A project report entitled

“Photoredox Catalysis: Synthesis of Photoredox Catalyst and its Application for Organic Transformation”

Dissertation submitted to Goa University in partial fulfillment of the requirement for the degree of

MASTER OF SCIENCE

IN

CHEMISTRY

By

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April 2020

STATEMENT

I hereby declare that the matter presented in this dissertation entitled, ”Photoredox Catalysis: Synthesis of Photoredox Catalyst and its Application in Organic Transformation” is based on the result of investigations carried by me in the School of Chemical Sciences , Goa University under the supervision of Prof.Sandesh Bugde and the same have not been submitted elsewhere for the award of a degree or diploma.

CERTIFICATE

This is to certify that the dissertation entitled, “Photoredox Catalysis: Synthesis of Catalyst and its Utilization in Organic Transformation” is bonafide work carried out by ‘Ashtreeda Cardozo’ under my supervision in partial fulfillment of the requirements for the award of the degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa University.

Dr. Sandesh T. Bugde

Guiding Teacher

School of Chemical Sciences

Goa University

ACKNOWLEDGEMENT

It gives me an immense pleasure to present this project report entitled “Photoredox Catalysis: Synthesis of Catalyst and its Utilization in Organic Transformation”.

The success and final outcome of this project required a lot of guidance and assistance from people 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 profound gratitude and deep regards to my guide Prof.Sandesh Bugde for his exemplary guidance, monitoring and constant encouragement throughout this project. The blessing, help and guidance given by him time to time shall carry me a long way in the journey of life on which I am about to embark.

I also take this opportunity to express a deep sense of gratitude to Prof.V.S.Nadkarni-Dean of School of Chemical Sciences, 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 towards the research student, Mr.Pritesh Kobrekar for helping me record IR spectra of my compounds and for his cordial support, valuable information which helped me in completing this task through various stages.

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

ABBREVIATIONS

GENERAL ABBREVIATIONS:

MEASUREMENTS:

Aq.	–	Aqueous
Equiv.	-	Equivalent
Fig.	-	Figure
g.	-	Grams
min.	-	Minutes
mmol	-	Millimol
m.p.	-	Melting point
r.t.	-	Room temperature
°C	-	Degree Celsius
hr	-	Hours

TECHNIQUES:

TLC	-	Thin Layer Chromatography
IR	-	Infrared Spectroscopy

COMPOUNDS:

RB	-	Rose Bengal
MB	-	Methylene Blue
EtOH	-	Ethanol
CH_3CN	-	Acetonitrile

GENETAL REMARKS

1. IR spectra were recorded on a Shimadzu FTIR Spectrophotometer (solid KBr pellets).

2. All melting points were measured by normal Thiele’s tube method and are corrected.

3. Distilled solvents were used in all cases.

4. Commercial reagents were used without further purification.

5. All solvents and reagents were purified and dried by Standard purification.

6. All the reactions were monitored by Thin Layer Chromatography (TLC) on silica gel.

7. Room temperature = 26-31°C

INDEX

Introduction

Photoredox catalysis is a branch of catalysis that harnesses the energy of light to accelerate a chemical reaction via single electron transfer events. This area is named as a combination of ‘photo’ referring to light and redox, a condensed expression for the chemical processes of reduction and oxidation[7]. In particular, Photoredox catalysis employs small quantities of light – sensitive compound that, when excited by light, can mediate the transfer electrons between chemical compounds that would usually not react at all. Photoredox catalysts are generally drawn from three classes of materials: transition-metal complexes, organic dyes and semiconductors. While organic Photoredox catalysts were dominant throughout the 1990s and early 2000s, soluble transition-metal complexes are more commonly used today[7].

Study of this branch of catalysis led to the development of new methods to accomplish known and new chemical transformations. Photoredox catalysts generate potent redox agents when exposed to light; they are unreactive under normal conditions. Photoredox catalysis is often applied to generate known reactive intermediate in a novel way and has led to the discovery of new organic reactions[7].

