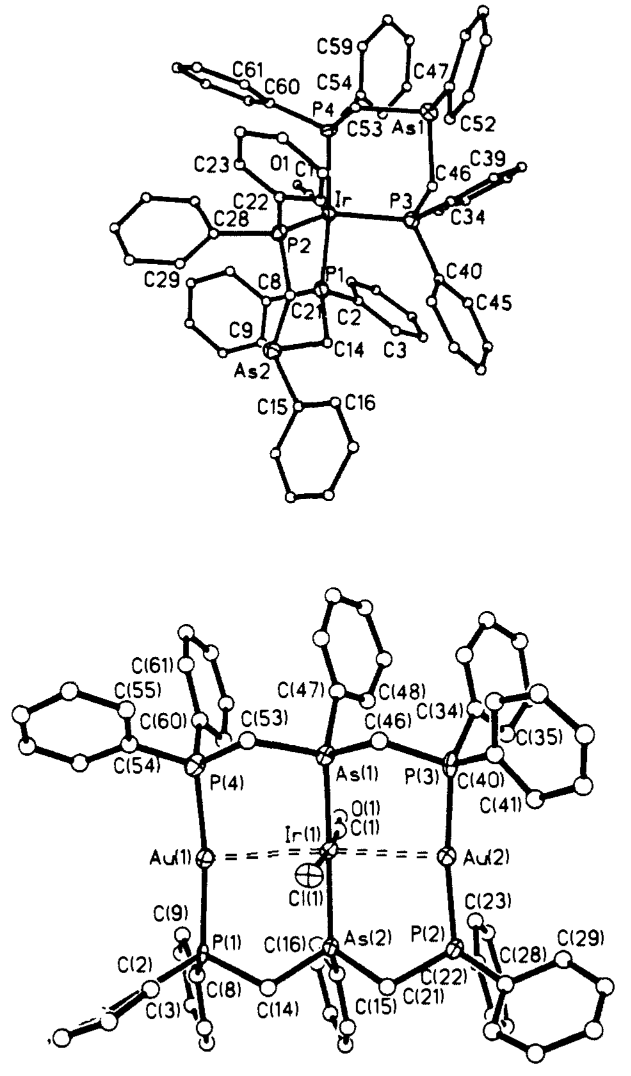

Figure 1. Top: Cation of **3**, $[Ir(CO)(dpma)_2]^+$; bond distances (angstroms), Ir-P(1), 2.367 (4); Ir-P(2), 2.400 (4); Ir-P(3), 2.358 (4); Ir-C(1), 1.853 (4); Ir···As(1), 4.316 (2); Ir···As(2), 4.384 (2); angles (degrees), P(1)-Ir-P(4), 169.1 (1); P(2)-Ir-P(3), 108.1 (1); P(2)-Ir-C(1), 127.3 (4); P(3)-Ir-C(1), 124.6 (4). Bottom: cation of **4**, $[Au_2Ir(CO)Cl(\mu\text{-dpma})_2]^+$; bond distances (angstroms), Au(1)-Ir(1), 3.013 (2), 3.014 (2); Au(2)-Ir(1), 2.985 (2), 3.025 (2); Au(1)-P(1), 2.318 (10), 2.306 (9); Au(1)-P(4), 2.306 (10), 2.303 (10); Au(2)-P(2), 2.286 (10), 2.318 (10); Au(2)-P(3), 2.315 (10), 2.297 (9); Ir(1)-As(1), 2.409 (4), 2.416 (4); Ir(1)-As(2), 2.407 (4), 2.408 (4); Ir(1)-Cl(1), 2.384 (11), 2.381 (10); Ir(1)-C(1), 1.78 (4), 1.84 (4); angles (degrees), Au(1)-Ir(1)-Au(2), 157.7 (1), 152.6 (1); P(1)-Au(1)-P(4), 169.4 (4), 173.8 (4); P(2)-Au(2)-P(3), 167.7 (4), 161.7 (4); As(1)-Ir(1)-As(2), 170.0 (2), 170.6 (2).

