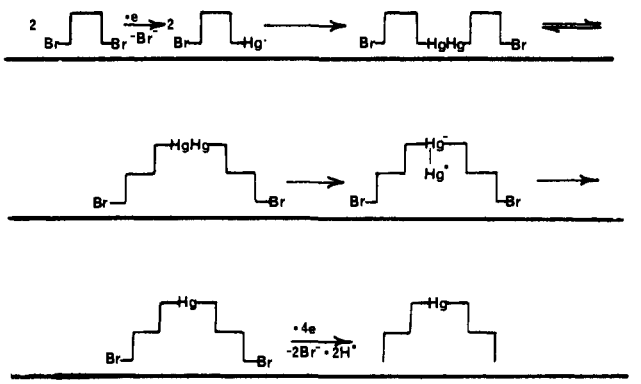

Figure 1.

(illustrated for a monobromide).[17] The most cogent aspects of the present proposal are the assumptions that, for step 4, $K_{eq} \gg 1$ and that disproportionation of $(RHg)_2$ occurs faster in the high field gradient near the electrode surface than it does in the bulk of the solution. If these assumptions are correct, the presence of a second C–Br bond in the dibromides will restrain the mercury(I) dimer to a region proximal to the electrode surface, where disproportionation can occur readily. Evidence for the radical $(RHg\cdot)$ in electroreductions is abundant.[6,18] Disposition of $(RHg\cdot)$ depend upon concentration, potential, and acid conditions.[18c,d] Electrolytic symmetrization of alkylmercuric halides is well documented.[19] The Jensen mechanism for disproportionation[20] (step 4, Scheme I), would be expected to lead to a marked increase in the rate of disproportionation near the electrode surface, where the field gradient may be as high as 10^6 V/cm and the chemistry of highly polarized species might well be affected.[21] Since we find that the first electron is consumed at a rate close to the rate of disappearance of starting material, there is little reason to invoke autocatalytic production of $RHgBr$[6,22] as an important intermediate, at least at these potentials.

Our present understanding of this unusual reaction is summarized in Figure 1, illustrated for the C_4 case. These results suggest a central role of adsorption in the fate of electroorganic processes. Work continues on the mechanism and scope of this process.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for partial support of this research. The authors are grateful to Joanne Murray, who carried out some of the preliminary experiments in this study.

(17) The bar over a formula denotes adsorption on the electrode surface.

(18) (a) C. A. Kraus, *J. Amer. Chem. Soc.*, **35**, 1732 (1913); (b) H. M. Billinge and B. G. Gowenlock, *J. Chem. Soc.*, 1201 (1962); (c) R. Benesch and R. E. Benesch, *J. Amer. Chem. Soc.*, **73**, 3391 (1951); (d) *J. Phys. Chem.*, **56**, 648 (1952).

(19) L. G. Marakova, "Organometallic Reactions," Vol. 2, E. I. Becker and M. Tsutsui, Ed., Wiley-Interscience, New York, N. Y., 1971, pp 374, 375.

(20) Reference 12b, p 142.

(21) Reference 7a, p 57.

(22) A. Kirrman and E. Kleine-Peter, *Bull. Soc. Chim. Fr.*, 894 (1957).

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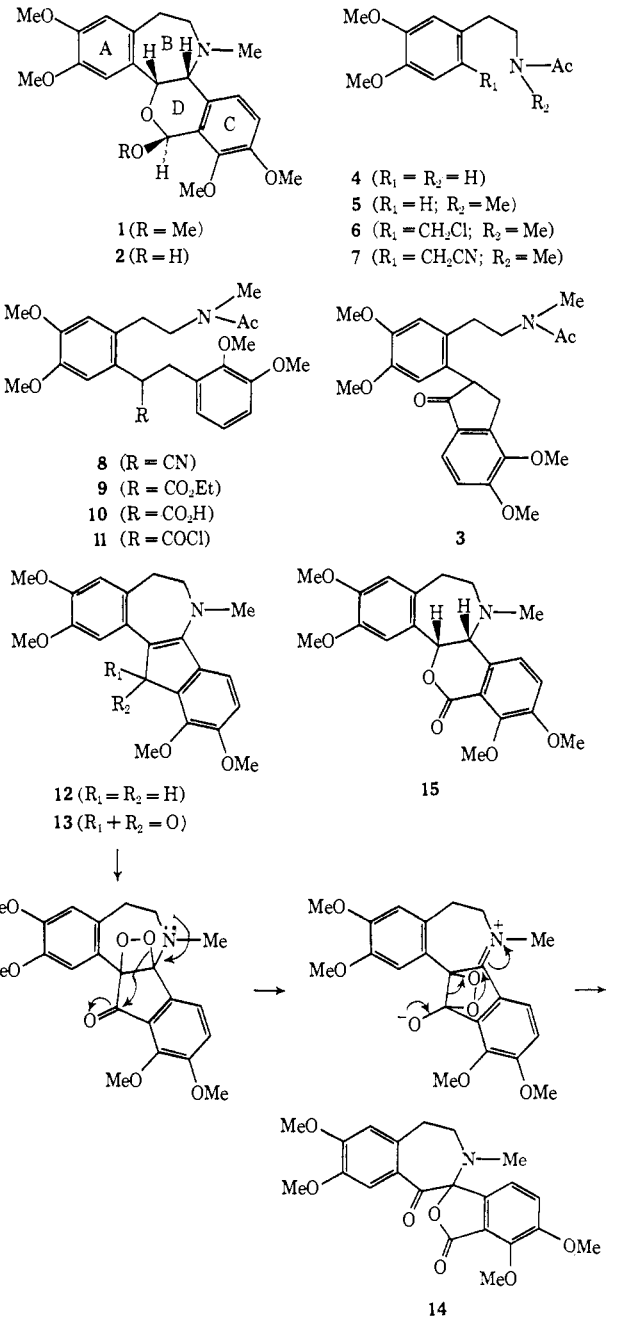
Received January 2, 1974

