VISIBLE-LIGHT-DRIVEN OXIDATIVE COUPLING BY ROSE BENGAL

AND

SYNTHESIS OF PHOTOREDOX CATALYST

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SUBJECT :- CGO-500

ROLL NO.:-CH-18-035

SCHOOL :- School of Chemical Science

Goa University

CERTIFICATE

This is to certify that the work included in the dissertation entitled," Visible-Light- Driven Oxidative Coupling by Rose Bengal and Synthesis of Photoredox Catalyst" is bonafide work done by 'Teja T. Kankonkar' during the period of study under my guidance in partial fulfilment of the requirements for the award of the degree of Master of Science in Chemistry at the School of Chemical Science, Goa University.

Dr. Sandesh Bugde

Guiding Teacher

School of Chemical Science

STATEMENT

I hereby declare that the matter presented in this dissertation entitled, "Visible-Light- Driven Oxidative Coupling by Rose Bengal and Synthesis of Photoredox Catalyst " is based on the result of investigation carried out by me in the Department of Chemistry, School of Chemical Science, Goa University under the supervision of Dr. Sandesh Bugde and the same has not been submitted elsewhere for the award of Degree.

ACKNOWLEDGEMENT

It gives me an immense pleasure to present this project report entitled, "Visible-Light-Driven Oxidative Coupling by Rose Bengal and Synthesis of Photoredox Catalyst ".

The success and final outcome of this project required a lot of guidance and assistance from many and I am extremely privileged to have got this all along the completion of my project. All that I have done is only due to such supervision and assistance and I would not forget to thank them.

I take this opportunity to express my deep gratitude and indebtedness to my project guide Dr. Sandesh Bugde, Assistant Professor, School of Chemical Science, Goa University for his valuable guidance, encouragement and thoughtful discussion during the course of work. I am very grateful to him to give us the opportunity and appreciating ideas and allowing us the freedom to take the tasks independently, helping us to explore the things and enriching us with the knowledge.

My sincere thanks to Prof. V. S. Nadkarni- Head of the School of Chemical Science, Goa University for permitting me to carry out this project work in our laboratory by providing all the necessary facilities during the project work.

I am grateful to the other teaching and non-teaching staff of the School of Chemical Science, Goa University.

I am grateful towards Research students, for helping me for doing flash chromatography and to record IR spectra.

My deep sense of gratitude goes to all my friends and classmates for helping me.

And last but not the least I would like to acknowledge the moving support and encouragement of my parents.

ABBREVIATIONS

General abbreviations

Min:- Minutes

Hrs:- Hours

CFL:- Compact Fluorescence Bulb

g :- Grams

mL:- Milliliter

Techniques

TLC plate :- Thin Layer Chromatography plate

ATRP :- Atom Transfer Radical Polymerization

Compounds

DMA :- Dimethylacetamide

DMSO :- Dimethyl Sulfoxide

DMF :- Dimethylformamide

DABCO :- 1,4-diazabicyclo[2.2.2]octane

TMEDA :- Tetramethylethylenediamine

PET Ether :- Petroleum Ether

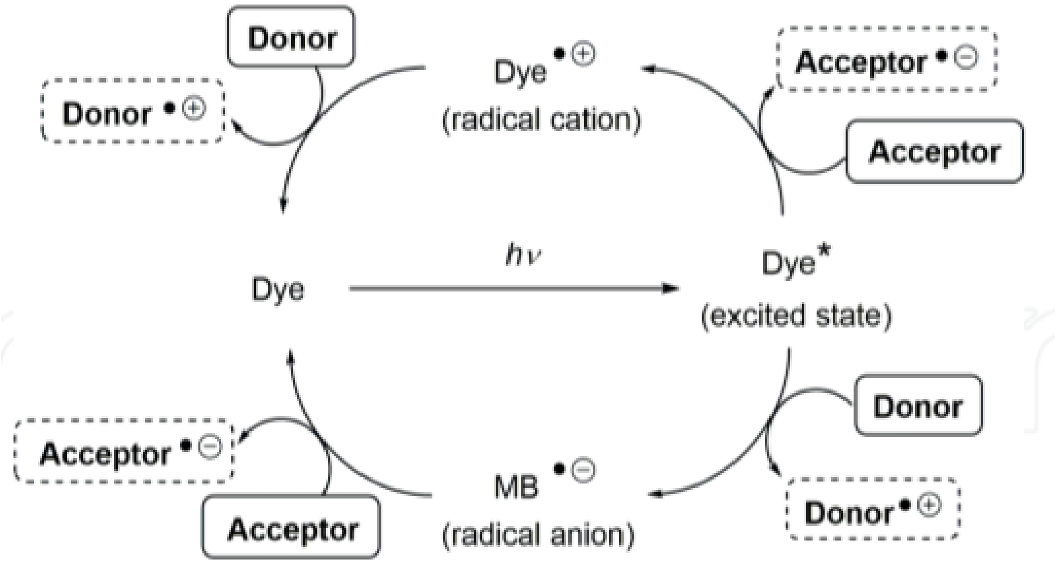
NaH :- Sodium Hydride

INDEX

INTRODUCTION

Photoredox catalysis is the branch of catalysis which uses light to accelerate the chemical reaction. This take place by single electron transfer. Photoredox catalysis involves small quantities of light sensitive compound that when excited facilitate the transfer of electron between chemical compounds that doesn't react at all.

The Photoredox Catalyst has open the door to develop the new methods for the synthesis of known compound and new chemical transformation are also possible. The Photoredox Catalyst are usually less toxic than traditional reagents like organotin compounds to generate the free radicals. The Photocatalyst have developed the several new modes of reactivity based on electron and energy transfer between Photoexcited Catalyst and various organic molecules. It has given the environmental friendly alternative to the most of the chemical transformations.



The Photoredox Cycle is initiated by the visible light irradiation of Photocatalyst in the ground state (cat) to the excited state (cat) *. In excited state the catalyst can either undergo the oxidative quenching or reductive quenching. If the excited catalyst (cat) *, donates it's electron to the substrate or oxidant then it form the radical cation (cat)$^{\cdot +}$ which then reduced by the substrate to (cat). Here the catalyst in excited state act as a reductant. If the excited catalyst (cat) *take electron from the substrate or reductant then it form the radical anion (cat)$^{\cdot -}$ This radical anion (cat)$^{\cdot -}$ is then oxidized by substrate to (cat). Here the excited catalyst act as a oxidant.

Mostly the metal polypyridyl complexes and organic dyes act as a Photoredox Catalyst. Organic

Photoredox Catalysis give a' metal free' approach for the synthesis of new compounds and for doing the Photoredox reaction. This is an alternative to the transition metals. It gives diversity of organic compounds that act as a Photoredox Catalysis which are unreactive for most synthetic context. It was found that the transition metal complexes are very much efficient to do many organic transformations and synthesis. But as these metals are costly, toxic and present in very less quantities in Earth crust. So for the sustainable and cost mediated issue the chemist found some organic molecules which act as a photoredox catalysts as a alternatives to them. These organic molecules are mostly organic dyes. They are easy to handle, cheaper and require the mild conditions.

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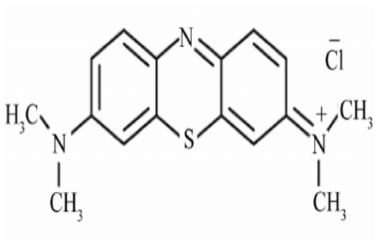
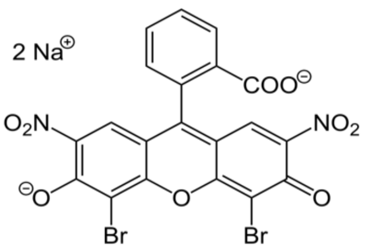
Some of the organic dyes which use as a Photocatalyst are

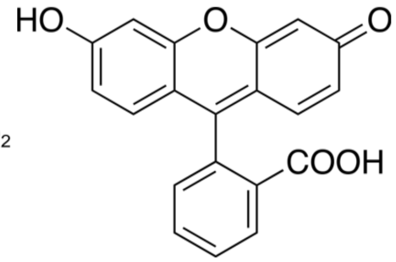
METHYLENE BLUE



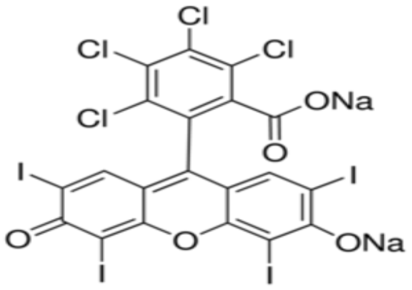
EOSIN B



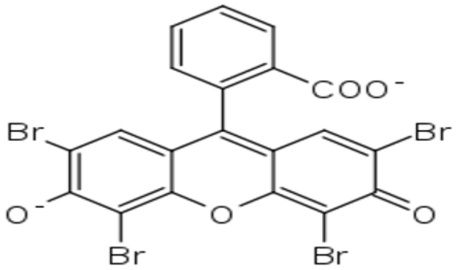
FLUORESCEIN



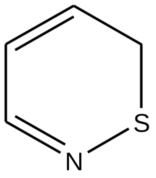
ROSE BENGAL



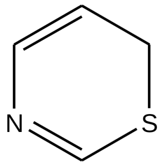
EOSIN Y



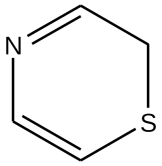
We will more concentrate on thiazine. Thiazine are the very important organic heterocycles which has the many uses in many branches of science like medicines, physics, chemistry, etc. There are three isomers of thiazine :- 1, 2- thiazine; 1,3- thiazine and 1,4- thiazine, which differ by the arrangement of the N & S atoms in the ring.



