Vapor-Phase Photochemistry of Dimethylpyridines

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Received March 9, 1999. Revised Manuscript Received April 30, 1999

Abstract: Irradiation of dimethylpyridine vapors (2−5 Torr) at 254 nm results in the formation of two sets of isomerization products. One set, formed in the larger yield, is substantially quenched when the irradiations are carried out in the presence of 15−21 Torr of nitrogen and is not formed when the irradiations are carried out with light of $\lambda > 290$ nm. In addition, a second set of reactions, which involve the interconversion of 2,3- and 2,5-dimethylpyridines, is enhanced by the addition of nitrogen, and these reactions are the only photoisomerization reactions observed when the irradiations are carried out with light of $\lambda > 290$ nm. In addition to the photoisomerizations, four of the dimethylpyridines also undergo demethylation to yield monomethylpyridines, and 2,6-dimethylpyridine undergoes methylation to yield a trimethylpyridine product. A variety of crossover experiments confirmed that the photoisomerizations are intramolecular. Based on the major phototransposition products, the six dimethylpyridines can be divided into two triads. Interconversion of the three members of each triad results in the major phototransposition products. These intra-triad interconversions are suggested to occur via 2,6-bonding, originating in a vibrationally excited S_2 (π,π^*) state of the dimethylpyridine, followed by nitrogen migration and rearomatization. This allows nitrogen to insert within each carbon−carbon bond. Phototransposition of 2,6-dideuterio-3,5-dimethylpyridine to a mixture of 5,6-dideuterio-2,4-dimethylpyridine and 3,4-dideuterio-2,5-dimethylpyridine is consistent with this mechanism. In addition to these intra-triad reactions, 2,5-dimethylpyridine, a member of triad 1, was observed to interconvert with 2,3-dimethylpyridine, a member of triad 2. These inter-triad reactions are suggested to occur via interconverting Dewar pyridine intermediates, formed from the triplet state of the dimethylpyridines. These Dewar pyridine intermediates were also observed by ^{1}H NMR spectroscopy after irradiation of the dimethylpyridines in CD₃CN at −30 °C.

When dimethylpyridines are irradiated in the vapor phase, they undergo photoisomerization as well as demethylation and methylation reactions. To account for the photoisomerizations they reported, Caplain and Lablache-Combier suggested a ring transposition mechanism involving azaprismane intermediates.[1] Such species could arise via Dewar isomers, initially formed by 2,5- (or 3,6-) bonding in the photoexcited dimethylpyridine. Indeed, the formation of Dewar pyridine was already known to result from irradiation of pyridine in liquid solution.[2]

A perplexing feature of the suggested transposition mechanism is the selectivity required to explain the products reported by Caplain and Lablache-Combier.[1] Thus, as shown in Scheme 1, the reported conversion of 2,6-dimethylpyridine (**4**) to 2,4-dimethylpyridine (**2**) requires that the reactant first undergoes 2,5- (or 3,6-) bonding (but not N_1−C_4 bonding) and regiospecific opening of the subsequently formed azaprismane via cleavage of the C_3−C_4 and C_5−C_6 bonds, but not of the C_2−C_3 and N_1−C_6 bonds, which would have resulted in the formation of 2,5-dimethylpyridine (**3**).

Alternatively, the reported conversion of 2,3-dimethylpyridine (**1**) to a mixture of 3,4-dimethylpyridine (**5**) and 2,5-dimethylpyridine (**3**) requires (Scheme 2) initial N_1−C_4 bonding (but not 2,5- or 3,6-bonding), followed by cleavage of the azapris-

(1) Caplain, S.; Lablache-Combier, A. *J. Chem. Soc., Chem. Commun.* **1969**, 1247−1248.
(2) Wilzbach, K. E.; Rausch, D. J. *J. Am. Chem. Soc.* **1970**, *92*, 2178−2179.

Scheme 1
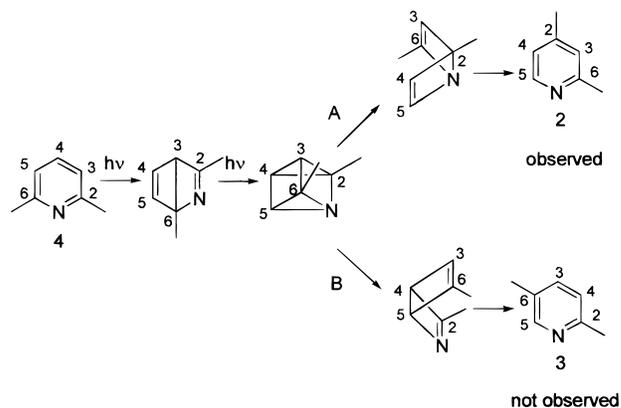
mane via both possible pathways. These examples illustrate the arbitrary selectivity that must be imposed upon the possible modes of formation of the initially formed Dewar pyridines as well as on the rearomatization of the subsequently formed azaprismanes.

As a result of these mechanistic ambiguities, we have reinvestigated the photochemistry of the six isomeric dimethylpyridines in the vapor phase. In this paper we report the results of this investigation which, to our initial surprise, are totally at variance with the results previously published by Caplain and Lablache-Combier.[1] Although we cannot account for the differences between our results and those previously published,

Scheme 2

our results are highly reproducible, and we have no reason to doubt their validity.[3]

Results and Discussion

Each dimethylpyridine (**1**−**6**) vapor, with a total pressure of 2−5 Torr, was irradiated through quartz at 254 nm or through Pyrex with light of wavelength >290 nm. In addition, a partial pressure of 2−5 Torr of each dimethylpyridine vapor (**1**−**6**) was diluted with 15−21 Torr of nitrogen, and each mixture was also irradiated through quartz at 254 nm. After each irradiation, the volatile materials were pumped out of the reaction flask, condensed, and dissolved in a standard volume of ether for quantitative GLC analysis. The recovered material accounted for approximately 45% of the mass of the original reactant. Products were identified by GLC retention times, by GLC co-injections with authentic samples, and, when possible, by mass spectroscopy. Photolyses were also accompanied by the formation of variable amounts of nonvolatile polymeric material which built up on the sides of the reaction flask and is responsible for the low mass balances shown in Tables 1 and 2. ^{1}H NMR analysis of this material showed the presence of aliphatic hydrogen but no absorptions due to aromatic protons, suggesting that polymerization is accompanied by ring opening. Photolyses of dimethylpyridines **3** and **6** were accompanied by the formation of substantially less polymeric material, and accordingly these reactions exhibited higher mass balances.

