While the authors recognize that the data are not as accurate at low concentrations as have been obtained in recent measurements on such materials as acetic acid, it is believed that this is due to the inherent difficulty in handling volatile amine solutions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Electron Sharing Ability of Organic Radicals. XI. *alpha*-Thienyl- and *alpha*-Mesitylpyrrolidines

BY J. G. KIRCHNER AND I. B. JOHNS

Studies on the alpha substituted pyrrolidines have been reported in earlier papers in this series.[1] In these chemical studies and in the insecticidal studies that have been carried along with them no α-substituted pyrrolidine has been used having an ionization constant lower than that of α-phenylpyrrolidine. In order to investigate these weaker bases α-thienyl- and α-mesitylpyrrolidine were prepared and their ionization constants determined.

The syntheses were accomplished by using the reaction of Cloke[2] as modified by Craig, Bulbrook and Hixon.[3]

Experimental

α-Thienyl-α-pyrroline.—Thiophene was treated with iodine and yellow mercuric oxide to yield the α-iodothiophene. From 24.3 g. (0.115 mole) of α-iodothiophene, 2.9 g. (0.115 atom) of magnesium, and 125 cc. of anhydrous ether a solution of α-thienylmagnesium iodide was prepared. As 12 g. of γ-chlorobutyronitrile in 125 cc. of ether was added a Grignard addition product precipitated and collected in the bottom of the flask as a dark liquid. After refluxing for thirty minutes the condenser was reversed, and xylene added as the ether distilled off. Heating this mixture for one hour changed the dark liquid to a gummy solid which was then hydrolyzed with a 10% solution of ammonium chloride. The xylene layer was separated, the water layer extracted with ether, and the latter combined with the xylene. Hydrochloric acid solution was used to recover the α-thienyl-α-pyrroline from the combined solvents. The acid solution was in turn washed with ether until the washings remained colorless and then heated to remove the ether. It was then treated with excess sodium hydroxide; the base extracted with ether and dried over solid potassium hydroxide. The compound was purified by crystallization from petroleum ether and by vacuum distillation. Four and eight-tenths grams of material boiling at 111.1–112.1° (4 mm.) was obtained, representing a yield of 27.5% based on the nitrile taken. α-Thienyl-α-pyrroline is a white crystalline solid melting at 57°.

Anal. Calcd. for C_8H_9NS: C, 63.54; H, 6.02; N, 9.24; S, 21.19. Found: C, 63.55; H, 6.09; N, 9.37; S, 21.10.

A picrate from alcohol melted at 197.7°.

α-Thienyl-α-pyrrolidine was obtained by reducing the above pyrroline with tin and hydrochloric acid. Four and three-tenths grams of base with excess tin and hydrochloric acid yielded 3.4 g. of the reduced compound: b. p. 88–89° (3 mm.); $n^{25}\mathrm{D}$ 1.5625.

Anal. Calcd. for $C_8H_{11}NS$: N, 9.14. Found: N, 9.10.

A picrate precipitated from ether solution and recrystallized from alcohol melted at 187.6°. It was found that picrates of these pyrrolidine bases precipitated from ether solutions with an ether solution of picric acid were much purer and required less recrystallizing than those prepared in alcohol solutions.

Reduction of the pyrroline was also attempted with sodium and alcohol. Two grams (0.013 mole) of base was treated with 4.2 g. of sodium and an excess of ethyl alcohol. During the reaction hydrogen sulfide was evolved, indicating that decomposition was taking place. Only a trace of an impure compound was recovered from the reaction mixture. Reduction of both rings probably occurred with the production of a highly unstable compound just as the complete reduction of α-pyrryl-α-pyrroline results in the spontaneously decomposable dipyrrolidine.[4] Likewise reduction of nicotine with sodium and alcohol results in the rupture of the pyrrolidine ring.[5]

α-Mesitylpyrroline was synthesized in the same general manner. A Grignard reagent was prepared from 24.9 g. (0.125 mole) of bromomesitylene and 3 g. (0.125 atom) of magnesium in 100 cc. of ether. In the preparation of this reagent it was necessary to heat the mixture for ten hours to complete the reaction. It was then cooled and 10.4 g. of nitrile added. A yield of 7.4 g. of pure base, representing 39.6% of the theoretical, was obtained. It is a colorless, rather unstable liquid which on standing turns dark red in color, b. p. 101–102° (cor.) (2 mm.).

Anal. Calcd. for $C_{13}H_{17}N$: C, 83.36; H, 9.15. Found: C, 83.6; H, 9.15.

A picrate recrystallized from alcohol melts at 180° (cor.).

Reduction of α-mesitylpyrroline was accomplished by means of sodium and alcohol. Eleven grams of sodium was added to a solution of 7 g. of base in 100 cc. of ethyl alcohol. After completion of the reaction the mixture was acidified, and the alcohol distilled off in a vacuum. It was necessary to keep the temperature below 50° during this concentra-

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(1) Craig and Hixon, THIS JOURNAL, **53**, 4367 (1931); Starr, Bulbrook and Hixon, *ibid.*, **54**, 3971 (1932); Goodhue and Hixon, *ibid.*, **56**, 1329 (1934).

(2) Cloke, *ibid.*, **51**, 1174 (1929).

(3) Craig, Bulbrook and Hixon, *ibid.*, **53**, 1831 (1931).

