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of uracil obtained from III showed a decreased signal at 5.86 ppm indicating that a considerable portion of the 5-H had been replaced by deuterium (Figure 1e).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

$$\begin{array}{c} H \\ | \\ (Rh) \\ \uparrow \\ B \end{array} + OH^- \rightleftharpoons \begin{array}{c} (Rh^I)^- \\ \uparrow \\ B \end{array} + H_2O \qquad (1)$$

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

$$\begin{array}{c} Cl \\ | \\ (Rh) \\ \uparrow \\ B \end{array} \xrightarrow[NaBH_4,OH^-]{} \begin{array}{c} (Rh^I)^- \\ \uparrow \\ B \end{array} \xrightarrow[-X^-]{+R-X} \begin{array}{c} R \\ | \\ (Rh) \\ \uparrow \\ B \end{array} \qquad (2)$$

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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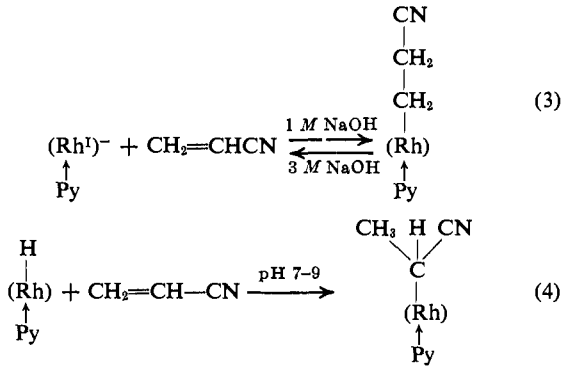
the near identity of the electronic environment of the methyl group in both compounds. *Anal.* Calcd for $C_9H_{19}N_4O_5Rh$: C, 29.51; H, 5.23; N, 15.30. Found: C, 29.47; H, 5.35; N, 15.15. In the optical spectrum of methylaquorhodoxime the band at lowest energy is observed at 403 mμ (ε $4.8.10^2$). The corresponding transition in the cobaloxime occurs at 448 mμ (ε $1.53.10^3$) and has been assigned to a metal–carbon CT transition. Methylaquorhodoxime is less sensitive to light than methylaquocobaloxime, yielding mainly methane as the termination product of the methyl radical formed on photolysis. The reaction of the methylaquorhodium compound with pyridine yields methylpyridinerhodoxime, mp ~162° dec. *Anal.* Calcd for $C_{14}H_{24}N_5O_4Rh$: C, 39.35; H, 5.20; N, 16.39. Found: C, 39.50; H, 5.31; N, 16.15. Ethylpyridinerhodoxime, mp ~171° dec, prepared similarly, produces ethylene on photolysis and thermal decomposition. *Anal.* Calcd for $C_{15}H_{24}N_5O_4Rh$: C, 40.82; H, 5.48; N, 15.87. Found: C, 40.78; H, 5.65; N, 15.67. The Rh(I) nucleophile reacts with acrylonitrile in 1 *M* NaOH to produce β-cyanoethylrhodoxime. The compound undergoes slow elimination back into acrylonitrile and rhodoxime(I) in 3 *M* aqueous NaOH (eq 3) and thus is more alkali resistant than the corresponding cobaloxime.[8] The rhodium hydride reacts with acrylo-



nitrile exclusively to produce the α-cyanoethyl derivative (eq 4), as has been noted in the cobaloxime system[8] and in reactions of acrylonitrile with Lewis-base adducts of hydridorhodium(III) chloride.[9] Both isomers have been characterized by analysis and their ir and nmr spectra. *Anal.* Calcd for $C_{16}H_{23}N_6O_4Rh$: C, 41.21; H, 4.97; N, 18.02. Found (β isomer): C, 41.25; H, 5.02; N, 18.16, mp ~170° dec. Found (α isomer): C, 41.22; H, 5.03; N, 18.12, mp ~221° dec. The striking analogy between cobaloximes and rhodoximes becomes obvious from the determination of the Pearson nucleophilicity[10] of $(Rh^I)^-$ under conditions identical with those employed for $(Co^I)^-$.[11] The average nucleophilicity of 13.7 ± 0.4 is smaller than that of the cobaloxime(I) (14.3 for OH^- as the axial base). The SN2 reactions of $(Rh^I)^-$ are slower compared to those of $(Co^I)^-$ presumably because of the greater size of the $4d_{z^2}$ orbital or $4d_{z^2}$–$5p_z$ hybrid compared to the analogous orbitals of cobalt. The relative rate profiles of Rh(I) and Co(I) reactions are very similar, however (Figure 1). The "iridoxime(I)" nucleophile, in contrast, is difficult to generate analogously due to the substitution inertness of, *e.g.*, $CpIr(Dmg)_2HCl$.[12] Ethylpyridineiridoxime, accordingly, is produced only in trace amounts by reductive alkylation. The compound (dec pt ~250°) is obtained in better yield by the Grignard procedure. The dark brown complex produces a 2:1 mixture of ethylene and ethane on pyrolysis. Organorhodoximes thus are surprisingly similar to cobaloximes except for a greater stability of the metal–carbon bonds. This suggests that corrins containing rhodium instead of cobalt could be interesting vitamin B_{12} inhibitors with little if any biological activity of their own. This prediction is supported by the established weak inhibiting effect of methylaquorhodoxime upon the corrin-dependent evolution of methane by cell extracts of *Methanobacillus omelianskii*,[13,14] where methylaquocobaloxime has been shown[15] to be a substrate almost as efficient as methylcobalamin.

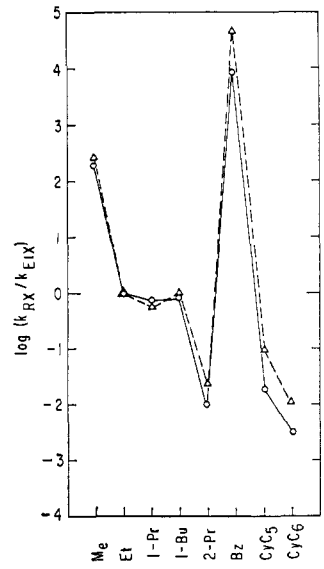


Figure 1. Rate profiles for SN2 reactions of rhodoxime(I) (axial base OH^-) (○—○) and of cobaloxime(I) (axial base tributylphosphine) (△- - -△) at 25°, 0.1 *F* in methanol.

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Selection Rules for Mass Spectrometry. An Example of a Photochemical Analogy

Sir:

We present the first complete study of a system designed to test selection rules for electrocyclic reactions induced by electron impact.