

mm. ("International Critical Tables" value 401 mm.) was stored in a 5-liter bulb (Section K, Fig. 1).

The experimental technique used was as follows: A reaction tube (Fig. 2) was sealed on the line (Section G, Fig. 1), evacuated and degassed. Dry air was then admitted through a phosphorus pentoxide drying column and a small hole was blown in the side tube (Section E, Fig. 2). An aluminum bromide capsule was then dropped into the side-arm after the tip had been broken. The hole was sealed and the tube re-evacuated. When the pressure had dropped to *ca.* 10^{-3} mm. of mercury the aluminum bromide was sublimed through the glass wool, into the U-tube (Section C, Fig. 2); Sections E and D were sealed off. The aluminum bromide was then sublimed into the reaction tube proper and Section C was sealed off. In later experiments the glass wool in D was eliminated. The oily film which is put on the glass during fabrication was difficult to remove and seemed to influence the results. The methylcyclopentane was next added, then the olefin, and finally the hydrogen bromide. The reaction tube was sealed off the line at A and warmed to room temperature. The tube was then placed in the constant temperature bath and agitated for the period of the experiment.

If no olefin or alkyl halide had been added the solution was clear; however, if either of these compounds was present in the reaction mixture, droplets of light yellow oil—insoluble in the hydrocarbon—were always noticed to be formed on the glass. When cyclohexyl bromide was used, cyclohexene was mixed with hydrogen bromide in equimolar amounts in a small capsule. The sealed capsule was then placed in the reaction tube. In this case all reagents except cyclohexene were added as previously described. After the aluminum bromide had dissolved in the methylcyclopentane, the tip of the capsule was broken by shaking the reaction tube. Immediately the whole solution became turbid and yellow; in a short while the oil separated on the glass. In the light of the variation in the experimental results mixing is a very serious problem with these rapid reactions.

After the agitation period, the tubes were attached to the line by sealing a ground joint on tube B, Fig. 2, and inserting this joint at E, Fig. 1. The tube was opened by dropping an iron weight enclosed in glass on the break-off in tube B, Fig. 2. The volatile gases were tested for the presence of non-condensables such as hydrogen or methane. In no case was more than 0.04 cc. S. T. P. of gas recovered (*ca.* 0.0001 mole per cent.). The value was determined with the aid of the Toepler pump (Section D, Fig. 1). The hydrogen bromide was difficult to separate quantitatively from methylcyclopentane so no analysis was attempted here. The hydrocarbon was analyzed by index of refraction and infrared spectroscopy. In no case did the infrared analysis reveal the presence of constituents other than cyclohexane and/or methylcyclopentane.

Summary

The reversible isomerization of methylcyclopentane to cyclohexane in the presence of aluminum bromide-hydrogen bromide catalyst has been studied using high vacuum technique. It was found that under certain controlled conditions methylcyclopentane does not undergo isomerization to cyclohexane unless cyclohexene or cyclohexyl bromide in amounts of about 0.05 mole per cent. or higher are present.

The effect of olefins, hydrogen bromide, and aluminum bromide concentrations upon the isomerization of methylcyclopentane has been studied.

A mechanism of isomerization has been proposed.

EVANSTON, ILLINOIS

RECEIVED DECEMBER 11, 1947

[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Synthesis of Syringaldehyde¹

BY IRWIN A. PEARL

In a study of the separation of guaiacyl from syringyl compounds in fractions obtained from lignin oxidations it was necessary to use large amounts of syringaldehyde. A review of the literature revealed numerous reported syntheses of syringaldehyde,²⁻⁸ but yields were all negligible or low, and syringaldehyde has remained more or less of a laboratory curiosity. However, one obvious synthesis of syringaldehyde has been overlooked by other investigators and that is the series of reactions analogous to the synthesis of vanillin from eugenol.

For years vanillin has been manufactured on a

(1) This paper represents a portion of the results obtained in the research program sponsored by the Sulphite Pulp Manufacturers' Research League and conducted for the League by The Institute of Paper Chemistry. Acknowledgment is made by the Institute for permission on the part of the League to publish these results.

(2) Graebe and Martz, *Ber.*, **36**, 1031 (1903).

(3) Guyot, *Compt. rend.*, **149**, 788 (1909).