Over the last century, the discovery, development, and use of light-mediated catalysis has enabled the invention of a wide variety of nontraditional bond constructions in organic chemistry. More recently, the field of photocatalysis has undergone a significant renaissance, and once again, a series of new activation modes have in turn seeded a large variety of new bond-forming protocols and synthetic methodologies[7]. Photocatalysis, the field, encompasses an ever-increasing number of generic activation modes in which photonic energy is selectively targeted to a specifically designed photon-absorbing catalyst (a photocatalyst) which, upon excitation, is able to induce an accompanying substrate, reagent, or secondary catalyst to participate in unique reaction pathways that were previously unattainable under thermal control. The most common mechanisms by which photocatalysts are able to convert light into chemical energy and at the same time perform selective molecule activation include (i) energy transfer, (ii) organometallic excitation, (iii) light-induced atom transfer, and (iv) photo redox catalysis[7].

Over the last four decades, photoredox catalysis has found widespread application in the fields of water splitting, carbon dioxide reduction, and the development of novel solar cell materials; however, only recently has the potential of applying this catalytic platform to organic synthesis begun to be fully realized. A key factor in the recent yet rapid growth of this activation platform has been the recognition that readily accessible metal polypyridyl complexes and organic dyes can facilitate the conversion of visible light into chemical energy under exceptionally mild conditions[6]. Upon excitation, these molecules can engage in single-electron transfer (SET) events with organic (and organometallic) substrates, providing facile access to open-shell reactive species. Here, irradiation with visible light, at wavelengths where common organic molecules do not absorb, effects selective excitation of the photoredox catalyst. The resultant excited species can act as both a strong oxidant and a strong reductant simultaneously, thereby providing access to a reaction environment that is unique for organic chemistry. Indeed, this electronic duality contrasts directly with traditional redox reaction manifolds (e.g., electrochemistry) wherein the reaction medium can be either oxidative or reductive (but not both) and, in turn, provides access to previously inaccessible redox-neutral reaction platforms9.

The field of photochemistry is rather broad, encompassing a range of processes including electron and energy transfer, isomerization and ligand substitution to name a few. Photo redox catalysis primarily deals with electron transfer processes that are initiated by the absorption of a photon by a chromophore (i.e., the photo catalyst). Such systems take advantage of the enhanced redox reactivity of the chromophore in its excited state to facilitate a reaction that would not proceed otherwise; in this sense, light provides the added energy needed to make the reaction thermodynamically viable. Although there have been reports of reactions driven by photo-induced energy transfer, the majority of the work in this area centers around photo-induced electron transfer processes utilizing charge-transfer chromophores being able to experimentally differentiate between electron and energy transfer processes is an important issue from a mechanistic perspective. In any photo catalytic cycle, the key step is the absorption of a photon that leads to the formation of an excited state that then engages in a chemical reaction[6].

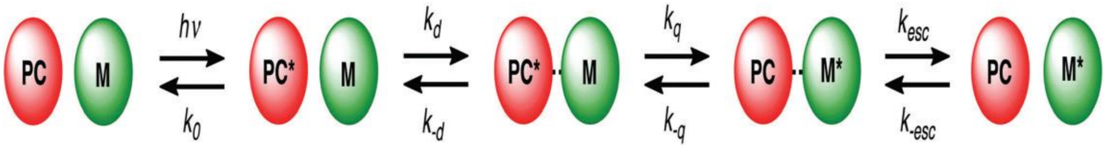


Figure 1.:Simplified kinetic scheme for a general quenching process.

Taken from chemical society reviews www.rsc.org/chemsocrev

Most steps in a photo redox catalytic cycle are bimolecular reactions and can be represented as shown in Figure 1. The first step is the absorption of a visible light photon by the photocatalyst in its ground state (PC) and its consequent promotion to an electronic excited state (PC*); k0 represents the rate of excited-state relaxation (in this case ground-state recovery). This process can be radiative (i.e., emission) and/or non-radiative. For the excited photocatalyst to react with a molecule (M), both species must diffuse towards each other, forming a ‘‘precursor complex’’. Then, these two species react. After the reaction, the products diffuse away from each other. If the two reactants cannot escape the solvent cage fast enough, an unwanted back reaction may take place. This is typically more of a concern with electron (as opposed to energy) transfer processes. This relatively simple scheme allows us to outline the main points that need to be considered when choosing and/or designing a photocatalyst[6].

