struction, **5** was dissolved in 6.8 M NH_4OAc, which was found to be capable of effecting solvolysis of the 1,4-lactone at 25 °C, and then heated (110 °C; 3 h) with 1.0 equiv of $Cu(OAc)_2$ and excess HCHO. These conditions were found to be optimal for the desired transformation. Workup (desalting on Biorex-70, crystallization from CH_3OH–EtOAc) gave N^{α}-acetyl-L-*erythro*-β-hydroxyhistidine as a pale green solid (Cu(II) complex of **3**) routinely in about 25% yield, $[\alpha]^{25}_D$ +28° (*c* 0.28, H_2O). As 2-acetamido-2-deoxy-D-mannono-1,4-lactones are known[10,11a] to epimerize readily at C-2 and to eliminate water in the presence of amines, and since an authentic sample of **3** decomposed slowly under the reaction conditions, careful characterization of the product was deemed necessary. After removal of Cu(II) (H_2S; Dowex 50-X8 (H^+ form)), the product was shown to be identical with authentic N^{α}-acetyl-DL-*erythro*-β-hydroxyhistidine as judged by paper chromatography in several solvent systems and NMR ((D_2O, external Me_4Si) δ 2.00 (s, 3), 4.66 (d, 1, J = 6 Hz), 5.28 (d, 1, J = 6 Hz), 7.41 (s, 1), and 8.66 (s, 1)), but not with an authentic sample of the N-acetylated threo isomer. Comparison with authentic samples after deacetylation in quantitative yield (1 M HCl, 3 h, 100 °C) demonstrated that the product had the erythro configuration; $[\alpha]^{25}_D$ +36° (*c* 0.96, H_2O).

Mechanistically, the formation of **4** must parallel the formation of other imidazoles from the respective α-hydroxyaldehydes and ketones. This could involve the well-precedented[15,16] Cu(II) oxidation of the α-hydroxyaldehyde derived from **5** to a dicarbonyl species, the latter of which could form the respective diimine. Condensation of the diimine with formaldehyde would then afford **3**. Alternatively, after solvolysis of **5** in aqueous NH_4OAc, the derived hydroxyaldehyde could react with 2 equiv of NH_3 to form a vicinal enediamine. Oxidation of this species before or after condensation with HCHO could also lead to the formation of **3**.[14,16] As Cu(II) binds tightly to **3**, it is also possible that the metal facilitates the transformation in a nonoxidative fashion. One may note, however, that formation of **3** using stoichiometric $Cu(OAc)_2$ in the absence of O_2, such that no Cu(II) was present at the end of the reaction, had essentially no effect on the yield of **3**.

Since the epimers of **4** were less easily accessible from imidazole-4-carboxaldehyde, it was also of interest to attempt their preparation in analogy with the transformations **2** → **3** → **4**. 2-Acetamido-2-deoxy-D-glucono-1,4-lactone was prepared as described[11b] and utilized for this purpose; its conversion to D-*threo*-β-hydroxyhistidine[17] was achieved in yields comparable to those obtained for **4**. On the basis of these experiments, it is suggested that 2-acetamido-2-deoxy-1,4-lactones may be of more general utility as convenient starting materials for the synthetic elaboration of amino acids having chirality at positions in addition to C^{α}.

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(7) In a typical experiment, imidazole-4-carboxaldehyde (7.5 g, 78 mmol) and *N*-pyruvylideneglycinatoaquocopper(II) dihydrate (19.5 g, 75 mmol) were stirred in 300 mL of H_2O for 4 h. The solution was acidified (HOAc, pH 4.5), treated with H_2S, and filtered.[8] After precipitation of the product from the neutralized filtrate with aqueous $HgCl_2$, the solid was dissolved in 1 M HCl and treated with H_2S; concentration of the filtrate (decolorization) gave DL-*erythro*-β-hydroxyhistidine hydrochloride (12.6 g, 81%) as a solid, contaminated with (<10%) DL-*threo*-β-hydroxyhistidine hydrochloride. Crystallization from H_2O–C_2H_5OH–*i*-C_3H_7OH gave **4** as colorless needles (11.0 g, 70%): mp 228 °C dec; NMR (D_2O, ext Me_4Si) δ 4.64 (d, 1, J = 3 Hz), 5.67 (d, 1, J = 3 Hz), 7.56 (s, 1), and 8.33 (s, 1).

