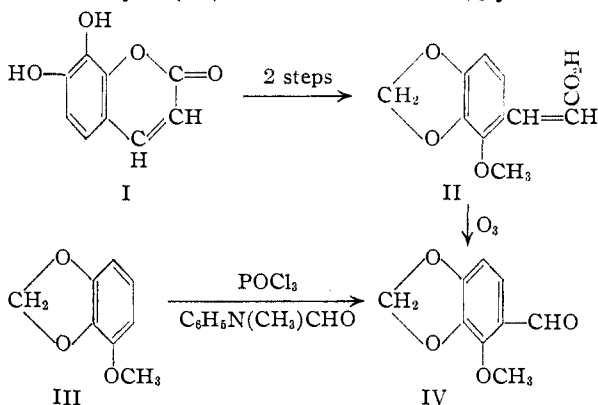


was desired. This aldehyde has been prepared<sup>2</sup> from daphnetin (I) by methylenation, followed by treatment with sodium hydroxide and dimethyl sulfate and ozonization of the resulting cinnamic acid (II).

As an approach to the synthesis of IV, 1-methoxy-2,3-methylenedioxybenzene (III) was treated with phosphorus oxychloride and N-methylformanilide.<sup>3</sup> The aldehyde (IV) was obtained in a 46% yield.



If the aldehydes required for the preparation of the azlactones are available, this reaction has distinct advantages in comparison with procedures described previously.<sup>3,4,5</sup>

**Phenylactic Acid.**—This process illustrates the general procedure. A mixture of 50 g. of azlactone (2-methyl-4-benzal-5-oxazalone), 100 g. of amalgamated zinc and 200 ml. of 6 N hydrochloric acid was refluxed for eight hours. The cold solution was saturated with sodium chloride and extracted repeatedly with ether. The ether was removed by distillation after drying over anhydrous sodium sulfate.

The crude acid recrystallized from carbon tetrachloride had m.p. 95.5–96.5° (uncor.).

*Anal.* Calcd. for C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>: C, 65.06; H, 6.02; neut. equiv., 166. Found: C, 64.81; H, 5.93; neut. equiv., 167.

*p*-Hydroxyphenylactic acid prepared using a similar procedure had m.p. 139–140° (uncor.).

*Anal.* Calcd. for C<sub>9</sub>H<sub>10</sub>O<sub>4</sub>: C, 59.34; H, 5.49; neut. equiv., 182. Found: C, 59.25; H, 5.39; neut. equiv., 178.

A number of benzene-substituted phenylactic acids have been prepared; physical constants and microbial activity will be reported in a later paper.

(3) V. K. La Mer and J. Greenspan, *THIS JOURNAL*, **56**, 1492 (1934).

(4) F. F. Blicke and H. H. Kaplan, *ibid.*, **65**, 1967 (1943).

(5) E. Erlenmeyer, *Ber.*, **13**, 303 (1880).

DEPARTMENT OF AGRICULTURAL CHEMISTRY

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Since III is readily prepared from *o*-vanillin by the method of Baker and co-workers,<sup>4</sup> the present work offers a convenient synthesis of croweacin aldehyde (IV).

#### Experimental

**Croweacin Aldehyde (IV).**—To 13.5 g. (0.1 mole) of N-methylformanilide there was added 15.3 g. (0.1 mole) of phosphorus oxychloride. The solution was allowed to stand for 30 minutes and then 6 g. (0.04 mole) of 1-methoxy-2,3-methylenedioxybenzene<sup>4a</sup> (III) was added. The reaction mixture was heated at 100° for two hours, cooled to room temperature and poured into ice-water. The solid product was collected by filtration and crystallized from dilute alcohol. The weight of material melting at 103° (lit.<sup>2</sup> 104°) was 3.3 g. (46%).

The 2,4-dinitrophenylhydrazone was prepared in the conventional manner and crystallized from ethyl acetate; m.p. 254–255° (lit.<sup>2</sup> 254°).

A portion of the aldehyde was oxidized with potassium permanganate to give croweacin acid, 2-methoxy-3,4-methylenedioxybenzoic acid, melting at 155° (lit.<sup>2</sup> 153°).

(2) A. R. Penfold, G. R. Ramage and J. L. Simonsen, *J. Chem. Soc.*, 756 (1938).

(3) L. N. Ferguson, *Chem. Revs.*, **38**, 231 (1946).

(4) (a) W. Baker, L. V. Montgomery and H. A. Smith, *J. Chem. Soc.*, 1281 (1932); (b) W. Baker and R. I. Savage, *ibid.*, 1607 (1938).

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### A Method of Synthesis of Phenylactic Acid and Substituted Phenylactic Acids<sup>1</sup>

BY EDWARD C. BUBL AND JOSEPH S. BUTTS

The need for large quantities of phenylactic acid for the continuation of metabolic studies was met by the application of a reductive hydrolysis of the azlactone. The azlactones were prepared from the aldehyde and acetylglycine using the well known general procedure.<sup>2</sup> When the azlactones were refluxed with amalgamated zinc and hydrochloric acid, they were converted into arylactic acids in good yields.

(1) Published as Technical Paper Number 658 with the approval of the Director of Oregon Agricultural Experiment Station.

(2) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1.

### Amine-catalyzed Condensations of Benzaldehydes with Phenylacetic Acids<sup>1</sup>

BY ROBERT E. BUCKLES, M. PETER BELLIS AND WILLIAM D. CODER, JR.

In an earlier report<sup>2</sup> the use<sup>3</sup> of triethylamine and tripropylamine as catalysts in the condensations of benzaldehyde and *p*-nitrobenzaldehyde with phenylacetic acid to yield the corresponding  $\alpha$ -phenylcinnamic acids was described. At the same time similar condensations with *p*-nitrophenylacetic acid were reported to give little or no product. Since that time improved methods for the isolation of products from these condensations have been developed, so that the yields of the few condensations originally reported have been raised substantially. A much more extensive survey of the condensations of phenylacetic acid and the nitrophenylacetic acids with various benzaldehydes in the presence of trialkylamines has now been carried out. The results of the reactions are summarized in Table I.

The method appears to be of general value for synthesizing  $\alpha$ -phenylcinnamic acids. The yields obtained were not always as high as those few reported for the Ogialoro<sup>4</sup> modification of the

(1) From the Ph.D. thesis of M. Peter Bellis and the M.S. thesis of William D. Coder, Jr.

(2) R. E. Buckles and E. A. Hausman, *THIS JOURNAL*, **70**, 415 (1948).

(3) M. Bakunin and D. Pecerrillo, *Gazz. chim. ital.*, **65**, 1145 (1935).

(4) (a) A. Ogialoro, *ibid.*, **9**, 428, 533 (1879); (b) A. Ogialoro and E. Rosini, *ibid.*, **20**, 396 (1890).