(1) Photocatalytic reactions make use of the enhanced reactivity of the photocatalyst in its excited state. For this reason, a photocatalyst must possess a good absorption cross-section, preferably over a broad range of wavelengths that the other species in the reaction mixture do not absorb.

(2) The yield of formation of the reactive excited state should be as high as possible. This will be influenced both by the intrinsic quantum yield of its formation (that is, the efficiency with which the reactive excited state is formed upon photon absorption) as well as the absorption cross-section as measured by the compound’s concentration and molar absorptivity.

(3) The excited state must persist long enough to undergo the desired reaction with the substrate. In the context of Figure 1, this means that the excited state of the photocatalyst must have a sufficiently long lifetime to enable it to diffuse to the reactant of interest before relaxing back to the ground state. Diffusion occurs on the nanosecond time scale in most solvents although increasing the concentration of reagents can offset diffusion to a certain extent, the bimolecular nature of the reaction places a practical upper limit of $\approx 10^9$s for k_0 of the excited photocatalyst.

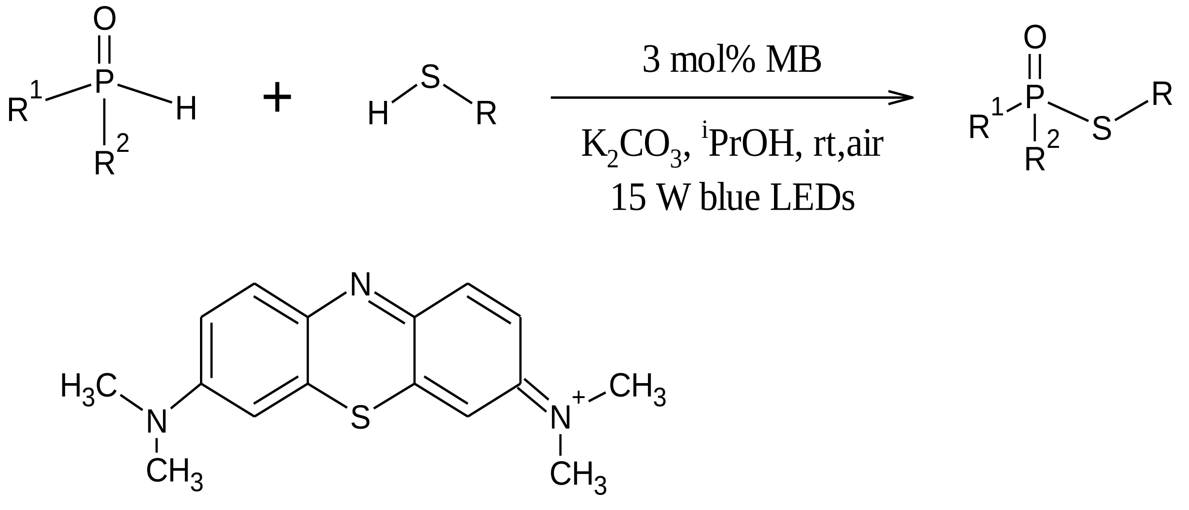
(4) The photo physics of the photocatalyst must be reversible (i.e., no photo degradation in the absence of quencher). In the case of electron transfer catalysis, the photocatalyst should exhibit reversible electrochemical behavior. Both of these characteristics are needed in order to maintain the viability of the chromophore as part of a catalytic cycle.

(5) If the catalytic cycle involves electron transfer, the excited and ground-state redox potentials of the photocatalyst must provide for an exothermic (or at worst weakly endothermic) reaction.

(6) Ideally, the excited-state properties of the photocatalyst should be easily tuned through synthetic modifications in order to facilitate tailoring the excited-state reactivity of the photocatalyst to the reaction being studied[6].

