

Even changing the nature of the ion produced no electrode action in liquid ammonia. In aqueous solutions at a high pH other ions, most frequently sodium ions, will take part in the transport of current, causing the well known "sodium error" of glass electrodes. The presence of a large excess of sodium ion in liquid ammonia solution did not produce an electrode response with any of the glasses tested.

Ammonium ions in liquid ammonia are the counterpart of hydronium ions in water: they change colors of pH indicators, catalyze solvolysis reactions, are displaced by certain metals and set up potentials with a hydrogen electrode.⁹ Glass electrode action might therefore also be expected in liquid ammonia solutions. Nevertheless, there are differences: the heat of solvation of the proton is 17 kcal./mole lower in liquid ammonia than in water, indicating a more stable system in ammonia. The low mobility of ammonium ions in ammonia as compared with hydronium ions shows that there is no "Grotthuss" conduction in liquid ammonia.

Though complete exchange exists between NH_4^+ and NH_3 ,¹² the dissociation of NH_4^+ into H^+ and NH_3 is very slight. Even in water ammonium ions have not been found to cause glass electrode "errors" such as sodium ions. In terms of Dole's statistical treatment of glass electrode action,¹³ the ammonium ion does not appear to have sufficient energy to exchange with the proton on the glass surface. Therefore, it seems plausible that the ammonium ions in liquid ammonia may not be in equilibrium with ions on the surface of the electrode.

Experimental

The Cell.—A cylindrical cell of 70 mm. diameter provided with a large ground glass joint and several smaller joints in the head for the lead-plated platinum reference electrode and glass electrode was used. The inside of the glass electrode was also filled with liquid ammonia and was provided with another reference electrode. The cell was cooled by immersion in a Dewar flask in acetone and Dry Ice.

Measuring Equipment.—A Beckman model G pH meter was used for the purpose of detecting pH response. A precision multirange test meter was used for all current measurements. With this meter 0.1 microampere can be detected. A 2400-volt d.c. power supply was placed in series with the cell and the ammeter. When pH measurements were attempted the power supply was removed and the pH meter inserted.

pH Sensitive Glasses.—Initial studies were confined entirely to Corning 015 type glass. In all cases the pH sensitivity of the membranes was first checked in water. The membranes were then subjected to evacuation followed by long periods of immersion in liquid ammonia. This procedure was adopted to ensure complete replacement of the water in the membrane by liquid ammonia.

Membranes composed of pH sensitive glasses of different compositions were similarly tested, *i.e.*, Beckman General Purpose glass and Beckman type E.

Measurements and Results.—A power supply of 300 and 2400 v. d.c., respectively, the cell and the microammeter were connected in series. The resistance of the glass membrane was calculated from Ohm's law. Measurements were made in aqueous solution between 6° and 52° for Corning 015 and Beckman general purpose glass and between 25° and 30° for the Beckman type E glass. The resistance for Corning 015 glass varied between 21 megohms at 52° to 1300 \pm 200 megohms at 6°. For Beckman General Purpose glass the resistance varied between 9 megohms at 50° and 600 megohms at 7°.

(12) C. J. Nyman, S. C. Fung and H. W. Dodgen, *THIS JOURNAL*, **72**, 1033 (1950).

(13) M. Dole, *J. Chem. Phys.*, **2**, 862 (1934).

Similar measurements were performed with aqueous alcohol solutions containing 80% of alcohol and containing a small amount of hydrochloric acid. Measurements could now be carried out to -33° , giving a resistance of 2×10^3 megohms for Corning 015 glass and 1.2×10^3 megohms for Beckman General Purpose glass.

In liquid ammonia solutions no current could be observed in the temperature range investigated, -35 to -1° .

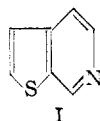
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Sulfur Analogs of Isoquinolines and β -Carbolines. III. The Pomeranz-Fritsch Reaction

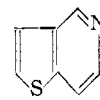
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RECEIVED JUNE 8, 1953

In a previous paper¹ it was demonstrated that isosteres of substituted isoquinolines may be prepared by applying the Bischler-Napieralski reaction to derivatives of thiophene. This work is being extended in our laboratory. It also seemed desirable to investigate the feasibility of synthesizing the parent substances, thieno[2,3-c]- (I) and thieno[3,2-c]pyridine (II) by means of the Pomeranz-Fritsch reaction² inasmuch as 2- and 3-thiophenealdehyde are readily available. A comparison of the properties of these substances with those of isoquinoline would be of great interest.



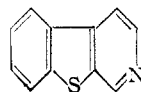
I



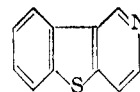
II

Although the condensation of the aldehydes with aminoacetal proceeded with great ease, cyclization of the resulting Schiff bases under the usual conditions gave only small yields of the desired thienopyridines I and II. This seems to be due largely to resinification under the influence of sulfuric acid at the temperatures necessary to effect cyclization. Slightly better yields were achieved by using a mixture of polyphosphoric acid and phosphorus oxychloride as cyclizing agent. To our knowledge this medium has not previously been used in such reactions.

