Table I. Rate of Reduction of Cobalt(III) Complexes by Chromium(II)[a]

	Complex	Rate, M^{-1} sec^{-1}	Ref
I.	$Co(NH_3)_5F^{2+}$	9×10^5	*b*
II.	$Co(NH_3)_5Cl^{2+}$	2.6×10^6	*b*
III.	$Co(NH_3)_5OH^{2+}$	1.7×10^6 [h]	*c*
IV.	$Co(NH_3)_5(OAc)^{2+}$	3.5×10^{-1}	*d*
V.	$Co(NH_3)_4(OAc)_2^+$	$15 + 50[H_3O^+]$	*e*
VI.	$Co(NH_3)_4(H_2O)(OAc)^{2+}$	$47 + 2.8[H_3O^+]^{-1}$	*e*
VII.	$Co(NH_3)_5(OOCCH_2OH)^{2+}$	3.1	*f*
VIII.	$Co(en)_2(HOCH_2COO)^{2+}$	38	*g*
IX.	$Co(en)_2(OCH_2COO)^+$	9.9×10^2	*g*
X.	$Co(en)_2(SCH_2COO)^+$	$>2 \times 10^6$	*g*

[a] μ = 1.0 *M*, 25°. [b] Reference 9. [c] A. Zwickel and H. Taube, *J. Amer. Chem. Soc.*, **81**, 1288 (1959). [d] Reference 7b. [e] Reference 4a,c. [f] Reference 6. [g] This work. [h] At 20°, μ = 1.20 *M*.

$$Co(en)_2(SCH_2COO)^+ + Cr(II) \xrightarrow{k_{S_2}} \text{products}$$

This reaction is also characterized by 1:1 stoichiometry (spectrally determined) yielding a red chromium(III) product which is indicative of a thiolate bridged reaction. Subsequent discussion will focus on the mechanistically comparable k_2 paths.

Table I summarizes our observations and relevant results from previous work on inner-sphere reductions. The glycollate complex appears unreactive relative to $Co(NH_3)_5OH^{2+}$. Steric hindrance of the alkoxide oxygen by the methylene group probably contributes substantially to this effect. A decreased stability of the precursor complex[7] is one likely consequence of the hindrance. We are studying the Cr(II)–$Co(NH_3)_5(HOCH_3)^{3+}$ [8] reaction to further evaluate the influence of alkoxide ligands.

The most significant reactivity influence evident in the results is that conferred by the thiolate ligand. The mercaptoacetate complex is more reactive toward reduction by Cr(II) than its oxygen analog by over three orders of magnitude. In spite of its potentially hindering methylene substituent, it approaches the highest reactivities observed for this class of reactants and may approach rate-limiting substitution on Cr(II).[7,9]

An important barrier to activation for the class of reactions under consideration is the apparent necessity, impressively supported experimentally,[10] to stretch the cobalt-bridging ligand bond prior to electron transfer.[11] A further influential factor may be the extent to which the ligand σ orbital overlaps the cobalt e_g orbital[11] although experimental evidence on this point is less convincing. The much greater reactivity which we have observed for the sulfur over the oxygen complex correlates nicely with a diminished steric hindrance of the larger thiolate sulfur by the methylene group and a lower bond strength and greater covalency expected for the cobalt–sulfur bond. The potential influences of the thermodynamic driving forces[7] and precursor complex stabilities[7] on the rate difference are difficult to assess at present except that the steric component of the latter influence should contribute in the observed direction.

Less dramatic effects than those we present have previously been reported for Co(III) complexes with ligands containing uncoordinated thio ether functions.[12] We are extending our studies to other reductants (particularly of the outer-sphere class), sulfur functions, and oxidizing centers.

Acknowledgment. We acknowledge with thanks support for this research provided by the National Science Foundation (Grants GP-6848 and GP-12223), the Petroleum Research Fund (Grant G-821), and the Public Health Service (National Institutes of Health Fellowship (GM 44691) to R. H. L. 1969–1970). We appreciate the support of the University of Florida for the stopped-flow spectrophotometer, an assistantship to R. H. L., and a summer research appointment to L. E. B. Our report has benefitted from comments by Professors Henry Taube and John Endicott and the referees.

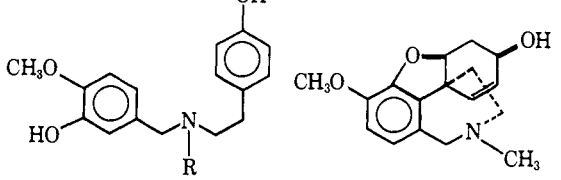
(12) E. S. Gould, *J. Amer. Chem. Soc.*, **88**, 2983 (1966).