Literature Review

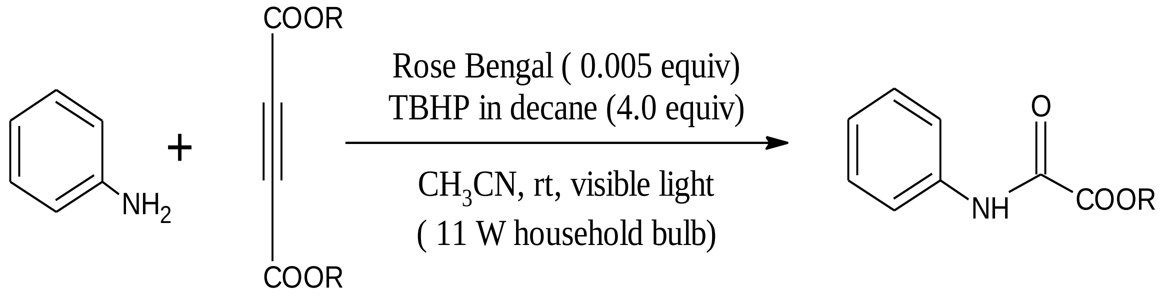
1. Visible Light Photoredox Catalyzed Thiophosphate Synthesis Using Methylene Blue as Promoter



Methyene blue

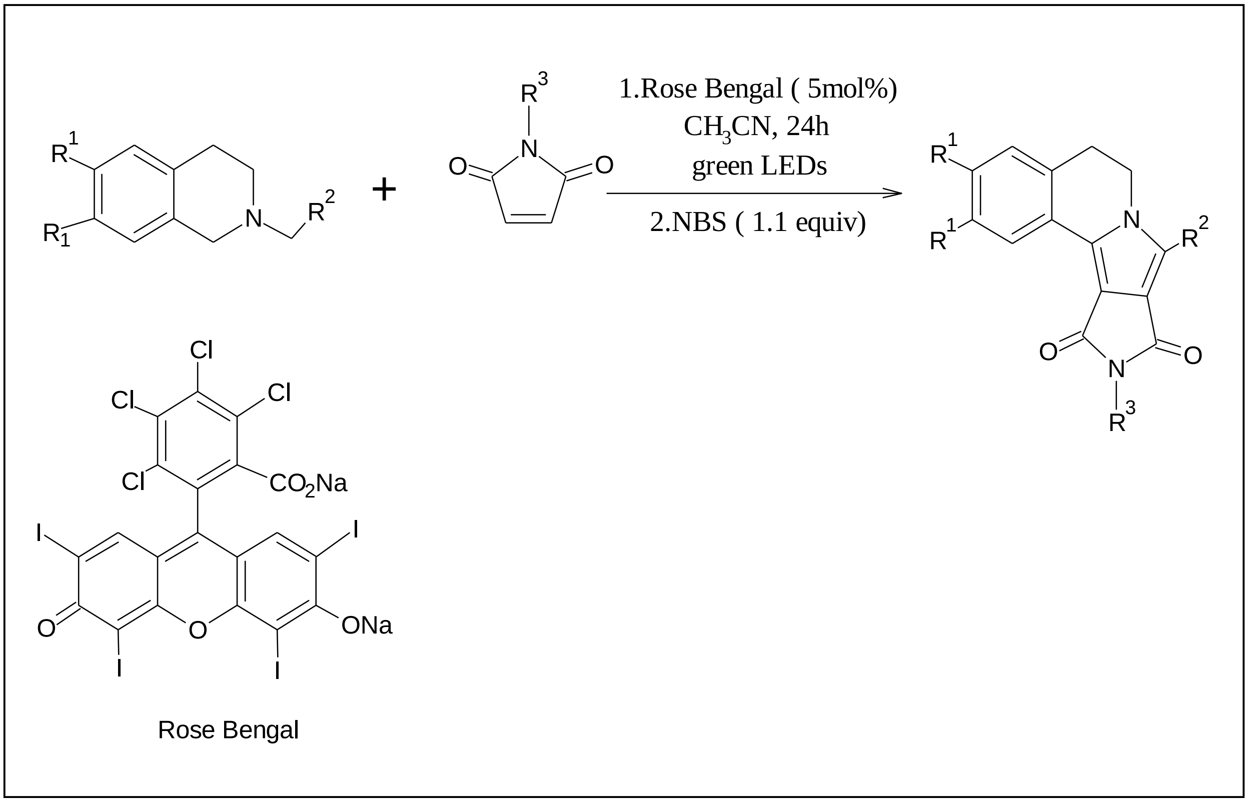
In 2018, Hao Zhang et al. reported synthesis of thiophosphate derivatives catalyzed by methylene blue with blue light irradiation under air atmosphere[13]. The thiophosphate products, which are found in many pharmaceuticals and pesticides, were obtained in moderate to good yields. Mild reaction conditions were used. When K_2CO_3 and ^iPrOH were used as base and solvent respectively 95% yield was obtained[14].

