to yield 22 g. (88%) of 4-hydroxy-3,5-dimethoxypropenylbenzene as a yellow oil, b. p. 107–108° at 0.05 mm., refractive index $n^{27}{}_D$ 1.5741.

Anal. Calcd. for $C_{11}H_{14}O_3$: CH_3O, 31.9. Found: CH_3O, 31.9.

Syringaldehyde.—The above reaction was carried through the cooling stage before the treatment with water. The solidified mixture was covered with 400 g. of nitrobenzene and 135 g. of 50% sodium hydroxide solution, and with vigorous stirring it was boiled under reflux for three hours. The reaction mixture was distilled with steam until almost no oil distilled with the steam. The mixture was then cooled, diluted with water, and extracted with ether. The aqueous solution was acidified with dilute hydrochloric acid and extracted with ether. The ether extract was extracted with 21% sodium bisulfite solution. The bisulfite extract was acidified with 50% sulfuric acid and aspirated with air while heating on the steam-bath. After all traces of sulfur dioxide were removed, the solution was allowed to cool. The heavy crystals which separated were filtered, washed with water and air dried to yield 53.5 g. (52%) of syringaldehyde melting at 109–110°. Recrystallization from petroleum ether (b. p. 65–110°) yielded very pale yellow needles melting at 109–110°.

Anal. Calcd. for $C_9H_{10}O_4$: CH_3O, 34.07. Found: CH_3O, 34.01.

The aqueous filtrate was extracted with ether, and the ether was dried with sodium sulfate and distilled, leaving an additional 16 g. (23%) of crude syringaldehyde melting at 108–110°. Recrystallization from petroleum ether raised the melting point to 109–110°.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra were determined with a Beckman model DU quartz spectrophotometer employing 1.0-cm. quartz cells and minimum slit widths. Measurements were made on freshly and accurately prepared solutions containing approximately 0.02 g. per liter in specially purified dioxane.

Acknowledgment.—The author is indebted to the Analytical Department of The Institute of Paper Chemistry for the analyses and ultraviolet absorption spectra reported in this paper.

Summary

Syringaldehyde has been synthesized from 4-hydroxy-3,5-dimethoxyallylbenzene by nitrobenzene oxidation in aniline solution. The intermediate 4-hydroxy-3,5-dimethoxypropenylbenzene has been isolated and characterized. This method affords a simple procedure for obtaining syringaldehyde from pyrogallol or pyrogallol 1,3-dimethyl ether. All steps in the synthesis give high yields. The ultraviolet absorption spectra of the intermediates have been determined.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ALBERTA]

Some Derivatives of Dibenzothiophene

BY ROBERT K. BROWN, ROBERT G. CHRISTIANSEN AND REUBEN B. SANDIN

The discovery of the carcinogenic action of the versatile 2-acetaminofluorene (VII) by Wilson, DeEds and Cox[1] has suggested the possibility that 3-acetaminodibenzothiophene might show similar activity. In this communication is described the preparation of this substance and some related compounds.

The orientation and derivatives of dibenzothiophene have been studied extensively by Gilman and co-workers.[2]

Recently Gilman and Nobis[3] have shown that 4-iododibenzothiophene undergoes an interesting rearrangement when treated with sodamide in liquid ammonia to give 3-aminodibenzothiophene.

In the present work it has been found that by using the sulfoxide of dibenzothiophene in which the oxygen is susceptible to reducing agents, a conversion of dibenzothiophene into 3-aminodibenzothiophene in an over-all yield of 45% can be accomplished. The preparation of dibenzothiophene-5-oxide from dibenzothiophene proceeds without difficulty and in high yields. Subsequent mono-nitration and reduction with stannous chloride and concentrated hydrochloric acid also proceed without difficulty and both reactions afford satisfactory yields of the desired products. The step-wise reduction of 3-nitrodibenzothiophene-5-oxide with stannous chloride and dilute hydrochloric acid has also been carried out, and has afforded 3-aminodibenzothiophene-5-oxide in good yield.

