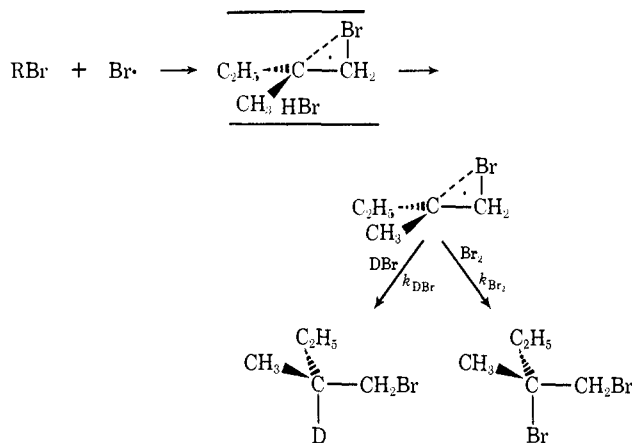


Scheme I



A second interesting aspect to this experiment is that it provides the hitherto elusive relative reactivities of bromine and hydrogen bromide.⁸ The amounts of dibromide and deuteriobromide produced in the experiments are approximately equal. Since the initial concentration ratios of the trapping agents, Br_2 and DBr , are $1/9$ to $1/14$, and the Br_2 is exhausted during the reaction, a maximum value of $k_{Br_2}/k_{DBr} \approx 9-14$ is indicated.^{9,10} Work in progress will refine this value. Other work in our laboratory has shown that k_{HBr} is approximately 50% greater than k_{DBr} .

Acknowledgment. The financial assistance of the Air Force Office of Scientific Research (Grant No. 1983) is acknowledged with gratitude.

(8) W. A. Thaler, "Methods in Free Radical Chemistry," Vol. 2, E. S. Huyser, Ed., Marcel Dekker, New York, N. Y., 1969, p 137.

(9) Hydrogen bromide (ca. 4 mmol) is generated during the photobromination. Its accumulation is not expected to significantly alter the estimated relative rate ratio since deuterium bromide is in large excess.

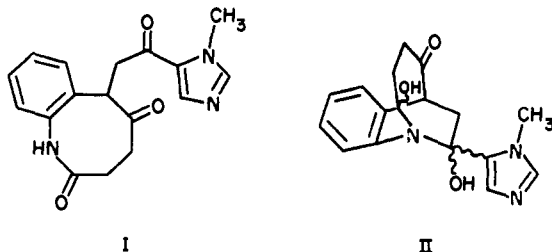
(10) A decrease in bromine concentration during the reaction places a lower limit on the k_{Br_2}/k_{DBr} ratio.

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Synthesis and Revised Structure of Dehydroisolongistrobine

Sir:

In 1969 Arndt, Eggers, and Jordaan reported the isolation of several alkaloids from *Macrorungia longistrobis*.¹ Dehydroisolongistrobine was assigned the structure I by these workers even though no absorption

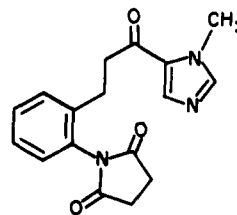


above 3000 cm^{-1} was apparent in its infrared spectrum. Furthermore, structure II was proposed to account for

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

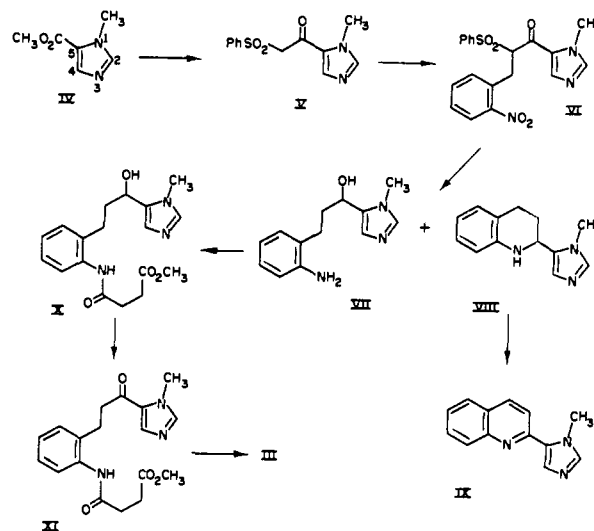
the spectral properties of isolongistrobine, for which carbonyl absorption was reported to lie at $1660-1680\text{ cm}^{-1}$. The ketonic carbonyl group of II would be expected to absorb at ca. 1710 cm^{-1} . The argument for the points of attachment of the succinic acid moiety in these structures rested primarily on rather unclear mass spectral labeling data.

