an additional hour. As the solution cooled, crystals separated and were collected on a filter, washed with cold glacial acetic acid and finally with water. Recrystallization of the product from alcohol yielded 0.9 g. (56%) of 3-acetylamino-6-bromoacenaphthene, m. p. 206–207°, identical with II-C obtained from ketone II-B.

The Oxidation of the Acetylhaloacenaphthenes.—The ketones were oxidized with a hypochlorite solution prepared according to the procedure of Fieser and Cason[13] to yield the following acids: 5-Bromo-3-acenaphthoic acid, m. p. 304–305° dec.

Anal. Calcd. for $C_{13}H_9O_2Br$: C, 56.34; H, 3.27. Found: C, 56.16; H, 3.44.

6-Bromo-3-acenaphthoic acid, m. p. 289–290° dec.

Anal. Calcd. for $C_{13}H_9O_2Br$: C, 56.34; H, 3.27. Found: C, 56.26; H, 3.47.

5-Chloro-3-acenaphthoic acid, m. p. 279–280° dec.

Anal. Calcd. for $C_{13}H_9O_2Cl$: C, 67.10; H, 3.90. Found: C, 67.07; H, 4.15.

6-Chloro-3-acenaphthoic acid, m. p. 264–265° dec.

Anal. Calcd. for $C_{13}H_9O_2Cl$: C, 67.10; H, 3.90. Found: C, 66.95; H, 4.03.

The Ultraviolet Absorption Spectra.—The spectra were measured by Dr. E. E. Pickett, a spectroscopist at the University of Missouri, with a Beckman Model DU spectrophotometer. The quartz cells were 1.00 cm. thick. The spectra were measured against the solvent, 95% alcohol, in a similar cell.

Summary

5-Bromo- and 5-chloroacenaphthene have been acylated in nitrobenzene solution with acetyl chloride and benzoyl chloride in the presence of aluminum chloride. The product from each acylation was a mixture from which two ketones were isolated: the 3-acyl-5-halo- and the 3-acyl-6-haloacenaphthenes.

The bromination of 3-acetylaminoacenaphthene in acetic acid solution yielded 3-acetylamino-6-bromoacenaphthene.

COLUMBIA, MISSOURI RECEIVED MAY 29, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Thienol

BY CHARLES D. HURD AND KENNETH L. KREUZ[1]

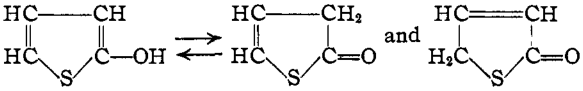
In the otherwise well-developed field of thiophene chemistry, the simple hydroxy derivative, 2-thienol,[2] is conspicuously absent; yet a survey of the literature shows but two attempts, both unsuccessful, toward its preparation.[3] Furthermore, while certain substituted thienols have been synthesized by ring-closure methods,[4] the introduction of the hydroxyl function into an existing thiophene nucleus has apparently not been recorded.

In the present work there is developed a preparative method for the simple thienols from thiophene, and a characterization of the more readily available isomer, 2-thienol.

The oxidation of aromatic Grignard reagents with oxygen ordinarily leads mainly to the formation of biaryls and tars. However, a modification involving the inclusion of a suitable aliphatic Grignard among the reactants has been found to repress these side-reactions, so that in the preparation of phenol by this method, the yield is increased from one-quarter to three-quarters of the theoretical.[5]

Analogous reactions have now been investigated for thiophene. Simple treatment of 2-thienylmagnesium bromide with oxygen was found to produce 2,2′-bithienyl in significant amounts, along with much hydrogen sulfide and resinous material, but no more than a trace of 2-thienol was formed. In the presence of somewhat more than an equivalent amount of isopropylmagnesium bromide these by-products were reduced sufficiently to permit isolation of the desired thienol in 25% yield.

2-Thienol is of considerable interest because it holds the possibility of enol–keto tautomerism, the "keto" forms being both 3- and 2-butenothiololactones



In general, compounds of the thiophene series exhibit a marked physical and chemical resemblance toward their benzene analogs. The extent to which 2-thienol resembles phenol, therefore, should depend on the tendency for it to exist in the enol form, which in turn is a measure of the aromatic character of the thiophene ring.

