the same manner as was VI above, light-yellow prisms from methanol, m. p. 283–284°, yield 55%. *Anal.* Calcd. for $C_{15}H_{10}N_2$: C, 82.56; H, 4.59; N, 12.83. Found: C, 82.21, 82.14; H, 5.98, 5.89; N, 12.57. In this case the ring closure yielded pure (V) directly so that no dehydrogenation was necessary. The isomeric 11H-pyrido[3,4-a]carbazole (IV)[1] melts at 280–282° but when it was mixed with (V) there was a thirty-degree depression of melting point.

10H-Pyrido[3,4-b]carbazole (I).—This was prepared from N-formyl-3-β-aminoethylcarbazole (N-formyl-IX) in the same manner as was VI above, light-yellow needles from methanol or acetone, m. p. 270–271°, yield 12%. *Anal.* Calcd. for $C_{15}H_{10}N_2$: C, 82.56; H, 4.59; N, 12.83. Found: C, 83.00, 82.92; H, 4.50, 4.49; N, 12.57. The pyridocarbazole (II)[1] obtained from 7-hydrazinoisoquinoline melts at 249–250°.

Summary

Three new pyridocarbazoles, namely, 6H-pyrido(4,3-b)-, 10H-pyrido(3,4-b)- and 7H-pyrido-[3,4,-c]carbazole have been synthesized by the ring closure of the N-formyl derivatives of 2-, 3- and 4-β-aminoethylcarbazole, respectively.

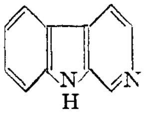
ONTARIO, CANADA RECEIVED APRIL 15, 1950

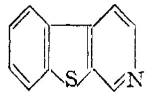
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

Sulfur Analogs of β-Carbolines

BY WERNER HERZ

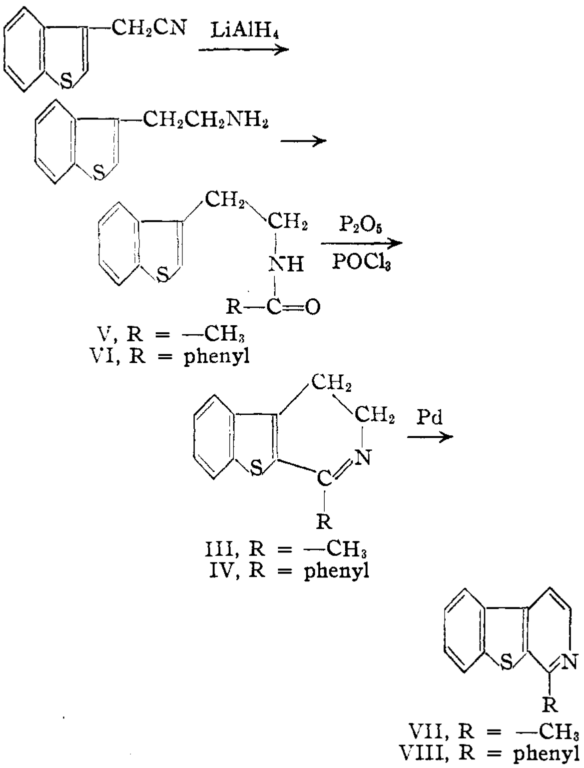
The presence of the β-carboline nucleus in a number of alkaloids, particularly those of *Peganum harmala* and yohimbé bark, has led to the development of several methods for the synthesis of β-carbolines.[1] The isosteric relationship between -NH- and sulfur groups demonstrated, for example, in the amino acid series[2] suggested the application of these methods to the synthesis of compounds of possible physiological interest in which the indole moiety of β-carboline (I) is replaced by a thianaphthene nucleus (II).


I


II

In this communication the preparation of two such compounds, 1-methyl- (III) and 1-phenylthianaphtheno(2,3-*C*)-pyridine (IV) is reported. III is the sulfur analog of the alkaloid harman and suitable variation of the starting materials might be expected to yield analogs of other indole alkaloids.

