Apart from the stability of these *tert*-butyl side chain protected derivatives, it is the special character of the acyl fluoride function itself that is likely to assure the widespread applicability of this general class of reagents. Thus, due to the nature of the C–F bond, acyl fluorides are of greater stability than the corresponding chlorides toward neutral oxygen nucleophiles such as water or methanol yet appear to be of equal or nearly equal reactivity toward anionic nucleophiles and amines.[11] Application of FMOC amino acid fluorides in the FMOC/polyamine rapid segment synthesis is possible with little if any difference in the time required for completion of the coupling step between the fluorides and chlorides.[12] More importantly a striking qualitative difference between the two classes of compounds toward tertiary amines allows direct application of the fluorides to solid-phase peptide coupling reactions. In the case of FMOC amino acid chlorides, necessary basic co-reagents (DIEA, NMM, pyridine, etc.) cause immediate conversion to the corresponding oxazolones, which are more sluggish in their further conversion to the desired acylation product than the acid chlorides themselves.[13] For solid-phase reactions, maximum speed in the coupling step can be achieved by prior conversion of the acid chloride to an active ester (e.g., the HOBt ester obtained via a 1:1 mixture of DIEA and HOBt).[3] In remarkable contrast, FMOC amino acid fluorides are stable to these same tertiary bases,[14] which then serve to catalyze the direct acylation step and bind the liberated acid.[15] Model racemization studies[2,3] showed no significant loss of chirality in either solution or solid-phase syntheses.

(10) These data exclude from consideration any question of an oxazolone hydrohalide structure for these compounds. Compare: Carter, H. E.; Hinman, J. W. *J. Biol. Chem.* **1949**, *178*, 403. Carter and Hinman discuss such structures in the case of *N*-acyl amino acid halides. See also: Ronwin, E. *Can. J. Chem.* **1957**, *35*, 1031.

(11) For a discussion of the marked differences between the reactivity of acid chlorides and acid fluorides, see: (a) Bunton, C. A.; Fendler, J. H. *J. Org. Chem.* **1966**, *31*, 2307. (b) Swain, C. G.; Scott, C. B. *J. Am. Chem. Soc.* **1953**, *75*, 246. (c) Bender, M. L.; Jones, J. M. *J. Org. Chem.* **1962**, *27*, 3771.

(12) As an example, the protected heptapeptide i was obtained in the normal manner by using TAEA[2b] except that FMOC-Asp($OCMe_3$)-F and FMOC-Ser(CMe_3)-F were used along with FMOC-Val-Cl and FMOC-Leu-Cl. Following flash chromatography on silica gel using $CHCl_3$/MeOH/HOAc (90/10/1), the pure protected heptapeptide was obtained in analytically pure form (33%) as white crystals, mp 245 °C dec, α^{23}_D −19.4° (*c* 0.18, DMF); MS/FAB 1255 (MH^+), calcd 1253.8 (M). TAEA deblocking of the FMOC group followed by 10% *m*-cresol in TFA/CH_2Cl_2 (1:1) for 2 h gave in 54.5% yield the free heptapeptide TFA salt, mp 210–220 °C dec; MS/FAB 808.4437 (MH^+), calcd MH^+ 808.4457. Amino acid analysis (48-h hydrolysis): Asp, 0.97 (1); Ser, 1.02 (1); Val, 1.72 (2); Leu, 2.05 (2); Tyr, 0.95 (1).

FMOC-Val-Asp($OCMe_3$)-Val-Leu-Leu-Ser(CMe_3)-Tyr(CMe_3)-$OCMe_3$
i

(13) For peptide coupling reactions in solution, this problem is avoided by slow addition of the FMOC amino acid chloride to a solution of the amino acid ester and the base taken as HCl acceptor. Direct reaction with the acid chloride competes favorably with oxazolone formation. Similarly, under two-phase conditions with $NaHCO_3$ or Na_2CO_3 in the aqueous phase, the desired direct reaction occurs quickly in the organic phase. If the amino acid ester is omitted, oxazolone builds up slowly (ca. 10 min) in the organic phase.