Robert H. Lane, Larry E. Bennett
Department of Chemistry, University of Florida
Gainesville, Florida 32601
Received January 16, 1970

Intramolecular Oxidative Phenol Coupling. II. A Biogenetic-Type Synthesis of (±)-Maritidine[1]

Sir:

Radioactive tracer experiments have verified that most, and probably all, of the Amaryllidaceae alkaloids are biosynthesized by way of intramolecular oxidative coupling of either O-methylnorbelladine (**1**) or O,N-dimethylnorbelladine (**2**).[2] Although it has been recognized that execution of this scheme in the laboratory would provide an exceedingly simple synthetic route to these alkaloids,[3] Barton and Kirby's[4] synthesis of galanthamine (**3**) remains the only reported biogenetic-type synthesis of an Amaryllidaceae alkaloid; these



1, R = H
2, R = CH_3

3

workers were able to effect the intramolecular *ortho–para* coupling of **2** in 1.4% yield. We recently described a new method for carrying out intramolecular oxidative phenol coupling[1] and wish now to report its use in the biogenetic-type synthesis of (±)-maritidine

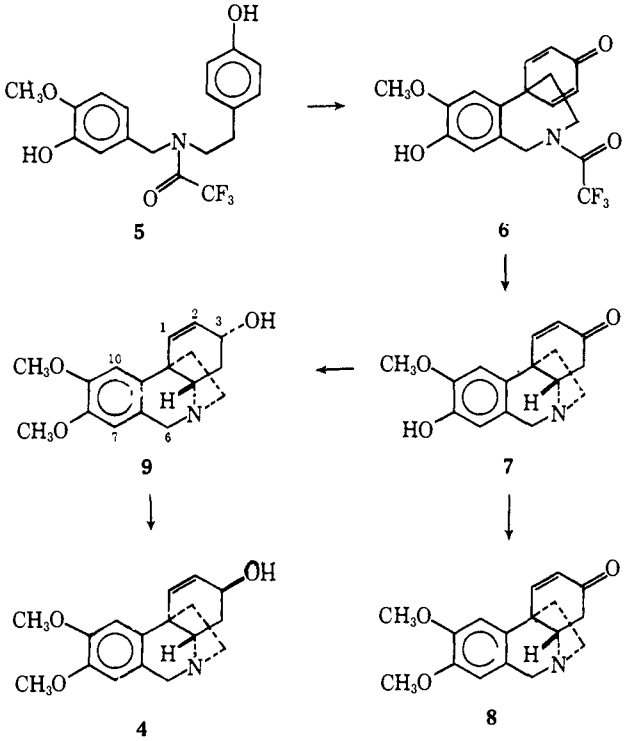
(7) (a) N. Sutin, *Accounts Chem. Res.*, 1, 225 (1968); (b) H. Taube and E. Gould, *ibid.*, 2, 321 (1969); (c) J. C. Patel, R. E. Ball, J. F. Endicott, and R. G. Hughes, *Inorg. Chem.*, 9, 23 (1970).
(8) R. B. Jordan, A. M. Sargeson, and H. Taube, *ibid.*, 5, 1091 (1966).
(9) J. P. Candlin and J. Halpern, *ibid.*, 4, 766 (1965).
(10) (a) R. K. Murmann, H. Taube, and F. A. Posey, *J. Amer. Chem. Soc.*, 79, 262 (1957); (b) M. Green, K. Schug, and H. Taube, *Inorg. Chem.*, 4, 1184 (1965); (c) H. Diebler, P. H. Dodel, and H. Taube, *ibid.*, 5, 1688 (1966).
(11) J. A. Stritar and H. Taube, *ibid.*, 8, 2281 (1969).

(1) Previous paper: M. A. Schwartz, R. A. Holton, and S. W. Scott, *J. Amer. Chem. Soc.*, **91**, 2800 (1969).
(2) For a comprehensive review, see W. C. Wildman, *Alkaloids*, **11**, 387 (1968).
(3) (a) R. A. Abramovitch and S. Takahashi, *Chem. Ind.* (London), 1039 (1963); (b) B. Franck and H. J. Lubs, *Angew. Chem. Intern. Ed. Engl.*, 7, 223 (1968); (c) B. Franck and H. J. Lubs, *Ann.*, 720, 131 (1969).
(4) D. H. R. Barton and G. W. Kirby, *J. Chem. Soc.*, 806 (1962).

