Formation of Fullerenes. One end of an 8-in. long, $^1/_8$-in. diameter, graphite rod was sharpened with a pencil sharpener, then weighed (~2.8 g). The flat end of the $^1/_8$-in. rod was secured to part A (see diagram above) and placed through the copper guide B (see diagram above), so that the point was resting in an indent carved into the $^1/_2$-in. graphite rod. The apparatus was connected to an ultrapure He cylinder and to a two-neck 5-L round-bottom flask (ballast). The second neck of the ballast was connected to an oil vacuum pump via a 2.5-cm outside diameter coarse frit to prevent soot from contaminating the oil pump. The apparatus was purged five times by He pump-filling cycles. The setup was then brought to 100 Torr He. The reactor was placed in a cold water bath (5-gal bucket), the power supply was set to 130 A, AC, and turned on. After the arc between graphite rods started, the power was reduced to a setting of "70" (ammeter reading of 55 A). In about 10 min. the $^1/_8$-in. rod was consumed (~6 in.) to the point that it could no longer make contact with the $^1/_2$-in. rod, and the power was shut off. The system was brought up to atmospheric pressure with He and allowed to cool for 20 min before moving the reactor to a hood and brushing the soot from the electrodes and the heat shield (baffle) into the kettle and extracted with 700 mL of benzene and the extract filtered using a 150-mL ASTM 10-15 M fritted-glass funnel. Sometimes "slag" forms on the $^1/_2$-in. bottom graphite rod; it should be removed before the next run, otherwise the $^1/_8$-in. rod will not burn uniformly or it will be difficult to start an arc. Another $^1/_8$-in. rod was put in place, and the process was repeated. This was done eight times at which point the kettle was moved into a hood. The solvent was removed in vacuo, giving 410 mg of extract from a total of 5.3 g of "burned" carbon (yield 7.7%). Pure C_{60}, 220 mg (53.7% by weight from extract), and C_{70}, 50 mg (~11% by weight from extract, still containing some C_{60}), were obtained by passing the extract through a column of Brockmann neutral activity grade I, 80-200-mesh Alumina, using 5 and 20% toluene in hexanes[4], respectively. When rods were burnt at 6 in./min with 130-A current, 12.5 g of graphite produced only 380 mg of extract (yield ~3%).

Summary and Conclusions

We described an apparatus for the facile preparation of buckminsterfullerenes. The reactor can be assembled mostly from commercial parts and fits in a standard preparative chemist's fume hood. The soot generated from graphite decomposition is easily and safely recovered. The yield of C_{60} is in the range of 3-4% based on graphite rod consumed.

Acknowledgment. We thank the National Science Foundation for support through Grants DMR-88-20933 and CHE89-08323. We are indebted to Rudi Stuber and his colleagues for help with the design and execution of the fullerene benchtop reactor.

Supplementary Material Available: Reproduction of photographs of the reactor (3 pages). Ordering information is given on any current masthead page.

Stereoselective Synthesis of Theonelladins A-D†

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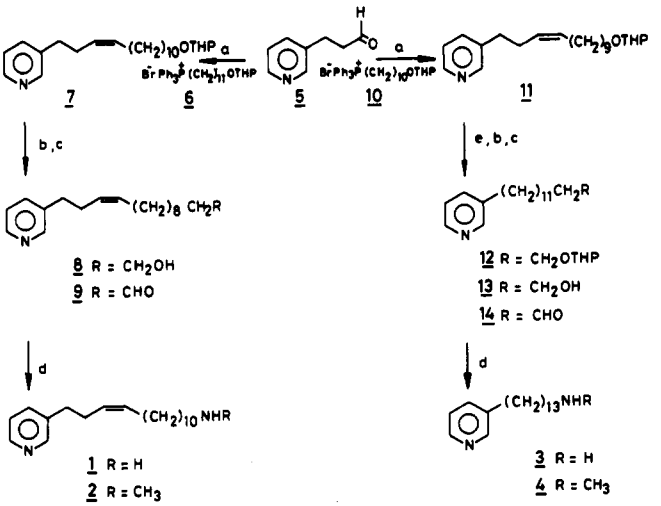
Introduction

