norbelladine derivative **3** (prepared in two steps[1a] from piperonal and tyramine in 85% yield) gave a 19% yield of the dienone **4**, mp 138–142°, upon treatment with excess TTFA in CH_2Cl_2. Hydrolysis of **4** with Na_2CO_3 in aqueous methanol afforded (±)-oxocrinine (**5**), mp 171–174° (lit.[5] mp 172–173°), indistinguishable spectrally and chromatographically from an authentic[6] sample of oxocrinine, in 95% yield.

The colchicine precursor[7] *O*-methylandrocymbine (**6**) seemed a particularly challenging synthetic goal for the new procedure, since previous attempts to prepare the alkaloid by oxidative coupling of the diphenol **7** had met with failure.[8] Accordingly, the phenethylisoquinoline **8**,[9] mp 136–138°, was treated with diborane in THF–$CHCl_3$, and the mixture was passed through silica gel to give the corresponding amine–borane **9** as a stable oil: ir ($CHCl_3$) 4.23 μ; nmr ($CDCl_3$) δ 2.58 (N–Me); molecular ion at m/e 401.2352 (calcd 401.2373). Oxidation of the protected[10] amine (**9**) with 2–3 molar equiv[11] of TTFA in CH_2Cl_2 (24 hr at 25°) gave, after removal of the blocking group with anhydrous Na_2CO_3 in refluxing methanol, (±)-*O*-methylandrocymbine (**6**), mp 155–157° (lit.[12a] mp 154–156.6°), in 20% overall yield.[12] The spectral properties of the synthetic alkaloid were in agreement with those reported.[12b,c]

Investigations into the nature of the by-products formed in these reactions, as well as into application of the method to other systems, are in progress. A representative experimental procedure for the TTFA oxidation of **3** follows.

To a slurry of 1.63 g (3.00 mmol) of TTFA (weighed and transferred in a drybox under nitrogen) in 275 ml of anhydrous CH_2Cl_2 was added a solution of 367 mg (1.00 mmol) of **3** in 75 ml of the same solvent, and the mixture was stirred at room temperature in the dark for 20 hr. The resulting clear pale-yellow solution was evaporated under reduced pressure; the thallium salts and other polar components were removed by

filtration of a solution of the residue in $CHCl_3$ through a column of silica gel, to give 163 mg of a viscous orange oil which exhibited two spots on thin layer chromatography ($CHCl_3$–2% CH_3OH). Separation of the mixture by preparative tlc afforded 68.4 mg (0.187 mmol) of the dienone **4**. The compound could be crystallized from CH_3OH–H_2O and exhibited ir, nmr, and mass spectra consistent with the assigned structure.

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General Synthetic Routes to Tetraaza Macrocycles. Preparation of the Corrin Inner Ring Structure

Sir:

The chemistry of synthetic tetraaza macrocycles and their metal complexes is in a stage of rapid development,[1,2] with much of the current interest derived from attempts to relate structural, electronic, and reactivity features with those of metalloporphyrins and corrins. In this context our current work is directed toward the immediate objectives of (i) synthesis of ring systems whose complexes reproduce the chelate ring size patterns of porphyrin (6-6-6-6) and corrin (6-5-6-6) complexes, and (ii) development of oxidative transformations of these complexes to, or direct synthesis of, species with total oxidation levels equivalent to those of the internal chelate rings of natural macrocycles. The two most readily accessible cyclic tetraaza systems, **1**[3] (cis, trans, $n = 2,3$) and **2**[4] ($n = 2$; 3; 2,3), are not entirely suitable[5] because of *gem*-dimethyl substitution (**1**) and the presence of reactive functional groups (**2**, $R_\beta =$

1   2
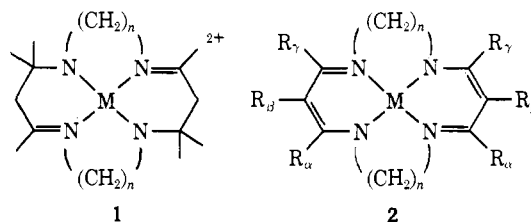
COR, COOR) requisite to their syntheses.[4,6] Our previous preparation[7] of the 6-5-6-5 complexes M(Me-HMe(en)$_2$) (**2**, $R_\alpha = R_\gamma = $ Me; $R_\beta = $ H; $n = 2$) has not yet proven capable of extension to larger ring systems.

