

only to slow bimolecular anthracene dimerization. Thus, the intramolecular photocycloaddition which occurs in ANP appears to be somewhat unique. Its closest analog is the recent work of Bouas-Laurent and Castellán⁸ who reported the photoaddition of various anthracenes to tetracene whose reactivity is vastly greater than that of naphthalene. The intramolecular addition of ethylene to benzene⁹ has also been observed. It seems reasonable to expect that the mixed dimers of other polycyclic hydrocarbons could be prepared under appropriate conditions and, further, that such adducts could be of significant value in the study of molecular interactions in sandwich dimers.

(8) H. Bouas-Laurent and A. Castellán, *Chem. Commun.*, 1648 (1970).

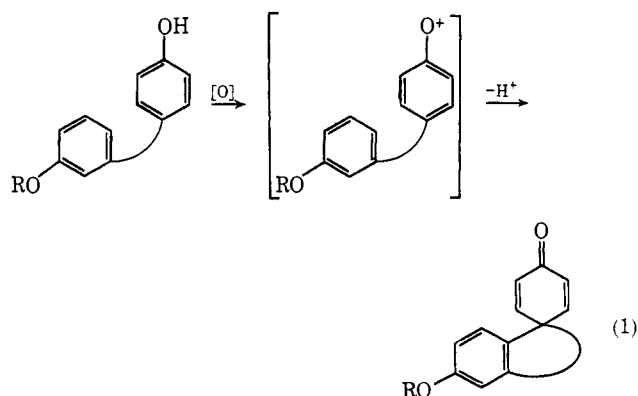
(9) H. Morrison and W. Ferree, *J. Chem. Soc. D*, 268 (1969).

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Intramolecular Oxidative Phenol Coupling. III. Two-Electron Oxidation with Thallium(III) Trifluoroacetate¹

Sir:

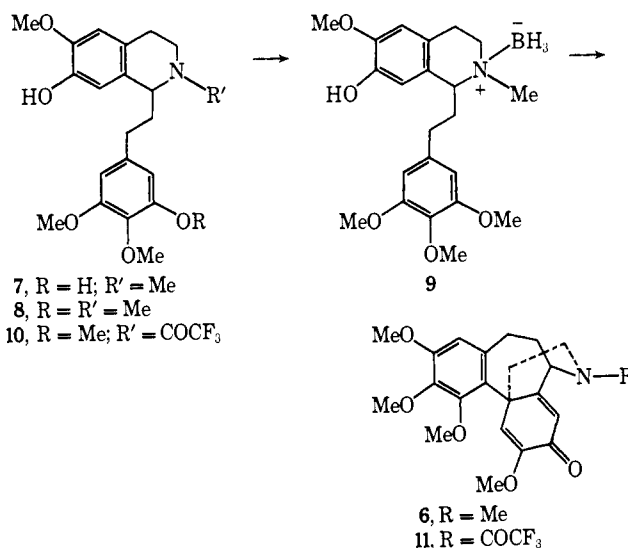
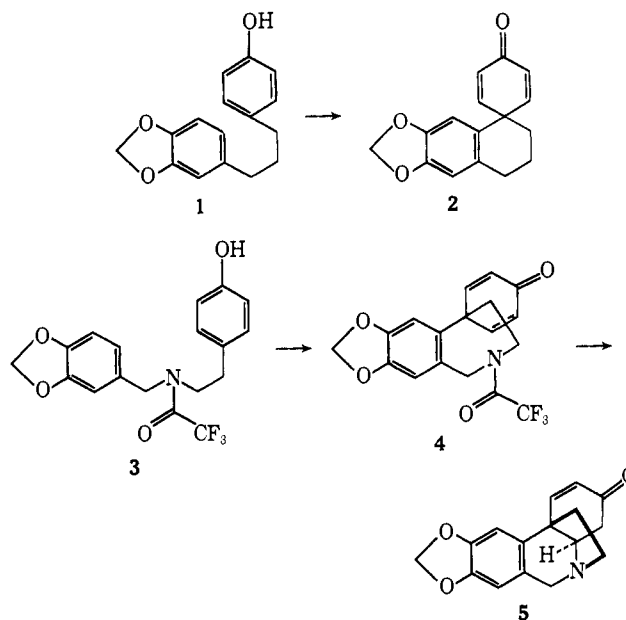
In a continuing effort to develop effective intramolecular oxidative phenol coupling methods for use in alkaloid synthesis,^{1a} we were interested in the possible utilization of a phenoxonium ion (or equivalent) mediated coupling, as outlined in eq 1. Although the generation of such intermediates has been investigated,²



(1) (a) Previous paper in series: M. A. Schwartz and R. A. Holton, *J. Amer. Chem. Soc.*, **92**, 1090 (1970). (b) This work was supported by Public Health Service Grant CA-10136 from the National Cancer Institute.

(2) J. W. A. Findlay, P. Gupta, and J. R. Lewis, *Chem. Commun.*, 206 (1969); M. Chauhan, F. M. Dean, K. Hindley, and M. Robinson, *ibid.*, 1141 (1971); D. G. Hewitt, *J. Chem. Soc., C*, 1750 (1971).

and an intermolecular analog of the desired transformation (eq 1) has been realized *via* anodic oxidation,³ no example of intramolecular carbon-carbon coupling by this method has been reported. The description by Taylor and coworkers⁴ of the oxidation of phenols to *p*-quinones with thallium(III) trifluoroacetate (TTFA) led us to examine the use of TTFA in the above scheme. We wish to report some success with this approach, leading to simple total syntheses of the alkaloids (\pm)-oxocrinine and (\pm)-*O*-methylandrocymbine.



