

mediately to localize the negative charge. It may also be that in our particular system the lowering of the singlet state energy which accompanies Jahn-Teller distortion is greater than the singlet-triplet energy difference. Thus our evidence does not conclusively demonstrate that cyclobutadiene and other members of this class of compounds will not have triplet ground states, but it is suggestive.

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TOTAL SYNTHESIS OF RACEMIC CONESSINE

Sir:

Barton and Morgan¹ recently have described an ingenious synthesis of conessine from Δ^5 -pregnene-3 β ,20 β -diol. In the present communication we wish to disclose a synthesis of the racemic form of the alkaloid starting from coal tar intermediates.

The tetracyclic ketone I, which is readily available from 5-methoxy-2-tetralone by successive (*in situ*) condensation with ethyl vinyl ketone followed by methyl vinyl ketone, has been stereoselectively converted into the hydroxy ketone II.² The present report discloses the transformation of this latter substance into racemic conessine.

Reaction of the hydroxy ketone II with excess methylolithium afforded a dihydroxy compound, m.p. 155–156°, which on treatment with acetic anhydride and pyridine was selectively acetylated to give the 3-acetate, m.p. 166–167°. Treatment of this hydroxy ester with phosphorus oxychloride and pyridine effected dehydration to yield a mixture of olefins which was rich in the desired 13,17a-dehydro isomer III (acetoxyl group at C₃) as shown by ozonolysis and subsequent work-up with formaldehyde to give the diketo 3-acetate IV, m.p. 79.5–80.5°. This last substance was cyclized smoothly with dilute alcoholic potassium hydroxide to the unsaturated ketone V, m.p. 72–74°, $\lambda_{\text{max}}^{\text{EtOH}}$ 257 m μ (ϵ 14,200) which on treatment with potassium cyanide and ammonium chloride in dimethylformamide³ was converted, in excellent yield, into a mixture of epimeric 13-cyano-3-hydroxy compounds, m.p. 144–145° and 169–171°, formed in approximately equal amounts. The cyano ketones were easily separated by chromatography, and the 171° compound proved to be the 13 β isomer VI as shown by its conversion to conessine as described below.^{3a}

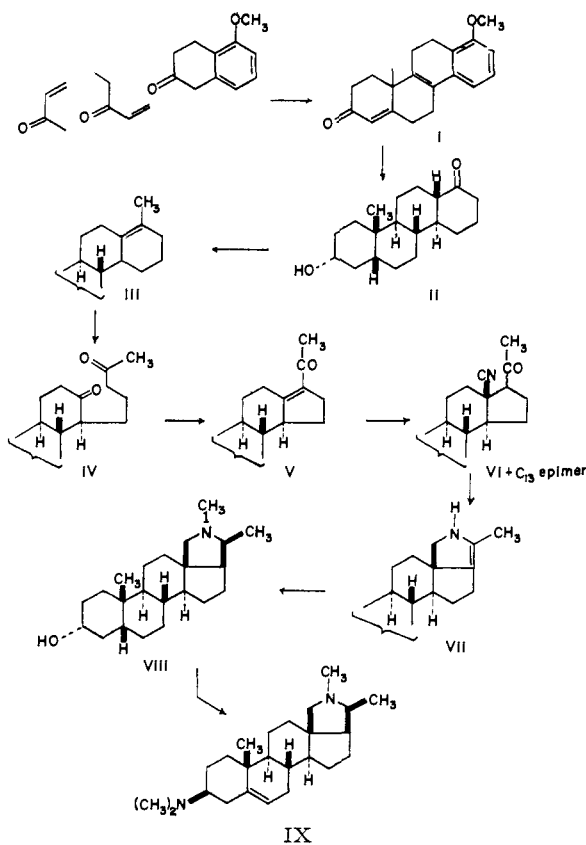
Preliminary attempts to effect direct conversion of the cyano ketone VI into N-desmethyl VIII by

(1) D. H. R. Barton and L. R. Morgan, *Proc. Chem. Soc.*, 206 (1961).

(2) W. S. Johnson, W. A. Vredenburg and J. E. Pike, *J. Am. Chem. Soc.*, **82**, 3409 (1960).

(3) Cf. the work of W. Nagata, I. Kikkawa and K. Takeda, *Chem. and Pharm. Bull. (Japan)*, **9**, 79 (1961), on the cyanation of the corresponding unsaturated ketone in the estratriene series. It also is to be noted that W. L. Meyer and I. F. Wolfe are studying the reaction in the model two-ring system, and we wish to thank Professor Meyer for advising us of his unpublished work.