In the corresponding equilibrium for phenol, the ΔH value for the tautomeric shift from keto to enol has been estimated at approximately -16 kcal.[6]; this value is only slightly greater than the difference in resonance energies (10–12 kcal.) between the benzene and thiophene rings. Other things being equal, one might on this basis roughly predict nearly equal stabilities for the two tautomers of 2-thienol. This suggested dual nature has already been observed in substituted thienols.[4] It is reflected in the physical and

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[1] The Texas Company Fellow, 1946–1948.

[2] The name "thienol" is based on the generally accepted use of the stem "thien" for the thienyl radical, C_4H_3S, analogous to the stem "phen" for the phienyl radical. Thus thienol and phenol are analogous terms, as are thienyl and phenyl. The name "2-thiophene-ol" (*cf. C. A.*, **39**, 5904 (1945)) obviously is poorly adapted for this substance, since thiophenol is generally used for C_6H_5SH.

[3] Thomas, *Compt. rend.*, **146**, 642 (1908); Mentzer and Billet, *Bull. soc. chim.*, **12**, 292 (1945).

[4] The simplest example, 5-methyl-2-thienol, is described by Steinkopf and Thormann, *Ann.*, **540**, 1 (1939).

[5] Kharasch and Reynolds, THIS JOURNAL, **65**, 501 (1943).

[6] Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 291.

chemical properties of 2-thienol itself, in so far as they have been elucidated in the present work.

In certain of its physical properties, such as crystalline form and solubility, 2-thienol resembles phenol, but its odor is non-phenolic and its boiling point is 37° higher than that of phenol. Since the calculated molecular refractions for the enol and the thiolactone forms nearly coincide (25.85 and 25.99, respectively), no conclusion can be drawn from the observed value of 25.93.

Spectroscopic evidence also points to the existence of tautomeric forms. The infrared data obtained on a Beckman infrared spectrophotometer given in Fig. 1 show peaks at 2.9 and 3.2μ, characteristic of the hydroxyl and the aromatic C–H linkages, respectively; as well as peaks at 3.35 and 6.0μ, indicative of the aliphatic C–H and the carbonyl linkages, respectively. The observed red shift from the usual carbonyl absorption region might be expected from the conjugated thiolactone form.

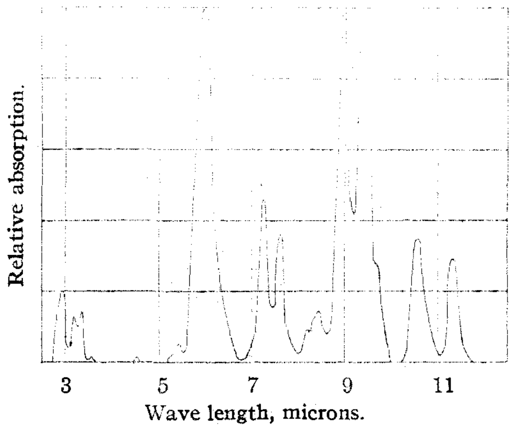

Fig. 1.—Infrared absorption spectrum of 2-thienol in carbon tetrachloride (56%).

The ultraviolet spectrum of 2-thienol shown in Fig. 2a, obtained on a Beckman quartz spectrophotometer, also can be interpreted in terms of the conjugated thiolactone form. Thus the strong band near 2200 Å. (log ϵ = 3.9) and the shoulder near 3200 Å. (log ϵ = 2.0) furnish a pattern similar to that noted by many investigators[7] for the conjugated system (C=C—C=O).

The chemical reactions of 2-thienol give further evidence of its dual nature. It yields a red color with ferric chloride and, like phenol, is a very weak acid. Exposure to air causes rapid deterioration at room temperature, but refluxing in nitrogen (217–219°) produces little change. It undergoes characteristic reactions of the phenolic hydroxyl group such as acetylation, benzoylation and methylation, and reacts readily with diazotized amines in alkaline solution to yield highly colored solids, part of which are alkali-soluble coupling products.