(14) For a recent citation to the similar stability of alkyl fluoroformates toward solvents such as DMSO relative to the analogous chloroformates, see: Dang, V. A.; Olofson, R. A. *J. Org. Chem.* **1990**, *55*, 1851.

(15) As a first model to confirm direct acylation via FMOC amino acid fluorides, prothrombin (1–9) ii was assembled manually on a batch synthesizer in DMF solution using 1 g of a TFA-sensitive polyamide resin bearing 0.1 mequiv/g of FMOC-valine. Glu, Leu, Phe, Gly, Lys, and Ala were incorporated as the FMOC amino acid fluorides (4 equiv of acid fluoride, 0.08 M in DMF, 4 equiv of DIEA) and Asn as pentafluorophenyl ester. Deblocking was carried out for 4 min twice with 20% piperidine in DMF. All washing steps involved DMF. Resin samples were removed after each 10-min coupling period and tested by the ninhydrin method. All couplings were complete by this time except for the Phe-to-Leu coupling, which was allowed to proceed for 25 min. No couplings were repeated. Final deblocking and removal from the resin (950 mg; at each coupling stage, 5–10 mg of resin was lost due to the ninhydrin tests) was achieved with 30 mL of TFA containing 5% H_2O and 5% *m*-cresol at 20 °C for 2 h to give 74 mg of peptide ii as the TFA salt, MS/FAB 1006 (MH^+), calcd 1005 (M), identified by coelution with an authentic sample.

H-Ala-Asn-Lys-Gly-Phe-Leu-Glu-Glu-Val-OH
ii

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Supplementary Material Available: HPLC trace of crude prothrombin ii (1 page). Ordering information is given on any current masthead page.

Biosynthesis of 3,6-Dideoxyhexoses: Stereochemical Analysis of the Deprotonation Catalyzed by the Pyridoxamine 5′-Phosphate Dependent Enzyme CDP-4-keto-6-deoxy-D-glucose-3-dehydrase Isolated from *Yersinia pseudotuberculosis*

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The 3,6-dideoxyhexoses are found in the O-specific side chains of cell wall lipopolysaccharides of a number of Gram-negative bacteria, where they have been identified as the dominant antigenic determinants.[1] Studies of the biosynthesis of CDP-ascarylose (**1**), the 3,6-dideoxy-L-*arabino*-hexopyranose derived from CDP-4-keto-6-deoxy-D-glucose (**2**), have shown that the C–O bond cleavage at C-3 is catalyzed by CDP-4-keto-6-deoxy-D-glucose-3-dehydrase (E_1), a pyridoxamine 5′-phosphate (PMP) dependent enzyme.[2] The proposed mechanism of this enzyme-catalyzed reaction involves the coupling of the coenzyme with the C-4 keto group of the substrate (**2**) to form a Schiff base (**3**) followed by a C-4′ proton abstraction from the resulting adduct (**3**) that triggers the expulsion of the C-3 hydroxy group (Scheme I).[2c,d] This enzymatic process is unique since it represents the only PMP-dependent catalysis that is not a transamination reaction. Although a reductive step catalyzed by an NAD(P)H-dependent reductase (E_3) has been shown to constitute the second phase of C-3 deoxygenation (Scheme I),[2a,d,3] the putative $\Delta^{3,4}$-glucoseen intermediate (**4**) has never been isolated or characterized.[2] In an attempt to explore the mechanism of this deoxygenation in detail, we have recently isolated an "E_1 equivalent" from *Yersinia pseudotuberculosis*[4] and determined the stereospecificity of its mediated deprotonation from the PMP–substrate adduct (**3**). Summarized in this paper are the results of this stereochemical

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(4) The original E_1 was isolated from *Pasturella pseudotuberculosis*,[2a] which is now classified as *Yersinia pseudotuberculosis*. However, the strains used in Strominger's studies and our current research are different. This recently purified enzyme consists of a single polypeptide chain with a molecular mass of 49 000 daltons.

