The Vapor-Phase Phototransposition Chemistry of Pyridine: Deuterium Labeling Studies

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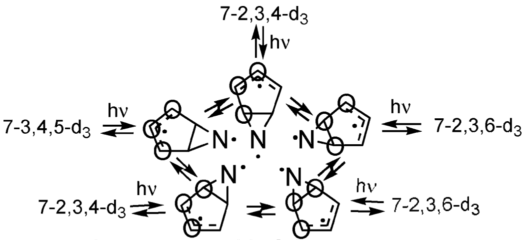
Received December 17, 2007



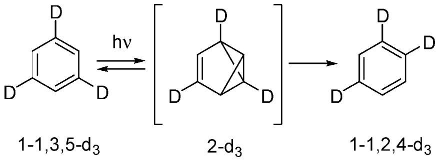
carbon atoms with O bear deuterium

The six isomeric trideuteriopyridines and the three isomeric tetradeuteriopyridines undergo phototransposition upon $S_0 \rightarrow S_2$ (π, π^*) excitation in the vapor phase at 254 nm. On the basis of the products formed, the six trideuteriopyridine isomers can be divided into two triads. Similarly, the three isomeric tetradeuteriopyridines also constitute a triad. Irradiation of any one member of each triad results in the formation of the other two members of that triad. These isomerizations are consistent with a mechanism involving photocyclization, nitrogen migration around the five sides of the cyclopentenyl ring, and rearomatization.

Introduction

It is well-known that benzene undergoes transposition upon irradiation in the vapor phase. Thus, $S_0 \rightarrow S_1$ (π, π^*) excitation of 1,3,5-trideuteriobenzene (**1-1,3,5-*d*$_3$**) vapor at 254 nm has been shown to result in the formation of 1,2,4-trideuteriobenzene,(**1-1,2,4-*d*$_3$**), as shown in Scheme 1. This photoisomerization was suggested to occur via the intermediacy of the valence isomer benzvalene-d_3 (**2-*d*$_3$**).[1]

SCHEME 1



Although irradiation of pyridine at 254 nm in solution at −15 °C was reported to form Dewar pyridine,[2] early studies led to the conclusion that pyridine is unreactive when irradiated in the vapor phase at 254 nm.[3−6] More recent studies, however, have shown that methylpyridines, cyanopyridines, and dimethylpyridines undergo phototransposition upon $S_0 \rightarrow S_2$ (π, π^*) excitation at 254 nm in the vapor phase.[7,8] Product formation and deuterium labeling studies were consistent with the phototransposition mechanism shown in Scheme 2 for the conversion of 2,6-dimethylpyridine (**3**) to 2,3-dimethylpyridine (**6**). This mechanism involves initial photocyclization converting **3** to azaprefulvene biradical[9] **4** followed by nitrogen migration and rearomatization of **5** to provide the observed product **6**. This mechanistic suggestion is consistent with theoretical

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[1] Wilzbach, K. E.; Harkness, A. L.; Kaplan, L. *J. Am. Chem. Soc.* **1968**, *90*, 1116.

[2] (a) Wilzbach, K. E.; Rausch, D. J. *J. Am. Chem. Soc.* **1970**, *92*, 2178. (b) Chapman, O. L.; McIntosh, C. L.; Pacansky, J. *J. Am. Chem. Soc.* **1973**, *95*, 614.

[3] Linnell, R. H.; Noyes, W. A. *J. Am. Chem. Soc*. **1951**, *73*, 3986.

[4] Cundall, R. B.; Fletcher, F. J.; Milne, D. G. *Trans. Faraday Soc.* **1964**, *60*, 1146.

[5] Lemaire, J. *J. Phys. Chem.* **1967**, *71*, 612.

[6] Irradiation at 193, 213.9, or 228.8 nm has been reported to result in ring cleavage. See: (a) Mathias, E.; Heicklen, J. *Mol. Photochem.* **1972**, *4*, 483. (b) Lin, M.-F.; Dyakov, Y. A.; Tseng, C.-M.; Mebel, A. M.; Lin, S. H.; Lee, Y. T.; Ni, C.-K. *J. Chem. Phys.* **2005**, *123*, 054309.

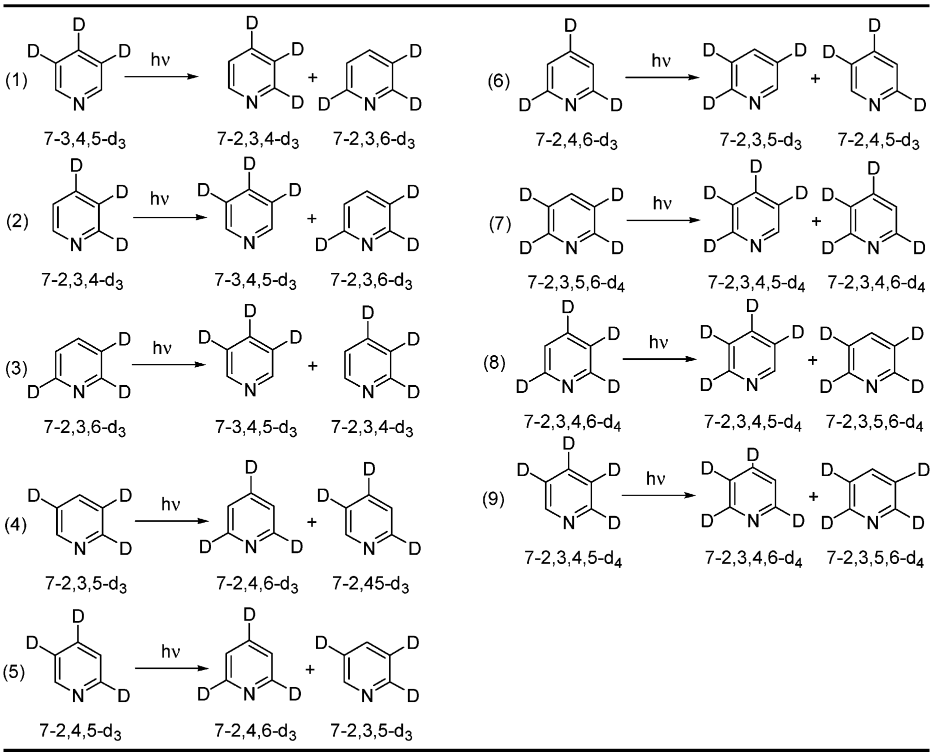
[7] Pavlik, J. W.; Kebede, N.; Thompson, M.; Day, A. C.; Barltrop, J. A. *J. Am. Chem. Soc.* **1999**, *121*, 5666.