Tables 1 and 2 show the products formed from each dimethylpyridine under each set of conditions. As noted earlier, the phototransposition products observed in this study are totally different than those previously reported by Caplain and Lablache-Combier.[1] As Tables 1 and 2 show, both phototransposition and photodemethylation and methylation products were observed. Although Caplain and Lablache-Combier reported that methylpyridines undergo phototransposition as well as demethylation and methylation upon irradiation in the vapor phase, they reported that dimethylpyridines undergo only photoisomerization.

Although these irradiations result in a variety of phototransposition products, inspection of Tables 1 and 2 reveals that they can be divided into two classes. For example, irradiation of pure 2,3-dimethylpyridine (**1**) vapor at 254 nm results in the formation of 2,6-dimethylpyridine (**4**), 3,4-dimethylpyridine (**5**), and 2,5-dimethylpyridine (**3**) in yields of 5.7, 0.9, and 0.8%, respectively.[5] Upon dilution of the reactant with N$_2$, the yields of **4** and **5** were substantially decreased to 1.8 and 0%,

(3) Caplain and Lablache-Combier also reported that 2-methylpyridine undergoes photoisomerization in the gas phase to yield 4-methylpyridine. This is in contrast to the report by Roebke that the gas-phase photolysis of 2-methylpyridine yields both 3- and 4-methylpyridine in a ratio of 10:1.[4]

(4) Roebke, W. *J. Phys. Chem.* **1970**, *74*, 4198−4203.

Table 1. Photolysis Products[a]

	4	**5**	**3**	**7**	**8**
−45.6[b]	5.7	0.9	0.8	1.6	0.2
−42.6[c]	1.8	—	1.5	0.7	1.3
−21.3[d]	—	—	0.9	—	2.4

	3	**6**	**7**	**9**
−40.4[b]	3.6	2.3	0.2	1.7
−48.2[c]	0.5	0.6	0.4	2.4
−15.6[d]	—	—	—	7.1

	2	**6**	**1**	**7**	**8**
−30.4[b]	13.7	3.7	3.5	1.0	1.9
−32.6[c]	2.8	3.7	5.0	2.7	7.2
−39.3[d]	—	—	3.9	2.3	—

[a] Numbers are percent of reactant consumed or the percent yields of products formed after irradiation. [b] Irradiation at 254 nm. [c] Irradiation at 254 nm in the presence of added N$_2$. [d] Irradiation at λ > 290 nm.

respectively, while the yield of 2,5-dimethylpyridine (**3**) increased from 0.8 to 1.5%. Furthermore, **3** is the only phototransposition product formed when **1** is irradiated with light of wavelength longer than 290 nm. These results indicate the operation of two mechanistically different phototransposition pathways. One pathway, leading to the formation of **4** and **5**, is substantially quenched upon dilution of the reactant with N$_2$ and does not operate upon irradiation with λ > 290 nm. In addition, a second pathway, leading to the formation of **3**, is also implicated, which is enhanced by dilution with N$_2$ and is the only pathway in operation upon irradiation at λ > 290 nm.

Irradiation of pure 2,5-dimethylpyridine (**3**) vapor at 254 nm also leads to the formation of three phototransposition products, 2,4-dimethylpyridine (**2**), 3,5-dimethylpyridine (**6**), and 2,3-dimethylpyridine (**1**), in yields of 13.7, 3.7, and 3.5%, respectively. Again, two mechanistic pathways are implicated since the yields of **2** and **6** are either reduced or unaffected by dilution with N$_2$, and neither product is formed upon irradiation of **3** at

(5) All yields reported are absolute yields determined from the number of moles of products formed and the number of moles of reactant consumed.

Table 2. Photolysis Products[a]

4 →	1	5	7	10
-37.0[b]	5.4	1.5	0.4	5.2
-37.0[c]	3.5	0.7	3.7	4.2
-26.2[d]	—	—	2.6	2.6

5 →	1	4	8	9
-64.0[b]	8.1	3.5	1.5	1.4
-89.0[c]	0.7	03	0.4	0.4
-35.8[d]	---	—	—	—

6 →	2	3
-44.8[b]	12.7	14.7
-45.8[c]	10.1	8.8
-0[d]	—	---

[a] Numbers are percent of reactant consumed or the percent yields of products formed after irradiation. [b] Irradiation at 254 nm. [c] Irradiation at 254 nm in the presence of added N_2. [d] Irradiation at $\lambda > 290$ nm.

$\lambda > 290$ nm. At the same time, however, the yield of 2,3-dimethylpyridine (**1**) is enhanced by the addition of N_2 and is the only product formed upon irradiation at $\lambda > 290$ nm.

Irradiation of 2,4-dimethylpyridine (**2**), 2,6-dimethylpyridine (**4**), 3,4-dimethylpyridine (**5**), or 3,5-dimethylpyridine (**6**) resulted in the formation of two transposition products in each case. Furthermore, in each case, the yields of both transposition products are decreased upon irradiation of the reactant in the presence of added N_2 gas and are not formed when the reactant is irradiated at $\lambda > 290$ nm.

Unsymmetrical dimethylpyridines **1**, **2**, **3**, and **5** each also underwent photodemethylation to yield two different mono-methylpyridine derivatives formed by loss of either of the two nonequivalent methyl groups. As expected, 2,6-dimethylpyridine (**4**) provided only one demethylation product, 2-methylpyridine (**7**), formed by loss of either of the two equivalent methyl groups. No demethylation product was detected after irradiation of 3,5-dimethylpyridine (**6**). In the case of 2,6-dimethylpyridine (**4**), a trimethylpyridine (**10**) was also detected as a product.

