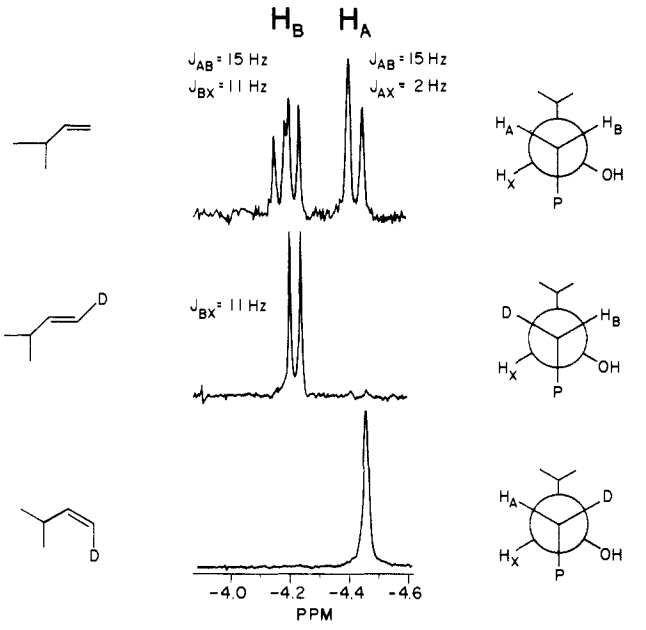

Figure 1. High-field ^{1}H NMR of *N*-alkylporphyrins from 3-methyl-1-butene and its *E*- and *Z*-1-deuterio isomers.

the biological system, epoxides do not form green pigments under our catalytic conditions.

The *N*-alkylporphyrin isolated from 3-methyl-1-butene has a ^{1}H NMR ($CDCl_3$) similar to that previously reported[2b] with a high-field pair of doublets for the methylene attached to the pyrrolic nitrogen (Figure 1). When the *E*- and *Z*-1-deuterio olefins are used, only one doublet is observed, indicative of a stereospecific reaction. The actual stereochemistry of addition was determined from the coupling constants, assuming a conformation with the bulky isopropyl group and the porphyrin trans (Figure 1). The anti coupling constant for the *E*-1-deuterio olefin requires that the N-alkylation must result from a syn addition of oxygen and nitrogen to the olefin. The *N*-alkylporphyrin from the *Z*-1-deuterio olefin confirms this stereospecificity (Figure 1). The same stereochemistry has been reported for P-450, using an indirect method.[4c] Analysis of recovered olefin showed no loss of stereochemistry, and the epoxide indicated a stereospecific syn addition.

Olefin partition numbers (moles of epoxide produced per mole of catalyst N-alkylated) were measured[7] and found to be highly structure dependent: 1-decene, 100; methylene cyclohexane, 800; styrene, 10000. These values resemble those observed for P-450 (200–230) with allylisopropylacetamide.[3a,b] The partition number for 1-decene is independent of both catalyst and olefin concentration. In addition, the presence of a competing olefin, cyclooctene, at a 1:10 and 1:2 (cyclooctene/1-decene) ratio while decreasing both epoxidation and N-alkylation rates does not affect the partition number for 1-decene. Such observations are consistent with (but do not require) the presence of a common intermediate that can partition between N-alkylation and epoxidation. That 1,1-disubstituted olefins and styrenes yield *N*-alkylporphyrins in this model system and not in the biological system may be due to a steric effect or simply due to the greater stability of this catalyst and the large partition numbers for these olefins.

Several pathways have been proposed for olefin epoxidation and N-alkylation: formation of an olefin–oxo π-complex,[9] an acyclic cation or radical,[3c,2b] an electron-transfer species followed by collapse to a radical or cation,[8] a metallacarbene,[9] or a metallacycle.[1a,2b] We have proposed a metallacyclic intermediate for olefin epoxidation[1a] and phenylacetaldehyde formation[1b] and believe a metallacycle could be involved in porphyrin N-alkylation. The observed regiospecificity of the N-alkylation and the dependence on olefin structure are easily explained by preference for one regioisomer of a putative metallacycle. We are continuing to explore the mechanism of these reactions.