In recent years several pyridine-derived alkaloids such as navenones,[1] pulo'upone,[2] halitoxins,[3] and niphatynes,[4] have been isolated from marine organisms. Theonelladins A-D[5] (1-4) belonging to the same group of alkaloids have been isolated from the Okinawan marine sponge *Theonella swinhoei*. The antileukemic Theonelladins A-D also exhibited potent antineoplastic activity against marine lymphomas L1210 and showed powerful Ca^{2+}-releasing activity from sarcoplasmic reticulum. These compounds were found to be 20 times more potent than caffeine, a well-known Ca^{2+} inducer. Here we describe the first total synthesis of these highly active compounds. This process will make it possible to obtain the title compounds in large quantities for biological screening.

Scheme I[a]



[a] Reagents and conditions: (a) *n*-BuLi, THF, 0 → -40 °C; (b) 3 N HCl, MeOH; (c) Swern oxidation; (d) NH_3 or $MeNH_2$, MeOH, $NaBH_4$; (e) Pd-C/H_2, EtOH.

Discussion of Results

The general strategy (Scheme I) utilized in the present synthesis involved a common approach for construction of the required carbon skeleton. Accordingly, the Wittig reaction has been utilized to our advantage, both for the chain elaboration as well as for the stereoselective introduction of the required C-9 double bond. The commercially available 3-γ-pyridinepropanol was chosen as the starting material for simple and straightforward synthesis of 1-4.

Swern oxidation[6] of 3-γ-pyridinepropanol in CH_2Cl_2 gave the aldehyde **5** in 78% yield. Construction of the required carbon skeleton was achieved by Wittig olefination,[7] where the aldehyde **5** in THF was reacted with phosphonium salt[8] **6** in the presence of *n*-butyllithium at -40 °C to afford compound **7**, thereby stereoselectively introducing the cis double bond. The configuration of the double bond was assigned by spectral studies (^1H and ^{13}C NMR). The coupling constant of the olefinic protons was found to be 10.6 Hz, corresponding to the literature value.[9] The ^{13}C

† IICT Communication No. 2728.

(1) Sleeper, H. L.; Fenical, W. *J. Am. Chem. Soc* **1977**, *99*, 2367.
(2) Coval, S. J.; Scheuer, P. J. *J. Org. Chem.* **1985**, *50*, 3025.
(3) Schmitz, F. J.; Hollenbeak, H. K.; Campbell, D. C. *J. Org. Chem.* **1978**, *43*, 3916.
(4) Quinoa, E.; Crews, P. *Tetrahedron Lett.* **1987**, *28*, 2467.
(5) Kobayashi, J.; Murayama, T.; Ohizumi, Y.; Sasaki, T.; Ohta, T.; Nozoe, S. *Tetrahedron Lett* **1989**, *30*, 4833.
(6) (a) Omura, K.; Swern, D. *Tetrahedron* **1978**, *30*, 1651. (b) Mancuso, A. J.; Brownfain, D. S.; Swern, D. *J. Org. Chem.* **1979**, *44*, 4148.
(7) Yamagiwa, Y.; Ohashi, K.; Sakamoto, Y.; Hirakawa, S.; Kamikawa, T. *Tetrahedron* **1989**, *43*, 3387.
(8) Novak, L.; Toth, M.; Balla, J.; Szantay, C. *Acta Chim. Sci. Hung.* **1979**, *102*, 135.

