TABLE I

	[a]Product of Clemmensen reduction of 1-methyl-2-ethyl-1-azacycloheptan-3-one	Product of Wolff–Kishner reduction of 1-methyl-2-ethyl-1-azacycloheptan-3-one	[a]1-Methyl-2-*n*-propylpiperidine prepared according to Lukes and Smetackova[3]	Reported for 1-methyl-2-*n*-propylpiperidine (*dl*-N-methylconiine)
B. p., °C. (mm.)	163–165 (759)	174–175 (755)	167–168 (757)	175.5[3]; 174[4]
$n^{20}D$	1.4491	1.4472	1.4500	1.4522[3]
Hydrochloride, m. p., °C.	168–168.5	.....	169–169.5	165–167[3]; 165–166[4]
Picrate, m. p., °C.	108.5–109	166.5–167.5	109.3–109.8	112–114[3]; 110.5[4]
Chloroaurate, m. p., °C.	88.5–90.5	.....	88.5–89.5	90[3]; 91[4]
Chloroplatinate, m. p., °C.	194.5–196	.....	196–197	197[3]; 194[4]

[a] The melting points of mixtures of the corresponding derivatives showed no depression.

tion of a saturated aqueous solution of potassium hydroxide. The white slurry thus obtained was subjected to steam distillation until the distillate was no longer basic to litmus paper. The organic layer was separated and the aqueous layer was extracted with four 40-ml. portions of ether. The organic layer and extracts were combined and dried and the ether was removed. Distillation of the residue yielded 1.49 g. (50%) of basic material, b. p. 61–63° (13 mm.); 163–165° (759 mm.); $n^{20}D$ 1.4491.

Anal. Calcd. for $C_9H_{19}N$: C, 76.53; H, 13.56; N, 9.92. Found: C, 76.13; H, 13.68; N, 9.99.

The **picrate** was prepared in ether and recrystallized from dilute ethanol as long light-yellow needles, m. p. 108.5–109°.

Anal. Calcd. for $C_{15}H_{22}N_4O_7$: C, 48.64; H, 5.99; N, 15.13. Found: C, 48.75; H, 6.19; N, 15.29.

The **chloroplatinate** was prepared by adding an aqueous solution of the amine hydrochloride to an aqueous solution of platinum chloride and was recrystallized from dilute ethanol as bright orange prisms, m. p. 194.5–196°.

The **chloroaurate** was prepared similarly, yielding greenish yellow needles, m. p. 88.5–90.5°.

The **hydrochloride** was formed in ether and deposited white needles when recrystallized from acetone, m. p. 168–168.5°.

1-Methyl-2-pyridone.—This compound was prepared by the method of Prill and McElvain[7] in a yield of 83%, b. p. 134–136° (18 mm.); $n^{20}D$ 1.5679.

(7) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 419.

1-Methyl-2-piperidone.—Fifty-five and four-tenths grams of 1-methyl-2-pyridone was dissolved in 200 ml. of glacial acetic acid and the solution was hydrogenated at 2–3.5 atmospheres and 26° in the presence of 0.5 g. of platinum oxide catalyst. Slightly more than the theoretical amount of hydrogen was taken up in seventeen hours. The catalyst was removed by filtration and the solvent was removed by evaporation under reduced pressure. Distillation of the residue yielded 50.36 g. (87.5%) of product, b. p. 102–106° (15 mm.); $n^{20}D$ 1.4711.

1-Methyl-2-*n*-propylpiperidine.—The method of Lukes and Smetackova[3] was used in the preparation of this material from 1-methyl-2-piperidone in a yield of 9.7%; b. p. 167–168° (757 mm.); $n^{20}D$ 1.4500. The derivatives of 1-methyl-2-*n*-propylpiperidine were made in the same manner as were the derivatives of the product of the Clemmensen reduction of 1-methyl-2-ethyl-1-azacycloheptan-3-one. They are listed in Table I.

Summary

It has been established that Clemmensen reduction converts 1-methyl-2-ethyl-1-azacycloheptan-3-one to the rearrangement product, 1-methyl-2-*n*-propylpiperidine (*dl*-N-methylconiine). The process involves ring contraction from seven to six members.

