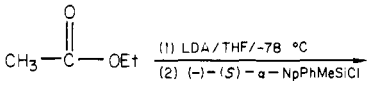
O-silylated material, **4** and **5**, respectively in quantitative yield (crude product). Moreover it was not possible to purify the desired C-silylated isomer (**4**) due to either decomposition or hydrolysis during all attempts.[10]

The C-silylation of butyrolactone and valerolactone proceeds exceedingly well to give the C-silylated lactones in high isolated yield. However, the product from the reaction with α-methyl butyrolactone (**7**) proved impossible to purify without the occurrence of decomposition or hydrolysis.[11]

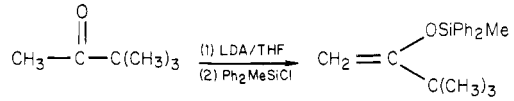
The displacement of the chloride on silicon by the enolate ion occurs with inversion of configuration at silicon as seen by entry 8[12] (eq 3). This inversion of configuration at silicon is expected



(+)-(*R*)-α-NpPhMeSiCH$_2$CO$_2$Et (3)

on the basis of Sommer's results on the nucleophilic displacement of the chloride leaving group from silicon.[14] Thus, we now have a route to α-silylated esters optically active at silicon from ester lithium enolates.

Finally, an attempt to prepare 1-(diphenylmethylsilyl)-3,3-dimethyl-2-butanone via diphenylmethylsilylation of the lithium enolate of pinacolone gave only the enol silyl ether in 90% isolated yield (eq 4). Thus under the present conditions the reaction does



(4)

not serve to C-silylate the lithium enolates of ketones.[15]

The silylation of ethyl propionate is representative of the general procedure. A dry, 100 mL, round-bottom flask equipped with magnetic stirring, cold bath, and a nitrogen inlet was charged with 10 mL of THF, 1.55 mL of diisopropylamine (12.0 mmol) and at −78 °C 6.70 mL (12.0 mmol) of 1.79 M *n*-butyllithium in hexane. The resulting solution was warmed to 25 °C for 15 min, cooled to −78 °C again, and 1.02 g (10.0 mmol) of ethyl propionate in 2 mL of THF added via syringe. The clear solution was stirred for 30 min at −78 °C and 2.33 g (10.0 mmol) of diphenylmethylchlorosilane in 10 mL of THF added dropwise via syringe. The reaction mixture was stirred at −78 °C for 1.5 h, warmed to 25 °C for 2 h, and hydrolyzed with 10 mL of 1.5 N HCl. The organic layer was dried over sodium sulfate, concentrated, and the crude sample purified by flash chromatography[16] on silica gel by utilizing 2% ethyl acetate/hexane to give 2.78 g (93.3%) of ethyl (diphenylmethylsilyl)propionate.

The results presented here should inspire greater use of α-silylated esters and lactones in organic synthesis[17] and a greater appreciation of the potential of the electronic nature of a silicon moiety as opposed to the more commonly invoked steric factors.

Acknowledgment. We thank the NIH-MBS (RR-1802-09) for financial support, Pfizer and Bristol Pharmaceuticals of Puerto Rico for generous gifts of chemicals, and the NSF (CHE-79-1462) for an instrument grant to purchase the Jeolco FX90Q NMR. We especially want to thank Professors L. Echegoyen and J. Szobota for valuable assistance in obtaining the ^{13}C spectra.

(10) Gentle hydrolysis (H_2O/pentane) of a 50:50 mixture of **4** and **5** gave a mixture of ethyl phenylacetate and diphenylmethylsilanol. Attempts to purify **4** by chromatography on a variety of silica gels and florisil at temperatures down to −30 °C resulted in hydrolysis. Kugelrohr distillation resulted in decomposition as did gas chromatography. The mixture of **4** and **5** showed a singlet at δ 3.28 for the α proton of **4** and resonances at δ 4.55 and 4.43 (2:1) for the two isomers of **5**. The IR spectrum showed bands at 1735 and 1650 cm^{-1}.