[8] Pavlik, J. W.; Laohhasurayotin, S.; Vongnakorn, T. *J. Org. Chem.* **2007**, *72*, 7116.

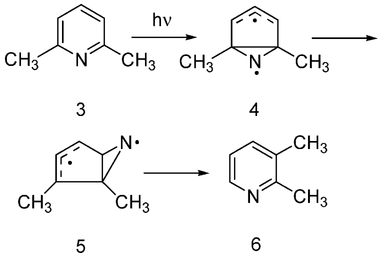
[9] A similar biradical structure called prefulvene was first suggested to be an intermediate in the photoisomerization of benzene. See: Bryce-Smith, D.; Longuet-Higgins, H. C. *J. Chem. Soc., Chem. Commun.* **1966**, *17*, 593.

10.1021/jo7026799 CCC: $40.75

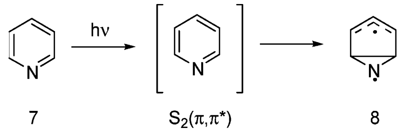
TABLE 1. Phototransposition Products



SCHEME 2



SCHEME 3



calculations that have indicated that the potential energy surfaces of the S_1 (n, π*) and S_2 (π, π*) states of pyridine have crossing points along the isomerization pathway leading to an azaprefulvene biradical.[10−12] In principle, cyclization could occur to yield a biradical in which nitrogen is part of the five-membered ring and the odd-electron is localized on a carbon atom. This is inconsistent with theoretical calculations which indicate that photoexcitation of pyridine leads to ring deformation with nitrogen above the plain of the carbocyclic ring.[10] Furthermore, cyclization followed by carbon migration does not lead to the experimentally observed products. The interconversion of azaprefulvenes has also been theoretically studied. It was suggested that the isomerization on the triplet surface occurs stepwise by way of an azafulvene species.[13]

Additional recent work, using femtosecond transient absorption spectroscopy, has shown that in the condensed phase the S_2 (π, π*) state of pyridine (**7**) passes through a conical intersection to the ground state of the azaprefulvene biradical **8** (Scheme 3).[14]

This species is then reported to revert to pyridine **7** in greater than 2 ns.[14] Considering the studies with mono- and disubstituted pyridines cited above,[7,8] it seems plausible that, during the lifetime of azaprefulvene **8**, nitrogen migration occurs leading to transposition of the ring atoms in pyridine.

In order to further test this mechanistic possibility, in our final investigation of pyridine photochemistry, we have undertaken a study of the synthesis[15] and vapor-phase photochemistry of the six possible isomeric trideuteriopyridines and the three possible isomeric tetradeuteriopyridines. As part of this study, we have recently reported[16] that irradiation of 3,4,5-trideuteriopyridine (**7-3,4,5-*d*$_3$**) in the vapor phase at 254 nm results in the formation of 2,3,4-trideuteriopyridine (**7-2,3,4-*d*$_3$**) and 2,3,6-trideuteriopyridine (**7-2,3,6-*d*$_3$**) as shown in Table 1(1). In this paper, we report the results of our study of the remaining five isomeric trideuteriopyridines and the three isomeric tetradeuteriopyridines.

Results and Discussion

The vapor of each deuterated pyridine, with a total pressure of 1.0−1.5 Torr, was irradiated through quartz at 254 nm. After

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(10) Sobolewski, A. L.; Domke, W. *Chem. Phys. Lett.* **1991**, *180*, 381.

(11) Sobolewski, A. L.; Woywod, C.; Domke, W. *J. Chem. Phys*. **1993**, *98*, 5627.

(12) Zhang, D.; Dian, E. W.-G.; Bernhardt, T.; De Feyter, S.; Roberts, J. D.; Zewail, A. H. *Chem. Phys. Lett*. **1998**, *298*, 129.

(13) Cao, Z.; Zhang, Q.; Peyerimhoff, S. D. *Chem.*−*Eur. J*. **2001**, *7*, 1927.

(14) Chachisvilis, M.; Zewail, A. H. *J. Phys. Chem. A* **1999**, *103*, 7408.

(15) Pavlik, J. W.; Laohhasurayoton, S. *J. Heterocycl. Chem*. **2007**, *44*, 1485.

(16) Pavlik, J. W.; Laohhasurayotin, S. *Tetrahedron Lett.* **2003**, *44*, 8109.

