Acknowledgment. We are grateful to the National Science Foundation (MP-57-21260) and Hoffmann-La Roche Inc. for support of this research.

References and Notes

(1) (a) K. B. Sharpless, D. W. Patrick, L. K. Truesdale, and S. A. Biller, *J. Am. Chem. Soc.*, **97**, 2305 (1975); (b) K. B. Sharpless, D. W. Patrick, L. K. Truesdale, and S. A. Biller [a full paper on the alkyl imido reagents (**1a**) is in preparation].
(2) It is surprising that Chloramine-T has been so little used in organic synthesis. It is inexpensive and is formally a nitrogen analogue of sodium hypochlorite (NaOCl). Whereas NaOCl is formally a source of ":Ö:", TsNClNa is formally a source of "TsN̈". We have also found recently that anhydrous TsNClNa reacts with selenium metal to produce a potent reagent for allylic amination of olefins [K. B. Sharpless, T. Hori, L. K. Truesdale, and C. O. Dietrich, *J. Am. Chem. Soc.*, **98**, 269 (1976).
(3) K. A. Hoffmann, *Chem. Ber.*, **45**, 3329 (1912).
(4) N. A. Milas and S. Sussman, *J. Am. Chem. Soc.*, **58**, 1302 (1936).
(5) When $AgNO_3$ is added to a stirred suspension of TsNClNa in *tert*-butyl alcohol at room temperature a new more flocculent precipitate is formed: this solid is the silver salt of Chloramine-T (TsNClAg). TsNClAg was prepared by a known method [G. Wittig and D. Hellwinkel, *Chem. Ber.*, **97**, 789 (1964)] and was found to have the same properties in these reactions as the combination of $AgNO_3$ + TsNClNa.
(6) Commercial bleach was diluted 5 to 1. This treatment converts the *p*-toluenesulfonamide, sometimes a by-product of these oxidations, to Chloramine-T, which is preferentially extracted into the aqueous phase. Although the *p*-toluenesulfonamide can also be extracted with aqueous NaOH, this procedure often removes some of the desired product as well.
(7) These crude products contain surprisingly little diol (usually <2%); recall that on the order of 1% diol is necessarily formed since the catalyst is added as osmium tetroxide. We have found that the solid osmate(VI) ester of pinacol also serves as a catalyst and results in no initial diol formation. However, we prefer to use osmium tetroxide because of the convenience of adding a solution.
(8) These $AgNO_3$ modifications were either run at 60 or at 25° as noted in Table I.
(9) Sodium naphthalene in glyme is also effective for the reductive cleavage of sulfonamides [S. Ji, L. B. Gantler, A. Waring, A. Battisti, S. Bank, and W. D. Closson, *J. Am. Chem. Soc.*, **89**, 5311 (1967)]; this procedure also works well for allylic and benzylic sulfonamides and thus should succeed with most of the hydroxy amides in Table I.
(10) Camille and Henry Dreyfus Teacher-Scholar Grant recipient; Alfred P. Sloan Fellow, 1973–1975.
(11) Rohm and Haas Graduate Fellow, 1974–1975.

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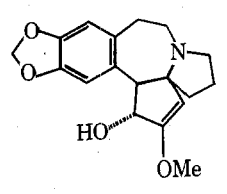
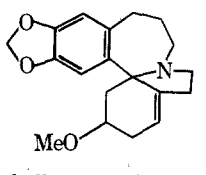
A Biogenetic-Type Approach to Homoerythrina Alkaloids[1]

Summary: A unified synthetic approach to homoerythrina alkaloids via the dibenz[*d,f*]azecine **11** has produced the schelhammera-type skeleton **12** and a new homoerysodienone skeleton **13.**

