCO_3$ (13.0 g) in water (10 mL). Enough water was added to dissolve the resulting solid, and the solution was extracted with CH_2Cl_2 (10 × 5 mL), combined, dried (Na_2SO_4), and concentrated and the residue purified by preparative GLC to give 3,4-dideuterio-1-methylpyrazole: ^1H NMR (200 MHz, $CDCl_3$) δ 3.90 (s, 3 H), 7.35 (s, H-5), and a low intensity signal (26.3 ± 3.2% of H-5) at 6.22 for residual H_4 protons; MS m/e 84.2 (100), 83.2 (91), 82.1 (27), 56.1 (33), 55.1 (46), 54.1 (27), 53.2 (17), 42.1 (47).

4-Deuterio-1,3-dimethylpyrazole ($18d_1$). 1,3-Dimethylpyrazole (2.0 g, 0.021 mol) was dissolved in D_2SO_4 (5.0 mL, 70%), protected from atmospheric moisture, and maintained at 70 °C for 6 days. NMR analysis indicated greater than 80% deuteration at the C-4 position. The resulting solution was neutralized by dropwise addition to a rapidly stirred suspension of aqueous sodium bicarbonate, extracted with dichloromethane, and concentrated. The residual oil was subjected to a second deuteration in 70% D_2SO_4. After 6 days, no residual hydrogen could be detected by NMR. Workup as above and distillation (Kugelröhr) provided 1.1 g of a colorless oil. Pure 4-deuterio-1,3-dimethylpyrazole was obtained by preparative GLC at 180 °C: ^1H NMR (200 MHz, DMSO-d_6) δ 2.11 (s, 3 H), 3.71 (s, 3 H), 7.50 (s, 1 H), and a low intensity signal at 5.93 for residual H_4 protons.

4-Deuterio-1,5-dimethylpyrazole ($22d_1$). 1,5-Dimethylpyrazole (2.0 g, 0.021 mol) was treated with 70% D_2SO_4 as de-

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scribed above. Workup and distillation (Kugelröhr) provided 1.0 g of a colorless oil. Pure 4-deuterio-1,5-dimethylpyrazole was obtained as above by preparative GLC: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.26 (s, 3 H), 3.76 (s, 3 H), 7.36 (s, 1 H) and a low intensity signal (0.1 H) at 6.00 due to residual H-4 protons.

Irradiation and Analysis Procedures. To monitor 1-methylpyrazole to 1-methylimidazole or (*N*-methylamino)-acrylonitrile photoconversions on an analytical scale, a solution of the appropriate 1-methylpyrazole or (*N*-methylamino)acrylonitrile (3.0 mL, 1.0×10^{-2} M or 12.0 mL, 1.0×10^{-2} M) in acetonitrile was placed in a quartz tube (7 mm i.d. or 14 mm i.d. × 13 cm long), sealed with a rubber septum, and purged with nitrogen for 5 min prior to irradiation. The tubes were suspended in an ambient temperature water bath adjacent to a water-cooled quartz immersion well containing a 450-W high-pressure Hg lamp. Preparative-scale reactions were carried out by irradiating a nitrogen-purged solution of the appropriate 1-methylpyrazole (25.0 mL, 1.0×10^{-2} M) in acetonitrile in a quartz tube (20 mm i.d. × 15 cm long).

Formation of 1-methylimidazoles was monitored by irradiating the appropriate 1-methylpyrazole solution for 60 min while removing aliquots every 5 min for GLC analysis on column A. Formation of (*N*-methylamino)acrylonitriles was monitored by irradiating the appropriate 1-methylpyrazole solution for 15 min, concentrating the resulting solution (10 to 1), and analyzing the resulting solution by GLC on column B. Upon direct irradiation of an (*N*-methylamino)acrylonitrile, reactant consumption was monitored by GLC on column B without concentration while 1-methylimidazole formation was determined by GLC on column A. The retentions of all products are given relative to the appropriate starting reactant. Solutions resulting from preparative-scale reactions were concentrated to less than 0.5 mL. Unconverted reactants and products were collected by preparative GLC at the temperature indicated.

Quantitative GLC analysis of reactant consumption and product formation was accomplished using calibration curves constructed for each reactant and product by plotting detector response vs a minimum of five standards of known concentrations. Correlation coefficients ranged from 0.993 to 0.999.

1-Methylpyrazole (1). GLC analysis of the irradiated solution at 145 °C showed the formation of 1-methylimidazole (3) with a relative retention of 3.4. GLC analysis of the concentrated solution showed the formation of 3-(*N*-methylamino)propenenitrile (17) with a relative retention of 5.0.

1,3-Dimethylpyrazole (18). GLC analysis of the irradiated solution at 145 °C showed the formation of 1,4-dimethylimidazole (20) and 1,2-dimethylimidazole (19) with relative retentions of 2.3 and 2.6, respectively. No additional products were detected by GLC analysis of the concentrated solution.

1,4-Dimethylpyrazole (21). GLC analysis of the irradiated solution at 145 °C showed the formation of 1,4-dimethylimidazole (20) with a relative retention of 2.8. GLC analysis of the concentrated solution showed the formation of 2-methyl-3-(*N*-methylamino)propenenitrile (24) with a relative retention of 3.0.

