SRI VENKATESWARA INTERNSHIP PROGRAM FOR RESEARCH IN ACADEMICS (SRI-VIPRA)

Project Report of 2022: SVP-2214

"Green routes to nitration of arenes-An Enquiry"

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SRIVIPRA PROJECT 2022

Title : Green routes to nitration of arenes-An Enquiry

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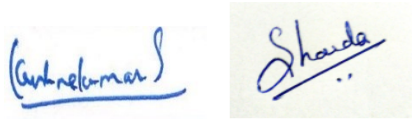
SRIVIPRA-2022
(Sri Venkateswara College Internship Program in Research and Academics)

This is to certify that this project on, "Green routes to nitration of arenes-An Enquiry" (SVP-2214) was registered under SRIVIPRA and completed under the mentorship of **Prof. Sharda Pasricha** during the period from 21st June to 7th October 2022.



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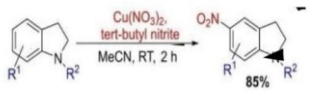
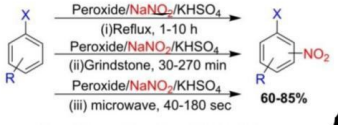
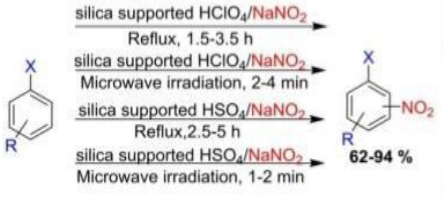
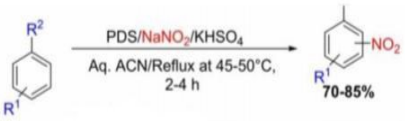
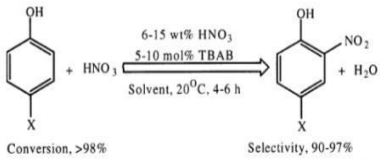
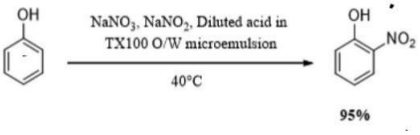
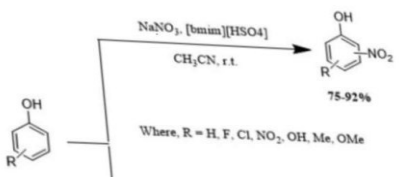
INTRODUCTION

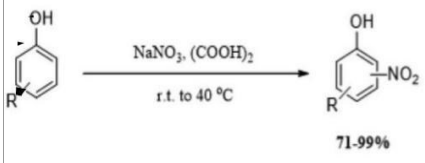
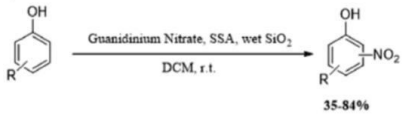
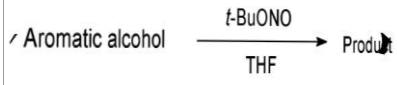
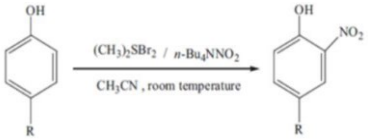
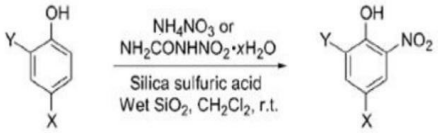
Nitroarenes are important synthetic precursors in industries like agrochemical, pesticides, pharmacology, dyes, polymers, etc. and preparations of those molecules are the most extensively studied chemical reactions. But the classical methods include the use of strong mineral acid like nitric and sulphuric acid. They have several drawbacks like low yield, corrosive nature, not handy, formation of side products, poor regioselectivity, and formation of large amount of waste. Therefore, a green approach for aromatic nitration may improve the yield, reduce the waste, avoid hazards and provide a benign and sustainable method.

Green chemistry refers to the design of chemical products and processes that lessen or do away with the use or production of hazardous materials. Green chemistry covers all aspects of a chemical product's life cycle, including its creation, use, and final disposal. It is based upon 12 principles which aim to minimize or eliminate the risks associated with chemical feedstocks, reagents, solvents, end products, and also decrease pollution at its source.

