Table III. INDO Hyperfine Coupling Constants (G) for the Benzoyl Radical[a]

	Planar[b] *cis*	Planar[b] *trans*	Linear[c]	Free rotation[d]	High barrier[e]	Experimental[f]
$a_{H(ortho)}$	1.21	−0.10	−5.49	0.30	0.56	<0.1
$a_{H(meta)}$	−0.13	2.72	3.08	1.36	1.30	1.16
$a_{H(para)}$	0.02	0.02	−4.92	−0.46	0.02	<0.1
$a^{13}C^{g}$	129.72	129.72	21.88	120.17	129.72	128.2

[a] The structure used for the calculations assumes a regular hexagon for the phenyl group with $d(C,C) = 1.39$, $d(C,H) = 1.08$, $d(C_1,C_7) = 1.40$, $d(C_7,O) = 1.21$ Å, and $\alpha(C_1,C_7,O) = 120°$. [b] The nomenclature *cis* and *trans* refers to the unpaired electron mainly localized in an sp^2 hybrid orbital on C_7. [c] Same assumed structural parameters except for $\alpha(C_1,C_7,O) = 180°$. [d] Isotropic average of the coupling constants calculated over a rotation of 180° about the C_1–C_7 bond in increments of 10°. [e] Average of the coupling constants for the *cis* and *trans* hydrogens. [f] Absolute values. [g] Coupling constant for C_7.

tive of delocalization of unpaired spin density directly into the σ system of the phenyl substituent.

Unfortunately, one cannot distinguish, on the basis of the results of Table III alone, between the two dynamic models in question, *i.e.*, free rotation of the carbonyl group about the C_1–C_7 bond or a sizable twofold barrier to rotation with a coplanar conformation at the minimum. The observation of a 1:2:1 triplet splitting due to the *meta* protons implies an averaging process which is fast compared with the hyperfine frequency difference of the *meta* protons. This averaging becomes incomplete, however, at temperatures below −120° as evidenced by a pronounced broadening[16] of the central line of the triplet. We infer that the rotation of the acyl moiety is hindered by a relatively small barrier and that the equilibrium conformation corresponds to the coplanar structure.[17,18] A quantitative treatment of the hindered rotation in the benzoyl radical is in progress.

Acknowledgments. We thank Dr. Paul Meakin for helpful discussion, and Mr. K. Eaby for assistance with the experimental work.

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(17) The equilibrium conformation with the C_1C_7O plane bisecting the phenyl ring, with *equivalent ortho* and *meta* hydrogens, cannot cause the observed line broadening.

(18) This relatively low barrier is surprising. Infrared[19] and nmr[20] studies indicate a barrier for benzaldehyde of the order of 7 kcal/mol. In two related radicals, α-hydroxybenzyl[8] and the benzaldehyde radical anion,[21] the barrier must also be very high since these radicals possess distinct *ortho* and *meta* hydrogens. The lower barrier in the benzoyl radical may be attributed to the relative stability of the bisected form where the loss of resonance interaction with the carbonyl group is partially compensated by the greater delocalization of the unpaired electron.

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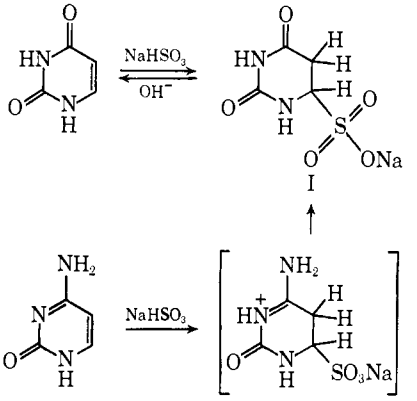
The Addition of Sodium Bisulfite to Uracil and to Cytosine

Sir:

Our recent discovery of an oxygen-mediated reaction between 4-thiouridine and sodium sulfite,[1] which brings about the formation of uridine-4-sulfonate,[2] has led us to investigate the effect of sodium sulfite on other nucleoside bases.

Uracil was found to react with $NaHSO_3$ at pH ~6. A typical reaction procedure is as follows. A suspension of uracil (224 mg, 2 mmol) in water (10 ml) was heated at 66°. Into it was added a mixture of $NaHSO_3$ (12 mmol) and Na_2SO_3 (3 mmol). A complete solution resulted within 1 min and precipitation of a product started in 3 min. After 30 min of heating, when the reaction was complete as judged by the loss of absorption at 260 mμ of the reaction solution ($A_{260\ m\mu}$ value of the supernatant solution was found to be less than 5% of the original value), the reaction mixture was chilled in ice and the prism crystals of the product (I) were collected by filtration (yield, 375 mg). No other product than I was detected in the reaction mixture by paper chromatographic analysis.