The accompanying diagram illustrates the method of synthesis which represents an adaptation of the scheme employed by Späth and Lederer[3] in the synthesis of harman and harmaline. Lithium aluminum hydride reduction[4] of 3-cyanomethylthianaphthene[5] gave β-3-thianaphthylethylamine in 30–35% yield. The acetyl (V) and benzoyl (VI) derivatives of this base were cyclized smoothly *via* the Bischler–Napieralski reaction,[6] using the method recommended by Whaley and Hartung.[7] The resulting 1-substituted 3,4-dihydrothianaphtheno-(2,3-*C*)-pyridines were converted to the desired aromatic compounds by dehydrogenation with palladium black.[3]



V, R = —CH_3
VI, R = phenyl

III, R = —CH_3
IV, R = phenyl

VII, R = —CH_3
VIII, R = phenyl

Fig. 1.

For comparison with reported spectra of β-carbolines[8] the ultraviolet absorption curves of compounds III, IV, VII and VIII are reproduced in Figs. 2 and 3. As expected, the increase in conjugation brought about by dehydrogenation results in displacement of the curves toward

---

[1] Henry, "The Plant Alkaloids," J. A. Churchill Ltd., London, 4th edition, 1949, p. 485, *et seq.*

[2] Herz, Dittmer and Cristol, THIS JOURNAL, **70**, 504 (1948).

[3] Späth and Lederer, *Ber.*, **63**, 120 (1930).

[4] Nystrom and Brown, THIS JOURNAL, **70**, 3738 (1948).

[5] Avakian, Moss and Martin, *ibid.*, **70**, 3075 (1948); Blicke and Sheets, *ibid.*, **70**, 3768 (1948).

[6] Bischler and Napieralski, *Ber.*, **26**, 1903 (1893).

[7] Whaley and Hartung, *J. Org. Chem.*, **14**, 650 (1949).

[8] Kharasch, Stanger, Bloodgood and Legault, *Science*, **83**, 36 (1936); Pruckner and Witkop, *Ann.*, **554**, 127 (1944); Raymond-Hamet, *Compt. rend.*, **221**, 387 (1945).

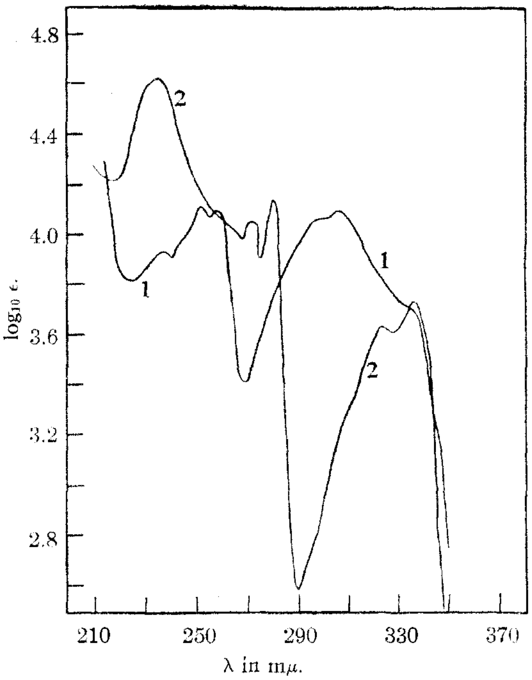


Fig. 2.—Ultraviolet absorption spectra in 95% ethanol: 1, compound III; 2, compound VII.

