Electrophilic Substitution Reaction Using ZnCl₂ Catalyst/SiCl₄-Nano3

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Abstract
Development of new Silane reagent derive from SiCl₄ was applied in the presence of NaNO₃ and ZnCl₂ (Homogeneous nitrating system). The nitration proceeds smoothly under mild conditions in good yield. Above reagent consider to be of economic advantage and environment friendly. Above reaction can be used for synthesis of potential drug.

Keywords: Nitration, Sodium Nitrate, Tetrachlorosilane

Introduction
Nitrated aryl compounds remained in dispensable over the last two centuries due to their industrial and commercial applications. They are used as plastics, explosives, agro chemicals, dyes, pigments and polymers. These compounds can be synthesized from aryl pre cursors employing various nitrating agents like nitric acid, metallic nitrates, nitronium salts and acetyl nitrates. But there are major drawbacks in using reagents. These are acidic corrosivity of the nitrating agents, poor regioselectivity and environmental pollutions. As nitrations are usually associated with heat, which may cause secondary reactions or decomposition of final product which leads to low purity and yield. Nitrate salts can be used but the reagent is not cheap. These are difficult to prepare, store and handle.

Method:
First it was used for the nitration of phenol. To a stirred solution of phenol in Dichloromethane (10 ml), NaNO₃ was added. TCS and ZnCl₂ were then added and the reaction mixture stirred at room temperature in the dark for about 40 minutes. After completion of the reactions, water was added and the reaction mixture was extracted with dichloromethane and dried over Na₂SO₄. The solvent is distilled off and resulting crude product can be separated by steam distillation. It can be successfully applied for the preparation of p-Iodonitrobenzene from Acetanilide.

4-Nitrophenol
Yield-55%, Yellow colored solid.
4-Nitrotoluene
Yield-65%, Yellow colored solid.
4-Iodonitrobenzene
Yield-70%, Black colored solid.

Reaction

\[
\text{SiCl}_4 + \text{ZnCl}_2 + \text{NaNO}_3 \rightarrow \text{NO}_2^- + + \text{ZnCl}_3^- + \text{Cl}_3 \text{SiOCl}_3 + \text{NaCl}
\]

…………… (1)……………

Aromatic compound + 1 → Nitrated Aromatic compound
### Table 1: Effect of solvents in the nitration of phenol with NaNO3/TCS

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Conversion of time (min.)</th>
<th>Substrates molar ratios Phenol: NaNO3:SiCl₄ᵃ</th>
<th>Products(s)</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethanol</td>
<td>0</td>
<td>1:1:1</td>
<td>b</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Ethanol</td>
<td>0</td>
<td>1:2:2</td>
<td>b</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Chloroform</td>
<td>260</td>
<td>1:2:2</td>
<td>o-Nitro phenol</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>p-Nitro phenol</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>Dichloromethane</td>
<td>30</td>
<td>1:1:1:5</td>
<td>o-Nitro phenol</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>p-Nitro phenol</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>Dichloromethane</td>
<td>30</td>
<td>1:1:2</td>
<td>o-Nitro phenol</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>p-Notro phenol</td>
<td>60</td>
</tr>
</tbody>
</table>

ᵃ. No reaction was observed in the absence of TCS;
ᵇ. The reaction was exothermic, low yielding.

### References