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Condensation of Vanillin Substitution Products with Acetophenone

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THE OXIDATION OF CITRIC ACID

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In the recent gasometric micro method for the determination of lactic acid in blood devised by Avery and Hastings¹ which measures the carbon dioxide evolved upon oxidation with permanganate, these investigators obtained more carbon dioxide than could be accounted for by the lactic acid known to be present. No other likely constituents of their blood filtrate yielded carbon dioxide and the source of this extra carbon dioxide was not explained. In view of the work on citric acid reported at the meeting of the Academy last year it seemed probable that this substance was the unknown source of this additional carbon dioxide and this led to a study of the oxidation of citric acid with the following results. Oxidation by permanganate in acid solution at 100°C. tends to yield three mols of carbon dioxide and one mol of acetone. At 60° and lower no acetone is formed and the oxidation proceeds along an entirely different path, tending to yield five mols of carbon dioxide. Further light on this unusual behavior has been obtained by studies of the oxidation of acetone dicarbonic acid and also of citric acid in the presence of potassium bromide. Further data on the oxidation of citric acid in the body and its variations in the blood were presented.

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CONDENSATION OF VANILLIN SUBSTITUTION PRODUCTS WITH ACETOPHENONE

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It has been found that the bromine and chlorine substitution products of vanillin² condense with acetophenone in the presence of sodium hydroxide to give mono- and diacetophenone derivatives. Of the vanillalacetophenones, the three monobromo-, the 2,6- and the 5,6-dibromo compounds are yellow; while the 2,5-dibromo and the 2,5,6-tribromo products are practically colorless. The chlorine compounds studied show similar differences. None of the diacetophenone compounds are colored. These products were prepared in order to obtain starting material with which to study further³ the rearrangement of hydrazones to pyrazolines.

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¹ Avery, B. F., and Hastings, A. B., *A. Gasometric Method for the Determination of Lactic Acid in Blood*. J. Biol. Chem. 94: 273-280. 1931.

² Raiford, L. C., and Lichty, J. G., Chlorine derivatives of vanillin and some of their reactions, J. Am. Chem. Soc., 52, 4576-4586 (1930).

³ Raiford, L. C., and Davis, H. L., Condensation products of benzalacetophenone and some of its derivatives. J. Am. Chem. Soc., 50, 156-162 (1928).