Acknowledgment. We thank Jeffrey P. Fitzgerald, Scott A. Raybuck, and Thomas J. Kodadek for advice and technical assistance and acknowledge support from the Bioorganic, Biomedical Mass Spectroscopy Resource (A. L. Burlingame, Director), supported by NIH Division of Research Resources Grant RR01614, the National Institutes of Health (NIH GM17880), and the National Science Foundation (NSF CHE83-18512).

(7) To determine partition numbers, aliquots of a mixture (20 mL) of olefin (0.1–2 M), PFIB (0.2–0.6 mmol), alkane standard (0.01–0.5 mmol), and Fe(TDCP)Cl (3–12 μmol) in CH_2Cl_2 at 17 °C were taken and excess oxidant was quenched with PPh_3. The disappearance of Fe(TDCP)Cl (416 nm Soret) and formation of *N*-alkylporphyrin (446 nm Soret) was isosbestic (four points) and first order in Fe(TDCP)Cl. Epoxide formation was followed by GC. Since the *N*-alkylporphyrins have a catalytic activity an order of magnitude lower than Fe(TDCP)Cl, the partition numbers were measured by determining the ratio of epoxide to total catalyst when formation of the *N*-alkylporphyrin was essentially complete. The actual partition numbers were found to be (within 15%) 1-decene, 130; methylene cyclohexane, 830; and styrene, 12000 by our best estimate considering the catalytic activity of the *N*-alkyl porphyrin. Similar partition numbers were obtained alternatively by measuring either the epoxide formation at half-conversion (one half-life) or the ratio of initial rates for both processes.

(8) Traylor, T. G.; Nakano, T.; Dunlap, B. E.; Traylor, P.; Dolphin, D. *J. Am. Chem. Soc.* **1986**, *108*, 2782.

(9) Groves, J. T. 41st Northwest Regional Meeting of the American Chemical Society, ACS, Portland OR, June 16–18, 1986.

Organic Synthesis Using Carbon Monoxide. Regiospecific Cobalt-Mediated Synthesis of 2*H*-Pyran-2-ones

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(η^3-Oxocyclobutenyl)(tricarbonyl)cobalt complexes **1** can be prepared in good yields by the reaction of readily available cyclopropenyl cations with the $[Co(CO)_4]^-$ anion.[1] This ring-expansion reaction incorporates one molecule of CO originally present on the metal into the oxocyclobutenyl framework. Excellent regioselectivity is obtained with unsymmetrically substituted cations, the unique substituent R on the cyclopropenyl ring invariably appearing adjacent to the ketone in the oxocyclobutenyl product.[1] We now report that reaction of these oxocyclobutenyl complexes with carbon or hydride nucleophiles under an atmosphere of CO results in conversion to the important 2*H*-pyran-2-one skeleton,[2] with regeneration of the $[Co(CO)_4]^-$ anion. A key step in the mechanism is shown to involve transfer of an acyl or formyl ligand from cobalt to the oxocyclobutenyl ring.

Reaction of the oxocyclobutenyl complex **1a**[1] with methyllithium (THF, −78 °C) under a CO atmosphere followed by warming to room temperature affords a solution whose IR spectrum contains a single band at 1887 cm^{-1}, indicating clean formation of the $[Co(CO)_4]^-$ anion.[3] Chromatographic workup affords the known[4] pyrone **2a**, identified by comparison of its spectral properties with

(1) Donaldson, W. A.; Hughes, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 4846–4859.

(2) The pyrone skeleton is an important component of human leukocyte elastase inhibitors: Spencer, W. B.; Copp, L. J.; Pfister, J. R. *J. Med. Chem.* **1985**, *28*, 1828–1832. Groutas, W. C.; Stanga, M. A.; Brubaker, M. J.; Huang, T. L.; Moi, M. K.; Carroll, R. T. *Ibid.* **1985**, *28*, 1106–1109. For a review of the synthesis and chemistry of 2*H*-pyran-2-ones, see: Staunton, J. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: Oxford, **1979**; Chapter 18.2.