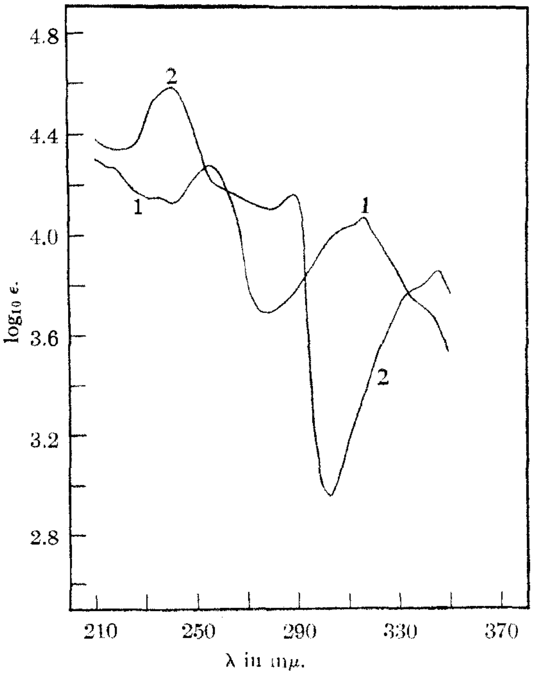


Fig. 3.—Ultraviolet absorption spectra in 95% ethanol: 1, compound IV; 2, compound VIII.

longer wave lengths, with the band near 310 mμ being considerably reduced in intensity. This displacement also seems to have caused the appearance of another high intensity band, formerly beyond instrument range, at shorter wave lengths.

Acknowledgment.—This work was supported in part by a grant from the Research Council of the Florida State University. The thianaphthene required was donated by the Jefferson Chemical Company, New York, N. Y. The author is indebted to Dr. Wilson M. Whaley for a number of discussions which led to the present study.

Experimental

β-3-Thianaphthylethylamine.—Fourteen grams of 3-cyanomethylthianaphthene purified by recrystallization from benzene–petroleum ether was dissolved in 300 ml. of absolute ether and added dropwise to a solution of 4 g. of lithium aluminum hydride in 300 ml. of anhydrous ether. Stirring was continued for fifteen minutes after addition was complete; then water was added cautiously to decompose the reagent. The mixture was treated with 200 ml. of 25% sodium potassium tartrate solution; the ether layer was separated and the aqueous layer was extracted with two 100-ml. portions of ether.

The combined ether layers were extracted with three 50-ml. portions of 5% hydrochloric acid. Considerable cloudiness, possibly due to the formation of an insoluble hydrochloride, was noted in the acid extract. The acid solution was made strongly basic with sodium hydroxide solution and the red oil which separated was extracted with three 100-ml. portions of ether. The combined ether extracts were washed with water and dried over sodium sulfate. Fractionation at reduced pressure yielded 4.5 g. (32%) of a basic liquid, b. p. 125° at 1 mm.

Anal.[9] Calcd. for $C_{10}H_{11}NS$: N, 7.90; S, 18.08. Found: N, 7.89; S, 18.12.

The amine was protected from the atmosphere or used immediately since it rapidly absorbed carbon dioxide. The picrate, prepared in the usual manner,[10] melted at 176.5–177°(dec.). Analysis showed that it contained two molecules of picric acid.

Anal. Calcd. for $C_{22}H_{17}N_7O_{14}S$: N, 15.43. Found: N, 15.11.

Removal of solvent from the ether layers freed from amine by extraction with hydrochloric acid yielded variable amounts of a neutral substance, b. p. 135° at 3–4 mm., presumably 1-(3-thianaphthyl)-2-hydroxyethane. Tests established the presence of a primary hydroxyl group. The alcohol did not yield a picrate.

Anal. Calcd. for $C_{10}H_{10}OS$: C, 67.36; H, 5.64; S, 17.98. Found: C, 67.44; H, 5.62; S, 17.67.

Its phenylurethan melted at 105–108°.

Anal. Calcd. for $C_{17}H_{15}NO_2S$: C, 68.65; H, 5.08; N, 4.71. Found: C, 68.17; H, 4.85; N, 4.53.

N-Acetyl-β-3-thianaphthylethylamine.—One and four-tenths grams of the amine was treated with 18 ml. of 20% sodium hydroxide solution and then portionwise with 5 ml. of acetic anhydride, accompanied by shaking and cooling. The product gradually solidified on standing and chilling. It was filtered and freed from water by boiling with benzene. Dilution with petroleum ether and cooling yielded 1.4 g. of crude product. Another recrystallization from benzene–ligroin gave shiny white needles, m. p. 68°.