(11) Chromatography on silica gel or florisil even at low temperature resulted in hydrolysis. Attempted distillation gave decomposition. The NMR spectrum of the crude product showed resonances at δ 3.62 (m) for the oxygenated methylene, 1.22 (s) for the alpha methyl and 0.47 (s) for the silyl methyl group. The IR showed a strong carbonyl band at 1770 cm^{-1}. We have been able to prepare and purify *tert*-butyl 2-(diphenylmethylsilyl)-2-methylpropionate (**10**), by methylation of the lithium enolate of *tert*-butyl 2-(diphenylmethylsilyl)propionate (**11**), in 93.1% yield. **11** was prepared also in 93.1% yield from methylation of the lithium enolate of **1**.

(12) Compound **9** showed $[\alpha]_D$ −4.69° (*c* 10.75, cyclohexane) which compared to Brook's $[\alpha]_D$ +4.65° for the compound formed from the reaction of (+)-α-naphthylphenylmethylchlorosilane and ethyl diazoacetate.[13]

(13) Brook, A. G.; Duffand, J. M.; Anderson, D. G. *J. Am. Chem. Soc.* **1972**, *92*, 7567.

(14) Sommer, L. H. "Stereochemistry, Mechanism and Silicon"; McGraw-Hill: New York, 1965.

(15) Rasmussen, J. K. *Synthesis* **1977**, 1.

(16) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(17) Studies related to the utility of α-silylated esters in synthesis are under way in our laboratory. Treatment of the lithium enolate of **2** (LDA/THF/−78 °C) with isobutyraldehyde gives an 85% yield of ethyl 4-methyl-2-butenoate (cis/trans 16:84). 2-(*tert*-butyldimethylsilyloxy)cyclopentanone gave ethyl (2-*tert*-butyldimethylsiloxy-(*Z*)-cyclopentylidene)acetate in 30% isolated yield. Thus, these α-(diphenylmethylsilyl) esters are useful precursors for a Peterson-type reaction to prepare α,β-unsaturated esters.

(18) **1**: ^{1}H NMR (CCl_4, Me_4Si) δ 7.1 (m, 10 H), 2.14 (s, 2 H), 1.13 (s, 9 H), 0.62 (s, 3 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 171.0, 135.0, 134.3, 129.3, 127.6, 79.4 27.7, 25.9, −4.0; IR 1712 cm^{-1}. **2**: ^{1}H NMR ($CDCl_3$/Me_4Si) δ 7.58 (m, 4 H), 7.36 (m, 6 H), 3.93 (q, 2 H, *J* = 7 Hz), 2.40 (s, 2 H), 0.97 (t, 3 H, *J* = 7 Hz), 0.68 (s, 3 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 171.9, 134.9, 134.3, 129.5, 127.8, 59.8, 24.8, 13.9, −3.9; IR 1721 cm^{-1}. **3**: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 7.60 (m, 4 H), 7.42 (m, 6 H), 3.92 (d, 2 H, *J* = 7.1 Hz), 2.58 (q, 1 H, *J* = 8 Hz), 0.59 (d, 3 H, *J* = 8 Hz), 0.94 (t, 3 H, *J* = 7.1 Hz), 0.66 (s, 3 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 175.7, 134.8, 134.3, 129.5, 127.8, 127.7, 59.8, 28.8, 13.9, 11.9, −5.6; IR 1720 cm^{-1}. **6**: ^{1}H NMR (CCl_4/Me_4Si) δ 7.3 (m, 10 H), 4.28–3.31 (m, 2 H), 2.81–1.80 (m, 3 H), 0.76 (s, 3 H); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 179.0, 134.6, 129.8, 127.9, 127.5, 67.1, 28.5, 25.0, −4.7; IR 1765 cm^{-1}. **8**: ^{1}H NMR ($CDCl_3$/Me_4Si) δ 7.30 (m, 10 H), 3.90–3.66 (m, 2 H), 2.86–1.40 (m, 4 H), 1.06 (t, 1 H), 0.63 (s, 3 H); ^{13}C NMR ($CDCl_3$/Me_4Si) 178.5, 134.8, 129.8, 128.1, 127.9, 75.6, 32.9, 30.4, 21.3, −4.5; IR 1765 cm^{-1}. **9**: ^{1}H NMR (CCl_4/Me_4Si) δ 6.92–8.02 (m, 12 H), 3.75 (q, 2 H, *J* = 7 Hz), 2.43 (s, 2 H), 0.80 (t, 3 H, *J* = 7 Hz), 0.76 (s, 3 H); IR 1735 cm^{-1}. $[\alpha]^{25}_D$ −4.69° (*c* 2.13, cyclohexane). Brook and co-workers[13] report +4.65° for the other enantiomer.

