

exchange compel interpretation of the three peaks in terms of absorption by the hydroxyl groups of the monomeric diol. The broad band at 3480  $\text{cm.}^{-1}$  may be assigned to O-H stretching vibrations of hydroxyl groups, the hydrogen atoms of which are *intramolecularly* hydrogen bonded to oxygen in a seven-membered ring.<sup>6</sup> The doublet (3640 and 3619  $\text{cm.}^{-1}$ ) may be attributed to O-H stretching vibrations of all of the hydroxyl groups, the hydrogen atoms of which are *not* engaged in hydrogen bonding. If such "free" hydroxyl groups all had the same conformation, a doublet would not be expected.<sup>7</sup> Therefore, it is highly probable that two or more conformations are significantly populated for diol A, at least one of which is the *intramolecularly hydrogen bonded twist conformation* (Ib or IIb).

The configuration of diol A may be assigned on the basis of the method of synthesis. Diol A most probably has structure I (although structure II cannot be rigorously excluded at this time). Structure I would result from 2,5-di-*t*-butylhydroquinone if a stereospecific addition of all six hydrogen atoms occurred from the same side of the plane of the ring to give an all *cis* configuration. The hydrogenation conditions used, when applied to other aromatic compounds, yield mostly *cis*-substituted cyclohexane derivatives.<sup>8</sup>

The author is indebted to the American Academy of Arts and Sciences for a grant from the Warren Fund, and to Dr. Richard C. Lord for use of equipment which made possible the initiation of this work. Continuing financial support by the National Science Foundation is gratefully acknowledged.

(6) G. C. Pimentel and McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, California, 1960, Chapters 3 and 5; L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

(7) R. Piccolini and S. Winstein, *Tetrahedron Letters*, No. 13, 4 (1959).

(8) R. D. Stolow, *J. Am. Chem. Soc.*, **81**, 5806 (1959), and refs. 29-31 therein.

CONTRIBUTION No. 257

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#### CHEMISTRY OF THE METAL CARBONYLS. X. TETRACARBONYLNITROSYLMANGANESE(O)<sup>1,2</sup>

Sir:

Treatment of manganese pentacarbonyl iodide with nitric oxide affords carbonyltrinitrosylmanganese.<sup>3a</sup> Synthesis of this compound significantly extended the "pseudo-nickel tetracarbonyl" series of nitrosyls, previous members of this series being the long established cobalt and iron complexes  $\text{Co}(\text{NO})(\text{CO})_3$  and  $\text{Fe}(\text{NO})_2(\text{CO})_2$ . Barraclough and Lewis<sup>3a</sup> have pointed out that manganese could conceivably form two monomeric carbonylnitrosyls with inert-gas configurations, *viz.*, Mn-

(1) Part IX R. B. King, T. A. Manuel and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961). For Part VIII see H. D. Kaesz, R. B. King and F. G. A. Stone, *Z. Naturforsch.*, **15b**, 763 (1960).

(2) We are indebted to the National Science Foundation for support of this work through Grant 14610.

(3) (a) C. G. Barraclough and J. Lewis, *J. Chem. Soc.*, 4842 (1960).

(b) R. F. Lambert and J. D. Johnston, *Chem. and Ind.*, 1267 (1960), have reported a compound  $(\text{C}_6\text{H}_5)_2\text{PMn}(\text{CO})_2\text{NO}$  which may be regarded as a derivative of  $\text{Mn}(\text{CO})_5\text{NO}$ .

$(\text{NO})_3\text{CO}$  and  $\text{Mn}(\text{NO})(\text{CO})_4$ , and that the latter if it existed would be a member of an entirely new "pseudo-iron pentacarbonyl" nitrosyl series. From arguments based on  $\pi$ -bonding, electronegativity, and stereochemical effects it was concluded that  $\text{Mn}(\text{NO})_3\text{CO}$  would be more stable than  $\text{Mn}(\text{NO})(\text{CO})_4$ , and thus isolation of the former in preference to the latter is understandable.<sup>3a</sup> We now describe tetracarbonylnitrosylmanganese(O).<sup>3b</sup>

A 9.2-g. (43 mmoles) sample of N-methyl-N-nitroso-*p*-toluenesulfonamide<sup>4</sup> was placed in a 1-l. Pyrex reaction bulb fitted with a stopcock. The bulb was attached to the vacuum line and evacuated, Diethyl ether (30 ml.) and manganese carbonyl hydride<sup>5</sup> (4.0 g., 20.4 mmoles) were distilled into the bulb, which was removed from the vacuum line and stored in the dark at room temperature for 16 hr. During this period the solution changed from pale yellow to deep red. The bulb was re-attached to the vacuum system and its contents fractionated. Dark red crystals of tetracarbonylnitrosylmanganese (2.24 g., 56% yield) collected in a trap cooled to  $-35^\circ$ . This compound melts at  $-1.5$  to  $0^\circ$  to a deep-red air-sensitive liquid, forming reddish-brown vapors, resembling bromine in appearance. The new nitrosyl is diamagnetic<sup>6</sup> and has a vapor pressure of about 8 mm. at  $25^\circ$ . *Anal.* Calcd. for  $\text{C}_4\text{NO}_5\text{Mn}$ : N, 7.1; Mn, 27.9; CO groups, 4.00; mol. wt., 197. Found: N, 7.2; Mn, 28.2; CO groups,<sup>7</sup> 4.00, 3.92; mol. wt. (from vapor density), 199, 200.