We concluded that structure III was in agreement



III

with the data presented for dehydroisolongistrobine and undertook its synthesis. The imidazole ester IV,



readily available *via* Jones' excellent procedure,² reacted with the Grignard reagent derived from methyl phenyl sulfone³ in the procedure of Stetter and Hesse,⁴ to give the β -keto sulfone V, mp $169-170.5^\circ$ (EtOAc), in 88.8% yield.⁵ Compound V, when treated in tetrahydrofuran at 60° under argon with an equivalent amount of potassium *tert*-butoxide in *tert*-butyl alcohol followed by addition of an equivalent amount of *o*-nitrobenzyl bromide in tetrahydrofuran and stirring at 60° overnight, provided the phenylsulfonyl nitro ketone VI, crystallized from absolute ethanol, mp $131-131.5^\circ$, in 77.4% yield.⁶

Compound VI, when reduced with aluminum amal-

(2) R. G. Jones, *J. Amer. Chem. Soc.*, **71**, 644 (1949).

(3) "Organic Syntheses" Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 674.

(4) H. Stetter and R. Hesse, *Monatsh. Chem.*, 755 (1967).

(5) Physical data for V: ir (KBr) 1660 cm^{-1} ; nmr ($CDCl_3$) δ 3.90 (3 H, s), 4.57 (2 H, s), 7.5-8.1 (7 H, m) ppm; uv (MeOH) λ_{max} 265 nm (ϵ 15,400) shifted to 246 nm (ϵ 12,100) in acid. Anal. Calcd for $C_{12}H_{12}N_2O_3S$: C, 54.54; H, 4.58; N, 10.60; S, 12.11. Found: C, 54.41; H, 4.65; N, 10.49; S, 12.08.

(6) Physical data for VI: ir (KBr) 1660 and 1530 cm^{-1} ; nmr ($CDCl_3$ 100 MHz) δ 3.64 (1 H, d, $J = 8\text{ Hz}$), 3.65 (1 H, d, $J = 6\text{ Hz}$), 3.82 (3 H, s), 5.20 (1 H, d of d, $J = 8, 6\text{ Hz}$), 7.2-7.9 (11 H, m) ppm; uv (MeOH): λ_{max} 271 nm (ϵ 16,500) shifted to 251 nm (ϵ 15,400) in acid. Anal. Calcd for $C_{19}H_{17}N_3O_5S$: C, 57.14; H, 4.29; N, 10.52; S, 8.01. Found: C, 57.04; H, 4.38; N, 10.54; S, 8.08.

gam in aqueous tetrahydrofuran,⁷ gave a mixture of two compounds which were separated by preparative plate chromatography on silica gel (9:1 CH₃CN-CH₃OH eluent). The less mobile of the two products, obtained in 64% yield at 0° as an off-white foam,^{8,9} showed nmr behavior (CDCl₃) which implied structure VII: δ 2.12 (2 H, m), 2.65 (2 H, m), 3.50 (3 H, s), 4.50 (4 H, broad; collapses to 1 H, m, upon addition of D₂O), 6.5-7.2 (6 H, m) ppm. The more mobile compound, produced in 39% yield at 60°,⁸ exhibited nmr behavior (CDCl₃) which led to the assignment of structure VIII: δ 2.08 (2 H, m), 2.82 (2 H, m), 3.58 (3 H, s), 4.42 (2 H, m; collapses to 1 H, d of d, $J = 5, 7$ Hz, upon addition of D₂O), 6.4-7.3 (6 H, m) ppm. The tetrahydroquinoline structure of VIII was further substantiated by its conversion, upon treatment with 10% Pd-C and sulfur in refluxing xylene for 2 days,¹⁰ to isomacrorine (IX), in 57% yield. This sample exhibited mass spectral and ultraviolet behavior as reported,^{11,12} and melted at 105-107° (lit.¹² mp 110°). Thus, this work constitutes a new synthesis of isomacrorine.¹³

Amino alcohol VII proved to be the key to the synthesis of dehydroisolongistrobine, for in its production from VI, the carbonyl group had been rendered incapable of intramolecular cyclization to a dihydroquinoline system. Compound VII, admixed with 1 equiv of pyridine in methylene chloride, was treated at 0° with an equivalent amount of β -carbomethoxypropionyl chloride¹⁴ to produce, after plate chromatography on silica gel (9:1 CH₃CN-CH₃OH eluent), hydroxyamido ester X as an off-white foam in 63% yield.¹⁵ Upon oxidation of X with Cornforth's reagent (CrO₃ in aqueous pyridine)¹⁶ and plate chromatography on silica gel (9:1 CH₃CN-CH₃OH eluent), the beautifully crystalline ketone XI, mp 119-120.5° (CH₂Cl₂-hexane), was obtained in 43% yield.¹⁷

When XI was heated *in vacuo* above its melting point for 5 min, III was obtained in 83% yield as splendid white needles mp 130.5-131.5° (lit.¹ mp 131°, nmp 130-131.5°¹⁸) from methylene chloride-hexane.¹⁹

(7) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **86**, 1639 (1964).

(8) At 0°, the ratio of VII to VIII was greater than 2:1; at 60°, *ca.* 1:1.