(4) Mauthner, *Ann.*, **395**, 273 (1913).

(5) Späth, *Monatsh.*, **41**, 278 (1920).

(6) Pauly and Strassberger, *Ber.*, **62**, 2277 (1929).

(7) McCord, *THIS JOURNAL*, **53**, 4181 (1931).

(8) Manske, Ledingham and Holmes, *Can. J. Research*, **22B**, 100 (1945).

large scale from eugenol (the chief constituent of oil of cloves and cinnamon leaf oil) by two general methods. In the first, eugenol is treated with alkali to isomerize it to isoeugenol which, in turn, is oxidized to vanillin by some mild oxidizing agent, such as nitrobenzene and alkali. In the second method, eugenol is acetylated to protect the hydroxyl group, and the acetyleugenol is oxidized by a strong oxidizing agent, such as dichromate and acid or permanganate. The resulting acetylvanillin is then hydrolyzed to vanillin. The present paper describes a synthesis of syringaldehyde analogous to the first of these vanillin syntheses.

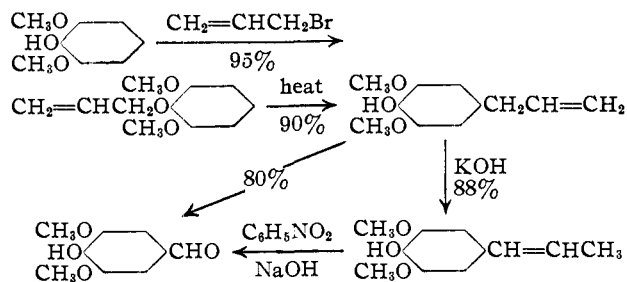
Although the syringyl analog of eugenol is not an easily obtained natural product or article of commerce, its preparation from pyrogallol 1,3-dimethyl ether in good yield has been recorded.^{9,10} Pyrogallol 1,3-dimethyl ether is easily prepared by the controlled methylation of pyrogallol according to Krauss and Crede.¹¹

(9) Mauthner, *Ann.*, **414**, 252 (1917).

(10) Hahn and Wassmuth, *Ber.*, **67**, 702 (1934).

(11) Krauss and Crede, *THIS JOURNAL*, **39**, 1433 (1917).

Pyrogallol 1,3-dimethyl ether was treated with allyl bromide in anhydrous acetone in the presence of anhydrous potassium carbonate and yielded 95% of 2-allyloxy-1,3-dimethoxybenzene; this underwent the Claisen rearrangement to 4-hydroxy-3,5-dimethoxyallylbenzene by boiling under reflux at 75 mm. pressure in a yield of 90%. Isomerization of 4-hydroxy-3,5-dimethoxyallylbenzene to 4-hydroxy-3,5-dimethoxypropenylbenzene by the action of alkali proved to be a more difficult problem. The methods ordinarily employed for isomerizing eugenol to isoeugenol were inoperative because the alkali metal salts of 4-hydroxy-3,5-dimethoxyallylbenzene are only slightly soluble in water. The use of aniline as a solvent solved the problem and a high yield of 4-hydroxy-3,5-dimethoxypropenylbenzene and of syringaldehyde was obtained by an adoption of the process described by Bots¹² for preparing vanillin from eugenol. 4-Hydroxy-3,5-dimethoxyallylbenzene was isomerized to 4-hydroxy-3,5-dimethoxypropenylbenzene by boiling with potassium hydroxide in aniline solution. The propenyl derivative could be isolated in 88% yield. Without separation of the propenyl compound, the entire reaction mixture was treated with more alkali and nitrobenzene and heated to yield 80% of syringaldehyde. The reactions involved are shown by the following formulas.



The ultraviolet absorption spectra of these compounds were determined in anhydrous dioxane with a Beckman spectrophotometer at minimum slit width. These spectra are shown in Fig. 1. The curve for syringaldehyde agrees fairly well with that reported by Patterson and Hibbert,¹³ who determined their curve in ethanol. However, the present curve shows the fine structure of the principal 3050 Å. band.