(4) Craig, *ibid.*, **56**, 1144 (1934).

(5) Blau, *Ber.*, **26**, 628 (1893).

tion to avoid decomposition of the hydrochloride. After freeing the base and drying over solid potassium hydroxide it was distilled at 124.2° (cor.) under 3.5 mm.

Anal. Calcd. for $C_{13}H_{19}N$: N, 7.40. Found: N, 7.43.

A picrate melted at 194.6°.

Measurement of Ionization Constants.—The method and apparatus used were the same as those previously employed by Goodhue[1] and by Oldham[6] in this Laboratory. The hydrogen-ion concentrations of half neutralized solutions of the bases were determined by means of the hydrogen electrode with a vacuum tube potentiometer. For the determinations in absolute methanol two 0.1 *f* sodium chloride–calomel reference electrodes were used having an e. m. f. of 0.1174 and 0.1175 v. For the determinations in water, the usual saturated potassium chloride–calomel reference electrode was used.

TABLE I

Compound	Solvent	E. m. f.	$-\log a_H$	$-\log K_B$
α-Thienyl-α-pyrrolidine	Methanol	0.7224	10.25	6.47
α-Thienyl-α-pyrrolidine	Water	.7980	9.35	4.65
α-Mesitylpyrrolidine	Methanol	.7062	9.99	6.73
α-Phenylpyrrolidine[a]	Methanol	.7576	10.87	5.83
α-Phenylpyrrolidine[b]	Water	.8143	9.65	4.35

[a,b] These values were taken from the data by Goodhue[1] and Craig,[1] respectively.

The values of these constants indicate that thienylpyrrolidine and mesitylpyrrolidine are distinctly weaker bases than phenylpyrrolidine.

Attempted Resolution of Optical Isomers.—The resolution of α-thienyl-α-pyrrolidine was attempted with *d*-tartaric acid, α-bromocamphorsulfonic acid, and *l*-malic acid without success. Glutamic acid yielded a crystalline salt but the free base isolated from it was inactive. Camphoric acid gave a crystalline salt: m. p. 128–129°; $[\alpha]^{21}\text{D}$ (ethanol *c*, 4.5) + 15.54°. The base isolated from this salt, $[\alpha]^{23}\text{D}$ (ethanol *c*, 12.5) − 3.12° was doubtless only partially resolved. Further purification failed.

The resolution of α-mesitylpyrrolidine was attempted with *d*-tartaric acid and with camphoric acid without success.

Summary

α-Thienyl-α-pyrroline, α-thienyl-α-pyrrolidine, α-mesitylpyrroline, and α-mesitylpyrrolidine have been prepared for the first time.

Ionization constants of the reduced compounds have been determined.

Attempts have been made to resolve these pyrrolidines.

AMES, IOWA

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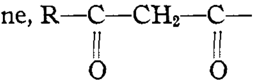
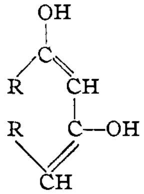
(6) Oldham and Johns, THIS JOURNAL, **61**, 3289 (1939).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

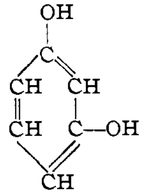
β-Diketones: Synthesis, Structure and Bactericidal Properties

BY CHARLES D. HURD AND CHARLES D. KELSO[1]

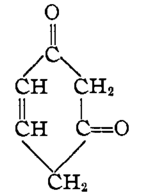
If one considers a β-diketone,  $R-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_2R$, in its completely enolized modification (I), it may be compared to resorcinol (II)



I



II



III

for which, incidentally, there is evidence of the diketo structure (III) on the basis of work with Raman spectra[2] and absorption spectra.[3] In view of the known effectiveness of hexylresorcinol as a germicide, it was of interest to see whether β-diketones containing eight to twelve carbon atoms per molecule would possess similar effectiveness.

Two reactions were considered for the synthesis of the diketones. One was the well-known Claisen condensation of an ester with a ketone. The other was the new reaction[4] between acetoacetyl chloride and a Grignard reagent

$$CH_3COCH_2COCl + RMgX \longrightarrow CH_3COCH_2COR + MgXCl$$

These four diketones were prepared by the Claisen condensation, the last two of them being new compounds: 2,4-octanedione from ethyl acetate and 2-hexanone; 2,4-decanedione from ethyl acetate and 2-octanone; 2-dodecene-4,6-dione from ethyl crotonate and 2-octanone

$$CH_3CH{=}CHCOOC_2H_5 + CH_3COC_6H_{13} \longrightarrow CH_3CH{=}CH{-}CO{-}CH_2COC_6H_{13} + C_2H_5OH$$

1-hendecene-3,5-dione, $CH_2{=}CH{-}CO{-}CH_2CO{-}C_6H_{13}$, from ethyl acrylate and 2-octanone.

2,4-Octanedione was prepared also from acetoacetyl chloride and butylmagnesium bromide.

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(1) Parke, Davis and Company Fellow, 1937–39.

(2) Hayashi, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **23**, 16 (1933); Kohlrausch and Pongrantz, *Monatsh.*, **65**, 6 (1934).

(3) Valyashko and Scherbaky, *J. Gen. Chem.* (U. S. S. R.), **8**, 1629 (1938).

(4) Hurd and Kelso, THIS JOURNAL, **62**, 1548 (1940).