For this discussion the small differences between the equatorial Co–N distances may be ignored. We shall thus only be concerned with the axial metal ligand distances. The Co(III)–NH_3 distance of 1.96 Å may be used to derive *via* covalent radii a Co(III)–O distance of ~1.94 Å (r_{III}). The Co(II)–O distance of 2.48 Å provides a value for r_{II}. The large difference is, of course, a consequence of Jahn–Teller distortion in the Co(II) system, an effect which is surely static as a consequence of the well-defined size of the N_4 girdle.

These structural results indicate that the $\mathrm{Co([14]dieneN_4)(OH_2)_2}^{2+}$ and $\mathrm{Co([14]dieneN_4)(OH_2)_2}^{3+}$ complexes are unique models for the study of intermolecular electron transfer processes since changes in bond lengths (and therefore inner sphere reorganizational barriers) are confined to one molecular axis. This is also the first known example of an essentially forbidden self-exchange reaction ($k_{\mathrm{exch}} = 2 \times 10^{-7}$ M^{-1} sec^{-1} at 70°)[15] between low-spin cobalt(II) and cobalt(III) complexes. Stranks' method[18] may be used to estimate the activation barrier which results from compressing the cobalt(II)–OH_2 bonds and stretching the cobalt(III)–OH_2 bonds until they are dimensionally equivalent. We find this bond distance in the activated complex to be $r^{\ddagger} = 2.10$ Å;[19,20] the corresponding reorganizational barrier[21] is approximately 21 kcal/mol. A reorganizational barrier of this magnitude is certainly compatible with the small self-exchange rate.

If one takes these cyclic complexes as models of "spin-allowed" intermolecular electron transfer between cobalt(III) and cobalt(II) complexes, then it appears that any "spin" constraint manifested in the $\mathrm{Co(NH_3)_6}^{3+}$–$\mathrm{Co(NH_3)_6}^{2+}$ self-exchange reaction may be attributed to the reorganizational barrier which results from the Jahn–Teller distortion accompanying the localization of electron density in a d_{z^2} orbital in the low-spin cobalt(II) intermediate.

All X-ray intensity data were collected on a card-controlled Picker four-circle diffractometer with Zr-filtered Mo Kα radiation. The θ–2θ scan technique was used with a scan speed of 2°/min and a minimum scan width of 2° plus allowance for spectral dispersion. Those data with $I \geq 2.5\ \sigma\ (I)$ were used for the solution and refinement of the structure. The space groups and lattice constants are as follows: $\mathrm{[Co[(14]dieneN_4)(OH_2)_2](BF_4)_2}$ $P2_1/c$, $a = 7.893\ (7)$ Å, $b = 9.518\ (7)$ Å, $c = 16.813\ (13)$ Å, $\beta = 107.16\ (2)°$; $\mathrm{[Co([14]dieneN_4)(NH_3)_2](ClO_4)_3}$ $A2/a$, $a = 9.596\ (9)$ Å, $b = 18.829\ (16)$ Å, $c = 15.550\ (14)$ Å, $\beta = 86.09\ (2)°$.

The structures were solved by a combination of Patterson and Fourier techniques and were refined by full-matrix least-squares with anisotropic thermal parameters for all atoms other than hydrogen atoms. The discrepancy factors for the Co(II) complex are $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.068$ and $wR = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2} = 0.074$ for 1442 data with sin $(\theta/\lambda) < 0.628$. The structure of the Co(III) complex involves a statistical disordering of one of the $\mathrm{ClO_4}^-$ groups about a twofold axis. The refinement in the centrosymmetric space group has resulted in discrepancy factors of $R = 0.066$ and $wR = 0.082$ for 1533 data with sin $(\theta/\lambda) < 0.596$. We are presently working on improved models for the disordered $\mathrm{ClO_4}^-$ counterion.