1,2-thiazine



1,3-thiazine



1,4-thiazine

From this 1,4- thiazine derivatives has the more significant in many branches. Traditionally phenothiazine used as a dyed & pigments. Also they gained prominent place in medicine as pharmacological lead structures. They used as the antihelmintic drug and insecticides. Recently these compounds and their derivatives have found application in organo-electronics and material sciences. Nowadays they also use as the photocatalyst such as Methylene Blue is use as the photocatalyst trifluoromethylation reaction, oxidative hydroxylation, dehalogenation reaction.

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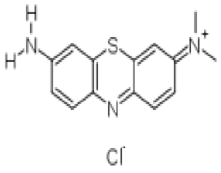
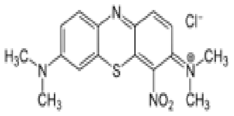
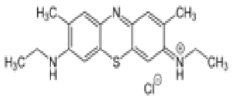
The some of the thiazine dyes as a Photocatalyst are



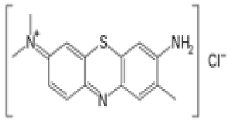
Azure A



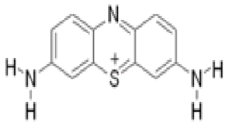
Methylene Green



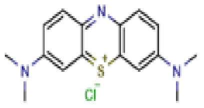
New Methylene Blue



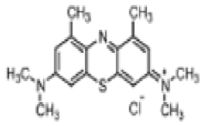
Toluidine Blue



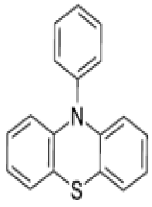
Thionin



Methylene Blue



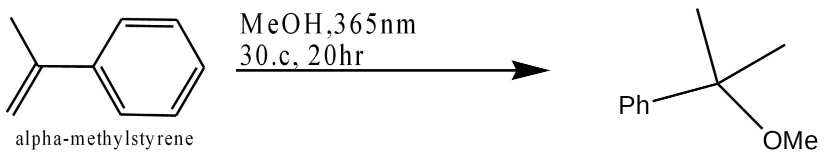
1,9-dimethyl methylene blue



N- phenylphenothiazine

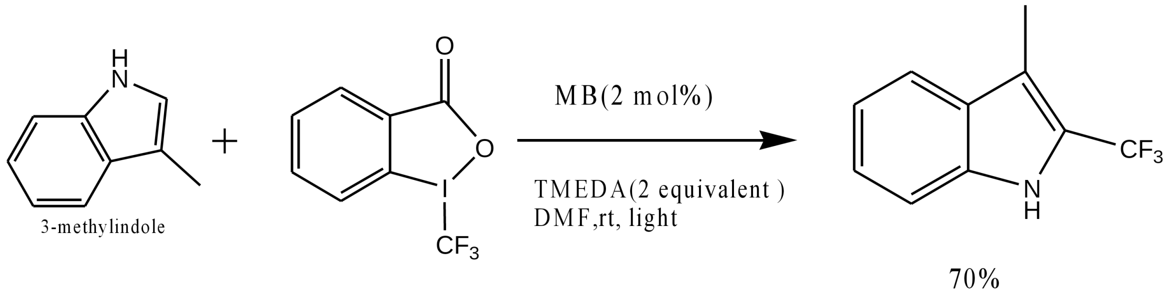
LITERATURE WORK

Nucleophilic addition of alcohols to alkene



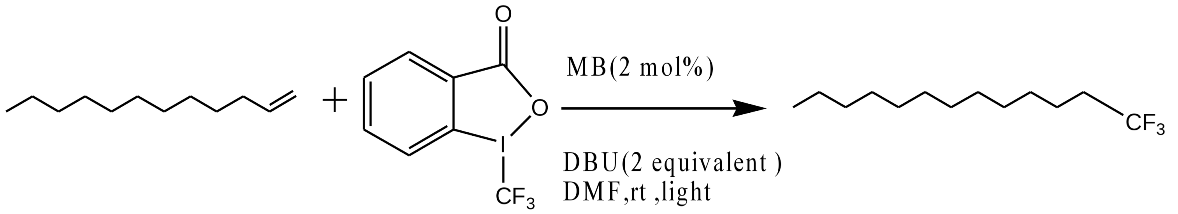
In 2019, Fabienne et. al. studied the nucleophilic addition of methanol to α-methylstyrene through photoredox catalysis. It was a Markovnikov type of addition. The use of many derivatives of N-phenyl phenothiazine were identified to be to be highly suitable for photoredox catalysis. It gave the yield upto 84%. α-Methylstyrene reacted with methanol through photoredox catalysis i.e derivatives of N-phenyl phenothiazine derivatives at 30°c for 65 hrs at 365nm. When the concentration of all components was increased at 170mM the reaction was completed within 20 hrs. The increased in the concentration above 170mM, slows down the rate to increase the yield of product, the concentration of α-methylstyrene should be high and the concentration of catalyst should be less. [1]

Trifluromethylation of electron rich heterocycles

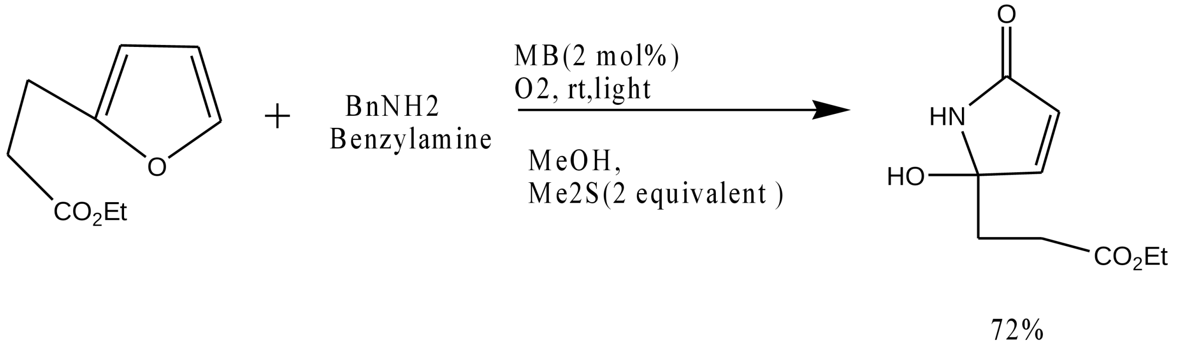


Scaiano's group studied the radical trifluoromethylation of electron rich heterocycles by the used of Togni's reagent as a CF_3 radical source, by using the Methylene Blue as a photoredox catalyst under visible light irradiation. In above reaction, TMEDA i.e N,N,N',N'-tetramethylenediamine was use as an electron donor and compounds were obtained in good yields.

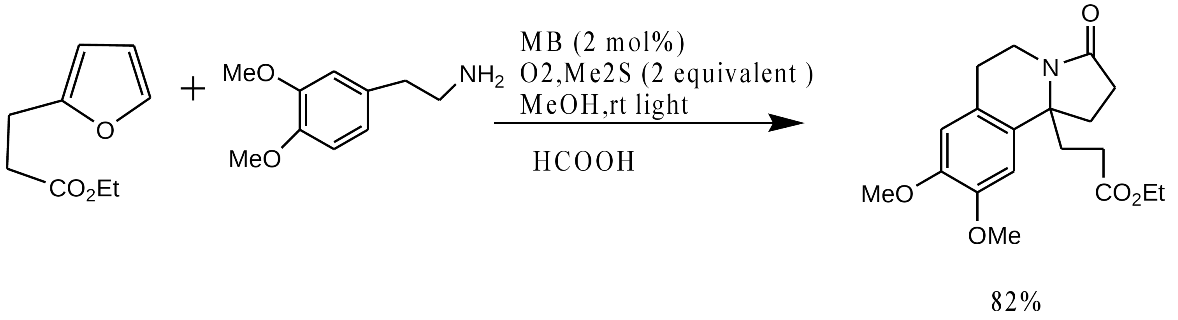
Aliphatic alkenes were also used to get hydrotrifluoromethylation product. Here DBU i.e 1,8-diazabicyclo[5.4.0]undec-7-ene was use as an electron donor.[2]



In this reaction, the visible light excited MB(MB*) was readily quenched by aliphatic amines such as TMEDA or DBU to form the semi- reduced MB as a radical anion and an α-amino radical. CF_3 radical was generated via the reduction of Togni's reagent with semi- reduced MB and /or an α-amino radical.



Authors also studied the reaction between Furan and amines. The transformation of furan into 5-hydroxy-1H-pyrrol-2(5H)-ones by using MB as a photocatalyst. The reaction of furan with benzylamine gave lactam i.e 5-hydroxy-1H-pyrrol-2(5H)-ones in 72% yield in the presence of MB and oxygen via the reduction of intermediate by Me_2S.

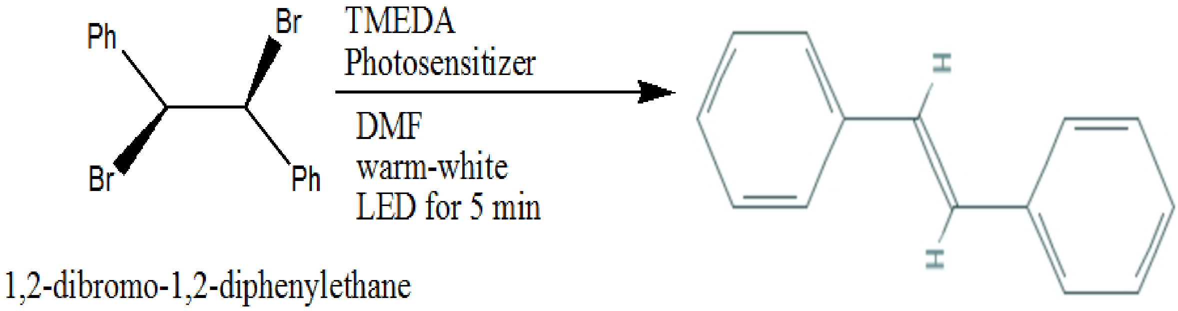


The use of 2-(3,4-dimethoxyphenyl) ethanamine instead of benzylamine led to the formation of tricycle via Pictet-Spengler cyclization process. For Pictet-Spengler cyclization process, HCOOH was added as an acid leading to N-acyliminium ion which spontaneously undergo in cyclization process.

