perature, probably liberate the isocyanide from part of I, which then adds to the rest of I to form II at low temperatures.

The possibility that the unstable species II is the hexacoordinated low-spin complex is supported by the esr spectrum: the five-line super-hf structure (5.5-G splitting) in one of the parallel peaks with intensity ratio of approximately 1:2:3:2:1 was proved by ^{15}N labeling to be caused by two nitrogen nuclei. Consequently, there must be two isocyanide groups in the axial positions. This fact, combined with the above observations, immediately points to the hexacoordinated structure. Furthermore, the observed $g_{\parallel}$ of II is considerably larger than any of the known tetra- and pentacoordinated phenyl isocyanide low-spin complexes of Co(II),[4] in which $g_{\parallel}$ (2.003–2.008) is closer to the free-spin value, 2.0023.

From all these observations, we conclude that the species II is in fact the complex ion, Co^{II}(phenyl isocyanide)$_6$. Recently Pratt and Silverman[3] reported visual observation of similar color change ("mauve" instead of "orange") with the corresponding methyl isocyanide complex. These authors presumed that the mauve species may be a hexa(isocyanide) complex, but no evidence was given. Several Co(II) complexes were reported by Stoufer and others,[5] in which the high- and low-spin states are apparently in equilibrium. The integrated intensity of the spectrum at 77°K of II represents all the Co(II) in the system within ±10%. Also II does not show the line broadening even at 248°K in significant contrast to the systems of Stoufer and others.

Since narrow esr absorption is obtained even near 0°, the geometrical structure of II must be axially distorted from the ideal octahedral symmetry so as to lift the degeneracy of e_g orbital levels, as, indeed, is indicated in the frozen spectrum. The axial distortion may be effected by interaction with surrounding molecules, especially with the counterions (ClO_4^-). It could also be due to the static Jahn–Teller effect, in which case the unpaired electron orbital would be the vibronic mixture[6] $\psi = \cos^2(\phi/2)\,(d_{3z^2-r^2}) + \sin^2(\phi/2)\,(d_{x^2-y^2})$. This is, indeed, consistent with the comparatively large positive deviation of $g_{\parallel}$, since $d_{x^2-y^2}$ will contribute to the positive shift through coupling with the lower t_{2g} orbitals. In this connection it is worth pointing out that similar positive shifts were also found with the low-spin cobalt(II) phthalocyanine with its axial site occupied by heterocyclic amines,[7] where the ligand field is expected to be near octahedral.

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The Photochemical Addition of Alcohols to Purine[1]

Sir:

We report here a new photoreaction of purine in deoxygenated alcohol solution which results in efficient addition of α-hydroxyalkyl groups to the purine 6 position. Figure 1 shows typical absorption spectrum changes resulting from irradiation of purine in methanol. The new peak near 292 nm and clean isosbestic points are also found after irradiation in deoxygenated ethanol, 2-propanol, and 1-butanol. Photolysis of purine in oxygen-saturated ethanol leads to different products, with bands near 280 and 310 nm.