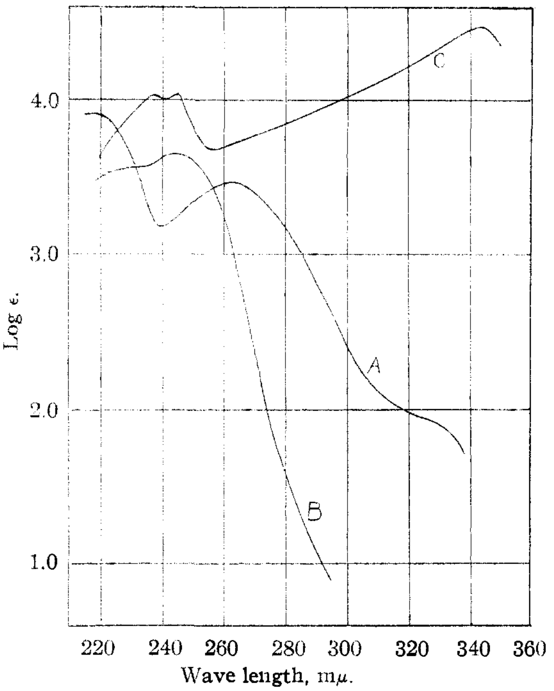

Fig. 2.—Ultraviolet absorption spectra: A, 2-thienol in water; B, methyl 2-thienyl ether in ethanol; C, reaction product of benzaldehyde and 2-thienol, in 2,2,4-trimethylpentane.

The acetyl and methyl derivatives of 2-thienol are practically indistinguishable from their benzene analogs as regards physical properties such as boiling point and odor. This is in marked contrast to 2-thienol itself. The ultraviolet spectrum of the methyl ether, Fig. 2b, emphasizes the fundamental structural differences between it and the parent compound.

Chemical evidence is available also for the thiolactone form of 2-thienol. Ring fission occurs at an appreciable rate in warm acidic or cold alkaline media, yielding hydrogen sulfide and an easily resinified acidic material. Fission is apparently also a major reaction during methylation with methyl iodide or methyl sulfate, which processes yield polymerizable oils. Furthermore, 2-thienol condenses readily with benzaldehyde to yield a neutral compound, apparently the 3- or 5-benzylidene derivative of the thiolactone. Analytical and molecular weight data were both satisfactory for $C_{11}H_8OS$. Its ultraviolet spectrum, given in Fig. 2c, shows strong absorption in the region of 3400 Å., denoting an extended conjugated system.

Finally, mention may be made of the behavior of 2-thienol toward bromine in carbon tetrachloride. Under conditions which sufficed for quantitative monobromination of phenol, 2-thienol consumed only one-third of an equivalent of bromine.

The above results indicate that 2-thienol may exist as a mixture of tautomers, in which the

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(7) Rasmussen, *et al.*, This Journal, **71**, 1068 (1949); Sponer and Teller, *Rev. Mod. Phys.*, **13**, 75 (1941).

thiolactone form is at least partly the 2-butenothiololactone. It is undetermined as yet which tautomer is represented in the crystalline state. Also the equilibrium position of the tautomeric system is not known.

Oxidation of 3-thienylmagnesium bromide in the above-mentioned fashion gave a low yield of a steam-volatile liquid, very weakly acidic and possessing a phenolic odor, which was presumably 3-thienol. Although difficulties in isolation prevented characterization, the material was found to yield an intense vermillion color with ferric chloride, and appeared to couple with diazotized aniline.

