EMR-II). S.B. and R.C. also thank CSIR for awarding them JRF and RA, respectively.

Supplementary Material Available: ^{1}H NMR data of 4-methylpent-1-yn-3-one, 1-phenylprop-2-yn-1-one, 1-(4-methoxyphenyl)prop-2-yn-1-one, 1-methoxy-5-methylhex-2-yn-4-one, and 1-phenyl-4-methoxybut-2-yn-1-one and ^{1}H NMR spectra of all the starting acetylenic ketones and compounds **1a-1f**, **2-7**, and **9** (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

New Preparation of Pyridines from Enamino Nitriles[1]

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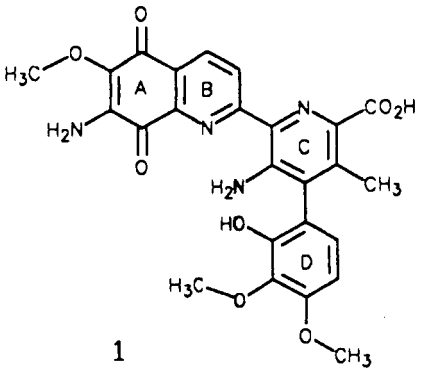
Numerous synthetic sources of the pyridine ring have been reviewed.[2-4] There remained a need for a pyridine preparation with few limitations. Indeed, the synthesis of the multisubstituted pyridine ring C of Streptonigrin (1),[5] with five different substituents, has presented quite



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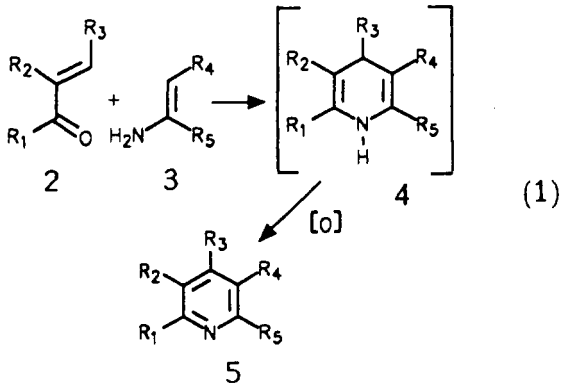
a synthetic challenge. It was the key to several reported total syntheses.[6,7] The construction of a pyridine ring C of Streptonigrin with five appropriate groups was best accomplished by sequential inverse electron demand aza Diels-Alder reactions.[6] However, these two steps achieved only a 28% yield of the desired pyridine due to lack of regiochemical control. Kelly and Liu[8] published an elegant "one-pot" but multiple-step pyridine synthesis from *N,N*-dimethylhydrazone enolates. Regioselective control was achieved, but the yields of products which had four or five substituents was low (14-45%). Therefore, we proposed to develop an alternate method for synthesizing multisubstituted pyridines which could similarly achieve regioselective control of all groups.

Background

The so-called "3 + 3" pyridine synthesis,[4] using α,β-unsaturated carbonyls **2** as the 3-carbon component and primary enamines **3** as the 2-carbon component, had the potential to meet our goals (eq 1).[9] Unsaturated ketones **2** are easily prepared with a variety of substituents R_1-R_3.[10,11] The Michael addition of enamines **3**, to these propenones **2**, followed by ring closure to **4**, allows regioselective control of substituents R_1-R_5.[12,13] This method has previously been only marginally successful. The dihydropyridines **4** initially formed often underwent further reactions, including disproportionation, to a mixture of products. Subsequent oxidation of the isolated dihydropyridines **4** with HNO_3, or other reagents, also gave pyridines **5** but with overall poor yield.



(1)

Primary enamines of type **3** are not stable unless conjugated with an electron-withdrawing group on the β-carbon. Before now, this has been the nature of substituent R_4. We envisioned including one additional leaving group on either substrate, **2** or **3**. For example, reaction of **2** with a **3** that was modified to include another elimination would directly afford an aromatic ring. Aromatization would also provide driving force for the reaction.