(3) Edgell, W. F.; Lyford, J.; Barbetta, A.; Jose, C. I. *J. Am. Chem. Soc.* **1971**, *93*, 6403–6406. In the absence of CO the IR spectrum of the solution is more complicated, although the organic product (vide infra) is still formed.

(4) For other syntheses of **2a,b**, see: Hayasi, Y.; Nozaki, H. *Tetrahedron* **1971**, *27*, 3085–3093. For **2e**, see: Ishibe, N.; Masui, J. *J. Am. Chem. Soc.* **1974**, *96*, 1152–1158.

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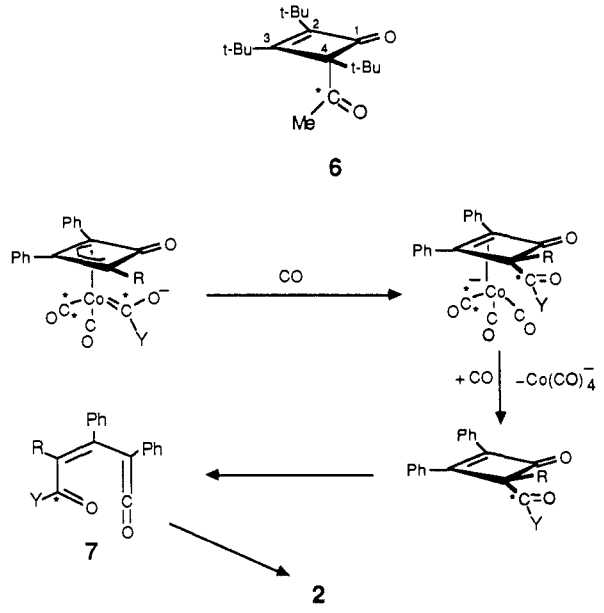
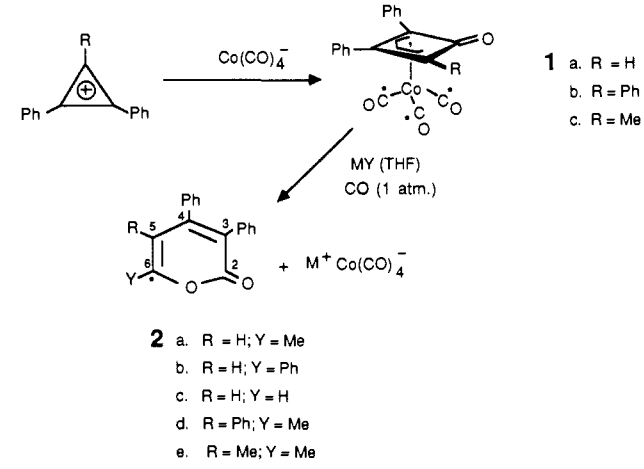
Scheme I

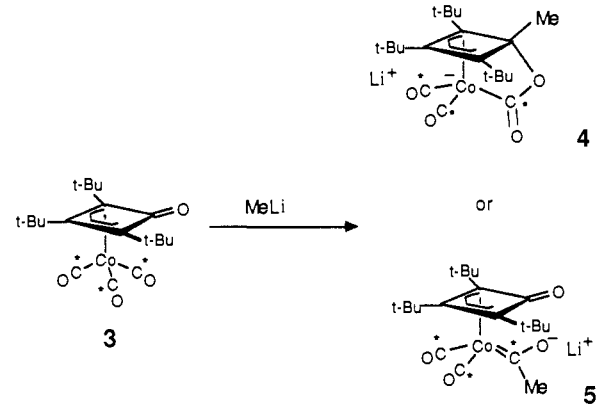


literature values.[5] Use of starting material **1a** selectively labeled with ^{13}CO at the metal carbonyl sites[6] affords **2a** which is labeled (*) only at C(6). Analogous results were obtained with phenyllithium or lithium triethylborohydride, affording pyrones **2b** and **2c**, respectively.[4,5] Other oxocyclobutenyl complexes **1b** and **1c** also form pyrones **2d** and **2e** on reaction with methyllithium under these conditions.[4,5]