These results show that irradiation of dimethylpyridine vapors at 254 nm results in the formation of two sets of isomerization

Scheme 3
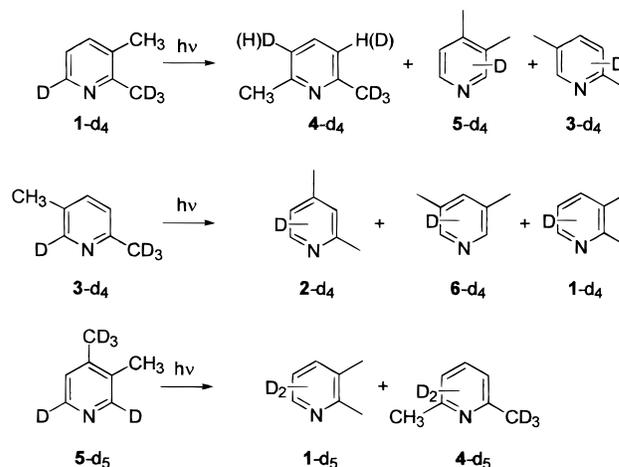
Triad 1   Traid 2

Scheme 4

products. One set, formed in the larger yield, is substantially quenched when the irradiations are carried out in the presence of 15−21 Torr of nitrogen and is not formed when the irradiations are carried out with light of $\lambda > 290$ nm. In contrast, the yields of the second set of products are lower when the reactant is irradiated at 254 nm but are increased by the addition of nitrogen and are the only photoisomerization products observed when the irradiations are carried out with light of $\lambda > 290$ nm.

Based on these major products, the dimethylpyridines can be divided into two triads, each containing three interconverting compounds. Triad 1, shown in Scheme 3, consists of 3,5-di-methylpyridine (**6**), 2,4-dimethylpyridine (**2**), and 2,5-dimethyl-pyridine (**3**), while triad 2 (Scheme 3) consists of 2,6-di-methylpyridine (**4**), 2,3-dimethylpyridine (**1**), and 3,4-dimethyl-pyridine (**5**).

Since irradiation also results in demethylation−methylation reactions, the possibility was considered that these phototrans-positions also occur by way of such a process. Although this explanation seems unlikely in view of the regioselectivity of these reactions, various photochemical crossover experiments were carried out in order to determine if these phototransposition reactions occur via an intermolecular demethylation−methyla-tion pathway.

Irradiation of 6-deuterio-2-trideuteriomethyl-3-methylpyridine (**1**-d_4) vapor at 254 nm gave rise (Scheme 4) to the formation of **4**, **5**, and **3** in yields of 1.6, 0.6, and 0.5%, respectively, which were all shown by mass spectral analysis to be d_4-labeled. This indicates that the transposition reaction occurred by way of an intramolecular process, since if **4**, **5**, and **3** were formed by intermolecular demethylation−methylation reactions the deu-

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Table 3. Crossover Experiments

Scheme 5

Triad 1

in triad 1, 3,5-dimethylpyridine (**6**) can be viewed as having the nitrogen inserted between C-2 and C-6 of the pyridine ring. Because of the symmetry of this molecule, insertion of nitrogen between C-2 and C-3 or between C-5 and C-6 results in the second member of the triad, 2,4-dimethylpyridine (**2**), while insertion of nitrogen between C-3 and C-4 or between C-4 and C-5 will result in the formation of 2,5-dimethylpyridine (**3**), the third member of the triad. Consideration of the members of triad 2 leads to a similar conclusion. Thus, because of the symmetry of 2,6-dimethylpyridine (**4**), insertion of nitrogen either between C-2 and C-3 or between C-5 and C-6 results in 2,3-dimethylpyridine (**1**), the second member of the triad, while insertion of nitrogen either between C-3 and C-4 or between C-4 and C-5 results in 3,4-dimethylpyridine (**5**), the third member of the triad. Thus, because of the symmetry of 3,5-dimethylpyridine (**6**) and 2,6-dimethylpyridine (**4**), each of these two compounds can be converted only into the other two members of their respective triads by a reaction mechanism involving nitrogen insertion within the carbon skeleton of the pyridine molecule.

A mechanism that allows for this selective nitrogen insertion involves electrocyclic ring closure, nitrogen migration around the sides of the cyclopentenyl ring, and rearomatization. Similar mechanisms have previously been employed to explain the phototransposition reaction of both five- and six-membered heteroaromatic compounds,[6] and a similar mechanism has been recently proposed by Pincock et al. to explain the photoisomerization reactions of isomeric cyanotoluenes.[7]

This mechanism for triad 1 is shown in Scheme 5. Thus, electrocyclic ring closure of 3,5-dimethylpyridine (**6**) results in the formation of azabicyclohexenyl species **6a**, shown here as a diradical. This structure is analogous to the bicyclic species originally named prevalene and suggested by Bryce-Smith to be the photochemically generated precursor of benzvalene.[8]

terium content would range from d_1 to d_7. In the case of **4**-d_4, the ring deuterium was determined to be at the C-3 or C-5 position since the ^{1}H NMR spectrum exhibited a doublet at δ 6.9 ($J = 8.4$ Hz), which means that the deuterium cannot be at C-4, since in that case both remaining ring protons would appear as a singlet in the spectrum. The position of the ring deuterium could not be determined in the case of **3**-d_4 or **5**-d_4 due to their low yields.