Oxime[2] and hydrazone derivatives[4,8] of 1,5-diketones **6** have been employed to provide for this type of elimination. Acidic conditions were required for ring closure as well as protonation of the leaving group for the final elimination to the aromatic pyridine **5**. There are far fewer examples of pyridines synthesized with leaving groups that are not attached to nitrogen.[4,12,14,15] Kronke's[15] use of the pyri-

(1) Presented in part at the 42nd Southeast/46th Southwest Combined Regional Meeting of the American Chemical Society, New Orleans, LA; December 1990; Abstr. 393.

(2) (a) Brody, F.; Rudy, P. R. In *Pyridine and Its Derivatives*; Klingsberg, E., Ed.; Interscience: New York, 1960; Vol. 14, Part 1, Chapter 2. (b) Boodman, N. S.; Hawthorne, J. O.; Masciantonio, P. X.; Simon, A. W. In *Pyridine and Its Derivatives*; Abramovitch, R. A., Ed.; Wiley-Interscience: New York, 1972; Vol. 14, Supplement Part 1, Chapter 2.

(3) Newkome, G. R.; Paudler, W. W. *Contemporary Heterocyclic Chemistry*; Wiley: New York, 1982.

(4) *Pyridine and Its Derivatives*; Newkome, G. R., Ed.; Wiley: New York, 1984; Vol. 14, Part 5.

(5) Rao, K. V.; Biemann, K.; Woodward, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2532.

(6) Boger, D. L.; Panek, J. S. *J. Am. Chem. Soc.* **1985**, *107*, 5745.

(7) (a) Weinreb, S. M.; Basha, F. Z.; Hibino, S.; Khatri, N. A.; Kim, D.; Pye, W. E.; Wu, T.-T. *J. Am. Chem. Soc.* **1982**, *104*, 536. (b) Kende, A. S.; Lorah, D. P.; Boatman, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 1271.

(8) Kelly, T. R.; Liu, H.-t. *J. Am. Chem. Soc.* **1985**, *107*, 4998.

(9) Substituent groups are represented generically: R is not limited to alkyl.

(10) The Perkin, Claisen-Schmidt, and Knoevenagel condensations have been extensively reviewed: (a) Johnson, J. R. *Org. React.* **1942**, *1*, 210. (b) Jones, G. *Ibid.* **1967**, *15*, 204. (c) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: Menlo Park, CA, 1972; Chapter 10.

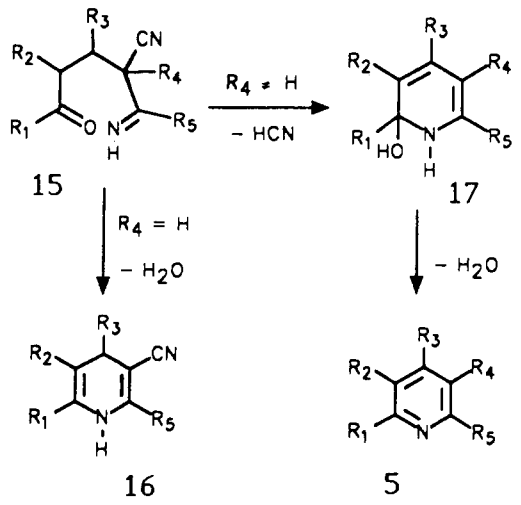
(11) A typical example is the preparation of chalcone (**10**): Kohler, E. P.; Chadwell, H. M. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, p 78.

(12) (a) Meyer, V.; Irmscher, J. *J. Prakt. Chem.* **1908**, *78*, 497. (b) Courts, A.; Petrow, V. *J. Chem. Soc.* **1952**, 1, 334. (c) Chatterjea, J. N.; Prasad, K. *J. Indian Chem. Soc.* **1955**, *32*, 371. (d) Chatterjea, J. N.; Prasad, K. *J. Sci. Ind. Res. (India)* **1955**, *14B*, 383.