Experimental[8]

Oxidation of 2-Thienylmagnesium Bromide.—A Grignard solution was prepared in a 500-cc. flask from 16.3 g. of 2-bromothiophene, b. p. 70–71° (50 mm.), 18.5 g. of isopropyl bromide, and 6.5 g. of magnesium in 200 cc. of anhydrous ether. Dry oxygen was passed into the solution at 0° with stirring. Absorption was rapid and exothermic, requiring a controlled rate of oxygen admission in order to maintain a reaction temperature of 0–5° by means of an ice–salt-bath. Approximately 0.1 mole (2350 cc., S. T. P.) of oxygen was absorbed during one hour, after which absorption ceased. The product, which contained a white granular solid, was stored overnight at −10°. It was then poured on solid carbon dioxide, followed by hydrolysis with a slight excess of cold dilute sulfuric acid. Hydrogen sulfide was evolved. After saturating with sodium chloride, the product was extracted with ether. The ether solution in turn was extracted with cold 20% sodium hydroxide. The resulting neutral material after removal of solvent was 2,2′-bithienyl, b. p. 103° (3 mm.), m. p. 31°, leaflets from ethanol; yield 2.4 g. (29%).

The alkaline extract was acidified immediately with cold dilute sulfuric acid, and extracted with ether after saturating with salt. Hydrogen sulfide was evolved again. This ether solution, after washing with sodium bicarbonate solution and drying over sodium sulfate, yielded 2.5 g. (25%) of light yellow liquid, b. p. 80–84° (6 mm.), which proved to be 2-thienol. On strong cooling, it formed long, colorless needles, which did not remelt at 0°. The distillation residue consisted of a small amount of a dark green solid, whose ether solution was decolorized by sodium hydrosulfite.

The above bicarbonate washings, after acidification with dilute sulfuric acid, extraction with ether, and drying of the ether extract over sodium sulfate, yielded approximately one gram of red-brown gummy oil, which failed to yield any 2-thenoic acid on extraction with hot water.

When the above oxidation was carried out at −5°, on a scale three times larger, there was obtained a 23% yield of 2-thienol and a 12% yield of 2,2′-bithienyl.

When the above oxidation was carried out without the isopropyl bromide but using 0.1-molar amounts of 2-bromothiophene and magnesium in 100 cc. of ether at 5°, oxygen absorption appeared to be very slight. The yield of bithienyl was 25%, but no 2-thienol was isolable. The product did, however, yield a red color with ferric chloride.

2-Thienol.—The combined thienol fractions from several runs were vacuum distilled in an atmosphere of nitrogen. The material distilled entirely at 70–80°, mainly at 75°, under 5 mm. pressure. Its odor was non-phenolic. The colorless center fraction on cooling formed long needles which melted and froze at 7–9°. In a nitrogen atmosphere it boiled at 217–219° under 760 mm. pressure with very slight discoloration. Other physical constants are $d^{20}{}_4$ 1.255; $n^{20}{}_\mathrm{D}$ 1.5644; molecular refraction, obsd., 25.93; calcd. for 2-thienol, 25.85; calcd. for 3-butenothiololactone, 25.99.

The solubility at 25° in hexane was 2%, in water, 6%. It was miscible with all other common solvents. On standing at room temperature, the pure material rather quickly assumed a red color; after 12 hours much resinification had occurred. At −10° it could be stored with only slight coloration.

Anal. Calcd. for C_4H_4OS: C, 47.98; H, 4.02. Found: C, 48.03; H, 4.15.

2-Thienyl Acetate.—Two grams of 2-thienol was dissolved in 12 cc. of 10% sodium hydroxide solution and cooled to 0°. Crushed ice was added, then 3 cc. of acetic anhydride, and the mixture was swirled vigorously for several minutes. A heavy oil separated from the red solution. The total product was extracted with ether. The ether extract was washed with cold 5% sodium hydroxide, then with water, and dried over sodium sulfate. After removal of solvent, the residue distilled at 96° under 25 mm. The colorless distillate had a strong ester-like odor, similar to that of phenyl acetate. It solidified at −10 to −20°; yield 1.6 g. (56%).

Anal. Calcd. for $C_6H_6O_2S$: C, 50.68; H, 4.25. Found: C, 50.81; H, 4.25.

2-Thienyl Benzoate.—To 0.3 g. of 2-thienol and 0.4 g. of benzoyl chloride was added 4 cc. of 10% sodium hydroxide. The mixture was heated to boiling with vigorous swirling, then cooled in ice-water. The oil which formed crystallized, yielding 0.4 g. (65%) of product. After recrystallization from a small amount of alcohol, fine, colorless crystals, m. p. 44–45°, were obtained.

