observed in the pulse radiolytic reduction of Co complexes[7] (k = 6×10^4, 1×10^4, 1.5×10^3 s^{-1}).

The conclusions drawn from these findings are as follows. The primary step in the charge-transfer photochemistry of $Co(NH_3)_5Cl^{2+}$ is oxidation of the Cl^- and elimination of the Cl atom. The intermediate observed by flash photolysis in the microsecond time scale and interpreted as NH_2Cl^- [6] may be the product of a reaction of this highly reactive Cl atom with the released ammonia or it could be $ClOH^-$ from reaction of Cl· with water[10] (at pH values higher than 3), which has a spectrum similar to that of Cl_2^- but with a lower extinction coefficient. Our observations show that the Cl atom is quickly complexed with Cl^- to Cl_2^-. The reduced Co complex releases the NH_3 ligands in five successive steps. The rates of these steps decrease by a factor of roughly 7 for each NH_3 eliminated. This observation leads to the conclusion that a particularly stable complex with four NH_3 ligands in a plane as would be expected for a low-spin Co(II) complex by analogy to the stable macrocyclic Co(II) complexes[12] is not present, and that the spin relaxation to the stable form of free Co(II) takes place in $<10^{-7}$ s. Measurements of the elimination of first NH_3 from $Co(NH_3)_6^{2+}$ will be reported in a further paper.[13]

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J. Lilie

Hahn-Meitner-Institut für Kernforschung Berlin GmbH
Bereich Strahlenchemie, D-1000 Berlin 39, West Germany

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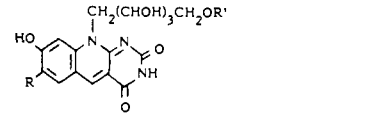
Synthesis of 7,8-Didemethyl-8-hydroxy-5-deazariboflavin and Confirmation of Its Identity with the Deazaisoalloxazine Chromophore of *Methanobacterium* Redox Coenzyme F_{420}

Sir:

Methane-producing bacteria contain at least two novel coenzymes which participate in the eight-electron reduction of CO_2 to CH_4 at the expense of H_2 oxidation: coenzyme M (β-mercaptoethanesulfonate),[1] proposed as a one-carbon carrier during CO_2 reduction, and factor 420,[2] a fluorescent redox cofactor which is an immediate acceptor of electrons from a methanogen hydrogenase. Reduced F_{420}, in turn, is a mobile reductant for cellular NADP. Wolfe and colleagues have isolated F_{420} and recently proposed that it has structure **1**,[3] based on spectroscopic evidence and similarity to known 8-hydroxyflavin[4] and 5-deazaflavin chromophores.[5,6] Factor 420 would then be the first example of a naturally occurring 5-deazaisoalloxazine, and independent structural corroboration, by synthesis, seems in order.

We report here the syntheses of 7,8-didemethyl-8-hydroxy-5-deazariboflavin (**2a**)[7] and 8-demethyl-8-hydroxy-5-deazariboflavin (**2b**)[7] as well as experiments confirming that **2a** is identical with the riboflavin level derivative (FO)[3] obtained by acid hydrolysis of factor 420.[3]