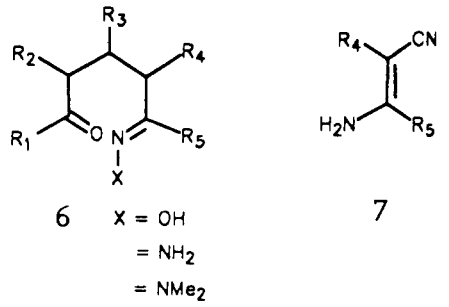
(13) Chatterjea, J. N. *J. Indian Chem. Soc.* **1952**, *29*, 323.

0022-3263/92/1957-7352$03.00/0

Scheme I

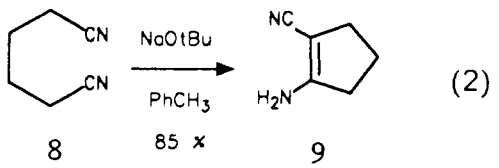


dinium ion as a leaving group requires either the 3- or 5-position of the product to be unsubstituted.



Synthetic Strategy

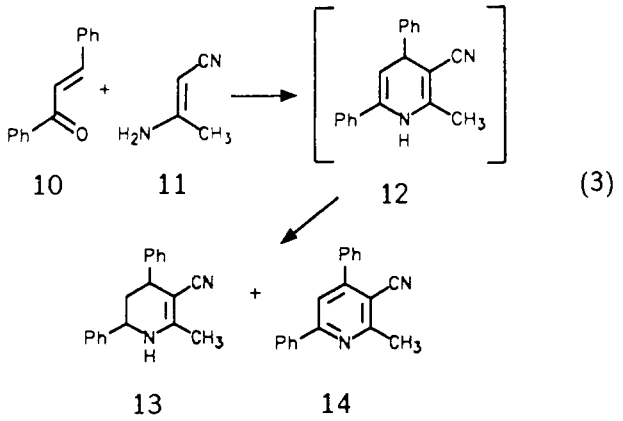
Initially, we chose to study enamino nitriles (7)[16] as the 2-carbon component of a "3 + 3" reaction for several reasons: (1) enamino nitriles contain the primary enamine synthon stabilized by conjugation with an electron-withdrawing cyano group, (2) cyanide is a good leaving group, (3) the leaving group is on carbon rather than nitrogen, and (4) enamino nitriles are readily available especially via the Thorpe–Ziegler reaction. For example, Thompson[17] published an improved procedure for the Thorpe–Ziegler cyclization of adiponitrile (8) to 1-amino-2-cyanocyclopentene (9) using sodium *tert*-butoxide in toluene (eq 2). Since then, lithium amide bases[18] and sodium or potassium hydride[19] have been used for similar cyclizations in aprotic solvents and gave very good yields.



(2)

(14) Palit, N. *J. Indian Chem. Soc.* **1950**, *27*, 71.
(15) Krohnke, F. *Synthesis* **1976**, 1 and references therein.
(16) Literature was reviewed in 1968: Taylor, E. C.; McKillop, A. *Advances in Organic Chemistry Vol. 7: The Chemistry of Cyclic Enaminonitriles and o-Aminonitriles*; Taylor, E. C., Ed.; Interscience: New York, 1970.
(17) Thompson, Q. E. *J. Am. Chem. Soc.* **1958**, *80*, 5483.
(18) (a) Kruger, C. R.; Rochow, E. G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 617. (b) Kulp, S. S. *Can. J. Chem.* **1967**, *45*, 1981. (c) Rodriquez-Hahn, L.; Parra, M. M.; Martinez, M. *Synth. Commun.* **1984**, *14*, 967.
(19) (a) Williams, J. K. *J. Org. Chem.* **1963**, *28*, 1054. (b) Brown, C. A. *Synthesis* **1975**, 326.