Green nitration may be defined as the nitration involving green and eco-friendly reagents, economically favoured conditions, high atom economy, energy efficient reactions. The protocols which are economical, have high atom economy and sustainable are need of the hour. Methods which can eliminate the use of hazardous chemicals (nitric acid and sulphuric acid used in conventional methods), use a renewable source of energy, involve a benign protocol, maximize yields, minimize waste at the molecular level and cause minimum environment pollution will be most suitable. etc. Some of the recently reported reactions for green nitration are illustrated in the **Table 1**.

Table 1: Recently reported Green Methods for Nitration of Arenes

	Substrate	Reagent	Time	Reaction	Pros
1	Indoline	tert-butyl nitrite and Cu(*catalyst*)	1-2 hr		Highly selective at the C-5 position, room temperature., Yield -85%
2	Aromatic and heteroaromatic compound	Peroxides, NaNO2, and KHSO4 (*catalyst*)	40 sec to 270 min		Mild reaction conditions, less time and high yield
3	Aromatic compounds	NaNO2 and SiO2/HClO4 & SiO2/KHSO4.(*catalyst*)	1 min to 3.5 hr		Eco-friendly, recyclable catalyst, less reaction time, and high yield.
4	Substituted phenols	Prussian blue, NaNO2, KHSO4 and CH3CN	1-3 hr		Eco-friendly reagents, mild reaction conditions , and high yield.
5	Substituted phenols and naphthols	PDS, NaNO2, KHSO4, ACN	2-4 hr		Mild condition, green reagents, less reaction time and good yield
6	Substituted Phenols	Glacial acetic acid, KNO3, and yttrium nitrate (*catalyst*)	3 min to 3 hr		High yield, less reaction time and mild reaction conditions
7	Substituted Phenols	(NaNO3) dilute sulfuric in TX100 [polyoxyethylene (10) isooctylphenyl ether] O/W microemulsion and dilHCl (*catalyst*)	----		Highly selective, high-yield, Non-toxic reagents, mild reaction conditions
8	Substituted Phenols	(SiCl4), (NaNO2), wet SiO2 in (DCM)	-----		Ortho-selective, high-yield, reusable silica gel, easily available reagents
9	Substituted phenols	NaNO3, CH3CN, Diethyl ether and ionic liquid (*catalyst*) ([bmim][HSO4])	30 min		Mile reaction conditions, highly selective, high-yield, less reaction time

10	Substituted phenols	Nano3 and oxalic acid (*catalyst*)	----		Solvent-free, room temperature, High yield
11	Substituted Phenols	Ionic Liquid [bbim]BF4 or ionic liquid ethyl ammonium nitrate, ferric nitrate	----		Less reaction time, high selectivity and recyclable ionic liquid
12	Substituted phenols	Guanidinium nitrate, silica sulphuric acid(*catalyst*), DCM, silica	15-420 min		Less reaction time, good yield, mild reaction conditions
13	Substituted phenols	THF, t-butyl nitrite.	1-3 hr		Highly selective, good yield, less reaction time, room temperature conditions
14	Substituted phenols	Bromodimethylsulfonium bromide (*catalyst*), tetrabutylammonium nitrite, CH3CN, NaHCO3	1-2 hr		Mild reaction conditions (Stirring at room temperature), high yield, High selectivity
15	Aromatic compounds	Silica sulphuric acid, poly(4-vinyl pyridinium nitrate), and DCM	1-3 hr		Mild reaction conditions (Stirring at room temperature) and goof yield

Present work:

In search of a green nitrating agent, we have carried out nitration of salicylic acid using several reagents, which are as follows:

1. Calcium Nitrate & Acetic acid.
2. Sodium nitrate, Sodium nitrite, oxalic acid.
3. Copper nitrate, Sodium nitrate, oxalic acid.
4. Calcium nitrate, Tartaric acid, Potassium persulphate, and Ethanol as solvent.
5. Calcium nitrate, Oxalic acid, Potassium persulphate, and Ethanol as solvent.
6. Calcium nitrate, Tartaric acid, Potassium persulphate, and Acetone as solvent.
7. Calcium nitrate, Oxalic acid, Potassium persulphate, and Acetone as solvent.

The solid obtained in each case was weighed for yield, and melting point of recrystallized sample was compared with the literature value of the intended product 5-nitrosalicylic acid. TLC of the sample was run with the standard sample to know the purity and identity of the sample. The characterization and identification is in progress.

Future aspect- We would like to continue with exploring and finding best nitrating agent for the reaction. The aim is to find a green method of nitration and replace the use of traditional nitrating agents; nitric acid and sulphuric acid used for nitration at undergraduate level.