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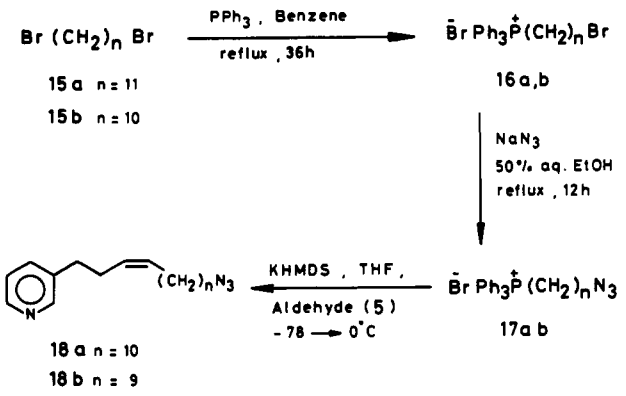
Scheme II



NMR spectrum showed the chemical shifts of C-8 (δ 29.5) and C-11 (δ 29.7) assigned to the two allylic carbons indicating that the double bond is cis.[10] Having obtained compound **7** with the required number of carbon atoms with a ω-functionality, we then aimed for its transformation to the target molecules involving a simple sequence of reactions.

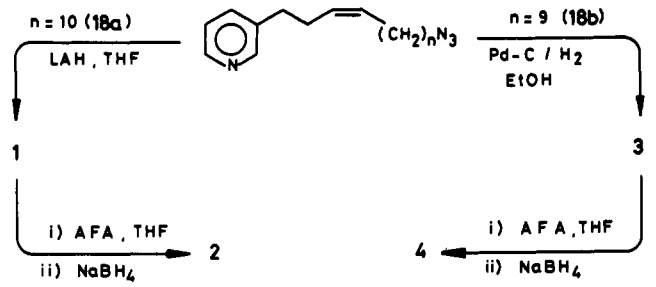
Thus, the exposure of the compound **7** to methanolic HCl gave the hydroxy compound **8**, which on Swern oxidation led to the formation of the common intermediate aldehyde **9**. The aldehyde **9** on reaction with excess ammonia and subsequent reduction[11] of the resultant imine with sodium borohydride afforded Theonelladin **1**, while condensation with methylamine[12] followed by sodium borohydride treatment gave Theonelladin **2**. The spectral data of these compounds was in full agreement with the reported values.

Theonelladins **3** and **4** were prepared (Scheme I) from aldehyde **5** following the same strategy applied for Theonelladins **1** and **2**. Thus, Wittig olefination of aldehyde **5** with the phosphonium salt[13] **10** afforded compound **11** in 78% yield. Catalytic hydrogenation over 10% Pd–C in ethanol yielded compound **12** in 96% yield. Depyranylation of compound **12** (methanolic HCl) followed by the Swern oxidation of the resultant alcohol **13** gave the aldehyde **14** in 78% yield. The aldehyde **14** on condensation with ammonia or methylamine followed by sodium borohydride reduction furnished Theonelladins **3** and **4** whose spectral data was found to be in agreement with the reported values.

Though the successful completion of the synthesis of **1–4** has been achieved by the above approach, the final introduction of the amino group into the molecule was not clean and involves the multistep sequence. Keeping in view this drawback, we have altered the synthetic sequence such that one can introduce the amino group indirectly. A recent report by Vaultier et al.[14] showed that the azido phosphonium salts can be successfully manipulated in Wittig olefination reactions. We felt the azido group would serve as a masked amino group which could be conveniently converted to the required amino group at an appropriate stage.

Accordingly, 1,11- and 1,10-dibromo compounds **15a** and **15b** on reaction with triphenylphosphine in refluxing benzene for 36 h afforded the corresponding (bromoalkyl)triphenylphosphonium bromides **16a** (mp 94–96 °C) and **16b** (mp 79–81 °C) in 84% yield (Scheme II). Subsequent reaction with sodium azide in refluxing mixture of ethanol–water (1:1) for 12 h yielded the required azidophosphonium bromides **17a** (mp 79–81 °C) and **17b** (mp 74–76 °C) in 90% yield. Thus, Wittig olefination of aldehyde **5** in THF with salt **17a** in the presence of potassium hexamethyl disilazide at −78 °C for 2 h exclusively afforded *Z* isomer[9,10] **18a** in 74% yield. Subsequent reduction of azido group in **18a** (Scheme III) with $LiAlH_4$ in THF furnished Theonelladin **1** in 90% yield. The compound **1** on formylation followed by reduction[15] with $LiAlH_4$ afforded **2** in 79% yield.