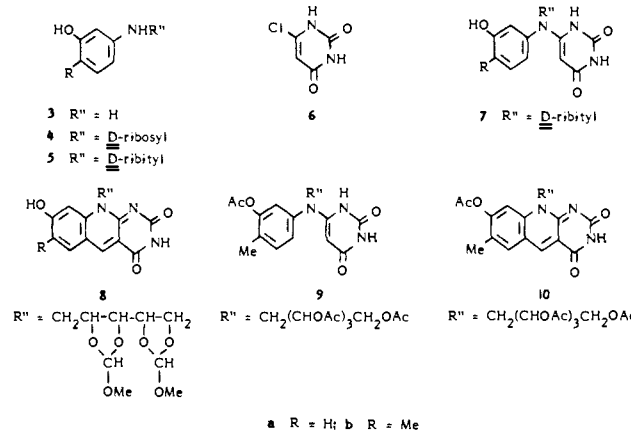


1 R = H, R' = P-OCH-CNHCH(CH$_2$)$_2$CNHCH(CH$_2$)$_2$CO$_2^-$ (Me, O$^-$, CO$_2^-$, CO$_2^-$)

2a R = H, R' = H

2b R = Me, R' = H

Syntheses of **2a,b** represent modifications of our earlier method for the preparation of 5-deazariboflavin.[8] Condensation of **3a** with ribose (MeOH, reflux, 4 h) gave a 79% yield of **4a** (mp 144 °C dec), which was unstable and was used directly. Attempted hydrogenation of **4a** in the presence of Raney Ni or Pd catalyst resulted in reduction of the aromatic ring as a major side reaction. However, treatment of **4a** (1 equiv) with $NaBH_3CN$ (4.8 equiv) in MeOH containing a small amount of AcOH (20 °C, 16 h) gave satisfactory reduction. After destruction of excess borohydride, chromatography on AG 50W-X8 cation-exchange resin (elution with 1% NH_4OH) afforded an 80% yield of **5a**: mp 133–135 °C dec; NMR[9] (Me_2SO-d_6) δ 5.9–6.2 (m, 3 H), 6.7–7.1 (m, 1 H), 8.87 (s, 1 H)). Compound **5a** (3 equiv) was reacted with 6-chlorouracil (**6**)[10] (1 equiv) in a small volume of H_2O (reflux, 14 h). The resulting solution was applied to a column of AG 50W-X8 resin. Elution with H_2O yielded **7a** (46% based on **6**, 70% based on recovered **5a**) as a glass which was suitable for use in the next reaction: NMR(Me_2SO-d_6) δ 4.08 (s, 1 H), 6.6–6.9 (m, 3 H), 7.1–7.4 (m, 1 H, partly superimposed on broad NH hump).



3 R" = H

4 R" = D-ribosyl

5 R" = D-ribityl

6

7 R" = D-ribityl

8 R" = CH$_2$CH-CH-CH-CH$_2$ (OMe, OMe)

9 R" = CH$_2$(CHOAc)$_3$CH$_2$OAc

10 R" = CH$_2$(CHOAc)$_3$CH$_2$OAc

a R = H; **b** R = Me

Cyclization of **7a** was accomplished by treatment with a large excess of trimethyl orthoformate in the presence of *p*-toluenesulfonic acid catalyst (reflux, 18 h). The product **8a** precipitated from the reaction mixture in 41% yield and was obtained as a golden yellow, fluorescent solid (mp >251 °C dec).[11] Treatment with 1 N HCl (steam bath, 0.5 h) converted **8a** into **2a** (83%), obtained as golden yellow crystals (mp 284–286 °C dec).[12]

The synthesis of **2b** was carried out by a modification of the above route. In contrast to **4a, 4b** was successfully converted into **5b** (mp 119–122 °C (after LC)); NMR(Me_2SO-d_6) δ 1.90 (s, 3 H), 5.9–6.1 (m, 2 H), 6.70 (d, J = 8 Hz, 1 H), 8.60 (s, 1 H)) by hydrogenation (600 psi of H_2, Raney Ni, 70 °C,

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7 h) without significant reduction of the aromatic ring. Compound **7b** was not isolated but was converted into **9** (Ac_2O-pyridine, 0 °C, 16 h) which was separated from peracetylated **7b** by column chromatography. Reaction of **9** (dark oil) with triethyl orthoformate in the presence of Me_2SO and a catalytic amount of *p*-toluenesulfonic acid (95–115 °C, 24 h) gave **10** (mp 180–184 °C (from EtOH)),[13] in 5% overall yield. Deacetylation of **10** with concentrated HCl (20 °C, 23 h) provided a 66% yield of 2b (mp 311–313 °C dec).[14] Alternatively, conversion of **7b** (isolated by cation-exchange chromatography; NMR (Me_2SO-d_6) δ 2.14 (s, 3 H), 4.11 (s, 1 H), 6.71 (d, J = 8 Hz, 1 H), 6.75 (s, 1 H), 7.18 (d, J = 8 Hz, 1 H)) into **8b** (mp 253–255 °C dec)[15] and then into **2b** by methods analogous to the synthesis of **2a** was accomplished in overall yield comparable with that via **9** and **10**.

Comparison of **2a** and **2b** with FO, generated from F_{420} by acid hydrolysis,[3] revealed the identity of **2a**, but not **2b**, with FO. FO and **2a** have identical UV-visible spectra (λ_{max} 420 nm (ϵ 42 000 to 44 000 M^{-1} cm^{-1})), while **2b** shows a 6-nm red shift (λ_{max} 426 nm (ϵ 45 000 M^{-1} cm^{-1})). Stoichiometric complexation of each compound with egg white flavin-binding apoprotein[16,17] produced a bathochromic shift of λ_{max} to 404 nm (ϵ 6000 M^{-1} cm^{-1}) for **2a** and FO, but to 410 nm (ϵ 6000 M^{-1} cm^{-1}) for **2b.** Curiously, **2b** is a substrate for conversion into the FMN and FAD levels by the *B. ammoniagenes* riboflavin kinase-FAD synthetase complex,[6] but **2a** and the FO sample were not. Reduction with borohydride or H_2–Pt bleached the 420- or 426-nm (**2b**) peak and produced the anticipated[3] new transition in the 320–322-nm region (ϵ 10 000), characteristic of the 1,5-dihydro-5-deazaisoalloxazine chromophore.[6] With 175 μg of crude hydrogenase from *Methanobacterium thermoautotrophicum* strain, ΔH, 10 nmol of FO and **2a** were quantitatively reduced in seconds, while **2b** was reduced ca. tenfold more slowly to the 1,5-dihydro species. One-electron reductants of appropriate potential (dithionite, *A. vinlandii* flavodoxin[18]) were ineffective, as in the parent 5-deazaflavin system,[5,6] strongly suggesting that in vivo reduction of F_{420} by methanogen hydrogenase is an obligate two-electron process involving transfer of a hydride equivalent to C-5 of F_{420}.[19] The slow autoxidation of dihydro-F_{420} by O_2 has been suggested[3] and is also a feature of **2a, 2b,** and FO.

