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The Role of Organoaluminum Compounds in the Friedel-Crafts Reaction

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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

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It was originally suggested by Friedel and Crafts¹ that the reactions which later came to bear their name proceed by way of organoaluminum compounds. Later Leone² 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

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

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

the possible intermediate formation of organoaluminum compounds.

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HIGH MOLECULAR WEIGHT FATTY ACID DERIVATIVES AND THE PHENOMENON OF HOMOLOGY

FRED W. HOYT, BYRON A. HUNTER AND HENRY GILMAN

The studies of compounds derived from lauric, myristic, palmitic and stearic acids have been advanced sufficiently to indicate that the generally accepted principles drawn from the phenomenon of homology apply to these *normal*, long-chained acid derivatives. It appears advisable not to compare all homologous acids, but to break up the series of acids (and their derivatives) so that comparisons are made of *normal* acids, of disubstituted acetic acids, and of trisubstituted acetic acids.

The present evidence is based on several classes of new compounds derived directly or indirectly from the acids: namely, primary, secondary and tertiary amines; ethanol amines; sulfides, sulfoxides and sulfones; (long-chained alkyl) (ethyl) malonates and their condensation products with urea; and organometallic compounds derived from the long-chained alkyl halides.

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MORPHINE ALKALOIDS AND SYNTHETIC DIBENZOFURAN DERIVATIVES

THOMAS H. COOK AND HENRY GILMAN

A continuation of studies patterning synthetic types after morphine alkaloids has now made possible the introduction of substituents into the critical 1-, 4-, 6- and 9-positions. The present report is concerned with methoxy and hydroxy groups in the 4- and 6-positions, and suitably substituted amino groups in the 1-position.