was 10/90 acetonitrile/sodium perchlorate (0.10 M) adjusted to pH 2.5 with perchloric acid; flow rate 1 mL/min; λ = 211 nm. The above solvent ratio for **5b** was 20/80; flow rate 2 mL/min; λ = 211 nm.

Chiral HPLC determinations were done on a 0.46 cm (i.d.) × 2.5 cm Chiracel OC column from J. T. Baker Chemical Co. using hexanes/2-propanol (65/35) at 1 mL/min; λ = 211 nm.

General Procedure for Synthesis of 4-Substituted 2-Oxazolidinones from Their Respective Amino Acids. A 5-L, three-necked, round-bottomed flask was equipped with the following: a mechanical stirrer, a heating mantle, a claisen adapter containing a 500-mL addition funnel with a nitrogen inlet on top, and a take-off claisen adapter with thermometer and a "Therm-O-Watch"[18] attached. On top of the take-off claisen was a 16-cm flood trap, two 25-cm condensers connected in series, and a nitrogen outlet bubbler. The flask was swept with nitrogen and filled with 2.65 mol of the amino acid and 2.5 L of ethylene glycol dimethyl ether (DME) and warmed to ≃67 °C. The addition funnel was charged with 397 mL (3.23 mol) of boron trifluoride etherate and added to the flask at ≃67 °C over 1 h under nitrogen. After the addition, the yellow homogeneous solution was allowed to stir at 67 °C for an additional 1 h and the *nitrogen flow was stopped* to reduce the volume of out-flowing gases.

The reaction solution was then heated to a solution temperature of 80 °C at which time 424 mL (4.24 mol) of borane methyl sulfide complex (10.0 M) was added very carefully over a 1.0–2.5-h period (a 1.0-h addition time was satisfactory for only phenylglycine). The usual rate of addition was 2.5–6.0 mL/min. The reaction solution temperature has to be maintained within the 80–86 °C range. ***Note**: Caution has to be exercised when adding the borane methyl sulfide complex, especially for **5a** and **5b**. The rate of addition should be such that the first condenser shows a vigorous reflux and the solution temperature should never be allowed to drop much less than 80 °C with the flask being externally heated during the addition. A faster rate of addition than that recommended above will result in a lowering of the solution temperature, which may result in a violent expulsion of gases and solvent.* If such an exotherm occurs it may be controlled by stopping the addition and removing the nitrogen inlet to equalize the pressure within the reaction apparatus. The stirring may also be stopped if necessary. After the borane addition, the solution was heated under reflux for 4 h and then allowed to cool to ambient temperature. The reaction mixture was checked for starting material by HPLC for **5b** and **5c** or by TLC for **5a** (10 mL:10 mL:1 mL; chloroform–methanol–concentrated ammonium hydroxide with ninhydrin as detector, R_f = 0.31). If starting material is found to be present, add at ambient temperature 5–10% more borane methyl sulfide and heat the reaction solution to reflux 1 h more.

Methanol (400 mL) was added carefully to the reaction mixture initially at ambient temperature. The solution was then heated to a solution temperature of ≃85 °C. Solvent was removed via the take-off claisen until the reaction solution was half to one-third its original volume (1.5–2.0 L of solvent was removed). Aqueous NaOH (6 N, 1440 mL) was added to the hot (≃80 °C) reaction mixture, and the solution was heated to 85 °C for 0.5 h. The flask was cooled to ambient temperature, and 1 L of methylene chloride was added.[19] The flask was then cooled to −15 to −20 °C using a dry ice/acetonitrile bath. The addition funnel was charged with 193 mL (1.60 mol) of trichloromethyl chloroformate (TCF) in 250 mL of methylene chloride. This solution was added to the cooled reaction flask with stirring at a temperature not warmer than −10 °C and kept within a pH range of 9.0–11.0 by adding 50% NaOH simultaneously via the claisen adapter as needed (usually ≃205 mL). The addition of TCF was done over 1–1.5 h. After the addition, the reaction mixture was stirred for 1 h at ambient temperature where the final pH should be within the 9.25–9.5 range.