2. Visible light-mediated photocatalytic oxidative cleavage of activated alkynes via hydroamination: a direct approach to oxamates



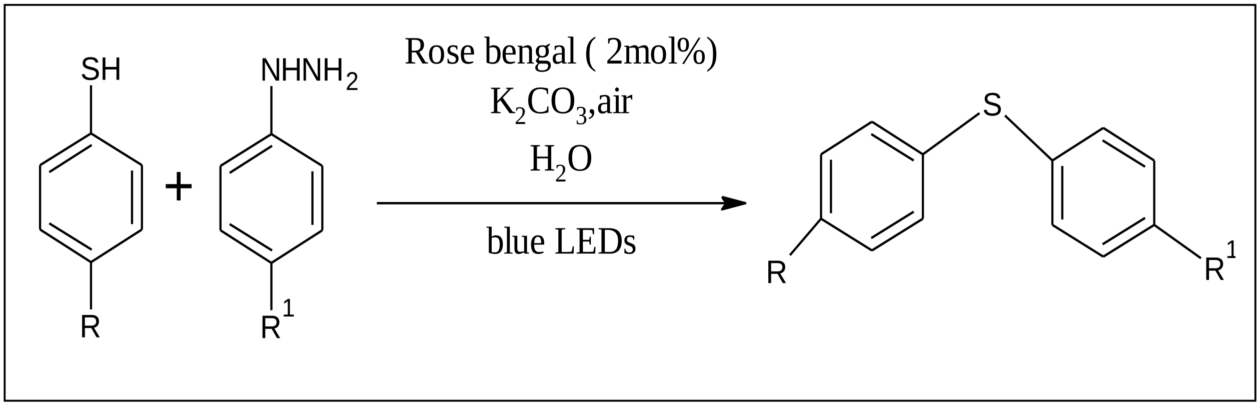
In 2020, Narenderreddy Katta et al. developed a visible light driven Rose Bengal photocatalysis oxidative cleavage of C–C triple bond through hydroamination for the direct synthesis of oxamates from amines and electron deficient alkynes as the starting material[3]. These reactions were carried out in the presence of acetonitrile, TBHP which play a dual role as “O” source and for the regeneration of the photocatalyst and 11W household bulb as the source of visible light[3].

3. Visible-light Photoredox Catalyzed Synthesis of Pyrroloisoquinolines via Organocatalytic Oxidation/[3+2] Cycloaddition /Oxidative Aromatization Reaction Cascade with Rose Bengal



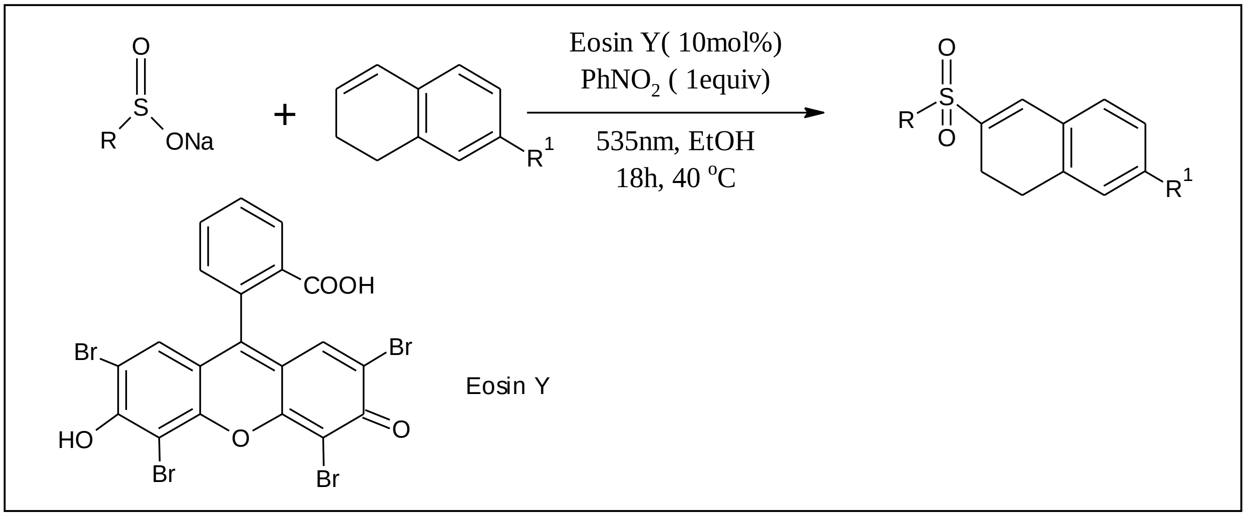
In 2014, Carlos Vila et al. developed a metal-free photoredox oxidation/[3 + 2] dipolar cycloaddition/oxidative aromatization cascade catalyzed by Rose Bengal using visible-light[13]. In this reaction pyrrolo [2,1-*a*]isoquinolines was synthesized from readily available maleimides and tetrahydroisoquinolines. Using rose bengal as organo-photocatalyst and CH_3CN as solvent with green light irradiation for 24 h upto 72% yield was obtained[13].

