

The other portions of these spectra are in accord with the assigned structures.¹⁰

(10) Satisfactory carbon and hydrogen analyses were obtained for all new compounds.

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Interconversion of the Aspidospermine Skeleton to the Refractine Type¹

Sir:

In the course of our work² on the structure of minosine³ (= minovincine⁴) I, an alkaloid isolated from *Vinca minor*,^{3,4} we discovered a reaction which made possible an experimentally facile transformation of a skeleton of the aspidospermine type⁵ into the pleiocarpine⁶-refractine⁷ class of alkaloids, an interconversion of considerable biogenetic interest.

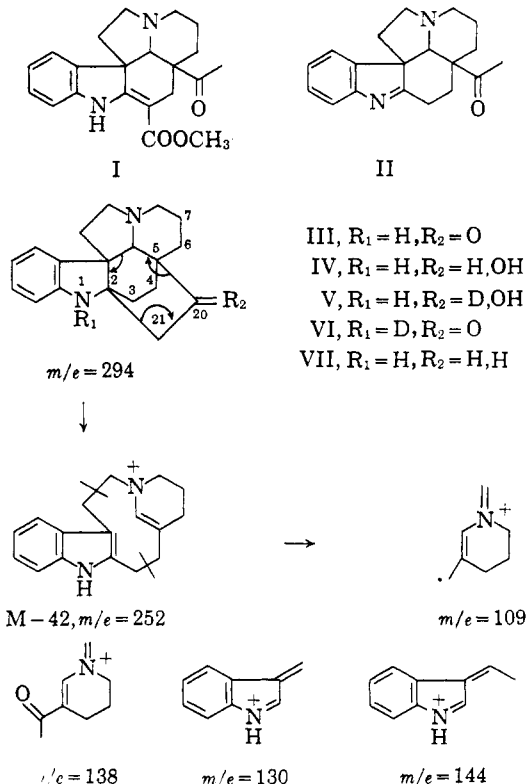
While our approach as well as the conclusions regarding the structure of I had closely paralleled those published at about that time by Janot, Djerassi, and their collaborators,⁴ we realized that an unexpected cyclization had occurred during one of the degradation reactions.

On heating of I in constant-boiling hydrochloric acid a crystalline compound (m.p. 176–177°, mol. wt. 294) was obtained to which we assign the hexacyclic structure III, a skeleton of the pleiocarpine type. Aside from its biogenetic significance, this observation contradicts the report⁴ cited above in which the apparently identical substance (same melting point and molecular weight, also obtained by acid decarboxylation of I) was considered—without citing much experimental evidence—to be the isomeric indolenine II, the product expected *a priori* in the hydrolysis of a carbomethoxymethyleneindole such as I.

The mass spectrum of the decarbomethoxylation product cannot be reconciled with structure II (it is very different from the one exhibited by the carbonyl-free analog of II⁸) and all our results are consistent with structure III instead: the ultraviolet spectrum is typically that of a dihydroindole: $\lambda_{\text{max}}^{\text{EtOH}}$ 241 (ϵ 7110) and 292 $m\mu$ (ϵ 3080), and from the infrared absorption at 1706 and 3350 cm^{-1} ketone and amino functions can be inferred. The molecular ion at $m/e = 294$ in the mass spectrum of III confirms the loss of the ester function and all other peaks are readily interpreted in terms of the assumed structure: loss of both 28 and 42 mass units from the molecular ion, the former representing carbon monoxide and ethylene,⁹ the

latter a ketene fragment resulting from the familiar retro Diels-Alder-type of fragmentation (see arrows), common for alkaloids of the aspidospermine¹⁰ and refractine classes.¹¹ The $M - 42$ fragment ($m/e = 252$) can then undergo simple bond fission as indicated to yield an ion of $m/e = 109$, a very characteristic phenomenon for systems such as III. Other important ions are the indole fragments of $m/e = 130$ and 143, 144, as well as the one at $m/e = 138$ which arises from the alicyclic part *via* a variation¹¹ of the general pathway outlined above. Further proof of the conversion of $\text{CH}_3\text{CO}-$ to $-\text{CH}_2\text{CO}-$ is derived from the base-catalyzed exchange of the α -hydrogens. Two atoms of deuterium were exchanged (under conditions leading to incorporation of three deuterium atoms into I) as judged from the mass spectrum of the product which also agrees with the above interpretation of the spectrum of III (peaks at $m/e = 109, 130, 140, 143, 144, 252$, and 296).