Sir: Recently, attention has been focused on the total synthesis of cephalotaxine[2] **1**, since it is the alkaloidal portion of the antitumor esters[3] of *Cephalotaxus harringtonia.* The presence of schelhammera-type alkaloids[4] such as 3-epischelhammericine **2** in species of *Cephalotaxus*[5] has led us and others[5a] to the proposal that both the schelhammera-type and *Cephalotaxus* alkaloids are biogenetically related and may be classified as homoerythrina alkaloids. We have been interested in testing in the laboratory a unified approach to homoerythrina skeletons via the substituted phenethylisoquinoline **3** and the pivotal dibenz[*d,f*]azecine **5**, shown in Scheme I. It seemed reasonable that compound **5** could be a possible biogenetic precursor[6] to the *Cephalotaxus* (pathway c, Scheme I) and the *Schelhammera* alkaloids (pathway a, Scheme I) as well as the hitherto unknown homoerysodienone skeleton **8** (pathway b, Scheme I). In fact, the dibenz[*d,f*]azecine **5** is also a homolog of the alkaloid erybidine.[7] In this communication, we wish to report the synthesis of the dibenz[*d,f*]azecine **11** and its oxidative transformation into two homoerythrinadienones **12** and **13.**

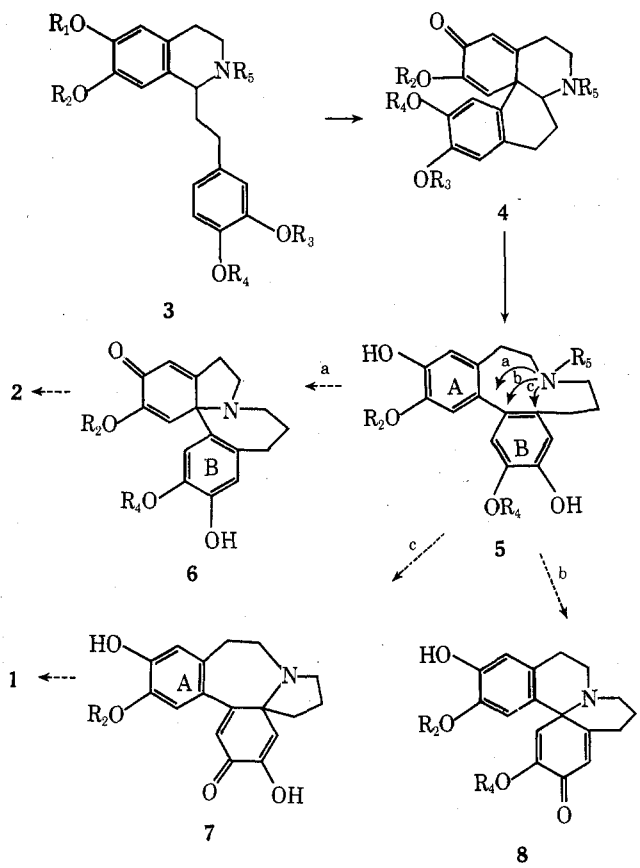


cephalotaxine **1**



schelhammercine **2**

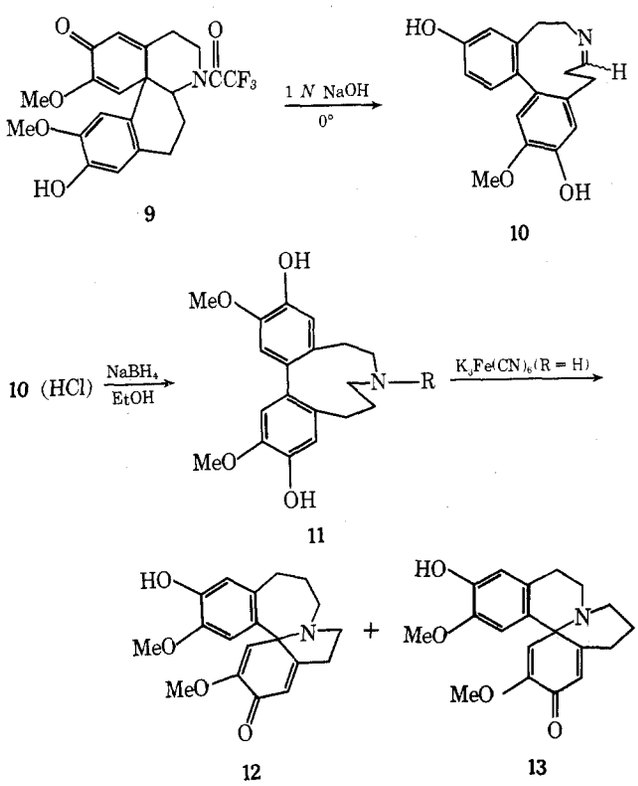
Scheme I



The preparation of the prohomoerythrinadienone derivative **9** from the corresponding phenylethylisoquinoline precursor has been previously described by us.[8] The hydrolytic fragmentation process, which was affected with 1 *N* hydroxide at 0° in methanol, yielded the bisphenolic imine **10** (Scheme II) in quantitative yield. The stereoelectronics of the base-induced bond cleavage requires that the compound **10** initially possess the unusual trans-imine moiety.[9] The bisphenolic imine **10** was converted into its hydrochloride salt (dp 237–239°) with anhydrous hydrogen chloride in ethanol. This imminium chloride was reduced efficiently with sodium borohydride in ethanol to the crystalline bisphenolic amine **11** (R = H, mp 211.5–212.5°).[10] The overall yield from **9** to pure bisphenolic amine **11** was 76%. The preparation of the dibenz[*d,f*]azecine **11** constitutes an efficient synthesis[11] of the homoerybidine skeleton which very likely may occur as a natural product.