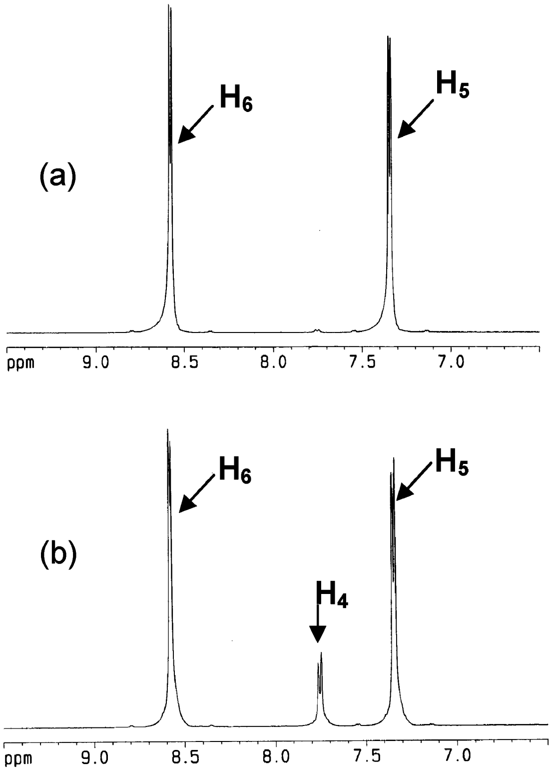

FIGURE 1. ^{1}H NMR spectrum from δ 6.5−9.5 of 2,3,4-trideuteriopyridine (**7-2,3,4-d_3**) in acetone-d_6 (a) before irradiation and (b) after irradiation for 12 h in the vapor phase at 254 nm.

each irradiation, the volatile materials were pumped out of the reaction flask, condensed, and analyzed by ^{1}H NMR spectroscopy. Pyridine products were identified by comparing the observed chemical shifts with the known chemical shifts of authentic deuterated pyridine samples.[15]

Trideuterated Pyridines. The ^{1}H NMR spectrum of 2,3,4-trideuteriopyridine (**7-2,3,4-d_3**) before photolysis in Figure 1a exhibits a doublet ($J = 4.8$ Hz) at δ 8.59 due to the proton at position 6 coupling with the proton at ring position 5.[17] Interestingly, the signal due to the latter proton appears as a doublet of triplets ($J = 4.8$ and 1.0 Hz) at δ 7.34 presumably due to the H5 proton coupling with H6 ($J_{\mathrm{H5,H6}} = 4.8$ Hz) and also with the deuterium at ring position 4 ($J_{\mathrm{H,D}} = 1.0$ Hz).

After 12 h of irradiation, the spectrum in Figure 1b shows the appearance of a new doublet ($J = 7.6$ Hz) at δ 7.76 due to the formation of a product with protons at ring positions 4 and 3 (5). This product must be 2,3,6-trideuteriopyridine (**7-2,3,6-d_3**). Scale expansion of the signal at δ 8.59 reveals that after irradiation a singlet is now superimposed on the doublet of the reactant. Since no other new signals are apparent in the spectrum, this new singlet must be due to a photoproduct with two equivalent protons at H2 and H6 and the second product must be 3,4,5-trideuteriopyridine (**7-3,4,5-d_3**) as shown in Table 1(2).

The ^{1}H NMR spectrum of 2,3,6-trideuteriopyridine (**7-2,3,6-d_3**) is shown in Figure 2a. Before photolysis, the spectrum shows two doublets ($J = 7.6$ Hz) at δ 7.76 and 7.34 for the H4 and H5 ring protons, respectively. After 12 h of irradiation, the spectrum in Figure 2b shows the formation of an intense signal at δ 8.58, where H2 and H6 absorb. Because of its intensity, this new signal must be due to more than one proton. Scale expansion shows that this signal can be resolved into a doublet overlapping with a singlet. Thus, the photoproduct with the doublet at δ 8.58 must have protons at both C6 and C5 and must be 2,3,4-trideuteriopyridine (**7-2,3,4-d_3**). The signal for H5 of this product must be overlapping with the signal for H5 at δ 7.34 for the unconsumed reactant. Scale expansion confirmed this by showing that this signal can be resolved into two overlapping doublets. The doublet with the larger coupling constant ($J \sim 7.6$ Hz) is due to **7-2,3,6-d_3**, while the second doublet with the smaller coupling constant ($J \sim 4.6$ Hz) is due to H5 of the photoproduct **7-2,3,4-d_3**.[17]

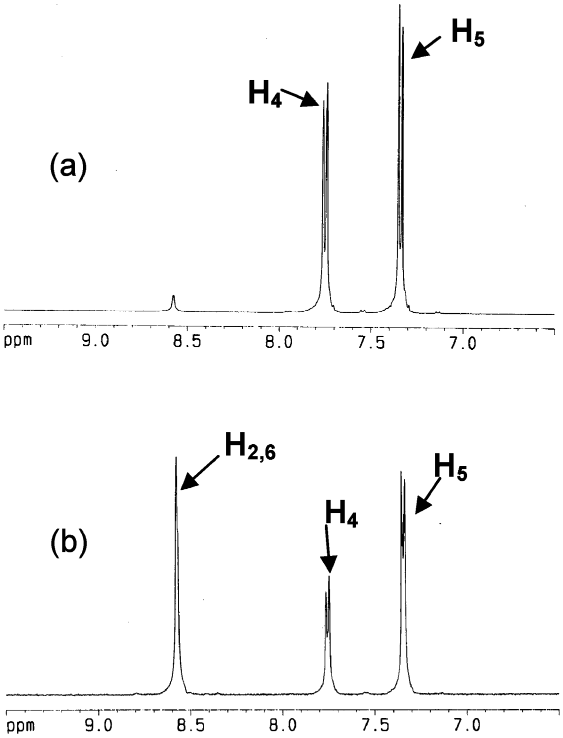

FIGURE 2. ^{1}H NMR spectrum from δ 6.5−9.5 of 2,3,6-trideuteriopyridine (**7-2,3,6-d_3**) in acetone-d_6 (a) before irradiation and (b) after irradiation for 12 h in the vapor phase at 254 nm.