Only two enaminonitriles have previously been reacted with enones.[12-14] Chatterjea reported[13] only two products from the reaction of 2-aminocrotononitrile (11) with chalcone (10). He found the cyanopyridine 14 and a compound, mp 207–8 °C, reported to be the dihydropyridine 12. No yields were reported. Therefore, we reinvestigated this reaction to look for other products as evidence of cyanide ion as a leaving group. No such evidence was found. The compound reported as 12 actually was found to be the tetrahydro compound 13. Compounds 13 and 14 are the products expected from disproportionation of the initially formed dihydropyridine (12) which we detected in trace amounts.

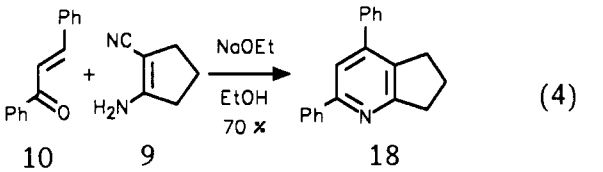


(3)

Separate mechanistic paths to pyridines from Michael adduct 15 are possible (Scheme I). If substituent R_4 is hydrogen, then it could easily form the conjugated enamine and cyclize to the 1,4-dihydropyridine (16). Conjugated vinylogous cyanamides such as 16 cannot readily lose cyanide without first undergoing an unfavorable tautomerization to a nonconjugated nitrile. On the other hand, if R_4 is a substituent other than hydrogen, such tautomeric equilibration from the imine to the enamine is precluded. Then, elimination of HCN, equilibration to the dienamine, ring closure, and dehydration would afford pyridine 5. To test the strategy of forcing cyanide to be a leaving group, we incorporated an alkyl group at R_4 and determined that this is precisely what occurs.

Results and Discussion

Under basic conditions (NaOEt/EtOH) chalcone (1) and 1-amino-2-cyanocyclopentene (9) afforded about 59–71% of 2,4-diphenyl-6,7-dihydro-5*H*-1-pyrindine (18) (eq 4).[20]



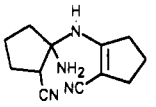
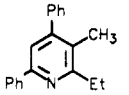
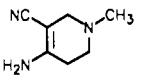
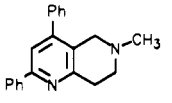
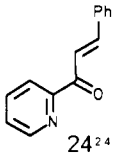
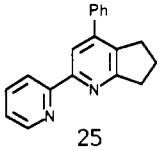
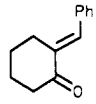
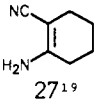
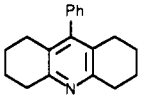
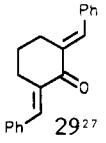
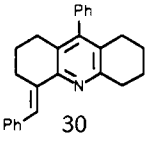
(4)

Potassium hydroxide in 95% ethanol gave a similar result. Interestingly, the dimer of 9,[17] 2-amino-2-[(2-cyano-1-penten-1-yl)amino]cyclopentanecarbonitrile (19) also reacts with 10 under basic conditions to give 18 in good yield. Under these conditions, retro-Michael addition will give 2 equiv of 9. The results are summarized in Table I.

This "3 + 3" reaction can also be conducted under acidic conditions. With equal proportions of 9 and 10 only a 42% yield of 18 is obtained with boiling AcOH/NH_4OAc. The enamino nitrile may be partially hydrolyzed during reac-

(20) (a) Stobbe, H.; Voland, H. *Ber.* **1902**, *35*, 3973. (b) Stobbe, H.; Striegler, C. *J. Prakt. Chem.* **1912**, *86*, 241.

Table I[a]

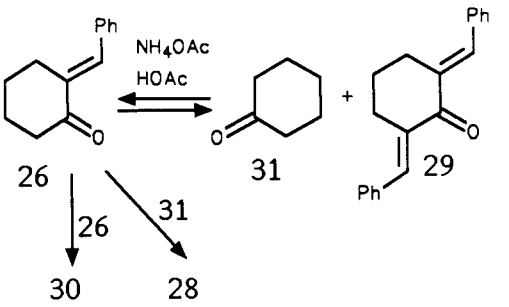
enone	enamino nitrile	pyridine	method/% yield[b]
10[11]	9[18c]	18[20,22]	1:1(B)/71[c] 1:2(A)/88
10	 19[17]	18	1:1(B)/79
10	 20[21]	 21[22]	1:2(B)/64
10	 22[23]	 23	1:2(B)/57
 24[24]	9	 25	1:2(A)/52
 26[25]	 27[19]	 28[26]	1:2(A)/20[d]
 29[27]	27	 30	1:2(A)/62

