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 mμ; corresponding log ε'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 ε'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 mμ 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 mμ. A somewhat similar situation is found in the spectra of the two isomeric thianaphthenopyridines III (maxima at 232, 272, 280, 328 and 338 mμ, log ε's 4.61, 3.88, 4.03, 3.53 and 3.60) and IV (maxima at 230, 252, 305 and 316 mμ, log ε's 4.70, 4.33, 3.15 and 3.21).

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Experimental[7]

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.), $n^{23}D$ 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-thiophenealdehyde[8] and amino acetal yielded 20.5 g. of product, b.p. 120–121° (1.8 mm.). The analytical sample boiled at 128° (3 mm.), $n^{23}D$ 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-thianaphthenealdehyde[9] 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.), $n^{23}D$ 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 $C_{13}H_8N_4SO_7$: 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 $C_{13}H_8N_4O_7S$: 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 $C_{17}H_{10}O_7N_4S$: N, 13.39. Found: N, 13.6.

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(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).

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Preparation of Normal and Secondary Butyl Hydroperoxides

BY E. G. LINDSTROM

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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. Medvedev[2] was

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

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

unable to isolate *n*-propyl hydroperoxide, although he obtained a good yield of isopropyl hydroperoxide. Harris and Egerton[3] succeeded in preparing *n*-propyl hydroperoxide in yields of only 1.3% per pass. Numerous attempts to prepare *s*-butyl hydroperoxide in our own laboratory following the procedures used by these earlier workers were entirely unsuccessful. We have now found that relatively good yields of *n*- and *s*-butyl hydroperoxides can be obtained by the classical procedure if most of the water employed as reaction solvent is replaced with methanol.

Although the reaction has not been extended to alkyl hydroperoxides higher than butyl, there is an excellent prospect that this improved procedure will prove to be a general one, and it is anticipated that this method may result in improved yields for some of the lower hydroperoxides. The success of the method apparently depends on the fact that methanol brings the alkyl sulfate, hydrogen peroxide and potassium hydroxide into solution in the same phase. Other alcohols and similar solvents may also serve as suitable reaction media.

n-, iso and *s*-butyl hydroperoxides have been previously reported,[4] but properties and methods of synthesis were not included.

Preliminary studies on *n*- and *s*-butyl hydroperoxides indicate that they are relatively stable compounds; detonation was not obtained by hammer blows or by heating with a free flame. In this respect primary and secondary butyl hydroperoxides are more similar to *t*-butyl hydroperoxide than to the relatively unstable methyl and ethyl hydroperoxides.

Experimental

***s*-Butyl Hydroperoxide.**—The preparative procedure employed was similar to that of Harris and Egerton[3] except that a 25% solution of potassium hydroxide in methanol was used in place of the 50% aqueous potassium hydroxide solution. A solution of 1.88 moles of potassium hydroxide in 400 ml. of methanol, chilled and decanted from solid carbonate, was added dropwise to 200 ml. of 30% hydrogen peroxide (2.3 moles) in a three-neck flask equipped with a stirrer. Then 395 g. (1.88 moles) of chilled *s*-butyl sulfate was added dropwise. The reaction mixture was held at −20 to −10° during these additions and then stirred at +2° (ice-bath) for 20 hours. The reaction mixture was added to 2 l. of ice and water; unreacted butyl sulfate was recovered by ether extraction. The aqueous phase was neutralized with 50% sulfuric acid at 0° and 3 pounds of ammonium sulfate was added. The *s*-butyl hydroperoxide was separated by three 200-ml. extractions with ether. Three hundred grams (1.44 moles) of butyl sulfate was recovered and the ether extract of the hydroperoxide contained 0.45 equiv. of peroxide.