1,5-Dimethylpyrazole (22). GLC analysis of the irradiated solution at 145 °C showed the formation of 1,4-dimethylimidazole (20), 1,2-dimethylimidazole (19), and 1,5-dimethylimidazole (23) with relative retentions of 2.1, 2.3, and 3.5, respectively. GLC analysis of the concentrated solution showed the formation of 3-(*N*-methylamino)butenenitrile (25) with a relative retention of 4.4.

3-Fluoro-1-methylpyrazole (26). GLC analysis of the irradiated solution showed the formation of 2-fluoro-1-methylimidazole (29) with a relative retention of 1.3.

4-Fluoro-1-methylpyrazole (27). GLC analysis of the irradiated solution showed the formation of 4-fluoro-1-methylimidazole (30) with a relative retention of 2.7.

5-Fluoro-1-methylpyrazole (28). GLC analysis of the irradiated solution showed the formation of 2-fluoro-1-methylimidazole (29) and 5-fluoro-1-methylimidazole (31) with relative retentions of 3.2 and 3.7, respectively.

3,4-Dideuterio-1-methylpyrazole ($1d_2$). A total of 400 mL of $1d_2$ (2.38×10^{-2} M) was irradiated in 25-mL portions until GLC analysis showed slightly less than 10% conversion of $1d_2$. The resulting solutions were combined and concentrated by fractional distillation through a Vigreux column. Unconverted $1d_2$ and dideuterio-1-methylimidazole ($3d_2$) were isolated by preparative GLC [120 °C (16 min), 120–190 °C at 32° min^{-1}, 190 °C (16 min)]. ^{1}H NMR (200 MHz): of $1d_2$ ($CDCl_3$) δ 3.90 (s, 3 H), 7.35 (s, H-5), and a low intensity signal (23% of H-5) at 6.22 for residual H-4 protons; of $3d_2$ (DMSO-d_6) δ 3.62 (s, 3 H), 6.73 (s, H-4, integral rise 8.6 ± 1.2 mm), 7.02 (s, H-5, integral rise 26.8 ± 1.1 mm), 7.41 (s, H-2, integral rise 26.5 ± 1.5 mm).

4-Deuterio-1-dimethylpyrazole ($18d_1$). A total of 500 mL $18d_1$ (2.1×10^{-2} M) was irradiated in 25-mL portions until GLC analysis showed slightly less than 10% conversion of $18d_1$. The resulting solutions were combined and concentrated by fractional distillation through a Vigreux column. The residue (~1.5 mL) was subjected to silica gel (8.0 g, 70–230 mesh) column chromatography. The column (7 cm long × 1.0 cm dia) was eluted with 70 mL of hexane–acetone (5:1), 30 mL of hexane–acetone (1:1), and 50 mL of acetone–CH_2Cl_2 (3:2); 2.0-mL fractions were collected. On the basis of GLC analysis, fractions 10–30 were combined and concentrated to recover unconverted $18d_1$ while fractions 52–75 were combined and concentrated to provide a mixture of deuterio-1,2-dimethylimidazole ($19d_1$) and deuterio-1,4-dimethylimidazole ($20d_1$). Unconverted $18d_1$ and the mixture of photoproducts $19d_1$ and $20d_1$ were collected by preparative GLC at 170 °C: ^{1}H NMR (200 MHz): of $18d_1$ (DMSO-d_6) δ 2.11 (s, 3 H), 3.71 (s, 3 H), 7.50 (s, 1 H), and a low intensity signal at 5.93 for residual H-4 protons; of $19d_1$ and $20d_1$ (DMSO-d_6) δ 2.06 (s, 3 H, C-4 CH_3 in $20d_1$), 2.28 (s 3 H, C-2 CH_3 in $19d_1$), 3.53 (s, 3 H, NCH_3 in $19d_1$), 6.97 (s, 1 H, H-5 in $19d_1$), 7.38 (s, 1 H, H-2 in $20d_1$), and very low intensity signals at 6.67 and 6.76 for residual C-4 protons in $19d_1$ and C-5 protons in $20d_1$, respectively.

3-(*N*-Methylamino)propenenitrile (17). GLC analysis after 20 min, or irradiation of 17 (86% cis, 14% trans) indicated no consumption of 17. Cis–trans isomerization was determined by comparing the UV–vis absorption spectrum of the solution (50 μL diluted to 10.0 mL) with the spectra of solutions of authentic samples of known concentration and cis–trans composition. This analysis indicated that the solution contained 19 ± 1% cis and 71 ± 1% trans after 20 min of irradiation. After 30 min of irradiation, GLC analysis indicated that less than 2% of 17 was consumed and that 1-methylimidazole (3) was formed. After 9 h of irradiation, GLC analysis indicated that 25% of 17 was consumed and that 3 was formed in 32% absolute yield.

2-Methyl-3-(*N*-methylamino)propenenitrile (24). GLC analysis after 10 min of irradiation indicated 53% consumption of 24 and formation of 1,4-dimethylimidazole (20) in less than 2% absolute yield.

3-(*N*-Methylamino)butenenitrile (25). GLC analysis after 30 min of irradiation indicated 18% consumption of 25 and formation of 1,5-dimethylimidazole (23) in 29% absolute yield.

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