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## Effect of Substituents in the Formation and Reactions of Certain Ethers

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to have the halogen in position 5 ( $\text{CHO} = 1$ ). Peratoner [Gazz. Chim. Ital., 28 (1) 235 (1898)] reported a monochloro compound in which the halogen was not oriented, but which may be a 5-derivative. The only dihalogenated vanillin on record is a diiodo compound obtained by Carles, for which no melting point was given, no derivatives prepared, and in which the halogen atoms were not oriented.

In the present work we have obtained the two remaining monobromo compounds, the 2- and 6-derivatives, and two of the possible dibromo substitution products, the 2, 5- and the 5, 6-compounds. Both mono- and dihalogenated compounds have been characterized by the study of several derivatives. All halogenated vanillins condense with amino compounds. No one of them has yet been found to undergo the benzoin condensation. Only one of the stereoisomeric oximes required by theory has been obtained in any case. The nitril obtained from the 5, 6-derivative, viz., 3-methoxy-4-hydroxy-5,6- dibromobenzonitril, resists hydrolysis with alkali to an extraordinary degree.

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## EFFECT OF SUBSTITUENTS IN THE FORMATION AND REACTIONS OF CERTAIN ETHERS

L. CHAS. RAIFORD AND GARRETT THIESSEN

In a previous report on this study it was found by Raiford and Colbert [Jour. Am. Chem. Soc., 48, 2652 (1926)] that the presence of a nitro radical in diphenyl ether interferes with the entrance of bromine to a much greater degree than could have been predicted on the ground of steric hindrance. Owing to lack of time the structures of several derivatives prepared to test this view were left undetermined, for future study. In the present study these have been determined in several cases and a number of other new halogenated derivatives prepared. These experiments have been conducted in the presence of aqueous alkali, a method which was in part standardized and designated in the previous work as the "wet method." In the present work this process has been shown to be capable of two modifications, each with somewhat specific applications which can, in general, be predicted.

A second point of interest in this work is the structure of the

tetrabromo derivative of diphenyl ether obtained some years ago by Cook [J. Am. Chem. Soc., 32, 1286 (1910)] by direct bromination. A number of derivatives of this product have been obtained, but there is still some doubt as to the exact structure of the compound. Negative results are due in part to the stability of diphenyl ether derivatives, which makes it difficult to "split" the compounds in such a way as to recognize the character of the radicals present.

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### ORGANO-LEAD COMPOUNDS IN THE TREATMENT OF CANCER

HENRY GILMAN AND JACK ROBINSON

New organo-lead compounds have been prepared by means of the Grignard reagent. These compounds are being tested in cancer studies, as anti-knock agents, and as reagents to combat some plant diseases. Grignard reagents are being prepared from tetra-*p*-bromophenyl-lead, diphenyl-di-*p*-bromophenyl-lead, and halogeno-alkyl lead types by reaction with the special magnesium-copper alloy using mercuric salts as catalysts. Solubilizing groups like dialkylamino, diethyl-aminoethyl, and various carboxylic acid groups are being attached to the R groups which in turn are attached to lead.

For allied purposes the same types are being prepared where the lead has been replaced by tin, antimony, selenium and tellurium.

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### SOME ABNORMAL REACTIONS OF ORGANOMAGNE- SIUM HALIDES

HENRY GILMAN, J. E. KIRBY, R. E. FOTHERGILL AND  
S. A. HARRIS

Nitro and nitroso groups react with methylmagnesium halides (and other RMgX compounds) to give methane and some ethane. The gases so evolved make it necessary to correct for the ordinary determination of active hydrogen by means of the Zerewitinoff method. Accordingly, the new hydroxy structure proposed for