The second photoproduct with the singlet at δ 8.58 must be either **7-3,4,5-d_3** or **7-2,4,5-d_3**. Since scale expansion of the signal at δ 7.34 revealed no evidence for the formation of a singlet which would be required by **7-2,4,5-d_3**, the new singlet at δ 8.58 must be due to two protons and the second photoproduct must be **7-3,4,5-d_3**. The reaction is shown in Table 1(3).

Figure 3a shows two intense singlets at δ 7.75 and 8.60 for H4 and H6, respectively, of 2,3,5-trideuteriopyridine (**7-2,3,5-d_3**). After 12 h of irradiation, the spectrum in Figure 3b shows the formation of a new singlet at δ 7.34, where H3 and H5 protons are known to absorb. The intensity of this signal suggests that it must be due to more than one proton. Considering the relative decrease in the intensity of the H4 signal at δ 7.75 due to the consumption of the reactant, this new signal must be due to the formation of products with three equivalent protons at ring positions 3 and 5. Since all of these protons appear as singlets, and since each photoproduct can have only two protons, the two photoproducts must be **7-2,4,6-d_3** and **7-2,4,5-d_3** as shown in Table 1(4).

The spectrum of 2,4,5-trideuteriopyridine (**7-2,4,5-d_3**) in Figure 4a shows singlets at δ 8.59 and 7.36 due to H6 and H3,

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[17] Castellano, S.; Sun, C.; Kostelnik, R. *J. Chem. Phys.* **1967**, 327.

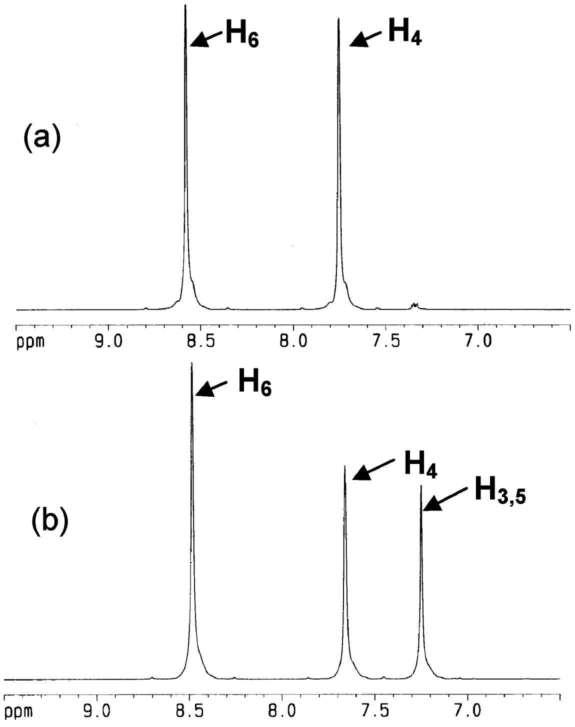


FIGURE 3. ^{1}H NMR spectrum from δ 6.5 to 9.5 of 2,3,5-trideuteriopyridine (**7-2,3,5-*d*$_3$**) in acetone-d_6 (a) before irradiation and (b) after irradiation for 12 h in the vapor phase at 254 nm.

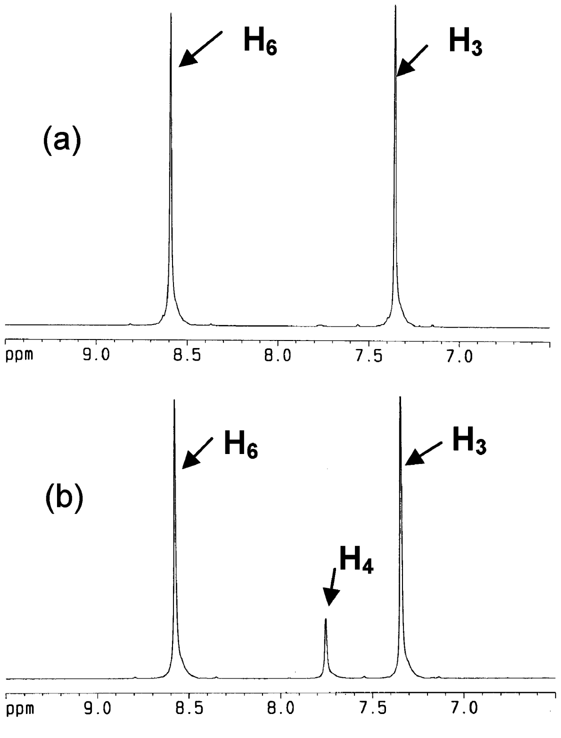


FIGURE 4. ^{1}H NMR spectrum from δ 6.5 to 9.5 of 2,4,5-trideuteriopyridine (**7-2,4,5-*d*$_3$**) in acetone-d_6 (a) before irradiation and (b) after irradiation for 12 h in the vapor phase at 254 nm.

respectively. After irradiation, the spectrum in Figure 4b shows the formation of a new singlet at δ 7.75 due to the formation of a product with a proton at ring position 4. Since this signal is a singlet, and since the product must have three deuterium atoms, the product must be **7-2,3,5-*d*$_3$** [Table 1(5)].