The contents of the reaction vessel were poured into a 12-L separatory funnel and 5-L of water was added. The bottom organic layer was removed, and the aqueous layer was washed with methylene chloride (3 × 1 L). The combined organic layer was washed with 1 L each of water and brine and then dried ($MgSO_4$). The dried solution was filtered and then concentrated under vacuum to near dryness. The crystalline mass was triturated with 400 mL of hexanes/ethyl acetate (4:1, v/v) cooled to ≃6 °C, treated with 400 mL more of hexanes, and allowed to stand overnight at ≃6 °C. The crystals were collected by filtration then recrystallized by dissolving in 0–4 L of methylene chloride, which was removed by distillation and replaced with about 500 mL of hexanes/ethyl acetate (4/1, v/v). The crystals that formed after standing overnight at ≃6 °C were collected by vacuum filtration and dried under vacuum.

Registry No. **1a**, 72-18-4; **1b**, 63-91-2; **1c**, 2935-35-5; **5a**, 17016-83-0; **5b**, 90719-32-7; **5c**, 99395-88-7; TCF, 503-38-8.

(18) Purchased from Instruments for Research and Industry (I^2R), Cheltenham, PA 19012.

(19) If desired, the amino alcohol may be isolated by methylene chloride extraction at this point.

Convenient Synthesis of Nickel [5,7,12,14,19,21,26,28-$^{13}C_8$]Phthalocyanine

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Metallophthalocyanines are convenient precursors for diverse low-dimensional electrical conductors. Recently we wished to prepare large quantities of nickel [5,7,12,14,19,21,26,28-$^{13}C_8$]phthalocyanine (**4**) with high isotopic enrichment. Previously macrocycle **4** had been prepared at five times natural abundance by the cyclization of 1,2-dicyanobenzene (**3**).[1] The partially labeled 1,2-dicyanobenzene (**3**) in turn was prepared from ^{13}C-enriched potassium cyanide through the use of copper(I) cyanide. However, we were reluctant to employ this methodology to achieve greater enrichment because of the high cost of 99% potassium [^{13}C]cyanide and low overall yield of the process. Herein we report an efficient method to prepare **4** using (arene)tricarbonylchromium chemistry.[2]

(1,2-Dichlorobenzene)tricarbonylchromium (**1**) was readily prepared from 1,2-dichlorobenzene and chromium hexacarbonyl.[3] The reaction of **1** with potassium [^{13}C]-cyanide and 18-crown-6[4] in DMSO solution smoothly provided the (1,2-di[^{13}C]cyanobenzene)tricarbonylchromium (**2**). This material was not isolated but was directly air-oxidized under photolytic conditions[5] to produce 1,2-di[^{13}C]cyanobenzene (**3**) (63%). The nucleophilic displacement reaction of **1** to produce **3** is notable on three counts. Firstly, excess cyanide is not required to ensure good conversion; the reaction is stoichiometric. Secondly, the yield in the reaction is easily reproducible. In our hands the conversion of 1,2-dihalobenzenes into phthalonitrile using copper(I) cyanide was capricious and depended critically on the copper reagent. Thirdly, the product **3** was not contaminated by 2-chlorobenzonitrile. Phthalonitrile prepared by using copper(I) cyanide fre-

(1) Toscano, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 437.

(2) For examples of nucleophilic substitution reactions of arene tricarbonyl complexes, see: Semmelhack, M. J.; Hall, H. T. *J. Am. Chem. Soc.* **1974**, *96*, 7091, 7092. Litvak, V. V.; Goryunov, L. I.; Shteingarts, V. D. *Zh. Org. Khim* **1986**, *22*, 157. Alemagna, A.; Baldoli, C.; Del Buttero, P.; Licandro, E.; Maiorana, S. *Gazz. Chim. Ital.* **1985**, *115*, 559. Nicholls, B.; Whiting, M. C. *J. Chem. Soc.* **1959**, 551.