As shown in Scheme 4, irradiation of 6-deuterio-2-trideuteriomethyl-5-methylpyridine (**3**-d_4) or 2,6-dideuterio-4-trideuteriomethyl-3-methylpridine (**5**-d_5) vapor at 254 nm led to the formation of only d_4 transposition products **2**-d_4 (2.2%), **6**-d_4 (2.8%), and **1**-d_4 (3.8%) or d_5 transposition products **1**-d_5 (4.9%) and **4**-d_5 (2.0%), respectively. In the case of **3**-d_4, no evidence could be detected for the formation of any d_1 or d_7 transposition products, while in the case of **5**-d_5, it was not possible to detect any d_2 or d_8 phototransposition products that would be expected if the transpositions involved intermolecular demethylation−methylation reactions.

Additional crossover experiments were carried out by irradiating the deuterated pyridines shown in Table 3 mixed with equal amounts of the corresponding undeuterated compound. Analysis of the product mixtures by GLC-MS provided no evidence for any crossover products that would implicate intermolecular demethylation−methylation reactions in the phototransposition reactions. Thus, irradiation of equimolar mixtures of **1**-d_4 and **1**-d_0, **2**-d_7 and **2**-d_0, **3**-d_4 and **3**-d_0, **4**-d_6 and **4**-d_0, **5**-d_5 and **5**-d_0, or **6**-d_2 and **6**-d_0 led to the detection of only d_4 and d_0, d_7 and d_0, d_4 and d_0, d_6 and d_0, d_5 and d_0, or d_7 and d_0 phototransposition products, respectively.

An inspection of the isomers in the two triads (Scheme 3) shows that the compounds of each triad differ in the position of nitrogen within the carbon skeleton of the pyridine ring. Thus,

(6) See, for example: Pavlik, J. W. Kurzweil, E. M. *J. Org. Chem.* **1991**, *56*, 6313−6320. Pavlik, J. W.; Tongcharoensirikul, P.; Bird, N. P.; Day, A. C.; Barltrop, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 2292−2300. Pavlik, J. W.; Patten, A. D.; Bolin, D. R.; Bradford, K. C.; Clennan, E. L. *J. Org. Chem.* **1984**, *49*, 4523−4531 and references therein.

(7) MacLeod, P. J.; Pincock, A. L.; Pincock, J. A.; Thompson, K. A. *J. Am. Chem. Soc.* **1998**, *120*, 6443−6450.

(8) Bryce-Smith, D.; Longuet-Higgins, H. C. *J. Chem. Soc., Chem. Commun.* **1966**, 593−594.

Scheme 6
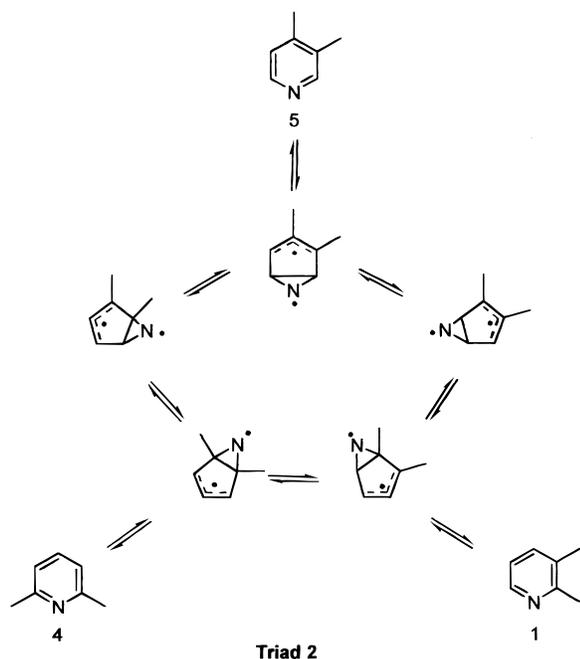
Scheme 7
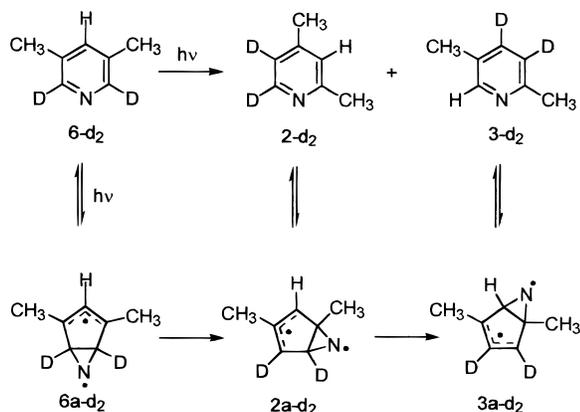
Sigmatropic shift of the nitrogen around the five sides of the cyclopentenyl ring thus allows interconversion of **6a** with azabicyclohexenyl species **2a** and **3a** which, after rearomatization, allows the interconversion of **6** with **2** and **3**, the two other members of the triad. It is not known whether the nitrogen actually migrates around all five sides of the cyclopentenyl ring. Indeed, conversion of **2a** to **6a** can occur by four consecutive migrations in a counterclockwise manner or by a one-step clockwise migration of nitrogen. The analogous mechanism for the interconversion of **1**, **4**, and **5**, the three members of triad 2, is shown in Scheme 6.

Nitrogen migration around the cyclopentenyl ring could occur via an azaniabenzvalene intermediate. Although such species have been implicated in the phototransposition reactions of *N*-methylpyridinium cations,[9] there is no compelling evidence to claim their intermediacy in the present case.

Deuterium labeling studies are consistent with the proposed mechanism. Thus, as shown in Scheme 7, irradiation of 2,6-dideuterio-3,5-dimethylpyridine (**6**-d_2) in the vapor phase at 254 nm yielded products that were identified by GLC and GLC-MS as **2**-d_2 and **3**-d_2. Furthermore, ^{1}H NMR analysis of the

(9) Kaplan, L.; Pavlik, J. W.; Wilzbach, K. E. *J. Am. Chem. Soc.* **1972**, *94*, 3283−3284.

product mixture revealed signals at δ 2.61 (CH$_3$ at C-2 for **2** and **3**) and singlets at δ 6.9 due to a C-3 or a C-5 ring proton and at δ 8.3 due to a hydrogen at C-6 of the pyridine ring. Since the C-3 proton of **3** is known to absorb at δ 7.0 and the C-3 and C-5 protons of **2** resonate at δ 6.9 and 6.8, respectively, the observed singlet at δ 6.9 was assigned to the C-3 proton of **2**, indicating that the two deuterium atoms are at ring positions 5 and 6, as in **2**-d_2. This requires that the observed signal at δ 8.3 must be due to the C-6 proton of **3**, which places the two deuterium atoms at positions 3 and 4, as in **3**-d_2.

