for $C_{14}H_{20}O$ [(*Z*)-1-(4-methylphenyl)-5-hepten-1-ol]: C, 82.30; H, 9.87. Found: C, 82.19; H, 10.03. Calcd for $C_{13}H_{18}O$ [(*Z*)-1-phenyl-5-hepten-1-ol]]: C, 82.06; H, 9.54. Found: C, 81.87; H, 9.79. Calcd for $C_{13}H_{17}OBr$ [(*Z*)-1-(4-bromophenyl)-5-hepten-1-ol]: C, 58.00; H, 6.37. Found: C, 58.26; H, 6.05. Calcd for $C_{13}H_{17}OBr$ [(*Z*)-1-(3-bromophenyl)-5-hepten-1-ol]: C, 58.00; H, 6.37. Found: C, 57.83; H, 6.26.

Solvolysis rates were followed as described previously.[2] The reported values are the mean of three to five independent measurements. In all cases the first-order rate law was obeyed up to at least 80% reaction completion. Rate constants were calculated by means of a nonlinear least-squares program.

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Registry No. **2U** (Y = *p*-OCH_3), 71434-71-4; **2U** (Y = *p*-CH_3), 71434-72-5; **2U** (Y = H), 71434-73-6; **2U** (Y = *p*-Br), 71434-74-7; **2U** (Y = *m*-Br), 71434-75-8; (*E*)-**3U** (Y = *p*-OCH_3), 85662-56-2; (*E*)-**3U** (Y = *p*-CH_3), 85662-57-3; (*E*)-**3U** (Y = H), 85662-58-4; (*E*)-**3U** (Y = *p*-Br), 85662-59-5; (*E*)-**3U** (Y = *m*-Br), 85662-60-8; (*Z*)-**3U** (Y = *p*-OCH_3), 85662-61-9; (*Z*)-**3U** (Y = *p*-CH_3), 85662-62-0; (*Z*)-**3U** (Y = H), 85662-63-1; (*Z*)-**3U** (Y = *p*-Br), 85662-64-2; (*Z*)-**3U** (Y = *m*-Br), 85662-65-3; **4U** (Y = *p*-OCH_3), 71434-50-9; **4U** (Y = *p*-CH_3), 71434-51-0; **4U** (Y = H), 71434-52-1; **4U** (Y = *p*-Br), 71434-53-2; **4U** (Y = *m*-Br), 71434-54-3; (*Z*)-1-(4-methoxyphenyl)-5-hepten-1-ol, 85662-66-4; (*Z*)-1-(4-methylphenyl)-5-hepten-1-ol, 85662-67-5; (*Z*)-1-phenyl-5-hepten-1-ol, 85662-68-6; (*Z*)-1-(4-bromophenyl)-5-hepten-1-ol, 85662-69-7; (*Z*)-1-(3-bromophenyl)-5-hepten-1-ol, 85662-70-0.

Solvent Isotope Effects on Equilibria of Mono- and Dihydration of Neutral Pteridine

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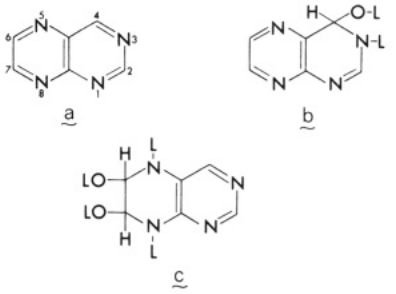
Reversible covalent hydration of C=N bonds has been observed in a number of heterocyclic compounds, of which unsubstituted pteridine is a prototype.[1] In a process that may resemble a partial reaction in substrate hydrolysis, adenosine deaminase catalyzes the stereospecific hydration of pteridine (Chart I, a) at the 3,4-position.[2] The product (Chart I, b) is a strong inhibitor.[3] Addition of D_2O to carbonyl compounds is known to proceed with an equilibrium constant substantially more favorable than that for addition of water,[4] and it seemed possible that fractionation factors might be useful in investigating interactions of pteridine with enzymes. In a thorough kinetic study of the nonenzymatic hydration of pteridine, Pocker et al.[5] reported results in which no substantial solvent isotope effect on the equilibrium of monohydration of pteridine was evident at pH values at and above neutrality. Reinvestigating this reaction, we have confirmed that the solvent isotope effect on the monohydration of pteridine is close to unity. We find in addition that pteridine *di*hydrate[6] (Chart I, c) is formed in neutral solution more slowly than the monohydrate. The dihydrate had been believed to be formed only as the cation in acid solution.[6]