Dehalogenation of meso – 1, 2- Dibromo -1, 2-diphenyl-ethane

In 2016 Spencer P. Pitre, Christopher D. McTiernan, and Juan C. Scaiano studied the Dehalogenation of meso – 1, 2- Dibromo-1, 2-diphenylethane by using various cationic organic dye.

The Authors also examined the dehalogenation of meso – 1, 2-Dibromo-1, 2-diphenylethane under visible light irradiation by using methylene blue. The irradiation for 1hr, yields trans stilbene i.e the dehalogenated product in quantitative amt. Decrease in the irradiation time to 5min, decrease the conversion of dibromo compound to 66%. With this it was noted that the only trans isomer of stilbene was observed under short period of irradiation.[3]

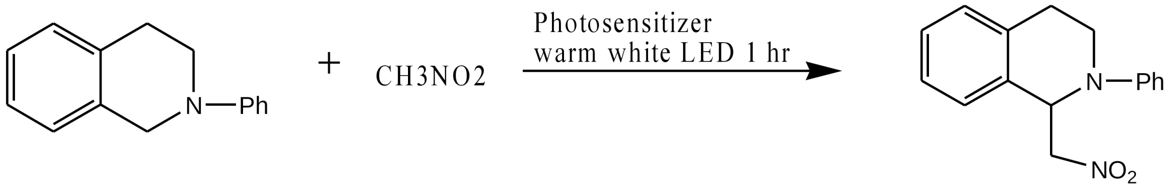


The meso -1,2-dibromo-1,2-diphenylethane was reacted with TMEDA in presence of methylene blue for 5 min to produce the reduce form of dye. Xanthene, Oxazine dyes, 9-mesityl-10-methyl acridinium perchlorate were less active for this reaction.

This reaction was also studied by using Ru(bpy)$_3$Cl$_2$ or fac-Ir(ppy)$_3$; they get both cis and trans –stilbene as a product as here the formed trans –stilbene outcompete TMEDA in the quenching of Ru(bpy)$_3$Cl$_2$ resulting in energy transfer and isomerization around the double bond.

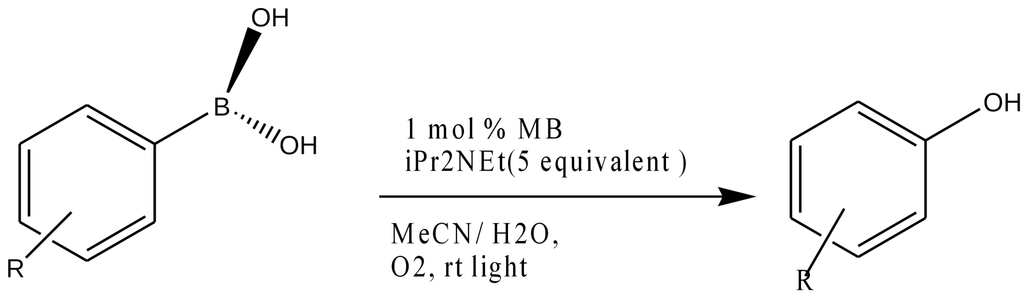
They also studied the Aza Henry reaction which was first studied by Stephenson and Coworkers in 2010. It is the most studied reaction in the field of photoredox catalysis; in fact, this reaction has become one of the gold standard for testing the activity of newly developed photocatalysts.

In this reaction, 2-phenyl-1,2,3,4-tetrahydroisoquinoline (PhTHIQ) was reacted with nitromethane (MeNO$_2$). In this PhTHIQ quench the molecular oxygen and not the photocatalyst. In absence of oxygen, the reaction doesn't proceed.

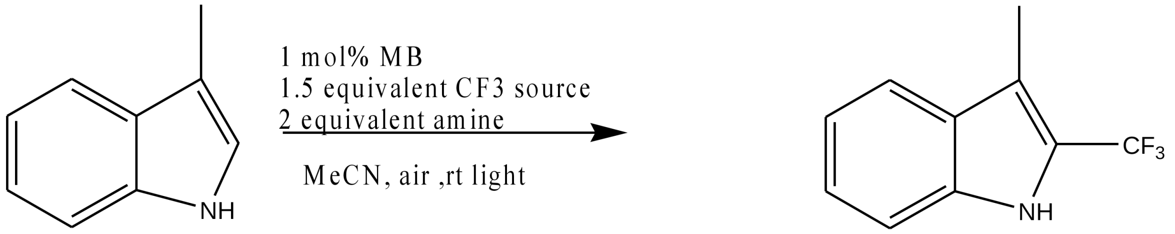


The similar results where obtained as that of the above dehalogenation reaction i.e 9-mesityl-10-acridinium perchlorate is less efficient.

Oxidative hydroxylation of Arylboronic acids

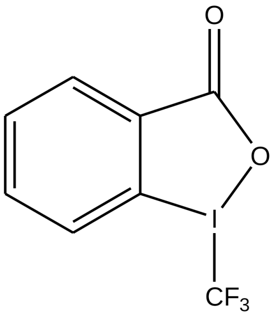


In 2016, Spencer et.al studied this reaction by using 1 mol% of MB and 94% yield whereas in $Ru(bpy)_3Cl_2$ about 58% yield. Here iPr2Net is used to quench the MB. Thus MB was more efficient then $Ru(bpy)_3Cl_2$ in this reaction.[4]

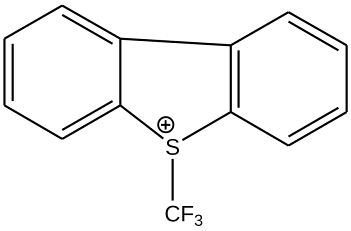


They also studied which will quench the photocatalyst and act as a good source of CF_3 in the trifluoromethylation of 3-methylindole. It was seen that Umemoto's reagent should be more efficient thermodynamically as it has more positive reduction potential. However they came to know that the Umemoto's reagent is less efficient than Togni's reagent.

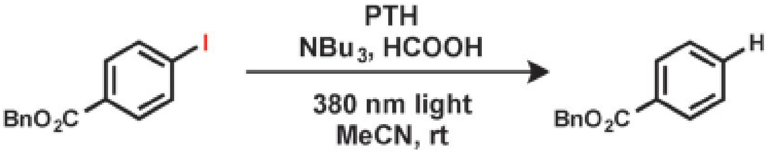
Togni's reagent



Umemoto's reagent

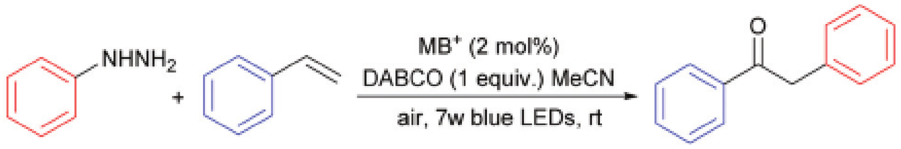


Dehalogenation reaction of aryl and alkyl iodide, bromide and chloride



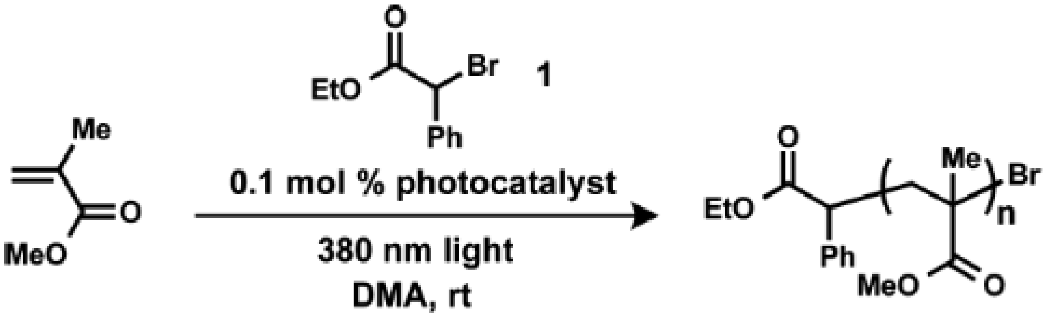
In 2015,Hawkers and coworkers use 10-phenylphenothiazine as a reducing Photocatalyst in dehalogenation reaction. It is the inexpensive way of doing this reaction which give good yields at room temperature. the electron rich aryl halides were also reduced; the substrate containing acid, phenol, amines was also reduced in good yield. 10-phenylphenothiazine, tributylamine, formic acid was use to dehalogenate the aryl or alkyl halides at room temperature under 380nm LED irradiation. In this, the Photocatalyst generate the carbon-centered radical intermediate which further reacted with mild hydrogen donar reagent to give the product. [6]

Synthesis of Ketones from Alkenes



In 2017, Ya Ding and coworkers provide the new route for the synthesis of Ketones from Aryl Hydrazine and Alkenes. Many Photocatalyst were screened and found that the Methylene Blue is good catalyst. In this, the carbon-centered radical was generated from the hydrazine by using the Photocatalyst and dioxygen. This radical is then added to the alkene to give ketone in the presence of oxygen. They took Aryl Hydrazine, Alkene, Methylene blue, DABCO and MeCN in air under room temperature and irradiated with 7W blue LED for 8hr.[7]