Chart I



When I was paper chromatographed (solvent: *t*-amyl alcohol–formic acid–H_2O, 3:2:1, v/v), no uv-absorbing spot was detectable on the chromatogram. After 0.1 *N* NaOH solution was sprayed on the chromatogram, however, a strongly uv-absorbing spot with an R_f value of 0.58 became detectable (R_f of uracil was 0.70). Uv absorption spectra of this alkali-treated I in acid and in alkali were identical with those of uracil. Paper chromatography of the alkali-treated I gave a single spot whose R_f value was the same as that of uracil. This fact has indicated that I readily regenerates uracil on treatment with alkali.

Interestingly, cytosine gave I upon treatment with sodium sulfite at pH about 6. Thus, when a solution of cytosine (2 mmol) in water (5 ml) was treated with a mixture of $NaHSO_3$ (12 mmol) and Na_2SO_3 (3 mmol) at 80° for 30 min, a crystalline product (340 mg) was obtained as an insoluble precipitate. Identity of this product with I was established by paper chromatography, paper electrophoresis (see below), uv and ir spectra, and the regeneration of uracil on treatment with alkali.

The following evidences have established the structure of I to be sodium 5,6-dihydrouracil-6-sulfonate.

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(2) H. Hayatsu and M. Yano, *Tetrahedron Lett.*, 755 (1969).

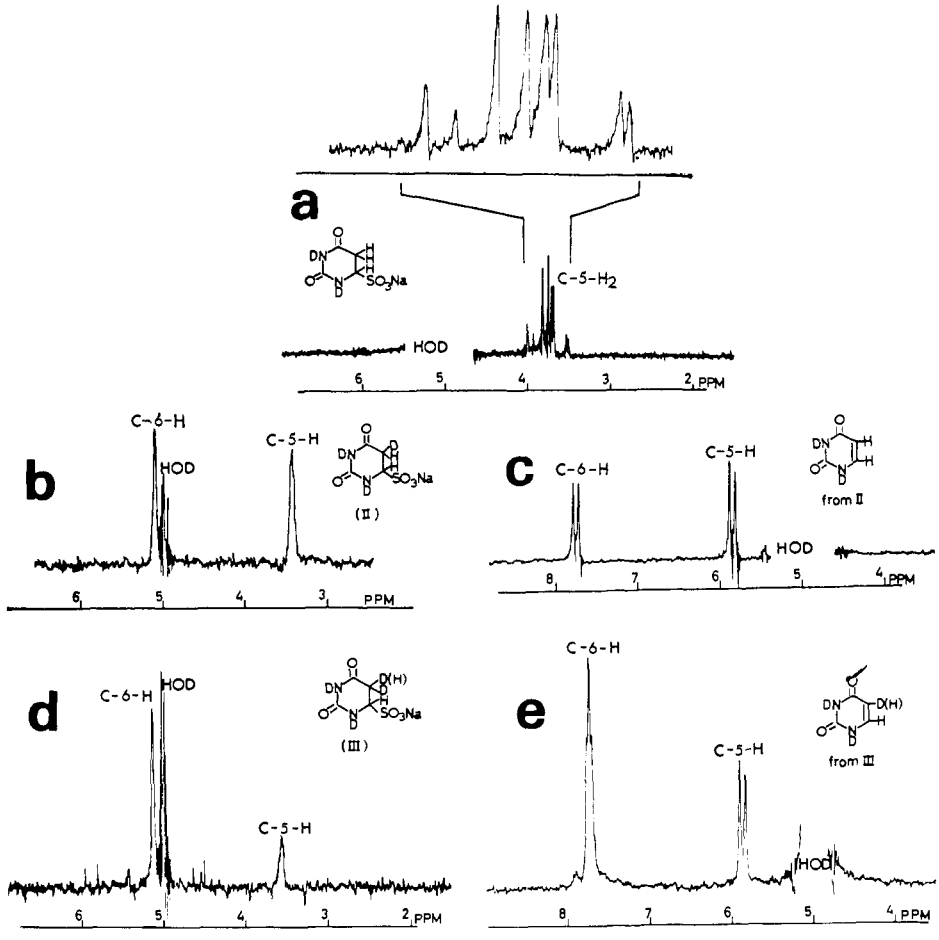

Figure 1. Nmr spectra (100 MHz) of 5,6-dihydrouracil-6-sulfonate and uracil (deuterated and nondeuterated). Spectra of D_2O solutions were recorded using a Jeol-NM 4H-100 nmr spectrometer. As a standard, the signal of HOD was adjusted to 5.00 ppm and the chemical shifts of other signals were read against this HOD signal. The composition of each solution and the recording temperature were as follows: a, 30 mg of I in 0.5 ml of D_2O (with a drop of concentrated DCl), at 55°; b, 37 mg of II in 0.5 ml of D_2O (DCl added), at 55°; c, 27 mg of uracil in 0.5 ml of 1 *N* NaOD, at 24°; d, 38 mg of III in 0.5 ml of D_2O (DCl added), at 57°; e, 44 mg of uracil in 0.5 ml of 1 *N* NaOD, at 24°.