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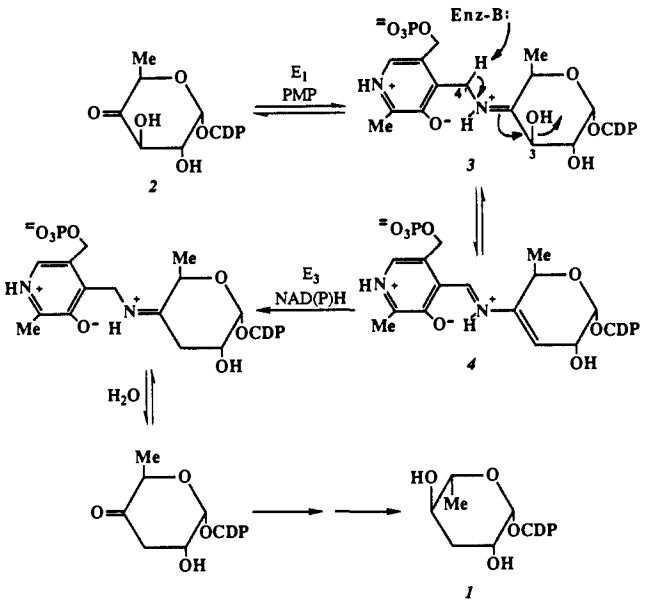
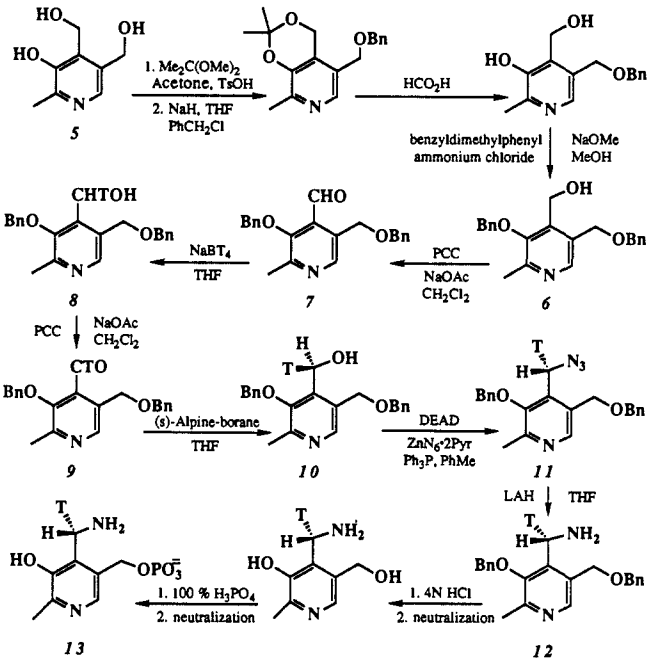
Scheme I



analysis and their implication to the mechanism of the key step initiating C-3 deoxygenation.

