

of other possible acid-catalyzed condensation and addition reactions, such as dioxane or polyethylene oxide formation.<sup>2</sup>

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## NEW COMPOUNDS

### 2-Methyl-4,6-Dichlorophenoxyacetic Acid

**2-Methyl-4,6-dichlorophenoxyacetic Acid.**—4,6-Dichloro-*o*-cresol<sup>1</sup> (3.82 g.) dissolved in 10 ml. of aq. 20% sodium hydroxide was added hot in 1-ml. portions to a hot solution of 4.75 g. of chloroacetic acid in 10 ml. of 20% sodium hydroxide, and the mixture refluxed for four hours. The solution was then made acid and the precipitate removed by filtration. It was dissolved in dilute sodium carbonate and the excess phenol extracted with ether. The product was precipitated from the carbonate solution with acid and crystallized from alcohol-water; yield 3.3 g., m. p. 187–187.5°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>8</sub>O<sub>3</sub>Cl<sub>2</sub>: C, 45.95; H, 3.40. Found: C, 45.87; H, 3.54.

This compound was checked for plant growth activity using the Avena test. The work was done by Dr. Robert Muir, Dept. of Botany, University of Iowa. The compound was found to be inactive. Complete results of these tests will be published elsewhere.

(1) Claus and Riemann, *Ber.*, **16**, 1598 (1883).

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### Some Derivatives of Benzylvanillin and Benzylvanillic Acid

The benzyl ethers of the monochloro and monobromo derivatives of vanillin and benzyl-2-nitrovanillin were prepared by the alkylation of the appropriate vanillin derivative and benzyl chloride in the presence of sodium hydroxide.<sup>1</sup>

**Benzyl Ethers of Derivatives of Vanillic Acid.**—Five grams of the benzyl ether of the requisite vanillin derivative was dissolved in 50 cc. of pyridine and the solution heated

(1) Späth, Orechhoff and Kufner, *Ber.*, **67B**, 1214–1217 (1934).

to 60–70°. A hot (90–100°), concentrated aqueous solution of 5 g. of potassium permanganate was added in small portions. A vigorous reaction ensued with the immediate precipitation of manganese dioxide. The mixture was cooled and filtered. The residue was washed with a little pyridine and the filtrate and washing were combined. The manganese dioxide in the residue was dissolved in sodium bisulfite solution and dilute hydrochloric acid. A white precipitate remained which was extracted with ethyl ether. The pyridine was removed from the filtrate by steam distillation and the residue was extracted with the ether previously used. The ether layer was repeatedly extracted with sodium hydroxide solution until acidification gave no precipitate. The aqueous extracts were combined, acidified and the resultant precipitate filtered, washed with water and dried. It was then recrystallized from the appropriate solvent (either aqueous ethanol or aqueous acetic acid). The properties of some benzyl ethers of derivatives of vanillin and vanillic acid are listed in the accompanying table. The ethers crystallized as colorless needles except where otherwise noted.

### BENZYL ETHERS OF DERIVATIVES OF VANILLIN AND OF VANILIC ACID

Substituent	Yield, %	M. p., °C.	Halogen, % Calcd.	% Found
Vanillin Derivatives				
2-Bromo-	48	99–99.5	24.88	24.61
5-Bromo-	52	49–50	24.88	24.80
6-Bromo-	71	96–97	24.88	24.83
2-Chloro-	73	94	12.81	12.79
5-Chloro-	54	43–44	12.81	12.80
6-Chloro-	58	101–102 <sup>a</sup>	12.81	12.92
2-Nitro-	41	106–107 <sup>b</sup>		
Vanillic Acid Derivatives				
2-Bromo-	74	162–163 <sup>c</sup>	23.70	23.73
5-Bromo-	83	157–157.2	23.70	23.77
6-Bromo-	76	173–174	23.70	23.64
2-Chloro-	74	149–150	12.11	11.94
5-Chloro-	81	154	12.11	12.01
6-Chloro-	60	164–165	12.11	12.09
2-Nitro-	78	183–184 <sup>d</sup>	4.62 <sup>e</sup>	5.08 <sup>e</sup>

<sup>a</sup> Pale orange prisms. <sup>b</sup> Brown needles. <sup>c</sup> Light yellow needles. <sup>d</sup> White plates. <sup>e</sup> % Nitrogen.

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