(4),[5,6] a representative of the 5,10b-ethanophenanthridine class of Amaryllidaceae alkaloids.

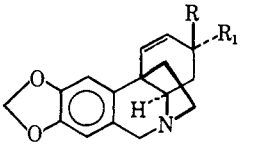
The synthetic route is outlined in Scheme I.[7] Treatment of O-methylnorbelladine (**1**)[8] with trifluoroacetic anhydride in pyridine followed by aqueous work-up afforded a 96% yield of the N-trifluoroacetyl derivative **5**: mp 66–74°; ir ($CHCl_3$) 5.93 μ; molecular ion at *m/e* 369.1194 (calcd 369.1188) (*Anal.* Found: C, 58.37; H, 4.90; N, 3.62). Oxidation of **5** with 3.5 mol

Scheme I



equiv of vanadium oxytrichloride[1] in anhydrous ether (3 hr at −78°, 10 hr at reflux) gave rise, after preparative thin-layer chromatography (tlc), to the *para–para* coupled dienone **6** in 24% yield (37% based on recovered starting material): ir ($CHCl_3$) 5.92 and 6.01 μ; nmr: olefinic hydrogens at 6.32 (2 H, d, J = 9.5) and 7.06 (2 H, d, J = 9.5), aromatic hydrogens at 6.52 (1 H, s) and 6.90 (1 H, s). As expected,[3b,9] removal of the N-trifluoroacetyl group from **6** (potassium carbonate in aqueous methanol) resulted in spontaneous cyclization to give the phenolic enone **7** in 95% yield: mp 250–252° dec; ir (KBr) 5.98 μ; nmr (DMSO-d_6): olefinic H at 5.96 (d, J = 10) and 8.01 (d, J = 10), aromatic H at 6.46 (s) and 7.09 (s), benzylic H at 4.19 (d, J = 17) (the higher field portion of this AB quartet was obscured by other resonances), and O-methyl H at 3.78 (s); molecular ion at *m/e* 271.1200 (calcd 271.1208).

That the enone **7** did in fact possess the desired structure and stereochemistry was demonstrated by methylation of it with phenyltrimethylammonium hydroxide[10] to afford (±)-oxomaritidine (**8**), mp 144–146°, indistinguishable from an authentic sample of (+)-oxomaritidine[11] by tlc and in its infrared, nmr, and mass spectra. The yield of the methylation reaction was low (24%; 41% based on recovered **7**), however, and could not be improved by using a variety of methods applied to either the enone **7** or dienone **6**. Consequently **7** was first reduced with sodium borohydride in methanol and then treated with diazomethane in ether–methanol to give (±)-epimaritidine (**9**) in 64% yield: mp 199–201°; infrared spectrum ($CHCl_3$) identical with that of (+)-maritidine[11] in the region 2.5–8.0 μ, but showing significant differences at longer wavelengths; nmr 6.49 (dd, J = 10 and 2, H-1), 5.82 (d, J = 10, H-2), *ca.* 4.4 (m, H-3), 4.53 (d, J = 17, H-6), 3.86 (d, J = 17, H-6), 6.54 (s, H-7), 6.81 (s, H-10), 3.88 (s, OMe), and 3.82 (s, OMe); molecular ion at *m/e* 287.1496 (calcd 287.1521). The assignment of stereochemistry at C-3 of epimaritidine (**9**) and maritidine (**4**) was made by comparison of their nmr spectra with those of crinine[11] (**10**) and epicrinine[11] (**11**). The coupling constants of the olefinic hydrogens with the proton at C-3 are con-



10, R = H; R_1 = OH
11, R = OH; R_1 = H

sistent with maritidine having the same pseudoaxial C-3 OH as is found in crinine (see Table I).[12]

Table I. Comparison of Nmr Spectra[a]

	4	9	10	11
δ(H-1)	6.66 d	6.49 dd	6.54 d	6.40 dd
δ(H-2)	6.01 dd	5.82 d	5.96 dd	5.78 d
δ(H-3)	~4.3 m	~4.4 m	4.31 m	~4.4 m
$J_{1,2}$	10	10	10	10
$J_{1,3}$	~0	2	~0	2
$J_{2,3}$	5	~0	5	~0

[a] See footnote 7.