Significant Au-Ir interactions exist within **4**. The Au-Ir distances are nearly equal, and the Au-Ir-Au angle is slightly bent. The electronic absorption spectrum of **4** shown in Figure 2 shows that the $IrP_2Cl(CO)$ chromophore [which has λ_{max} = 438, 387, 339 in $Ir(CO)Cl(PPh_3)_2$][9] is strongly perturbed by the proximity of the two gold ions. The spectrum is remarkably similar to that of **2** (λ_{max} = 508, ϵ = 32 000). Complex **4** is strongly luminescent in solution. As seen in Figure 2, there are two emission bands, both of which have excitation profiles that resemble the absorption spectrum. The high-energy emission is attributed to fluorescence while the lower energy band is probably due to phosphorescence. The temperature dependence of the spectrum supports this assignment. On cooling to −196 °C, the intensity of the low-energy emission increases relative to that of the higher energy emission as shown in Figure 2. These electronic spectral features can readily be accounted for by modifying the simple molecular orbital picture developed for the $d^8d^{10}d^8$ Ir^I–Au^I–Ir^I chain to this $d^{10}d^8d^{10}$ chain in which the predominant interactions involve the filled d_{z^2} and empty p_z orbitals that are directed along the Au-Ir-Au axis.[2]

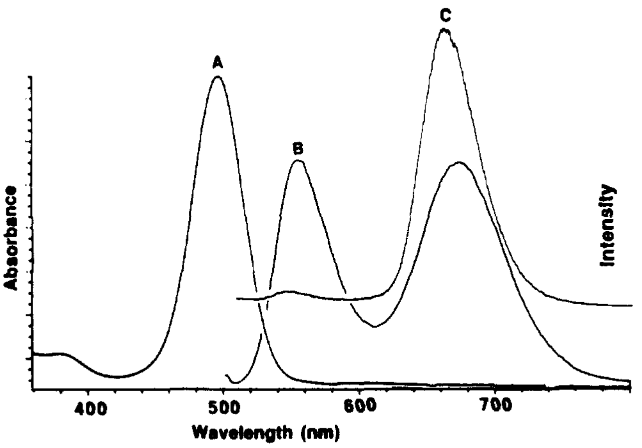

Figure 2. A, electronic absorption (λ_{max} = 498 nm, ϵ = 31 400 L mol^{-1} cm^{-1}); B, uncorrected emission [λ(excitation) = 500 nm] spectra for $[Au_2Ir(CO)Cl(\mu\text{-dpma})_2][PF_6]_2$ in dichloromethane solution at 23 °C; C, uncorrected emission at 77 K.

Preliminary results indicate that **3** reacts with a variety of other transition-metal ions including Ag^I, Pd^{II}, and Ir^I. The structures and properties of the products are under investigation.

Acknowledgment. We thank the National Science Foundation (CHE-8941209 and CHE-8519557) for support, Johnson Matthey, Inc., for a loan of precious metal salts, and Professor H. Hope for experimental assistance. The diffraction and computing equipment used in this study were purchased under NSF Grant CHE-8802721 to the University of California, Davis.

Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and data collection parameters for **3** and **4** (23 pages). Ordering information is given on any current masthead page.

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Reactivity of a Sc-Si Bond toward CO and $CN(2,6\text{-}Me_2C_6H_3)$. Generation and Reactivity of an Apparent Silene Intermediate Resulting from Isocyanide Coupling at Scandium

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Electron-deficient alkyl and silyl complexes of d^0 metals generally combine with CO or CNR (isocyanides) to form reactive η^2-COR′ or η^2-C(NR)R′ derivatives.[1,2] In some cases, products

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of CO–CO or CNR–CNR coupling result.[2] Although it appears that transient ketene or ketene-like intermediates can play an important role in the observed reaction chemistry, the indirect evidence for these intermediates leaves them rather ill-defined.[2a,b,d] The reaction chemistry derived from these apparent ketene complexes is dependent on the nature of the d^0 center, but few of these trends are presently understood. We are surveying the reactivity of various d^0 metal silyl complexes toward unsaturated substrates and have examined reactions of the scandium silyl $Cp_2Sc[Si(SiMe_3)_3](THF)$ (**1**) with carbon monoxide and the isocyanide CN(Xyl) (Xyl = $2,6\text{-}Me_2C_6H_3$). These reactions reveal new chemical processes involving CO–CO and CNR–CNR coupling promoted by a d^0 metal center. The isocyanide coupling reaction reported here affects cleavage of the $Si(SiMe_3)_3$ group via a remarkable metal-mediated rearrangement that probably involves a reactive silene intermediate.