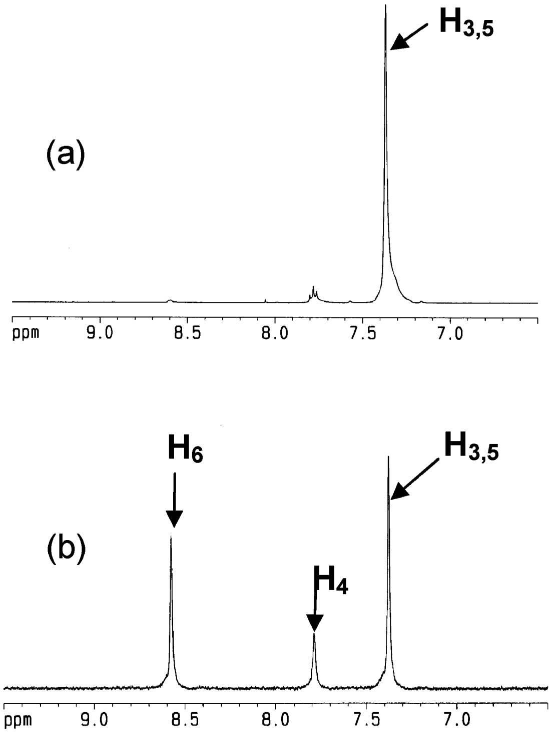


FIGURE 5. ^{1}H NMR spectrum from δ 6.5 to 9.5 of 2,4,6-trideuteriopyridine (**7-2,4,6-*d*$_3$**) in acetone-d_6 (a) before irradiation and (b) after irradiation for 11 h in the vapor phase at 254 nm.

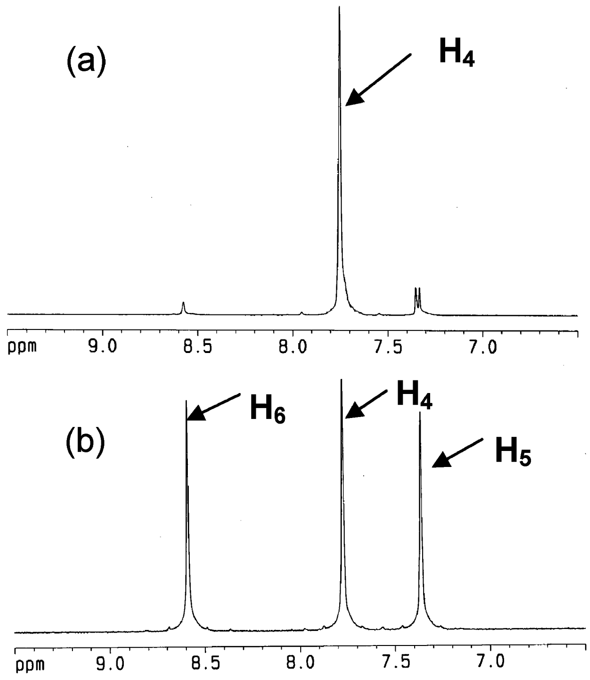


FIGURE 6. ^{1}H NMR spectrum from δ 6.5 to 9.5 of 2,3,5,6-tetradeuteriopyridine (**7-2,3,5,6-*d*$_4$**) in acetone-d_6 (a) before irradiation and (b) after irradiation for 12 h in the vapor phase at 254 nm.

The second product must have protons at ring positions 3(5) and/or 2(6) which all appear as singlets that are overlapping with the signals of **7-2,4,5-*d*$_3$**. Excluding **7-2,4,5-*d*$_3$**, of the six trideuterated pyridines, only **7-2,4,6-*d*$_3$** and **7-3,4,5-*d*$_3$** are possible structures. As seen in Figure 6b, the intensities of the signals at δ 7.35 due to H3(5) and δ 8.60 due to H2(6) remain essentially constant after irradiation. On this basis, **7-3,4,5-d_3** can be eliminated as a product since the formation of **7-2,3,5-d_3** and **7-3,4,5-d_3** would require that the intensity of the signal at δ 8.60 due to H2(6) be much larger than the intensity of the signal at δ 7.35 due to H3(5). Accordingly, the second product must be **7-2,4,6-d_3**. Whereas the formation of **7-2,3,5-d_3** would result in an increase in the intensity of the signal at δ 8.60 due to the H6 proton, the formation of **7-2,4,6-d_3** would result in a 2-fold increase in the intensity of the signal at δ 7.35 due to new protons at both ring positions 3 and 5. Since the intensities at δ 7.35 and 8.60 remain identical, it appears that the ratio of the yields of **7-2,3,5-d_3** and **7-2,4,6-d_3** is 2:1. The photoreaction is summarized in Table 1(5).

Figure 5a shows that the ^{1}H NMR spectrum of 2,4,6-trideuteriopyridine (**7-2,4,6-d_3**) before photolysis exhibits an intense singlet at δ 7.37 due to the equivalent H3 and H5 protons. After 11 h of irradiation, the spectrum in Figure 5b shows a singlet at δ 7.37 due to unconsumed reactant and new singlets at δ 8.58, where H2 and H6 are known to absorb, and at δ 7.79, where the H4 proton absorbs, in an integrated ratio of 2:1. According to the chemical shifts and multiplicities of these signals, one of the photoproducts must have a proton at ring position 4 with deuterium atoms at positions 3 and 5. The third deuterium atom must be at position 2, while the second proton must be at ring position 6. Accordingly, this photoproduct must be 2,3,5-trideuteriopyridine (**7-2,3,5-d_3**).

The second photoproduct must have one proton at ring position 6. According to the spectrum, the second proton cannot be at ring positions 2, 4, or 5. This proton must therefore be at ring position 3, and the product must be 2,4,5-trideuteriopyridine (**7-2,4,5-d_3**). These results are shown in Table 1(6).