Completion of the synthetic scheme required epimerization at C-3 of (±)-epimaritidine (**9**), which was accomplished by refluxing **9** for 1 hr in 10% hydrochloric acid.[13] Preparative tlc afforded 33% of **9** and 29% of (±)-maritidine (**4**), mp 230–233° dec, identical with the natural material in tlc behavior and in its infrared, nmr, and mass spectra.

We are at present investigating the use of this same general approach in the synthesis of lycorine-type and other Amaryllidaceae alkaloids.

(5) (a) Reference 2, p 356; (b) G. G. DeAngelis and W. C. Wildman, *Tetrahedron Lett.*, 729 (1969).

(6) Structure **4** depicts the absolute configuration of (+)-maritidine.[5b] The hydroxyl group stereochemistry shown in **4** was assigned as a result of the present work (see later).

(7) High-resolution mass spectra were obtained using an Associated Electronics Industries MS 902 instrument. Nmr spectra were obtained at 90 MHz (in $CDCl_3$ unless otherwise specified) using a Bruker HS-9 spectrometer; chemical shifts are expressed in parts per million downfield from tetramethylsilane and coupling constants in hertz.

(8) D. H. R. Barton, G. W. Kirby, J. B. Taylor, and G. M. Thomas, *J. Chem. Soc.*, 4545 (1963). We find that **1** can be conveniently prepared in 90% yield by *in situ* sodium borohydride reduction of the imine formed from isovanillin and tyramine.

(9) A. Goosen, E. V. O. John, F. L. Warren, and K. C. Yates, *ibid.*, 4038 (1961).

(10) W. Rodionow, *Bull. Soc. Chim. Fr.*, **39**, 305 (1926).

(11) We are very grateful to Professor W. C. Wildman for providing samples of oxomaritidine, maritidine, epicrinine, and crinine.

(12) The same nmr behavior has been observed and explained for derivatives of haemanthamine and crinamine: R. D. Haugwitz, P. W. Jeffs, and E. Wenkert, *J. Chem. Soc.*, 2001 (1965).

(13) H. W. Whitlock, Jr., and G. L. Smith, *J. Amer. Chem. Soc.*, **89**, 3600 (1967).

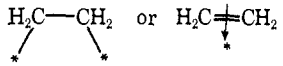
Acknowledgments. We thank Professor R. C. Dougherty for determination of the high-resolution mass spectra. The mass spectrometers and the Bruker nmr spectrometer were purchased with funds from the National Science Foundation. This work was supported by Public Health Service Grant CA-10136 from the National Cancer Institute.

Martin A. Schwartz, Robert A. Holton
Department of Chemistry, The Florida State University
Tallahassee, Florida 32306
Received December 17, 1969

Formation of π-Allyl Complexes by Adsorption of Propylene on Zinc Oxide

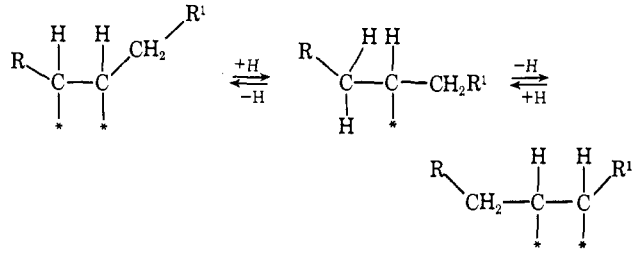
Sir:

Many of the mechanistic features of heterogeneous hydrogenation catalysts are accommodated by the assumption that adsorbed olefin reacts (reversibly or irreversibly) with an adsorbed hydrogen atom to form a surface alkyl which subsequently reacts with another adsorbed hydrogen atom to form alkane.[1] It is traditionally assumed that the adsorbed olefin is bound to the surface either by two σ bonds (I) or by a single π bond (II), *e.g.*



I II

where * stands for a surface atom. Isomerization of olefins, which accompanies hydrogenation, is also included in this scheme as follows.



