



Available online at: www.basra-science-journal.org

ISSN -1817-2695



Fries rearrangement of 3,5-dimethoxyphenyl acetate

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Accepted 1998

Abstract

3,5-dimethoxyphenyl acetate was studied in the presence of Lewis acid catalyst in different type of solvent (CS_2 , CH_2Cl_2 , $\text{C}_6\text{H}_5\text{Cl}$ and CH_3NO_2) and different temperatures (25°C and reflux). All the products of the rearrangement were isolated and identified by spectrophotometrically methods. The products were checked by using gas - liquid chromatography and the ortho isomer was the major one and in many times was the unique.

Key words: Fries rearrangement, 3,5-dimethoxyphenyl acetate,

Introduction :

Phenolic esters [1] can be rearranged by heating with Friedel-Crafts catalysts in a synthetically useful reaction known as the Fries rearrangement [2-5]. Both ortho and para acetylphenols may be produced. The o/p ratio is depended on the temperature, solvents and the amount of catalyst used [6].

The reaction as a whole and specially the catalyst should be anhydrous lewis acid and the ratio of catalyst : ester is important. Though exception that the para product will favour low temperature and the ortho product will favour high temperature.

Many studies were done by using equal moles of ester and catalyst with or without using solvents, the excess of catalyst (2

moles or more) will introduce not only the migration of acyl groupbut also any alkyl group present in the molecule studied [7].

The mechanism of Fries rearrangement till now was unclear, it will be either an intramolecular [3] or intermolecular [8,9] rearrangement . Blatt [10] was proved by cross over experiment that both inter and intramolecular mechanism was found in Fries reaction.

Finally, Fries rearrangement look like Friedel-Crafts reaction due to the presence of unreacted lewis acid which interferes the compounds which are formed from the dissociation of ester to the corresponding phenols or its salt and the acyl chloride.