The formation of **2**-d_2 and **3**-d_2 from **6**-d_2 is consistent with the mechanism proposed in Scheme 5. Thus, as shown in Scheme 7, **2**-d_2 would be formed by a single sigmatropic shift of nitrogen, converting **6a**-d_2 to **2a**-d_2, followed by rearomatization, while two consecutive shifts of nitrogen followed by rearomatization will result in the formation of **3**-d_2 via **3a**-d_2.

The 2,6-bridging heteroatom migration mechanism accounts for the interconversions of the three members of each triad but predicts that there should be no interconversion of the members of triad 1 with members of triad 2. Experimental results, however, clearly show that the two triads are connected via the interconversion of 2,5-dimethylpyridine (**3**), a member of triad 1, and 2,3-dimethylpyridine (**1**), a member of triad 2. These inter-triad reactions clearly require a different mechanistic interpretation.

The interconversion of **1** and **3** can be viewed as reversible 1,3-shifts of the methyl group from ring position 3 in **1** to ring position 5 in **3**. Although this interconversion can be rationalized by a mechanism involving formation and cleavage of an azaprismane intermediate, such a pathway would allow both 1,2- and 1,3-shifts. Thus, the observed specificity for only a 1,3-shift is inconsistent with an azaprismane mechanism.

A mechanism involving interconverting Dewar pyridine intermediates, however, is consistent with the observed regiospecificity. Scheme 8 shows the products predicted from 2,3-dimethylpyridine (**1**) by the interconverting Dewar pyridine mechanism. Thus, initial 2,5-bridging (Scheme 8a) in the excited state of **1** would result in the formation of Dewar pyridine **1b**. Isomerization via 1,3-shifts of nitrogen or carbon would convert **1b** to the isomeric Dewar pyridines **3b**, **3c**, **5b**, and **5c**, and rearomatization would result in the formation of 2,5-dimethylpyridine (**3**) and 3,4-dimethylpyridine (**5**).

Alternatively, 3,6-bonding in excited **1** (Scheme 8b) would lead to the formation of Dewar pyridine **1c**, which is predicted to isomerize via 1,3-shifts of nitrogen and carbon, followed by rearomatization to 2,3-dimethylpyridine (**1**) and 2,5-dimethylpyridine (**3**).

This mechanistic pathway thus predicts that 2,3-dimethylpyridine (**1**), a member of triad 2, should transpose to 2,5-dimethylpyridine (**3**), a member of triad 1, by either initial 2,5- or 3,6-bonding and accordingly accounts for the observed inter-triad conversion. Interestingly, this mechanism also predicts that **1** should also transpose to 3,4-dimethylpyridine (**5**), which is also a member of triad 2 and which is, therefore, also predicted to result from **1** via the 2,6-bridging heteroatom shift mechanism (Scheme 6) that accounts for the intra-triad interconversions. It is possible, therefore, that **1** and **5** interconvert by both mechanistic pathways, which in the absence of suitable labeling cannot be distinguished.

The inter-triad interconversion of 2,3-dimethylpyridine (**1**) and 2,5-dimethylpyridine (**3**) was enhanced when either isomer was irradiated at 254 nm in the presence of N$_2$ and was the only phototransposition reaction observed when the reactant was irradiated with light of wavelengths greater than 290 nm. This

Scheme 8
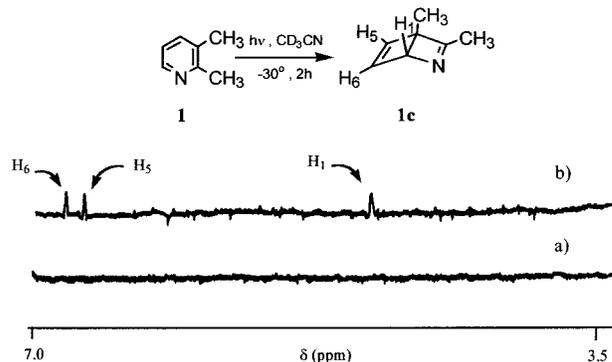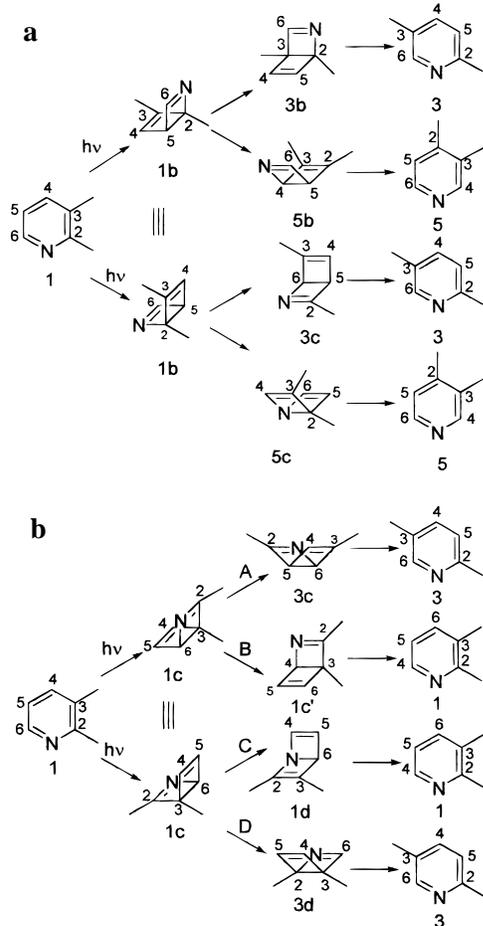
Figure 1. ^{1}H NMR spectrum from δ 3.5 to 7.0 of 2,3-dimethylpyridine (**1**) in CD$_3$CN (a) at -30 °C before irradiation and (b) after irradiation at 254 nm at -30 °C for 2 h.
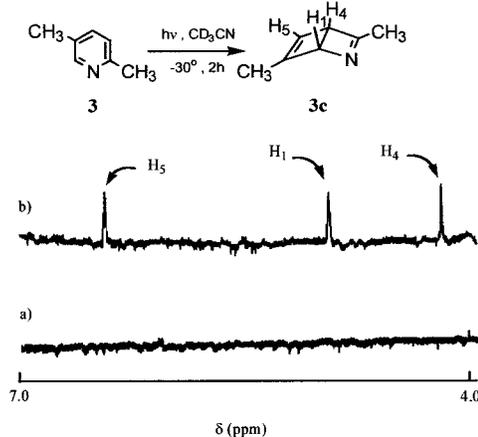
Figure 2. ^{1}H NMR spectrum from δ 3.7 to 7.0 of 2,5-dimethylpyridine (**3**) in CD$_3$CN (a) at -30 °C before irradiation and (b) after irradiation at 254 nm at -30 °C for 2 h.