Chemical transformations of III support the assignment: lithium aluminum hydride reduction produced a dihydroindole alcohol IV (mol. wt. 296), the mass spectrum of which had the expected peaks at $m/e = 252$ ($M - 44$), 140 ($= 138 + 2$), and 109. Similarly, reduction with lithium aluminum deuteride furnished the C-20 deuterated derivative V, whose mass spectrum showed the appropriate shifts $M = 297$, $m/e = 252$ ($M - 45$), 141 ($= 138 + 3$), and 109. Partial exchange of the active hydrogen on nitrogen in III for deuterium led to a compound (VI) which showed doublets in its mass spectrum at $m/e = 295, 294$ (M^+), 267, 266 ($M - 28$), 252, 253 ($M - 42$), 145, 144, and



(1) Paper XXIII on the Application of Mass Spectrometry to Structure Problems. For paper XXII see K. Biemann, P. Bommer, A. L. Burlingame, and W. J. McMurray, *J. Am. Chem. Soc.*, **86**, 4624 (1964).

(2) In collaboration with Dr. J. Mokry and his colleagues, Chemical Institute of Slovak Academy of Sciences, Bratislava, Czechoslovakia.

(3) J. Mokry, I. Kompiš, L. Dubravková, and P. Šefčovič, Paper presented at the Second International Symposium on the Chemistry of Natural Products, 1962, Prague, Czechoslovakia.

(4) M. Plat, J. Le Men, M.-M. Janot, H. Budzikiewicz, J. M. Wilson, L. J. Durham, and C. Djerassi, *Bull. soc. chim. France*, 2237 (1962).

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(6) W. G. Kump, D. J. Le Count, A. R. Battersby, and H. Schmid, *Helv. Chim. Acta*, **45**, 854 (1962).

(7) C. Djerassi, T. George, N. Finch, H. F. Lodish, H. Budzikiewicz, and B. Gilbert, *J. Am. Chem. Soc.*, **84**, 1499 (1962).

(8) K. Biemann and G. Spiteller, *ibid.*, **84**, 4578 (1962).

(9) In a 1:1 ratio, as determined by high-resolution mass spectrometry.

(10) K. Biemann, M. Spiteller-Friedmann, and G. Spiteller, *J. Am. Chem. Soc.*, **85**, 631 (1963).

(11) C. Djerassi, H. Budzikiewicz, R. J. Owellen, J. M. Wilson, W. G. Kump, D. J. LeCount, A. R. Battersby, and H. Schmid, *Helv. Chim. Acta*, **46**, 742 (1963).

131, 130, but singlets at $m/e = 138$ and 109, a result which clearly locates the amino function in the indole part of the molecule. Finally, Wolff-Kishner reduction of III furnished VII, the mass spectrum of which is practically identical with that of the recently isolated aspidofractinine¹¹ (major peaks at $m/e = 280$ (M), 252 (M - 28), 124, and 109).

Attempts to effect the cyclization of I to III with retention of the carbomethoxy grouping at C-3 have thus far proved unsuccessful, a major handicap being the lack of sufficient material to identify clearly the components of the product mixtures obtained in various experiments.

The unexpectedly facile formation of III from minovincine may be understood if one considers the indolenine II and its enol form as the intermediate in the decarboxylation-cyclization process. Molecular models show that the methyl group of the side chain is situated within bond-forming distance above C-2, and an aldol-type condensation should thus proceed fairly readily once the enol is formed. The fact that most of the refractine-type alkaloids isolated so far bear a substituent (usually carbomethoxy) at C-3 would seem to implicate minovincine and related α -methyleneindole alkaloids as actual biogenetic precursors of this skeleton.

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An Arylazo Derivative of Molybdenum¹

Sir:

Reactions between aryl diazonium salts and many anions are useful both for the preparation of substituted aromatic compounds and for the preparation of arylazo compounds often useful as dyes.² In attempts to prepare interesting aryl or arylazo complexes of various transition metals we have been investigating reactions between various aryl diazonium salts and various metal carbonyl anions. By this synthetic technique we have prepared the first compound with an arylazo group, $RN=N$, directly bonded to a transition metal.