[a] References are for suitable preparations or identifications. [b] Ratio of enone to enamino nitrile. A or B indicates acid (NH_4OAc/HOAc) or base (NaOEt/EtOH) conditions. Yields were estimated by GC/MS and external standards. Isolated yields were somewhat lower. [c] Actual isolated yield. [d] **30** was the major product (40%).

tion in this acidic medium. As the reaction progresses, the water produced as a byproduct undoubtedly contributes to this hydrolysis. The yield of **18** was increased to 88% by reacting 2 equiv of the enamino nitrile **9** with 1 equiv of the enone **10** under the same conditions. In contrast, slow addition of a solution of **10** to **9** in acidic conditions gave only a 45% yield.

The reaction of (*E*)-3-amino-2-methyl-2-pentenonitrile (**20**)[21] with chalcone (**10**) shows that acyclic enamino nitriles also afford the same "3 + 3" reaction. Compound **20** is somewhat less reactive than **9**. Again, an increase in the concentration of enamino nitrile improves the yield of product significantly and a 64% yield of 2-ethyl-3-methyl-4,6-diphenylpyridine (**21**)[22] is obtained.

Scheme II



Also shown in Table I are 6-methyl-2,4-diphenyl-5,6,7,8-tetrahydro-1,6-naphthyridine (**23**), 4-phenyl-2-(2-pyridyl)-6,7-dihydro-5*H*-1-pyrindine (**25**), and two 2,3:5,6-dicyclohexeno-4-phenylpyridines (**28** and **30**). These compounds show the versatility of our pyridine synthesis and represent a fused heterocyclic ring system, a bispyridyl chelator, and pentasubtituted pyridine rings, respectively. The latter two compounds may be useful as building blocks for hexagonal lattice receptors.[28] The reaction of enone **26** with enamino nitrile **27** gave only the desired pentasubstituted pyridine **28** as a minor product (20%). To our surprise the major product (40%) was **30**. This unexpected product is probably formed by Hantzsch pyridine synthesis in which 2 mol of **26** reacted, with either nitrogen source, to afford **30**. That **27** could serve as a source of nitrogen for this type of reaction was demonstrated by boiling **26** and **27** in AcOH only. Essentially the same amounts of products were produced again, 38% of **30** and 16% of **28**. When the enamino nitrile **27** was removed as a nitrogen source and **26** boiled under nitrogen for 2 days in AcOH/NH_4OAc, **28** (31%), **30** (29%), a dihydro **30** (10%), and about 16% of **29** were obtained (Scheme II). Presumably, **26** is disproportionating under these conditions to **29** and cyclohexanone (**31**). Formation of **28** from the available cyclohexanone and **26** provides support for this disproportionation. Thus, attempted reaction of **26** with **27** to form **28** in a direct manner was precluded by a more facile Hantzsch pyridine synthesis. Upon reaction of pure **29** with **27**, the yield of **30** increased to 62% as expected with the normal enamino nitrile synthesis.

Work up of these reactions is worth mentioning. Routine precautions for cyanide ion and HCN gas are noted in the Experimental Section. Excess enamino nitrile is converted into the base-soluble cyano ketone upon treatment with dilute HCl.[17,19] This facilitates the use of higher stoichiometric ratios of enamino nitrile to improve the yield without causing any difficulty in the isolation of a product.