Scheme III



Similar treatment of aldehyde **5** with salt **17b** afforded **18b** in 78% yield. Subsequent exhaustive reduction of **18b** (Scheme III) under catalytic hydrogenation (10% Pd–C) yielded Theonelladin **3**. The compound **3** on reaction with acetic formic mixed anhydride and subsequent reduction by $LiAlH_4$ gave Theonelladin **4** in 79% yield.

In conclusion, the Wittig approach adopted in this simple strategy has successfully provided the biologically active Theonelladins **1–4**.

Experimental Section

General Procedures. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer 1310 spectrophotometer, and mass spectra were recorded on a Finnigan Mat 1210 spectrometer. ^1H NMR spectra were recorded on a Varian Gemini 200 and Bruker 300 instrument in $CDCl_3$ solutions containing TMS as an internal reference. Microanalyses were performed by IDPL laboratories, Hyderabad. Flash Chromatography was performed on Em Kieselgel 60 (~230 mesh).

All reactions were carried out under a positive pressure of N_2, unless otherwise noted. Tetrahydrofuran (THF) was distilled immediately before use from sodium benzophenone ketyl. Methylene chloride (CH_2Cl_2) was freshly distilled from P_2O_5 before use. Benzene, DMSO, and triethylamine were distilled from CaH_2. Methanol and ethanol were distilled from Mg turnings before use.

3-[14-(Tetrahydro-2-pyranyloxy)-3(*Z*)-tetradecenyl]-pyridine (7). To a stirred suspension of compound **6** (1.5 g, 2.51 mmol) in THF (10 mL) at 0 °C was added dropwise *n*-butyllithium (1.56 mL, 2.51 mmol, 1.6 M) at 0 °C under argon atmosphere. After 30 min it was cooled to −40 °C and a solution of compound **5** (0.34 g, 2.51 mmol) in THF (6 mL) was added. The reaction mixture was stirred for an additional 40 min and allowed to attain room temperature. It was quenched with water followed by methanol and extracted with EtOAc (3 × 20 mL). The organic layer was washed with brine, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by flash column chromatography (SiO_2, 7:3 hexane–EtOAc) to afford **7** (0.72 g) in 77% yield as a pale yellow oil. IR ($CHCl_3$): 2850, 1715, 1585, 1420, 1270, 1110, 1075, 1020, 785, 695 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.36 (br s, H-2), 8.34 (d, J = 5.2 Hz, H-6), 7.46 (d, J = 7.8 Hz, H-4), 7.12 (q, J = 5.0 and 7.9 Hz, H-5), 5.38 (m, 2 H, J = 10.6 Hz, H-9 and H-10),

(9) Reitz, A. B.; Nortey, S. O.; Jordan, A. D., Jr.; Mutter, M. S.; Maryanoff, B. E. *J. Org. Chem.* **1986**, *51*, 3302.
(10) Sakemi, S.; Totton, L. E.; Sun, H. H. *J. Nat. Prod.* **1990**, *53*, 995.
(11) Schellenberg, K. A. *J. Org. Chem.* **1963**, *28*, 3259.
(12) Layer, R. W. *Chem. Rev.* **1963**, *63*, 489.
(13) Bestmann, H. J.; Koschatzky, K. H.; Schatzke, W.; Sub, J.; Vostrowsky, O. *Leibigs Ann. Chem.* **1981**, *9*, 1705.
(14) Chhen, A.; Vaultier, M.; Carrie, R. *Tetrahedron Lett.* **1989**, *30*, 4953.
(15) Huebner, C. F.; Donoghue, E. M.; Plummer, A. J.; Furness, P. A. *J. Med. Chem.* **1966**, *9*, 830.