Synthesis of **1** from $[Cp_2ScCl]_2$ and $(THF)_3LiSi(SiMe_3)_3$ follows analogous procedures for other d^0 $M\text{–}Si(SiMe_3)_3$ derivatives.[3] This yellow, crystalline complex appears to be the first silyl derivative reported for a group 3 transition metal.[4,5]

Carbonylation of **1** in methyltetrahydrofuran (50 psi of CO) gave an orange complex (**2**), that was characterized in solution by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of **2**-$^{13}C_2$ (prepared from **1** and ^{13}CO) contains doublets at δ 142.21 and 158.57 ($^1J_{CC}$ = 84 Hz), indicating coupling of two CO molecules. Since these NMR parameters are in close agreement with those observed for $Cp^*Cl_3Ta[O^{13}C(SiMe_3)^{13}C(2,6\text{-}Me_2NC_5H_3)O]$ (d, δ 139.7 and d, δ 149.7; $^1J_{CC}$ = 84 Hz),[2a] we characterize **2** as the ketene adduct shown in Scheme I. Note that an analogous derivative of tantalum, $Cp^*Cl_3Ta[OC(SiMe_3)C(OC_5H_{10})O]$, appears to decompose rapidly via ether cleavage to $Cp^*Cl_3Ta[OCH(SiMe_3)C(O)O(CH_2)_3CH{=}CH_2]$.[2a] Removal of solvent from **2** results in isolation of a green solid, which exhibits spectroscopic properties distinct from those of **2**. This green complex (**3**), which may be crystallized from pentane, results from loss of methyltetrahydrofuran from **2** and can also be prepared directly from **1** by carbonylation in nonpolar solvents. Its characterization as an enedione diolate (see Scheme I) was facilitated by mass spectroscopy and the ^{13}C NMR spectrum of **3**-$^{13}C_2$, which exhibits two well-resolved AA′BB′ multiplets centered at δ 243.97 and 155.89.[5] Two enedione diolate structures are possible:[2b,d] the one shown in Scheme I and its rotamer with six-membered chelate rings.[6] The apparent lability of the methyltetrahydrofuran in **2** suggests that formation of enedione diolate complexes such as **3** may occur via dimerization of a ketene derivative.

Unlike carbon monoxide, isoelectronic CN(Xyl) reacts with **1** to afford an isolable monoinsertion product, the yellow η^2-iminosilaacyl **4**. Compound **4** is characterized by a ν(CN) stretching frequency in the infrared spectrum at 1500 cm^{-1} and a ^{13}C NMR

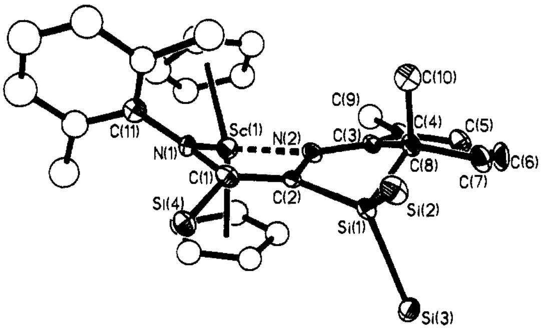
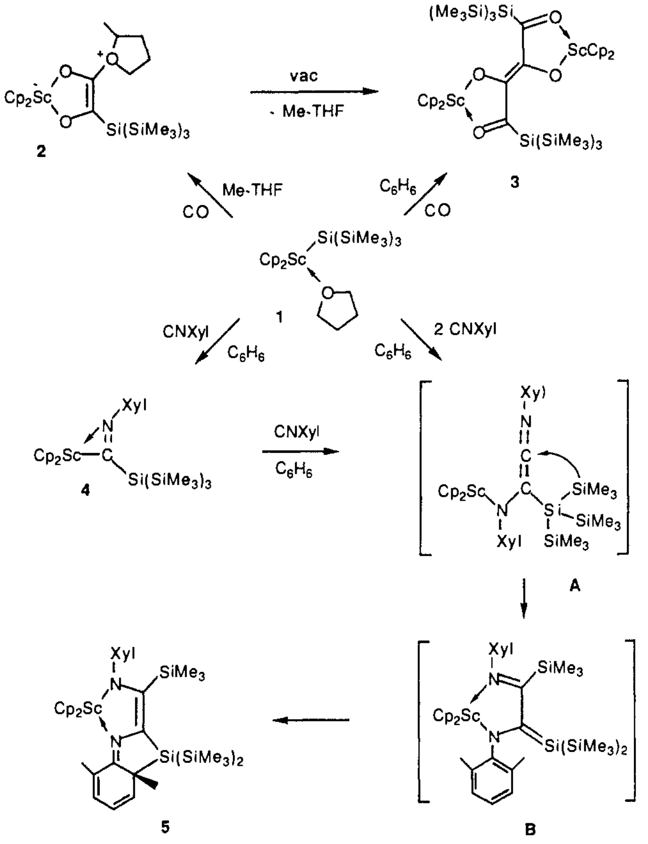