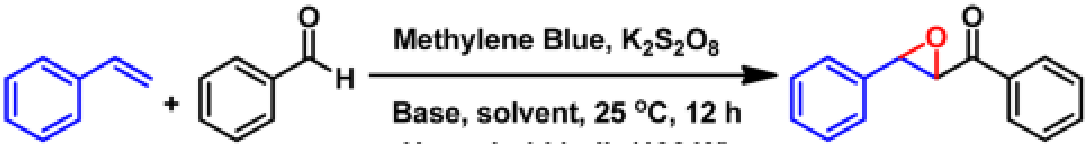
Metal-free ATRP process



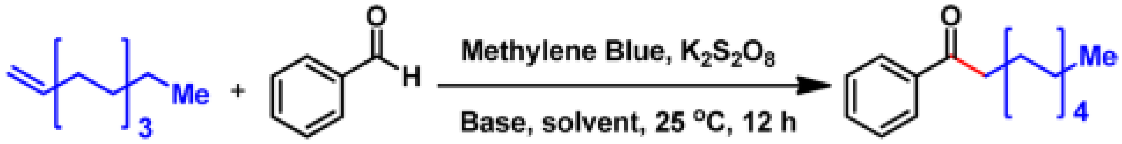
In 2014, Hawker et. al. came up with the metal free ATRP process. They use vinyl monomers and organic Photocatalyst I. e. 10- phenylphenothiazine and methylphenothiazine to accurately control over the molecular weight of polymers, low dispersity and high retention of end groups. This also helps in preparation of block copolymers in sequences. In this, the methyl methacrylate, initiator, Photocatalyst in DMA at room temperature with irradiation from 380nm.[8]

Epoxyacylation and Hydroacylation of Olefins

Epoxyacylation of olefins

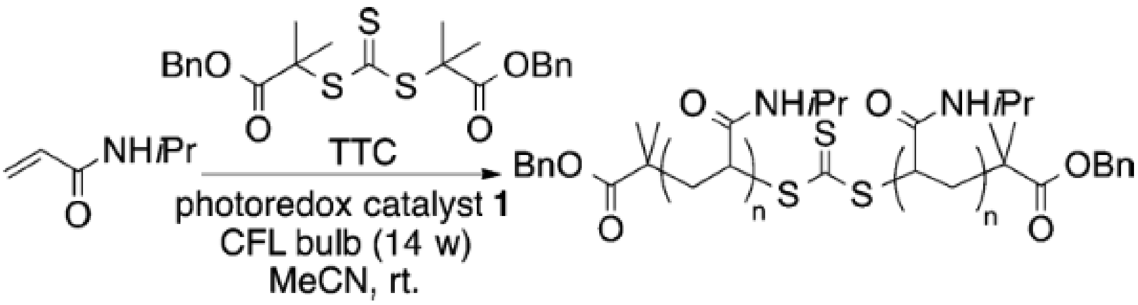


Hydroacylation of olefins



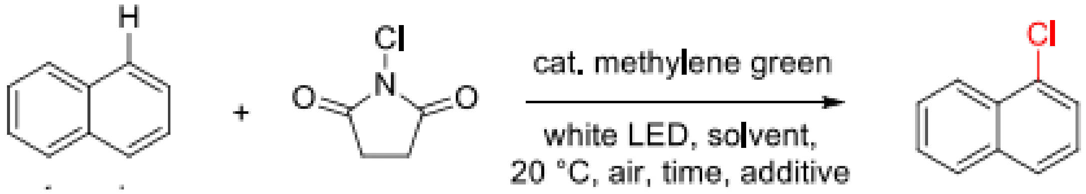
In 2018,Gabriela and coworkers use the Methylene blue as a Photocatalyst in epoxyacylation and Hydroacylation reaction. In this, they used several aromatic and aliphatic as well as conjugate and non-conjugated olefins to gave Ketones and epoxyketones. This is the inexpensive and green method. In this, persulfate was use as a oxidant and water as a solvent. If aldehydes was reacted with conjugated olefins then epoxyketones were obtained and upon reaction of aldehydes with non-conjugated olefins Ketones were major product. [9]

Living Radical Polymerization from Trithiocarbonate Iniferter



In 2015,Jonhson and coworkers reported the controlled living radical polymerization of acrylates and acylamides from trithiocarbonate iniferters by using the 10-phenylphenothiazine, the molecular weight was controlled by using the light. The polymer show the low polydispersity. This involve N-isopropyl acrylamide, trithiocarbonate and 10-phenylphenothiazine in MeCN at room temperature with irradiation from CFL bulb, it yields 93% of products. [10]

Chlorination of Arenes and Heteroarenes



In 2019, Rogers et. al Chlorination the Arenes and Heteroarenes by using N-chlorosuccinimide under visible light. Many organic dyes of acridine, xanthene, oxazine, azine, thiazine families were screened; out of which a dye from thiazine family I. e. methylene blue was found to be a good for this reaction as it gives moderate to good yields. The presence of air and external oxidant like $(NH_4)_2S_2O_8$ increase the efficiency of the reaction. In absence of Photocatalyst, the product formation was reduce from 72% to 6%.[11]

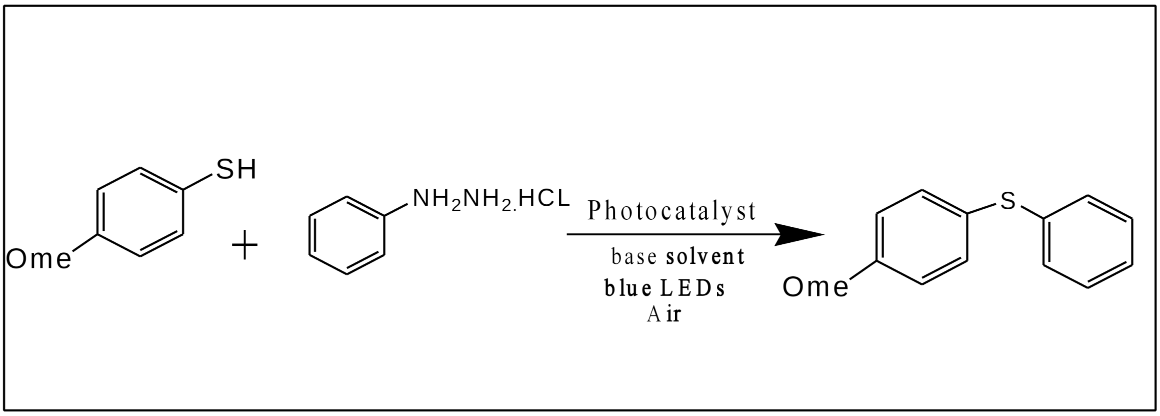
RESULT AND DISCUSSION

This project has two part

Part 1:- Use of rose Bengal as a photocatalyst for oxidative coupling reactions.

Part 2:- Synthesis of new photocatalyst.

PART I :- USE OF ROSE BENGAL FOR THE OXIDATIVE COUPLING

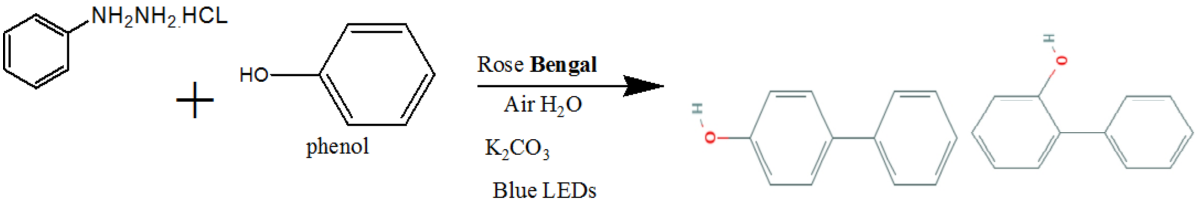


The above reaction, is the oxidative coupling between thiols and arylhydrazines take place to give the diaryl sulfides using a rose bengal as photocatalyst under aerobic conditions. They synthesize many unsymmetrical diaryl sulfides in good yields at room temperature.

We wanted to carry out similar coupling reactions with dyes as photoredox catalysts. We thought of carrying out similar reactions using phenol, bromobenzene and anisole.

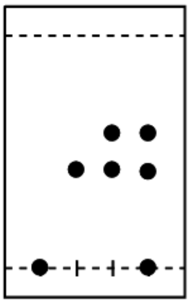
The photocatalyst rose Bengal was use for the oxidative coupling of the arylhydrazine and different substrates like phenol, anisole and bromobenzene.

Reaction :-1



Excepted products

TLC of the reaction in 20% of solvent

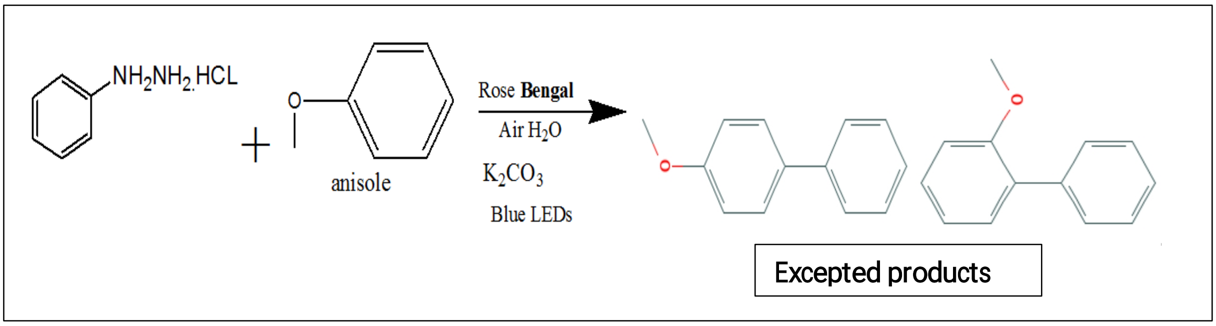


A-	Phenylhydrazine
B-	Phenol
C-	Reaction mixture
D-	Co

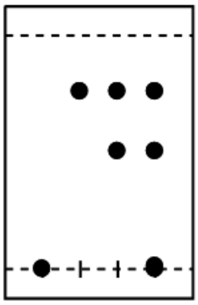
TLC Analysis:- The top spot in reaction mixture was the new one. So the product was formed. The reactant was present.