(3a) ADDED IN PROOF.—On April 2, 1962, we discovered that the 13a-cyano ketone, on heating at 350°, rapidly loses hydrogen cyanide and is smoothly reconverted to unsaturated ketone in excellent yield. Through this recycling process, the synthesis of conessine reported here is thus rendered stereoselective at every stage.



catalytic hydrogenation were unpromising; therefore the cyano ketone was converted to the ethylene ketal which, without purification, was treated in turn with lithium aluminum hydride to reduce the cyano group, then with dilute acid to hydrolyze the ketal, and finally with hydrogen in the presence of platinum oxide in order to reduce the enamine VII ($\lambda_{\text{max}}^{\text{EtOH}}$ 6.03 μ). The crude basic material was treated with formaldehyde and formic acid⁴ to effect N-methylation, and the product, m.p. 168.5–170°, was shown to be the racemic form of the hydroxy compound VIII by virtue of the complete identity of the infrared and high temperature mass spectra with those of D-VIII derived from natural conessine.⁵ Oxidation of racemic VIII with chromium trioxide and perchloric acid in acetic acid afforded the corresponding 3-keto compound, m.p. 147–149°, having an infrared spectrum indistinguishable from that of naturally derived D-material.⁵ Bromination followed by dehydrobromination gave the racemic 3-keto- Δ^4 -unsaturated derivative which was transformed into the N,N-dimethylenamine and reduced with sodium borohydride and acetic acid.^{5b,6} The product melted at 127–128.5° and was shown to be racemic conessine by the complete identity of

(4) R. Tschesche and A. C. Roy, *Ber.*, **89**, 1288 (1956).

(5) Cf. (a) R. Pappo, U. S. Patent No. 2,913,455, Nov. 17, 1959 [*Chem. Abstr.*, **54**, 3527 (1960)]; (b) W. S. Johnson, V. J. Bauer and R. W. Franck, *Tetrahedron Letters*, No. 2, 72 (1961).

(6) Since our previous work (ref. 5b), we have found that reaction occurs only after acetic acid is added to the mixture of borohydride and enamine in dioxane. Since better yields are obtained after refluxing the acidified mixture (a treatment originally done in order to hydrolyze any unreacted enamine), we suspect that the reduction process may involve hydroboration followed by hydrolysis, as suggested by G. Stork and G. Birnbaum, *Tetrahedron Letters*, No. 10, 313 (1961).

the infrared and mass spectra with those of the natural product.⁷

Acknowledgment.—We are grateful to R. W. Franck for working out procedures for the conversion of VIII to the 3-keto- Δ^4 -compound in the natural series. We also wish to thank H. Budzikiewicz for performing the mass spectrographic analyses, and the U.S. Public Health Service and the National Science Foundation for providing support for this study.

(7) Satisfactory compositional analyses have been obtained for all substances for which melting points are recorded.

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NICKEL-NICKEL BOND IN NICKEL DIMETHYLGLYOXIME¹

Sir:

Godycki and Rundle² postulated that nickel-nickel bonding is a fundamental feature of the nickel dimethylglyoxime, $[\text{Ni}(\text{DMG})_2]$, crystal and that this feature offered an explanation of the great difference in the aqueous solubility of the nickel and copper dimethylglyoxime, $[\text{Cu}(\text{DMG})_2]$, complexes. From the heats of solution of $\text{Ni}(\text{DMG})_2$ and $\text{Cu}(\text{DMG})_2$ in *n*-heptane, Fleischer³ concluded that the crystal energy of the latter may be greater than that of the former by 2 to 3 kcal. and that if a nickel-nickel bond does exist in the crystal, it would have to be extremely weak.

TABLE I
THERMODYNAMIC QUANTITIES FOR THE SOLUBILITY OF $\text{Ni}(\text{DMG})_2$ AND $\text{Ni}(\text{EMG})_2$

Solvent	Complex	$-\log X_2$ at °C.		ΔH° , kcal.	ΔF° , kcal.	ΔS , ^b e. u.
		25	35			
<i>n</i> -Heptane	$\text{Ni}(\text{DMG})_2$	7.44 ^a	7.08 ^a	15.1	10.15	16.62
	$\text{Ni}(\text{EMG})_2$	6.74	5.62	5.8	9.19	-11.39
CCl_4	$\text{Ni}(\text{DMG})_2$	6.24	5.92	15.3	8.50	22.8
	$\text{Ni}(\text{EMG})_2$	4.10	4.03	4.0	5.59	-5.34

^a Values taken from Fleischer.³ ^b Calculated for 25°.