Figure 1. ORTEP view of **5**. Methyl groups on Si(2), Si(3), and Si(4) are omitted for clarity. Important bond distances (angstroms) and angles (degrees) are as follows: Sc(1)–N(1) 2.133 (7), Sc(1)–N(2) 2.324 (8), N(1)–C(11) 1.416 (9), N(1)–C(1) 1.413 (12), C(1)–C(2) 1.375 (12), C(2)–N(2) 1.469 (11), N(2)–C(3) 1.322 (11), C(3)–C(4) 1.452 (12), C(4)–C(5) 1.344 (15), C(5)–C(6) 1.419 (17), C(6)–C(7) 1.322 (14), C(7)–C(8) 1.509 (13), C(3)–C(8) 1.504 (15), N(1)–Sc(1)–N(2) 76.6 (3), Sc(1)–N(1)–C(1) 110.5 (5), Sc(1)–N(2)–C(2) 105.3 (5), C(2)–N(2)–C(3) 113.6 (7), C(2)–Si(1)–C(8) 86.6 (4), Si(2)–Si(1)–Si(3) 111.0 (2).

Scheme I



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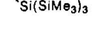
[5] For **1**: ^1H NMR (benzene-d_6, 300 MHz, 25 °C) δ 0.50 (s, 27 H), 0.98 (m, 4 H), 2.99 (m, 4 H), 6.12 (s, 10 H). Anal. C, H. An X-ray structure for **1** has been determined.[4] For **2**-^{13}C: ^{13}C NMR (methyltetrahydrofuran, benzene-d_6 reference, 75.5 MHz, 25 °C) δ 142.21 (d, $^1J_{CC}$ = 84 Hz), 158.57 (d, $^1J_{CC}$ = 84 Hz). For **3**: ^1H NMR (benzene-d_6, 300 MHz, 25 °C) δ 0.36 (s, 54 H), 6.24 (s, 20 H); $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 25 °C, INEPTR) δ −61.46 ($\mathit{Si}(SiMe_3)_3$), −11.07 ($Si(\mathit{Si}Me_3)_3$). For **3**-$^{13}C_2$, computer simulation of the ^{13}C spectrum yielded the following: J_{AB} = 48.9 Hz, $J_{BB'}$ = 73.4 Hz, $J_{AB'}$ = 8.8 Hz, $J_{AA'}$ = 0.2 Hz. MS (EI): parent ion observed at *m/e* 956. Anal. C, H. For **4**: ^1H NMR (benzene-d_6, 300 MHz, 25 °C) δ 0.22 (s, 27 H, $SiMe_3$), 2.25 (s, 6 H, $\mathit{Me}_2C_6H_3$), 6.12 (s, 10 H, Cp), 6.86 (m, 3 H, $Me_2C_6\mathit{H}_3$). Anal. C, H. For **5**: ^1H NMR (benzene-d_6, 300 MHz, 25 °C) δ 0.07 (s, 9 H, $SiMe_3$), 0.20 (s, 9 H, $SiMe_3$), 0.35 (s, 9 H, $SiMe_3$), 5.87 (s, 5 H, C_5H_5), 6.22 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 25 °C) δ 2.30 ($Si\mathit{C}H_3$), 2.83 ($Si\mathit{C}H_3$), 3.12 ($Si\mathit{C}H_3$), 110.55 (C_5H_5), 111.80 (C_5H_5). Anal. C, H.

[6] The alternative structure (see ref 2d) is



chemical shift for the iminosilaacyl carbon at δ 299.07.[3a,b] Addition of 1 equiv of CN(Xyl) to a benzene solution of **4**, or reaction of **1** with 2 equiv of CN(Xyl), results in formation of a blue complex **5**. The combustion analysis of isolated **5** is consistent with a 1:2 adduct of **1** with isocyanide, $Cp_2Sc(CN(Xyl))_2Si(SiMe_3)_3$. However, ^1H NMR data for **5** indicate a complex structure and the presence of three inequivalent $SiMe_3$ groups in a 1:1:1 ratio.[5] Formation of X-ray-quality, blue crystals from diethyl ether allowed complete characterization of this compound.

