ray structural[9] and combustion data[10] make such possibilities, except in a dynamic sense or in an excited state, both structurally and energetically unlikely. A similar instance of this same difficulty has been seen in the empirical application of the usual Hückel $(4n + 2)$ aromatic rules to the end products of the metallotetraphenylporphin type monocations under electron impact in mass spectroscopy,[11] where the phenyl π electrons must be added to those of the porphin ring to make simple sense of the observed data.

These empirical correlations therefore all suggest some interesting problems either with the behavior of porphyrin structures or, perhaps, with the conventional interpretation of resonance phenomena and parameters. In particular, they suggest that the usual inferences drawn from Hammett parameter correlations may still be susceptible to alternative explanations. If so, a continued study of such phenomena could considerably deepen our understanding of electronic effects in molecular structures.

They also demonstrate the utility of porphyrins in discovering and exploring structural relationships. Thus the above data can be combined to demonstrate a relationship between a relative spectral shift (a molecular property parameter) and a relative specific reaction rate (a reactivity parameter).

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Radiation Chemistry of Nucleic Acids. Isolation and Characterization of Thymine Glycols[1]

Sir:

Since the discovery by Muller[2] in the late twenties that X-rays cause mutagenic effects, the radiation chemistry of nucleic acids has received considerable attention.[3] Radiation effects on thymine have been in the forefront, and 5,6-dihydroxy-5,6-dihydrothymines of trans (I) and cis (II) configurations have been indicated as products.[4] However, the actual isolation and identification of I has not been previously accomplished. We now wish to report the successful characterization of I and the chemistry of I and II.

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Thymine, dissolved in triply distilled water, was saturated with oxygen. The solution (375 ml/run, 3×10^{-2} *M*, pH ~6) was irradiated with ^{137}Cs-Gammator[5] at a dose rate of 2 krads/min[6] for a total of 10 hr, and resaturated with oxygen at 2-hr intervals. The irradiated solution was evaporated (35°) until dry and the residue was extracted with methanol. The combined methanolic extract was concentrated, applied on Whatman No. 3 paper, and eluted with *n*-butyl alcohol saturated with water. Materials with R_f values of 0.47 and 0.40 were cut out and rechromatographed twice. The purified material was recrystallized from methanol.

The R_f 0.40 material was found to have identical ir, uv, and nmr spectra as the *cis*-thymine glycol (II)[4b,7] prepared by permanganate oxidation of thymine[8] at pH 6.8.

The trans isomer (I), R_f 0.47, has mp 145–147° dec, shows only end absorption in the uv region, has peaks for CH_3 (s, δ 1.60), C(6)H (d, δ 4.70, J = 2.0 Hz), C(5)OH (s, δ 6.15), C(6)OH (m, δ 6.60) N(1)H (d, δ 8.32, J = 2.0 Hz), and N(3)H (s, δ 9.65) in the nmr spectrum (in $(CD_3)_2SO$ at 100 MHz with internal standard $(CH_3)_4Si$), and displays bands at 3430 (sh) and 3370 cm^{-1} for OH groups in its ir spectrum (KBr pellet). A mass spectrum of I gives no parent ion, but an M − 18 peak. However, after silylation with Regisil No. 27002 in pyridine, a molecular ion peak at *m/e* 448 corresponding to a tetratrimethylsilyl derivative of I was evident. Compound I slowly decomposes when stored in a vacuum desiccator at ambient temperature. When paper chromatography with *n*-propyl alcohol–water (10:3) was carried out with this material, another compound (R_f 0.38) was detected in addition to the unchanged I. This new compound was shown to be 2,3,4,5-tetrahydro-2,4-dioxy-5-hydroxy-5-methylpyrimidine (III). It shows only end absorption in the uv region, has peaks for CH_3 (s, δ 1.60), C(6)H (s, δ 7.57), C(5)OH (br, δ 7.18), and N(3)H (br, δ 9.60) in the nmr spectrum in $(CD_3)_2SO$ (addition of D_2O eliminates the signals for OH and NH protons), and it displays an ir band at 3360 cm^{-1} for the OH group. A mass spectrum of III gives the parent ion at *m/e* 142.

With the purified I on hand, the interrelation of I and II could then be examined. When a solution of II (20 mg/ml of H_2O) was heated at 90° for 4 hr, four products with R_f 0.27, 0.32, 0.39, and 0.57 (I) were detected together with II (0.47) by Fink's reagent on tlc (Eastman 6065, cellulose, with fluorescent indicator *n*-PrOH–HOH). The formation of I was also followed chromatographically by examining samples withdrawn at 30-min intervals. Although a very weak spot of I appeared for the 30-min sample, it never exceeded 2% at the end of 4 hr. When the solution of II was allowed to stand at 37° for 10 hr, only I and II could be detected. A time study revealed that I began to appear