Frasson, Bardi and Bezzi⁴ have shown that in $\text{Cu}(\text{DMG})_2$ the copper is bonded to four nitrogen atoms and with an oxygen atom in a nearby molecule forming a dimer. Dyrssen and Hennichs⁵ in a very recent study of the solubilities of the nickel and copper complexes of dimethylglyoxime have concluded that the crystal energies must be about the same and that the large difference in water-solubility must be due to the greater tendency of the $\text{Cu}(\text{DMG})_2$ to become solvated, perhaps forming $\text{Cu}(\text{DMG})_2 \cdot \text{H}_2\text{O}$ in aqueous solution.

Frasson and Panattoni⁶ have shown that in nickel ethylmethylglyoxime, $[\text{Ni}(\text{EMG})_2]$, the packing system is completely different from that in $\text{Ni}(\text{DMG})_2$. In fact, the nickel-nickel direction is not perpendicular to the plane of the molecule

and the nickel-nickel distance (4.75 Å.) is so great that nickel-nickel bonding is not possible. Also the distance between the nickel and the closest oxygen of an overlying molecule is much too great (3.44 Å.) to involve coordination.

This suggests that a study of the heats of solution of $\text{Ni}(\text{DMG})_2$ and $\text{Ni}(\text{EMG})_2$ in non-coordinating solvents such as *n*-heptane and carbon tetrachloride would give a measure of the relative stabilities of these two crystals and, in fact, might give a good measure of the strength of the nickel-nickel bond in $\text{Ni}(\text{DMG})_2$.

Saturated solutions of the nickel(II)-*vic*-dioxime complexes in *n*-heptane and carbon tetrachloride were prepared at various temperatures. The solubility in *n*-heptane was so low that it was necessary to extract the nickel into an aqueous hydrochloric acid solution, adjust the pH to 6-7, add additional ethylmethylglyoxime, and concentrate the $\text{Ni}(\text{EMG})_2$ by reextraction into chloroform.⁷ The absorbancies were measured in the chloroform at 328 $m\mu$. The solubility of $\text{Ni}(\text{DMG})_2$ in carbon tetrachloride was determined by the extraction procedure outlined above. The absorbancies were measured in chloroform at 374 $m\mu$. The solubility of $\text{Ni}(\text{EMG})_2$ was determined directly by measuring the absorbancies in the carbon tetrachloride at 378 $m\mu$. Concentrations were obtained by comparison with calibration curves.

The heats of solution were calculated from the temperature dependence of the solubility. The standard state for the solute was taken as the hypo-

thetical mole fraction, X_2 , of one and 298°K. (Table I).

The ΔH° values in Table I show that the crystal energy of $\text{Ni}(\text{DMG})_2$ is about 9 to 11 kcal. more stable than that of $\text{Ni}(\text{EMG})_2$. In view of the X-ray crystal structure studies,^{1,4} and the observations that such properties of these complexes as the "abnormal" dichroism,⁸ solubility product,⁹ and intrinsic solubility¹⁰ correlate rather well with the metal-metal distances in these complexes, it seems reasonable to attribute a large part of this great difference in the crystal energies to the presence of nickel-nickel bonding.

It now appears that $\text{Ni}(\text{DMG})_2$ is less soluble in water than $\text{Ni}(\text{EMG})_2$ because of the increased stability arising from the nickel-nickel bonding in the crystalline state of the former complex, whereas $\text{Ni}(\text{DMG})_2$ is less soluble in water than

(1) Contribution No. 1117. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

(3) D. Fleischer, Ph.D. Thesis, University of Pittsburgh, 1959, University Microfilms 59-2396, Ann Arbor, Michigan.

(4) E. Frasson, R. Bardi, and S. Bezzi, *Acta Cryst.*, **12**, 201 (1959).

(5) D. Dyrssen and M. Hennichs, *Acta Chem. Scand.*, **15**, 47 (1961).

(6) E. Frasson and C. Panattoni, *Acta Cryst.*, **13**, 893 (1960).

(7) H. Christopherson and E. B. Sandell, *Anal. Chim. Acta*, **10**, 1 (1954).

(8) C. V. Banks and D. W. Barnum, *J. Am. Chem. Soc.*, **80**, 4767 (1958).

(9) C. V. Banks and D. W. Barnum, *ibid.*, **80**, 3579 (1958).

(10) C. V. Banks and S. Anderson, unpublished work.