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## Preparation and Some Properties of Isomeric Carboaryloxyaminoanilines

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is formed with sulfuric acid. The compound from N-chloro-di-n-butylamine has been isolated as a white solid and analysed.

With N-chloro-N-methyl-n-octylamine ring closure apparently occurs with the fifth carbon from nitrogen to form a substituted piperidine. However, complete identification of the compound has not yet been made.

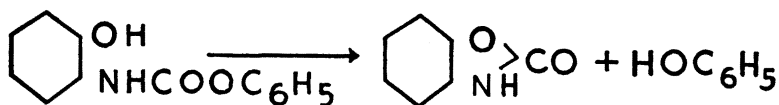
In the application of this method to primary amines n-butylamine was converted to N-chloro-N-n-butyl-p-toluenesulfonamide. Under the usual conditions of ring closure there was formed from this compound a 50% yield of pyrrolidine with a 35% recovery of N-n-butyl-p-toluenesulfonamide.

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## PREPARATION AND SOME PROPERTIES OF ISOMERIC CARBOARYLOXYAMINOANILINES

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Heating 2-aminophenylurethane above its melting point causes loss of alcohol and formation of o-phenyleneurea [Ber., 12, 1296 (1879)]. Attempts to acylate the hydroxyl group of 2-carbophenoxyaminophenol splits off phenol and closes the benzoxazolone ring [J. Am. Chem. Soc., 56, 1590 (1934)], as shown below.



It is now found that when 2-carbophenoxyaminoaniline is heated above its melting point phenol is lost and o-phenyleneurea is formed. If the same aminoaniline derivative is dissolved in caustic alkali solution and the resulting liquid is acidified with dilute mineral acid the cyclic urea indicated above is precipitated. The formation of this urea is favored by the presence of certain substituents in the carbophenoxy radical. Thus, 2-carbo-(2-chlorophenoxy)-aminoaniline decomposes into o-phenyleneurea and 2-chlorophenol in attempts to crystallize the aniline from alcohol. The isomeric meta and para derivatives are much more stable and do not form cyclic ureas under these conditions.

The carbophenoxyaminoanilines required in this work could not be prepared directly from the corresponding phenylenediamines, but were obtained by reduction of the related carboaryloxyamino-nitrobenzenes in acid mixtures. The products were further characterized by study of their simple and mixed diacyl derivatives.

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### THE RÔLE OF ORGANOALUMINUM COMPOUNDS IN THE FRIEDEL-CRAFTS REACTION

ALBERT H. HAUBEIN, LESTER D. APPERSON AND HENRY GILMAN

It was originally suggested by Friedel and Crafts<sup>1</sup> that the reactions which later came to bear their name proceed by way of organoaluminum compounds. Later Leone<sup>2</sup> and co-workers studied the possibility of organoaluminum intermediates by reacting organoaluminum iodide etherates with alkyl halides, acid halides, and ketones. With alkyl halides they obtained small quantities of homologs of benzene together with large amounts of resins, whereas acid halides and ketones gave chiefly condensation products. They concluded that alkylation may proceed by way of an organoaluminum compound, but that ketone synthesis does not involve intermediate organoaluminum compounds because of condensation reactions.

Ketones usually exist as complexes with aluminum chloride in the Friedel-Crafts reaction, and it has been found that these complexes do not give condensation products when treated with organoaluminum halides under moderate conditions. An excellent recovery of ketone was obtained upon hydrolysis. Furthermore, good yields of ketones were obtained by interaction of ether-free organoaluminum halides with either acid chlorides or complexes formed from acid chlorides and aluminum chloride. Likewise, acid anhydrides give good yields of the expected ketones or keto-acids when reacted with ether-free organoaluminum halides.

One may conclude, therefore, that the formation of carbonyl derivatives in the Friedel-Crafts reaction is not inconsistent with

<sup>1</sup> Friedel and Crafts, *Ann. chim. phys.*, [6] 14, 433 (1888).

<sup>2</sup> Leone, *Gazz. chim. ital.*, 55, 294-306 (1925); *Atti II. Congr. naz. chim. pura applicata*, (1926), 1332-7 [*Chem. Zentr. I*, 2174 (1928)].