4.58 (br s, 1 H), 3.85 (m, 1 H), 3.78 (dt, 1 H, J = 6.8 and 10.2 Hz), 3.45 (m, 1 H), 3.38 (dt, 1 H, J = 7.0 and 10.0 Hz), 2.60 (t, J = 7.2 Hz, H-7), 2.38 (q, J = 7.2 and 13.6 Hz, H-8), 1.90 (br t, H-11), 1.52 (m, H-19), 1.17-1.37 (m, H-12-H-18, 14 H), MS (m/e): 373 (M^+). Anal. Calcd for $C_{24}H_{39}NO_2$: C, 77.16; H, 10.52; N, 3.75. Found: C, 77.06; H, 10.58; N, 3.67.

(Z)-N-Methyl-14-(3-pyridinyl)-11-tetradecen-1-amine (2). To a solution of compound **9** (0.5 g, 1.74 mmol) in methanol (5 mL) was added 40% aqueous $MeNH_2$ (0.15 mL, 1.93 mmol) at 0 °C and stirred for 40 min. The reaction mixture was treated with sodium borohydride (0.1 g, 2.63 mmol) and stirred for additional 40 min. It was quenched with 2 N HCl (2 mL), the volatiles were removed under reduced pressure, and the residue was basified (pH ~10), with 1 N NaOH (~6 mL) and extracted with EtOAc (3 × 15 mL); the organic layer was washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, 1:9 MeOH-$CHCl_3$) to give **2** (0.4 g) in 76% yield as a pale yellow oil. IR ($CHCl_3$): 3350, 2910, 1620, 1580, 1438, 1268, 1110, 1075, 1020, 785, and 650 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.36 (br s, H-2), 8.34 (d, J = 5.0 Hz, H-6), 7.46 (d, J = 7.9 Hz, H-4), 7.17 (q, J = 5.0 and 7.9 Hz, H-5), 5.38 (m, 2 H, J = 10.6 Hz, H-9 and H-10), 3.30 (br s, 1 H, N*H*), 2.60 (t, J = 7.40 Hz, H-7), 2.52 (t, J = 7.4 Hz, H-20), 2.40 (s, H-22), 2.38 (q, J = 7.4 and 13.6 Hz, H-8), 1.90 (br t, H-11), 1.60 (m, H-19), 1.17-1.37 (m, 14 H, H-12-H-18). ^{13}C ($CDCl_3$): δ 149.8, 147.4, 139.0, 137.8, 132.0, 127.8, 122.8, 50.2, 34.8, 33.1, 29.9-30.8 (6 C), 29.7, 29.5, 28.0, and 27.8. MS (m/e): 302 (M^+). Anal. Calcd for $C_{20}H_{34}N_2$: C, 79.41; H, 11.33; N, 9.26. Found: C, 79.38; H, 11.25; N, 9.33.

3-[14-Azido-3(Z)-tetradecenyl]pyridine (18a). To a stirred suspension of compound **17a** (1.5 g, 2.78 mmol) in THF (8 mL) was added potassium hexamethyl disilizide (27.8 mmol, 0.1 M) in THF at -78 °C under argon atmosphere. After 1 h, a solution of aldehyde **5** (0.37 g, 2.78 mmol) was added in THF (4 mL) and stirred for an additional 1 h. It was allowed to attain room temperature, quenched with methanol (3 mL), and extracted with EtOAc (3 × 20 mL). The organic layer was washed with brine, dried (Na_2SO_4) and evaporated in vacuo. The residue was purified by flash column chromatography (SiO_2, 7:3 hexane-EtOAc) to give **18a** (0.67 g) in 78% yield as a colorless oil. IR ($CHCl_3$): 2910, 2100, 1840, 1570, 1450, 1415, 1255, 1010, 790, and 700 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.36 (br s, H-2), 8.34 (d, J = 5.0 Hz, H-6), 7.46 (d, J = 7.9 Hz, H-4), 7.12 (q, J = 5.0 and 7.9 Hz, H-5), 5.30 (m, 2 H, J = 10.6 Hz, H-9 and H-10), 3.20 (t, J = 6.5 Hz, H-20), 2.60 (t, J = 7.48 Hz, H-7), 2.30 (q, J = 7.4 and 13.6 Hz, H-8), 1.90 (br s, H-11), 1.52 (m, H-19), 1.17-1.37 (m, 14 H, H-13-H-18). MS (m/e): 314 (M^+). Anal. Calcd for $C_{19}H_{30}N_4$: C, 72.56; H, 9.62; N, 17.82. Found: C, 72.52; H, 9.60; N, 17.80.