4. Visible-Light-Mediated Synthesis of Unsymmetrical Diaryl Sulfides via Oxidative Coupling of Arylhydrazine with Thiol



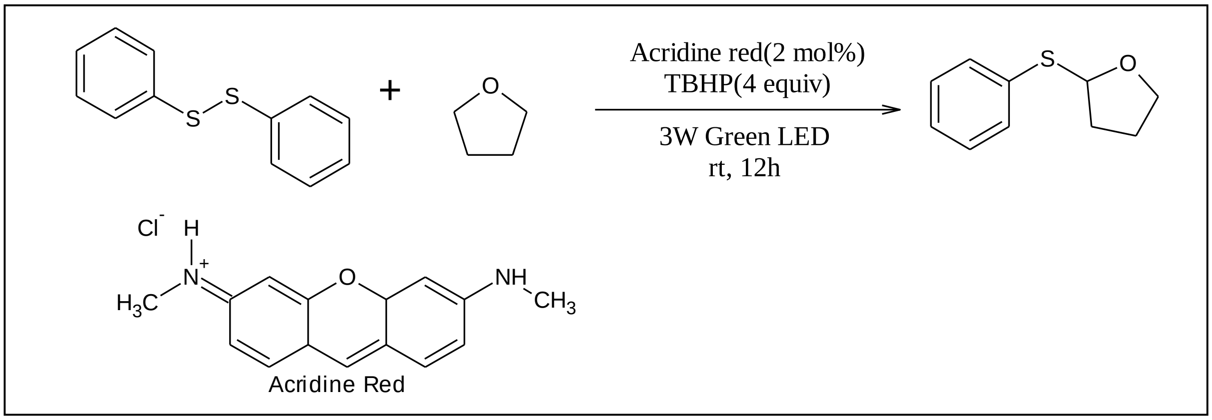
In 2018, Golam Kibriya et al. reported a metal-free visible-light-promoted oxidative coupling between thiols and arylhydrazines to afford diaryl sulfides using a catalytic amount of rose Bengal as photocatalyst under[2]. Using Na_2CO_3 as the base and H_2O as solvent at ambient temperature under aerobic conditions unsymmetrical diaryl sulfides with broad functionalities were synthesized in good yields[2].