Conclusion:- The product was formed but the reactant was still present, the column chromatography was carried out to separate them.

Reaction:-2



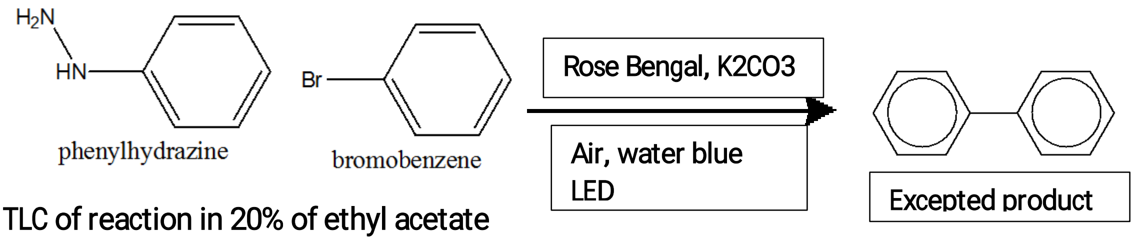
TLC of reaction in 20% of solvent



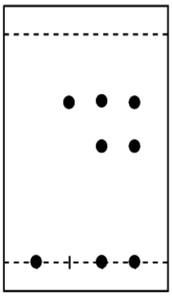
A-	Phenylhydrazine
B-	Anisole
C-	Reaction mixture
D-	Co

TLC Analysis:- The reaction mixture shows the new spot, so the product was formed. The reactant was still present.

Reaction 3:-



TLC of reaction in 20% of ethyl acetate



A-	Phenylhydrazine
B-	Bromobenzene
C-	Reaction mixture
D-	Co

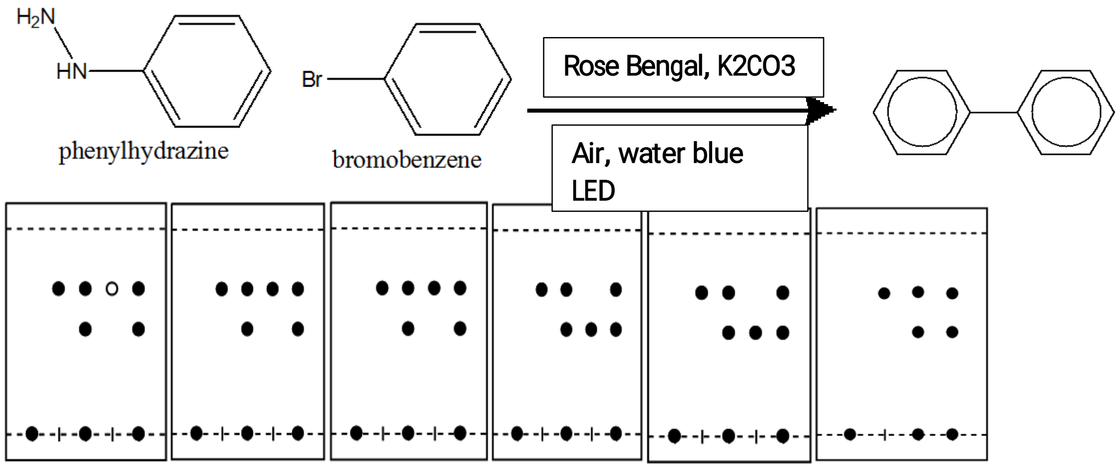
TLC Analysis:- The top spot in reaction mixture was the new one. So the product was formed. The reactant was present.

Table:- 1

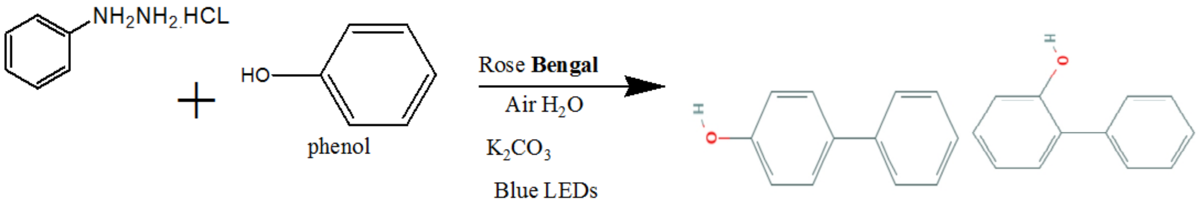
Sr.No.	Reactant A	Reactant B	Yields
1.	Phenylhydrazine	Anisole	30%
2.	Phenylhydrazine	Bromobenzene	30%
3.	Phenylhydrazine	Phenol	30%

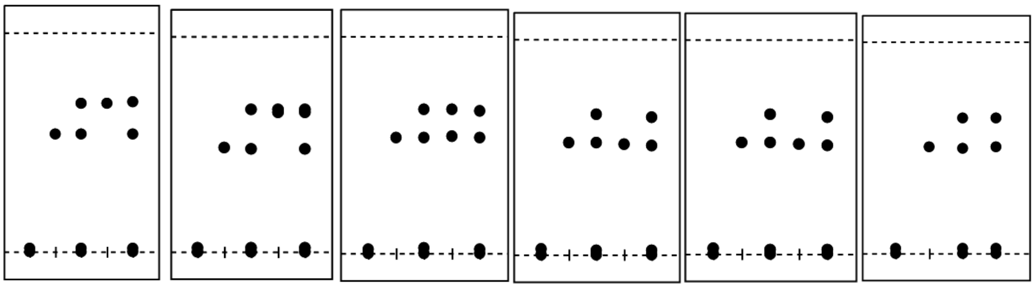
All the reactions tried are depicted in table 1. Oxidative coupling reaction though yielded new compound, which was analysed by TLC. Almost all the reaction were having impurities along with reactant, which was unutilized in the reaction. To separate the new spot from reaction mixtures, column chromatography was tried .