Most of the ether was removed at atmospheric pressure from the hydroperoxide fraction; 200 ml. of water was added producing two phases and the mixture was distilled in a three-foot spinning band column at 20:1 reflux ratio and 35 mm. There was obtained 16.2 g. (40% based on butyl sulfate which reacted) of *s*-butyl hydroperoxide as an azeotrope along with an equal volume of water at 30–31°. In other preparations this azeotrope distilled at 36° at 100 mm. and 47° at 150 mm. The azeotropic mixture was saturated with ammonium sulfate and the hydroperoxide layer was dried with anhydrous cupric sulfate; $n^{20}D$ 1.4052, d^{20}_4 0.9094. The active oxygen was determined by reaction with potassium iodide in acetic acid solution.

Anal. Calcd. for $C_4H_{10}O_2$: C, 53.31; H, 11.19; active (O), 17.76. Found: C, 52.13, 52.39; H, 11.26, 10.92; active (O), 16.1, 16.0.

***n*-Butyl hydroperoxide** was prepared in an analogous manner. Eleven ml. (20% yield based on 0.78 moles of reacted *n*-butyl sulfate) was obtained as an azeotrope (b.p. 28–29° at 100 mm.). A heart cut of the hydroperoxide was dried and redistilled at 5 mm.; $n^{20}D$ 1.4032, d^{20}_4 0.9078.

Anal. Calcd. for $C_4H_{10}O_2$: active (O), 17.76. Found: active (O) 16.4, 15.2.

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2-Thienol

BY CHARLES D. HURD AND HUGH J. ANDERSON[1]

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The original synthesis[2] of 2-thienol involved oxidation of a mixture of 2-thienylmagnesium bromide and isopropylmagnesium bromide, the yield being about 25% of the theoretical. The present work describes some new synthetical approaches, but it is interesting to note that none gave yields as high as the original method. These results were obtained.

(a) A 10% yield by treatment of 2-thienyllithium with 1,2,3,4-tetrahydro-1-naphthyl hydrogen peroxide, which method gave a nearly quantitative yield of phenol[3] from phenyllithium. (b) A 5% yield by treatment of a mixture of 2-thienylmagnesium bromide and isopropylmagnesium bromide with 1,2,3,4-tetrahydro-1-naphthyl hydrogen peroxide. (c) No 2-thienol following reaction of 2-thienyldimethylcarbinol in glacial acetic acid with 30% hydrogen peroxide and either aluminum chloride, zinc chloride or titanium tetrachloride. This was adapted from Kharasch's procedure[4] for the preparation of phenol from phenyldimethylcarbinol.

Experimental

Oxidation of 2-Thienyllithium.—A solution of 0.1 mole of 2-thienyllithium[5] in 300 ml. of dry ether was forced through a plug of glass wool into a dropping funnel. It was added slowly, with cooling and stirring, into a solution of 0.05 mole of 1,2,3,4-tetrahydro-1-naphthyl hydrogen peroxide[6] in 100 ml. of dry ether. After standing overnight at −10°, the mixture was poured on Dry Ice and decomposed with dilute sulfuric acid. The ether layer was removed and the aqueous layer was saturated with salt. After two more extractions with ether, the combined ether solutions were washed with three 50-ml. portions of 20% sodium hydroxide solution. The almost black basic solution was cooled and neutralized rapidly with cold dilute sulfuric acid and saturated with salt. This solution was then extracted with four 50-ml. portions of ether, the ether dried and removed to give 1.0 g. of thienol, b.p. 82–87° at 8 mm., a 10% yield. The product was characterized by means of the benzoate, m.p. 43–44°.

The same procedure applied to phenyllithium gave a 75% yield of phenol.

Oxidation of 2-Thienylmagnesium Bromide.—A mixture[2] of 0.1 mole of 2-thienylmagnesium bromide and 0.15 mole of isopropylmagnesium bromide was forced through a plug of glass wool into a dropping funnel. It was then added slowly with stirring and cooling to a solution of 1,2,3,4-tetrahydro-1-naphthyl hydrogen peroxide in 100 ml. of dry ether. After storing overnight at −10° it was processed

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