

103.5° alone and when mixed with a sample prepared from authentic 2-propylphenanthrene.

*Anal.* Calcd. for  $C_{17}H_{16}C_8H_8O_6N_2$ : C, 63.7; H, 4.4. Found: C, 63.7; H, 4.4.

**2-Phenanthrene-*t*-butyl Alcohol (XXI).** (A) From XX. —A solution of 100 mg. of the ketone in 5 cc. of benzene was treated with excess methylmagnesium iodide and allowed to stand for twelve hours at room temperature. After hydrolysis and extraction of the product with benzene, the carbinol was crystallized from benzene-petroleum ether giving a total of 100 mg. (93%) of material melting at 118.5–119.5°. Another recrystallization of the compound raised this m. p. to 119–119.5°.

(B) From XXII.—When 100 mg. of the ester XXII was refluxed in benzene solution for four hours with excess methylmagnesium iodide and the carbinol isolated as before, there was obtained a total of 95 mg. (95%); m. p. 119–120°. Recrystallization from benzene-petroleum ether gave material melting at 119.5–120°; when mixed with the carbinol prepared in (A) this product melted at 119–120°. Both samples gave dark brown crystals with sulfuric acid with but little color in the liquid.

*Anal.* Calcd. for  $C_{18}H_{18}O$ : C, 86.4; H, 7.2. Found: C, 86.6; H, 7.0.

**1-(2'-Phenanthryl)-propanol-2.**—Reduction of 0.5 g. of the ketone XX with 10 cc. of a *M* solution of aluminum isopropoxide in isopropyl alcohol according to the method of Lund<sup>28</sup> gave 0.44 g. (88%) of the secondary alcohol; m. p. 105–107°. Another recrystallization of the compound from

(26) Lund, *Ber.*, **70**, 1520 (1937).

benzene-petroleum ether raised the m. p. to 107–107.5°.

*Anal.* Calcd. for  $C_{17}H_{16}O$ : C, 86.4; H, 6.8. Found: C, 86.8; H, 6.7.

**Attempt to Convert XIII to Ethyl 2-Phenanthreneacetate.**—Evaporative distillation of this furan derivative at 200° at 0.3 mm. and recrystallization of the acidic material after hydrolysis gave 10% of a mixture; m. p. 200–210°. Similarly, boiling a solution of XIII in acetic acid for fifteen hours, followed by alkaline hydrolysis of the product, gave a mixture of acids melting at 120–170°; after recrystallization from methanol the mixture had the m. p. 145–172°.

### Summary

1. The synthesis of  $\Delta^{1,1'-2'}$ -keto-3,4-dihydro-1,2-cyclopentenophenanthrene is reported.

2. Catalytic reduction of the unsaturated ketone to 2'-keto-1,2,3,4-tetrahydro-1,2-cyclopentanophenanthrene is described, and the extension of the method to the synthesis of compounds of interest in connection with the sex hormones is discussed.

3. Cyclization of ethyl 1-ketotetrahydrophenanthrene-2-acetoacetate to phenanthro[1.2-*b*]furan derivatives is described.

4. 1-Acetyl-2-hydroxy-10,11-dihydrophenanthro[1.2-*b*]furan was converted by heat into 2-phenanthreneacetone.

MADISON, WISCONSIN

RECEIVED MARCH 11, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AND THE LIGNIN AND CELLULOSE RESEARCH LABORATORIES OF THE UNIVERSITY OF WASHINGTON]

## Vanillin from Lignin Materials

BY IRWIN A. PEARL\*

Recently numerous investigators<sup>1-6</sup> have reported high yields of vanillin from lignin containing materials by oxidation with nitrobenzene and aqueous alkali under pressure. These successful experiments with nitrobenzene prompted the use of other low potential oxidizing agents in attempts to obtain high yields of vanillin from lignin materials.

The oxidizing mixture of copper hydroxide in alkaline solution reported by Pearl and Dehn<sup>7</sup> was

\* Present address: Institute of Paper Chemistry, Appleton, Wisconsin.

(1) Freudenberg, Lautsch and Engler, *Ber.*, **73**, 167 (1940).

