

*SYNTHESIS OF SOME AROMATIC AND HETEROCYCLIC
COMPOUNDS CONTAINING NITROGEN ATOM*



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WALEED ELSAYED BORAIE



Department of Chemistry
Faculty of Science
Ain shams University
Cairo, Egypt
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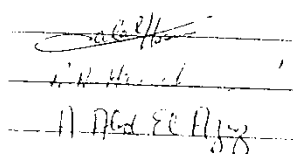
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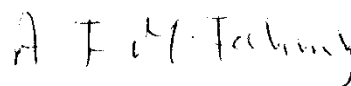
Prof. Dr. G.H. Sayed

Prof.Dr.Ashraf A.M. Hamed

Prof.Dr. A.S Abd-El- Aziz

Thesis approved





Head of Chemistry Department

Prof.Dr. Fahmy , A.F.M .

ABSTRACT

Time-dependent oxidation reactions of η^6 -alkylaniline- η^5 -cyclopentadienyliron hexafluorophosphate, allowed for the preparation of nitrobenzene complexes with alkyl or keto substituents. Alkyl nitroarene complexes were prepared by the oxidation of their corresponding aniline complexes with H_2O_2 in CF_3COOH for 20 minutes. Increasing the reaction time to 24 hours gave rise to nitroarene complexes with keto substituents in lower yields. The use of nitroarenes as starting materials in the synthesis of alkanolic acid esters is of importance since it allows for the preparation of a large number of this class of compounds with a variety of alkyl substituents. Two different approaches were utilized to allow for the synthesis of alkanolic acid esters. The first approach involved nucleophilic aromatic substitution reactions of alkyl nitrobenzene complexes with ethyl alkylacetoacetates followed by demetallation to give alkanolic acid esters. This methodology allowed for the preparation of these esters with a variety of alkyl substituents in either the meta or para positions. Another route outlined the reaction of phenylsulphonylacetonitrile with nitroarene complexes to prepare alkanolic acid precursors with alkyl substituents in the ortho, meta, and para positions. The preparation of a large pool of nitroarene complexes clearly demonstrates the advantage of using the cyclopentadienyliron arene complexes in the synthesis of alkanolic acid esters or their precursors, arylated phenylsulphonylacetonitriles, over traditional synthetic routes. Also, addition of cyanide anions to substituted arene cyclopentadienyliron complexes

containing electron-donating group like alkyl and electron-withdrawing group such as nitrogroup, was investigated. Cyanide addition with these complexes proved to be highly selective, allowing for the formation of one adduct while in the case of sec-butyl group in p-position for nitroarene iron complex gave rise to two isomers due to the asymmetric carbon. Also, the reaction of cyanide anion with p-keto nitroarene complex gave rise to two isomers; one is ortho addition and the other is ipso addition. Selective addition of the cyanide anion with various alkylarylsulphonyl di-iron complexes gave rise to one adduct ortho to the electron-withdrawing sulphonyl group.

Formation of cyanide adducts of poly-iron systems were achieved by selective addition to ortho position of methyl group in polycyclopentadienyliron arene complex with etheric bridges. The nature of some of these adduct were identified by ¹H COSY NMR techniques. Oxidative demetallation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) yielded the substituted benzonitrile and the functionalized uncomplexed polyaromatic ether with cyano groups in good yield and free diaromatic sulfoxide alkane with cyano group in good yield.

Formation of cinnolines cyclopentadienyliron complexes was carried out in two steps. First formation of the hydrazone on a keto group in position 2 of the side chain of o-chloro (substituted benzene) cyclopentadienyliron complex. Second, the nucleophilic substitution carried out on the o-chloro group by the second amino group of hydrazone gave rise the Cp₂Fe complexes of 3-mono-, or 3,4-disubstituted 1,4-dihydrocinnoline.

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