Mechanistic insight was provided by treatment of the tri-*tert*-butyloxocyclobutenyl complex **3**[7] with methyllithium to afford a pale yellow solid in quantitative yield.[8] This compound exhibited IR bands at 1992 and 1940 cm^{-1}, indicative of a dicarbonylcobalt species and an additional ketonic absorption at 1618 cm^{-1}. The presence of a symmetry plane bisecting the four-membered ring was evidenced in its ^1H NMR spectrum by the observation of two



tert-butyl singlets (ratio 2:1) and a methyl singlet. These data are consistent either with structure **4** arising from nucleophilic attack at the oxocyclobutenyl ketone followed by attack at the resulting *endo*-alkoxide on a coordinated CO ligand or **5** which would obtain from direct nucleophilic attack at coordinated CO.



When **3** enriched with ^{13}CO at the metal carbonyl sites was used, the ^{13}C NMR spectrum of the product contained a ^{13}C-enriched low-field resonance at 297 ppm together with an enriched CO resonance at 214 ppm; natural-abundance peaks due to the ketone, two *tert*-butyl groups, a methyl group, and two additional ring carbon peaks were also observed.[8] Significantly, only the methyl peak exhibited coupling to ^{13}C, consistent with structure **5** but inconsistent with **4**. In agreement, the IR spectrum of **5** prepared from ^{13}CO-enriched **3** showed the expected isotopic shifts for the metal carbonyl bands but not for the ketone absorption. When **5** was refluxed in THF under CO, the $[Co(CO)_4]^-$ anion was formed cleanly, and the acetylcyclobutenone **6** was isolated as the only organic product.[9] ^{13}CO-enriched **5** gave **6** which was enriched exclusively at the acetyl carbonyl site, as shown by the observation of ^{13}C coupling to the methyl group.

Formation of the diketone **6** from the acylate precursor **5** in the presence of CO requires formal reductive coupling of acyl and allylic ligands, followed by loss of the organic fragment and coordination of CO. As precedent, coupling of a methyl and a formyl ligand in the anionic complex $[CpMo(CO)_2(CH_3)(CHO)]^-$ has been observed[10] to give the anionic acetaldehyde complex $[CpMo(CO)_2(CH_3CHO)]^-$. Our labeling studies suggest that a similar path is followed in all the reactions reported above but that in the absence of bulky *tert*-butyl substituents the acyl-

(5) **2a**: IR (CCl_4) ν_{CO} 1728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.8–7.4 (m, 10 H, Ph), 6.21 (s, 1 H, CH), 2.35 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, enriched peaks labeled *) δ 163.4 (C_2), 160.0* (C_6), 152.6 (C_4), 137.4, 133.8, 130.7, 128.5, 128.2, 127.8, 127.4 (Ph), 121.8 (C_3), 107.0 (C_5, $^1J_{C-C}$ = 70 Hz), 19.8 (CH_3, $^1J_{C-C}$ = 52 Hz); MS, *m/e* 262 (38%, P^+), 234 (100%, P^+ – CO), 83 ($P^+ - C_3H_3O_2$). **2b**: IR (CCl_4) ν_{CO} 1722 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1–8.0 (m, 15 H, Ph), 6.83 (s, 1 H, CH); ^{13}C NMR ($CDCl_3$) δ 162.7 (C_2), 158.2 (C_6), 152.7 (C_4), 137.7, 133.8, 131.3, 130.9, 130.7, 128.9, 128.7, 128.6, 128.4, 127.9, 127.6, 125.5 (Ph), 123.1 (C_3), 104.9 (C_5); MS, *m/e* 324 (34%, P^+), 296 (100%, P^+ – CO), 191 (42%, $P^+ - C_8H_5O_2$), 105 (64%, $P^+ - C_{16}H_{11}O$), 77 (68%, $P^+ - C_{17}H_{11}O_2$). **2c**: IR (CCl_4) ν_{CO} 1729 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.06–7.28 (m, 10 H, Ph), 7.53 (d, $^3J_{H-H}$ = 5 Hz, 1 H, CH), 6.40 (d, $^3J_{H-H}$ = 5 Hz, 1 H, CH); ^{13}C NMR ($CDCl_3$) δ 162.6 (C_2), 151.5 (C_4), 149.3 (C_6), 137.0, 133.6, 130.6, 128.8, 128.6, 128.3, 127.9, 127.7 (Ph), 109.8 (C_5); MS, *m/e* 248 (85%, P^+), 220 (92%, P^+ – CO), 191 (100%, $P^+ - C_2HO_2$). **2d**: IR (CCl_4) ν_{CO} 1719 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.2–7.8 (m, 15 H, Ph), 2.20 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 162.8 (C_2), 158.1 (C_6), 154.8 (C_4), 136.1, 135.1, 134.2, 133.6, 130.5, 129.3, 128.1, 127.6, 127.2 (Ph), 18.9 (CH_3); MS, *m/e* 338 (32%, P^+), 310 (100%, P^+ – CO), 267 (100%, $P^+ - C_2H_3O_2$). **2e**: IR (CCl_4) ν_{CO} 1722 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.8–7.4 (m, 10 H, Ph), 2.35 (s, 3 H, C_6–CH_3), 1.74 (s, 3 H, C_5–CH_3); ^{13}C NMR ($CDCl_3$) δ 163.0 (C_2), 156.5 (C_6), 156.3 (C_4), 136.7, 134.3, 130.5, 128.4, 128.1, 127.7, 127. , 127.1 (Ph), 124.0 (C_3), 111.2 (C_5), 18.1 (C_6–CH_3), 14.6 (C_5–CH_3); MS, *m/e* 276 (37%, P^+), 248 (100%, P^+ – CO), 205 (56%, $P^+ - C_2H_3O_2$).