Photosensitized Oxidation of an Enaminoketone. The Total Synthesis of a Rhoeadine Alkaloid

Sir:

The oxidation of enamines by singlet oxygen has been reported[1] to proceed *via* a dioxetan intermediate which undergoes facile decomposition to carbonyl compounds in a process promoted by the pair of electrons on the nitrogen atom. We now report that in extending this reaction to an enaminoketone system, the decomposition of the corresponding dioxetan is accompanied by a novel and useful rearrangement. Specifically, the enaminoketone **13** has been oxidatively rearranged to the ketolactone **14** by this method thus



providing a convenient solution to the problem of achieving the desired substitution pattern in ring C of

(1) J. E. Huber, *Tetrahedron Lett.*, 3271 (1968); T. Matsuura and I. Saito, *ibid.*, 3273 (1968).

the rhoeadine alkaloids.[2] In this manner the alkaloids (±)-*cis*-alpinine (**1**) and (±)-*cis*-alpinigenine (**2**) have been synthesized without the necessity of preforming a 1,2,3,4-substituted benzene precursor for rings C/D, usually a tedious and low-yielding operation.[3,4]

The synthesis of the indanone **3**, achieved by standard methods, will be detailed elsewhere. Thus *N*-acetylhomoveratrylamine **4** was successively *N*-methylated (sodium hydride–methyl iodide in tetrahydrofuran–dimethylformamide) to **5**, chloromethylated[5] (formaldehyde–dry hydrogen chloride) to **6**, converted to the nitrile **7** (sodium cyanide–dimethyl sulfoxide), and condensed with 2,3-dimethoxybenzaldehyde under base catalysis to the stilbene which was reduced directly (2% sodium amalgam in ethanol) to **8**. The nitrile was successively hydrolyzed (ethanolic hydrogen chloride) to the ester **9** and the acid **10** (brief treatment with 5% methanolic potassium hydroxide). Friedel–Crafts cyclization of the acid chloride **11** (aluminum chloride–nitrobenzene) produced the desired indanone **3**. The yields in each step of the above sequence were 70% or better, and the properties of all compounds were consistent with the assigned structures.

Base hydrolysis of **3** (10% potassium hydroxide in 50% aqueous ethanol under reflux for 20 hr) produced the indene **12** (62% yield, mp 133–134°) which possessed the 3-benzazepine moiety characteristic of the rhoeadine alkaloids, fused in the correct manner to a potential CD system with the desired substitution pattern. The indene **12** was identical with a rearrangement product of a tetramethoxyspirobenzylisoquinoline[3b] which had been assigned the same structure on the basis of its spectroscopic properties. This provided an independent verification of our synthesis at this stage and unequivocally established the structure of the rearrangement product.

Base-catalyzed oxidation of compound **12** (Triton B in pyridine–molecular oxygen) produced the bright red indenone **13** (79% yield; mp 159–161°, $\nu_{max}^{CHCl_3}$ 1700 cm^{-1}; λ_{max}^{EtOH} 225 (sh), 242 (sh), 308 (sh), 319, and 503 nm; ϵ_{max} 15,400, 15,800, 18,800, 19,300, and 4100, respectively; $\delta(CDCl_3)$ 2.8–3.1 (m, 2H), 3.6–3.9 (m, 2H), 3.40 (s, 3H), 3.97, 4.04 (s, 2 × 3H), 3.84 (s, 6H), 6.62, 7.93 (s, 2 × 1H), 6.73 and 7.13 (q, 2H, J_{AB} = 8 Hz); M^+ = 381) which on Rose Bengal sensitized photooxidation yielded *inter alia* the ketolactone **14** analogous to those described earlier[4] (37% yield; mp 214–215°; $\nu_{max}^{CHCl_3}$ 1767 and 1690 cm^{-1}; λ_{max}^{EtOH} 223, 240 (sh), 284 and 321 nm; ϵ_{max} 22,600, 18,300, 11,300, and 14,000, respectively; $\delta(CDCl_3)$ 2.37 (s, 3H), 3.0–3.6 (m, 4H), 3.80, 3.93, 3.98, 4.17 (s, 4 × 3H), 6.77, 6.97 (s, 2 × 1H), 6.98 and 7.19 (q, 2H, J_{AB} = 8 Hz); M^+ = 413). A systematic examination of this reaction is now underway; in particular it is envisaged that the yields may be improved, the by-products identified, and the scope defined. Other oxidative methods are available in principle for achieving an equivalent transformation (**13** → **14**) and these possibilities are being explored.