(8) After filtration of Cu_2S, **4** could be obtained directly (albeit in lower yield) by adjusting the solution to pH 6.3–6.4 and permitting the free base to precipitate. Purification was then completed by recrystallization from water (personal communication from Dr. W. A. Szabo, Aldrich Chemical Co.).

(9) D-Glucosamine was oxidized to D-glucosaminic acid (69% yield) with yellow HgO (M. L. Wolfrom and M. J. Cron, *J. Am. Chem. Soc.*, **74**, 1715 (1952)) and then converted to 2-amino-2-deoxy-D-manno-1,4-lactone (77%) as described (P. A. Levene, *J. Biol. Chem.*, **36**, 73 (1918)). Acetylation (Ac_2O; Dowex 1-X4 (HCO_3^- form); vigorous stirring) gave **4** as colorless crystals in 81% yield. The same compound could also be obtained in a single step[10] by Br_2 oxidation of commercially available, albeit expensive, *N*-acetyl-D-mannosamine.

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(17) D-*threo*-β-Hydroxyhistidine hydrochloride was obtained as a pale yellow solid (NMR (D_2O, ext Me_4Si) δ 4.60 (1 H, d, J = 4 Hz), 5.73 (1 H, d, J = 4 Hz), 7.70 (1 H, d, J = 1 Hz), and 8.87 (1 H, d, J = 1); $[\alpha]^{25}_D$ +15° (*c* 1.2, H_2O)) by acid hydrolysis of the initially formed N^{α}-acetyl-D-*threo*-β-hydroxyhistidine (NMR (D_2O, ext Me_4Si) δ 2.03 (3 H, s), 4.62 (1 H, d, J = 3.5 Hz), 5.48 (1 H, d, J = 3.5 Hz), 7.37 (1 H, s), and 8.47 (1 H, s); $[\alpha]^{25}_D$ −17° (*c* 1.25, H_2O)). Limited (<10%) conversion to the erythro species was observed during the synthesis of the threo isomer, presumably reflecting the greater thermodynamic stability of the former; the specific rotations given above for (N^{α}-acetyl)-D-*threo*-β-hydroxyhistidine are not corrected for the epimeric impurities.

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(19) National Science Foundation Predoctoral Fellow, 1975–1978.

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A Facile Synthesis of Substituted *N*-Hydroxy-2-azetidinones. A Biogenetic Type β-Lactam Synthesis

Sir:

Synthesis of 2-azetidinones **1**, the basic structural unit of the β-lactam antibiotics, remains the object of considerable interest, especially because of the recent discovery of unusual, naturally occurring β-lactams.[1] β-Lactam ring synthesis has been approached from nearly every conceivable way.[2-4] For-

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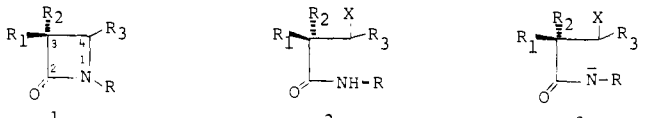