Anal. Calcd. for $C_{12}H_{13}NOS$: C, 65.71; H, 5.97; N, 6.39. Found: C, 65.10; H, 6.17; N, 6.28.

N-Benzoyl-β-3-thianaphthylethylamine.—To a mixture of 0.4 g. of the amine and 0.5 ml. of benzoyl chloride was added gradually with shaking and cooling 3.5 ml. of 20% sodium hydroxide solution. An oil separated and solidified on keeping in the refrigerator overnight. It was

---

(9) Analyses by Clark Microanalytical Laboratory, Urbana, Illinois.

(10) Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1948, third edition, p. 180.

taken up in 15 ml. of ethanol, treated with charcoal, filtered, diluted with water until barely cloudy at 40°, reheated and allowed to cool. The yield of white needles was 0.45 g. Another crystallization from ethanol–water gave material melting at 93°.

Anal. Calcd. for $C_{17}H_{15}NOS$: C, 72.56; H, 5.37; N, 4.98. Found: C, 72.73; H, 5.49; N, 5.04.

1-**Methyl-3,4-dihydrothianaphtheno(2,3-*C*)pyridine.**—One and two-tenths grams of V was refluxed with 2.4 g. of phosphorus pentoxide and 2.4 g. of phosphorus oxychloride in anhydrous xylene for one hour. The cold mixture was decomposed with ice. The aqueous layer was separated, washed with benzene, made basic with concentrated sodium hydroxide solution and extracted with three 25-ml. portions of benzene. The combined benzene extracts were dried over sodium sulfate and concentrated at reduced pressure. The residual red sirup solidified on stirring with a little petroleum ether and was taken up in 100 ml. of that solvent. The solution was decolorized with charcoal, filtered and concentrated to 15 ml. on chilling; 0.6 g. of white product separated. Another recrystallization gave crystals melting at 73.5°, soluble in dilute acid with yellow color, insoluble in base.

Anal. Calcd. for $C_{12}H_{11}NS$: C, 71.59; H, 5.51; N, 6.96. Found: C, 71.66; H, 5.54; N, 6.86.

Addition of picric acid solution to a solution of the product in ethanol immediately precipitated the picrate. After recrystallization from a large volume of ethanol it decomposed at 227–228° when the capillary was immersed at a temperature of 220°.

Anal. Calcd. for $C_{18}H_{14}N_4O_7S$: N, 13.02. Found: N, 12.61.

1-**Phenyl-3,4-dihydrothianaphtheno(2,3-*C*)pyridine.**—Cyclization of 1 g. of the benzoyl derivative in the same manner yielded 0.65 g. of crude product. The white needles melted at 64° after recrystallization from petroleum ether.

Anal. Calcd. for $C_{17}H_{13}NS$: C, 77.54; H, 4.98; N, 5.32. Found: C, 77.70; H, 4.79; N, 5.35.

The picrate decomposed at 196–198°.

Anal. Calcd. for $C_{23}H_{16}N_4O_7S$: N, 11.37. Found: N, 1.02.

1-**Methylthianaphtheno(2,3-*C*)pyridine.**—One gram of the dihydro compound was heated with 1 g. of palladium black in a small test-tube at 190–200° for thirty minutes. The cold mixture was extracted thoroughly with acetone, the acetone was treated with charcoal, filtered and evaporated to dryness at reduced pressure. The residue was taken up in 50 ml. of low-boiling petroleum ether, decolorized with charcoal and concentrated to 5 ml. On chilling, 0.4 g. of white crystals, m. p. 109°, was obtained. Sublimation at 100° (0.5 mm.) yielded a product melting at 110°.

Anal. Calcd. for $C_{12}H_9NS$: C, 72.32; H, 4.56; N, 7.03. Found: C, 72.65; H, 4.51; N, 6.82.

