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## The Chlorine Derivatives of Vanillin

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## THE CHLORINE DERIVATIVES OF VANILLIN

L. CHAS. RAIFORD AND J. G. LICHTY

The purpose of this work was to complete the possible list of chlorine derivatives of vanillin, and to use these products in testing further the theory that the presence of acidic substituents favors the formation of stereoisomeric aldoximes.

Previous to the work here summarized, only one chlorovanillin was known, the 5-derivative.<sup>1</sup> That product was obtained in this work by the action of chlorine on a chloroform solution of vanillin. 2-Chlorovanillin was prepared from 2-aminovanillin<sup>2</sup> by means of the Sandmeyer reaction. 6-Chlorovanillin was secured by treatment of 3-methoxy-4-acetoxybenzal diacetate with chlorine. Further treatment with chlorine gave the 5, 6-derivative. The 2, 5- and 2, 6-dichloro and the trichloro compounds were obtained by following the methods of Raiford and Stoesser.<sup>3</sup> All compounds have been further characterized by the study of typical aldehyde derivatives. Special attention was given to the oximes. No evidence of steric hindrance was noted in these preparations, and no stereoisomeric oximes have been obtained.

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## MECHANISMS OF ADDITION AND SUBSTITUTION REACTIONS OF FURFURAL AND DERIVATIVES

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In a complete series of substitution reactions (such as halogenation, nitration, mercuration, etc.,) of furfural and its derivatives, it appears that substitution is preceded by addition. For example, in bromination, two atoms of bromine first add to give a relatively unstable intermediate which then loses hydrogen bromide. These preliminary additions may be 1, 2- or 1, 4- or 1, 6- additions depending upon reactants and upon experimental conditions. Accom-

<sup>1</sup> Hann, *J. Am. Chem. Soc.*, 47, 2000 (1925).

<sup>2</sup> Sumuleanu, *Ann. Sci. Univ. Jassy*, 2, 131 (1902).

<sup>3</sup> Raiford and Stoesser, *J. Am. Chem. Soc.*, 50, 2556 (1928).