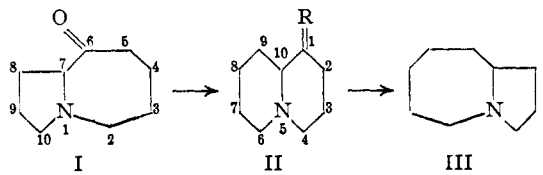
URBANA, ILLINOIS RECEIVED FEBRUARY 23, 1949

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Rearrangement of α-Aminoketones During Clemmensen Reduction. IV. Contraction of a Seven-membered Ring in the Bicyclic Series

BY NELSON J. LEONARD AND WILLIAM C. WILDMAN[1]

In a previous communication[2] the authors showed that the rearrangement of 1-ketoquinolizidine (IIb) to 1-azabicyclo[5.3.0]decane (III), under conditions of the Clemmensen reduction, proceeds with contraction of the ketonic ring and expansion of the non-ketonic ring, and a mechanism was suggested for this transformation. Now we have shown that the 1-azabicyclo[5.3.0]decane ring system can be transformed to the quinolizidine ring system by the same process. The Clemmensen reduction of 6-keto-1-azabicyclo[5.3.0]-decane (I) produced the rearrangement product, quinolizidine (1-azabicyclo[4.4.0]decane) (IIa).



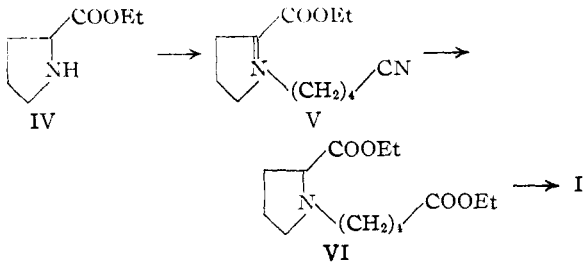
I II III

(a, R = H_2; b, R = O)

The synthesis of I was accomplished by the Dieckmann ring closure of ethyl δ-N-(2-carbethoxypyrrolidyl)-valerate (VI) without isolation of the intermediate ketoester. The diester VI was obtained by ethanolysis of δ-N-(2-carbethoxypyrrolidyl)-valeronitrile (V), product of the condensa-

(1) Present address: Department of Chemistry, University of Wisconsin, Madison, Wisconsin.

(2) Leonard and Wildman, THIS JOURNAL, 71, 3098 (1949).



tion of ethylproline (IV) with δ-bromovaleronitrile.

The normal carbonyl reduction product of 6-keto-1-azabicyclo[5.3.0]decane (I) was obtained by the Wolff–Kishner method and was identified as 1-azabicyclo[5.3.0]decane (III). The Clemmensen reduction product of I was the result of rearrangement and was identified as quinolizidine (IIa). Authentic samples of IIa and III were available for direct comparison with these reduction products. The conversion of I to IIa under Clemmensen conditions thus proceeds with the contraction of the seven-membered ketonic ring and expansion of the five-membered non-ketonic ring. The contraction of a seven-membered ring has also been observed in the Clemmensen reduction of a monocyclic α-aminoketone.[3]

Experimental[4]

δ-Bromovaleronitrile.—A solution of 783 g. (3.62 moles) of tetramethylene bromide, 47.0 g. (0.724 mole) of potassium cyanide, and 600 ml. of methanol was heated under reflux for twenty-four hours. The methanol was removed by distillation. The residue was washed twice with water, dried over anhydrous magnesium sulfate, and fractionally distilled. After removal of the excess tetramethylene bromide, the δ-bromovaleronitrile was obtained as a colorless liquid, b. p. 114–115° (12 mm.); $n^{21.5}D$ 1.4795; yield, 50.0 g. (42.7%).

Ethyl Proline.—The ester was prepared by the procedure of Kapfhammer and Matthes[5] except that the ethanolic solution of proline ethyl ester hydrochloride was concentrated, redissolved in 100 ml. of absolute ethanol, and resaturated with hydrogen chloride. The solution then was concentrated under reduced pressure and treated with ether and anhydrous ammonia as described.[5] This modification resulted in yields as high as 80%.