suggested that the inter-triad reactions might also occur in condensed media at low temperature, where the proposed Dewar pyridine intermediates might be observed. Indeed, Wilzbach and Rausch observed the parent Dewar pyridine by ^{1}H NMR spectroscopy at -25 °C after irradiation of pyridine at 254 nm in butane at -15 °C.[2]

In an attempt to observe the Dewar pyridine isomers of dimethylpyridines **1** and **3**, each isomer was irradiated at 254 nm in CD$_3$CN solution at -30 °C and examined at that temperature by ^{1}H NMR spectroscopy.[10]

Figure 1 shows a portion of the ^{1}H NMR spectrum from δ 3.5 to 7.0 of 2,3-dimethylpyridine (**1**) in CD$_3$CN at -30 °C (a) before irradiation and (b) after the sample had been irradiated at 254 nm at -30 °C for 2 h. The latter spectrum shows the formation of three new low-intensity signals of equal area due to the formation of Dewar pyridine **1c** resulting from 3,6-bonding (Scheme 8b) in excited **1**. Based on the ^{1}H NMR spectrum of the unsubstituted Dewar pyridine,[2] **1c** would be expected to exhibit two signals near δ 6.5 for the C-5 and C-6 vinyl protons and one signal near δ 5.0 due to the C-1 bridgehead proton. The other possible Dewar pyridine isomer **1b** (Scheme 8a), resulting from 2,5-bonding, can be excluded since this isomer would be expected to show a signal at δ 4.0 due to the C-4 bridgehead proton and only one signal in the vinyl region near δ 6.5. All of the observed signals disappeared after the sample was warmed to room temperature. GLC analysis of the resulting solution showed the formation of a very small quantity of 2,5-dimethylpyridine (**3**), the inter-triad product, as

(10) We would like to thank Dr. Pakamas Tongcharoensirikul for technical assistance in recording these low-temperature ^{1}H NMR spectra.

well as the demethylation products, 2-methylpyridine (**7**) and 3-methylpyridine (**8**). Neither 2,6-dimethylpyridine (**4**) nor 3,4-dimethylpyridine (**5**), the intra-triad products which were the major products formed when **1** vapor was irradiated at 254 nm, could be detected in the present solution.

Figure 2 shows a portion of the ^{1}H NMR spectrum from δ 3.7–7.0 of 2,5-dimethylpyridine (**3**) in CD$_3$CN at -30 °C (a) before irradiation and (b) after irradiation of the sample at -30 °C for 2 h. The latter spectrum shows that irradiation results in the formation of three new signals at δ 4.0, 4.8, and 6.4 that are of greater intensity than the signals observed from the irradiation of **1**.

These signals are consistent with Dewar pyridine **3c** (Scheme 8b), since this isomer would be expected to show one-proton signals near δ 4.0 and 5.0 for the C-4 and C-1 bridgehead protons, respectively, and a one-proton signal below δ 6.0 for the C-5 vinyl proton. The other possible Dewar pyridine **3b** can be excluded since this isomer would exhibit signals only in the vinyl region between δ 6.0 and 6.5. These new signals disappeared upon warming of the solution to room temperature. GLC analysis of the resulting solution showed the formation of 2,3-dimethylpyridine (**1**), the inter-triad product, as the major product, much lower yields of 2,4-dimethylpyridine (**2**) and 3,5-dimethylpyridine (**6**), the intra-triad products, and small quantities of 2-methylpyridine (**7**) and 3-methylpyridine (**8**), the demethylation products.

Although both 2,5- and 3,6-bonding were considered in Scheme 8, the ^{1}H NMR spectral data in Figure 1 shows that

Scheme 9

2,3-dimethylpyridine (**1**) undergoes only 3,6-bonding to yield **1c**. 1,3-Sigmatropic shift of nitrogen from C-6 to C4 (path B, Scheme 8b) or of C-4 from C-3 to N (path C, Scheme 8b), followed by rearomatization of **1c′** (an enantiomer of **1c**) or **1d**, results only in the regeneration of **1**, the reactant. Alternatively, **1c** could also rearrange via 1,3-sigmatropic shift of C-2 from C-3 to C-5 (path A, Scheme 8b) or of C-5 from C-6 to C-2 (path D, Scheme 8b), followed by rearomatization of **3c** or **3d**, to result in the 2,5-dimethylpyridine (**3**), the inter-triad product.