(3) Alemagna, A.; Cremonesi, P.; Del Buttero, P.; Licandro, E.; Maiorana, S. *J. Org. Chem.* **1983**, *48*, 3114.

(4) For a review on crown-enhanced nucleophilic displacement reactions, see: Gokel, G. W.; Durst, H. D. *Synthesis* **1976**, 168.

(5) For an example of photolytic aerobic decomplexation, see: Nechvatal, G.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1982**, 467.

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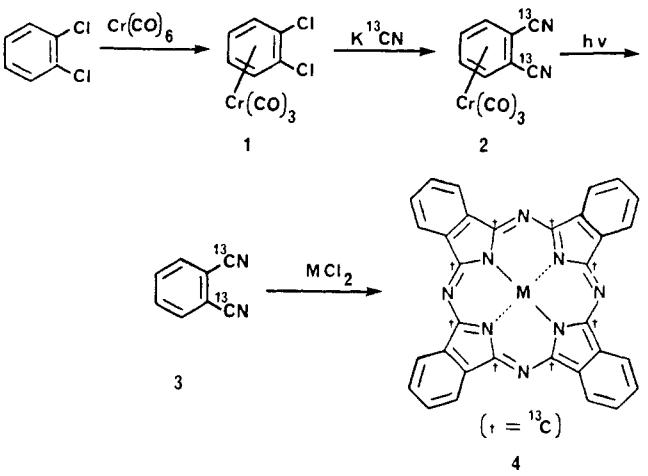

quently contains this impurity. Reaction of **3** with nickel(II) chloride[1] in quinoline gave the required phthalocyanine complex **4** (M = Ni) (63%). Spectroscopic data for both **3** and **4** were fully in accord with the required high level of isotopic enrichment. The copper complex **4** (M = Cu) was prepared in exactly the same way. It is clear from these results that (arene)tricarbonylchromium chemistry is particularly useful in labeled phthalocyanine construction.

Experimental Section

Melting points were determined by using a Reichert Jung hot-stage microscope. IR data were obtained on a Mattson spectrometer. Solution ^1H and ^{13}C NMR spectra were obtained with a Varian VXR-400 instrument and CP-MAS ^{13}C NMR spectra with a Varian XLA-300 instrument. Mass spectra were recorded by using a VG-70-250SE instrument.

1,2-Di[^{13}C]cyanobenzene (3). Potassium [^{13}C]cyanide[6] (99% ^{13}C, 0.91 g, 15 mmol) and 18-crown-6 (3.84 g, 14 mmol) were dissolved in DMSO (16 mL) under nitrogen. (η^6-1,2-Dichlorobenzene)tricarbonylchromium[3] (2.0 g, 7.1 mmol) was added, and the solution was stirred for 3 h, under nitrogen, in the dark. An equal volume of water was added to this solution on ice, and the resulting mixture was extracted with CH_2Cl_2 (5 × 30 mL). The red-orange extract was exposed to either bright sunlight or a UV light source (Hg vapor arc lamp) for ca. 3 days in order to decomplex **2**. The mixture was filtered through Celite daily to remove the green flocculent, oxidized-chromium precipitate and expedite the photodecomplexation. When the filtrate appeared clear and colorless, the solution volume was reduced to a minimum by rotary evaporation and cold H_2O (50 mL) was added. The resulting tan-white precipitate was filtered off, dissolved in hot ethanol (20 mL), and decolorized with a small amount of charcoal. After filtering, warm H_2O (30 mL) was added to the ethanolic solution, which was chilled on ice. The resulting white crystalline precipitate was filtered and recrystallized from hot ethanol/H_2O (1:1) to give **3** (0.50 g, 63%): mp 139–141 °C; IR (KBr) 3079 (w), 3040 (w), 2177 (s, C≡N), 1483 (m), 1355 (m), 1277 (s), 1221 (w), 1206 (w), 1206 (w), 1145 (sh), 1118 (s), 965 cm^{-1} (m) (the C≡N stretch in unlabeled 1,2-dicyanobenzene appears at 2232 cm^{-1}); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.78 (m); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 115.32; mass spectrum (EI) m/e 130 ($M^{+\cdot}$).