There are certain limitations to the present "3 + 3" method. Conjugate bases of these enamino nitrile exhibited little reactivity in aprotic solvents. Retrospectively, this stability of salts may in part explain the excellent yields of recent preparations of enamino nitriles in aprotic media.[18,19] Another limitation is where $R_1 = CH_3$, or $R_2 = NO_2$, CO_2Et, or Bz. These enones are too reactive and give a variety of products, none of which is the desired pyridine. Therefore, this new pyridine synthesis method does not allow the direct preparation of a Streptonigrin ring-C precursor with a nitro group at R_2. Some structural limitations in this synthetic method may be overcome by a complimentary "3 + 3" pyridine synthesis in which the leaving group is placed on the enone rather than on the enamine. This will be the subject of a following paper.

(21) Adkins, H.; Whitman, G. M. *J. Am. Chem. Soc.* **1942**, *64*, 150. We obtained a better yield (83% vs 42%) using Kulp's method (ref 18b).
(22) Katritzky, A. R.; El-Mowafy, A. M.; Musummara, G.; Sakizadeh, K.; Sana-Ullah, C.; El-Shafie, S. M. M.; Thind, S. S. *J. Org. Chem.* **1981**, *46*, 3823 who made, in two steps, **18** in 19% and **21** in 17%.
(23) (a) Cook, A. H.; Reed, K. J. *J. Chem. Soc.* **1945**, 399. (b) Kotelo, A.; Mikolajewska, H.; Zajaczkowska, B. *Acta Polon. Pharm.* **1960**, *17*, 361; *Chem. Abstr.* **1961**, *55*, 14295d.
(24) Marvel, C. S.; Coleman, L. E.; Scott, G. P. *J. Org. Chem.* **1955**, *20*, 1785.
(25) Baltzly, R.; Lorz, E.; Russell, P. B.; Smith, F. M. *J. Am. Chem. Soc.* **1955**, *77*, 624.
(26) (a) Yang, S.-S.; Huang, W.-Y.; Chen, S.-M. *Chemistry (Taipei)* **1962**, 65; *Chem. Abstr.* **1963**, *59*, 3893b. (b) Tilichenko, M. N.; Kharchenko, V. G. *Zhur. Obshchei. Khim.* **1960**, *30*, 2283; *Chem. Abstr.* **1961**, *55*, 9400a.
(27) Vorlander, D.; Kunze, K. *Ber.* **1926**, *59*, 2078.
(28) Bell, T. W.; Cho, Y.-M.; Firestone, A.; Healy, K.; Liu, J.; Ludwig, R.; Rothenberger, S. D. *Org. Synth.* **1990**, *69*, 226 and references therein.

Experimental Section

General. FTIR spectra for solids were obtained by diffuse reflectance. IR data are reported in cm^{-1}. Analyses by GC/MS (EI and CI-H_2 modes) employed a HP-1 (0.2-mm-i.d. × 12.5-m and 0.33-μm film, β = 150) capillary column while HPLC/PB/MS used a 5-μm C18 column with MeOH/H_2O solvents. Routine NMR spectra, ^1H (80 MHz) and ^{13}C (20 MHz), were run in $CDCl_3$ vs TMS. Other NMR data are specifically noted. Suitable data and spectra were obtained to match the literature data for all known compounds. When spectral data for known compounds was not available in the literature, it was included herein. Preparative plate chromatography was done on 20- × 20-cm silica gel 60 (PLK-F254) plates. Melting points were taken in capillary tubes and are reported uncorrected. Representative procedures are included.

Chalcone (10) and 2-Aminocrotononitrile (11) (Chatterjea's Reaction).[13] NaOEt/EtOH was generated by adding Na chips (1.0 g, 43.5 mmol) to 25 mL of absolute EtOH under N_2. After cooling 11 (3.28 g, ~85%, ~43.5 mmol) was added. After a short time, 10 (4.16 g, 20.0 mmol) was added, and the mixture was refluxed for 2 h. The reaction mixture was allowed to cool and recrystallize at rt for several days before being poured into 5% aqueous HCl and extracted with CH_2Cl_2. The solvent was dryed with anhyd Na_2SO_4 and evaporated in vacuo. The residual oil was recrystallized from hexane/acetone to give 0.92 g (16.9%) of 3-cyano-2-methyl-4,6-diphenyl-1,4,5,6-tetrahydropyridine (13): mp 201–206 °C [lit.[13] mp 207–208 °C (incorrectly reported as the dihydro compound)]; IR 3292 (NH), 2185 (C≡N); MS 274 (M^+, 100), 273 (26), 197 (24), 169 (28), 104 (42).