The potential utility of the method was demonstrated when oxidation of the diarylpropane derivative **1** (mp 73.5–74°, prepared from the corresponding chalcone) with a suspension of 1 molar equiv of TTFA in anhydrous CH_2Cl_2 (3 hr at 25°) afforded the dienone **2** in 87% yield: mp 171°; ir (CHCl_3) 6.03 μ ; nmr (CDCl_3) δ 1.97 (m, 4), 2.82 (m, 2), 5.85 (s, 2), 6.23 (d, $J = 10$ Hz, 2), 6.40 (s, 1), 6.60 (s, 1), 6.97 (d, $J = 10$ Hz, 2). Extension of the method to the Amaryllidaceae alkaloid system was accomplished with ease, but with a substantial decrease in yield. The *N*-trifluoroacetyl-

(3) A. Ronlán, *Chem. Commun.*, 1643 (1971).

(4) A. McKillop, B. P. Swann, and E. C. Taylor, *Tetrahedron*, **26**, 4031 (1970).

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 CH₂Cl₂. Hydrolysis of **4** with Na₂CO₃ in aqueous methanol afforded (±)-oxocrinine (**5**), mp 171–174° (lit.⁵ mp 172–173°), indistinguishable spectrally and chromatographically from an authentic⁶ sample of oxocrinine, in 95% yield.

The colchicine precursor⁷ *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–CHCl₃, and the mixture was passed through silica gel to give the corresponding amine–borane **9** as a stable oil: ir (CHCl₃) 4.23 μ; nmr (CDCl₃) δ 2.58 (N–Me); molecular ion at *m/e* 401.2352 (calcd 401.2373). Oxidation of the protected¹⁰ amine (**9**) with 2–3 molar equiv¹¹ of TTFA in CH₂Cl₂ (24 hr at 25°) gave, after removal of the blocking group with anhydrous Na₂CO₃ 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 CH₂Cl₂ 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

(5) H. Muxfeldt, R. S. Schneider, and J. B. Mooberry, *J. Amer. Chem. Soc.*, **88**, 3670 (1966).

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

(7) A. R. Battersby, R. B. Herbert, E. McDonald, R. Ramage, and J. H. Clements, *Chem. Commun.*, 603 (1966); A. C. Barker, A. R. Battersby, E. McDonald, R. Ramage, and J. H. Clements, *ibid.*, 390 (1967).

(8) T. Kametani, H. Yagi, F. Satoh, and K. Fukumoto, *J. Chem. Soc.*, C, 271 (1968).

(9) A. Brossi, J. Van Burik, and S. Teitel, *Helv. Chim. Acta*, **51**, 1965 (1965).

(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–BH₃ group served to prevent N oxidation, although it suffered modification¹¹ 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 CH₂Cl₂ gave a major product which could be isolated by chromatography on silica gel, and which exhibited CF₃COO– as well as diminished B–H absorption in the ir. Hydrolysis of the material in refluxing methanol containing Na₂CO₃ 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.

filtration of a solution of the residue in CHCl₃ through a column of silica gel, to give 163 mg of a viscous orange oil which exhibited two spots on thin layer chromatography (CHCl₃–2% CH₃OH). Separation of the mixture by preparative tlc afforded 68.4 mg (0.187 mmol) of the dienone **4**. The compound could be crystallized from CH₃OH–H₂O and exhibited ir, nmr, and mass spectra consistent with the assigned structure.

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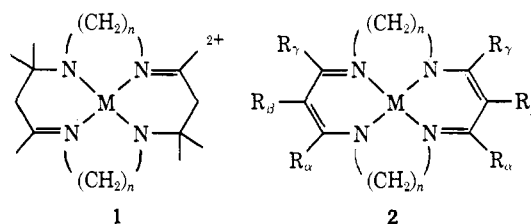
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General Synthetic Routes to Tetraaza Macrocycles. Preparation of the Corrin Inner Ring Structure

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 suitable⁵ because of *gem*-dimethyl substitution (**1**) and the presence of reactive functional groups (**2**, R_β =



COR, COOR) requisite to their syntheses.^{4,6} Our previous preparation⁷ of the 6-5-6-5 complexes M(Me–HMe(en)₂) (**2**, R_α = R_γ = Me; R_β = 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

(1) L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, **6**, 1 (1971).

(2) D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Advan. Chem. Ser.*, No. 100, 44 (1971).

(3) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

(4) E.-G. Jäger, *Z. Chem.*, **8**, 30, 392, 470 (1968); *Z. Anorg. Allg. Chem.*, **364**, 177 (1969).

(5) Complexes of type **1** can be oxidatively dehydrogenated to 6-π and 8-π species: N. F. Curtis, *J. Chem. Soc. A*, 2834 (1971); E. K. Barefield and D. H. Busch, *Inorg. Chem.*, **10**, 108 (1971); V. L. Goedken and D. H. Busch, *ibid.*, **10**, 2679 (1971).

(6) P. Bamfield, *J. Chem. Soc. A*, 2021 (1969).

(7) T. J. Truex and R. H. Holm, *J. Amer. Chem. Soc.*, **94**, 4529 (1972).

(8) H. Prinzbach and E. Futterer, *Advan. Heterocycl. Chem.*, **7**, 39 (1967).

(9) E. Klingsberg, *J. Amer. Chem. Soc.*, **83**, 2934 (1961).