Indole Alkaloid Synthesis via Claisen Rearrangement. Total Synthesis of Secodine[1]

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Received December 22, 1980

It has been over a decade since dehydrosecodine (**1**) was postulated[2] as a key intermediate both in the later stages of the biosynthesis of *Aspidosperma* and *Iboga* alkaloids[3] and in the biomimetic interconversion of certain alkaloids.[4] To date, presumably due to its inherent lability, **1** has not been isolated from natural sources or synthesized as a discrete, isolable substance; however, a number of more highly reduced alkaloids related to **1** have been isolated from *Rhazya* species.[5] These alkaloids include secodine (**2**), 16,17-dihydrosecodin-17-ol (**3**), and 16,17-dihydrosecodine (**4**).[5]

We now wish to report the total synthesis of **2**, utilizing a synthetic strategy which is based upon the Claisen ortho ester

† Fellow of the Alfred P. Sloan Foundation, 1980–1982.

‡ Chevron Graduate Fellow, 1980.

(1) Synthesis via Sigmatropic Rearrangements. 6. For previous paper in this series, see: Raucher, S.; Burks, J. E., Jr.; Hwang, K.-J.; Svedberg, D. P. *J. Am. Chem. Soc.* **1981**, *103*, 1853.

(2) Qureshi, A. A.; Scott, A. I. *J. Chem. Soc., Chem. Commun.* **1968**, 945.

(3) Scott, A. I. *Bioorg. Chem.* **1972**, *94*, 8266.

(4) Scott, A. I.; Qureshi, A. A. *Tetrahedron* **1974**, *30*, 2993 and references cited therein.

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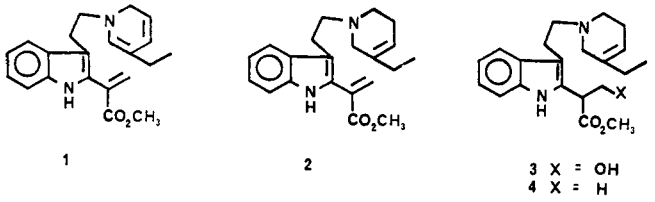
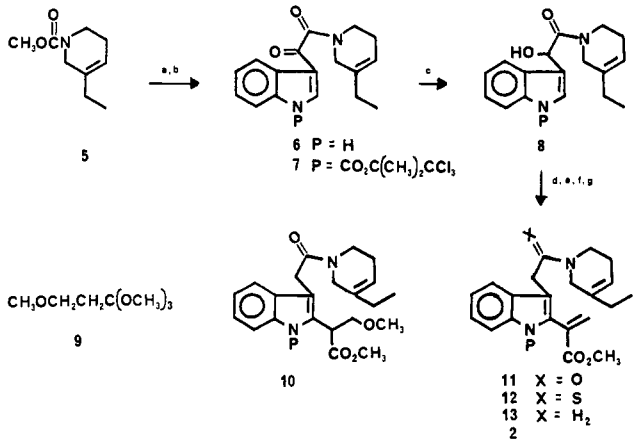


rearrangement[6,7] of the readily prepared indole-3-glycolamide **8** with trimethyl β-methoxyorthopropionate (**9**)[8] to give the 2,3-disubstituted indole **10** and subsequent elimination of methanol to afford