It should be apparent, as delineated in Scheme I, that determining the stereospecificity of this enzymatic deprotonation requires the incubation of PMP samples stereospecifically labeled at the C-4′ position. The labeled unphosphorylated coenzyme is commonly prepared by incubating pyridoxal and glutamate with apoaspartate aminotransferase in tritiated buffer.[5] It had also been synthesized by reducing an L-threonine–pyridoxal–metal complex with sodium [^{3}H]borohydride.[6] However, the enzymatic method is laborious and limited to microscale preparation, while the chemical method shows poor asymmetric induction, giving products with low enantiomeric purity. To circumvent these difficulties, we have developed a reaction sequence producing the requisite chirally labeled PMP with high stereochemical purity in satisfactory yield. As shown in Scheme II, the key intermediate **7**, derived from pyridoxine **5** via a series of reactions (overall 56% yield),[7] was reduced with sodium [^{3}H]borohydride. The resulting pyridoxine **8** (85% yield, 3.1 mCi/mmol) was then oxidized by pyridinium chlorochromate (PCC). Since a large kinetic isotope effect was expected for the PCC oxidation,[8] the isolated pyridoxal **9** was found, as anticipated, to retain most of the isotopic labeling (94% yield, 3.0 mCi/mmol). Conversion of **9** to the *pro-R* chirally labeled pyridoxine **10** was accomplished by treatment with *S*-Alpine-Borane in THF, a well-defined asymmetric reduction (85% yield).[9] The stereospecificity of this step was determined to be greater than 94% based on ^{1}H NMR analysis of the mandelic ester of **10**,[10] which was separately prepared under identical conditions from deuterated **9**.[11] A zinc azide/bispyridine-mediated Mitsunobu substitution[12] of **10** led to **11** (93% yield) which, upon

Scheme II



treatment with lithium aluminum hydride, was swiftly transformed to the (4′*S*)-[4′-^{3}H]pyridoxamine (**12**; 88% yield).[13] Acid hydrolysis to remove the benzyl protecting groups[14] followed by phosphorylation[15] completed the synthesis of (4′*S*)-[4′-^{3}H]PMP (**13**). The overall yield, starting from **5**, was nearly 20%. The same reaction sequence was also used to make (4′*R*)-[4′-^{3}H]PMP by substituting *S*-Alpine-Borane with *R*-Alpine-Borane.

Samples of the chirally labeled PMP coenzymes were then incubated with purified E_1 and substrate **2** that was synthesized in situ from CDP-D-glucose by CDP-D-glucose oxidoreductase.[16,17] An identical mixture containing no CDP-D-glucose was run in parallel as the control. If E_1-catalyzed dehydration is a stereospecific reaction, such an incubation would liberate only one of the C-4′ diastereotopic hydrogens from the ketimine complex **3**. Thus, the incubations were allowed to proceed for 1 h and were then quenched with a 10% aqueous suspension of activated charcoal to absorb PMP.[2c,18] The stereochemical course of this process was deduced by comparing the tritium washout in the supernatant of these samples. Based on this strategy, the incubation of (4′-*S*)-[4′-^{3}H]PMP was found to release 9.5 times as much radioactivity as the 4′-*R*-labeled PMP. Clearly, E_1 is a chiral catalyst that preferentially removes the *pro-S* hydrogen.

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(11) The deuterated analogue of **9** was prepared from **6** via permanganate oxidation, diazomethane esterification, lithium aluminum deuteride reduction, and PCC oxidation.
(12) (a) Viaud, M. C.; Rollin, P. *Synthesis* **1990**, 130. (b) Mitsunobu, O. *Synthesis* **1981**, 1.
(13) The enantiomeric purity of this sample was estimated to be greater than 89% (ee) based on ^{1}H NMR analysis of the camphanic ester of the corresponding deuterated species that was prepared under identical conditions from deuterated **10**: Gerlach, H.; Zagalak, B. *J. Chem. Soc., Chem. Commun.* **1973**, 274. Clearly, the zinc azide/bispyridine-mediated substitution proceeded with clean inversion.
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(16) The CDP-D-glucose oxidoreductase used in these experiments was purified from the same *Y. pseudotuberculosis* strain. It consists of two identical subunits, each with a molecular mass of 42 500 daltons.
(17) The substrate **2** was prepared by incubating CDP-D-glucose (0.4 μmol) and NAD^+ (0.4 μmol) with CDP-D-glucose oxidoreductase (40–60 μg) in potassium phosphate buffer (10 mM, pH 7.5, total volume 220 μL) at 27 °C for 30 min. An aliquot (40 μL) of this mixture was then added to an assay solution containing the labeled PMP coenzyme (4.2 nmol) and E_1 (130 μg) in the same potassium phosphate buffer (total volume 200 μL). The reaction was allowed to proceed at 27 °C for 1 h.
(18) Activated charcoal (10% solution, 200 μL) was added to the reaction mixture at the end of the incubation. The resulting solution was mixed vigorously on a vortex mixer for 1 min followed by centrifugation to precipitate the charcoal. The supernatant (150 μL) was then removed and analyzed by scintillation counting.