Tetracarbonylnitrosylmanganese could have either a trigonal bipyramidal or a tetragonal pyramidal structure. Moreover, depending on the position of substitution of the nitric oxide group a trigonal bipyramidal configuration would have  $\text{C}_{3v}$  or  $\text{C}_{2v}$  symmetry, and a tetragonal pyramidal arrangement  $\text{C}_{4v}$  or  $\text{C}_s$  symmetry. The infrared spectrum of  $\text{Mn}(\text{CO})_4\text{NO}$  was examined in an attempt to establish structure. The compound showed three carbonyl stretching bands at 2095 (m), 2019 (s), and 1972 (s)  $\text{cm.}^{-1}$ , and a nitric oxide stretching frequency at 1759 (s)  $\text{cm.}^{-1}$ .<sup>8</sup> Of the possible structures mentioned above, only the trigonal bipyramidal structure having the NO group at an apex ( $\text{C}_{3v}$ ) would show three infrared active carbonyl stretches. In possessing a trigonal bipyramidal structure tetracarbonylnitrosylmanganese is thus similar to iron pentacarbonyl.<sup>9</sup>

(4) A reagent previously used to prepare the nitrosyl  $\pi\text{-C}_6\text{H}_5\text{Mo}(\text{CO})_2\text{NO}$  (T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956)).

(5) We are indebted to the Ethyl Corporation for a gift of manganese carbonyl from which the hydride may be made; see W. Hieber and G. Wagner, *Z. Naturforsch.*, **13b**, 338 (1958).

(6) Diamagnetism was established by the n.m.r. method described by D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(7) Determined by heating at  $150^\circ$  weighed samples of the nitrosyl with excess of iodine. No nitric oxide was released, but carbon monoxide was formed and measured with an automatic Sprengel pump (B. Bartocha, W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **6**, 119 (1958)). Identity of the carbon monoxide was established by quantitative combustion of the gas over copper oxide at  $800^\circ$  to form carbon dioxide, which was identified by its infrared spectrum.

(8) Spectra were taken in tetrachloroethylene solution with a Perkin-Elmer Model 221 Prism-Grating spectrophotometer. We thank Professor M. K. Wilson of Tufts University for making this high-resolution instrument available for our use.

(9) H. Stammreich, Oswaldo Sala and Yara Tavares, *J. Chem. Phys.*, **30**, 856 (1959).

A characteristic of iron pentacarbonyl is the reaction it undergoes on irradiation to produce diiron nonacarbonyl and carbon monoxide. Accordingly, the *pseudo*-iron pentacarbonyl  $\text{Mn}(\text{CO})_4\text{NO}$  was irradiated in an attempt to obtain  $\text{Mn}_2(\text{CO})_7(\text{NO})_2$ , a compound analogous to  $\text{Fe}_2(\text{CO})_9$ . This treatment gave heptacarbonyldinitrosyldimanganese (30% yield) as deep red crystals (decomp. without melting at  $\sim 140^\circ$ ), carbon monoxide, and lesser amounts of manganese carbonyl and carbonyltrinitrosylmanganese. Heptacarbonyldinitrosyldimanganese(0), very air sensitive, subliming at  $25^\circ$  (0.1 mm.), and exceedingly difficult to purify from manganese carbonyl, probably has a structure analogous to that of  $\text{Fe}_2(\text{CO})_9$ ,<sup>10</sup> *viz.*,  $\text{ON}(\text{CO})_2\text{Mn}(\text{CO})_3\text{Mn}(\text{CO})_2\text{NO}$ , with some metal-metal bonding between manganese atoms. The infrared spectrum<sup>8</sup> shows carbonyl stretching bands at 2101 (w), 2042 (vs), 2006 (vs), 1995 (w, sh) and 1776 (s)  $\text{cm}^{-1}$ . Bands in the bridging carbonyl region and the nitrosyl stretching region occur at 1743 (m), 1735 (m), 1731 (w), 1726 (w) and 1710 (m)  $\text{cm}^{-1}$ .

(10) H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 286 (1939).  
(11) National Science Foundation Predoctoral Fellow.