(6) Obtained by refluxing a hexane solution of **1a** under an atmosphere of ^{13}CO. Selective enrichment (ca. 50%) at the terminal CO sites was confirmed by IR observation of the expected isotopic shifts and by exclusive enhancement of the M–CO resonance in the ^{13}C NMR spectrum.

(7) Hughes, R. P.; Lambert, J. M. J.; Whitman, D. W.; Hubbard, J. L.; Henry, W. P.; Rheingold, A. L. *Organometallics* **1986**, *5*, 789–797.

(8) (a) **5**: IR (Et_2O) ν_{CO} 1992, 1940, 1618 cm^{-1}; ^1H NMR (THF-d_8) δ 2.54 (s, 3 H, CH_3CO), 1.19 (s, 9 H, $C(CH_3)_3$), 1.15 (s, 18 H, $C(CH_3)_3$); ^{13}C NMR (THF-d_8, enriched peaks labeled *) δ 297.4* (CH_3—*C*=O, appears as a quartet, $^2J_{C-H}$ = 5 Hz, in the ^1H-coupled spectrum), 214.1* (Co—*C*O), 157.6 (*C*=O), 97.9 (*C*—$C(CH_3)_3$), 87.2 (*C*—$C(CH_3)_3$), 52.5 (CH_3—CO, $^1J_{C-C}$ = 17 Hz)[8b], 34.2 ($C(CH_3)_3$), 33.0 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$). (b) It is unclear why this value of $^1J_{C-C}$ is small (cf. values for **2a**[5]). The effects of transition metals on the magnitude of such couplings do not appear to have been explored.

(9) **6**: IR (hexane) ν_{CO} 1748, 1708 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.11 (s, 3 H, CH_3CO), 1.32 (s, 18 H, $C(CH_3)_3$), 1.12 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$, enriched peaks labeled *) δ 206.7* (CH_3—*C*=O), 189.4 (C_1), 181.1 (C_3), 160.9 (C_2), 87.6 (C_4), 35.9 (*C*(CH_3)$_3$), 34.4 (*C*(CH_3)$_3$), 33.0 ($C(CH_3)_3$), 30.5 ($C(CH_3)_3$), 29.5 (*C*(CH_3)$_3$), 29.0 ($C(CH_3)_3$), 28.7 (*C*H_3CO); MS, *m/e* 278 (0.2%, P^+), 250 (7%, P^+ – CO), 222 (8%, P^+ –2CO), 207 (100%, $P^+ - C_3H_3O_2$), 194 (30%, $P^+ - C_6H_{12}$), 57 (89%, $P^+ - C_{12}H_{21}O_2$).