δ-N-(2-Carbethoxypyrrolidyl)-valeronitrile.—A mixture of 20.0 g. (0.14 mole) of proline ethyl ester, 22.7 g. (0.14 mole) of δ-bromovaleronitrile, and 22.1 g. (0.16 mole) of anhydrous potassium carbonate was heated at 100° for six hours. The reaction mixture was cooled, and water was added to dissolve the inorganic salts. The cyano ester was separated, and the aqueous layer was extracted with ether. The cyano ester and ether extract were combined, washed with water, dried over anhydrous magnesium sulfate, and distilled. The nitrile was obtained as a colorless liquid, b. p. 102–103° (0.5 mm.); $n^{20}D$ 1.4630; d^{20}_4 1.0333; yield, 23.1 g. (74%).

Anal. Calcd. for $C_{12}H_{20}N_2O_2$: C, 64.28; H, 8.99; N, 12.50; *MR*D 60.75. Found: C, 64.38; H, 9.00; N, 12.65; *MR*D 59.76.

Ethyl δ-N-(2-Carbethoxypyrrolidyl)-valerate.—A solution of 22.6 g. (0.105 mole) of δ-N-(2-carbethoxypyrrolidyl)-valeronitrile in 125 ml. of absolute ethanol, cooled in ice and protected from moisture, was saturated with dry hydrogen chloride. The solution was allowed to stand at room temperature for two hours and then was boiled under reflux for two hours. The ammonium chloride was removed by filtration, and the ethanolic solution of the diester was concentrated under reduced pressure. The residue was dissolved in 50 ml. of water, cooled to 0°, and made alkaline with 15% potassium hydroxide solution. The organic layer was separated, and the aqueous solution was extracted with ether. The diester and the ether extract were combined, dried over anhydrous magnesium sulfate, and distilled. The product was obtained as a colorless liquid, b. p. 110–113° (0.3 mm.); $n^{20}D$ 1.4563; d^{20}_4 1.0413; yield, 16.2 g. (60%).

Anal. Calcd. for $C_{14}H_{25}NO_4$: C, 61.97; H, 9.29; N, 5.16; *MR*D 71.90. Found: C, 62.01; H, 9.31; N, 5.37; *MR*D 70.88.

Dieckmann Ring Closure of Ethyl δ-N-(2-Carbethoxypyrrolidyl)-valerate. 6-Keto-1-azabicyclo[5.3.0]decane.—Sodium ethoxide[6] was prepared from 1.36 g. (0.058 mole) of sodium in a 500-ml. three-necked flask fitted with a mercury-sealed stirrer, a dropping funnel, and a Vigreux fractionating column. A thermometer was inserted in the head of the column, and the side-arm was set for downward distillation. A solution of 15.9 g. (0.058 mole) of the diester in 200 ml. of dry xylene was added to the sodium ethoxide at 25°. The solution was caused to reflux gently in the Vigreux column. The bath temperature was raised periodically, and the ethanol-xylene mixture was distilled until the boiling point of pure xylene was attained. At the end of eighteen hours no ethanol was found in the distillate. The solution was cooled and extracted three times with water. The xylene layer then was extracted with dilute hydrochloric acid until ferric chloride reagent gave a negative test for the enol function. The aqueous extracts were combined and refluxed three hours with 50 ml. of concentrated hydrochloric acid. The solution was concentrated *in vacuo*, cooled to 0°, and made basic with 30% potassium hydroxide solution. The amino ketone was extracted with ether and dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure through a ten-inch column packed with glass helices. The 6-keto-1-azabicyclo[5.3.0]decane was obtained as a colorless liquid, b. p. 105–106° (12 mm.); yield, 2.43 g. (27.4%). The amino ketone darkened rapidly on standing. To prevent further decomposition, it was dissolved in absolute ether, and the solution was saturated with dry hydrogen chloride.

6-Keto-1-azabicyclo[5.3.0]decane Picrate.—Prepared in ether and recrystallized three times from ethanol, the picrate formed golden needles, m. p. 170–171°.