This strategy incorporates two modifications of the Claisen ortho ester rearrangement which we have recently reported.[7,8] The first modification involves the application of our discovery that the [3,3]-sigmatropic rearrangement of benzyl vinyl ethers, although not generally observed,[9] is markedly facilitated by a carboxyl functionality at the benzylic position.[7] The second modification entails the use of trimethyl β-methoxyorthopropionate (**9**) as a trimethyl orthoacrylate equivalent in the Claisen ortho ester arrangement.[8,10] The combination of the above methods provides easy access to structures with the functionality necessary for elaboration to the desired alkaloids.[12]

The indole-3-glycolamide **8** necessary for the Claisen ortho ester rearrangement was prepared by the following route.[13] Reaction of *N*-(carbomethoxy)-3-ethyl-1,2,5,6-tetrahydropyridine (**5**)[14] with methyllithium (3 equiv) in diethyl ether (1 M, 0 °C, 20 min), quenching with anhydrous HCl (3 equiv) in diethyl ether, addition of triethylamine (3 equiv) followed by freshly prepared indole-3-glyoxyloyl chloride[15] (1.0 equiv), and stirring at 0 °C for 4 h gave (90%) **6** [mp 120–122° (ether–hexane); ^{1}H NMR ($CDCl_3$) δ 1.10 (t, J = 7 Hz, 3 H), 1.5–2.4 (m, 4 H), 3.2–4.2 (m, 4 H), 5.45 (br s, 1 H), 7.0–7.4 (m, 3 H), 7.70 (d, J = 3 Hz, 1 H), 8.1–8.4 (m, 1 H)]. Protection of the indole nitrogen[16] with $ClCO_2C(CH_3)_2CCl_3$[17] (1.1 equiv) and triethylamine (1.4 equiv) in CH_2Cl_2 (0.5 M, 0–25 °C, 30 min) afforded (80%) **7** [mp 132.5–135° (CH_3OH); ^{1}H NMR $CDCl_3$ δ 1.10 (t, J = 7 Hz, 3 H), 1.7–2.4 (m) and 2.08 (s) (total 10 H), 3.3–4.2 (m, 4 H), 5.50 (br s, 1 H), 7.15–7.60 (m, 2 H), 8.20–8.40 (m, 3 H)]. Addition of a solution of $NaBH_4$ (1.0 equiv) in methanol (0.5 mL per mmol) to a solution of **7** in THF (0.2 M, 0 °C, 20 min) and purification by flash chromatography[18] (3% EtOAc–CH_2Cl_2) gave (63%) the requisite indole-3-glycolamide **8**[13] [^{1}H NMR ($CDCl_3$) δ 0.7–1.3 (m, 3 H), 1.6–2.5 (m) and 2.08 (s) (total 10 H), 3.0–4.2 (m, 4 H), 4.60 (d, J = 6 Hz, 1 H, CHO*H*), 5.25–5.60 (m, 2 H), C*H*OH and –C*H*=C<), 7.10–8.40 (m, 5 H)] as a light yellow oil.

Scheme I[a]



[a] (a) MeLi; HCl; Et_3N; indole-3-glyoxyloyl chloride. (b) $ClCO_2CMe_2CCl_3$, Et_3N. (c) $NaBH_4$. (d) **9**, $ArCO_2H$, Δ. (e) $(CH_3OC_6H_4)_2P_2S_4$. (f) $Et_3O^+BF_4^-$; $NaBH_3CN$, HOAc. (g) Zn, HOAc.

The Claisen ortho ester rearrangement of **8** with **9** was examined under a variety of conditions. Although it was possible to isolate **10** if the reaction was carried out for shorter times, the best overall yields were obtained if the Claisen ortho ester rearrangement and subsequent elimination were effected concomitantly in the same reaction vessel. Thus, a solution of **8** and 2,4,6-trimethylbenzoic acid (2 equiv)[19] in **9** (15 mL per mmol of **8**) under argon in a round bottomed flask fitted with a 15-cm Vigreux column topped with a short-path distillation head was heated in an oil bath at 210 °C for 20 min and then at 225 °C for 100 min. Methanol was allowed to distill out of the reaction mixture as it was formed. Excess ortho ester was removed in vacuo (60–80 °C, 0.5 mm), and the residue was purified by flash chromatography[18] (40% EtOAc–hexane) to give **11**[13] [^{1}H NMR ($CDCl_3$) δ 1.00 (t, J = 7 Hz, 3 H), 1.7–2.2 (m) and 2.03 (s) (total 10 H), 3.2–4.2 (m) and 3.70 (s) (total 9 H), 5.47 (br s, 1 H), 5.85 (d, J = 2 Hz, 1 H), 6.58 (d, J = 2 Hz, 1 H), 7.05–8.45 (m, 4 H)] as a light yellow oil in 65% overall yield from **8**.