Chart I



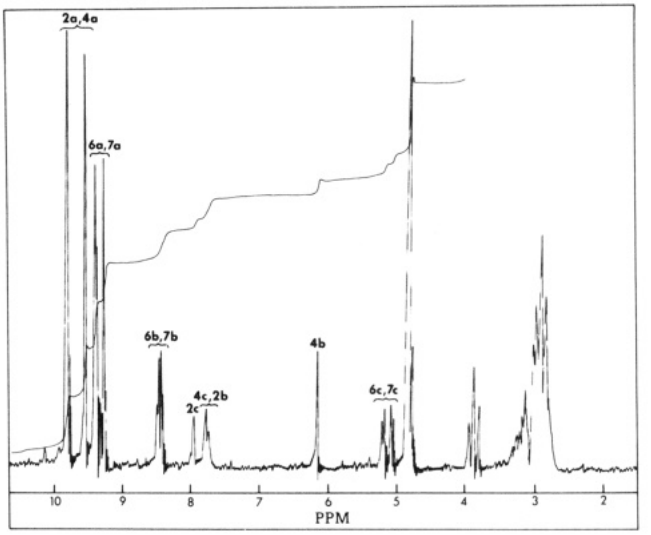


Figure 1. NMR spectrum of pteridine incubated in D_2O (0.17 M Hepes, pD = 8.2) at 34.2 °C for 8 h. The numbers indicate assignments of protons to the ring positions indicated Chart I, a–c. L refers to protium or deuterium.

Like monohydration, the equilibrium of dihydration appears to be almost completely insensitive to the replacement of water by D_2O.

Results and Discussion

The 90-MHz proton NMR spectrum of pteridine in buffered D_2O, after having been allowed to stand at 34.2 °C for 8 h, is shown in Figure 1. A similar spectrum was generated when pteridine (0.07 M) was allowed to act as its own buffer and incubated in D_2O, in which case the pD (pH meter reading + 0.4) was 7.7 immediately after the pteridine was dissolved, and gradually rose during the course of the experiment to 8.3. Thus the buffer (and relatively highly concentration of pteridine) is not responsible for the differences between the NMR spectrum in Figure 1 and those reported by Albert et al.[6] The earlier observations were evidently made at lower temperatures and/or shorter times than the present ones, as only resonances for the monohydrate and free pteridine appeared. A relatively high concentration of pteridine was used to obtain the data in Figure 1, because it was found that similar measurements could be made in H_2O with some precision at 0.7 M, allowing the determination of an approximate solvent isotope effect on the equilibrium constant for formation of the dihydrate. All of the resonances observed in D_2O were also observed in H_2O except for the dihydrate pair of doublets at 5.1–5.3 ppm. After incubation of pteridine for about 12 h in H_2O (or 30 h in D_2O) at 34.2 °C, more signals began to appear in the NMR spectrum. We were unable to assign these late resonances, as they overlapped considerably with the dihydrate and monohydrate ones; however, they appeared at such a rate as to require only minor corrections of the integrated in-

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tensities for the unhydrated, monohydrated, and dihydrated forms at apparent equilibrium.

Peaks for the monohydrate reached half their final heights at approximately 30 min in D_2O and 5 min in H_2O. Peaks for the dihydrate reached half their final heights after approximately 110 min in D_2O and 80 min in H_2O. After 1100 minutes in D_2O, the observed equilibrium constant for formation of the monohydrate (K_{eq} = (monohydrate)/(free pteridine)) was 0.30 ± 0.03, and the observed equilibrium constant for formation of the dihydrate (K_{eq} = (pteridine dihydrate)/(free pteridine)) was 0.22 ± 0.02. After 800 min in H_2O, the observed equilibrium constant for formation of the monohydrate was 0.29 ± 0.03, and the observed equilibrium constant for formation of the dihydrate was 0.23 ± 0.02. Thus the solvent isotope effects (K_{H_2O}/K_{D_2O}) were 0.97 ± 0.14 for the monohydrate and 1.0 ± 0.13 for the dihydrate. This value for formation of the monohydrate is consistent with the data reported by Pocker et al.,[5] who used UV spectrophotometry to study the kinetics and equilibria of formation of pteridine monohydrate. These investigators reported infinity point drifts in their runs, for which appropriate correction was made.