Synthetic entry to three basic types of macrocycles containing 14-, 15-, and 16-membered rings is based on the electrophilic reactivity of 1,2-dithiolium cations.[8] Treatment of 1 equiv of **3**[9] with 1 equiv of ethylenediamine (en; ethanol, 25°) or trimethylenediamine

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(6) We thank Professor W. C. Wildman for providing us with this sample.

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(10) Attempted oxidation of the free amine **8** with TTFA led to a myriad of products, at least partially due to oxidation at nitrogen. The N–BH$_3$ group served to prevent N oxidation, although it suffered modification[11] during the course of the reaction. This rather unique blocking group is under further investigation. The *N*-trifluoroacetyl blocking group was also utilized. Treatment of the amide **10** with TTFA gave the dienone **11** in 10% yield.

(11) Oxidation of **9** with only 1 molar equiv of TTFA in CH_2Cl_2 gave a major product which could be isolated by chromatography on silica gel, and which exhibited CF_3COO^- as well as diminished B–H absorption in the ir. Hydrolysis of the material in refluxing methanol containing Na_2CO_3 gave the starting amine **8** as the sole organic product, thus indicating that oxidation at boron had occurred. Resubmission of the material to the reaction conditions with another molar equivalent of TTFA gave, after hydrolysis, *O*-methylandrocymbine.

(12) (±)-*O*-Methylandrocymbine has been previously synthesized by photolytic cyclization of bromo-[12a] and diazophenethylisoquinoline[12b] derivatives in yields of 3 and 8%, respectively: (a) T. Kametani, Y. Satoh, S. Shibuya, M. Koizumi, and K. Fukumoto, *J. Org. Chem.*, **36**, 3733 (1971); (b) T. Kametani, M. Koizumi, K. Shishido, and K. Fukumoto, *J. Chem. Soc. C*, 1923 (1971). (c) We thank Professor Kametani for providing us with a copy of the ir spectrum of *O*-methylandrocymbine.

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Communications to the Editor

(tn; benzene, 25°) afforded the aminothiones[10] **4** and **5** (60–80%), which proved susceptible to ring closure by further condensation. Reaction of **4** with en (2 equiv), tn (2 equiv), and tn (6 equiv) in benzene (70°, 1 hr) yielded after separation from by-products the macrocycles **6** (40%, mp 286–289°), **7**[11] (~30%, mp 220–222°), and **8** (30%, mp 147–148°), respectively, as white solids from chloroform–ethanol. Macrocycle **8** is better obtained from **5** and tn (2.5 equiv, benzene, 70°); yields of 90% have been achieved by this route.[12] Molecular weights of **6–8** were confirmed by high-resolution mass spectra (*e.g.*, calcd for $^{12}C_{24}{}^{1}H_{28}{}^{14}N_4$ (**8**), 372.2314; found, 372.2304).
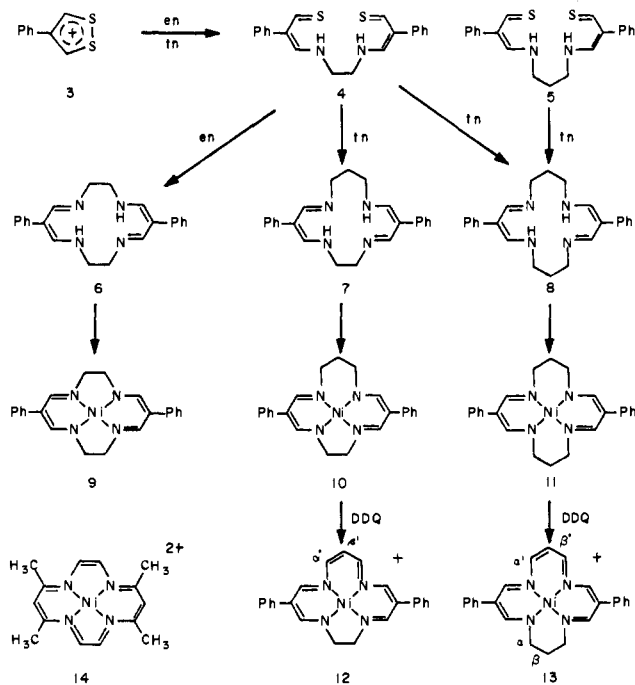
Reaction of **6**, **7**, and **8** (plus 1 equiv of tn) with nickel(II) acetate in hot DMF gave the complexes **9** (84%, red, mp 320–322°), **10** (~80%, green, mp 276–277°), and **11** (50%, green, mp 269–270°), respectively. The three complexes are diamagnetic and their pmr spectra are consistent with the indicated structures. Complexes **10** and **11** were subjected to dehydrogenation reactions. Treatment of **11** with 4 equiv of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in trichloroethylene (85°, 8 hr) followed by metathesis (NaPF₆–ethanol) and recrystallization (ethanol–acetone) yielded the partially dehydrogenated 14-π cation **13** as its PF_6^- salt (58%, green, mp 279–280°): pmr (CD₃CN) δ 8.00 (d, 2, α'-H), 7.85, 7.58 (both s, 2, ring H), 7.42 (10, Ph), 6.14 (t, 1, β'-H), 4.01 (t, 4, α-CH₂), 2.11 (CD₃NO₂, m, 2, β-CH₂). An analogous reaction of **10** afforded the PF_6^- salt of **12** (~30%, orange-brown, mp 257–258°): pmr (CD₃CN) δ 8.32, 7.83 (both s, 2, ring H), 8.22 (d, 2, α'-H), 7.41 (10, Ph), 6.32 (t, 1, β'-H), 4.01 (s, 4, CH₂). Increased ligand conjugation is evidenced by absorption bands at 489 (**12**, 17,400) and 516 nm