Conversion of **11** to secodine (**2**) requires only the reduction of the amide and removal of the indole nitrogen protecting group. The reduction of the amide **11** was effected by a new, highly selective, and mild procedure[20] which involves preparation of the thioamide **12** (71% yield after purification by flash chromatography[18] with 30% EtOAc–hexane) by reaction with $(CH_3OC_6H_4)_2P_2S_4$[21] (0.5 equiv) in refluxing benzene for 2 h, followed by alkylation with $Et_3O^+BF_4^-$ (1.5 equiv) in CH_2Cl_2 and reduction with $NaBH_3CN$ (3.0 equiv) in methanol containing HOAc (9.0 equiv) at 0 °C to give **13**[13] [^{1}H NMR ($CDCl_3$) δ 1.02 (t, J = 7 Hz, 3 H), 1.70–3.25 (m) and 2.08 (s) (total 18 H), 3.72 (s, 3 H),

(6) (a) Johnson, W. S.; Werthemann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T.-T.; Faulkner, D. J.; Peterson, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 741. For recent reviews, see: (b) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1. (c) Ziegler, F. *Acc. Chem. Res.* **1977**, *10*, 227. (d) Bennett, G. B. *Synthesis* **1977**, 589.

(7) (a) Raucher, S.; Lui, A. S.-T. *J. Am. Chem. Soc.* **1978**, *100*, 4902. (b) Raucher, S.; Lui, A. S.-T.; Macdonald, J. E. *J. Org. Chem.* **1978**, *43*, 3794.

(8) Raucher, S.; Macdonald, J. E.; Lawrence, R. F. *Tetrahedron Lett.* **1980**, 4335.

(9) For pertinent references, see ref 7a, footnote 3.

(10) Although triethyl orthoacrylate is readily prepared,[11] attempts to effect Claisen ortho ester rearrangement with this substance have not proved to be encouraging: (a) Raucher, S.; Hwang, K.-J. Macdonald, J. E. *Tetrahedron Lett.* **1979**, 3057. (b) Saucy, G.; Cohen, N.; Banner, B. L.; Trullinger, D. P. *J. Org. Chem.* **1980**, *45*, 2080. For an alternative method for the introduction of an α-substituted acrylate moiety via [3,3]-sigmatropic rearrangement, see: (c) Still, W. C.; Schneider, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 948. This procedure is not applicable to esters derived from **8** due to the acidity of the benzylic proton.

(11) Stetter, H.; Uerdingen, W. *Synthesis* **1973**, 207.

(12) For other approaches to α-(2-indolyl)acrylates, see: (a) Ziegler, F. E.; Spitzner, E. B. *J. Am. Chem. Soc.* **1973**, *95*, 7146. (b) Kuehne, M. E.; Roland, D. M.; Hafter, R. *J. Org. Chem.* **1978**, *43*, 3705. (c) Kuehne, M. E.; Kirkemo, C. L.; Matsko, T. H.; Bohnert, J. C. *Ibid.* **1980**, *45*, 3259. (d) Sundberg, R. J.; Bloom, J. D. *J. Org. Chem.* **1980**, *45*, 3382. (e) Weinstein, B.; Lin, L.-C. C.; Fowler, F. W. *Ibid.* **1980**, *45*, 1657.

(13) All new compounds exhibited satisfactory infrared, proton magnetic resonance, mass spectroscopic, and/or combustion analysis data. Yield refer to isolated, chromatographically (TLC, HPLC) homogeneous material.