(2) Schulz, U. S. Patent 2,187,366 (1940).

(3) Lautsch, Plankenhorn and Klink, *Angew. Chem.*, **53**, 450 (1940).

(4) Lautsch and Piazzolo, *Ber.*, **73**, 317 (1940).

(5) Creighton, McCarthy and Hibbert, *THIS JOURNAL*, **63**, 312 (1941).

(6) Creighton, McCarthy and Hibbert, *ibid.*, **63**, 3049 (1941).

(7) Pearl and Dehn, *ibid.*, **60**, 57 (1938).

tried on sulfite waste liquor solids, butanol lignin, and Meadol. High vanillin yields (10–20%) were obtained. Lautsch, Plankenhorn and Klink<sup>3</sup> reported very low yields (3–5%) of vanillin by oxidation of "Cuproxam" or hydrochloric acid lignin with alkali in the presence of lead, silver or copper oxide.

In addition to the oxidations with alkaline copper hydroxide experiments were made using Fehling solution and using copper hydroxide-calcium hydroxide mixtures on the three previously mentioned lignin materials. Yields of 9–16% vanillin were obtained on the basis of the lignin present (Table I).

Vanillin was determined by extracting the acidified reaction mixture with ether. The ether was then extracted successively with 5% sodium bicarbonate and sodium hydroxide solutions. The

TABLE I

Expt.	Reaction mixture	g.	Temp., °C.	Time, hr.	Vanillin, g. <sup>a</sup>	Vanillin, % <sup>b</sup>
1	SWL solids <sup>c</sup>	40	160	5	3.55	21.9
	NaOH	70				
	CuSO <sub>4</sub> ·5H <sub>2</sub> O	80				
	H <sub>2</sub> O	400				
2	SWL solids	50	102	16	2.72	13.5
	NaOH	100				
	CuSO <sub>4</sub> ·5H <sub>2</sub> O	125				
	H <sub>2</sub> O	700				
3	Butanol lignin	5	102	10 <sup>d</sup>	0.60	12.0
	NaOH	20				
	CuSO <sub>4</sub> ·5H <sub>2</sub> O	25				
	H <sub>2</sub> O	150				
4	Meadol	30	102	5 <sup>d</sup>	0.88	2.93
	NaOH	100				
	CuSO <sub>4</sub> ·5H <sub>2</sub> O	125				
	H <sub>2</sub> O	1000				
5	SWL solids	10	102	1	0.39	9.7
	Fehling soln. <sup>e</sup>	500				
6	Butanol lignin	5	102	2	0.69	13.8
	Fehling soln.	500				
7	Meadol	10	102	3	0.37	3.7
	Fehling soln.	600				
8	SWL solids	25	160	8	1.57	15.6
	CaO	100				
	CuSO <sub>4</sub> ·5H <sub>2</sub> O	500				
	H <sub>2</sub> O	100				

<sup>a</sup> Vanillin yields are calculated from the weight of vanillin-2,4-dinitrophenylhydrazones. <sup>b</sup> Vanillin is reported as percentage of initial lignin present in the starting material. <sup>c</sup> SWL abbreviates sulfite waste liquor. <sup>d</sup> All the cupric oxide was not reduced after this time. <sup>e</sup> Fehling solution prepared according to A. O. A. C.<sup>8</sup>

sodium hydroxide extract was acidified, and the vanillin present was estimated by precipitation with 2,4-dinitrophenylhydrazine. In the oxidations of Meadol syringaldehyde was precipitated simultaneously with the vanillin.

The estimation of vanillin as the 2,4-dinitrophenylhydrazone was studied. Brickman, Hawkins and Hibbert<sup>9</sup> used 2,4-dinitrophenylhydrazine to precipitate vanillin and vanilloyl methyl ketone prior to subsequent separation of the two compounds, but no analytical method for vanillin was reported.