COLUMN CHROMATOGRAPHY OF BROMOBENZENE AND PHENYLHYDRAZINE

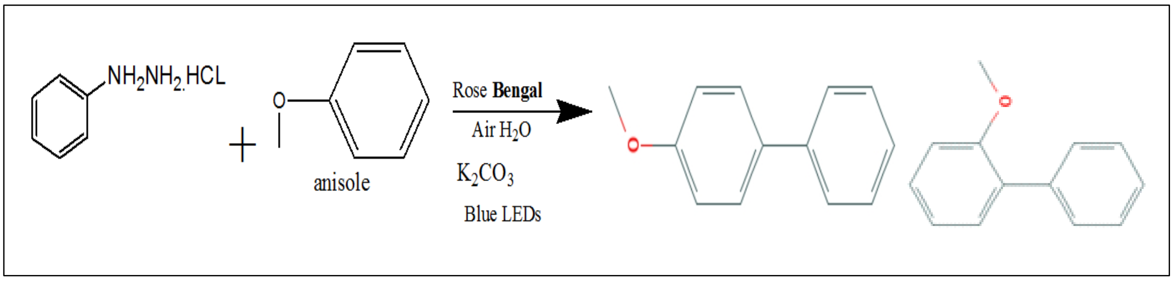


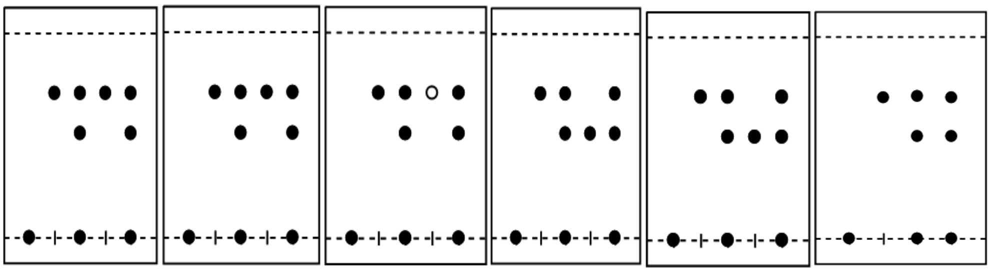
COLUMN CHROMATOGRAPHY OF PHENOL AND PHENYLHYDRAZINE





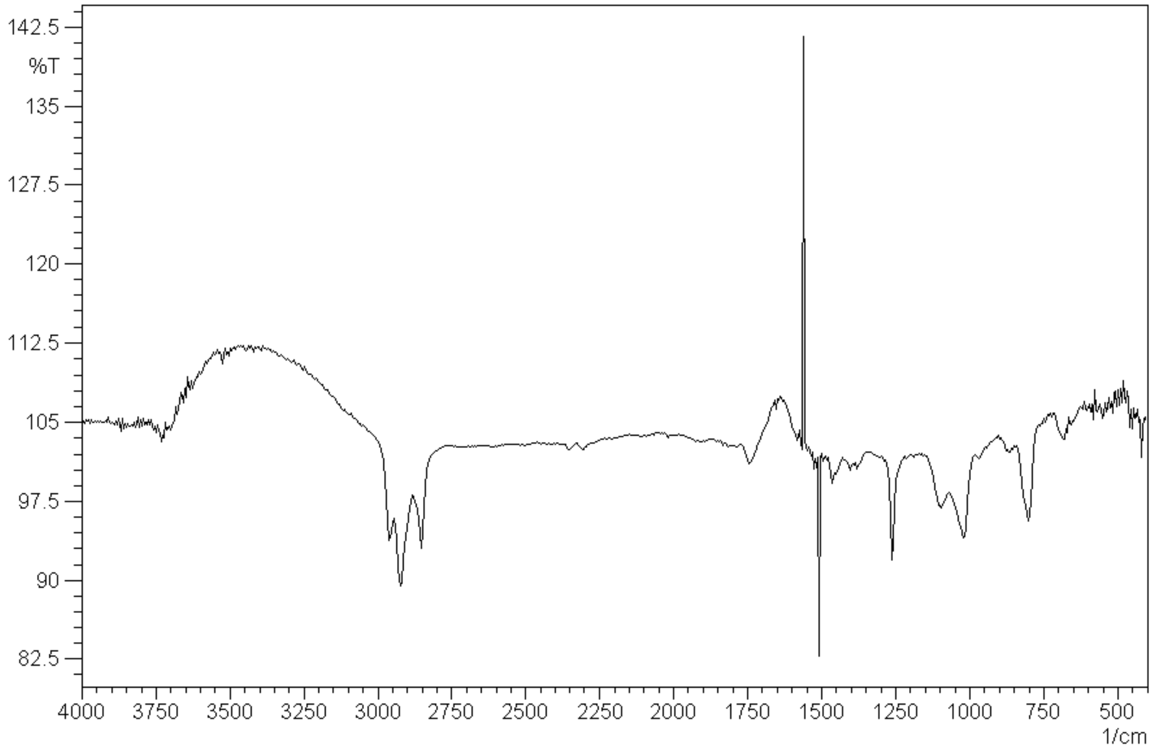
COLUMN CHROMATOGRAPHY OF ANISOLE AND PHENYLHYDRAZINE





Conclusion :- the single spot was obtained for the product which were collected and the solvents were removed and the compounds were weighed.

IR spectra of the compound A (reaction between Phenylhydrazine and Anisole)

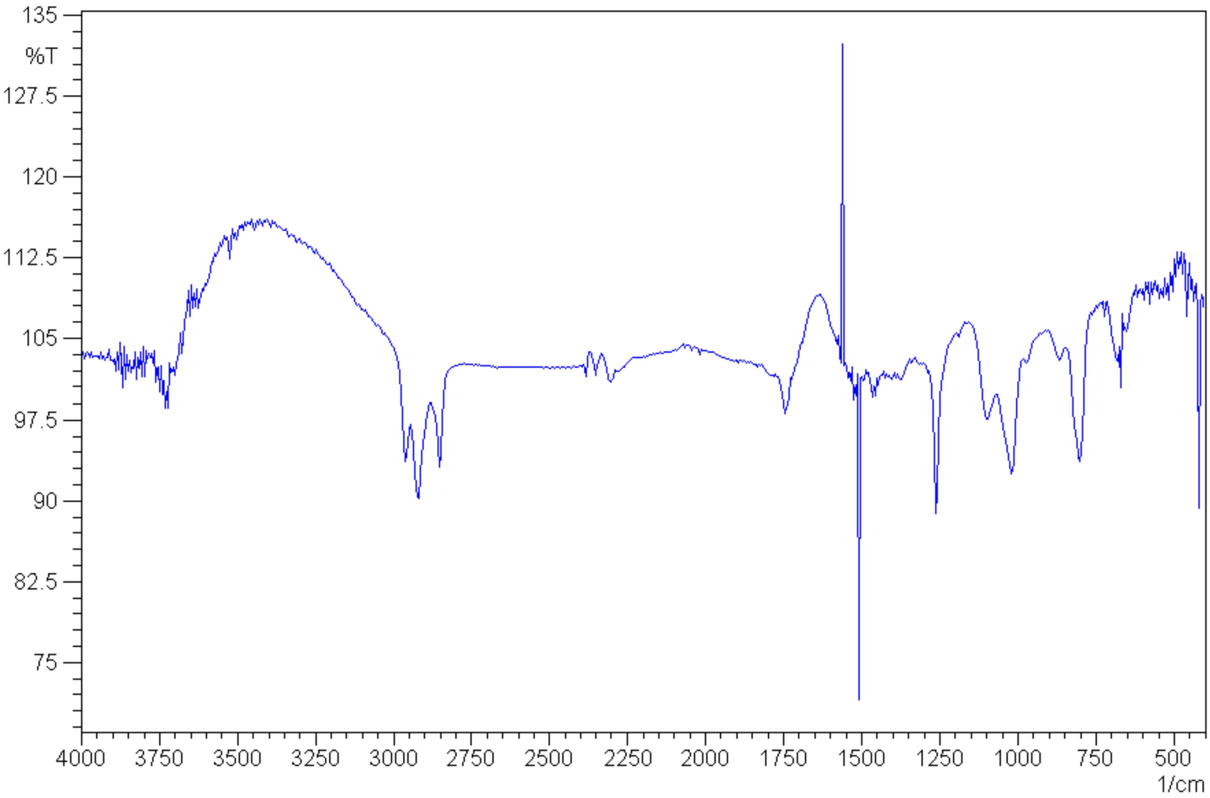


IR spectra analysis :-

2950 cm^{-1} ➔ sp^2 C-H (stretching)

1500 cm^{-1} ➔C=C bond, aromatic (stretching)

IR spectra of compound B (reaction between Phenylhydrazine and Bromobenzene)



IR spectra analysis :-

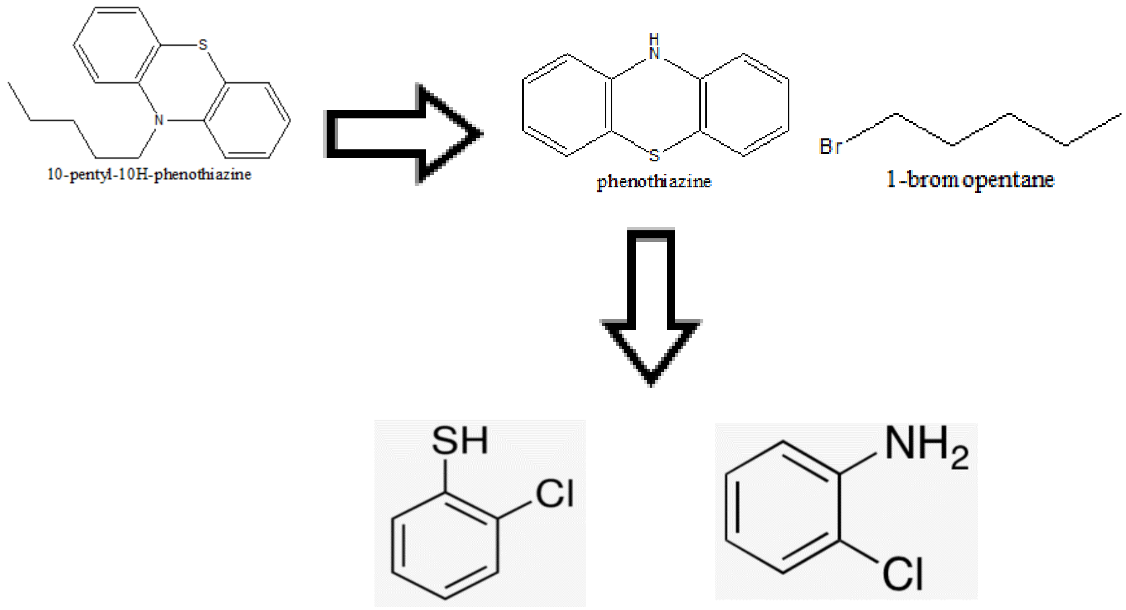
2950 cm^{-1} ➔ sp^2 C-H (stretching)

1500 cm^{-1} ➔C=C bond, aromatic (stretching)

Conclusion :- As both the IR spectra of the compounds were similar, the compounds formed with Anisole and Bromobezene was same.

PART II:- SYNTHESIS OF CATALYST

We had envisioned the synthesis of new phenothiazine derivatives as photoredox catalyst. The retrosynthetic scheme is depicted below.

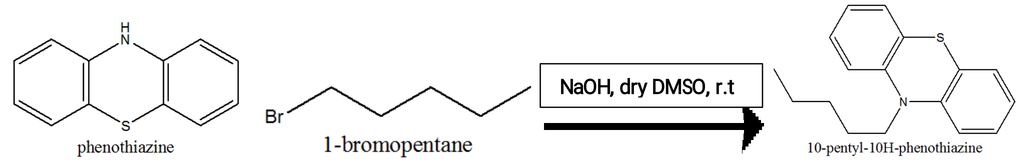


Scheme: Retrosynthesis of 10-Pentyl-10H-Phenothiazine

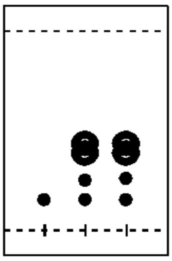
The new photocatalyst was prepared by using the phenothiazine and 1-bromopentane through N-alkylation process. These photocatalyst was absorb in the UV region.

It is the reducing photocatalyst.

