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Synthesis and Spectral Characterization of Haloarens by Novel Greener Approach via Thermal Methodology

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ABSTRACT:
A highly greener and cost effective method for the synthèsis of haloarens compound has been acheived through a greener approach via high-thermal method. The main studies of this work are preparing haloarenes reaction without catalyst and confirm the molecule by NMR.

KEYWORDS:
Green-Chlorination, Haloarens, NMR, Thermal Chlorination

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I. INTRODUCTION

The word "Green Chemistry" defined by US environmental protection agency (EPA) as the development of a set of principles that reduces or eliminates the use or generation of hazardous substances in the intend, produce and application of chemical products are widely accepted. Excellent reviews on green chemistry are available [1, 2]. Chlorination it happens with or without catalyst and desire molecule obtained. In producing green synthetic strategies, scientists mainly concentrate on avoiding environmentally non compatible chemicals and that is reagents. Mainly we focus on synthetic routes to decrease number of steps and increase overall process efficiency, use of newer catalyst and simplification of reaction procedure.

During the past decades, researchers focused on the development of more efficient and selective processes for the chlorination of benzene [4–5]. Nowadays, organic chemistry is increasingly moving toward green chemistry, where both homogeneous and heterogeneous catalysis are at the core of this concept. In other concept we focused on de-nitro chlorination reaction without using any catalyst. The combination of these properties led them to exhibit high conversions and excellent selectivitie's in targeted reactions,

Different methods of preparation of chlorofluorobenzenes are known in the art. Pallash (Acta Chim. Acad. Sci. Hung 10:227-232, 1956) have reported by diazotization of 2,4-dichloroaniline and introduced the fluorine using Balz - Scheimann reaction. Also 3-chloro -4- aniline was transformed into 2,4-dichlorofluorobenzene using sandmeyer reaction for introducing chlorine function. The cost of the raw materials used in the above two processes was high and diazotization methods are difficult for operation on commercial scale. Subsequently a new method involving denitrochlorination of a suitably substituted fluorine containing nitrobenzene was applied. Thus 2,4-dinitrofluorobenzene used for denitrochlorination at higher temperature to give 2,4-dichlorofluorobenzene.

Haloarenes are valuable starting molecules in fine chemistry, for the synthesis of dyes, bio-active compounds such as pesticides or pharmaceuticals [3,4]. The chlorination of nitrohaloarenes is a very important process for the production of series of useful compounds in agro chemistry [5,6.7]. It is worthy to study the chlorination of nitrohaloarenes in

order to produce valuable intermediates for the synthesis of azo dyes, [8,9]. agro intermediates.

The aim of the present study is therefore to develop a new chlorination process of deactivated aromatics, being more environmental-friendly by without using any catalyst. In order to achieve this goal, we set up both process to chlorinate nitrohaloarenes without using chlorination agent. We applied greener approach to achieve quality and quantity of the specified molecule.

II. EXPERIMENTAL METHODS

All chemical used in this study were laboratory grade including Orthohalonitroarene, Chlorine, Conc. H_2SO_4 (98%), Conc. HCl (33%), all chemicals were purchased from sigma Aldrich. Bruker Ultra shield 300 MHz spectrometer (Germany) using tetramethylsilane (TMS) as an internal standard.

All solvents were dried and purified by standard techniques just before use. The progress of the reaction was monitored by Gas chromatography (Shemadzu) Melting points (m.p. values) were determined on melting point apparatus and are uncorrected. The 1H and 13C NMR spectra were recorded on Bruker Ultrashield 300 MHz spectrometer (Germany) using tetramethylsilane (TMS) as an internal standard. The chemical shift values are recorded on δ scale and the coupling constants (J) are in Hertz. GC Mass spectrometry was recorded on waters, Q-TOF MICROMASS (GC-MS).

III. RESULTS AND DISCUSSION

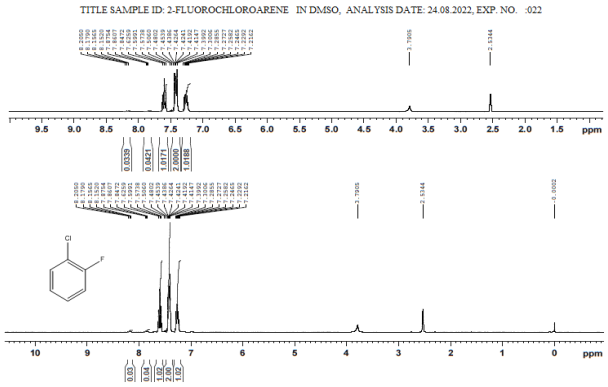
In the present work, Orthohaloarene, prepared by De-nitro chlorination reaction of Orthohalonitroarene, using anhydrous chlorine gas purging at 165□C temperature. Large number of organic reactions can be carried out in higher yield, shorter reaction time and milder conditions. It was observed that the reaction time decreased considerably and the yield of the products increases.

A. Synthesis of Orthohalonitroarene

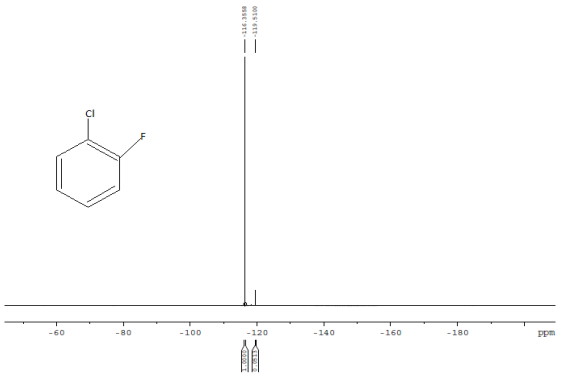
Reaction taken in 50ml 4N RBF, gas purging tube, and reflux condenser all set up over oil bath, Charge 20 g (0.14mol) of Orthohalonitroarene and 25.15 g (0.35 mol) chlorine gas was introduced at a rate of 1.2 g/hr at 165°C for 19-20 hours. The reaction monitoring by Gas chromatography, whereby the conversion of the starting material to Orthohaloarene was 96%. Purification done by distillation under vacuum 16.4 gm **(Yield: 88.4%)**

B. Spectral Characterization

1H-NMR: Orthohaloarene



C13-NMR: Orthohaloarene



C. Properties of Haloarens:

Final Products	Molecular Formula	Molecular weight	Melting point	Boiling point	Density (g/ml)
2-FCA	C_6H_4ClF	130.55	-43.5□C	136.8□C	1.22

D. Reaction parameters to prepare haloarenes:

Compounds	Molecular Formula	Reaction Temperature	Cl2 Rate	Theoretical Yield Gm/%	Practical Yield Gm/%
2-FCA	C_6H_4ClF	160-175□C	1.2 g/hr	18.66/100	16.4/88.4

CONCLUSIONS

From the above spectral characterization H-NMR and C-NMR of data the synthesized compounds containing fluoro & chloro group at ortho state of positions and boiling point matches to confirm that molecule.

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