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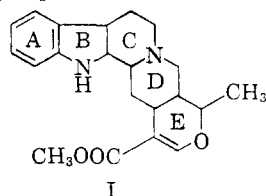
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#### THE TOTAL SYNTHESIS OF *dl*-AJMALICINE

Sir:

Of the numerous and widely distributed E-heterocyclic indole alkaloids, the *Rauwolfia* component ajmalicine (tetrahydroserpentine,  $\delta$ -yohimbine) (I),<sup>1</sup> a peripheral vasodilator effective in the



treatment of angina and other physical disorders, is a notable example. In this Communication, we summarize operations leading to *dl*-ajmalicine, which represent the first synthesis of a member of this important natural product group.<sup>2</sup>

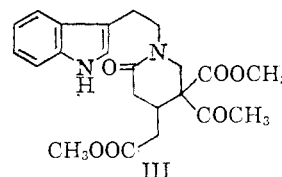
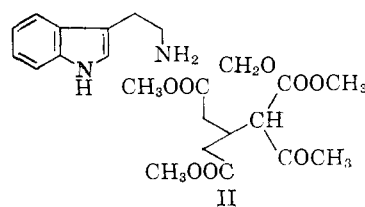
In a key step which roughly parallels the presumed biogenetic process,<sup>3</sup> the essentials of the desired alkaloidal system are efficiently assembled at the outset: tryptamine, formaldehyde and the keto triester II<sup>4</sup> undergo a Mannich condensation

(1) Isolation and characterization: (a) S. Siddiqui and R. H. Siddiqui, *J. Ind. Chem. Soc.*, **8**, 667 (1931); **9**, 539 (1932); **12**, 37 (1935); **16**, 421 (1939); (b) H. Heineman, *Ber.*, **67**, 15 (1934). Gross structure: R. Goutarel and A. LeHir, *Bull. Soc. chim.*, **18**, 909 (1951). Partial stereochemical structure: (a) E. Wenkert and D. K. Roychaudhuri, *J. Am. Chem. Soc.*, **79**, 1519 (1957); **80**, 1613 (1958); (b) N. Neuss and H. E. Boaz, *J. Org. Chem.*, **22**, 1001 (1957).

(2) First announced (March 28, 1961) at the 139th Meeting of the American Chemical Society, St. Louis, Missouri.

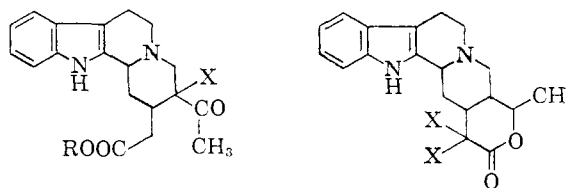
(3) E. Wenkert and N. V. Bringli, *J. Am. Chem. Soc.*, **81**, 1474 (1959).

(4) Secured through Michael addition of methyl acetoacetate to dimethylglutaconate (*cf.* M. H. Dreifuss and C. K. Ingold, *J. Chem. Soc.*, **123**, 2964 (1923).



in *tert*-butyl alcohol, providing the lactam III in nearly quantitative yield.<sup>5</sup> Although the lactam was found to be neither distillable nor crystallizable, it could be purified by column chromatography; material so obtained displayed consonant spectral properties (infrared absorption at 2.88, 5.75, 5.80 and 6.09  $\mu$ ) ( $\lambda_{\text{max}}$  221, 276, 284 and 292  $m\mu$ ) and was suitable for the succeeding steps.

First of all, ring-C was fashioned, carried out by means of phosphorus oxychloride closure to the tetracyclic  $\Delta^3$ -dehydro base ( $\text{PO}_2\text{Cl}_2^-$  salt, m.p.



IVa (X =  $-\text{COOCH}_3$ ;  
R =  $-\text{CH}_3$ )

IVb (X =  $-\text{H}$ ; R =  $-\text{H}$ )

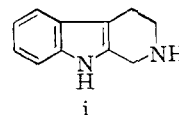
Va (X =  $-\text{H}$ )  
Vb (X =  $=\text{CHOH}$ )

148–150°) ( $\lambda_{\text{max}}$  247, 358  $m\mu$ ,  $\epsilon = 11,900$ ; 23,500) and then reduction over palladium-on-carbon in ethanol to the keto diester IVa (HCl salt, m.p. 152.5–154°).

Removal of the ester function from the  $\beta$ -keto ester moiety was accomplished next, effected by prolonged heating of the keto diester IVa in refluxing dilute hydrochloric acid. The resulting keto acid IVb, isolated and purified as the hydrochloride (m.p. 236.5–238°), was accompanied by varying amounts of *diacid* (m.p. 268–269°) formed by acid-catalyzed deacetylation of IVa.

In preparation for the construction of the E-ring, keto acid IVb was reduced with sodium borohydride to the hydroxy acid (m.p. 248–251°), which, on treatment with *N,N'*-dicyclohexylcarbodiimide in pyridine, was converted to the  $\delta$ -lactone Va (HCl salt, m.p. 236–238°) (infrared absorption

(5) Use in this case of traditional Mannich conditions, *viz.*, formaldehyde, active hydrogen component and amine in an *acidic* medium, leads to formation of tetrahydro- $\beta$ -carboline (i), but no product of the type III. When the reaction is carried out in *tert*-butyl alcohol and



in the absence of added acid, formation of tetrahydro- $\beta$ -carboline is suppressed, and lactam III is produced instead. These observations will be treated appropriately in the future full publication.