(Z)-14-(3-Pyridinyl)-11-tetradecen-1-amine (1). A mixture of $LiAlH_4$ (0.09 g, 2.36 (mmol) and azide **18a** (0.5 g, 1.59 mmol) in THF (8 mL) was stirred at room temperature for 2 h. The reaction mixture was quenched with 1 N NaOH (0.2 mL), and the solids obtained were filtered and washed with EtOAc, the filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (SiO_2, 1:9 MeOH-$CHCl_3$) to give compound **1** (0.41 g) in 90% yield as a pale yellow oil. IR ($CHCl_3$): 3350, 2905, 1716, 1580, 1420, 1270, 1110, 1075, 1020, 785, and 690 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.36 (br s, H-2), 8.34 (d, J = 5.0 Hz, H-6), 7.46 (d, J = 7.9 Hz, H-4), 7.17 (q, J = 5.0 and 7.9 Hz, H-5), 5.8 (br s, 2 H, NH_2), 5.38 (m, 2 H, J = 10.6 Hz, H-9 and H-10), 2.79 (t, J = 5.2 Hz, H-20), 2.60 (t, J = 7.4 Hz, H-7), 2.38 (q, J = 7.4 and 13.6 Hz, H-8), 1.90 (br t, H-11), 1.52 (m, H-19), 1.17-1.37 (m, H-12-H-18). ^{13}C ($CDCl_3$): δ 149.8, 147.1, 138.6, 137.8, 131.6, 127.8, 122.8, 42.1, 33.1, 29.8-30.6 (5 C), 29.7, 29.5, 28.0, and 27.9. MS (m/e): 288 (M^+). Anal. Calcd for $C_{19}H_{32}N_2$: C, 79.11; H, 11.8; N, 9.71. Found: C, 78.81; H, 10.95; N, 9.69.

3-Pyridinetridecanamine (3). To a solution of **18b** (0.5 g, 1.66 mmol) in absolute ethanol (5 mL) was added 10% Pd-C (50 mg, 10% w/w), and the mixture was stirred under a hydrogen atmosphere (1 atm) for 4 h at room temperature. The reaction mixture was filtered over Celite, the filtrate was concentrated, and residue was purified by column chromatography (SiO_2, 1:9 MeOH-$CHCl_3$) to give **3** (0.41 g) in 90% yield as a pale yellow oil. IR ($CHCl_3$): 3349, 2910, 1552, 1452, 738, and 710 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.36 (br s, H-2), 8.34 (d, J = 5.0 Hz, H-6), 7.46 (d, J = 7.9 Hz, H-4), 7.17 (q, J = 5.0 and 7.9 Hz, H-5), 5.9 (br s, 2 H, NH_2), 2.81 (t, J = 5.2 Hz, H-19), 2.60 (t, J = 7.4 Hz, H-7), 1.52 (t, J = 6.95 Hz, H-8), 1.12-1.38 (m, 20 H, H-9-H-18). ^{13}C ($CDCl_3$): δ 150.3, 147.5, 139.6, 138.5, 125.1, 42.1, 33.3, 29.9-30.6 (8C), 29.8, 29.6, 28.2. MS (m/e): 276 (M^+). Anal. Calcd for $C_{18}H_{32}N_2$: C, 78.20; H, 11.67; N, 10.13. Found: C, 78.18; H, 11.62; N, 10.08.