^{1}H NMR spectroscopy (Figure 2) also revealed that 2,5-dimethylpyridine (**3**) undergoes 3,6-bonding to form **3c′**. 1,3-Sigmatropic shift of nitrogen from C-6 to C-4 (path A, Scheme 9) would convert **3c′** into its enantiomer **3c**. Rearomatization thus regenerates 2,5-dimethylpyridine (**3**). 1,3-Sigmatropic shift of C-2 from C-3 to C-5 (path B, Scheme 9), followed by rearomatization of **1c′**, results in the formation of 2,3-dimethylpyridine (**1**), the inter-triad product.

The relative intensities of the ^{1}H NMR spectral signals for Dewar pyridines **1c** and **3c**, formed from dimethylpyridines **1** and **3**, indicate that, after the same duration of irradiation, the yield of **3c** from **3** is larger than the yield of **1c** from **1**. This may be due to the greater stability of **3c**, which bears methyl substituents at both the C=C and C=N double bonds as compared to **1c**, which has one of its methyl groups at a bridgehead position. These relative yields of the Dewar pyridines are consistent with the yields of the inter-triad reactions observed. Thus, as shown in Table 1, 2,5-dimethylpyridine (**3**), which in the condensed phase gives Dewar pyridine in the greater yield, is also converted in the gas phase to the inter-triad product 2,3-dimethylpyridine (**1**) in the greater yield. Conversely, 2,3-dimethylpyridine (**1**), which in the condensed phase gives the Dewar pyridine in the lower yield, is also converted in the gas phase to the inter-triad product **3** in the lower yield.

The 0−0 bands for $S_o{\to}S_1$ and $S_o{\to}S_2$ absorptions in pyridine vapor occur at 34 769 and 38 350 cm^{-1}, respectively.[11] This corresponds to Es$_1$ (n,π*) and Es$_2$ (π,π) at 99.4 and 109.7 kcal mol^{-1}, respectively. Methyl substitution in pyridine significantly lowers the S_2 energy level, while the S_1 level is nearly unchanged.[11] The energies of the S_1 (n, π*) and S_2 (π,π*) states in 2,6-dimethylpyridine (**4**), for example, are 100.4 and 105.5 kcal mol^{-1}, and the six dimethylpyridines are expected to have excited-state energies similar to these values.[11] Photochemical excitation of dimethylpyridines with light of 254 nm is thus expected to result in the population of S_2 (π,π*) excited states with excess vibrational energy.

The nonradiative decay properties of pyridine are reported to be similar to those of benzene. Thus, the ϕ_F in both pyridine[11−13] and benzene[14] shows a characteristic dependence on excess vibrational energy in the lowest π,π* excited state.

The sudden decrease in ϕ_F suggests the existence of a decay channel, which has been referred to as "channel three".[15] In benzene, this decay pathway, which originates in a vibrationally excited π,π* state, results in the formation of the ground-state diradical prefulvene, the presumed precursor of benvalene.[16]

Although the analogous meta-bonded valence isomer of pyridine, azabenzvalene, has never been isolated or definitively detected, theoretical calculations predict that the S_2 (π,π*) state of pyridine crosses both the S_1 (n,π*) and S_o states along a concerted pathway, leading to the ground-state azaprefulvene diradical,[17] the suggested intermediate responsible for intra-triad isomerizations (Schemes 5 and 6). Quenching of these intra-triad reactions by added N_2 is consistent with their origin from an excited state possessing excess vibrational energy.

In contrast to the intra-triad reactions, the inter-triad interconversions of 2,3- and 2,5-dimethylpyridines (**1**) and (**3**) are enhanced by the addition of N_2, are the major products observed upon irradiation in condensed media, and are the only photoisomerization products formed upon irradiation with light of wavelength >290 nm. Furthermore, the suggested Dewar pyridine intermediates (Scheme 8) can also be detected upon irradiation of **1** or **3** in the condensed phase at low temperature. Accordingly, these reactions occur from an excited state of lower energy. A number of facts indicate that this lower energy state is the T_1 state of the dimethylpyridine.

In the case of pyridine and methylpyridines, the quantum yield for intersystem crossing is known to increase substantially as the excitation energy is decreased from $S_o{\to}S_2$ (π,π*) absorption to the $S_o{\to}S_1$ (n,π*) region.[18,19] Thus, the net effect of decreasing the excitation energy is to increase the triplet population. Although no evidence has been detected for any triplet state, gas-phase chemistry in pyridine,[20] photolysis of pyridine at 254 nm in an argon matrix has been shown to result in the formation of Dewar pyridine.[21] Furthermore, this reaction was enhanced when the matrix was changed to xenon. This enhancement in xenon indicates strongly that the triplet state of pyridine is involved in the isomerization.[21]

Both experimental[22] and theoretical studies[23] point to the existence of two triplet forms of pyridine with different intrinsic lifetimes, brought about by strong pseudo-Jahn−Teller vibronic coupling of the nearly degenerate $^3\pi$,π* and ^{3}n,π* states. This results in a double minimum in the lowest triplet surface, yielding a vibrationally relaxed triplet state with a boat-shaped geometry which is suggested to be involved in the photochemical generation of Dewar pyridine.[22]

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Although the demethylation−methylation reactions were not studied in detail, it appears that these reactions occur by extrusion or insertion of a CH_2 group from CH_3 or a CD_2 group from CD_3. Thus, irradiation of 6-deuterio-2-trideuteriomethyl-5-methylpyridine (3-d_4) resulted in the formation of 6-deuterio-2-trideuteriomethylpyridine (7-d_4) and 2,6-dideuterio-3-methylpyridine (8-d_2) as a result of the expulsion of CH_2 and CD_2, respectively. Similarly, irradiation of 2,6-dideuterio-4-trideuteriomethyl-3-methylpyridine (2-d_5) led to the formation of 2,6-dideuterio-4-trideuteriomethylpyridine (9-d_5) and 2,4,6-trideuterio-3-methylpyridine (8-d_3), also by expulsion of CH_2 and CD_2, respectively.