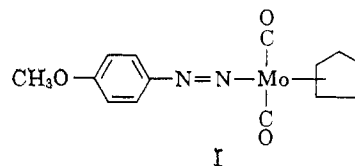
Solid *p*-anisyl diazonium tetrafluoroborate was added gradually to excess $NaMo(CO)_3C_6H_5$ ³ in tetrahydrofuran at room temperature. After several hours solvent was removed and product extracted from the residue with dichloromethane. After evaporation of the dichloromethane, further purification was accomplished by chromatography on alumina in diethyl ether solution and by low temperature crystallization from pentane to give red-orange crystals, m.p. 78–79°, of $p-CH_3OC_6H_4N_2Mo(CO)_2C_6H_5$ in ~20% yield. *Anal.* Calcd.: C, 47.7; H, 3.4; N, 8.0; Mo, 27.2; O, 13.6; mol. wt., 352. Found: C, 47.8; H, 3.7; N, 8.0; Mo, 26.9; O, 13.9; mol. wt., 338 (Mechrolab vapor pressure osmometer in benzene solution). In some ex-

periments where excess *p*-anisyl diazonium tetrafluoroborate was present, no $p-CH_3OC_6H_4N_2Mo(CO)_2C_6H_5$ was obtained. Instead most of the molybdenum was converted to a red-purple solid insoluble in pentane and benzene but soluble in tetrahydrofuran. The nature of this material is still unknown, but its infrared spectrum clearly demonstrates the absence of carbonyl groups and the presence of the BF_4^- anion.

This new molybdenum complex $p-CH_3OC_6H_4N_2Mo(CO)_2C_6H_5$ is a red-orange crystalline solid readily soluble in all organic solvents but insoluble in water. On exposure to air its solutions decompose over several hours. Its acetone solution (4.15×10^{-4} M) possesses a low conductivity similar to that of pure acetone.

The infrared spectrum (KBr pellet) of $p-CH_3OC_6H_4N_2Mo(CO)_2C_6H_5$ exhibits two sharp strong metal carbonyl bands at 1960 and 1900 cm^{-1} . Comparison of the infrared spectrum of *p*-anisyl diazonium tetrafluoroborate with that of $p-CH_3OC_6H_4N_2Mo(CO)_2C_6H_5$ indicates that the ν_{NN} , the nitrogen-nitrogen multiple bond stretching frequency, of 2225 cm^{-1} in the diazonium salt has decreased to 1600 cm^{-1} in the molybdenum complex.⁴ This large lowering of ν_{NN} in $p-CH_3OC_6H_4N_2Mo(CO)_2C_6H_5$ to a value very similar to the ν_{NO} of the nitrosyl group in metal nitrosyls (e.g., ν_{NO} of $C_6H_5W(CO)_2NO$ at 1630 cm^{-1}) suggests a large decrease in the nitrogen-nitrogen bond order from the triple bond in the aryl diazonium salt.

The proton n.m.r. spectrum besides demonstrating $p-CH_3OC_6H_4N_2Mo(CO)_2C_6H_5$ to be diamagnetic exhibits two coupled ($J = 9$ c.p.s.) doublets at τ 2.80 and 3.20 attributed to the four protons on the *para*-substituted benzene ring, a single sharp resonance at τ 4.37 attributed to the five equivalent π -cyclopentadienyl protons, and another single sharp resonance at τ 6.25 attributed to the three protons of the methoxy group. All of these data are in agreement with the expected structure I for $p-CH_3OC_6H_4N_2Mo(CO)_2C_6H_5$.



The diamagnetism of the compound suggests an inert gas configuration for the molybdenum atom. If this is indeed the case and if the π -cyclopentadienyl and carbonyl groups donate the usual numbers of electrons to the metal atom, then the neutral *p*-anisylazo ligand must be acting as a three-electron donor.⁵ The compound $p-CH_3OC_6H_4N_2Mo(CO)_2C_6H_5$ would therefore be isoelectronic with the known compounds $C_6H_5Mo(CO)_2NO$,^{3,6} $C_6H_5Mo(CO)_2C_6H_5$,⁷ $C_6H_5Mo(CO)_2CH_2SCH_3$,⁸ $C_6H_5Mo(CO)_2C_7H_7$,⁹ etc. Indeed, replace-

(1) We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-580-64.

(2) For detailed discussions on the chemistry of diazonium salts see K. H. Saunders, "The Aromatic Diazo Compounds and Their Technical Applications," Longmans, Green and Co., New York, N. Y., 1949, and H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961.

(3) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1955).

(4) Absorption due to the aromatic rings partially obscures ν_{NN} of $p-CH_3OC_6H_4N_2Mo(CO)_2C_6H_5$ in its infrared spectrum making a comparison with the spectrum of *p*-anisyl diazonium tetrafluoroborate essential for unambiguous identification of ν_{NN} .

(5) Alternatively, in I the cationic *p*-anisylazo ligand can be considered as a two-electron donor similar to NO^+ combining with an anionic metal carbonyl fragment.

(6) E. O. Fischer, O. Beckert, W. Hafner, and H. O. Stahl, *Z. Naturforsch.*, **10b**, 598 (1955).

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(9) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964).