1, 4 R=OH
11 $R=OCH_2Ph$, $R_1=R_2=CH_3$, $R_3=H$
12 11; $R=OCOC(CH_3)_3$
13 11; R=OH
14 11; R=H

2, 5 $R=OCH_2Ph$
6 $R=OCOC(CH_3)_3$
9 $R=OCH_2Ph$, $R_1=R_2=CH_3$, $R_3=H$; X=Cl
10 9; $R=OCOC(CH_3)_3$

3, 7, 8

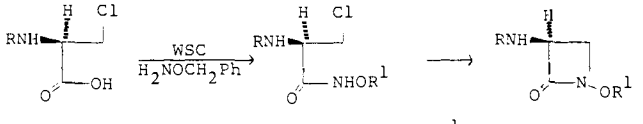
mation of the N-C_4 bond, the method which mimics the proposed biosynthesis, is usually accomplished by cyclization of β-haloamides **2**. Although recent elegant modifications have been devised,[5-10] this approach still requires the use of strong base to form the requisite amide nitrogen anion **3**. Consequently, additional protective steps must be incorporated to avoid competitive elimination and racemization, especially when C_3 is monosubstituted with an amide group as in most β-lactam antibiotics (**1**, R^1 = RCONH, R^2 = H). We describe here a mild, facile N-C_4 bond closure that provides related substituted *N*-hydroxy-2-azetidinones **4** (**1**, R = OH) in a manner compatible with peripheral functionality.

The NH bond of *O*-acyl- and *O*-alkylhydroxamic acids has a p*K* of 6-10;[11,12] yet the corresponding anions can be alkylated inter-[13] or intramolecularly[14] without competitive Lossen rearrangement.[12] Thus, preparation of substituted *N*-hydroxy analogues (**5** and **6**) of the β-lactam precursor **2** was anticipated to allow selective N-H ionization to **7** or **8** and subsequent cyclization under conditions compatible with peripheral functionality (R_1 = RCONH) and retention of configuration at C_3 (R_2 = H).

The model compounds **9** (84%)[15] and **10** (88%) were synthesized by reaction of the corresponding carboxylic acid and O-substituted hydroxylamine with the water-soluble 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (WSC) in DMF-H_2O (~1:4) at pH 4.5.[12] Both compounds cyclized readily (**9** → **11** (oil; IR 1780 cm^{-1}), NaH, DMF, 20 °C, 1 h, 94%; and **10** → **12** (mp 42.5-43.5 °C; IR 1770 cm^{-1}), Li_2CO_3, DMF, 20 °C, 24 h, 76%)). Similar cyclizations providing *N*-alkoxy-3,3-dialkyl-2-azetidinones have been accomplished in pyridine at 90-100 °C.[14,16] Aminolysis of **12**, with benzylamine in THF, cleanly gave the *N*-hydroxy compound **13** (oil, unstable to long storage at −20 °C; IR 1755 cm^{-1}; p*K* = 6.85) as did hydrogenation of **11** (1 atm H_2, 10% Pd/C; CH_3OH; 30 min). In one case, longer hydrogenation (1.5 h) of **11** also produced some of the N-O reduced product **14**[17] (16.5%).

These results encouraged the synthesis of chiral models to test the differentiation of the hydroxamate nitrogen anion and potential anions at either C_3 or a peripheral amide. Thus, *N*-carbobenzoxy-L-β-chloroalanine[18] (**15**, $[\alpha]^{20}_D$ +23.8°; as the dicyclohexylammonium salt[19] in DMF) and *tert*-butoxycarbonyl-L-β-chloroalanine (**16**, mp 123-125 °C dec; $[\alpha]^{20}_D$ + 22.9° (*c* 2, CH_3OH)) were prepared by standard procedures.[20] WSC-mediated coupling of **15** and **16** with *O*-benzylhydroxylamine (DMF-H_2O (1:4), pH 4.5, 30 min) gave the corresponding hydroxamates **17** (mp 146.5-148.5 °C; $[\alpha]^{20}_D$ −32.4° (*c* 2, CH_3OH)) and **18** (mp 89.5-92 °C; $[\alpha]^{20}_D$ −43.8° (*c* 2.2, CH_3OH)), quantitatively (see Scheme I).[21] Cyclization (100 mol % NaH; DMF-CH_2Cl_2 (1:1); 50 °C; 12 h) of **17** and **18** provided the lactams **19** (74-86%; mp 89.5-91 °C; $[\alpha]^{20}_D$ −9 ± 3° (*c* 2, CH_3OH)) and **20** (75-88%; mp 91-92 °C dec; $[\alpha]^{20}_D$ −3.3 ± 0.5° (*c* 2, CH_3OH)). No dehydrohalogenation products were detected; however, if attempted at high concentrations (>0.1 M) traces of polymeric material formed. Performing the reaction for shorter periods (3-4 h) decreased the yield but allowed recovery of starting material with complete retention of optical activity.[22] Reductive hydrolysis (6 N HCl; $Na_2S_2O_4$; 110 °C; 48 h) of **19** gave an amino acid which was identical with L-2,3-diaminopropionic acid (DAPA) by amino acid analysis.[23] Gentle catalytic hydrogenation (1 atm of H_2; 10% Pd-C; CH_3OH; 1 h) of **20** quantitatively produced the *N*-hydroxy compound **21** (mp 122-124.5 °C dec; $[\alpha]^{20}_D$ −21.1 ± 1.6° (*c* 1.07, CH_3OH), p*K* = 6.5).