(10) Gauntlett, J. T.; Taylor, B. F.; Winter, M. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1815–1820.

cyclobutenone rapidly opens to give a vinylketene **7**, which then undergoes rapid intramolecular trapping by the acyl group in an allowed 6-electron ring closure[11] to give the observed pyrone (Scheme I).[12] While we cannot exclude the possibility that the transformation **6** → **7** occurs within the coordination sphere of the metal, it has been shown that free cyclobutenones undergo such facile openings to produce vinylketenes[12,13] and that ring opening is dramatically accelerated by the presence of phenyl groups.[14] Presumably such a mechanism is sterically disfavored for the *tert*-butyl derivative **6** because it would require an intermediate containing three coplanar *tert*-butyl groups on contiguous carbon atoms. Our results indicate that the acyl–allyl coupling step is regiospecific, occurring at the less hindered allylic terminus, and that acetyl, benzoyl, and formyl ligands all undergo this reaction. This transformation effectively involves generation of an acyl anion equivalent, followed by intramolecular attack at the allylic ligand.

This process represents a novel organometallic route to an important organic ring system,[2] in which two carbon monoxide molecules are incorporated into the product. The reaction appears to be versatile in the range of nucleophiles and substituent groups which can be employed and has the advantage of regenerating the anionic organometallic reagent. Extensions to the syntheses of biologically significant pyrones are in progress.

Acknowledgment. We are grateful to the National Science Foundation, to the donors of the Petroleum Research Fund, Administered by the American Chemical Society, and to the Air Force Office of Scientific Research (Grant AFOSR-86-0075) for generous financial support of our research.

(11) Marvel, E. N. *Thermal Electrocyclic Reactions*; Academic Press: New York, 1980.

(12) Vinylketenes analogous to **7** have been postulated as intermediates in other pyrone syntheses.[4] Analogous ring opening of a vinylcyclobutenone, followed by electrocyclic closure to a 2,4-cyclohexadienone, has also been reported: Danheiser, R. L.; Gee, S. K. *J. Org. Chem.* **1984**, *49*, 1674–1676.

(13) For examples, see: Danheiser, R. L.; Gee, S. K.; Sard, H. *J. Am. Chem. Soc.* **1982**, *104*, 7670–7672. Buttinelli, P.; Loreto, M. A.; Pellacani, L.; Tardella, P. A. *J. Chem. Res., Synop.* **1985**, 158–159. Huisgen, R.; Mayr, H. *J. Chem. Soc., Chem. Commun.* **1976**, 55–56.

(14) Mayr, H.; Huisgen, R. *J. Chem. Soc., Chem. Commun.* **1976**, 57–58.

Synthesis of the First Highly Potent Bridged Nicotinoid. 9-Azabicyclo[4.2.1]nona[2,3-*c*]pyridine (Pyrido[3,4-*b*]homotropane)†

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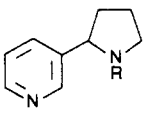
Attempts to determine the bioactive conformation of a given agonist at its receptor frequently involve the synthesis of conformationally restricted structures.[1] Significant efforts along these lines have been made in the nicotine (**1**) area.[2] Up to this time, however, there have been no reports of a bridged nicotinoid with bioactivity equaling or surpassing that of the conformationally free parent. We now report the design, synthesis, and biological activity of pyrido[3,4-*b*]homotropane (**2**)—the first highly potent bridged nicotinoid.

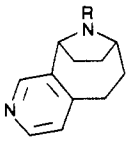
Table I

agent	IC_{50}[a] (M)	LD_{50}[b] (mg/Kg)
±-nornicotine	8×10^{-8}	1.0
±-pyrido[3,4-*b*]homotropane	5×10^{-9}	0.3

[a] Receptor binding (rat-brain membrane). IC_{50} = concentration of agent necessary to produce 50% inhibition of [^{3}H]nicotine (concentration of (-[^{3}H]nicotine in assay was 1×10^{-9}).[18] [b] Lethal dose for 50% of test animals[19] by intravenous tail injection of male mice.