In order to supplement our earlier work on the preparation of sulfur analogs of β -carbolines³ studies were also carried out which had as their aim the preparation of thianaphtheno[3,2-c]- (III) and thianaphtheno[2,3-c]pyridine (IV) from the aminoacetals derived from 2- and 3-thianaphthenealdehyde. III⁴ and IV⁵ have since been prepared by different, somewhat less convenient, routes. The cyclization did not proceed in sulfuric acid solution, but using polyphosphoric acid-phosphorus oxychloride the



III



IV

(1) W. Herz, *THIS JOURNAL*, **73**, 351 (1951).

(2) W. J. Gensler, *Organic Reactions*, **6**, 191 (1951).

(3) W. Herz, *THIS JOURNAL*, **73**, 4999 (1950).

(4) H. Kotake and T. Sakan, *J. Inst. Polytech. Osaka City Univ., Ser. C*, **2**, No. 1, 25 (1951); *C.A.*, **46**, 6121 (1952).

(5) D. B. Capps and C. S. Hamilton, *THIS JOURNAL*, **75**, 697 (1953).

yields of thianaphthenopyridines were 18 and 12%. This suggests that polyphosphoric acid may be a useful cyclizing agent for other syntheses using the Pomeranz-Fritsch method.

The ultraviolet spectrum of I in isoöctane solution (maxima at 223, 227, shoulder at 242, maxima at 293, 299 and 304 μ ; corresponding $\log \epsilon$'s 4.24, 4.23, 3.68, 3.88, 3.76) exhibits marked resemblance to that of isoquinoline,⁶ but that of II (maxima at 222, 238, 256, shoulder at 274, maxima at 281, 291 and 337 μ , $\log \epsilon$'s 4.55, 3.58, 3.63, 3.45, 3.43, 3.30, 2.35) does not possess this similarity in the longer wave length region. It may be that in the spectrum of II the 290–310 μ band of I is sufficiently reduced in intensity and displaced toward shorter wave lengths to give rise to the less well pronounced maxima in the region 270–295 μ . A somewhat similar situation is found in the spectra of the two isomeric thianaphthenopyridines III (maxima at 232, 272, 280, 328 and 338 μ , $\log \epsilon$'s 4.61, 3.88, 4.03, 3.53 and 3.60) and IV (maxima at 230, 252, 305 and 316 μ , $\log \epsilon$'s 4.70, 4.33, 3.15 and 3.21).

Acknowledgment.—This work was supported in part by a grant from the U. S. Public Health Service, Department of Health, Education and Welfare.

Experimental⁷

Diethyl 2-Thenylideneaminoacetal.—A mixture of 11.2 g. of 2-thiophenealdehyde and 14 g. of aminoacetal was heated on the steam-bath. After two hours ether was added and the mixture was dried over sodium sulfate. Removal of ether followed by fractionation *in vacuo* yielded 19.6 g. (86%) of condensation product, b.p. 125–128° (2.5 mm.). The analytical sample boiled at 115–118° (1.9 mm.), n_D^{20} 1.5231.

Anal. Calcd. for $C_{11}H_{17}NSO_2$: C, 58.12; H, 7.54. Found: C, 58.16; H, 7.55.

Diethyl 3-Thenylideneaminoacetal.—Condensation of similar quantities of 3-thiophenealdehyde⁸ and aminoacetal yielded 20.5 g. of product, b.p. 120–121° (1.8 mm.). The analytical sample boiled at 128° (3 mm.), n_D^{20} 1.5179.

Anal. Calcd. for $C_{11}H_{17}NSO_2$: C, 58.12; H, 7.54. Found: C, 58.24; H, 7.39.

Diethyl 2-Thianaphthenylideneaminoacetal.—The yield of condensation product from 14.4 g. of 2-thianaphthenealdehyde⁹ and 12 g. of aminoacetal was 19 g. (78%), b.p. 155–161° (0.2 mm.). The liquid solidified upon standing and was sublimed for analysis at a bath temperature of 110–125° (0.5 mm.), m.p. 45–46°.

Anal. Calcd. for $C_{15}H_{19}O_2NS$: C, 64.95; H, 6.90; N, 5.05. Found: C, 65.05; H, 7.17; N, 5.15.

Diethyl 3-Thianaphthenylideneaminoacetal.—The yield of product, b.p. 155–165° (1.5 mm.), was 20.4 g. (83%). The analytical sample boiled at 162–165° (1.5 mm.), n_D^{20} 1.5711.

Anal. Calcd. for $C_{15}H_{19}NSO_2$: C, 64.95; H, 6.90. Found: C, 64.93; H, 6.82.

