Br RBr + Br. C.H. ----ĊH. CH<sub>a</sub> HBr C<sub>0</sub>H<sub>2</sub> CH.  $C_2H_5$  $CH_{34}$ CH.Br  $CH_2Br$ 

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<sub>2</sub> and DBr, are 1/9 to 1/14, and the Br<sub>2</sub> is exhausted during the reaction, a maximum value of  $k_{\rm Br_2}/k_{\rm DBr} \approx 9-14$  is indicated.<sup>9,10</sup> Work in progress will refine this value. Other work in our laboratory has shown that  $k_{HBr}$  is approximately 50% greater than  $k_{\text{DBr}}$ .

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 photo-

bromination. 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  $k_{\rm Br_2}/k_{\rm DBr}$  ratio.

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## Synthesis and Revised Structure of **Dehvdroisolongistrobine**

Sir

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



above 3000 cm<sup>-1</sup> 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).

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

We concluded that structure III was in agreement



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



readily available via Jones' excellent procedure,<sup>2</sup> reacted with the Grignard reagent derived from methyl phenyl sulfone<sup>3</sup> in the procedure of Stetter and Hesse,<sup>4</sup> to give the  $\beta$ -keto sulfone V, mp 169–170.5° (EtOAc), in 88.8% yield.<sup>5</sup> 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°, 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)

(4) H. Steller and R. Hesse, *Monatsh. Chem.*, 155 (1907). (5) Physical data for V: ir (KBr) 1660 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>)  $\delta$  3.90 (3 H, s), 4.57 (2 H, s), 7.5–8.1 (7 H, m) ppm; uv (MeOH)  $\lambda_{max}$  265 nm ( $\epsilon$  15,400) shifted to 246 nm ( $\epsilon$  12,100) in acid. Anal. Calcd for C12-H12N2O3S: 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<sup>-1</sup>; nmr (CDCl<sub>3</sub> (a) Fuysical data for V1: If (NBF) food and F30 cm<sup>-2</sup>; him (CDC)a 100 MHz)  $\delta$  3.64 (1 H, d, J = 8 Hz), 3.65 (1 H, d, J = 6 Hz), 3.82 (3 H, s), 5.20 (1 H, d of d, J = 8, 6 Hz), 7.2–7.9 (11 H, m) ppm; uv (MeOH):  $\lambda_{max}$  271 nm ( $\epsilon$  16,500) shifted to 251 nm ( $\epsilon$  15,400) in acid. Anal. Calcd for C<sub>19</sub>H<sub>17</sub>N<sub>8</sub>O<sub>5</sub>S: 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,<sup>7</sup> gave a mixture of two compounds which were separated by preparative plate chromatography on silica gel (9:1 CH<sub>3</sub>CN-CH<sub>3</sub>OH eluent). The less mobile of the two products, obtained in 64% yield at 0° as an off-white foam,<sup>8,9</sup> showed nmr behavior (CDCl<sub>3</sub>) 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  $D_2O$ ), 6.5-7.2 (6 H, m) ppm. The more mobile compound, produced in 39% yield at 60°,8 exhibited nmr behavior  $(CDCl_3)$  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  $D_2O$ ), 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,<sup>10</sup> to isomacrorine (IX), in 57% yield. This sample exhibited mass spectral and ultraviolet behavior as reported,<sup>11,12</sup> and melted at 105-107° (lit.<sup>12</sup> 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  $0^{\circ}$  with an equivalent amount of  $\beta$ -carbomethoxypropionyl chloride14 to produce, after plate chromatography on silica gel (9:1 CH<sub>3</sub>CN-CH<sub>3</sub>OH eluent), hydroxyamido ester X as an off-white foam in 63% yield.<sup>15</sup> Upon oxidation of X with Cornforth's reagent (CrO<sub>3</sub> in aqueous pyridine)<sup>16</sup> and plate chromatography on silica gel (9:1 CH<sub>3</sub>CN-CH<sub>3</sub>OH eluent), the beautifully crystalline ketone XI, mp 119-120.5° (CH<sub>2</sub>Cl<sub>2</sub>-hexane), was obtained in 43% yield.<sup>17</sup>

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.<sup>1</sup> 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  $0^{\circ}$ , the ratio of VII to VIII was greater than 2:1; at  $60^{\circ}$ , ca. 1:1.

(9) Exact mass measurement of parent peak of VII. Calcd for  $C_{13}$ -H11N3O: 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<sup>-1</sup>; 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<sup>-1</sup>; nmr (CDCl<sub>3</sub>, 100 MHz)  $\delta$  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)  $\lambda_{max}$  254 nm ( $\epsilon$  16,100) shifted to 232 nm ( $\epsilon$  15,900) in acid; mass spectrum (70 eV) m/e 82, 83, 109, 110, 234, 256, and 343 (parent). *Anal.* Calcd for C<sub>15</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>: 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 reported<sup>1</sup> for dehydroisolongistrobine. The infrared spectra of natural and synthetic samples of the alkaloid were identical, showing bands at 1780 (weak), 1710 (very strong),<sup>20</sup> and 1665 (strong)  $cm^{-1}$ . It should be noted that only the  $1710\text{-cm}^{-1}$  band was reported by Arndt, et al.<sup>1</sup> 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



proposed structure II, is strongly indicated for isolongistrobine, on the basis of the now-substantiated 5-[ $\beta$ -(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.

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

(19) Anal. Calculation of Antitactic C, 60000, 14, 6100, 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,<sup>1</sup> as well as peroxide<sup>2</sup> and base-catalyzed<sup>3</sup> addition of  $\equiv$ 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

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

<sup>(2)</sup> C. A. Burkhard and R. H. Krieble, J. Amer. Chem. Soc., 69, 2687 (1947); J. C. Saam and J. L. Speier, ibid., 80, 4104 (1958).

<sup>(3)</sup> R. A. Pike, J. Org. Chem., 27, 2186 (1962).