In line with the above, hydrogen is a cocatalyst for the isomerization of olefins over a number of metals.[2,3] Over cobalt,[4] however, isomerization is detectable in the absence of hydrogen (although it proceeds at a much lower rate), and over chromia isomerization of olefins may be faster in the absence of hydrogen than when it is present.[5] Clearly, isomerization in the absence of hydrogen calls for a different mode of olefin adsorption. Burwell, *et al.*,[6] proposed that dissociative adsorption of olefins to form allylic species could explain the results over chromia. Later, Rooney and coworkers[7] suggested that many of the features of exchange, isomerization, and racemization reactions related to hydrogenation are better explained if we assume olefins can form a π-allyl complex on the surface. Evidence for such π-allyl species stems largely from mechanistic considerations. In this paper we present infrared evidence that on at least one hydrogenation catalyst, zinc oxide, olefins adsorb to form allyl species in which the π bond appears to contribute to the bonding to the surface. Zinc oxide is particularly well suited for such a study of dissociatively adsorbed olefin because surface hydrogen species (formed from hydrogen adsorption) are known to give rise to strong bands at 3500 and 1710 cm^{-1} which have been assigned to surface OH and ZnH, respectively.[8] Both of these bands are shifted somewhat in the presence of olefins.[9]

At room temperature propylene adsorbs rapidly on zinc oxide to form a species not removable by evacuation at room temperature for 16 hr. This adsorbed species, however, is completely removed by evacuation at 125° for 2 hr, and collection and analysis of the desorbed gas reveal that it is essentially pure propylene. By way of contrast adsorbed ethylene, also recoverable unchanged, can be removed by brief evacuation at room temperature.[9] This dramatic difference in the strength of chemisorption for these two olefins clearly suggests a basically different mode of adsorption.

If the spectrum of the zinc oxide is observed during admission of propylene, one sees the immediate appearance of bands at 3590 and 1545 cm^{-1} as well as bands in the C–H stretching and deformation region. The band at 3590 cm^{-1} can be reasonably assigned to a surface OH, whereas the band at 1545 cm^{-1} occurs in a region characteristic of a weakened C=C bond such as that found in π complexes.[10,11] This assignment can be checked by examination of the spectrum of adsorbed perdeuteriopropylene. A band corresponding to a surface OD appears at 2655 cm^{-1}; the relative isotope shift for this band is essentially the same as that encountered for the OH and OD bands formed by adsorption of H_2 and D_2, respectively.[8,9] As well as the expected shifts for C–D bands, a band appears at 1475 cm^{-1} which corresponds to the 1545-cm^{-1} band for adsorbed C_3H_6. This isotope shift is too small for either a ZnH or CH bond, but it is comparable to the shift in C=C stretch found for gaseous propylene on deuteration, *i.e.*, from 1652 to 1588 cm^{-1}.[12]

Further details on the nature of adsorbed propylene are supplied by the spectra of deuterium-labeled propylenes. Adsorption of 2-deuteriopropylene yields a surface OH band and a spectrum consistent with adsorbed propylene with one C–D stretch; this spectrum does not change over a period of several hours. Absorption of 1,1-dideuteriopropylene yields initially a surface OH band and a spectrum consistent with adsorbed propylene with more than one C–D stretch. In time, however, the spectrum changes; the OH band intensity decreases and an OD band appears. The growth in intensity of the OD band is coordinated with the decrease in in-

(1) G. C. Bond, "Catalysis by Metals," Academic Press, New York, N. Y., 1962, pp 254–258.
(2) P. B. Wells and G. R. Wilson, *J. Catal.*, **9**, 70 (1967).
(3) J. P. Bartek and R. J. Kokes, unpublished results.
(4) J. J. Phillipson and P. W. Wells, *Proc. Chem. Soc.*, 222 (1964).
(5) (a) A. B. Littlewood and R. L. Burwell, Jr., *J. Amer. Chem. Soc.*, **82**, 6287 (1960); (b) R. L. Burwell, Jr., G. L. Haller, K. C. Taylor, and J. F. Read, *Advan. Catal.*, **20**, 1 (1969).
(6) R. L. Burwell, Jr., A. B. Littlewood, M. Cardew, G. Pass, and C. T. H. Stoddart, *J. Amer. Chem. Soc.*, **82**, 6272 (1960).
(7) See J. J. Rooney and G. Webb, *J. Catal.*, **3**, 488 (1964), for a comprehensive review. A more recent discussion is given by R. L. Burwell, Jr., *Accounts Chem. Res.*, 2, 289 (1969).
(8) R. P. Eischens, W. A. Pliskin, and M. J. D. Low, *J. Catal.*, **1**, 180 (1962).
(9) A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, **73**, 3772, 3781 (1969).
(10) J. Pradilla-Sorzano and J. P. Fackler, Jr., *J. Mol. Spectrosc.*, 22, 80 (1967).
(11) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Amer. Chem. Soc.*, **83**, 1601 (1961).
(12) R. C. Lord and P. Venkataswarlu, *J. Opt. Soc. Amer.*, **43**, 1079 (1953).