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The photochemistry of 3,4,5-trideuteriopyridine

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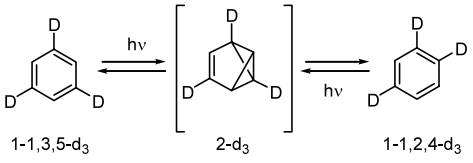
Abstract—Irradiation of 3,4,5-trideuteriopyridine at 254 nm in the vapor phase results in the formation of a mixture of 2,3,4-trideuteriopyridine and 2,3,6-trideuteriopyridine. The formation of these products is consistent with a photoisomerization mechanism involving equilibrating azaprefulvene intermediates. This is the first direct evidence that pyridine vapor undergoes photoisomerization resulting in transposition of the pyridine ring atoms.

It is well-known that benzene in the vapor phase undergoes phototransposition upon $S_0 \rightarrow S_1$ (π,π^*) excitation at 254 nm. Thus, irradiation of 1,3,5-trideuteriobenzene **1**-1,3,5-d_3 vapor at 254 nm was shown to result in the formation of 1,2,4-trideuteriobenzene, **1**-1,2,4-d_3 as shown in Scheme 1.[1]

This phototransposition was considered to occur via the formation and isomerization of the valence isomer, benzvalene **2**-d_3. Although irradiation of pyridine in butane solution at −15°C was found to lead to Dewar–pyridine,[2] early studies led to the conclusion that pyridine vapor is unreactive when irradiated at 254 nm.[3–5]

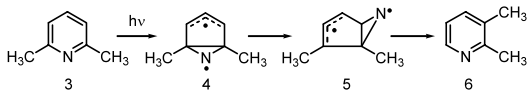
More recent studies have shown, however, that dimethylpyridines undergo phototransposition upon $S_0 \rightarrow S_2$ (π,π^*) excitation at 254 nm in the vapor phase.[6] Product formation and deuterium labeling studies were consistent with the phototransposition mechanism shown in Scheme 2 involving electrocyclic ring closure leading to an azaprefulvene species **4**, presumed to be a diradical, followed by nitrogen migration and rearomatization of **5** as illustrated for the transposition of 2,6-dimethylpyridine **3** to 2,3-dimethylpyridine **6**. In contrast, four of the six dimethylpyridine isomers do not transpose upon $S_0 \rightarrow S_1$ (n,π^*) excitation at λ>290 nm.[7]



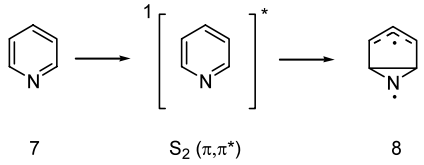
Scheme 1.

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

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



Scheme 2.



Scheme 3.

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We now report that irradiation of 3,4,5-trideuteriopyridine **7**-3,4,5-d_3 in the vapor phase at 254 nm results in deuterium scrambling that is consistent with the formation and isomerization of an azaprefulvene intermediate.

In these studies the trideuterated pyridine **7**-3,4,5-d_3[9] was allowed to vaporize into an evacuated 3 l quartz vessel to a total pressure of 1.5 Torr. The vessel was irradiated at 254 nm in a Rayonet Photochemical Reactor equipped with 16 low pressure Hg lamps. After the appropriate irradiation time the resulting vapor was pumped out of the reaction vessel and condensed in an acetone–dry ice trap. The condensate was dissolved in acetone-d_6 and examined by ^{1}H NMR spectroscopy.

Figure 1a shows that the ^{1}H NMR spectrum of 3,4,5-trideuteriopyridine **7**-3,4,5-d_3 before irradiation exhibits only a singlet at δ 8.6 due to the equivalent H2 and H6 protons.

After irradiation the spectrum in Figure 1b shows that a new signal has appeared as a doublet at δ 7.75, where H4 of pyridine absorbs, and a multiplet at δ 7.35 where the H 3,5 protons of pyridine are observed. These results are consistent with the formation of a mixture of 2,3,4-trideuteriopyridine **7**-2,3,4-d_3 and 2,3,6-trideuteriopyridine **7**-2,3,6-d_3 (Scheme 4).

The ^{1}H NMR spectrum of such a mixture would exhibit a doublet for the H4 proton of **7**-2,3,6-d_3 and