5. Eosin Y (EY) Photoredox-Catalyzed Sulfonylation of Alkenes: Scope and Mechanism



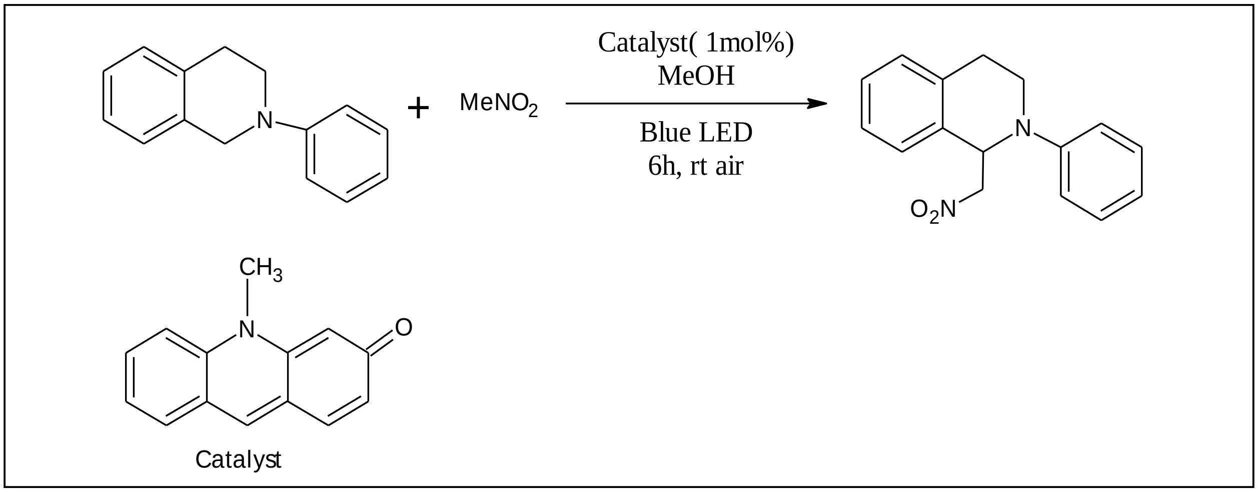
In 2016, Andreas Uwe Meyer et al. reported synthesis of alkyl and aryl vinyl sulfones by eosin Y (EY)-mediated visible-light photooxidation of sulfinate salts and the reaction of the resulting S-centered radicals with alkenes[8]. Nitrobenzene is a strong quencher and preferentially oxidizes the excited catalyst. Using ethanol as solvent at 40°C under irradiation of visible light for 18h resulted in moderate to good yields of vinyl sulfones from corresponding starting materials[8].

6. Visible-Light -Induced Direct Thiolation at α‑C (sp3)−H of Ethers with Disulfides Using Acridine Red as Photocatalyst



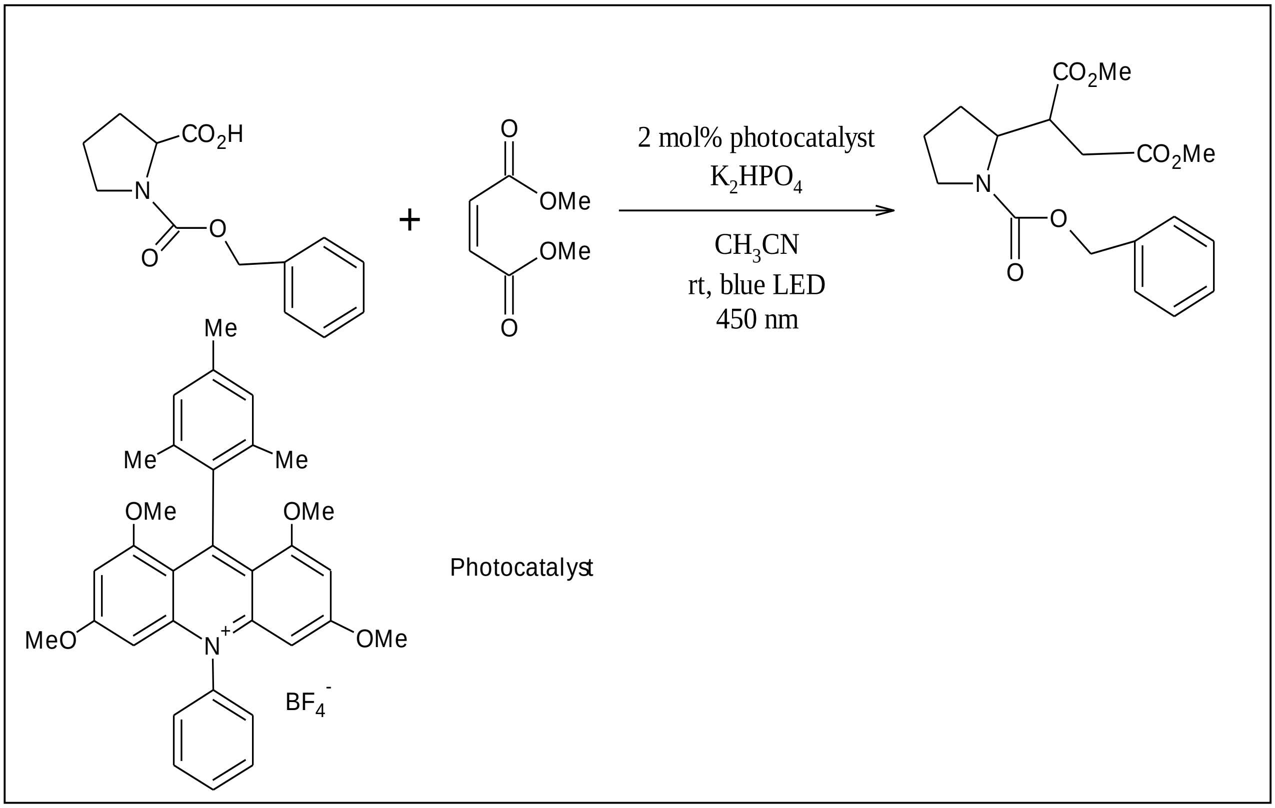
In 2016, Xianjin Zhu et al. developed a simple and efficient method for the preparation of α-arylthioethers through a visible-light-induced direct thiolation at α-C(sp3)−H of ethers with diaryl disulfides for 12 h using acridine red as a photocatalyst and tert-butyl hydroperoxide(TBHP) as oxidant. The reactions occurred at ambient conditions and generated the corresponding products in good to excellent yields[15].