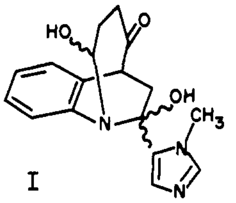
Acknowledgment. The authors are grateful to Dr. D. P. Rillema for obtaining suitable crystals of the cobalt complexes.

M. D. Glick,* J. M. Kuszaj, J. F. Endicott
Department of Chemistry, Wayne State University
Detroit, Michigan 48202
Received April 21, 1973

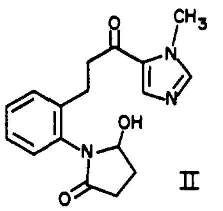
Synthesis and Revised Structure of Isolongistrobine[1]

Sir:

Our recent synthesis[1] of dehydroisolongistrobine cast doubt on the structure of a congeneric alkaloid, isolongistrobine. The latter alkaloid was assigned structure I by Arndt, *et al.*, who reported the isolation of these alkaloids in 1969.[2] Isolongistrobine exhibited no optical activity. Its uv spectrum suggested the presence of an acylimidazole. In accordance with our revised structure for dehydroisolongistrobine, we postulated structure II for isolongistrobine.[1]

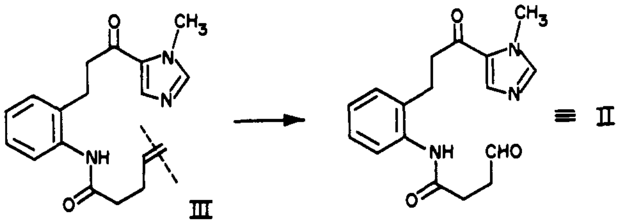


I



II

We planned to generate the proposed carbinol lactam of isolongistrobine (II) by oxidative cleavage of the vinyl group of a 4-pentenoamide (III) by ozone or its equivalent. Synthesis of III followed a sequence similar to that used in the preparation of the β-carbomethoxypropionamide[1] corresponding to 4-pentenoamide (III).



Acylation of amino alcohol IV[1] was effected by adding 4-pentenoyl chloride[3] to an equimolar mixture of IV and pyridine in dry methylene chloride at 0°. Plate chromatography on silica gel (9:1 CH_3CN–CH_3OH eluent) gave rise to amido alcohol V, a white

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[18] D. R. Stranks, *Discuss. Faraday Soc.*, **29**, 116 (1960).

[19] For $r^{\ddagger} = (k_{\mathrm{II}}r_{\mathrm{II}} + k_{\mathrm{III}}r_{\mathrm{III}})/(k_{\mathrm{II}} + k_{\mathrm{III}})$, in which k_{II} and k_{III}, are force constants for the cobalt(II)–OH_2 and cobalt(III)–OH_2 stretching vibrations, respectively. In the actual calculation we used $k_{\mathrm{II}} \simeq 0.7 \times 10^5$ dyn cm^{-1} and $k_{\mathrm{III}} \simeq 1.7 \times 10^5$ dyn cm^{-1} which are values for the respective cobalt–NH_3 vibrations. Cobalt–water force constants would be expected to be somewhat larger than cobalt–ammine force constants.[20]

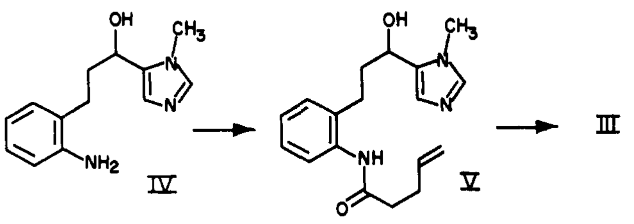
[20] K. Nakamoto, "Infrared Spectra of Coordination Compounds," Wiley, New York, N. Y., 1963.

[21] Estimated from $E_{\mathrm{total}} = 2(E_{\mathrm{II}} + E_{\mathrm{III}})$ where $E_{\mathrm{N}} = k_{\mathrm{N}}(\Delta r)^2$.

[1] Imidazole Alkaloids. II. Part I: M. A. Wuonola and R. B. Woodward, *J. Amer. Chem. Soc.*, **95**, 284 (1973).