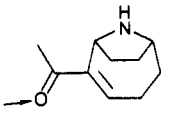


1a: R = H (nornicotine)
b: R = CH_3 (nicotine)

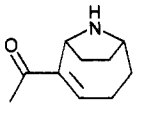


2: R = H
11: R = CH_2Ph

The semirigid alkaloid anatoxin *a* (**3**)[3] is known to possess high activity at the nicotinic acetylcholine receptor.[4] Nornicotine (**1a**),



3a (s-cis)



3b (s-trans)

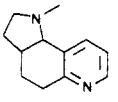
a potent agonist in its own right, has an activity significantly less than that of anatoxin *a*.[4] The present work was prompted by the recognition that one of the conformers of nornicotine would position the pyrrolidine nitrogen and a hydrogen-bond acceptor in the same spacial orientation as that found in the s-cis conformation (**3a**) of anatoxin *a*. The H-bond acceptor of **2** (pyridine nitrogen lone pair) corresponds specifically to the distal lone pair on the carbonyl of *s-cis*-anatoxin *a* (see arrow). Insertion of a two-carbon bridge in nornicotine between the $C_{5'}$ of the pyrrolidine and C_4 of the pyridine would "freeze" the structure in the desired conformation to yield the novel pyrido[3,4-*b*]homotropane (**2**).

Treatment of 1,2-oxido-5-cyclooctene[5] with benzylamine (2.0 equiv) in methanol (pot temperature 110 °C) for 3 h gave, after bulb-to-bulb distillation, an 84% yield of the *trans*-benzylamino alcohol **4**.[6,7] Aminomercuration[8] of **4** with 1 equiv of $Hg(OAc)_2$ in THF at 4 °C for 1.5 h, followed by demercuration with $NaBH_4$, yielded the bicyclic amino alcohol **5** (70% yield).[9] Jones oxidation of **5**, followed by chromatography on silica (CH_2Cl_2), yielded the

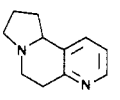
† Presented at the IXth International Symposium on Medicinal Chemistry, Berlin (West), Sept. 14–18, 1986.

(1) (a) Cannon, J. G.; Rege, A. B.; Grunen, J. L. *J. Med. Chem.* **1970**, *15*, 71–75 and references therein. (b) Low, S.-J.; Morgan, J. M.; Masten, L. W.; Borne, R. F.; Arana, G. W.; Kula, N. S.; Baldessarini, R. J. *J. Med. Chem.* **1982**, *25*, 213–216. (c) Woodruff, G. N. *Trends Pharmacol. Sci.* **1982**, *3*, 59–61.

(2) Two bridged nicotines, i[4a] and ii,[4b] have been reported previously. (a)



i



ii

Chavdarian, C. G.; Seeman, J. I.; Wooten, J. B. *J. Org. Chem.* **1983**, *48*, 492–494. (b) Catka, T. E.; Leete, E. *J. Org. Chem.* **1978**, *43*, 2125–2127.

(3) Carmichael, W. W.; Biggs, D. F.; Gorham, P. R. *Science* (Washington, D.C.) **1975**, *187*, 542.

(4) Spivak, C. E.; Waters, T.; Witkop, B.; Albuquerque, E. X. *Molec. Pharmacol.* **1983**, *23*, 337–343. Aronstam, R. S.; Witkop, B. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 4639–4643. Koskinen, A. M. P.; Rapoport, H. *J. Med. Chem.* **1985**, *28*, 1301–1309.

(5) U.S. Patent 3987073, 1976.

(6) Barrelle, M.; Apparu, M. *Tetrahedron* **1977**, *33*, 1309–1319.

(7) Satisfactory infrared (IR), proton magnetic resonance (^{1}H NMR), ^{13}C NMR, and high-resolution mass spectral data were obtained on chromatographically homogeneous samples of each stable compound reported herein.

(8) Brown, H. C.; Geoghegan, P. J. *J. Org. Chem.* **1970**, *35*, 1844–1850.

(9) A 10:1 mix of the [4.2.1] and [3.3.1] bicyclic systems is obtained which may be chromatographically separated on silica with hexane/CH_2Cl_2/ether (3/3/1).

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