The curves for the isomers—2-allyloxy-1,3-dimethoxybenzene, 4-hydroxy-3,5-dimethoxyallylbenzene and 4-hydroxy-3,5-dimethoxypropenylbenzene—illustrate the effect of structure on the ultraviolet absorption spectra and emphasize the difference between a conjugated and unconjugated unsaturated side chain. The double bond only becomes a strong resonator in this portion of the ultraviolet when it is conjugated with the ring. Change from an oxygen-allyl linkage to a carbon-allyl linkage results only in slight bathochromic

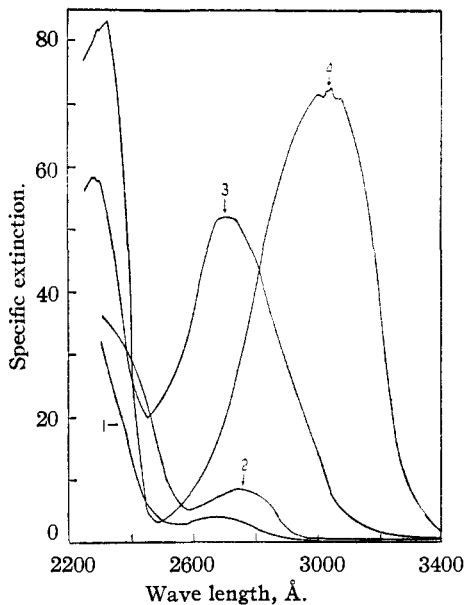


Fig. 1.—1, 2-Allyloxy-1,3-dimethoxybenzene; 2, 4-hydroxy-3,5-dimethoxyallylbenzene; 3, 4-hydroxy-3,5-dimethoxypropenylbenzene; 4, syringaldehyde.

and hyperchromic shifts. These data concur with those of Patterson and Hibbert for eugenol and isoeugenol.

Experimental

All melting points and boiling points are uncorrected.

2-Allyloxy-1,3-dimethoxybenzene.—Pyrogallol 1,3-dimethyl ether (154 g., 1.0 mole) was treated with 121 g. (1.1 mole) of allyl bromide and 180 g. (1.3 moles) of finely powdered anhydrous potassium carbonate in 400 ml. of anhydrous acetone according to the general procedure described by Hahn and Wassmuth.¹⁰ 2-Allyloxy-1,3-dimethoxybenzene was obtained in 184 g. (95%) yield as a colorless fluid oil, b. p. 102° at 2 mm., refractive index n_D^{20} 1.5301.

4-Hydroxy-3,5-dimethoxyallylbenzene.—2-Allyloxy-1,3-dimethoxybenzene was boiled under reflux at 75 mm. pressure according to Hahn and Wassmuth¹⁰ to yield 90% of 4-hydroxy-3,5-dimethoxyallylbenzene as a colorless viscous oil, b. p. 123–125° at 2 mm., refractive index n_D^{20} 1.5478.

4-Hydroxy-3,5-dimethoxypropenylbenzene.—Into a one-liter flask was placed a mixture of 100 g. of 4-hydroxy-3,5-dimethoxyallylbenzene and 50 g. of potassium hydroxide dissolved in 200 g. of water. The flask was connected to a distillation assembly and heated to boiling. After approximately 75 cc. of water had distilled, the boiling temperature began to rise. When the temperature of the mixture reached 110°, 450 g. of aniline was added and the mixture was distilled again. After about 100 ml. of distillate was collected, the boiling solution became thick with precipitate, but all precipitate dissolved when the last traces of water distilled and the temperature of the mixture began to rise. Approximately 150 ml. of distillate had been collected at this point. The distillation was continued until approximately 100 ml. of aniline was collected. The temperature at this point was 179–180°. The mixture was allowed to cool, and the solid material was treated with an excess of water and extracted with ether. The aqueous layer was acidified with hydrochloric acid and extracted with ether. The ether extract was thoroughly washed with dilute hydrochloric acid, and then with water, and finally dried with sodium sulfate and distilled. The residual oil was distilled under vacuum

(12) Bots, U. S. Patent 1,643,805 (Sept. 27, 1927).

(13) Patterson and Hibbert, THIS JOURNAL, 65, 1862 (1943).

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_D^{25} 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.

APPLETON, WISCONSIN

RECEIVED JANUARY 22, 1948

[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 Cox¹ 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 Nobis³ 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.

Experimental⁴

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 Vogt⁵ 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 Jacoby² 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

(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).