The picrate, recrystallized from a large volume of ethanol, decomposed at 262°.

Anal. Calcd. for $C_{18}H_{12}N_4O_7S$: N, 13.08. Found: N, 12.89.

1-**Phenylthianaphtheno(2,3-*C*)pyridine.**—Dehydrogenation of 1.35 g. of VIII was carried out in the manner described above. The acetone extract was treated with charcoal and concentrated to 15 ml. On cooling 0.52 g. of slightly-colored crystals separated. Concentration of the filtrate to 5 ml. and addition of a few drops of water yielded an additional 0.21 g. The product melted at 152.5° after recrystallization from acetone.

Anal. Calcd. for $C_{17}H_{11}NS$: C, 78.09; H, 4.24; N, 5.37. Found: C, 78.41; H, 4.33; N, 5.41.

The picrate was recrystallized from ethanol, m. p. 208–209° (dec.).

Anal. Calcd. for $C_{23}H_{14}N_4O_7S$: N, 11.38. Found: N, 11.73.

Summary

The synthesis of 1-methyl- and 1-phenylthianaphtheno(2,3-*C*)pyridine is reported. The former is the sulfur analog of harman.

TALLAHASSEE, FLORIDA RECEIVED APRIL 28, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY AND NUTRITION, TEXAS AGRICULTURAL EXPERIMENT STATION, TEXAS AGRICULTURAL AND MECHANICAL COLLEGE SYSTEM, COLLEGE STATION]

Separation and Stabilization of Fatty Acids by Urea Complexes[1]

BY HERMAN SCHLENK AND RALPH T. HOLMAN

After Bengen[2] had discovered the phenomenon of urea complex formation with normal aliphatic compounds in 1940, further research was carried on in the Oppau laboratory of the former I. G. Farbenindustrie A. G. The results of their detailed investigations of the structure and formation of the complexes, steric limitations, and energy relationships appeared in 1949.[3,4] Since the release of the Technical Oil Mission reports,[5] considerable interest has been aroused in this country. Attention was called to urea complexes by the group at Standard Oil Laboratories in 1949.[6,7] Recently the principal results of Schlenk were confirmed[8,9] and separations based upon urea complexes have been achieved in pilot plant scale.[10]

The earlier reports indicated that normal compounds could be separated from branched compounds. Such separations are based upon differences in molecular shape, and it seemed likely that unsaturation might cause sufficient change in the shape of normal compounds to

---

[1] Supported in part by a contract between the Office of Naval Research and the Texas A. and M. Research Foundation. Presented at the 117th A. C. S. meeting, Houston, Texas, March, 1950.

(2) F. Bengen, German patent application (March 18, 1940).

(3) F. Bengen and W. Schlenk, Jr., *Experientia*, **5**, 200 (1949).

(4) W. Schlenk, Jr., *Annalen*, **565**, 204 (1949).

(5) Technical Oil Mission Reel 6, frames 263–270 in German, Reel 143, pages 185–189 in English (Copies and translations of ref. 2).

(6) W. J. Zimmerschied, R. A. Dinerstein, A. W. Weitkamp and R. F. Marschner, THIS JOURNAL, **71**, 2947 (1949).

(7) W. J. Zimmerschied, R. A. Dinerstein, A. W. Weitkamp and R. Marschner, *Ind. Eng. Chem.*, **42**, 1300 (1950).

(8) O. Redlich, C. M. Gable, A. K. Dunlop and R. W. Millar, THIS JOURNAL, **72**, 4153 (1950).

(9) H. A. Newey, E. C. Shokal, A. C. Mueller, T. F. Bradley and L. C. Fetterly, Abst. 117th ACS Meeting, Detroit, April 1950, p. 5-M.

(10) W. A. Bailey, Jr., R. A. Bannerot, L. C. Fetterly and A. G. Smith, Abst. 117th ACS Meeting, Houston, March 1950, p. 12-N.