Cyclizations. (A) Sulfuric Acid Method.—To 6 g. of ice-cold sulfuric acid was gradually added 3 g. of the aminoacetal, then another 9 g. of sulfuric acid and 2 g. of phosphorus oxychloride. The mixture was kept at 160° for 1.5 hours, in the course of which it resinified, cooled and diluted with water. The filtered solution was extracted with ether (this fraction usually yielded aldehyde formed by hydrolytic cleavage of the acetal), made basic and again extracted with ether. The basic fraction after drying and

removal of ether was distilled or dissolved in a little ethanol and treated with 5 ml. of a saturated solution of picric acid in ethanol. The picrate was collected after chilling and recrystallized from ethanol.

(B) Polyphosphoric Acid Method.—A solution of 1 g. of phosphorus oxychloride in 30 g. of polyphosphoric acid was heated to the desired temperature in an oil-bath, the aminoacetal added with stirring, the mixture stirred for 5 to 30 minutes and then poured into ice-water. The aqueous solution was extracted with ether, made basic, saturated with ammonium sulfate and again extracted with ether. The ethereal solution was dried and the solvent removed under reduced pressure. The residue was sublimed *in vacuo*.

Thieno(2,3-c)pyridine (I).—Procedure A yielded 102 mg. of a picrate which decomposed at 207.5–208.5°.

Anal. Calcd. for $C_7H_5N_2SO_7$: C, 42.86; H, 2.21; N, 15.38. Found: C, 43.42; H, 2.26; N, 15.26.

Procedure B, using 10 g. of Schiff base in 200 g. of polyphosphoric acid and 10 g. of phosphorus oxychloride at 120° for 30 minutes, yielded 225 mg. of crude thieno(2,3-c)pyridine by fractional sublimation *in vacuo* of the basic residue. Two sublimations at a bath temperature of 70° (0.5 mm.) furnished colorless crystals, m.p. 54–55°.

Anal. Calcd. for C_7H_5NS : C, 62.19; H, 3.73. Found: C, 62.39; H, 3.90.

After collection of the first fraction, the bath temperature was raised to 130–140° and 90 mg. of a higher-melting solid, m.p. 142–144°, was obtained. This material has not yet been identified.

Thieno(3,2-c)pyridine (II).—Two and three-tenths grams of the Schiff base in 15 g. of polyphosphoric acid and 1 g. of phosphorus oxychloride at 120–130° for 10 minutes yielded 150 mg. of crude base. Resublimation at room temperature (0.25 mm.) furnished an analytical sample, m.p. 42–43°.

Anal. Calcd. for C_7H_5NS : C, 62.19; H, 3.73; N, 10.36. Found: C, 61.72; H, 3.69; N, 10.01.

The picrate melted at 224.5°.

Anal. Calcd. for $C_{13}H_9N_4O_7S$: C, 42.86; H, 2.21; N, 15.38. Found: C, 42.88; H, 2.27; N, 14.9.

Procedure A yielded 201 mg. of picrate.

Thianaphtheno(2,3-c)pyridine (III).—From 1.3 g. of the Schiff base in 31 g. of polyphosphoric acid and 1 g. of phosphorus oxychloride at 150–160° for 20 minutes there was obtained 240 mg. of the base. This was purified first by recrystallization from ether–petroleum ether and finally by sublimation at 0.2 mm., m.p. 96–98° (lit.⁴ 98–99°). The picrate decomposed at 256° (lit.⁴ 258–260°).

No cyclization was effected by means of 96% sulfuric acid at 5° for 10 hours as well as at 100° for two hours with a mixture of phosphorus oxychloride and sulfuric acid.

Thianaphtheno(3,2-c)pyridine (IV).—From 1.6 g. of the Schiff base in 30 g. of polyphosphoric acid and 1 g. of phosphorus oxychloride at 90–100° for 20 minutes there was obtained 0.2 g. of the base. Recrystallization from petroleum ether furnished colorless needles, m.p. 71–71.5° (lit.⁵ 69–70.5°). The picrate melted at 248°.

Anal. Calcd. for $C_{17}H_{13}O_7N_4S$: N, 13.39. Found: N, 13.6.

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Preparation of Normal and Secondary Butyl Hydroperoxides

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RECEIVED JULY 6, 1953

The classical method of preparing methyl and ethyl hydroperoxides is the reaction of the appropriate alkyl sulfate with hydrogen peroxide in concentrated aqueous potassium hydroxide solution.¹ It appears, however, that the method is not applicable to higher members of the series. Medvedev² was

(6) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.

(7) Melting points and boiling points are uncorrected. Analyses by Clark Microanalytical Laboratory, Urbana, Illinois, and Drs. Weiler and Strauss, Oxford.

(8) E. Campaigne and W. LeSuer, *THIS JOURNAL*, **70**, 1555 (1948).

(9) D. A. Shirley and M. J. Danzig, *ibid.*, **74**, 2935 (1952).

(1) A. Baeyer and V. Villiger, *Ber.*, **34**, 738 (1901).

(2) S. S. Medvedev and E. N. Alekseeva, *ibid.*, **65B**, 133 (1932).