(**13**, ϵ 17,200), whereas the 12-π precursors **9–11** show only weak d–d bands above 450 nm.

The nickel(II) cation **12** is the initial example of a complex whose cyclic ligand framework is comprised exclusively of the 14-π corrin inner ring structure.[13] This structure is evidently mildly perturbed by the phenyl substituents since the lowest energy intense band in Ni(II) corrinoid complexes with exterior saturated ring framework occurs at 420–450 nm.[14] Voltammetry of **12** reveals a one-electron reduction whose potential ($E_{1/2}$ −0.79 V *vs.* sce, acetonitrile) is slightly more cathodic than that recently predicted[15] (*ca.* −0.55 V) for Ni(II) corrins. Reduction of **13**, a possible precursor to the porphyrin inner ring structure by further oxidative dehydrogenation, occurs at −0.76 V. These values are less negative than those for reduction of Ni(II) porphyrins[16] but substantially more negative than the potentials (+0.70, +0.10 V) for stepwise reduction of the 14-π Ni(II) cation **14**.[7] These results, which provide further demonstration of the influence of ligand structures on redox properties of macrocycles,[17] together with elaboration of the synthetic methods herein will be the subject of future reports.

(13) Recently several dibenzo corrin-type ("dibenzocorromin") complexes have been reported: D. St. C. Black and A. J. Hartshorn, *J. Chem. Soc., Chem. Commun.*, 706 (1972).

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(15) N. S. Hush and I. S. Woolsey, *J. Amer. Chem. Soc.*, 94, 4107 (1972).

(16) A. Wolberg and J. Manassen, *ibid.*, 92, 2982 (1970).

(17) See, *e.g.*, J. C. Dabrowiak, F. V. Lovecchio, V. L. Goedken, and D. H. Busch, *ibid.*, 94, 5502 (1972).

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Cyclobutadiene[1]

Sir:

Cyclobutadiene has been the object of significant research effort since the initial attempt at its synthesis by Kekulé 100 years ago.[2] Synthetic methods for generation of cyclobutadiene as a reactive intermediate have been developed.[3–6] Physical evidence for the

(1) Photochemical Transformations. XLVIII. Presented at the European Photochemistry Association Symposium, Reading, England, July 1972.

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(10) All new compounds gave satisfactory elemental analyses and were further identified by pmr and, where necessary, by mass spectrometry.

(11) The crude product is contaminated with ~10% of **6** and **8** (identified by mass spectrum and pmr), which were removed by fractional recrystallization (benzene).

(12) Alternatively, the Ni(II) complex of **5** with excess neat tn (35°, 1 hr) afforded metal-free **8** (69%) in an apparent template reaction.