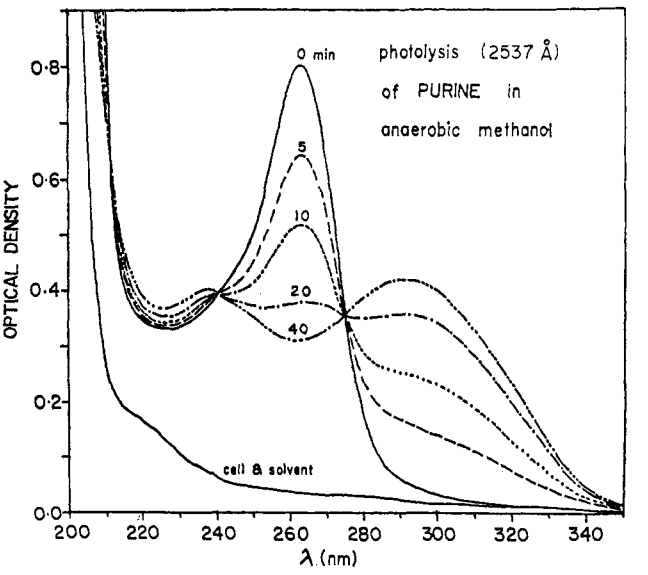

Figure 1. Spectral changes during photolysis (2537 Å) of purine in degassed methanol. Initial purine concentration 7.0×10^{-5} *M*; $I_0 = 6 \times 10^{-8}$ einstein/(cm^2 min); cell path = 14.7 mm; time in minutes.

Photoproducts of the anaerobic reaction with methanol, ethanol, and 2-propanol were recovered by evaporation, followed by recrystallization from dry ethylene chloride–methanol. The ethanol reaction yields two isomeric products in about equal amounts which were separated by fractional crystallization from ethylene chloride–methanol and chloroform–ethanol. Elemental analyses and mass spectrometer molecular weights correspond to 1:1 purine–alcohol adducts. Group analyses showed negligible alkoxyl or N-alkyl content. The nmr spectra of the four adducts in DMSO-d_6 solution all show a band at δ 4.6–4.9 ppm (one proton) relative to TMS and two sharp singlets at 6.9 and 7.2 ppm, above a broad absorption in the 6–8-ppm region. Addition of excess D_2O eliminates the broad absorption, producing a three-proton HOD peak and leaving one proton each for the 6.9- and 7.2-ppm singlets. We assign the three exchangeable protons to one OH and two NH groups and the two downfield protons (6.9 and 7.2 ppm) to ring CH groups associated with residual conjugation. The isopropyl adduct (Figure 2) shows sharp singlets at 0.97 and 1.18 ppm (three protons each) which can arise only from two *nonequivalent* methyl groups on the alcohol moiety. The remaining proton at 4.62 ppm must therefore be the purine CH at the site of addition. The nmr spectra for the other adducts are assignable in a similar manner by successively replacing the methyls of 2-propanol with hydrogens and retaining the nonequivalence of the a,b positions. In all cases, the spectra (further studied

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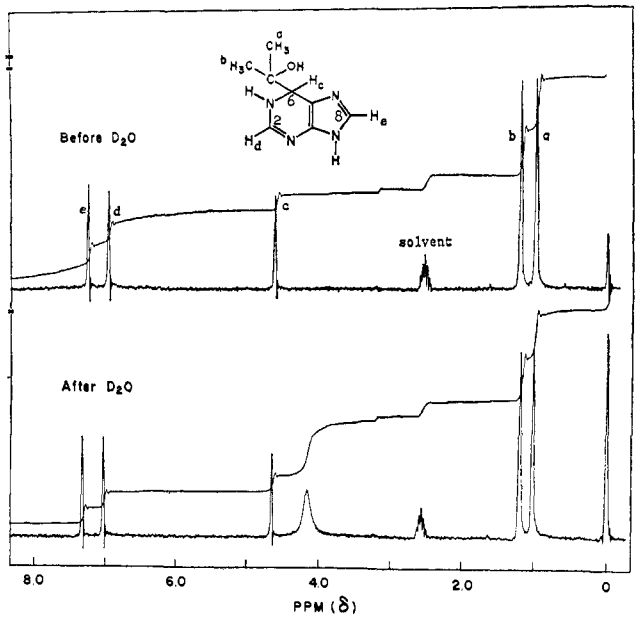

Figure 2. Nmr spectra (Varian A60-A) of 2-propanol–purine photoadduct (10 wt %) in DMSO-d_6 before (upper) and after (lower) addition of D_2O; chemical shifts (δ) referred to internal TMS standard. Very broad underlying band in the 6–8-ppm region is established by the integrated absorption curve. Recrystallizing solvent band (methanol) at 3.2 ppm has been deleted for clarity.

under high resolution) unambiguously require addition of the carbinol carbon of the alcohol to a purine ring carbon.