N-Methyl-3-pyridinetridecanamine (4). To a solution of acetic formic anhydride (0.04 g, 0.462 mmol) in THF (1 mL) was added a solution of compound **3** (0.1 g, 0.362 mmol) in THF (1 mL), and the mixture was stirred for 4 h at room temperature. It was diluted with EtOAc and washed with saturated $NaHCO_3$ solution, water, and brine, dried (Na_2SO_4), and concentrated in vacuo. This crude product and $LiAlH_4$ (0.02 g, 0.52 mmol) in THF (2 mL) were heated at reflux for 1 h. The reaction mixture was cooled and quenched with 1 N NaOH, and the solids obtained were filtered. It was washed with EtOAc, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (SiO_2, 1:9 MeOH-$CHCl_3$) to give compound **4** (0.082 g) in 78% yield as a pale yellow oil. IR ($CHCl_3$): 3350, 2905, 1565, 1450, and 700 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.36 (br s, H-2), 8.34 (t, J = 5.0 Hz, H-6), 7.46 (d, J = 7.9 Hz, H-4), 7.17 (q, J = 5.0 and 7.9 Hz, H-5), 3.8 (br s, 1 H, *NH*), 2.60 (t, J = 6.40 Hz, H-7), 2.52 (t, J = 7.5 Hz, H-19), 2.40 (s, H-20), 1.52 (t, J = 7.0 Hz, H-8), 1.38 (m, H-18), 1.12-1.34 (m, 18 H, H-9-H17). ^{13}C ($CDCl_3$): δ 150.0, 147.6, 139.4, 137.4, 125.0, 50.4, 33.3, 29.7-30.6 (8 C), 29.8, 29.6, 28.2. MS (m/e): 290 (M^+). Anal. Calcd for $C_{19}H_{34}N_2$: C, 78.56; H, 11.80; N, 9.64. Found: C, 78.52; H, 11.78; N, 9.61.

Registry No. **1**, 125289-09-0; **2**, 125289-10-3; **3**, 125289-11-4; **4**, 125289-12-5; **5**, 1802-16-0; **5** alchol, 2859-67-8; **6**, 73010-80-7; **7**, 133850-33-6; **8**, 133835-21-9; **9**, 133835-22-0; **10**, 79837-78-8; **11**, 133850-34-7; **12**, 133850-35-8; **13**, 133835-23-1; **14**, 133835-24-2; **15a**, 16696-65-4; **15b**, 4101-68-2; **16a**, 133835-25-3; **16b**, 120677-73-8; **17a**, 133835-26-4; **17b**, 133835-27-5; **18a**, 133835-28-6; **18b**, 133835-29-7.

Supplementary Material Available: Experimental data for **1-5**, **8**, **9**, **11-14**, **16a**, **17a**, and **16b-18b** (8 pages). Ordering information is given on any current masthead page.

Synthesis of Glycosyl Phosphates Using the Fraser-Reid Activation

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Glycosyl phosphates are biologically important, both as intermediates in metabolism[1] and as constituents of cell walls.[2-5] Polymers of glycosyl phosphates are an immunologically active part of the capsule or cell wall of several microorganisms.[4,5] A convenient synthetic route to this important class of compounds would be useful. Although enzymatic syntheses[6] appear attractive in principle, they are now practical only in the galactose series. The enzymes involved in formation of most sugar phosphates catalyze equilibria unfavorable to the sugar 1-phosphates,[7] although galactokinase (EC 2.7.1.6) catalyzes the direct phosphorylation at the anomeric center by ATP and is thermo-

(1) Rawn, D. J. *Biochemistry*; Harper & Row: New York, 1983.
(2) Sharon, N. *Complex Carbohydrates, Their Chemistry, Biosynthesis and Function*; Addison-Wesley: Reading, MA, 1975.
(3) Kennedy, J. F.; White, C. A. *Bioactive Carbohydrates*; Ellis Horwood Ltd.: West Sussex, 1983.
(4) *The Glycoconjugates*; Horowitz, M. I., Ed.; Academic: New York, 1977-1982.
(5) *The Polysaccharides*; Aspinall, G. O., Ed.; Academic: New York, 1982-1983.
(6) Toone, E. J.; Simon, E. S.; Bednarski, M. D.; Whitesides, G. M. *Tetrahedron* **1989**, *45*, 5365-5422.
(7) *The Enzymes*, 3rd ed.; Boyer, P., Eds.; Academic: New York, 1973.

0022-3263/91/1956-4547$02.50/0 © 1991 American Chemical Society