Anal. Calcd. for $C_{15}H_{18}N_4O_8$: C, 47.12; H, 4.75; N, 14.66. Found: C, 47.11; H, 4.87; N, 14.54.

6-Keto-1-azabicyclo[5.3.0]decane Picrolonate.—Prepared in ether and recrystallized from ethanol, the picrolonate formed orange platelets, m. p. 165–166°.

Anal. Calcd. for $C_{19}H_{23}N_5O_6$: C, 54.67; H, 5.55; N, 16.78. Found: C, 54.70; H, 5.65; N, 16.97.

Clemmensen Reduction of 6-Keto-1-azabicyclo[5.3.0]-decane. Quinolizidine.—Seven grams of mossy zinc was amalgamated with 1 g. of mercuric chloride, 1 ml. of concentrated hydrochloric acid, and 15 ml. of water. The mixture was swirled for five minutes. The aqueous layer was decanted, and the zinc was washed once with water. A mixture of 1 g. (0.0053 mole) of 6-keto-1-azabicyclo-[5.3.0]decane hydrochloride, 7 g. (0.107 mole) of amalgamated zinc, and 20 ml. of concentrated hydrochloric acid was refluxed for ten hours. An additional 10 ml. of acid was added every two hours during this time. The solution was cooled and made basic with 50% sodium hydroxide solution. The zinc hydroxide was removed by filtration using Super-Cel as a filtering aid. The filtrate was distilled until no basic material was found in the distillate. The distillate was saturated with potassium carbonate and extracted four times with ether. The ethereal

(3) Leonard and Barthel, *ibid.*, **71**, 3098 (1949).

(4) All melting points are corrected.

(5) Kapfhammer and Matthes, *Z. physiol. Chem.*, **223**, 43 (1934).

(6) Hauser and Hudson, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 279.

solution of the amine was dried over anhydrous magnesium sulfate and used for the preparation of derivatives.

Quinolizidine Picrate.—Prepared in ether and recrystallized from methanol, the picrate formed yellow elongated plates, m. p. 197.5–198.5°.

Quinolizidine Picrolonate.—Prepared in ether and recrystallized from ethanol, the picrolonate formed orange plates, m. p. 244–245° (dec.).

Quinolizidine Methiodide.—Prepared in ether and recrystallized from ethanol-ether, the methiodide formed colorless cubes, m. p. 329–330° (dec.).

Wolff-Kishner Reduction of 6-Keto-1-azabicyclo[5.3.0]decane. 1-Azabicyclo[5.3.0]decane.—A solution of 0.5 g. (0.0026 mole) of 6-keto-1-azabicyclo[5.3.0]decane hydrochloride, 1 g. (0.017 mole) of hydrazine hydrate (85%) and 1.5 g. (0.027 mole) of potassium hydroxide in 10 ml. of triethylene glycol was refluxed for one hour. The solution was then distilled until no basic material was found in the distillate. The distillate was saturated with potassium carbonate, extracted twice with ether, and dried over anhydrous magnesium sulfate. The derivatives were prepared from the ethereal solution.

1-Azabicyclo[5.3.0]decane Picrate.—Prepared in ether and recrystallized three times from methanol, the picrate formed yellow elongated plates, m. p. 213–214°. The melting point of a mixture with authentic 1-azabicyclo-[5.3.0]decane picrate[2] was not depressed.

1-Azabicyclo[5.3.0]decane Methiodide.—Prepared in ether and recrystallized from ethanol-ether, the methiodide formed colorless needles, m. p. 282–283°.

Quinolizidine.—Quinolizidine was prepared by the method of Boekelheide and Rothchild[7] from diethyl β-(2-pyridyl)-ethyl malonate in 70% yield, b. p. 72° (12 mm.); $n^{20}D$ 1.4765. The picrate, picrolonate and methiodide were prepared and were recrystallized from the same solvents as were the derivatives of the Clemmensen reduction product of 6-keto-1-azabicyclo[5.3.0]decane: **picrate,** m. p. 197–198°; **picrolonate,** m. p. 244–245° (dec.); **methiodide,** m. p. 329–330° (dec.). No depressions in melting points were observed when corresponding derivatives of the amines from the two syntheses were mixed.