Nickel [5,7,12,14,19,21,26,28-$^{13}C_8$]Phthalocyanine (4) (M = Ni). 1,2-Di[^{13}C]cyanobenzene (**3**) (0.50 g) and $NiCl_2 \cdot 6H_2O$ (0.50 g) in quinoline (6 mL) were heated to 180 °C and maintained at that temperature for 15 h. The resulting solid mass was broken up in acetone, filtered, and washed with acetone and H_2O. The purple crude material was sublimed at ca. 400 °C (10^{-3} Torr) to give **4** (M = Ni) (0.35 g, 63%) as lustrous, purple needles: IR (KBr) 2928, 2851, 1383, 1375, 1363, 1362, 1332, 1288, 1261, 1163, 1119, 1079, 1021, 906, 803, 775, 749, 722 cm^{-1}; UV-vis (1,2,4-trichlorobenzene) λ_{max} 672 (log ϵ = 5.00), 640 (4.51), 604 (4.53), 336 nm (4.66); ^{13}C CP-MAS NMR (75 MHz) δ 143.6; mass spectrum (EI) m/e 578 ($M^{+\cdot}$).

Copper [5,7,12,14,19,21,26,28-$^{13}C_8$]Phthalocyanine (4) (M = Cu). Reaction of **3** with $CuCl_2$ gave **4** (M = Cu) (28%): IR (KBr) 2962, 2917, 1383, 1375, 1363, 1332, 1331, 1284, 1261, 1162, 1116, 1077, 1022, 891, 802, 775, 748, 718 cm^{-1}; UV-vis (1,2,4-trichlorobenzene) λ_{max} 677 (log ϵ = 5.16) 648, (4.40), 610 (4.47), 345 nm (4.68), mass spectrum (EI) m/e 583, 584, 585 ($M^{+\cdot}$).

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Registry No. **1**, 70140-19-1; **2**, 120771-51-9; **3**, 120788-97-8; **4** (M = Ni), 99476-50-3; **4** (M = Cu), 120771-52-0; 18-crown-6, 17455-13-9; potassium [^{13}C]cyanide, 25909-68-6; 1,2-dichlorobenzene, 95-50-1.

(6) Potassium [^{13}C]cyanide (99% label) was purchased from the Aldrich Chemical Company.

Three New Polyhydroxylated Sterols with the 5β-Configuration from the Sponge *Dysidea etheria*[1]

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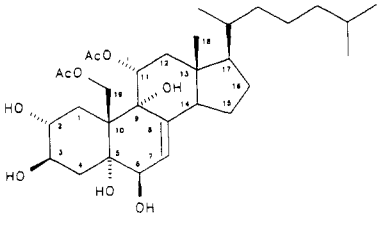
We recently reported the isolation of eight new, highly oxygenated sterols from the sponge *Dysidea etheria*, represented by **1**.[2] In the course of examining slightly less polar fractions of the extract for less oxidized or more highly acylated steroids, we uncovered a series of sterols analogous to those disclosed earlier, but distinguished by a 5β skeleton (cis AB ring juncture). It appears that herbasterol, a secosteroid isolated from *Dysidea herbacea*,[3] and a series of coprostanols from *Petrosia ficiformis*[4] are the only other examples of 5β sterols found in the phylum Porifera. The isolation, structure elucidation, and initial biological testing of three new 5β steroids with seven oxygen functionalities comprise this report.



As was noted earlier,[2] solvent partitioning[5] of the crude organic extracts of *D. etheria*, collected in Bermuda, yielded a chloroform-soluble fraction with a high concentration of highly functionalized steroids. Gel permeation chromatography (Sephadex LH-20, Bio-Beads S-X4) of

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