The crystal structure[7] (Figure 1) shows that **5** is the product of an isocyanide-coupling reaction that results in further rearrangements. The structure drawn in Scheme I reflects the observed structural parameters. The chelate ring of **5** is derived from the two isocyanide groups and contains a Sc(1)–N(1) single bond (2.133 (7) Å), a longer (dative) Sc(1)–N(2) bond (2.324 (8) Å), and a C=C double bond (C(1)–C(2) = 1.375 (12) Å). Migration of an $SiMe_3$ group to C(1) results in reduction of the C(1)–N(1) bond order, which exhibits a C–N bond distance (1.413 (12) Å) that is intermediate between those observed for single and double bonds. The C(2)–N(2) distance is significantly longer, 1.469 (11) Å, and more typical for a C–N single bond, while the C(3)–N(2) distance (1.322 (11) Å) clearly reflects double-bond character. The $Si(SiMe_3)_2$ group is incorporated as part of a five-membered ring that is fused to both the chelate ring and a cyclohexadiene ring derived from the xylyl group of an isocyanide.

A possible mechanism for formation of **5** from **4** and CN(Xyl) is given in Scheme I. Precedents in η^2-silaacyl chemistry suggest that the iminosilaacyl group of **4** should be susceptible to nucleophilic attack by isocyanide to give a ketenimine intermediate (A).[2a,3a] A closely related ketenimine complex, $Cp_2(Cl)Zr[OC(SiMe_3)(CN(Xyl))]$, has been characterized in solution.[3a] Migration of a trimethylsilyl group to the α-carbon of the ketenimine ligand results in intermediate B, which possesses a reactive Si=C double bond. Ishikawa and co-workers have observed 1,3-silyl shifts from silicon to carbon to generate silene (Si=C) intermediates in the coordination sphere of nickel.[8] Cycloaddition of the Si=C double bond in B to the adjacent xylyl ring then gives the connectivity observed for the product. Although attempts to trap the proposed silene intermediate with $(MeO)_3SiH$, Me_3SiOMe, and 2,3-dimethylbutadiene were unsuccessful, this is not unexpected since intramolecular rearrangement of high-energy intermediate B to **5** should be quite rapid. It is hoped that further insight into mechanistic details of this unprecedented rearrangement will result from future investigations.

Acknowledgment is made to the Air Force Office of Scientific Research, Air Force Systems Command, USAF, for support of this work under Grant No. AFOSR-88-0273. T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988–1990).

Supplementary Material Available: Characterization data for **1** and **3–5** and tables of crystal, data collection, and refinement parameters, atomic coordinates and isotropic displacement parameters, bond distances and angles, and hydrogen atom coordinates for **5** (10 pages); listings of observed and calculated structure factors for **5** (14 pages). Ordering information is given on any current masthead page.

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(7) $C_{37}H_{46}N_2Si_4Sc$: monoclinic, $P2_1/c$, a = 17.97 (1) Å, b = 8.613 (5) Å, c = 25.88 (2) Å, β = 101.86 (7)°, V = 3921 (5) $Å^3$, Z = 4, μ = 3.32 cm^{-1}, Mo Kα radiation (λ = 0.71073 Å), 297 K (24 °C), Nicolet R3m/V diffractometer with graphite monochromator; 4166 reflections were collected (3° $\leq 2\theta \leq$ 40°), using 2θ scans. Of these, 3674 reflections were unique (R_{int} = 3.26%) and 2171 were considered observed ($F > 6.0\sigma(F)$). Solution was by Patterson methods and refinement by full-matrix least-squares methods (SHELXTL PLUS computer programs, Nicolet Instrument Corp., Madison, WI). Due to limited data, only the scandium, silicon, nitrogen, and C(1)–C(8) atoms were refined anisotropically, and hydrogen atoms were refined in fixed and idealized positions. The Cp ligands were refined as rigid, idealized pentagons, and the C(11)–C(16) aromatic ring was refined as an idealized hexagon. R_F = 6.21%, R_{wF} = 6.72%, data/parameter = 9.8, GOF = 2.07, largest Δ/σ = 0.033, highest peak = 0.53 $e/Å^3$.

(8) (a) Ishikawa, M.; Ono, T.; Saheki, Y.; Minato, A.; Okinoshima, H. *J. Organomet. Chem.* **1989**, *363*, C1. (b) Ohshita, J.; Isomura, Y.; Ishikawa, M. *Organometallics* **1989**, *8*, 2050.