Sodium borohydride reduction of **14** followed by dilute hydrochloric acid treatment yielded the *cis*-lactone[4b] **15** (90% yield; mp 195–196°; $\nu_{max}^{CHCl_3}$ 1735 cm^{-1}; λ_{max}^{EtOH} 221, 237 (sh), 287, and 308 nm; ϵ_{max} 23,100, 20,100, 8600, and 5800, respectively; $\delta(CDCl_3)$ 2.20 (s, 3H), 3.35 and 5.23 (br s, J = <1 Hz), 3.82, 3.88, 3.92, 4.02 (s, 4 × 3H), 6.72, 6.75 (s, 2 × 1H), 7.05 and 7.07 (q, 2H, J = 9 Hz); M^+ = 399). The lactone was reduced with diisobutylaluminum hydride in toluene to the lactol **2** (94% yield; mp 183–184°; λ_{max}^{EtOH} 239 and 282 nm; ϵ_{max} 5800 and 5400, respectively; $\delta(CDCl_3)$ 2.20 (s, 3H), 3.13 and 4.59 (br s, J = <1 Hz), 3.80, 3.91 (s, 2 × 3H), 3.89 (s, 6H), 6.40 (s, 1H), 6.88 (s, 2H), 6.69 (s, 2H)) which was stable to refluxing 0.25 *N* hydrochloric acid (3 hr) and is therefore (±)-*cis*-alpinigenine **2**, with the relative configuration[2,6] as shown. Its pmr spectrum and tlc behavior were identical with those of an authentic sample of (+)-*cis*-alpinigenine.[6] This was methylated with methanolic hydrogen chloride in the usual manner[7] to (±)-*cis*-alpinine **1** which resisted crystallization. The pmr spectrum of **1** was identical with published data[8] for the compound and the mass spectra of **1** and **2** were virtually identical with published spectra[8] of (+)-alpinine and (+)-alpinigenine, respectively. **1** was converted to a crystalline methiodide (mp 207–208°) which provided satisfactory analytical figures.[9]

This synthetic scheme is not only a valid model for the preparation of the other cis-fused rhoeadine alkaloids[10] but also promises to lead to alkaloids of the spirobenzylisoquinoline (from **3**) and phthalideisoquinoline (from **14**[4b]) types.

Acknowledgment. We thank the National Research Council of Canada for financial support.

(2) For reviews see (a) F. Šantavý, *Alkaloids*, **12**, 398 (1970); (b) M. Shamma, "The Isoquinoline Alkaloids: Chemistry and Pharmacology," Academic Press, New York, N. Y., 1972, p 399.

(3) Two previous syntheses of rhoeadine alkaloids have been achieved by rearrangements of alkaloidal materials. See (a) H. Irie, S. Tani, and H. Yamane, *Chem. Commun.*, 1713 (1970); (b) *J. Chem. Soc., Perkin Trans. 1*, 2986 (1972).

(4) (a) W. Klötzer, S. Teitel, J. F. Blount, and A. Brossi, *J. Amer. Chem. Soc.*, **93**, 4321 (1971); (b) *Monatsh. Chem.*, **103**, 435 (1972); (c) W. Klötzer, S. Teitel, and A. Brossi, *Helv. Chim. Acta*, **54**, 2057 (1971), *ibid.*, **55**, 2228 (1972).

(5) B. Pecherer, R. C. Sunbury, and A. Brossi, *J. Heterocycl. Chem.*, **9**, 609 (1972).

(6) H. Rönsch, *Tetrahedron Lett.*, 4431 (1972). We thank Professor Rönsch for a copy of the pmr spectrum of (+)*cis*-alpinigenine and for 3.7 mg of the alkaloid.

(7) J. Slavik, L. Dolejš, L. Vokáč, and V. Hanuš, *Collect. Czech. Chem. Commun.*, **30**, 2864 (1965).

(8) M. Maturová, H. Potůšilová, F. Šantavý, A. D. Cross, V. Hanuš, and L. Dolejš, *Collect. Czech. Chem. Commun.*, **32**, 419 (1967).

(9) Satisfactory elemental analyses were obtained for compounds **2–15**.

(10) M. Shamma and L. Töke, *Chem. Commun.*, 740 (1973), have reported the synthesis of an *N*-benzoylated *trans*-rhoeadine system.

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Received September 25, 1973

Reactions of Molybdenum and Tungsten Atoms. Syntheses of Bisarene Sandwich Compounds

Sir:

Benzene sandwich compounds of molybdenum and tungsten have been reported by Fischer, Scherer, and Stahl,[1] and prepared by reduction of metal salts with aluminum–aluminum chloride in the presence of ben-

(1) E. O. Fischer, F. Scherer, and H. O. Stahl, *Chem. Ber.*, **93**, 2065 (1960).