(5) Model M Gammator, Radiation Machinery Corp., Parsippany, N. J.
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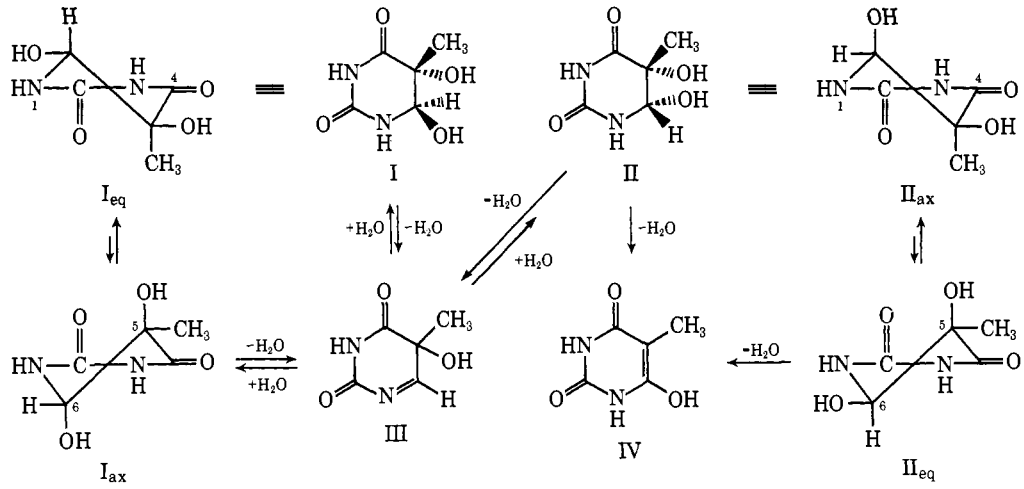
Scheme I



only after standing for 5 hr; however, the amount seemed to be very minor at all times.

The major product (R_f 0.39) from II when heated at 90° was isolated and identified as 1,2,3,4-tetrahydro-2,4-dioxy-5-methyl-6-hydroxypyrimidine (5-methylbarbituric acid (IV)) by uv and ir spectra. Thus, the results suggest that the conversion of II to IV is a facile process, but that conversion of II to I is inefficient at best, in contrast to earlier reports.[4a,4e]

On the other hand, when a solution of freshly prepared I (100 mg/15 ml of H_2O) was heated at 90° for 30 min, or allowed to stand at 37° for 3 hr, six and five spots, respectively, appeared on tlc. The major products were II (~4%) and III (~4%) in each case with ~85% of I unchanged.

Based on stereochemical considerations, a mechanistic explanation of the above discussed reactions may be given. The most predominant conformer of II was suggested to have an equatorial C(5)OH.[4c] Also, the same C(5)OH configuration may be assigned to I by examining the molecular structure of its analog, thymine–thymine adduct.[9] Thus, the major conformer for I and II may be I_{eq} and II_{ax} with equatorial and axial C(6)OH, respectively, as shown. Since the stereorequirement for a trans elimination process is favored by a trans planar conformation,[10,11] I_{ax} and II_{eq}, the minor conformers, are the species favored for dehydration. Thus, in neutral aqueous solutions, II possibly dehydrates at elevated temperature to give IV as the major product. By the same consideration, elimination of water from I should be difficult between C(5)OH and C(6)H, but is possible for C(6)OH and N(1)H to give III.[12] In aqueous solutions, addition of water to III would result in the formation of I or II. Thus I → III → I + II provides a route for the conversion of I to II (see Scheme I). This is a minor process since I, although unstable when dry, is stable in neutral aqueous solutions. On the other hand, II may also form III in the absence of its formation of IV. Although II → III → I is expected, II → IV is a favored process. Thus, the conversion of II to I occurs only in trace quantities. The above results may rule out the possibility of efficient cis and trans isomerization of I and II *via* a common intermediate,[4a,4e] by ring-chain tautomerization.

These findings are probably of significance to our understanding of the initial steps of the radiation chemistry of thymine in aqueous solution.

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Nonatetraenyl Anions. The 6-Vinylcycloheptadienyl–Nonatetraenyl Anion Rearrangement

Sir:

We wish to report four successful preparative routes to nonatetraenyl anions, two of which involve 6-vinylcycloheptadienyl–nonatetraenyl anion rearrangements.

Nonatetraenyl anion (I, R = H) was prepared in quantitative yield from 1,3,6,8-nonatetraene (II)[1] by metalation with *n*-butyllithium in THF–hexane at −70°. The nmr parameters[2] on structure I (for the parent anion, with R = H) clearly show this anion to exist predominantly in the extended planar conformation, as do the lower vinylogs allyl, pentadienyl, and heptatrienyl anions;[3] since the charge is delocalized over more atoms in I, the chemical shifts of the protons attached to the odd-numbered carbon atoms absorb slightly downfield from the corresponding atoms in heptatrienyl anion. The colors in the series range from none (allyl) through yellow (pentadienyl) and red (heptatrienyl) to blue-black (nonatetraenyl). Unlike heptatrienyl anions, which cyclize to cycloheptadienyl anions at −30°,[3] nonatetraenyl anion is stable at room temperature and could not be induced to cyclize; heating to 70° caused the separation of a black substance of unknown structure.

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