Elemental analysis of I, after recrystallization from dilute acetic acid, has given values indicating that I is a 1:1 addition compound between uracil and sodium bisulfite (*Anal.* Calcd for $C_4H_4N_2O_2 \cdot NaHSO_3 \cdot H_2O$: C, 20.51; H, 3.01; N, 11.96; S, 13.69. Found: C, 20.73; H, 3.00; N, 11.94; S, 14.09). The ir spectrum of I gave two strong bands in the carbonyl region (1692 and 1729 cm^{-1}) assignable to two C=O groups at the 2 and 4 positions.[3] This observation, together with the fact that I gives end absorptions in the uv region, has indicated that I bears a 5,6-dihydrouracil type structure. The nmr spectrum of the pyridinium salt of I, taken in dimethyl-d_6 sulfoxide, gave a multiplet signal centered at 2.76 ppm (downfield from internal tetramethylsilane) which was assignable to two protons at C-5, and a multiplet signal further downfield at 3.92 ppm due to a proton at C-6. These assignments were carried out in reference to the nmr spectra of 5,6-dihydrouracil,[4] 5,6-dihydro-6-hydroxyuridine,[5] and 5,6-dihydro-5-S-cysteine uracil.[4] Thus, the site of attachment of the sulfite group to uracil was concluded to be C-6. This view was unequivocally confirmed by a deuterium exchange experiment described below.

For the structure of I, there are two possible modes of linkage between C-6 and the sulfite group: the sulfonic acid type and the sulfite ester type. A strong support for the sulfonic acid structure was exhibited by ir and Raman spectra. Ir of the trimethylammonium salt of I gave absorptions characteristic of a CSO_3^- group: ν S–O at 1226, 1174, and 1054 cm^{-1}; ν C–S at 733 cm^{-1}; δ S–O at 516 cm^{-1}. A sulfite ester structure is not consistent with this spectrum.[6] The Raman spectrum of I (trimethylammonium salt) gave very strong absorptions at 1055 cm^{-1} (ν S–O), 740 cm^{-1} (ν C–S), and 520 cm^{-1} (δ S–O). It has been reported[6] that strong Raman bands in these regions are characteristic of alkyl sulfonic acid salts and can be employed for the distinction of such sulfonic acid structure from isomeric sulfite ester structure.

The anionic character of I was demonstrated by paper electrophoresis. Thus, at pH 4, I traveled toward the anode, and the mobility was equal to that of 1-methyluracil-4-sulfonate[2] which was simultaneously run in the electrophoresis.

The sulfite addition reactions to uracil and cytosine were carried out in deuterium oxide. The products II and III, respectively, were isolated and then they were treated with alkali at pH 12 for 5 min at room tempera-

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(5) W. J. Wechter and K. C. Smith, *ibid.*, **7**, 4064 (1968).
(6) H. G. Houlton and H. V. Tartar, *J. Amer. Chem. Soc.*, **60**, 544 (1938).

ture to regenerate uracil. These compounds were examined by nmr spectroscopy taken in D_2O (Figure 1). Uracil obtained from II gave normal 5-H and 6-H signals of nondeuterated uracil, indicating that the deuterium present in II was stereospecifically eliminated by the alkali treatment (Figure 1c). This fact has suggested that the addition and elimination of sodium sulfite take place in a way with stereochemically equal specificity: *trans* and *trans* or *cis* and *cis*. A *trans*-addition and *trans*-elimination mechanism is favored on the basis of the known mechanism of bimolecular ionic addition and elimination.[7] The spectrum of uracil obtained from III showed a decreased signal at 5.86 ppm indicating that a considerable portion of the 5-H had been replaced by deuterium (Figure 1e). The 3.56-ppm signal of III, whose intensity was much smaller than that of the corresponding signal of II, must have resulted from an extensive double deuteration at the 5 position of III (Figure 1b and d). The nondeuterated product I gave a multiplet signal typical of an ABX system at *ca.* 3.8 ppm due to two nonequivalent protons at the 5 position (Figure 1a). These observations confirmed the site of attachment of the sulfite group to uracil to be the 6 position. An alternative structure in which the sulfite attaches to the 5 position does not explain the experimental facts described above. The deuterium exchange reactions can be explained by a mechanism analogous to that of hydrolytic deamination of cytidine proposed by Wechter and Kelly.[8]

Although the addition of sulfite to double bonds has been reported previously,[9] the present work represents the first example in pyrimidines. This finding may be of considerable importance in the biology of nucleic acids.