Anal. Calcd. for $C_{11}H_8O_2S$: C, 64.68; H, 3.95. Found: C, 64.47; H, 3.93.

Treatment with bromine in carbon tetrachloride gave a halogen-containing solid, m. p. 75–76°.

Methyl 2-Thienyl Ether.—A cold solution of 1.8 g. of potassium hydroxide in 5 cc. of water was added to a mixture of 2 g. of 2-thienol and 3 g. of methyl sulfate cooled in an ice–salt-bath. The mixture was shaken for ten minutes with occasional cooling, then was diluted with water. The red oil which separated was taken up in ether, washed with water and dried over sodium sulfate. Removal of solvent left a residue which yielded 0.5 g. (22%) of a colorless liquid distilling at 70° (50 mm.). There remained a large amount of a red sirup having an objectionable odor. The sirup was converted to a semi-solid on extended heating, but could apparently be distilled at lower pressures. The lower-boiling distillate showed a boiling point of 153–155°, and had the odor of anisole. It was unaffected by warm alkali.

Anal. Calcd. for C_5H_6OS: C, 52.60; H, 5.29. Found: C, 52.77; H, 5.50.

None of this ether was formed by the action of methanolic hydrogen chloride on 2-thienol, or by treating 2-thienol with methyl iodide and anhydrous potassium carbonate in refluxing acetone. In the latter experiment there was obtained a yellow, viscous oil, b. p. 90–100° (15 mm.), resembling the by-product of the methyl sulfate reaction.

Diazomethane reacted with 2-thienol in ether solution without appreciable evolution of nitrogen. An insoluble yellow solid was formed.

5-Phenylazo-2-thienol.—One gram of aniline was diazotized in hydrochloric acid solution and added to 0.6 g. of 2-thienol dissolved in 20 cc. of 10% potassium hydroxide. There immediately resulted an intense violet-colored solution along with some dark red solid. An odor resembling phenylhydrazine was detected. Acidification of the filtered solution yielded 0.7 g. of red 5-phenylazo-2-thienol which melted indistinctly at 120–125°.

Anal. Calcd. for $C_{10}H_8N_2OS$: N, 13.72. Found: N, 14.10.

When the reaction was carried out in sodium acetate solution, coupling was less rapid, but a red solid formed within one minute. No reaction was observed in acid solution.

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[8] All melting and boiling points are corrected. Analyses were carried out by J. Anderson, M. Ledyard, P. Craig and N. Mold.

On substituting *p*-nitroaniline for aniline, immediate coupling occurred in alkaline solution to yield a red dye, similar in appearance to that obtained with aniline.

2(or 4)-Benzylidene-3-(or 2)-butenothiololactone.—To a solution of 0.2 g. of 2-thienol and 0.5 g. of benzaldehyde in 5 cc. of ethanol was added a drop of concentrated hydrochloric acid. Warming on the steam-bath for five minutes, then steam distillation to remove excess of aldehyde, furnished 0.2 g. of a solid which, on two recrystallizations from ethanol, was obtained as light yellow needles, m. p. 97.5–98.5°. The product was insoluble in alkali.

Anal. Calcd. for $C_{11}H_8OS$: C, 70.19; H, 4.28. Found: C, 70.17; H, 4.34.

This synthesis was repeated by Mr. Hugh J. Anderson, who determined its molecular weight cryoscopically in camphor: found, 191; calcd., 188.

Reaction of 2-Thienol with Bromine.—A solution of a weighed amount of 2-thienol in carbon tetrachloride was treated with a known excess of 0.2 *N* bromine in carbon tetrachloride solution in a closed system at −5°. After momentary mixing, the excess bromine was consumed by the addition of potassium iodide solution, and the resulting iodine titrated with thiosulfate. It was thus found that 0.31 mole of bromine had reacted for each mole of thienol present. An identical experiment using phenol in place of 2-thienol consumed 1.00 mole of bromine per mole of phenol.