A variety of oxidative cyclizations were attempted on the free amine **11** (R = H) and its trifluoroacetamide **11** (R =

Scheme II



CH_3CO). It was our original intention to affect the oxidation of the trifluoroacetamide of **11** in order to produce the corresponding diphenoquinone. A suitably substituted dipheno-*p*-quinone could then be transformed into the cephalotaxine precursor **7** via an intramolecular Michael addition of the nitrogen.[5] Attempted oxidation of **11** (R = CH_3CO) with dichlorodicyanoquinone, potassium hexacyanoferrate, silver oxide, or the ferric chloride–DMF complex[12] yielded only starting material. Thallium trifluoroacetate oxidation of the trifluoroacetamide of **11** (R = CH_3CO) produced a dimer (35% yield) derived from oxygen–carbon coupling. Lead tetraacetate oxidation of **11** (R = CH_3CO) in glacial acetic acid produced in high yield a bis-*o*-quinol acetate. The above results reflect the difficulty in oxidizing **11** (R = CH_3CO) to the corresponding dipheno-*p*-quinone, presumably because of the orthogonality of the aromatic rings of **11**. Thus, each aromatic ring of **11** (R = CH_3CO) behaves independently toward oxidation.

In contrast to the oxidations of the trifluoroacetamide of **11**, the free amine **11** (R = H) was cleanly transformed into two cyclized homoerythrina skeletons with potassium hexacyanoferrate in methylene chloride–sodium bicarbonate solution. After preparative layer chromatography on silica gel of the crude reaction mixture, a 45% yield of crystalline dienone **12** (mp 166–167°, from 2-propanol) was isolated along with 15% crystalline homoerysodienone **13** (mp 195.5–197.5°, from 2-propanol) and 35% recovered starting bisphenolic amine **11** (R = H). The isolation of the schelhammera-type skeleton[13] **12** and the new homoerysodienone skeleton **13** is consistent with standard phenolic coupling of the amine nitrogen para to a free hydroxyl group (paths a and b, Scheme I). The ratio of **12** to **13** is probably a good indication of the conformational preference for ring closure via path a vs. closure via path b. That no cephalotaxine precursor (path c) was observed in the above oxidation suggests the absence of a dipheno-*p*-quinone intermediate or a suitably disposed *p*-hydroxy group (**5**, R_4 = H). We are presently exploring the preparation of the biscatechol derivative of **11** and its transformation into a cephalotaxine precursor, via an *o*-quinone.

