have been shown to react with biphenyl in Friedel–Crafts reactions to give *p*-substitution products. The structure of the products has been proved by the preparation of derivatives.

2. Vinyl chloride, under variable temperature conditions, forms complex products which cannot be separated by fractional vacuum distillation.

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[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

Rotenone. XXXI. The Synthesis of 2-Hydroxy-4,5-dimethoxyphenylacetic Acid

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By the action of chloromethyl ether on the sodium compound of 2-hydroxy-4,5-dimethoxybenzaldehyde, the corresponding methoxymethyl ether was obtained; by condensation with hippuric acid this compound readily yielded an azlactone from which the 2-hydroxy-4,5-dimethoxyphenylacetic acid was obtained by saponification and oxidation in the usual manner.

Experimental Part

Sodium Compound of 2-Hydroxy-4,5-dimethoxybenzaldehyde.—Six grams of 2-hydroxy-4,5-dimethoxybenzaldehyde was added to a hot solution of sodium ethylate prepared by dissolving 0.8 g. of sodium in 50 cc. of absolute alcohol. The difficultly soluble sodium compound separated on cooling; it was removed by filtration, washed with alcohol and ether, and dried in a vacuum desiccator. The yield was 5.8 g. The alcohol–ether filtrate was evaporated to dryness; the residue was dissolved in a little dilute aqueous alkali, filtered, and the solution was acidified. The recovery was 0.8 g. of unchanged aldehyde.

Methoxymethyl Ether of 2-Hydroxy-4,5-dimethoxybenzaldehyde.—Six and two-tenths grams of the sodium compound was suspended in 30 cc. of dry toluene, and 2.4 g. of chloromethyl ether was added. The suspension was shaken from time to time at room temperature and after two hours 20 cc. of 5% aqueous sodium hydroxide solution was added, together with the same volume of ether. After separation from the aqueous portion, the ether–toluene solution was washed with water, dried, and evaporated. An oily product, which crystallized to a solid mass, remained. The yield was 3.4 g. After recrystallization from petroleum ether it melted at 61°.

Anal. Calcd. for $C_{11}H_{14}O_5$: C, 58.40; H, 6.19. Found: C, 58.33; H, 6.05.

One and a half grams of unchanged 2-hydroxy-4,5-dimethoxybenzaldehyde was recovered by acidification of the aqueous alkaline solution.

Azlactone of Methoxymethyl Ether of 2-Hydroxy-4,5-dimethoxybenzaldehyde.—Two grams of the substituted benzaldehyde, 1.75 g. of hippuric acid, 1 g. of anhydrous sodium acetate and 6 cc. of acetic anhydride were mixed together and heated on the steam-bath for two hours. After cooling, the acetic anhydride was decomposed with water, and the solid products were separated by filtration and washed with water and alcohol. The material was then recrystallized from ethyl alcohol. It separated from concentrated solutions in this solvent as red cubes and from dilute solutions as yellow needles. Both forms melted at 168°, the yellow form turning red at about 150°. The yield was 2.6 g.

Anal. Calcd. for $C_{20}H_{19}O_6N$: OCH_3 (3), 25.2. Found: OCH_3, 24.81.

2-Hydroxy-4,5-dimethoxyphenylacetic Acid.—A suspension of 2 g. of the azlactone in 20 cc. of 10% potassium hydroxide was boiled under reflux for five hours. The solution was then cooled, treated with 10 cc. of 10% hydrogen peroxide added in small portions and allowed to stand overnight. Dilute hydrochloric acid was added carefully until the solution gave a slightly acid reaction to congo paper. The solution was then extracted with five portions of ether, and the ethereal solution was dried over sodium sulfate. The solvent was removed, and the residue was subjected to steam distillation to remove the benzoic acid. At the same time hydrolysis of the methoxymethyl group occurred. The aqueous solution remaining after steam distillation was boiled with decolorizing carbon and filtered. The filtrate was saturated with sodium chloride and extracted repeatedly with ether. The ethereal extract yielded 0.8 g. of substance. It was recrystallized from water. The product obtained melted at 102° but contained water of crystallization, which can be removed by drying to constant weight at about 100°. The anhydrous material melted at 138°.

Anal. Calcd. for $C_{10}H_{12}O_5$: C, 56.6; H, 5.66; OCH_3 (2), 29.24; mol. wt., 212. Found: C, 56.36; H, 6.04; CH_3O, 28.9; mol. wt. (by titration), 217.

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