Scheme I

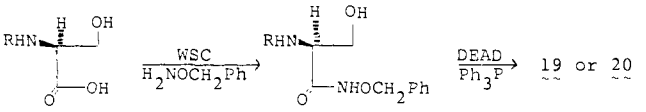


15 R=CBZ
16 R=t-BOC

17 R=CBZ, $R^1=CH_2Ph$ 19
18 R=t-BOC, $R^1=CH_2Ph$ 20
R=t-BOC, R^1=H 21

With the facility of the cyclization process demonstrated, a more convenient process, which would avoid the preparation of intermediate β-chloro-L-alanine derivatives, was sought. Thus, *N*-carbobenzyloxy- and *N*-*tert*-butoxycarbonyl-L-serine (**22** and **23**, Sigma) were each converted to the corresponding hydroxamic acid **24** (WSC; H_2NOCH_2Ph; DMF-H_2O (1:4); pH 4.5; <30 min; 89%; mp 125-127 °C; $[\alpha]^{20}_D$ −25.9° (*c* 3.2, CH_3OH)) and **25** (80-90%; mp 130-131 °C; $[\alpha]^{20}_D$ −37.6° (*c* 2.46, CH_3OH)). No serine hydroxyl group protection was required for this reaction. The products precipitated from the aqueous reaction mixture. Treatment of **24** and **25** directly with diethyl azodicarboxylate (DEAD) and triphenylphosphine[24,25] (100 mol % each at 0.06-0.1 M in THF; 50 °C 6 h or 20 °C, 20 h) followed by chromatography and recrystallization afforded the lactams **19** and **20** in 54-82 and 80-90% yields, respectively. These compounds were identical in all respects, including optical rotation, with those produced from **17** and **18**. Again, no elimination product (dehydroalanine) was detected. Thus, this process (Scheme II) allows the efficient

Scheme II



22 R=CBZ 24
23 R=t-BOC 25

preparation of substituted *N*-hydroxy-β-lactams in two steps from commercially available N-protected L-serine derivatives with retention of chirality at C_3. By employing a N-C_4 bond closure, this method also mimics the proposed biosynthesis of β-lactams.[5-8]

Since Ph_3P is also a thiophile, this process might also be applied to cysteine derivatives. These and further studies related to efficient N-O reduction and conversion of the resulting N-unsubstituted lactams to β-lactam antibiotics, including the monocyclic nocardicins,[1a,26] will be reported subsequently. Particular attention is also called to the fact that the *N*-hydroxylactams prepared demonstrate unusual properties (i.e. p*K* = 6.5-7) and might themselves be biologically interesting.

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(22) Intermolecular displacement reactions on β-chloro-L-alanine derivatives have previously been used to prepare chiral amino acids.[18,19]
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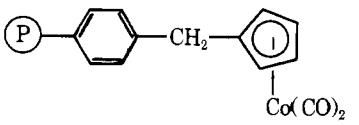
Polymer-Supported η^5-Cyclopentadienylcobalt, An Immobilized "Homogeneous" Fischer–Tropsch Catalyst

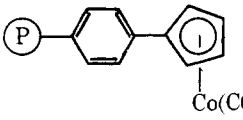
Sir:

The attachment of soluble, homogeneous catalysts to polymer supports has been the subject of considerable recent research activity.[1,2] Depending on bead and pore size, catalyst distribution, number and structure of pores, concentration and kind of attached ligands, degree of cross-linking, swelling properties of the polymer, and solvent, changes in rate and product distribution[3] have been observed in catalytic processes effected by these catalysts when compared with their mobile counterparts. Never, however, has there been the observation of new catalytic activity on immobilization. We wish to report that polystyrene-supported η^5-cyclopentadienylcobalt is catalytically active in the hydrogenation of carbon monoxide to give hydrocarbons, that this activity must be due to a defined attached homogeneous cobalt species and not to deposited metal crystallites, and that, in contrast, soluble $CpCo(CO)_2$ is inactive and decomposed under hydrogenating conditions. The observed data characterize the title compound as the first catalyst activated to *new* activity on polymer attachment and the first immobilized homogeneous Fischer–Tropsch catalyst.

We recently developed synthetic methodology en route to complex molecules employing cooligomerizations of alkynes catalyzed by $CpCo(CO)_2$.[4] In an effort to improve the efficiency of this approach, to stabilize the metal, and to facilitate its separation, we turned to a polymer-supported version of this catalyst. The method of Grubbs[3a,5] was used for the synthesis of two variants of polymer-supported cyclopentadiene. Treatment with $Co_2(CO)_8$ in refluxing CH_2Cl_2[6] followed by Soxhlet extraction of the resin with CH_2Cl_2 or C_6H_6 gave species **1**[7] and **2**, characterized by elemental analysis and the



1, P = 1% divinylbenzene–cross-linked microporous polystyrene; 0.35–0.50 mmol of Co/g; orange



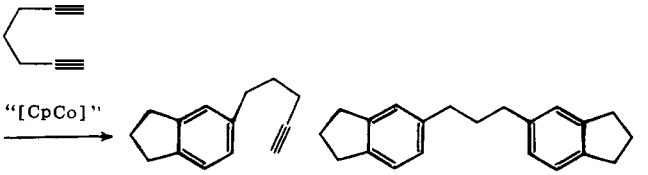
2, P = 3% divinylbenzene–cross-linked macroporous polystyrene; 0.8–1.0 mmol of Co/g; tan

characteristic infrared absorptions at 2012 and 1953 cm^{-1} (KBr) [cf. $CpCo(CO)_2$: 2033, 1972 (C_6H_{12}); 2017, 1954 cm^{-1} (acetone)]. In a swelling solvent (CH_2Cl_2, C_6H_6) both resins turned brown. Exposure to air led to slow oxidation (green color), although some resin-bound $CpCo(CO)_2$ was left even after 1 month's exposure (28%).

Decarbonylation of **1** and **2** could be effected by irradiation (Pyrex, −20 °C, toluene). In this reaction, resin **1**, in contrast to resin **2**, and a more highly cross-linked species,[7] revealed the formation of two *bridged* dicobalt carbonyl species (ν_{CO} 1790, 1773 cm^{-1}) assigned to the polymer-bound analogues of $Cp_2Co_2(CO)_3$[8] and $(CpCoCO)_2$,[9] formed under similar conditions from $CpCo(CO)_2$ in solution.

Analogously, vacuum pyrolysis of either resin (185 °C, 10^{-3} Torr, 112 h) led to complete decarbonylation. Microporous polymer **1** again revealed the formation of a bridged carbonyl during the course of CO removal. Significantly (vide infra), *the original species could be completely regenerated on exposure to CO pressure* (IR, analysis) (110 atm, 200 °C, benzene).

The catalytic activity of **1** or **2** in alkyne cyclizations proved to be disappointing. For example,[10] whereas $CpCo(CO)_2$ (0.5 mmol) will trimerize 1,6-heptadiyne (10 mmol, refluxing purified *n*-octane, syringe pump addition, 88 h) to **4** in 40% yield



3 **4**

(**3** is absent as a product), resin **1** and **2** *rapidly deactivate* after several turnovers to give substantial amounts of starting material, in addition to predominant formation of **3** at the expense of **4**.[10] Strong steric inhibition is apparent, trimethylsilylated alkynes being virtually inert to catalyst.

Limited hydroformylation[11] and isomerization activity under mild conditions was noted with 1-pentene [resin **2** sus-

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