(14) Prepared by the reduction of *N*-benzyl-3-ethylpyridinium chloride with $NaBH_4$ (4 equiv) in methanol at 0 °C to give *N*-benzyl-3-ethyl-1,2,5,6-tetrahydropyridine in 90% yield, followed by debenzylation with CH_3OCOCl (1.3 equiv) in benzene at reflux for 20 h to give **5** in 90% yield. GS/MS analysis indicated that **5** contained approximately 5% of *N*-(carbomethoxy)-3-ethyl-1,2,3,6-tetrahydropyridine. The series of compounds containing minor isomers was carried along and was separated by flash chromatography during the purification of **7**.

(15) Shaw, K. N. F.; McMillan, A.; Gundmundson, A. G.; Armstrong, M. D. *J. Org. Chem.* **1958**, *23*, 1171.

(16) Protection of the indole nitrogen with an electron-withdrawing group is necessary for the success of the Claisen rearrangement. The analogous series of transformations were carried out in comparable yields for compounds **7**–**13** with P = 4-$CH_3C_6H_4SO_2$; however, difficulties were encountered during attempts to remove this protecting group. Attempts to effect reduction of **7** (P = $CO_2CH_2CCl_3$) with $NaBH_4$ or Claisen ortho ester rearrangement of **8** [P = $CO_2C(CH_3)_3$] led to cleavage of the protecting group.

(17) Eckert, H.; Listl, M.; Ugi, I. *Angew Chem., Int. Ed. Engl.* **1978**, *17*, 361.

(18) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(19) It is noteworthy that the majority of the acid catalyst is esterified under these conditions. For example, methyl 2,4,6-trimethylbenzoate was obtained in greater than 98% yield from this reaction.

(20) Raucher, S.; Klein, P. *Tetrahedron Lett.* **1980**, 4061. Also see ref 12d.

(21) Scheibye, S.; Pedersen, B. S.; Lawesson, S. O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 229.

5.53 (br s, 1 H), 5.82 (d, J = 2 Hz, 1 H), 6.61 (d, J = 2 Hz, 1 H), 7.20–7.80 (m, 3 H), 8.20–8.40 (m, 1 H)] as a light yellow oil in 81% overall yield from **12**.

The total synthesis of secodine was completed by removal of the β,β,β-trichloro-*tert*-butyl carbamate protecting group by treatment of a solution of **13** in 10:1 methanol–acetic acid (0.02 M) with excess powdered zinc (20 equiv) at 0 °C for 20 min, aqueous $NaHCO_3$ workup, rapid removal of solvents at 0 °C, and purification by flash chromatography[18] (20% 2-propanol–CH_2Cl_2) to give **2**[13] [^{1}H NMR ($CDCl_3$) δ 1.00 (t, J = 7 Hz, 3 H), 1.6–3.3 (m, 12 H), 3.80 (s, 3 H), 5.45 (m, 1 H), 6.11 (d, J = 1 Hz, 1 H), 6.47 (d, J = 1 Hz, 1 H), 7.0–7.8 (m, 4 H), 9.2 (br s, 1 H); m/e Calcd for $C_{21}H_{26}O_2N_2$: 338.1994. Found: 338.1930] as a viscous oil in 76% yield.[13,22]

The above synthesis clearly demonstrates the applicability of the Claisen ortho ester rearrangement of indole-3-glycolamides for the construction of 2,3-disubstituted indoles, as well as the utility of **9** for the introduction of an α-substituted acrylate moiety under mild, nonbasic conditions. We are currently investigating the use of this strategy for the synthesis of a number of *Aspidosperma* and *Iboga* alkaloids.

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(22) Although secodine dimerizes rapidly at room temperature, the protected precursor **13** is stable for several weeks when stored under argon at 0 °C. For studies concerning the related, naturally occurring dimeric alkaloids, the secamines and presecamines, see: (a) Evans, D. A.; Smith, G. F.; Smith, G. N.; Stapleford, K. S. J. *J. Chem. Soc., Chem. Commun.* **1968**, 859. (b) Cordell, G. A.; Smith, G. F.; Smith, G. N. *Ibid.* **1970**, 191.