[2] R. R. Arndt, S. H. Eggers, and A. Jordaan, *Tetrahedron*, **25**, 2767 (1969).

[3] Prepared from 4-pentenoic acid and thionyl chloride, bp 103–122°, 73.7%. *Cf.* L. Henry and C. Aschmann, *Chem. Zentralbl.*, **69** (II), 663 (1898); H. Wohlgemuth, *Ann. Chim.* (*Paris*), **2** (9), 329 (1914).



foam, in 59.5% yield.[4] Upon oxidation of V with CrO_3 in aqueous pyridine (Cornforth's reagent[5]) overnight at ambient temperature, III, the desired precursor to isolongistrobine, was obtained in 52% yield, as white crystals (CH_2Cl_2–hexane), mp 105.5–107°.[6]

Oxidative cleavage of the vinyl group of III to the aldehyde equivalent to II was accomplished by means of 2 equiv of sodium periodate and a catalytic amount of osmium tetroxide in 10:3 dioxane-water at ambient temperature[7] for 1.5 hr. Compound II, obtained in 85% yield[8] (mp 134–139°, lit.[2] mp 132–136°), was identical in all respects (ir, uv, nmr, and mass spectra) with natural isolongistrobine.[9]

On the basis of this work a 4-acyl-1-methylimidazole structure, analogous to II, can be inferred for longistrobine.

Acknowledgments. M. A. W. thanks Professor R. B. Woodward for a Research Assistantship (1971–1973). Thanks are also due to Mr. W. J. Pegg for mass spectra and to Dr. P. Balaram and Dr. G. Dudek for nmr spectra. Elemental analyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark.

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[4] Physical data for V: ir (NaCl plate) 3300 (broad), 1660, and 1530 cm^{-1}; mass spectrum (70 eV) m/e 111, 125, 213, 295, and 313 (parent).

[5] R. H. Cornforth, J. W. Cornforth, and G. Popják, *Tetrahedron*, **18**, 1351 (1962).

[6] Physical data for III: ir (KBr) 3400, 1670, 1685, and 1540 cm^{-1}; uv (MeOH) λ_{max} 255 nm (ϵ 11,000) shifted to 232 nm (ϵ 11,400) in acid; nmr ($CDCl_3$, 100 MHz) δ 2.60 (4 H, br s), 2.95 (2 H, t, J = 6 Hz), 3.26 (2 H, t, J = 6 Hz), 3.89 (3 H, s), 4.9–5.3 (2 H, m), 5.6–6.2 (1 H, m), 7.0–7.9 (6 H, m), and 8.95 (1 H, br s) ppm; mass spectrum (70 eV) m/e 82, 109, 202, 213, 256, and 311 (parent). *Anal.* Calcd for $C_{18}H_{21}N_3O_2$: C, 69.43; H, 6.80; N, 13.50. Found: C, 69.25; H, 6.82; N, 13.51.

[7] R. Pappo, D. S. Allen, Jr., R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).

[8] *Anal.* Calcd for $C_{17}H_{19}N_3O_3$: C, 65.16; H, 6.11; N, 13.41. Found: C, 65.12; H, 6.22; N, 13.28.

[9] We are indebted to Dr. A. Jordaan for a sample of isolongistrobine from natural sources.

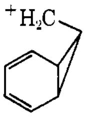
Mark A. Wuonola, R. B. Woodward*
Converse Memorial Laboratories
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received April 2, 1973

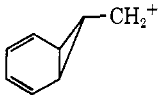
A Norcaradienylcarbinyl Cation. Effective π Participation in a σ-Delocalized Cyclopropylcarbinyl System. The Magnitude of the Norcaradiene–Cycloheptatriene Energy Gap[1]

Sir:

The question of the precise nature of the interactions which occur in norcaradienylcarbinyl cations has taken on increased importance since Sargent[2] originally suggested their intermediacy in the solvolysis of cycloheptatrienylcarbinyl 3,5-dinitrobenzoate. Subsequently, Hoffmann[3] pointed out that electron donation from cyclopropane to an adjacent (partially) positively charged center could be a prime factor in determining certain norcaradiene–cycloheptatriene equilibria (*e.g.*, that of 7,7-dicyanonorcaradiene[4]). Although Hoffmann did not consider the stereochemistry of the norcaradiene, it is apparent that, in the syn orientation (**1**), the symmetry of the orbitals is such that the diene could donate electron density directly (through space) to the positive center (stereochemically impossible for the anti analog **2**, however).

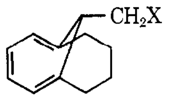


1

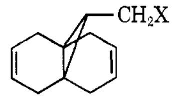


2

3-*syn*-



3-*anti*-



4

Recently, Wilcox[5] has seemingly eliminated the possibility that the double bonds of **1** or **2** could stabilize the positive center *via* π conjugation, by elegantly demonstrating the lack of such participation in other cyclopropylcarbinyl systems. In apparent accord with this, Paquette[6] has just reported that solvolysis of the epimers of **3**, thought to proceed *via* the intermediacy of norcaradienes, is unaccelerated relative to suitable models (*e.g.*, **4**). However, no firm conclusions can be drawn from studies of **3**, since the solvolyses are dependent upon preequilibria (introducing K_{eq} values of unknown magnitude). Nevertheless, Paquette concludes that conformational factors (*i.e.*, **1** *vs.* **2**) play an insignificant role in solvolyses where such ions intervene.

Clearly, direct evidence on the nature of ions such as **1** and **2** can only be obtained from an investigation of compounds whose ground-state structure is of the norcaradiene type.[7] We herein report such a study. The compounds chosen were derivatives of the tricyclo[4.3.1.0^{1,6}]decane series, the diene of which has been shown, by Vogel,[8] to exist "exclusively" in the norcaradiene form. All syntheses proceeded normally.[9] The vital distinction of stereochemistry was unambiguously made *via* iodolactonization of a precursor to the syn isomer, **9** (separations were made at this point[9]). Table I summarizes the kinetic solvolysis data obtained in 70% (v/v) acetone–water.[10]

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[1] We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

[2] G. D. Sargent, N. Lowry, and S. D. Reich, *J. Amer. Chem. Soc.*, **89**, 4085 (1967).

[3] R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970).

[4] E. Ciganek, *J. Amer. Chem. Soc.*, **87**, 652 (1965).

[5] C. F. Wilcox, Jr., and H. D. Banks, *ibid.*, **94**, 8232 (1972).

[6] L. A. Paquette and G. L. Thompson, *ibid.*, **95**, 2364 (1973).

[7] For a review of the norcaradiene–cycloheptatriene equilibrium problem, see G. Maier, *Angew. Chem., Int. Ed. Engl.*, **6**, 402 (1967).

[8] E. Vogel, W. Wiedemann, H. Kiefer, and W. Harrison, *Tetrahedron Lett.*, 673 (1963).

[9] Details of our synthetic approaches will appear in the full paper on the subject. Complete characterization (nmr, ir, mass spectra, analyses) of all key intermediates and products (except for **10**-OH, which was not obtained pure) was obtained.

0) (1Product studies on **7** and **10** in both unbuffered and urea-buffered 70% aqueous acetone showed 4-vinylindan to be the only identifiable product (≥80% yield). Also, **7**-OH was shown to be stable under even the unbuffered conditions. Therefore, we are confident of the absence of acyl–oxygen cleavage. The 4-vinylindan formed is completely analogous to Paquette's results,[6,11] and presumably arises *via* the same mechanism.[11] With respect to **5**, **6**, **8**, and **9**, the products are exclusively of the allylcarbinyl variety.

[11] In footnote 8 of ref 6, Paquette reports formation of 1-vinyltetralin. However, from the context, this clearly should be 5-vinyltetralin.