The *pro-S* stereospecificity unearthed in E_1-catalyzed deprotonation agrees with the stereochemical convergency found for all PLP/PMP-dependent catalysis in which bond cleavage and formation have been demonstrated to occur only at the *si* face of C-4′ in the Schiff base complex.[19,20] Thus, despite the fact that E_1-mediated dehydration represents an unique offshoot of PMP-dependent catalysis, the stereochemical consistency of E_1 and all other PLP/PMP enzymes suggests that E_1 behaves as a normal vitamin B_6 dependent catalyst and C-3 deoxygenation follows the well-established PLP/PMP cofactor chemistry. This result also supports Dunathan's hypothesis that this class of enzymes, regardless of its catalytic diversity, evolved from a common progenitor.[19,21]

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Entry to the Solution Chemistry of Niobium and Tantalum Sulfides: Synthesis of Soluble Forms of the Tetrathiometalates $[MS_4]^{3-}$

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The tetrathiometalates $[MS_4]^{2-}$ are fundamental structural and reactive entities in transition-metal sulfide chemistry.[2] They serve as primary precursors for the synthesis of a diverse array of compounds ranging from small metal–sulfide anions to heterometal clusters.[2,3] The species $[VS_4]^{3-}$, $[MoS_4]^{2-}$, $[WS_4]^{2-}$, and $[ReS_4]^{1-}$ are generally prepared by action of H_2S on a strongly alkaline solution of the appropriate oxometalate[2] and have been obtained as soluble compounds. The existence of $[VS_4]^{3-}$, recently obtained as a soluble and stable Li^+ salt,[4] imples stability of $[MS_4]^{3-}$ (M = Nb, Ta), a matter confirmed by the high-temperature synthesis of $K_3[MS_4]$ from the elements (8 d, 1150 K).[5] These compounds are described as soluble in nonaqueous solvents, but characterization of solution species has not been reported. Low-temperature preparations of $[MS_4]^{3-}$ have been hampered by the lack of suitable oxometalate precursors, and as products of solution reactions these species have remained elusive. We report here facile *solution* syntheses of $[MS_4]^{3-}$.

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$Li_3[NbS_4]\cdot 2TMEDA$

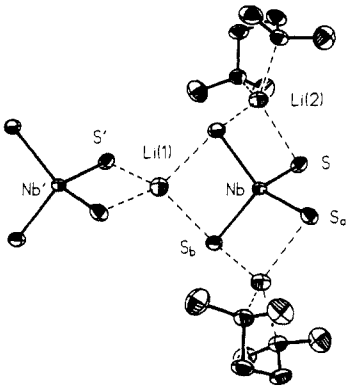

Figure 1. The structure of $Li_3[NbS_4]\cdot 2TMEDA$, showing 50% thermal ellipsoids and the atom-labeling scheme. The structure of $Li_3[TaS_4]\cdot 2TMEDA$ is isomorphous. Bond distances (Nb/Ta, Å): M–S, 2.274 (1)/2.280 (2); Li(1)–S, 2.512 (1)/2.518 (2); Li(2)–S, 2.465 (4)/2.40 (1). S–M–S bond angles (Nb/Ta, deg): 106.98 (4)/107.1 (1), bridged by Li(1); 106.92 (2)/104.0 (2), bridged by Li(2); 114.64 (3)/117.7 (2), unbridged.