The mother liquid was evaporated and the residue recrystallized from EtOH to give in two crops 1.675 g (31.1%) of 3-cyano-2-methyl-4,6-diphenylpyridine (14): mp 117.5–118 °C (lit.[29] mp 121.5–122.5 °C).

General Procedure Using Base. 9 (1.08 g, 10.0 mmol) was dissolved in 25 mL of EtOH containing NaOEt (14 mmol). 10 (1.04 g, 5.0 mmol) was added, and the mixture was boiled under N_2 for 44 h. The EtOH was removed. The residue was partioned between CH_2Cl_2 and water. *NOTE: The water layer was treated with bleach before disposal to convert any free cyanide to harmless cyanate ion.* The CH_2Cl_2 was then treated with 3 M HCl [**HOOD**!] with efficient mixing for 30 min. Finally, the CH_2Cl_2 layer was extracted with 5% NaOH solution (to remove cyano ketone), washed with water, dried, and filtered through a short pad of silica gel. The column was sequentially rinsed with 50 mL each of $CHCl_3$ and EtOAc. Evaporation of the solvents gave 1.23 g of crude mixture. Analysis by GC/MS showed this to contain 786 mg (2.91 mmol, 58.3%) of 2,4-diphenyl-6,7-dihydro-5*H*-1-pyrindine (18). Recrystallization from cyclohexane/EtOAc gave material with mp 141–3 °C. Sublimation gave pure 18: mp 147–8 °C (lit.[20,22] mp 144–146 °C); MS 271 (M^+, 76), 270 (100), 215 (5), 165 (8); ^1H NMR (300 MHz) δ 2.20 (m, 2 H), 3.10 (t, 2 H, J = 7.28), 3.20 (t, 2 H, J = 7.63), 7.35–7.60 (m, 9 H), 8.01–8.05 (m, 2 H); ^{13}C NMR (75.7 MHz), δ 23.52, 30.62, 34.79, 118.06, 126.98, 128.15, 128.22, 128.42, 128.60, 128.63, 133.05, 139.06, 139.98, 145.88, 156.50, 166.67. Neutralization of the 3 M HCl and extractive workup gave only 59 mg of crude products, containing only a trace (0.6%) of 18. A similar reaction used a 1:1 ratio of 9 to 10. It was boiled overnite and allowed to stand for several days before workup. A 71% yield of 18 was obtained.

General Procedure Using Acid. 9 (1.08 g, 10.0 mmol) and 10 (1.04 g, 5.0 mmol) were added to NH_4OAc (1.16 g, 15 mmol) in 15 mL of HOAc and boiled under N_2 for 17 h. The HOAc was evaporated. The residue was partitioned between water [NOTE: see above caution] and CH_2Cl_2. The CH_2Cl_2 layer was treated with 3 M HCl [**HOOD**] for 30 min before being extracted with 5% NaOH solution. The organic layer was dried with $CaCl_2$ and evaporated to give 1.34 g of product. GC/MS analysis (external standard) indicated that 89% of this was 18, which calculates to an 88% yield of the desired product.

2-Aminocyclopentanecarbonitrile (9):[18] ^1H NMR δ 1.86–1.98 (m, 2 H), 2.40–2.49 (m, 2 H), 2.5–2.6 (m, 2 H), 4.57 (s, 2 H); ^{13}C NMR δ 21.90, 31.15, 34.18, 74.17, 119.0, 162.44.