These near-unit solvent isotope effects on formation of both the mono- and the dihydrate are of special interest in view of the reported isotopic fractionation factors for *gem*-diol protons. These values averaged 1.25 per proton.[4] If the two hemiaminal protons in pteridine monohydrate were to exhibit this fractionation factor, the expected solvent isotope effect (K_{H_2O}/K_{D_2O}) would be 0.64. The four hemiaminal protons in pteridine dihydrate would result in an expected solvent isotope effect (K_{H_2O}/K_{D_2O}) of 0.41. Evidently the force constants acting on the hemiaminal protons are substantially different from those acting on *gem*-diol protons.

Experimental Section

Pteridine was prepared as described by Albert et al.[7] and was twice sublimed before use. The material gave no detectable NMR signals other than those characteristic of unhydrated pteridine[6] when spectra where taken in $CDCl_3$ or in D_2O before hydrate signals appeared. All spectra were measured with a Varian EM390 NMR spectrometer with a probe temperature of 34.2 °C. A H_2O solution of sodium 3-(trimethylsilyl)propanesulfonate in H_2O was used as an external shift standard.

Buffer solutions in H_2O and D_2O of the nonnucleophilic buffer *N*-(2-hydroxyethyl)piperazine-*N*′-2-ethanesulfonic acid (Hepes) (Sigma Chemical Co.) were prepared from a single solid mixture of the acidic and basic (Na^+ salt) components of the buffer in order to preserve the same buffer ratio. Equilibrium constants were calculated from the integrated peak intensities by using the assignments indicated in Figure 1. The standard error observed in measurement of the integrals within a run was approximately 7% while interrun error was 10%. A Model 501 Orion pH meter was used to measure pH or pD values (pD = meter reading + 0.4).[8] The pH or pD varied by about 0.05 unit during the course of each run when Hepes buffer, 0.17 M, was used.

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Registry No. a, 91-18-9; b (L = D), 85649-64-5; c (L = D), 14130-91-7; deuterium oxide, 7789-20-0; deuterium, 7782-39-0.

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Photochemistry of Diaryl Ketones: A New Photocyclization Reaction

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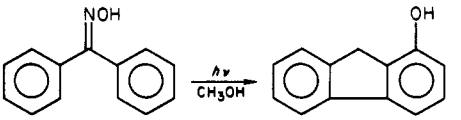
The photochemistry of oximes of aldehyde and ketones has been extensively studied. The reactions these systems undergo in the excited states are of many types,[1-6] e.g., syn–anti isomerization, photo-Beckmann rearrangement, regeneration of the parent ketone through an oxaziridine intermediate, and the formation of the iminyl radicals. However, our experience with benzophenone oxime[7] has been entirely different, and herein we report the results of an investigation on the photochemistry of diaryl keto oximes.

Results and Discussion

Benzophenone oxime in methanol (0.02 M) on photolysis (quartz filter) underwent a series of reactions involving regiospecific hydroxylation, cyclization of proximate phenyl groups, and Wolff–Kishner reduction, leading to 1-hydroxyfluorene in 34% yield. Its acetyl derivative showed mp 90 °C lit.[8] mp 90–91.5 °C). Structure 1 was



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further supported by NMR and mass spectra and elemental analysis. This is the first such reported reaction in the study of oximes. At this stage the following questions arose: (1) Is the photocyclization that of benzophenone oxime or is some other photoproduct undergoing a secondary reaction? (2) What is the effect of varying the solvent system on the reaction course? (3) What possible mechanisms for hydroxylation and what is the source of the hydrogens at C-9 of the fluorene nucleus? (4) What is the effect of oxygen and is the reaction caused by some impurities present in the solvents?

When benzophenone oxime along with benzophenone (0.1 M) was photolyzed under exactly the same conditions (except Pyrex filter), the yield of 1-hydroxyfluorene increased to 64% (see Table I). When other oximes, 2-methyl-, 3-methyl-, and 4-methylbenzophenone oximes, were photolyzed separately with benzophenone under the same conditions, the major product (55–75%) obtained in all those cases was 1-hydroxyfluorene and not the methyl-substituted fluorene.

Photolysis of a solution containing both benzophenone oxime and 4-methylbenzophenone gave a mixture of methyl-substituted hydroxyfluorenes **2** and **3**(15%) along with traces of 1-hydroxyfluorene. However, when a solu-

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