Our first attempt to prepare $[MS_4]^{3-}$ (reaction 1, X = Et_4NCl) instead afforded the cages $[M_6S_{17}]^{4-}$[6] (reaction 2), heretofore the

$$M(OEt)_5 + 4(Me_3Si)_2S + \text{X} \xrightarrow{\text{MeCN}} \begin{cases} (Et_4N)_3[MS_4] + 5Me_3SiOEt + 3Me_3SiCl & (1) \\ (Et_4N)_4[M_6S_{17}] & (2) \\ Li_3[MS_4] + 5Me_3SiOEt + 3Me_3SiOMe & (3) \end{cases}$$

only known soluble sulfides of Nb/Ta. However, anaerobic reaction 3 (X = LiOMe) generated after 3 h an orange-to-red supernatant and a precipitate, presumably $Li_3[NbS_4]\cdot 4MeCN$. Separation and dissolution of the latter in a solution of 6 equiv of *N,N,N′,N′*-tetramethylethylenediamine in acetonitrile followed by precipitation with ether afforded light-yellow $Li_3[MS_4]\cdot 2TMEDA$ (ca. 60%; M = Nb, Ta).[7] Compound identities were established by spectroscopy[8] and X-ray crystallography.[9]

The two compounds are isomorphous and isometric;[9] their structures are shown in Figure 1. The M = Nb/Ta atom resides on a position of 222 site symmetry, requiring D_{2d} anion symmetry with a distorted tetrahedral arrangement of sulfur atoms. Atom Li(1), also on a 222 site, interacts with four sulfur atoms from two adjacent anions, forming a linear polymeric chain. Symmetry-related atoms Li(2) bind to opposite pairs of sulfur atoms

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(7) Also, addition of THF to the M = Nb reaction mixture containing the precipitate resulted in a homogeneous solution; ether diffusion yielded pale yellow, readily desolvated $Li_3[NbS_4]\cdot 4MeCN$, which was identified crystallographically.

(8) λ_{max} (ϵ_M) (acetonitrile): 274 (ν_2, 14900), 340 (ν_1, 10000) nm ($[NbS_4]^{3-}$); 241 (ν_2, 17500), 249 (ν_2, sh, 16000), 300 (ν_1, 10700) nm ($[TaS_4]^{3-}$). ^{93}Nb NMR (CD_3CN/TMEDA. $(Et_4N)[NbCl_6]$ external reference): 1214 ppm, $\Delta H_{1/2} \approx 2000$ Hz). ν_{MS} (KBr) 458 (Nb), 435 (Ta) cm^{-1}.

(9) X-ray data were collected on a Nicolet P3F diffractometer with Mo Kα radiation. Structures were solved by direct methods or Patterson synthesis. Crystallographic data are given as *a*, *b*, *c*; α, β, γ; space group, *Z*, $2\theta_{min/max}$, unique data ($F_o^2 \geq 3\sigma(F_o^2)$), *R* (%). $Li_3[NbS_4]\cdot 2TMEDA$ (180 K): 13.983 (6), 13.983 (6), 6.152 (3) Å; $P\bar{4}n2$, 2, 3.0°/50.0°, 880, 2.23, $Li_3[TaS_4]\cdot 2TMEDA$ (180 K): 13.994 (2), 13.994 (2), 6.163 (1) Å; $P\bar{4}n2$, 2, 3.0°/55.0°, 1026, 6.10. $(Me_4N)_3[NbFe_2S_4Cl_4]\cdot DMF$ (180 K): 11.639 (2), 15.788 (3), 19.560 (3) Å; 70.11 (1)°, 89.59 (2)°, 86.83 (2)°; $P\bar{1}$, 4, 3.0°/50.0°, 9450, 3.23. $(Et_4N)_3[TaFe_2S_4Cl_4]$ (298 K): 13.212 (4), 18.515 (5), 18.039 (4) Å; 90°, 111.09 (2)°, 90°; $P2_1/n$, 4. The structure of this compound was only partially refined owing to extreme cation disorder; however, the refinement demonstrated that the anion is isostructural with $[NbFe_2S_4Cl_4]^{3-}$.

0002-7863/90/1512-9654$02.50/0