(9) Exact mass measurement of parent peak of VII. Calcd for C₁₈H₁₇N₃O: 231.1372. Found: 231.1378.

(10) Cf. H. S. Blair, M. Crawford, J. M. Spence, and V. R. Supanekar, *J. Chem. Soc.*, 3313 (1960); M. Crawford and V. R. Supanekar, *ibid.*, 2380 (1964).

(11) V. P. Joynt, R. R. Arndt, A. Jordaan, K. Biemann, and J. L. Occolowitz, *J. Chem. Soc. B*, 980 (1966).

(12) R. R. Arndt, A. Jordaan, and V. P. Joynt, *J. Chem. Soc., Suppl.* **2**, 5969 (1964).

(13) Cf. A. Jordaan, V. P. Joynt, and R. R. Arndt, *J. Chem. Soc. B*, 3001 (1965).

(14) "Organic Syntheses" Collect. Vol III, Wiley, New York, N. Y., 1955, p 169.

(15) Physical data for X: ir (NaCl plate) 3300 (very broad), 1735, 1665, and 1530 cm⁻¹; mass spectrum (70 eV) m/e 111, 125, and 345 (parent).

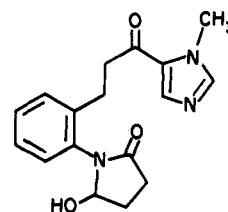
(16) R. H. Cornforth, J. W. Cornforth, and G. Popjak, *Tetrahedron*, **18**, 1351 (1962).

(17) Physical data for XI: ir (KBr) 3330, 1735, 1665, 1660, and 1530 cm⁻¹; nmr (CDCl₃, 100 MHz) δ 2.83 (4 H, s), 2.99 (2 H, t, $J = 6$ Hz), 3.26 (2 H, t, $J = 6$ Hz), 3.73 (3 H, s), 3.92 (3 H, s), 7.0-7.9 (6 H, m), and 8.96 (1 H, broad s) ppm; uv (MeOH) λ_{max} 254 nm (ϵ 16,100) shifted to 232 nm (ϵ 15,900) in acid; mass spectrum (70 eV) m/e 82, 83, 109, 110, 234, 256, and 343 (parent). Anal. Calcd for C₁₅H₂₁N₃O₄: C, 62.96; H, 6.16; N, 12.24. Found: C, 62.77; H, 6.22; N, 12.33.

(18) We are grateful to Dr. A. Jordaan for a sample of dehydroisolongistrobine from natural sources, which we recrystallized twice (mp 130.5-131.5°).

Uv and nmr spectra were in agreement with those reported¹ for dehydroisolongistrobine. The infrared spectra of natural and synthetic samples of the alkaloid were identical, showing bands at 1780 (weak), 1710 (very strong),²⁰ and 1665 (strong) cm⁻¹. It should be noted that only the 1710-cm⁻¹ band was reported by Arndt, *et al.*¹ In addition, mass spectra of natural and synthetic samples of dehydroisolongistrobine run under identical conditions were the same. Prominent peaks were observed at m/e 311 (parent), 110, 109, and 82.

On the basis of this work, structure III is firmly established for dehydroisolongistrobine, in preference to I. Furthermore, structure XII, rather than the previously



XII

proposed structure II, is strongly indicated for isolongistrobine, on the basis of the now-substantiated 5-[β -(*o*-anilino)propionyl]-1-methylimidazole skeleton and the spectral and chemical data reported by the original workers.

Further work on these alkaloids is in progress in our laboratories.

Acknowledgments. One of us (M. A. W.) thanks the NSF for a predoctoral fellowship (1969-1971). Thanks are also due to W. J. Pegg and G. W. Busby III for determination of mass spectra. Elemental analyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark.

(19) Anal. Calcd for C₁₇H₁₇N₃O₃: C, 65.58; H, 5.50; N, 13.50. Found: C, 65.48; H, 5.47; N, 13.37.

(20) The 1780-1710-cm⁻¹ doublet is characteristic of *N*-arylsuccinimides: K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 47; M. A. Wuonola, unpublished observations.

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A New Synthesis of Internally Substituted Alkyl Silanes

Sir:

Previous methods for preparing internally substituted alkyl silanes include the coupling of branched organometallics with the appropriate silicon compound,¹ as well as peroxide² and base-catalyzed³ addition of $\equiv\text{SiH}$ to internal olefins. The methods are tedious, some requiring long reaction times, and generally do not produce the alkyl silanes in good yield.

Hydrosilylation of olefins with trichlorosilane, catalyzed by transition metals on various supports or

(1) For typical examples, see J. W. Jenkins and H. W. Post, *J. Org. Chem.*, **15**, 552 (1950).

(2) C. A. Burkhard and R. H. Kriebel, *J. Amer. Chem. Soc.*, **69**, 2687 (1947); J. C. Saam and J. L. Speier, *ibid.*, **80**, 4104 (1958).

(3) R. A. Pike, *J. Org. Chem.*, **27**, 2186 (1962).