Figures 6a, 7a, and 8a show the ^{1}H NMR spectra of 2,3,5,6-tetradeuteriopyridine (**7-2,3,5,6-d_4**), 2,3,4,6-tetradeuteriopyridine (**7-2,3,4,6-d_4**), and 2,3,4,5-tetradeuteriopyridine (**7-2,3,4,5-d_4**), respectively. Each of these spectra show one intense singlet due to the H4, H5, and H6 protons, respectively. Figures 6b, 7b, and 8b show the ^{1}H NMR spectra of each of these three isomers after 12 h of irradiation in the vapor phase.

In addition to the singlet at δ 7.75 due to the H4 proton of **7-2,3,5,6-d_4**, after irradiation, the ^{1}H NMR spectrum in Figure 6b exhibits new singlets at δ 7.34, where H3/5 protons absorb, and a new singlet at δ 8.56, where the H2/6 protons absorb, in an integrated ratio of 1:1. Since each new photoproduct can have only one ring proton, these results show that **7-2,3,5,6-d_4** has phototransposed to a mixture of 2,3,4,5-tetradeuteriopyridine (**7-2,3,4,5-d_4**) and 2,3,4,6-tetradeuteriopyridine (**7-2,3,4,6-d_4**) as shown in Table 1(7).

After irradiation of **7-2,3,4,6-d_4**, the spectrum in Figure 7b shows a singlet at δ 7.36 due to the H5 proton of the reactant and two new singlets at δ 8.58 due to protons at ring positions 2(6) and at δ 7.79 due to a proton at ring position 4 in an integrated ratio of 2:1. The appearance of singlets for protons at ring positions 2 and 4 indicate that the photoisomerization of **7-2,3,4,6-d_4** resulted in the formation of 2,3,4,5-tetradeuteriopyridine (**7-2,3,4,5-d_4**) and 2,3,5,6-tetradeuteriopyridine (**7-2,3,5,6-d_4**) as shown in Table 1(8) in a ratio of 2:1.

The spectrum in Figure 8b shows a singlet at δ 8.60 due to the H6 proton of **7-2,3,4,5-d_4** and new singlets at δ 7.78 and 7.36 due to protons at ring positions 4 and 3(5), respectively, in a ratio of 1:2. These new signals show that **7-2,3,4,5-d_4** has undergone phototransposition leading to the formation of 2,3,5,6-tetradeuteriopyridine (**7-2,3,5,6-d_4**) and 2,3,4,6-tetradeuteriopyridine (**7-2,3,4,6-d_4**) as shown in Table 1(9) in a ratio of 1:2.

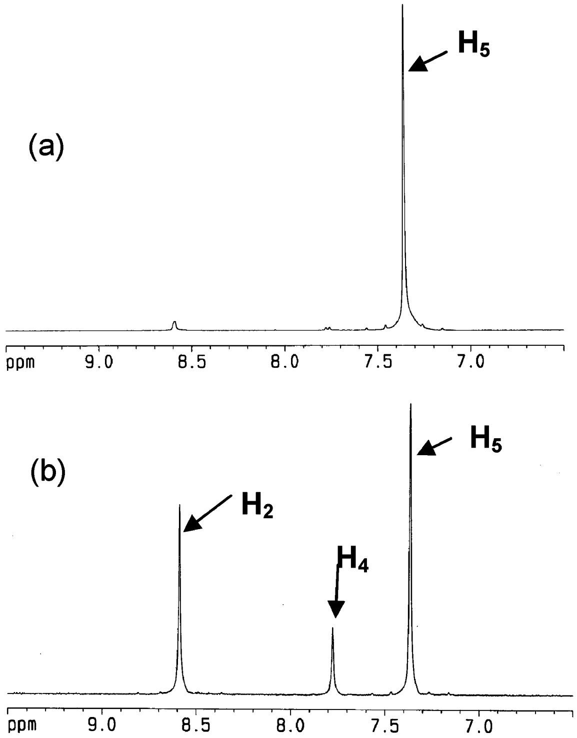


FIGURE 7. ^{1}H NMR spectrum from δ 6.5 to 9.5 of 2,3,4,6-tetradeuteriopyridine (**7-2,3,4,6-d_4**) in acetone-d_6 (a) before irradiation and (b) after irradiation for 12 h in the vapor phase at 254 nm.