Recovery experiments indicated that vanillin was precipitated quantitatively by 2,4-dinitrophenylhydrazine in the presence of excess hydrochloric acid. This method of vanillin determination has certain advantages over the currently used *m*-nitrobenzoylhydrazine method first reported by Hanus<sup>10</sup> and improved by Tomlinson and Hibbert.<sup>11</sup> The precipitation of the dinitrophenylhydrazone takes place under a wide variety of acid concentrations, thus differing from the *m*-

nitrobenzoylhydrazone precipitation. Furthermore, the vanillin-2,4-dinitrophenylhydrazone is always precipitated in a form which is easily filtered, and the filtered precipitate can be dried rapidly in an oven at 110°, thus hastening analysis time. The precipitated vanillin-2,4-dinitrophenylhydrazone is substantially pure, having a methoxyl content of 9.27–9.36% (calcd. 9.34%).

The ratios of syringaldehyde to vanillin in the oxidations of Meadol were determined from the methoxyl contents of the precipitated 2,4-dinitrophenylhydrazones. The obtained values of 2.83:1 in Expt. 4 and 3.11:1 in Expt. 7 agree with the ratio of syringaldehyde to vanillin (approximately 3:1) reported by Creighton, McCarthy and Hibbert.<sup>5,6</sup>

### Experimental

**Starting Materials.**—The sulfite waste liquor solids were of hemlock origin. The waste liquor was substantially freed of sugars by treating with calcium oxide until a pH of 10 was reached. At this point a great deal of the inorganic calcium precipitated. After decanting from the inorganic sludge the liquor was precipitated by alcohol. The precipitated solids were dried and powdered and were used without further purification. They contained 6.51% methoxyl and 13.8% ash. Using Freudenberg's<sup>1</sup> method, the lignin content was estimated by assuming that 90% of the methoxyl was due to lignin and that the lignin in the solids contained 14.5% methoxyl. Thus the solids contained 40.4% lignin.

The butanol lignin was of hemlock origin and was obtained from Dr. A. Bailey at the University of Washington.

The Meadol was kindly furnished by the Mead Corporation of Chillicothe, Ohio. It had a methoxyl content of 22.14% and an ash content of 1.71%.

**Pressure Oxidations.**—To a solution of 80 g. of hydrated copper sulfate in 350 cc. of water contained in a 600-cc. iron autoclave was added with stirring 40 g. of sulfite waste liquor solids. Seventy grams of sodium hydroxide dissolved in 100 cc. of water was then stirred in, and the mixture was heated to boiling with constant stirring. Mixing was stopped, and the autoclave was sealed and placed in an oil-bath at 160°. Heating to 160° was continued for five hours after which time the reaction mixture was allowed to cool. The autoclave contents were transferred to a volumetric flask and made to volume. An aliquot portion (1/50) was taken for vanillin determination.

The pressure oxidation with copper sulfate and lime was performed in the same manner except that the lime was added in a slurry instead of in solution.

**Atmospheric Oxidation with Precipitated Cupric Oxide.**—In a 2-liter 3-neck flask fitted with a reflux condenser, a thermometer reaching below the level of the liquid and a mercury-sealed stirrer were mixed with stirring solutions of 100 g. of sodium hydroxide in 200 cc. of water and 125 g. of hydrated copper sulfate in 500 cc. of water. Fifty grams of powdered sulfite waste liquor solids was gradually added to the alkaline copper solution, and the mixture was

(8) Association of Official Agricultural Chemists, "Methods of Analysis," 1935, p. 482.

(9) Brickman, Hawkins and Hibbert, *ibid.*, **62**, 2149 (1940).

(10) Hanus, *Z. Untersuch. Nahr. Genuss.*, **10**, 586 (1905).

(11) Tomlinson and Hibbert, *THIS JOURNAL*, **58**, 345 (1936).

heated to boiling with constant stirring. Boiling and stirring were continued for sixteen hours. After cooling, the contents of the flask were transferred to a volumetric flask and made to volume. An aliquot portion was taken for vanillin determination.

In like manner butanol lignin and Meadol were oxidized by precipitated cupric oxide in alkaline solution.

In the oxidation of Meadol (Expt. 4) the 15.10% methoxyl content of the 2,4-dinitrophenylhydrazone precipitate indicated that the latter was not the 2,4-dinitrophenylhydrazone of vanillin only, but probably an admixture with the 2,4-dinitrophenylhydrazone of syringaldehyde.