Irradiation of an equimolar mixture of 2,6-dimethylpyridine (4-d_0) and 2,6-bis(trideuteriomethyl)pyridine (4-d_6) resulted in intramolecular phototransposition to provide 1-d_0 and 1-d_6 and 5-d_0 and 5-d_6, loss of CH_2 and CD_2 to give 7-d_0 and 7-d_4, respectively, and the formation of a trimethylpyridine as a mixture of 10-d_0, 10-d_2, 10-d_6, and 10-d_8. These would result by insertion of CH_2 into 4-d_0 and 4-d_6 or insertion of CD_2 into 4-d_0 and 4-d_6.

The distribution of the demethylation products as a function of the reaction conditions also suggests that they arise from different excited states. Thus, as shown in Table 1, 2,3-dimethylpyridine (1) undergoes demethylation upon irradiation at 254 nm to yield 2-methylpyridine (7) and 3-methylpyridine (8) in a ratio of 8:1. When the irradiation of 1 is carried out in the presence of N_2, the yield of 7 is quenched while the yield of 8 is enhanced and is the only product observed when 1 is irradiated with light of $\lambda > 290$ nm. Thus, the formation of 2-methylpyridine (7) follows the profile of the intra-triad products 4 and 5, while the profile of the formation of 3-methylpyridine (8) is similar to the formation of the inter-triad product 3.

The situation is not as clear, however, in other cases. Thus, upon irradiation of 2,5-dimethylpyridine (3), the yields of both demethylation products 7 and 8 are enhanced by the addition of N_2, but only 2-methylpyridine (7), the isomer which is less affected by N_2, is observed upon irradiation at $\lambda > 290$ nm. Interestingly, in the case of 2,4-dimethylpyridine (2) and 2,6-dimethylpyridine (4), although irradiation at $\lambda > 290$ nm does not result in any photoisomerization products, demethylation was still observed. In the case of 3,4-dimethylpyridine (5), neither photoisomerization nor demethylation was observed upon irradiation at $\lambda > 290$ nm.

Experimental Section

Instrumentation. ^{1}H NMR spectra were recorded at 200 or 400 MHz on a Brucker FT-NMR system. GLC analyses were performed on a PE-9000 FID instrument equipped with a 15-m × 3-μm Carbowax-20 M bonded phase capillary column at a temperature of 80 °C. Mass spectra were recorded with an HP5970 mass-selective detector interfaced to an HP 5880 capillary gas chromatograph.

Materials. Dimethylpyridines were commercially available and were purified by distillation. Deuterated dimethylpyridines were prepared by heating the dimethylpyridines in D_2O containing potassium carbonate.[24]

Irradiation Procedures. The dimethylpyridine (0.185 g, 1.73 mmol) was placed in a Pyrex tube, attached to the vacuum line, and subjected to three freeze−thaw cycles. The remaining material was then allowed to vaporize into a 3-L quartz reaction flask which had been evacuated overnight. The resulting pressure in the reaction flask ranged from 1.10 Torr for 3,5-dimethylpyridine (6) to 3.62 Torr for 2,6-dimethylpyridine (4). The flask was irradiated in a Rayonet reactor equipped with 16 2537-Å lamps for 3 h.

Irradiation at 254 nm in the Presence of Added N_2. After the dimethylpyridine was allowed to vaporize into the 3-L quartz flask, N_2 gas was added to the flask until the final pressure in the reaction flask was approximately 20 Torr. The reaction flask was then removed from the vacuum line and irradiated as above.

Irradiation of $\lambda > 290$ nm. The 3-L quartz reaction flask containing a low pressure of the dimethylpyridine was removed from the vacuum line and irradiated through a cylindrical Pyrex sleeve in a Rayonet reactor equipped with 16 3000-Å lamps for 24 h.

Analysis Procedure. After irradiation by one of the above procedures, the 3-L reaction flask was attached to the vacuum line, and the volatile contents were recovered by pumping it out through a trap cooled in an acetone−dry ice bath. The contents of the trap were weighed and dissolved in a known volume of diethyl ether for GLC analysis. At 80 °C and a helium flow rate of 10.0 mL/min, the three methylpyridines and the six dimethylpyridines elute in the order 2-methylpyridine (7), 2,6-dimethylpyridine (4), 3-methylpyridine (8), 4-methylpyridine (9), 2,5-dimethylpyridine (3), 2,4-dimethylpyridine (2), 2,3-dimethylpyridine (1), 3,5-dimethylpyridine (6), and 3,4-dimethylpyridine (5), with retentions [relative to 2-methylpyridine (7)] of 1.00, 1.44, 2.32, 2.44, 2.96, 3.24, 3.92, 5.72, and 9.28, respectively.

Quantitative GLC analysis of reactant consumption and product formation was accomplished using calibration curves constructed for each methylpyridine and for each dimethylpyridine by plotting detector responses vs six standards of known concentrations. Correlation coefficients range from 0.976 to 1.000. Quantitative results for reactant consumption and product formation after 3.0 h of irradiation are given in Tables 1 and 2.

Cross-Over Experiments: Irradiation of Pure Deuterated Compounds. 6-Deuterio-2-trideuteriomethyl-3-methylpyridine (1-d_4), 6-deuterio-2-trideuteriomethyl-5-methylpyridine (3-d_4), or 2,6-dideuterio-4-trideuteriomethyl-3-methylpyridine (5-d_5) vapors were irradiated at 254 nm as described for the undeuterated dimethylpyridines. GLC-MS analyses of the resulting volatile products showed that 1-d_4, 3-d_4, and 5-d_4 were converted to d_4, d_4, or d_5 products, respectively, as shown in Scheme 4.

Irradiation of Mixtures of Deuterated and Underterated Dimethylpyridines. Equimolar mixtures of 1-d_4 and 1-d_0, 2-d_7 and 2-d_0, 3-d_4 and 3-d_0, 4-d_6 and 4-d_0, 5-d_5 and 5-d_0, or 6-d_2 and 6-d_0 vapors were irradiated as previously described. GLC-MS analyses of the resulting volatile products led to the results shown in Table 3.

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