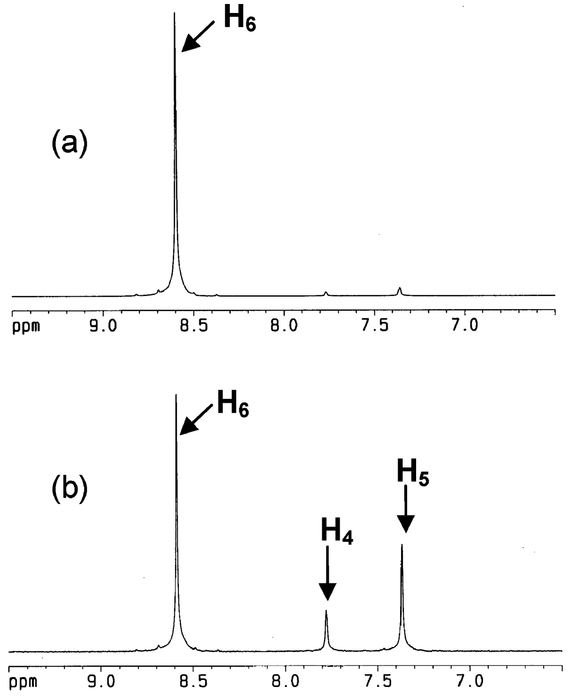
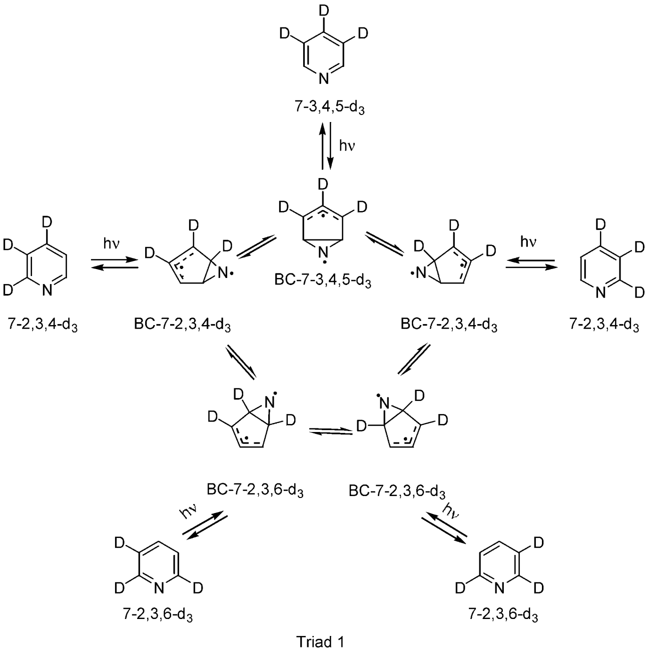


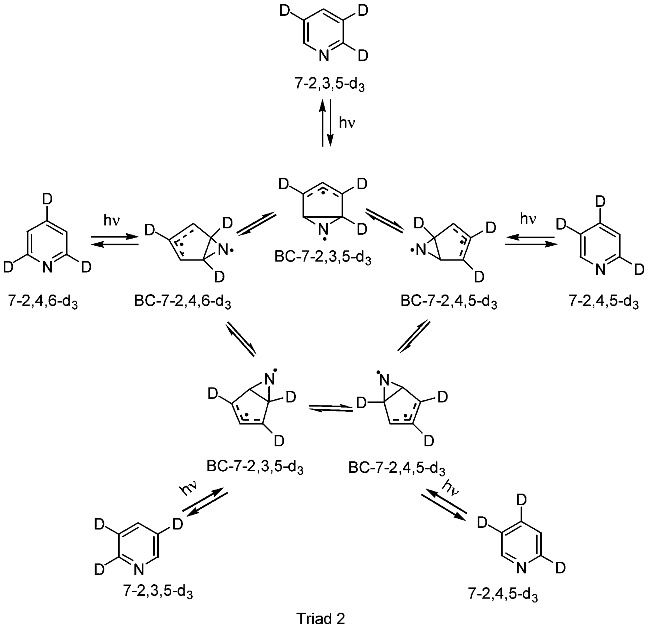
FIGURE 8. ^{1}H NMR spectrum from δ 6.5 to 9.5 of 2,3,4,5-tetradeuteriopyridine (**7-2,3,4,5-d_4**) in acetone-d_6 (a) before irradiation and (b) after irradiation for 12 h in the vapor phase at 254 nm.

The reactions summarized in Table 1 provide unambiguous evidence that pyridine undergoes transposition upon irradiation in the vapor phase at 254 nm. Furthermore, the observed

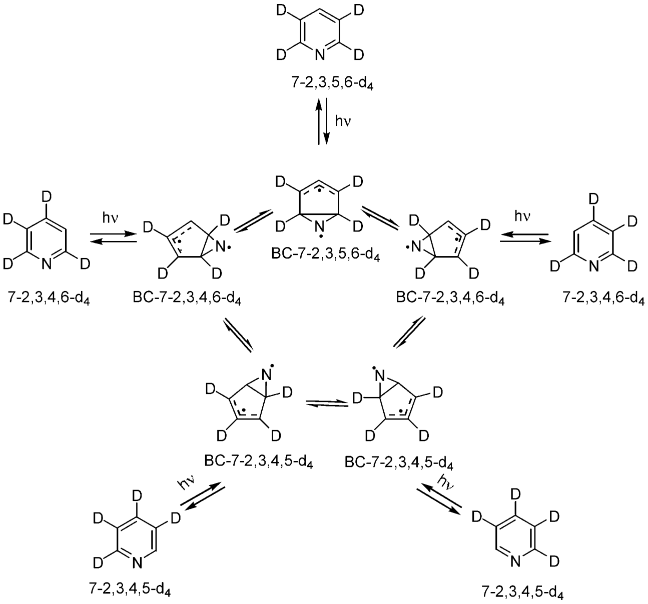
SCHEME 4



SCHEME 5



SCHEME 6



reactions show that the transpositions do not involve random scrambling of the deuterium labels. Instead, the reactions follow a well-defined transposition pattern. Thus, each trideuteriopyridine isomer undergoes phototransposition to yield two isomeric trideuteriopyridine products. On the basis of the observed products, the six trideuteriopyridines can be divided into two triads of compounds. Triad 1 consists of **7-3,4,5-d_3**, **7-2,3,4-d_3**, and **7-2,3,6-d_3**, whereas Triad 2 consists of **7-2,3,5-d_3**, **7-2,4,5-d_3**, and **7-2,4,6-d_3**. Irradiation of any one member of either triad in the vapor phase at 254 nm results in the formation of the other two members of the triad. The photochemistry of these six pyridines each bearing two ring hydrogens is almost identical to the photochemistry of the six isomeric dimethylpyridines.[7] In that case, the six isomers could also be divided into two triads of three interconverting compounds. Although, in the case of the dimethylpyridines, a leakage between the two triads was observed,[7] in the case of the trideuteriopyridines, no interconversion of any member of Triad 1 with any member of Triad 2 was detected.[18]