Attempts to separate the original aldehyde fraction by the methods of Hunter and Hibbert<sup>12</sup> and Pyle, Brickman and Hibbert<sup>13</sup> led to the isolation of small quantities of syringaldehyde, but no quantitative separation could be obtained. The syringaldehyde was identified by its 2,4-dinitrophenylhydrazone (m. p. 234–236°) and its semicarbazone (m. p. 186–188°).

Because of the similarity of this reaction to those of Creighton, McCarthy and Hibbert,<sup>5,6</sup> and because of the method of purification before the precipitation with 2,4-dinitrophenylhydrazine, it was assumed that the precipitate obtained with 2,4-dinitrophenylhydrazine was composed substantially of the 2,4-dinitrophenylhydrazones of vanillin and syringaldehyde. The ratio of the two aldehydes was calculated from the methoxyl content of the dinitrophenylhydrazone precipitate.

**Atmospheric Oxidation with Fehling Solution.**—Ten grams of sulfite waste liquor solids dissolved in 200 cc. of water was gradually added with stirring to 500 cc. of mixed Fehling solution and the resulting mixture was boiled under reflux with vigorous stirring for one hour. The reaction mixture was treated as in the preceding experiments.

In the Fehling solution oxidations of Meadol and butanol lignin the lignins were dissolved in dilute sodium hydroxide.

The ratio of vanillin to syringaldehyde in Expt. 7 was calculated in the same manner as in Expt. 4.

**New Method for Vanillin Determination.**—An aliquot of the alkaline oxidation mixture was acidified with dilute

sulfuric acid. The acid solution was extracted ten times by shaking with an equal volume of ether. The combined ether solutions were first extracted five times with 25 cc. of 5% sodium bicarbonate solution to remove acidic substances<sup>14</sup> and then 8–10 times with dilute sodium hydroxide. The combined sodium hydroxide extracts were strongly acidified with hydrochloric acid, filtered if necessary, warmed on the steam-bath, and treated with an excess of a warm filtered solution of 2,4-dinitrophenylhydrazine in dilute hydrochloric acid. Brick red vanillin-2,4-dinitrophenylhydrazone precipitated immediately. The mixture was digested on the steam-bath for one-half hour and then allowed to stand for several hours until cool.<sup>15</sup> The precipitate was filtered through a weighed sintered glass or Gooch crucible, washed with distilled water and dried in an oven at 110°. *Anal.* of original oven-dried precipitate. Calcd. for vanillin-2,4-dinitrophenylhydrazone: OCH<sub>3</sub>, 9.34. Found: OCH<sub>3</sub>, 9.27–9.36. Melting points of oven-dried precipitates ranged from 245° to 260°; recrystallization from dilute dioxane yielded microscopic crystals melting at 263–265°; mixed melting points with an authentic sample of vanillin-2,4-dinitrophenylhydrazone<sup>16</sup> showed no depression. Gravimetric factor = 0.4578.

### Summary

Increased yields of vanillin have been obtained by oxidation of lignin materials with alkaline copper solutions. A new, more rapid method for vanillin determination has been proposed.

Further studies on the oxidation of lignin are in progress.

SEATTLE, WASHINGTON RECEIVED DECEMBER 20, 1941

(14) Cerezo and Olay [*Añales soc. españ. fis. quim.*, **32**, 1090 (1934)] have shown that acids form hydrazides with 2,4-dinitrophenylhydrazine in mineral acid solution.

(15) Iddles and Jackson [*Ind. Eng. Chem., Anal. Ed.*, **6**, 455 (1934)] have shown that at 0° 2,4-dinitrophenylhydrazine precipitates vanillin in 102% yield.

(16) Macbeth and Price, *J. Chem. Soc.*, 152 (1935).

(12) Hunter and Hibbert, *THIS JOURNAL*, **61**, 2193 (1939).

(13) Pyle, Brickman and Hibbert, *ibid.*, **61**, 2199 (1939).