2-Amino-2-[(2-cyano-1-penten-1-yl)amino]cyclopentanecarbonitrile (19):[17] IR 3397 and 3344 (NH_2), 3142 (NH), 2256 and 2182 (C≡N); MS 216 (M^+, 0.15), 176 (42), 162 (13), 149 (100), 109 (9), 54 (9); ^1H NMR δ 1.6–3.1 (m, 12 H), 4.0–5.5 (3 broad signals, 4 H).

(*E*)-3-Amino-2-methyl-2-pentenonitrile (20):[21] IR 3362 and 3239 (NH_2), 2181 (C≡N); MS 110 (M^+, 100), 109 (87), 95 (9), 82 (38), 69 (28), 56 (76).

2-Ethyl-3-methyl-4,6-diphenylpyridine (21):[22] bp 155 °C (0.1 Torr); MS 273 (M^+, 31), 272 (100), 257 (6), 244 (4).

4-Amino-1,2,5,6-tetrahydro-1-methylnicotinonitrile (22):[23] IR 3400 and 3169 (NH_2), 2176 (C≡N); MS 137 (M^+, 33), 136 (100), 119 (14), 95 (14), 94 (15).

6-Methyl-2,4-diphenyl-5,6,7,8-tetrahydro-1,6-naphthyridine (23): mp 141–6 °C; IR 776 and 698 (Ar); MS 300 (M^+, 52), 299 (100), 285 (12), 256 (6), 215 (7), 154 (11); ^1H NMR (300 MHz) δ 2.379 (s, 3 H), 2.807 (t, 2 H), 3.223 (t, 2 H), 3.47 (s, 2 H), 7.2–7.5 (m, 9 H), 7.96–7.99 (m, 2 H); ^{13}C NMR (75.47 MHz) δ 32.96, 45.95, 52.91, 55.87, 118.92, 125.83, 126.75, 127.93, 128.19, 128.34, 128.49, 138.56, 148.41, 154.64, 154.97; MS (high-resolution) calcd for $C_{21}H_{20}N_2$ 300.16265, found 300.16193.

(*E*)-3-Phenyl-1-(2-pyridyl)prop-2-en-1-one (24):[24] IR 1698 and 1670 (C=O); MS 209 (M^+, 73), 181 (19), 180 (100), 131 (27), 103 (45), 102 (33), 77 (19).

4-Phenyl-2-(2-pyridyl)-6,7-dihydro-5*H*-1-pyrindine (25): mp 133–135 °C; IR 775 and 700 (Ar); MS 272 (M^+, 67), 271 (100), 193 (4), 165 (4), 135 (5), 78 (8), 51 (7). Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29. Found: C, 83.71; H, 6.00; N, 10.30.

(*E*)-2-Benzylidenecyclohexanone (26):[25] IR 1680(C=O); MS 186 (M^+, 61), 185 (100), 129 (43), 115 (48), 102 (12).

9-Phenyl-1,2,3,4,5,6,7,8-octahydroacridine (28):[26] MS 263 (M^+, 100), 262 (96), 234 (16), 165 (11), 109 (10).

(*E*,*E*)-2,6-Dibenzylidenecyclohexanone (29):[27] IR 1662 (C=O); MS 274 (M^+, 76), 273 (100), 217 (14), 129 (10), 128 (14), 115 (36), 91 (12), 77 (11); ^1H NMR δ 1.74 (m, 2 H), 2.88 (m, 4 H), 7.27–7.47 (m, 10 H), 7.79 (m, 2 H).

1-Benzylidine-9-phenyl-1,2,3,4,5,6,7,8-octahydroacridine (30): mp 167–169 °C; IR 754 and 694 (Ar); MS 351 (M^+, 57), 350 (100), 322 (13), 274 (10), 91 (9). Anal. Calcd for $C_{28}H_{25}N$: C, 88.85; H, 7.17; N, 3.98. Found: C, 88.48; H, 7.11; N, 3.96.

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Synthesis of a 1,2-Phenylene-Bridged Triporphyrin

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Since the first report of a covalently-linked cofacial triporphyrin,[1] several cofacial triporphyrins[2] have appeared

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