Summary

It has been established that Clemmensen reduction converts 6-keto-1-azabicyclo[5.3.0]decane to the rearrangement product, quinolizidine.

(7) Boekelheide and Rothchild, THIS JOURNAL, **69**, 3149 (1947).

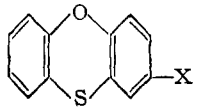
URBANA, ILLINOIS RECEIVED MARCH 28, 1949

[CONTRIBUTION FROM THE PITTSFIELD LABORATORY, APPARATUS DEPARTMENT, GENERAL ELECTRIC COMPANY]

Vinyl Compounds: Phenoxathiin and Dibenzothiophene Derivatives

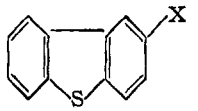
BY RALPH G. FLOWERS AND LEOLA WILLS FLOWERS

During an investigation of the properties of different polymeric materials, several phenoxathiin and dibenzothiophene derivatives were prepared. Interest in these compounds was centered upon the role played by the sulfur atom in determining their electrical properties. The vinylphenoxathiin was synthesized by the hydrogenation of the ketone to the carbinol with subsequent dehydration.



I, X = —$COCH_3$
II, X = —$CHOHCH_3$
III, X = —$CH{=}CH_2$

A similar scheme was carried out in the synthesis of the vinyldibenzothiophene.



IV, X = —$COCH_3$
V, X = —$CHOHCH_3$
VI, X = —$CH{=}CH_2$

The 2-acetylphenoxathiin (I) was prepared by a Friedel–Crafts reaction, using a modification of the work reported by Suter, McKenzie and Maxwell.[1] 2-(α-Hydroxyethyl)-phenoxathiin (II), prepared by the hydrogenation of I, was dehydrated in the vapor phase to 2-vinylphenoxathiin (III), m. p. 39.5–41°. The low melting point of this monomer allows it to be used for impregnation applications as well as in the form of its polymer and copolymers.

A number of investigators[2] have prepared the 2-acetyldibenzothiophene (IV) which we have hydrogenated to the 2-(α-hydroxyethyl)-dibenzothiophene (V). No evidence of catalyst poisoning was observed during the hydrogenation of these sulfur compounds or in subsequent runs using the same bombs with other materials. Two methods for the dehydration of V to 2-vinyldibenzothiophene (VI) were carried out in the present work. VI is also a low melting monomer, m. p. 45.0–45.5°, which may be utilized under the same conditions as those for III.

Experimental[3]

2-Acetylphenoxathiin (I).—One hundred thirty-five grams of anhydrous aluminum chloride and 300 cc. of carbon disulfide were placed in a 2-liter, 3-necked flask, equipped with an efficient stirrer, separatory funnel, condenser and a thermometer. A mixture of 200 g. of phenoxathiin in 700 cc. of carbon disulfide and 85 g. of acetyl chloride was added dropwise through the separatory funnel. The addition of the reactants took about six hours after which the mixture was allowed to stand one-half hour.

A yellow precipitate, which was obtained by hydrolyzing the mixture with ice and hydrochloric acid, was collected in a Büchner funnel and washed several times before drying. The fraction which distilled over at 165–185° at 1 mm. was recrystallized two times from ethyl alcohol: 74 g., 31% yield, of I was obtained which had a melting point of 111–112°.

2-(α-Hydroxyethyl)-phenoxathiin (II).—Seventy and one-half grams of I, dissolved in 1 liter of absolute methyl alcohol, and 5 g. of copper-chromium oxide catalyst[4] were placed in a glass lined, high pressure bomb. The reaction was carried out in the presence of hydrogen at 160° at

(1) Suter, McKenzie and Maxwell, THIS JOURNAL, **58**, 719 (1936).

(2) (a) Burger, Waterman and Lutz, *ibid.*, **60**, 2628 (1939); (b) Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1939); (c) Burger and Bryant, *ibid.*, **4**, 119 (1939).

(3) Analyses were made by Miss F. Durkee of this Laboratory and by Dr. Carl Tiedcke.

(4) Adkins, "Reactions of Hydrogen," Univ. of Wisconsin Press, Madison, Wisconsin.