Experimental[4]

Dibenzothiophene-5-oxide (II).—Dibenzothiophene (I) was prepared by the excellent method of Gilman and Jacoby.[2] For the preparation of the sulfoxide the procedure of Fries and Vogt[5] was used. A solution of 15 g. of I in carbon tetrachloride (150 ml.) was treated at 0–5° with chlorine until 6 g. had been added. The solution became red and the addition compound which was produced was hydrolyzed by vigorously shaking the reaction mixture with ice and water. The solid was filtered off and washed with water. The yield of dibenzothiophene-5-oxide melting at 174–180° was 15.8 g. (97%). It was crystallized from benzene and the yield of pure compound was 12.5 g. (77%); m. p. 185–187°.

Anal. Calcd. for $C_{12}H_8OS$: S, 16.0. Found: S, 16.15.

The reduction of dibenzothiophene-5-oxide with stannous chloride and concentrated hydrochloric acid afforded an 85% yield of pure dibenzothiophene.

3-Nitrodibenzothiophene-5-oxide (III).—The nitration of II was carried out by the procedure developed by Gilman and Jacoby[2] for the nitration of the corresponding dioxide. To an ice-cold mixture of 15 g. of II, 33 ml. of glacial acetic acid and 33 ml. of concentrated sulfuric acid, was added with stirring 36 ml. of fuming nitric acid (sp. gr. 1.5) during a period of fifteen minutes. After the resulting clear solution had stood at 0–5° for thirty

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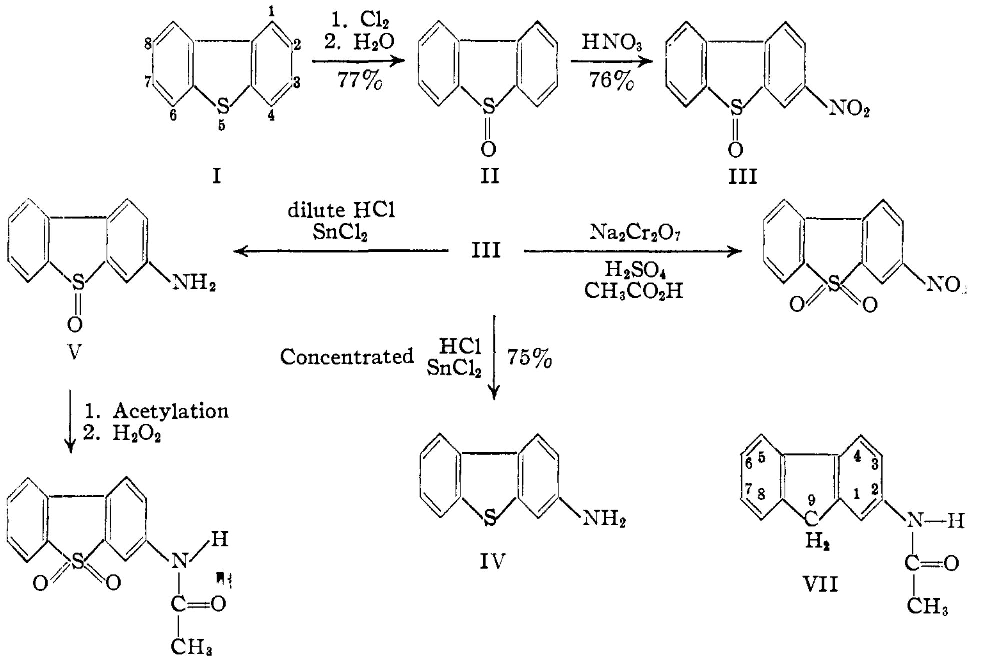
[1] Wilson, DeEds and Cox, *Cancer Research*, **1**, 595 (1941).

[2] Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938); Gilman, Jacoby and Pacevitz, *ibid.*, **3**, 120 (1938).

