

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<sup>2</sup> 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<sup>7</sup> from diethyl  $\beta$ -(2-pyridyl)-ethyl malonate in 70% yield, b. p. 72° (12 mm.);  $n_D^{20}$  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

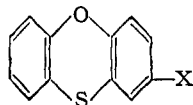
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[CONTRIBUTION FROM THE PITTSFIELD LABORATORY, APPARATUS DEPARTMENT, GENERAL ELECTRIC COMPANY]

## Vinyl Compounds: Phenoxathiin and Dibenzothiophene Derivatives

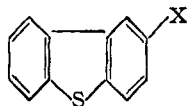
BY RALPH G. FLOWERS AND LEOLA WILLS FLOWERS

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 =  $-\text{COCH}_3$   
 II, X =  $-\text{CHOHCH}_3$   
 III, X =  $-\text{CH}=\text{CH}_2$

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



IV, X =  $-\text{COCH}_3$   
 V, X =  $-\text{CHOHCH}_3$   
 VI, X =  $-\text{CH}=\text{CH}_2$

The 2-acetylphenoxathiin (I) was prepared by a Friedel-Crafts reaction, using a modification of the work reported by Suter, McKenzie and Maxwell.<sup>1</sup> 2-( $\alpha$ -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<sup>2</sup> have prepared the 2-

(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.*, **8**, 108 (1939); (c) Burger and Bryant, *ibid.*, **4**, 119 (1939).

acetyldibenzothiophene (IV) which we have hydrogenated to the 2-( $\alpha$ -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<sup>3</sup>

**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-( $\alpha$ -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<sup>4</sup> were placed in a glass lined, high pressure bomb. The reaction was carried out in the presence of hydrogen at 160° at

(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.

pressures ranging from 2000 to 2400 p.s.i. with shaking for five hours. The reaction mixture was filtered to remove the catalyst. After the solvent had been distilled off, 64 g. (90% yield) was crystallized out of ligroin as small white needles, m. p. 65–67°.

*Anal.* Calcd. for  $C_{14}H_{12}O_2S$ : C, 68.84; H, 4.95. Found: C, 68.59; H, 4.99.

**2-Vinylphenoxathiin (III).**—Forty-seven grams of II was dissolved in 100 cc. of benzene, and introduced into the top of a vertical stainless steel column 1" in diameter and 18 in. long. This reaction column was packed with alumina pellets<sup>5</sup> and maintained at a temperature of 340–360° and a pressure of 10–20 mm. The reaction products were collected in an ice-cooled receiver and then recrystallized from alcohol: 35 g., 79% yield, of III was obtained which had a melting point of 39.5–41°. The infrared absorption spectrum of this compound was marked by the absence of absorption bands due to the contributions of the carbonyl and hydroxyl groups.

*Anal.* Calcd. for  $C_{14}H_{10}OS$ : C, 74.33; H, 4.47. Found: C, 74.30; H, 4.69.

**Polymers of III.**—This monomer was found to polymerize very readily with heat or with any of several catalysts.<sup>6</sup> Such catalysts as boron trifluoride, benzoyl peroxide, *t*-butyl hydroperoxide and potassium persulfate were employed. These polymers were precipitated from benzene solution with methyl alcohol as white powders having softening points of about 200°.

A disk of polyvinylphenoxathiin prepared by heating the monomer in an open beaker at 130° for one hour, was hard, transparent and brittle at room temperature but it was very pliable at temperatures above 200°. The electrical properties of the disk were determined at 25°. At 60 cycles, the polymer had a power factor of 0.108% and a dielectric constant of 3.42. At one megacycle, the power factor was 0.15% and the dielectric constant was 3.34.

**Copolymers of III.**—One part of III was copolymerized with 0.8 part vinyl acetate, 1.0 part acenaphthylene, 1.0 part styrene, 0.6 part acrylonitrile, 1.0 part maleic anhydride and 0.35 part butadiene.<sup>7</sup> The butadiene-III copolymer was made by polymerizing in an emulsion. This product formed a tough, pliable film with good electrical properties.

**2-( $\alpha$ -Hydroxyethyl)-dibenzothiophene (V).**—Ninety-eight grams of IV, dissolved in 1400 cc. of absolute methyl alcohol, was heated with shaking in the presence of a copper-chromium oxide catalyst and 2000 p. s. i. of hydrogen.

(5) Harshaw Chemical Company, Cleveland, Ohio.

(6) Flowers and Flowers, U. S. Patent 2,449,527; *C. A.*, **43**, 904 (1949).

(7) Flowers and Flowers, U. S. Patent 2,449,528; *C. A.*, **43**, 1223 (1949).

After reacting for five hours at 130°, the product was filtered to remove the catalyst and then recrystallized from dilute alcohol: 90 g., 91% yield, of white needles, m. p. 61.0–62.0° was obtained.

*Anal.* Calcd. for  $C_{14}H_{12}OS$ : C, 73.65; H, 5.26; S, 14.03. Found: C, 73.87; H, 5.13; S, 13.85.

**2-Vinyldibenzothiophene (VI).**—Thirty-eight grams of V was dissolved in 200 cc. of benzene and this solution was then added dropwise into the top of the vertical reaction column. The column was packed with alumina pellets<sup>5</sup> and maintained at a temperature of 325–350° and a pressure of 10 mm. during the reaction. The product was recrystallized from ethyl alcohol as small white needles, m. p. 45.0–45.5°; 17.5 g., 50% yield, was obtained from the conversion.

In an alternative procedure V and *p*-*t*-butylcatechol, as a polymerization inhibitor, were gently heated in a porcelain crucible until molten. Anhydrous copper sulfate was added to the mixture and heated a few minutes longer. The product was then recrystallized from alcohol.

*Anal.* Calcd. for  $C_{14}H_{10}S$ : C, 79.96; H, 4.76; S, 15.23. Found: C, 79.98; H, 4.77; S, 15.09.

**Polymers of VI.**—Products with high softening points and good electrical properties were prepared by polymerizing the monomer, both with catalysts and with heat alone. In one example VI was placed in a 125° oven for forty hours to give a hard brittle mass. This polymer when molded into a disk at 150° and 20,000 p.s.i. had a power factor of 0.1% and a dielectric constant of 2.8 at one megacycle.

**Copolymers of VI.**—Copolymers which are white powders with softening points ranging from 174° to above 220° were obtained by polymerizing one part of VI with one part of the following monomers: styrene, vinyl acetate, *N*-vinylcarbazole, *N*-vinylphthalimide, acrylonitrile and acenaphthylene.

**Acknowledgment.**—The authors wish to thank Mr. E. D. Elliott, Jr., of this Laboratory for his work on the emulsion polymerization of 2-vinylphenoxathiin.

### Summary

The synthesis and properties are given for 2-( $\alpha$ -hydroxyethyl)-phenoxathiin, 2-vinylphenoxathiin, 2-( $\alpha$ -hydroxyethyl)-dibenzothiophene and 2-vinyldibenzothiophene. Polymers and copolymers have been prepared from the 2-vinylphenoxathiin and from the 2-vinyldibenzothiophene.

PITTSFIELD, MASS.

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