The aggregate chemical and biochemical data support the identity of **2a**, but not **2b**, with the riboflavin level acid hydrolysis product (FO) of F_{420} and confirm the proposed[3] structure of the methanogen redox coenzyme as a 7,8-didemethyl-8-hydroxy-5-deazariboflavin derivative.[20] The availability of synthetic material may facilitate studies of the redox role and electron-transfer mechanism of F_{420} in biological methane formation.

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(12) NMR (Me_2SO-d_6) δ 7.04 (d, J = 9 Hz, 1 H, H-7), 7.40 (br s, 1 H, H-9), 8.01 (d, J = 9 Hz, 1 H, H-6), 8.89 (s, 1 H, H-5), 11.01 (s, 1 H, exchangeable), 11.2 (v br hump, 1 H, exchangeable); NMR (D_2O–7.5% Na_2CO_3) δ 6.3 (s, 1 H, superimposed on adjacent d, H-9), 6.43 (d, J = 9 Hz, 1 H, H-7), 7.04 (d, J = 9 Hz, 1 H, H-6), 7.58 (s, 1 H, H-5) (cf. ref 3); field desorption mass spectrum *m/e* 364 (M^+ + 1); $[\alpha]^{25}_D$ +38° (*c* 0.5, 0.1 N NaOH).
(13) NMR ($CDCl_3$) δ 1.74, 2.07, 2.23, 2.29, 2.36, 2.45 (s, each 3 H), 7.60 (s, 1 H), 7.76 (s, 1 H), 8.79 (s, 1 H), 9.06 (br s, 1 H, exchangeable); mass spectrum *m/e* 587, 588 (M^+, M^+ + 1).
(14) NMR (Me_2SO-d_6) δ 2.30 (s, 3 H, CH_3), 7.57 (s, 1 H, H-9), 8.01 (s, 1 H, H-6), 8.95 (s, 1 H, H-5), 11.11 (s, 1 H, exchangeable); field desorption mass spectrum *m/e* 378 (M^+ + 1).
(15) NMR (Me_2SO-d_6) δ 2.26 (s, 3 H), 3.13 (s, 3 H), 3.28 (s, 3 H), 5.97, 5.99 (overlapping s, total 2 H), 7.24 (s, 1 H), 7.88 (s, 1 H), 8.78 (s, 1 H), 10.91 (s, 1 H), 11.39 (br s, 1 H).
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(19) Reduction of **2a** and FO with D_2–Pt followed by reoxidation with O_2 yielded reoxidized **2a** and FO with >90% deuterium at C-5 by 60 -MHz FT NMR analysis.
(20) Evidence for the D-ribityl side chain in F_{420} was obtained by limited acid hydrolysis to the FMN level and stoichiometric complexation with *A. vinlandii* apoflavodoxin[18] ($K_D \leq 10^{-9}$ M), a protein known to be highly specific for the D-ribityl side chain of FMN derivatives.

Wallace T. Ashton,* Ronald D. Brown
Merck Sharp & Dohme Research Laboratories
Rahway, New Jersey 07065

Fredric Jacobson, Christopher Walsh*
Departments of Chemistry and Biology
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Received March 23, 1979

Regiospecific Photosensitized Oxygenation of Vinylsilanes. A Method for Converting Saturated Ketones to 1,2-Transposed Allylic Alcohols. Possible Role of Silicon in Directing the Regioselectivity of Epoxysilane Cleavage Reactions

Sir:

The considerable importance of regiospecificity to organic synthesis makes continued search for such methodology a high priority challenge. Herein we describe the development of a simple procedure capable of shifting the position of a ketone carbonyl by one carbon in an entirely predictable manner with concomitant introduction of a double bond. The new sequence broadens the scope of previously developed carbonyl transposition chemistry[1] and also provides access to α-silylated allylic alcohols, a less well-known class of compounds.[2]

Our approach is based on an awareness that α,β-epoxysilanes experience ring opening with a regioselectivity contrary to that followed by epoxides lacking carbon–metal bonds. Thus, exposure of **1** and its congeners to a variety of reagents, which include Brønsted[3-6] and Lewis acids,[5-8] cuprates,[9] and

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