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Bisdimethylglyoximatorhodium Derivatives. Analogs of Cobaloximes

Sir:

Recent reports in the Russian literature[1-3] and the results of an X-ray structure determination[4] suggest a resemblance of bisdimethylglyoximatorhodium complexes to the corresponding cobalt derivatives.[5] However, although a "rhodoxime" hydride, $HRh(Dmg)_2P(C_6H_5)_3$ and a rhodoxime(II) dimer with Rh–Rh bond have been characterized,[3,4] nothing is known about the properties of the hypothetical rhodoxime(I) nucleophiles. The blue to dark brown rhodoxime hydrides with axial bases such as triphenylphosphine, pyridine, or H_2O may be regarded as acids. They are sparingly soluble in neutral or mildly acidic aqueous solution but dissolve in alkali, in accord with the equilibrium

$$\underset{\uparrow \mathrm{B}}{\overset{\mathrm{H}}{|}\mathrm{(Rh)}} + \mathrm{OH^-} \rightleftharpoons \underset{\uparrow \mathrm{B}}{\mathrm{(Rh^I)^-}} + \mathrm{H_2O} \qquad (1)$$

Estimates of the pK_a's of rhodoxime hydrides with the axial components $P(C_6H_5)_3$, H_2O, or pyridine yield values of between 10.8 and 9.3. The rhodoxime hydrides thus are weak acids and comparable in strength to the less stable cobaloxime derivatives, which, unlike the rhodoxime hydrides, tend to decompose under hydrogen evolution.[6] The rhodoxime(I) nucleophiles, $(Rh^I)^-$, may be generated by adding NaOH to aqueous suspensions of the hydrides, which in turn are readily accessible from rhodoxime(III) starting materials such as $ClRh(Dmg)_2 \cdot P(C_6H_5)_3$[1] or $ClRh(Dmg)_2HCl$,[7] by reduction in neutral aqueous solution or suspension with stoichiometric $NaBH_4$. If the reductions are carried out in 0.1 *M* NaOH or in more strongly alkaline solution the nucleophiles are formed directly. In further analogy to the cobaloximes, the dimeric rhodoxime(II) derivatives, *e.g.*, $(C_6H_5)_3P \cdot (Dmg)_2RhRh(Dmg)_2 \cdot P(C_6H_5)_3$, also disproportionate into Rh^I and Rh^{III} in alkaline medium (3–6 *M* NaOH solution in H_2O–CH_3OH). The Rh(I) nucleophiles are recognized by their oxygen sensitivity and red-brown to brown-green color which is due to ligand-field transitions in the visible region. The band at lowest energy is assigned to the $4d_{z^2} \rightarrow 4d_{x^2-y^2}$ transition. Its λ_{max} is at 594 mμ (with OH^- as the axial base). In the corresponding cobaloxime the band is at 629 mμ.[6] Organorhodoximes are formed on reaction of the rhodoxime nucleophiles with alkylating agents (eq 2). The new organorhodium

$$\underset{\uparrow \mathrm{B}}{\overset{\mathrm{Cl}}{|}\mathrm{(Rh)}} \xrightarrow[\mathrm{NaBH_4,OH^-}]{} \underset{\uparrow \mathrm{B}}{\mathrm{(Rh^I)^-}} \xrightarrow[-\mathrm{X^-}]{+\mathrm{R\text{-}X}} \underset{\uparrow \mathrm{B}}{\overset{\mathrm{R}}{|}\mathrm{(Rh)}} \qquad (2)$$

compounds prepared in this fashion and isolated in crystalline form from CH_2Cl_2 extracts of the acidified aqueous solutions in many ways resemble the organocobaloximes. Methylaquorhodoxime, mp ~265° dec, exhibits the signal of the methyl protons in the nmr spectrum at 0.64 ppm (in alkaline D_2O). The signal is split symmetrically due to coupling with $^{103}Rh(I) = {}^1/_2$, $J = 2.6$ cps, thus proving the attachment of the methyl group to Rh. The Dmg protons appear as a single peak at 2.30 ppm. The Co-methyl protons in methylaquocobaloxime under identical conditions of measurement are observed at 0.64 ppm, demonstrating

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