Reaction 4:-



TLC of reaction in 10% ethyl acetate

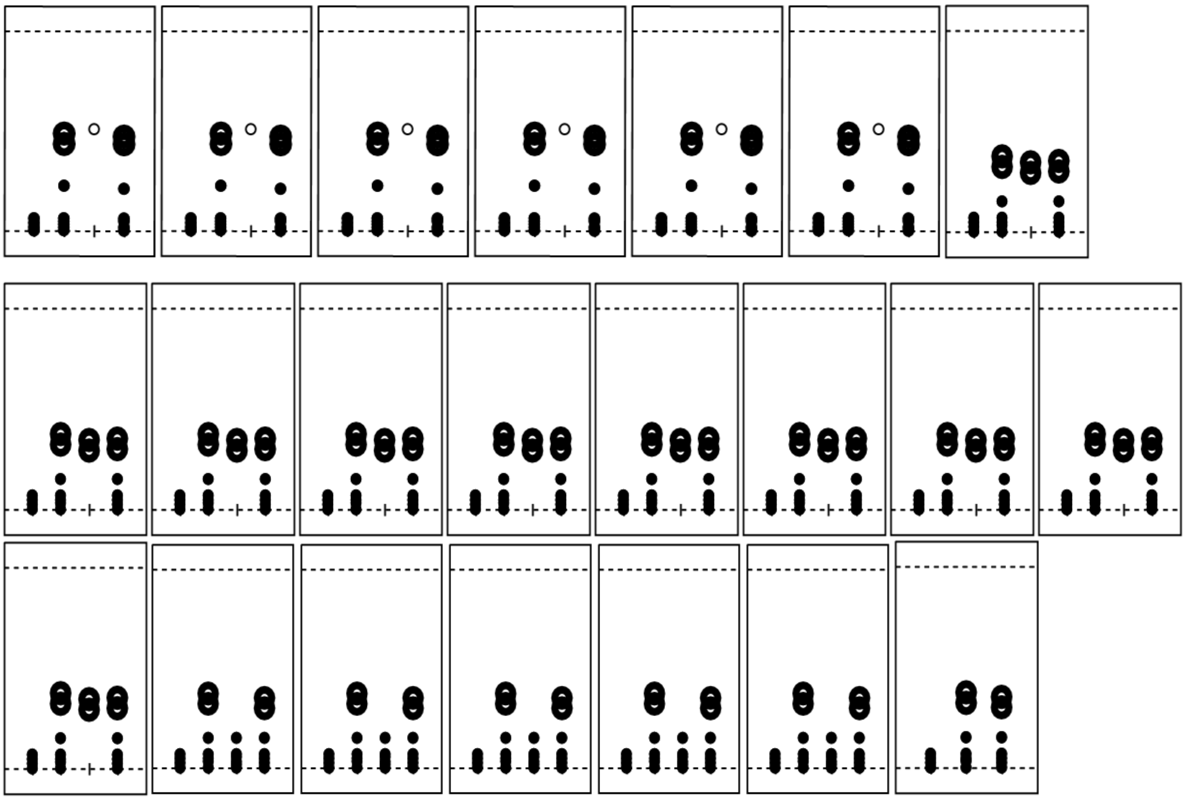


A-	Phenothiazine
B-	Reaction mixture
C-	Co

<u>TLC Analysis:-</u> Some new spots were seen. So the product was formed but had to separate each spots and will have to analyze them.

Column of these reaction was done to separate each spots by using earlier column chromatography process.

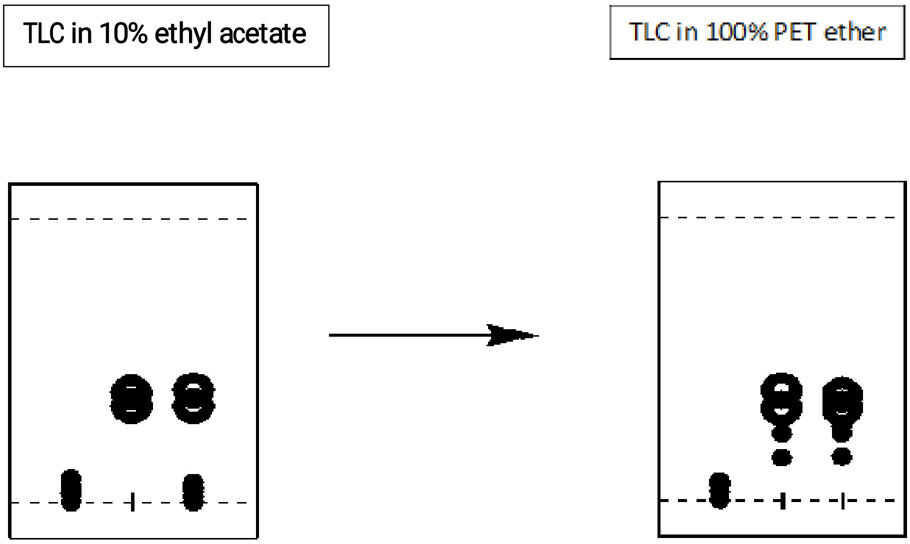
A-Phenothiazine, B- Reference, C-Extract, D- Co



1. The extract from 1 to 6 we're collected and the solvent was removed. It is a yellow colour solid.
2. The extract from 7to 16 were collected and the solvent was removed. It was a orange colour

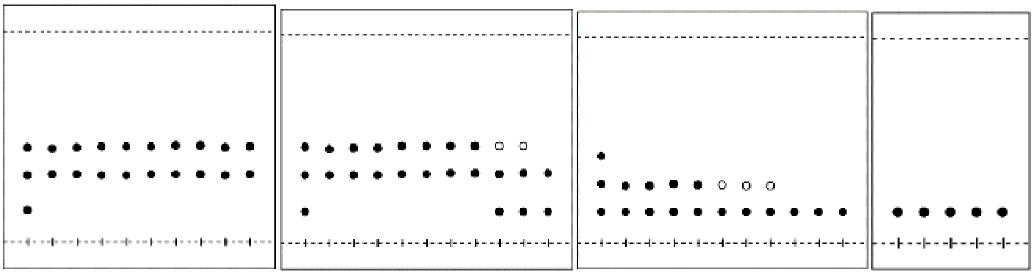
viscous liquid. But it was a mixture, so flash chromatography was use to separate them.
3. Other extract were collected.

The spots which gave the viscous liquid, was spotted on TLC plate and run on the 100%PET Ether.



TLC Analysis:- The two spots in 100% PET Ether gave four different spots. These was tried to separate by using the flash chromatography.

FLASH CHROMATOGRAPHY OF VISCOUS LIQUID

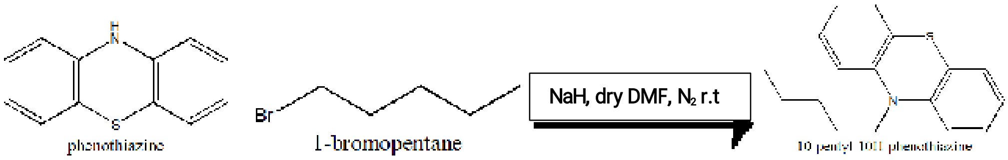


TLC Analysis:- In first extract only the mixture appeared. So the mixture was not separate.

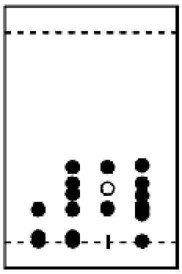
Conclusion:- In this reaction, the product was formed but it is impure and can't purified as the spots remove in 100% PET Ether only.

So the new reaction was use to get N-alkylation product by using the NaH and dry DMF in inert atmosphere.

Reaction 5:-



TLC of reaction mixture in 100% PET Ether



A-	Phenothiazine
B-	Reaction mixture with DMSO
C-	Reaction mixture with DMF
D-	co

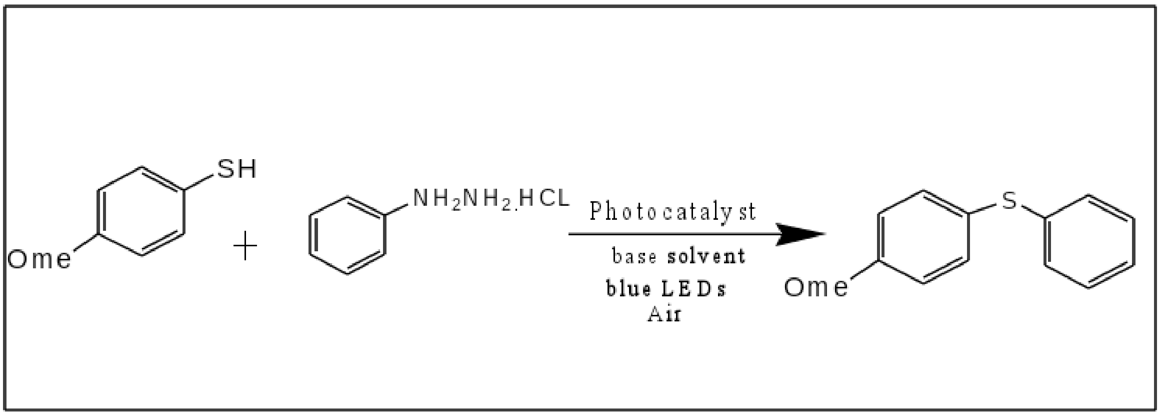
<u>TLC Analysis :-</u> The second spot in the reaction mixture with DMF is light than the reaction mixture with DMSO. Hence can be separated by the Column Chromatography .

<u>Conclusion :-</u> The reaction mixture was separated by the Column Chromatography. The top spot was separated by the slow elution and collected separately.