The equations in Table 1(7−9) also show that each of the three isomeric tetradeuteriopyridines undergoes phototransposition, leading to the other two isomers. These three pyridines, each bearing one ring hydrogen atom, constitute a photochemical triad and are analogous to the monosubstituted methyl and cyanopyridines.[8]

Since the observed transposition patterns of these tri- and tetradeuteriopyridines are identical to the transposition patterns previously observed for mono- and disubstituted pyridines, it is reasonable to assume that all of these compounds react by a common mechanistic pathway. The interconversions within each of the three triads of deuterated pyridines are consistent with the transposition mechanism shown in Schemes 4−6 involving photocyclization, nitrogen migration around the five sides of the cyclopentenyl ring, and rearomatization as previously suggested for the phototransposition reactions of other pyridine derivatives. Although the isomerizations are shown to occur via the intermediacy of azaprefulvene biradicals, the involvement of azabenzvalene valence isomers cannot be excluded. The strength of this mechanism, with or without the intermediacy of azabenzvalene, is that it predicts all of the transpositions observed for a wide variety of pyridine derivatives and does not suggest any other transpositions that were not observed. It should also be emphasized that the well-defined deuterium transpositions shown in Table 1 cannot be rationalized by an alternative mechanism involving Dewar pyridine intermediates. Transpositions via Dewar pyridine intermediates would lead to a substantially different set of deuterated pyridine isomers.[19]

The azaprefulvene mechanism not only predicts the correct products but also predicts the product ratios. The mechanism

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[18] In the present study, since product mixtures could not be analyzed by glpc, small amounts of leakage products would be difficult to detect.

[19] Pyridine phototranspositions were originally suggested to occur via Dewar pyridine intermediates. See: Caplain, S.; Lablache-Combier, A. *J. Chem. Soc., Chem. Commun.* **1969**, 1247. Subsequent work showed that Dewar pyridines are only minor intermediates in these reactions. See ref 7.

in Scheme 4, for example, shows that 3,4,5-trideuteriopyridine (**7-3,4,5-d_3**) can phototranspose via two identical one N-migration pathways leading to **7-2,3,4-d_3** or by the two identical two N-migration pathways leading to **7-2,3,6-d_3**. The observed product ratio of 1:1 is consistent with this mechanistic pathway. Inspection of Scheme 5 shows that, within Triad 2, whereas there are four pathways by which **7-2,4,5-d_3** can transpose to **7-2,3,5-d_3**, there are only two pathways by which it can isomerizes to **7-2,4,6-d_3**, indicating that the two products should be formed in a ratio of 2:1. A similar analysis indicates that **7-2,4,6-d_3** is expected to transpose to **7-2,3,5-d_3** and **7-2,4,5-d_3** in a ratio of 1:1. In both cases, these were the ratios that were experimentally observed. Finally, whereas the mechanism shown in Scheme 6 predicts that **7-2,3,5,6-d_4** should transpose to a 1:1 mixture of **7-2,3,4,5-d_4** and **7-2,3,4,6-d_4**, it also predicts that **7-2,3,4,6-d_4** should isomerize to **7-2,3,4,5-d_4** and **7-2,3,5,6-d_4** and that **7-2,3,4,5-d_4** should be converted to **7-2,3,4,6-d_4** and **7-2,3,5,6-d_4** in ratios of 2:1 and 1:2, respectively. These are the ratios that were experimentally observed.

Conclusion

Irradiation of tri- and tetradeuteriopyridines in the vapor phase at 254 nm leads to phototransposition of the ring atoms in reactions that are analogous to the phototransposition reactions of mono- and disubstituted pyridine derivatives previously reported. These reactions of deuterated pyridines are also analogous to the well-known phototransposition of 1,3,5-trideuteriobenzene.

Experimental Section

Instrumentation. ^{1}H NMR spectra were recorded in acetone-d_6 at 400 MHz on a FT-NMR system.

Materials. Tri- and tetradeuteriopyridines were prepared by procedures described elsewhere.[15]

Irradiation Procedure. The deuteriopyridine 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 that had been evacuated overnight. The resulting pressure in the reaction flask ranged from 1.0 to 1.5 Torr. The flask was irradiated in a Rayonet reactor equipped with 16 2537 Å lamps. The mass of reactants and products recovered are tabulated in Table 2.

TABLE 2. Mass of Reactants and Recovered Products

reactant	mass of reactant (mg)	mass of products (mg)
7-3,4,5-d_3	20	3
7-2,4,6-d_3	20	5
7-2,3,6-d_3	14	10
7-2,3,4-d_3	20	19
7-2,3,5-d_3	20	19
7-2,4,5-d_3	25	21
7-2,3,4,5-d_4	20	10
7-2,3,4,6-d_4	20	7
7-2,3,5,6-d_4	20	8

Analysis Procedure. After irradiation by the above procedure, 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 acetone-d_6 for ^{1}H NMR analysis. Products were identified by comparison of the observed chemical shifts with the ^{1}H NMR data of the known tri- and tetradeuteriopyridines given in ref 15.

Irradiations were also accompanied by the formation of small amounts of nonvolatile polymeric material on the walls of the reaction flask and are partially responsible for the low mass balances observed in some of the reactions. The substantial volatility of the deuteriopyridines also accounted for some of the observed material loss.

Supporting Information Available: Copies of the ^{1}H and ^{13}C NMR spectra of all tri- and tetradeuteriopyridines and the scale expansions referred to in the paper are available. This material is available free of charge via the Internet at http://pubs.acs.org.

JO7026799