Guest-Host Association by Transition-Metal Complexes Containing Permanent Voids—Progress toward Models for the Ternary Complex of Cytochrome P450

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Cytochrome P450 monooxygenase enzymes[1,2] produce highly selective oxygenations[3,4] of organic substrates by simultaneously activating dioxygen[5,6] and undergoing a hydrophobic[6] guest–host association between the enzyme and the target substrate. We are concerned with the design, synthesis, and study of totally synthetic transition-metal species having the ability to emulate cytochrome P450 by forming ternary complexes of this kind. Structure I shows a family of bicyclic ligands whose cobalt(II) and iron(II) complexes exhibit exceptional O_2-carrying capacities.[7,8] The earlier studies used relatively small bridging groups R^1 (structure I) that produced a limited cavity having sufficient volume to accommodate *only* small ligands such as O_2,[7,8] CO,[9] NCS^-,[10] etc.

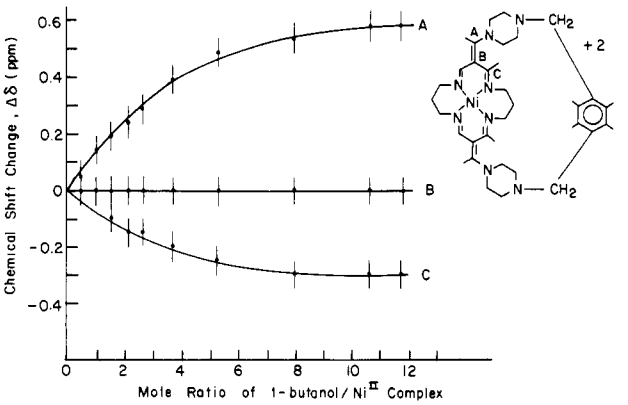
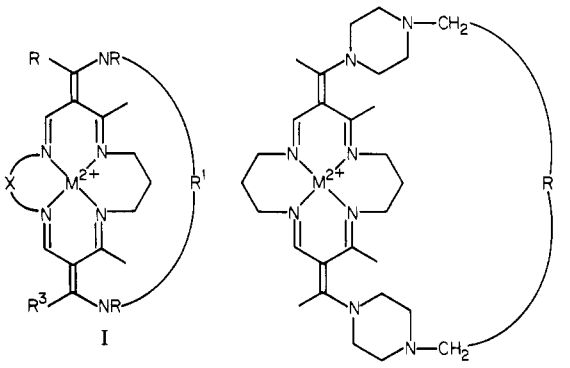


Figure 1. ^{13}C NMR, changes in chemical shifts for atoms of the host (Ni^{2+} complex of structure II, R = durene) as the concentration of guest (*n*-butyl alcohol) is changed, D_2O solution, ~30 °C.



Redesign of the bridging unit has now produced related structures having sufficiently commodious persistent voids to engulf many potential organic substrates (structure II, R = anthracene, benzene, durene, or pyridine). By deriving structure II from structure I, we are assured that the appropriate metal complexes will interact with O_2 as required for the formation of the ternary complex. The interaction that remained to be demonstrated is the guest–host association and that is the subject of this report. Guest–host associations resulting from hydrophobic interactions have been most widely studied with oligomeric cyclodextrins[11] and paracyclophanes[12,13] acting as hosts. Although there are several examples of cyclodextrins containing metal ions,[14] we are aware of no previous examples in which a transition metal is an essential part of the wall of a permanent void designed to serve as host for a hydrophobic guest.

The preparation of these complexes is illustrated by the anthracene derivative as follows. [Ni{(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$}](PF$_6$)$_2$[15] (0.005 mol) in acetonitrile was added dropwise to piperazine (0.1 mol) in methanol. An orange crystalline product (III) was isolated from the acetonitrile/methanol solution; yield, 1.2 g (29.2%). Anal. Calcd for $NiC_{26}H_{44}N_8P_2F_{12}$: C, 38.20; H, 5.43; N, 13.71. Found: C, 38.14; H, 5.58; N, 13.65. The product [Ni{(piperazineEthi)$_2$Me$_2$[16]tetraeneN$_4$}](PF$_6$)$_2$ (0.00244 mol)

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