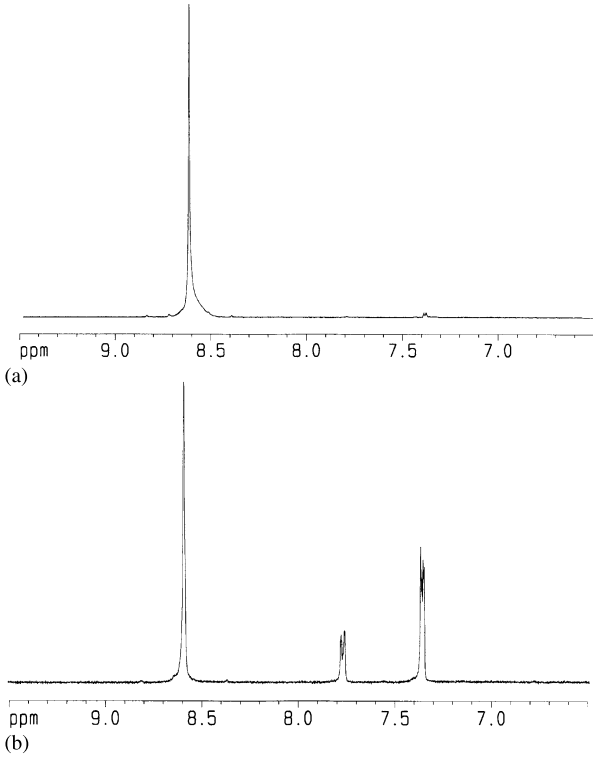
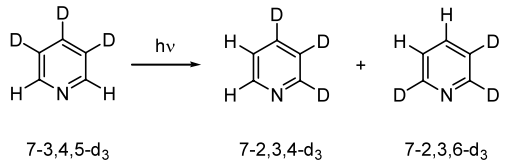
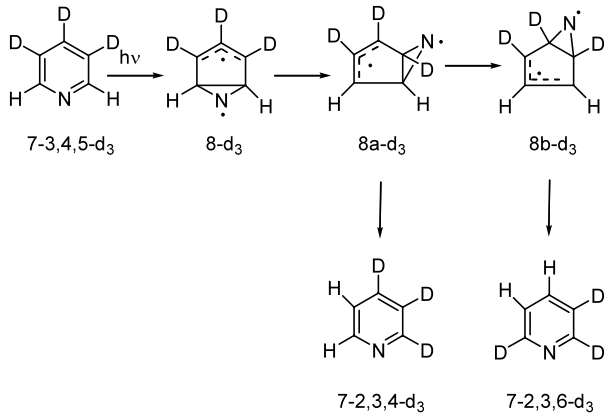


Figure 1. (a) ^{1}H NMR spectrum of 3,4,5-trideuteriopyridine before irradiation. (b) ^{1}H NMR spectrum of 3,4,5-trideuteriopyridine after irradiation.



Scheme 4.



Scheme 5.

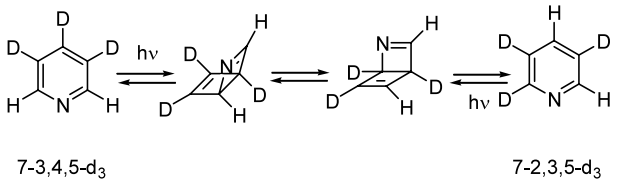
two overlapping doublets for the H3,5 protons of **7**-2,3,4-d_3 and **7**-2,3,6-d_3. The signal for the H6 proton of **7**-2,3,4-d_3 is obscured by the signal for the H2,6 protons of the reactant. Furthermore, as expected for an equimolar mixture of **7**-2,3,4-d_3 and **7**-2,3,6-d_3, the signals for the H3,5 and H4 protons are observed in Figure 1b in an integrated ratio of approximately 2:1.

The mass spectrum of **7**-3,4,5-d_3 exhibited a molecular ion as the base peak at m/z 82 with smaller signals at m/z 81(12.46% of M^+) and 83 (9.37% of M^+). Furthermore, the ratio of the 81:83 peaks after irradiation (1.32±0.001) was the same as before irradiation (1.33± 0.01). This indicates that there has been no change in the isotropic distribution and that the transposition does not involve bimolecular H–D exchange reactions.

These deuterium scrambling results are consistent with the mechanistic pathway shown in Scheme 5. Thus, excitation of 3,4,5-trideuteriopyridine **7**-3,4,5-d_3 at 254 nm [$S_{2(0,0)}$ for pyridine = 260.7 nm] leads to the formation of pyridine molecules in the S_2 (π,π^*) singlet state which evolve to the ground state of azaprefulvene **8**-d_3.

Two successive [1,3] sigmatropic shifts of nitrogen would be expected to yield an equilibrating mixture of azaprefulvenes **8a**-d_3 and **8b**-d_3.[10] Rearomatization of this mixture would then result in the formation of the observed 1:1 mixture of **7**-2,3,4-d_3 and **7**-2,3,6-d_3.

The observed deuterium scrambling is not consistent with phototransposition via interconverting Dewar–pyridines. Such a mechanism would lead to the formation of **7**-2,3,5-d_3 and the observation of a singlet for H4 in the ^{1}H NMR spectra (Scheme 6).



Scheme 6.

These results are the first direct demonstration that pyridine vapor is not inert to irradiation at 254 nm but rather undergoes phototransposition via interconverting azaprefulvene intermediates resulting in interchange of the pyridine ring positions.

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10. Although it is plausible that azaniabenzvalenes are intermediates in the interconversion of the azaprefulvenes **8**-d_3, **8a**-d_3, and **8b**-d_3, we see no compelling evidence to suggest their involvement.