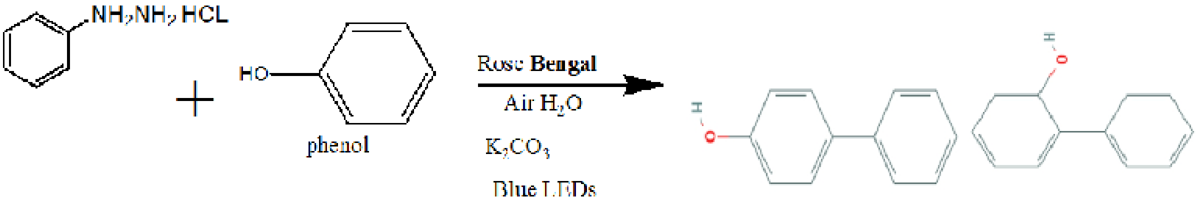
EXPERIMENTAL PROCEDURES

I.USING ROSE BENGAL FOR THE OXIDATIVE COUPLING

Scheme



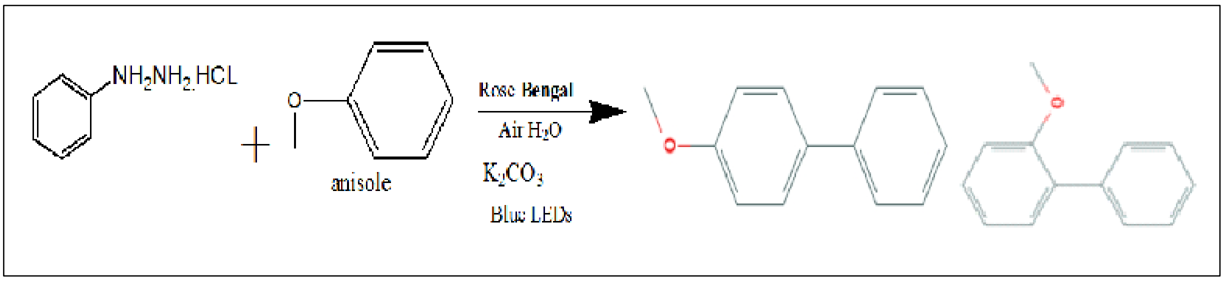
Reaction :-1



PROCEDURE:-

The phenylhydrazine (0.2mmol) was taken in a clean, dried round bottom flask. The phenol (0.4mmol), Acetonitrile (3 mL) as a solvent and K_2CO_3 as a base (0.2mmol) was then added to it along with the Rose Bengal (0.3 mol%) as a photocatalyst.The reaction mixture was stirred for 18 hrs in presence of blue LEDs. The progress of the reaction was monitor using TLCs.

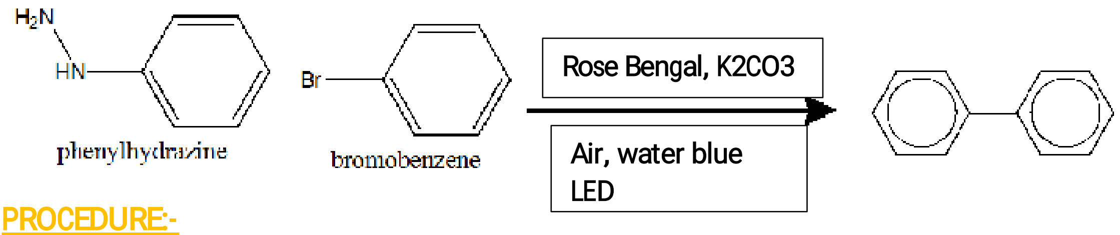
Reaction:-2



PROCEDURE:-

The phenylhydrazine (0.2mmol) was taken in a clean, dried round bottom flask. The Anisole (0.4mmol), Acetonitrile (3 mL) as a solvent and k_2CO_3 as a base (0.2mmol) was then added to it along with the Rose Bengal (0.3 mol%) as a photocatalyst.The reaction mixture was stirred for 18 hrs in presence of blue LEDs. The progress of the reaction was monitor using TLCs.

Reaction :-3



PROCEDURE:-

The phenylhydrazine (0.2mmol) was taken in a clean, dried round bottom flask. The Bromobezene (0.4mmol), Acetonitrile (3 mL) as a solvent and K_2CO_3 as a base (0.2mmol) was then added to it along with the Rose Bengal (0.3 mol%) as a photocatalyst.The reaction mixture was stirred for 18 hrs in presence of blue LEDs. The progress of the reaction was monitor using TLCs.

Through the TLC we came to know that, there was a reactant impurity in our product so we purify our product by using the column chromatography.

II. PROCEDURE OF THE COLUMN CHROMATOGRAPHY

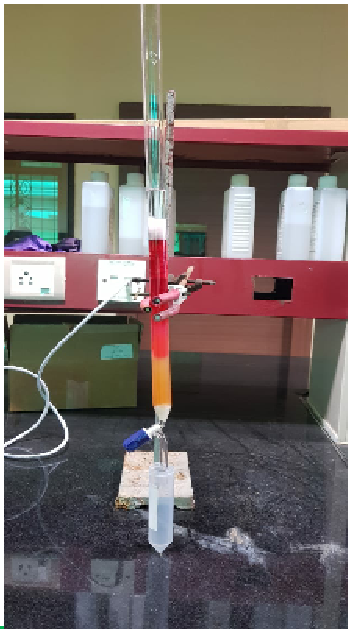
First the work up of the reactions was done by dissolving our reaction mixture in minimum amount of the ethyl acetate. These was then transfer into the separating funnel. The water was add to these and the organic layer was extracted. These was then concentrated on the water bath.

Preparation of column chromatography

The clean, dry column was taken and then the cotton was added into it with the help of glass rod.The PET ether was added to this column.The slurry of silica was prepared using the silica of 60-120 mesh and PET ether.This slurry was poured into the column through funnel on the top of the column along with continues tapping on the column so that the slurry settles down.The slurry of silica was continuously added in the same way till the required length of the silica bed was obtained.

Loading of reaction mixture or sample

Sample was loaded in the form of slurry.Some amount of silica was taken in round bottom flask and then added reaction mixture into it along with some amount of DCM i.e. Dichloromethane to make slurry of our sample. Again rinsed the reaction mixture beaker with DCM and added in same flask.The DCM was evaporated from the above slurry on the water bath till the slurry became free flowing.This slurry was added to the column with tapping on it through the funnel.Put the cotton after the sample bed.



Elution of the sample

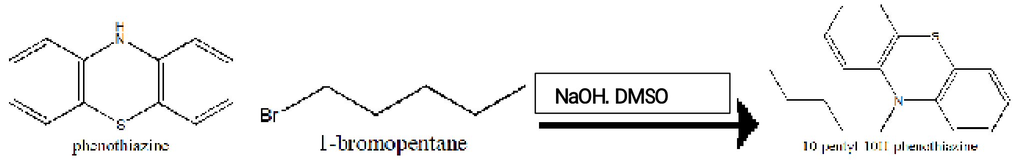
After the sample was loaded, the solvent was added to the column and the fractions were collected. Each time the polarity of the solvent was increased e.g. 10%, 20%, 30%, etc. and the fractions were collected.

Analysis of the fractions

The each collected fraction was then distilled out each time till the small amount was remained.TLC of these was taken, developed in 20% ethyl acetate solvent and observed under the UV chamber.If any spot for the product in the TLC then that fractions were collected in the clean and dry test tube along with washings of ethyl acetate which we gave to the round bottom flask. This way we separated the reactant and product.

III. SYNTHESIS OF NEW CATALYST

A new catalyst was prepared by using a phenothiazine as a starting material. The catalyst 10-Pentyl-10H-phenothiazine was prepared from phenothiazine and 1-bromopentane. 10-pentyl-10H-phenothiazine is a reducing Photocatalyst which absorbs in UV region.



PROCEDURE TO PREPARE 10-PENTYL-10H-PHENOTHIAZINE

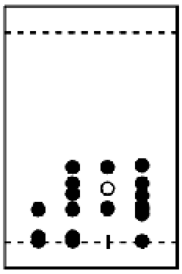
9.96g of Phenothiazine in 150mL of dry DMSO in clean , dried round bottom flask.16g of NaOH and 10.8mL of 1-bromopentane were added at room temperature in it and refluxed for 24hr.The reaction was then poured into the water.And extracted with the Ethyl Acetate.The organic layer was then dried over anhydrous $MgSO_4$.The solvent was removed and purified by column chromatography using Ethyl Acetate and PET Ether.

Other reaction of N-alkylation of phenothiazine was put by using the NaH as a base and DMF as a solvent.

PROCEDURE

5g of phenothiazine in 10 mL of dry DMF in a 50mL round bottom flask covered with septum. 1.02g of NaH in 10 mL of dry DMF in a 100mL three necked flask. Purged the vaccum and N_2 gas alternatively for three times in flask containing NaH solution. Then put the phenothiazine solution in that flask with syringe. Then 4mL of 1- bromopentane was added with syringe. Stired for 18hrs at room temperature. Extracted with Ethyl Acetate and dried over the anhydrous $MgSO_4$.The column chromatography was done to purified it by using the 100% PET Ether.

TLC of reaction mixture in 100% PET Ether



A:- Phenothiazene

B:- Reaction mixture with DMSO

C:- Reaction mixture with DMF

D:- Co

TLC Analysis :- The second spot in the reaction mixture with DMF is light than the reaction mixture with DMSO. Hence can be separated by the Column Chromatography .

Conclusion :- The reaction mixture was separated by the Column Chromatography. The top spot was separated by the slow elution and collected separately.

CONCLUSION

In Conclusion,

The rose Bengal dye was utilized as photoredox catalyst for C-C oxidative coupling reaction between phenyl hydrazine and various substrate. The reaction were successful to give new compounds, which were observed by TLC. Further purification process is underway to characterize new products obtain form the photoredox reactions.

Also, new photocatalyst I. e 10-pentyl-10H-phenothiazine which is successfully prepared via N-alkylation of phenothiazine. The utilization of synthesised catalyst remains to be explored.

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