Repetition of the experiment with 2-thienol, but at 25° for a reaction period of ten minutes resulted in the consumption of 1.09 moles of bromine per mole of thienol present.

Miscellaneous Reactions of 2-Thienol.—When an aqueous solution of 2-thienol was treated with dilute ferric chloride, a light red color appeared. On standing a red flocculent precipitate gradually formed.

A dilute solution of 2-thienol in 20% potassium hydroxide converted a suspension of cadmium carbonate to the yellow cadmium sulfide within 15 minutes at room temperature.

A dilute solution of 2-thienol in 15% sulfuric acid evolved hydrogen sulfide when warmed on the steam-bath.

Addition of a drop of 2-thienol to 10 cc. of ammoniacal silver nitrate resulted in the formation of a silver mirror within one minute.

The characteristic deep blue color of the indophenin test was generated when 2-thienol in thiophene-free benzene was treated with isatin and sulfuric acid.

Oxidation of 3-Thienylmagnesium Bromide.—A Grignard solution was prepared from 54 g. of 3-bromothiophene,[9] b. p. 156°, 54 g. of ethyl bromide and 19.5 g. of magnesium in 500 cc. of ether. This was added under nitrogen to a solution of isopropylmagnesium bromide prepared from 50 g. of isopropyl bromide and 10 g. of magnesium in 150 cc. of ether. The resulting mixture was treated with oxygen at 0–10° and worked up as previously described for 2-thienol. There was obtained approximately 4 g. of an alkali-soluble, bicarbonate-insoluble liquid having a phenolic odor. Attempts to purify this material by distillation or crystallization were unsuccessful. The crude product gave an immediate bright-red color with dilute ferric chloride. Treatment with diazotized aniline in alkaline solution yielded a red-brown solid product.

Twenty-two grams of 3-bromothiophene was recovered from the original oxidation product.

When a Grignard solution was prepared from 3-bromothiophene as described above and poured on solid carbon dioxide, the yield of 3-thenoic acid was 28%. One-half of the 3-bromothiophene was recovered unchanged.

Summary

A method has been developed for introduction of the hydroxyl function into the thiophene nucleus by oxidation of the thienylmagnesium bromide. 2-Thienol has been isolated and characterized. Its behavior indicates the existence of tautomeric forms. Evidence was obtained also for 3-thienol but it was not isolated as such.

[9] Steinkopf, *Ann.*, **543**, 128 (1940).

EVANSTON, ILLINOIS RECEIVED JUNE 22, 1950

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Polymerization Induced by Catalytic Decomposition of Formic Acid at Platinum Surfaces

BY GIUSEPPE PARRAVANO

In a previous communication[1] it has been shown that addition polymerization reactions of a vinyl monomer can be obtained during the catalytic decomposition of hydrazine solutions at palladium surfaces. This effect has been interpreted in terms of chain reactions, initiated at catalytic surfaces and proceeding in the surrounding liquid medium, away from the initiating center.

A similar mechanism is found to be operative during the heterogeneous catalyzed decomposition of formic acid solutions at room temperature. Polymerization reactions have been observed in an aqueous solution of methyl methacrylate in the presence of formic acid or sodium formate solutions and catalytic surfaces such as platinum, palladium, silver and charcoal. In this communication we present the results obtained in the more detailed study of the decomposition of formic acid solutions at platinum surfaces.

It is known[2] that the decomposition of formic acid at metal surfaces involves a dehydrogenation reaction which yields carbon dioxide and hydrogen. At room temperature, however, the catalytic activity of platinum metal is very low, but can be markedly increased by the presence of oxygen.[2] This may be attributed to strong adsorption of the product hydrogen on the pure metal and its oxidation to water in presence of oxygen. The present work confirms the fact that no significant decomposition of formic acid can be detected at room temperature if oxygen is thoroughly excluded from the system. When oxygen is present, a small fraction of the total decomposition processes gives rise to radicals

[1] Parravano, THIS JOURNAL, **72**, 3856 (1950).

[2] Müller and Schwabe, *Z. Elektrochem.*, **34**, 170 (1928).