Deoxyribose-5-phosphate Aldolase as a Synthetic Catalyst[1]

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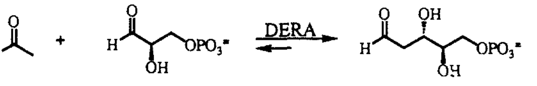
Received November 29, 1989

Enzyme-catalyzed stereocontrolled aldol condensations are valuable in organic synthesis, particularly in the synthesis of carbohydrates and related substances.[2,3] We report here an initial study on the synthetic utility of a bacterial 2-deoxyribose-5-phosphate aldolase (DERA, EC 4.1.2.4) overexpressed in *Escherichia coli*.[4] The enzyme DERA catalyzes the reversible aldol reaction of acetaldehyde and D-glyceraldehyde 3-phosphate to form 2-deoxyribose 5-phosphate[5] (eq 1). This enzyme is unique among the aldolases in that it is the only aldolase that condenses two aldehydes. Other aldolases use ketones as aldol dononors and aldehydes as acceptors.



(1)

The purified DERA[4] showed optimal activity at pH 7.5 with the following kinetic constants: V_{max} = 210 units/mg based on the cleavage of 2-deoxyribose 5-phosphate (k_{cat} = 521.1 s^{-1}) and K_m for 2-deoxyribose 5-phosphate = 1.93 mM. At 25 °C in 0.1 M triethanolamine buffer (TEA), pH 7.5, the enzyme is fairly stable, with 70% of the original activity retained after 10 days.

Examination of the substrate specificity[6] of DERA (Tables I and II) indicates that acetone, fluoroacetone, and propionaldehyde can replace acetaldehyde as the nucleophilic component in the aldol reaction. Substitution at C-2 of acetaldehyde with other than a single methyl group is not tolerated. It is of particular interest that the bond formation for fluoroacetone occurs regioselectively at the nonfluorinated carbon. With regard to the specificity of acceptors, many aldehydes as well as aldose sugars and their phosphates are accepted as weak substrates.

Although the enzyme possesses such a broad substrate specificity, the rates of condensation with unnatural substrate are relatively low and a relatively large amount of enzyme is required to achieve useful synthesis. The high stability and specific activity and the ready availability of the enzyme, however, appear to outweigh this shortcoming.

The following are representative syntheses with DERA.

(*S*)-4-Hydroxy-5-methylhexan-2-one. To a 100-mL solution containing 0.2 M acetone, 0.1 M isobutyraldehyde, 0.1 M TEA, and 1 mM EDTA was added 1000 units of DERA in a dialysis bag.[2] The reaction vessel was stoppered, and the solution was stirred for 3 days at room temperature and then continuously extracted with ether for 16 h. The solvent was removed by slow fractional distillation to yield the crude product, which was chromatographed on silica gel (ether/hexane, 1:1), to yield 0.56 g, 44% yield of the title compound: $[\alpha]_D$ –55.0° (c 1.4, $CHCl_3$);

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(1) Taken from the Ph.D. Thesis of C.F.B. at Texas A&M University, 1989. This work was supported by the NIH (GM 44154-01).

(2) Toone, E. J.; Simon, E. S.; Bednarski, M. D.; Whitesides, G. M. *Tetrahedron* **1989**, *45*, 5365 and references cited.

(3) Wong, C.-H. *Science* **1989**, *244*, 1145 and references cited.

(4) To construct an overproducing *E. coli* species, plasmid p VH 17 which contains the deo C gene (Valentin-Hansen, P.; Aiba, H.; Schumperli, D. *EMBO J.* **1982**, *1*, 317) was introduced into *E. coli* EM2929. A 6-L growth of *E. coli* EM2929/pVH17 produced approximately 124000 units of the aldolase. One unit = 1 μmol of 2-deoxyribose 5-phosphate cleaved per minute. About 3.1 × 10^4 units can be prepared for synthesis.

(5) The equilibrium constant for the condensation is 4.2 × 10^3 M^{-1} (Pricer, W. E.; Horecker, B. L. *J. Biol. Chem.* **1960**, *235*, 1292).

(6) The substrate specificity of *E. coli* DERA was not reported previously. The enzyme from *Lactobacillus plantarum* was reported to accept glycoaldehyde phoshate, D-ribose 5-phosphate, and D-erythrose 4-phosphate as acceptor substrate, and propionaldehyde as donor according to the activity assay (Rosen, O. M.; Hoffee, P.; Horecker, B. L. *J. Biol. Chem.* **1965**, *240*, 1517.

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