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## Mechanisms of Addition and Substitution Reactions of Furfural and Derivatives

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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

HENRY GILMAN, G. F. WRIGHT, J. B. DICKEY  
AND A. P. HEWLETT

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).

panying some of these transformations are ring fission and ring closure, and rearrangements involving unsaturated linkages. Typical illustrations of these changes were presented.

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THE TOXICITIES OF SOME ORGANO-LEAD COM-  
POUNDS FOR CANCER AND RELATED STUDIES

HENRY GILMAN, O. M. GRUHZIT, J. D. ROBINSON  
AND E. B. TOWNE

In connection with the application of organo-lead compounds in cancer, some plant diseases and as anti-knock reagents, a pharmacological study has been made of the relative toxicities of a miscellany of products derived from alkyl and aryl lead compounds. Some of the salts reported at this time have varying appreciable solubilities in water.

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THE PREPARATION OF *m*-HYDROXYBENZONITRILE

JAMES B. CULBERTSON, ERWIN L. CARPENTER  
AND ERNEST K. NIELSEN

It has been a general project in this laboratory to prepare the three monohydroxy diphenyl ketimines upon which certain studies have been planned. Last year the preparation of the 2-hydroxy and 4-hydroxy diphenyl ketimines were reported in these Proceedings. The present work has been directed toward the 3-hydroxy diphenyl ketimine. The former pair of ketimines were obtained by the action of the Grignard reagent, magnesium phenyl bromide, upon the corresponding hydroxybenzonitriles. To employ this same synthesis for the 3- or *m*-hydroxy diphenyl ketimine it has been necessary to prepare the appropriate hydroxybenzonitrile. Much greater difficulty has arisen in the preparation of this last nitrile than with the other two.

Ahrens<sup>1</sup> reported the preparation of this nitrile through the application of the Sandmeyer reaction to *m*-aminophenol, replacing the amine group by the nitrile. We have employed his directions

<sup>1</sup> Ahrens, *Ber.* 20, 2953-54 (1887).