The site of addition on the ring was established by experiments with purine substituted by deuterium at the 6 and 8 positions, respectively.[2] In the nmr spectrum of the methanol photoadduct of 8-deuteriopurine, the singlet at 7.2 ppm is absent but the spectrum is otherwise unchanged. On the other hand, in the spectrum of the 6-deuteriopurine–methanol adduct, the 6.9- and 7.2-ppm peaks are unchanged, but the 4.89-ppm band (corresponding to the 4.62-ppm line in Figure 2) is absent. The splitting pattern of the two CH alcohol protons further upfield is simplified accordingly. We conclude that the site of methanol addition is the 6 position of purine, and that the 6.9- and 7.2-ppm singlets correspond respectively to the C-2 and C-8 purine protons. Similar experiments with the ethanol adducts show that addition occurs again at the 6 position in *both* isomers. The two compounds must therefore be diastereomers. We assume that 2-propanol also adds at the same site. The assignment of the hydrogen positions among the four possible tautomeric structures is still uncertain. The interesting nonequivalence of the a and b positions implies a preferred conformation around the C_6–C_α bond. This may involve either an intramolecular hydrogen bond or specific intermolecular interactions.

Ferrioxalate actinometry[3] gave $\varphi = 0.24 \pm 0.03$ for the room temperature photoreaction (2537 Å) of purine in all three neat alcohols, at concentrations near 10^{-4} *M* and intensities around 10^{-8} einstein/(cm^2 min). The quantum yield of the methanol reaction decreases sharply to about 0.18 on addition of cyclohexene, up to about 10^{-2} *M*, but remains unchanged on further additions up to 0.1 *M*. Two pathways seem to be involved in this reaction.

Absorption spectrum changes generally similar to those seen in the purine reaction have been observed after irradiation of deoxygenated ethanol solutions of many heterocyclic molecules, including pyridine, pyrazine, pyrimidine, benzimidazole, benzoxazole, quinoline, isoquinoline, quinoxaline, 1,4,5-triazanaphthalene, and phenazine. It would appear that the photoaddition of alcohols to heteroaromatic molecules may be a quite general reaction. We note that photolysis of acridine in anaerobic methanol or ethanol has been shown to give the respective 9-α-hydroxyalkyl-9,10-dihydroacridines.[4]

A detailed account of this work will be given elsewhere.[5] Further studies on the mechanism and generality of the reaction are in progress.

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Aranotin and Related Metabolites from *Arachniotus Aureus*. I. Determination of Structure

Sir:

The antiviral activity[1] produced by a fungus provisionally designated as *Arachniotus aureus* (Eidam) Schroeter prompted a detailed investigation of its metabolites. These metabolites[2] belong to the class of sulfur-containing diketopiperazines such as gliotoxin[3] and sporidesmins.[4]

One of the active[1] metabolites is aranotin (**3a**), $C_{20}H_{18}O_7N_2S_2$, mp 198–200° dec. Acetylation of aranotin afforded another metabolite, acetylaranotin (**3**), $C_{22}H_{20}O_8N_2S_2$; mp 201–215° dec; mass spectra, *m/e* 440, accompanied by ions at *m/e* 64 due to loss of S_2;[5] ir (Nujol) 1740, 1230 (acetyl), and 1665 cm^{-1} (amide); uv (C_2H_5OH) end absorption with shoulders at 270 (ϵ 1800) and 222 mμ (ϵ 10,200); CD (CH_3OH), two Cotton effects, a positive at 267 and a negative at 230 mμ. The major metabolite is bisdethiodi(methylthio)acetylaranotin (BDA) (**4**), $C_{24}H_{26}O_8N_2S_2$; mp 213–217° dec; nmr τ 4.24

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(2) Fermentation conditions will be described elsewhere by M. Stark and coworkers.

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