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References and Notes

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(3) K. L. Mikolajczak, R. G. Powell, and C. R. Smith, Jr., *Tetrahedron*, **28**, 1995 (1972).
(4) (a) J. S. Fitzgerald, S. R. Johns, J. A. Lamberton, and A. A. Sioumis, *Aust. J. Chem.*, **22**, 2187 (1969); (b) S. R. Johns, J. A. Lamberton, and A. A. Sioumis, *ibid.*, **22**, 2219 (1969); (c) N. Langlois, B. Das, and L. Lacomb, *Bull. Soc. Chim. Fr.*, 3535 (1970).
(5) (a) R. G. Powell, *Phytochemistry*, **11**, 1467 (1972); (b) R. G. Powell and K. L. Mikolajczak, *ibid.*, **12**, 2987 (1973); (c) W. W. Paudler and J. McKay, *J. Org. Chem.*, **38**, 2210 (1973); (d) S. Asada, *Yakugaku Zasshi*, **93**, 916 (1973).
(6) R. J. Parry and J. M. Schwab, *J. Am. Chem. Soc.*, **97**, 2555 (1975). These workers have reported compelling evidence that labeled tyrosine was incorporated into cephalotaxine via an alternative biosynthetic pathway. At the present time, this work does not rule out elements of Scheme I as a possible biogenetic route to other homoerythrina alkaloids.
(7) M. Shamma, "The Isoquinoline Alkaloids," Academic Press, New York, N.Y., 1972, p 425.
(8) J. P. Marino and J. M. Samanen, *Tetrahedron Lett.*, 4553 (1973).
(9) Analysis of the NMR and ir spectra of **10** could not definitively confirm the trans stereochemistry for the imine. We have also not ruled out the possibility that the initially formed trans amine **10** has isomerized to the cis imine.
(10) All new compounds gave satisfactory elemental analyses and gave NMR, uv, ir, and MS data consistent with the assigned structures.
(11) For a recent and different approach to the dibenz[*d,f*]azecine system, see S. Kano, T. Ogawa, T. Koyomatsu, E. Komiyama, and S. Shibuya, *Tetrahedron Lett.*, 1063 (1974).
(12) S. Tobinaga and E. Kotani, *J. Am. Chem. Soc.*, **94**, 309 (1972).
(13) Dienone **12** was previously prepared by Kametani and Fukumoto in 4.2% yield from a phenethylphenylpropylamine: T. Kametani and K. Fukumoto, *J. Chem. Soc., C*, 2156 (1968).

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Thermal Rearrangement of Allyl Substituted 2*H*-Azirines to 3-Azabicyclo[3.1.0]hex-2-enes

Summary: The thermal rearrangement of 2-allyl substituted 2*H*-azirines to 3-azabicyclo[3.1.0]hex-2-enes proceeds in high yield. The reactions can best be rationalized in terms of an equilibration of the 2*H*-azirine with a transient vinyl nitrene which subsequently adds to the adjacent π bond.

Sir: Photolysis of 2*H*-azirines leads to irreversible ring opening and the formation of nitrile ylides as intermediates.[1,2] These species may be intercepted by a variety of dipolarophiles to form five-membered heterocyclic rings. In certain cases the initially formed 1,3 dipole can be intramolecularly trapped[3] to give novel azabicyclohexenes.[4] For example, irradiation of allyl substituted 2*H*-azirines (**1**) produce 2-azabicyclo[3.1.0]hex-2-enes (**2**) via an unusual 1,1 cycloaddition reaction of the 1,3 dipole.[4] This observation stimulated us to begin a general investigation of the scope and mechanistic details of the intramolecular cyclization of unsaturated azirines. In this communication we wish to report on the thermolysis of a number of allyl substituted