[3] Gilman and Nobis, THIS JOURNAL, **67**, 1479 (1945).

[4] All melting points are uncorrected.

[5] Fries and Vogt, *Ann.*, **381**, 341 (1911).



minutes, it was poured into 200 g. of cracked ice. The gummy solid which was formed soon hardened and was filtered off and washed with water. The crude material weighed 16.5 g. (87%) and melted at 201–205°. After crystallization from ethyl alcohol the pure 3-nitrodibenzothiophene-5-oxide weighed 14 g. (76%) and melted at 209.5–210.5°.

Anal. Calcd. for $C_{12}H_7O_3NS$: S, 13.06. Found: S, 13.15.

3-Nitrodibenzothiophene-5-oxide was oxidized with a mixture of sodium dichromate, acetic acid and dilute sulfuric acid (1:1). The product after crystallization from acetone was shown to be identical with an authentic sample of 3-nitrodibenzothiophene-5-dioxide.[2]

3-Aminodibenzothiophene (IV).—To a solution of 10 g. of III in 100 ml. of glacial acetic acid was added a solution of 51 g. of hydrated stannous chloride in 65 ml. of concentrated hydrochloric acid. The reaction was exothermic and a solid was formed. After standing at room temperature for twelve hours the solid was filtered off and washed with a mixture of equal parts of glacial acetic and concentrated hydrochloric acid. The amine was liberated with dilute sodium hydroxide solution and the weight of crude material, melting at 113–117°, was 8.1 g. (99%). The pure compound after crystallization from dilute ethyl alcohol weighed 6.1 g. (75%), and melted at 121–122.5°. A mixed melting point with the above amine and the amine prepared by the action of sodamide in liquid ammonia on 4-iododibenzothiophene (kindly furnished by Drs. Gilman and Nobis), was not depressed.

The acetylation of 3-aminodibenzothiophene was readily accomplished by the procedure of Gilman and Nobis.[3] After purification from ethyl alcohol it melted at 196–197°.

3-Aminodibenzothiophene-5-oxide (V).—To a solution of 5 g. of III in 60 ml. of glacial acetic acid was added 26 g. of hydrated stannous chloride in 40 ml. of dilute (6 *N*) hydrochloric acid. The reaction mixture was kept at 40° for thirty minutes and then allowed to stand at room temperature for three hours, after which it was cooled to 0° and the yellow solid was then filtered off. The amine was liberated with sodium hydroxide solution and afforded 4 g. (91%) of compound melting at 206–207.5°. The light yellow compound slowly darkened on exposure to air. For analytical purposes it was crystallized from dilute alcohol, m. p. 208–209°.

Anal. Calcd. for $C_{12}H_9ONS$: S, 14.87. Found: S, 15.05.

The amino sulfoxide is sensitive to heat and for that reason a temperature below 60° during the process of crystallization is desirable.

3-Acetaminodibenzothiophene-5-oxide (VI).—To a solution of 1.8 g. of V in 30 ml. of benzene was added 4 ml. of acetic anhydride. The reaction mixture was allowed to stand for twelve hours. The light yellow solid which was formed melted at 262–264°; yield, 95%. It was crystallized from absolute alcohol; m. p. 265–267°.

Anal. Calcd. for $C_{14}H_{11}O_2NS$: S, 12.44. Found: S, 12.47.

The oxidation of VI in glacial acetic acid with 30% hydrogen peroxide afforded 3-acetaminodibenzothiophene-5-dioxide, m. p. 308–310° (cor. m. p. 322–324°). A mixed melting point carried out with an authentic sample of 3-acetaminodibenzothiophene-5-dioxide[3] was not depressed.

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Summary

The reduction of 3-nitrodibenzothiophene-5-oxide with stannous chloride and concentrated hydrochloric acid affords 3-aminodibenzothiophene. With stannous chloride and dilute hydrochloric acid reduction to 3-aminodibenzothiophene-5-oxide can be accomplished. Some new derivatives of dibenzothiophene have been prepared.

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