7. N-substituted-3(10H)-acridones as visible-light photosensitizers for organic photoredox catalysis



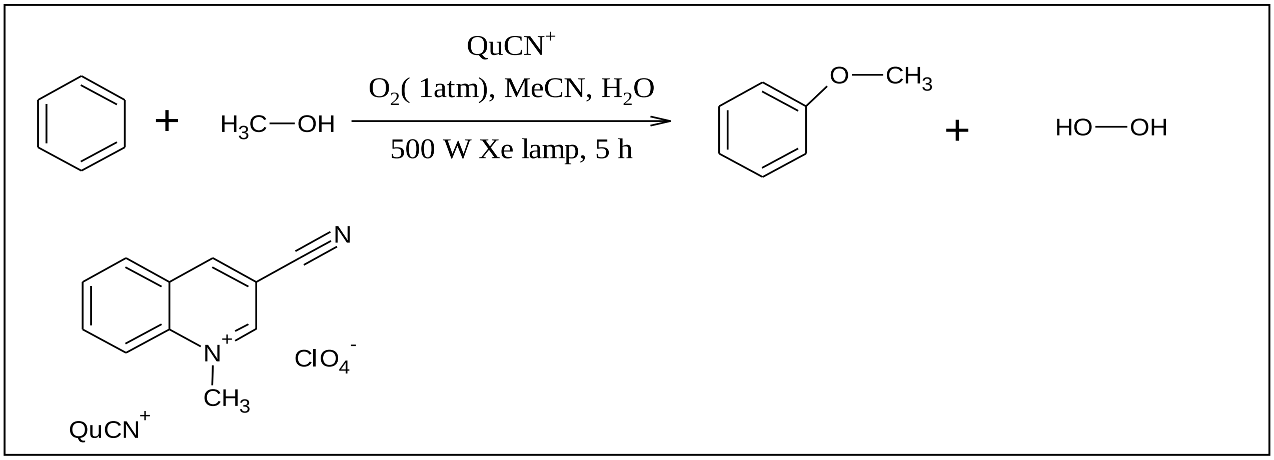
In 2017, Kun Chen et al. reported N-Substituted-3(10H)-acridones as a visible-light organic photocatalyst[4]. These photosensitizers are efficient for oxidative coupling reaction of N-aryl tetrahydroisoquinolines with various nucleophiles with blue LEDs as source of light methanol as the solvent. This catalyst is stable and can be cost effectively prepared[5].

8. Acridinium-Based Photocatalysts: A Sustainable Option in Photoredox Catalysis



In 2016, Amruta Joshi-Pangu et al. reported 1,3,5,6-substituted acridinium salts as organic alternatives to transition-metal-based photocatalysts that combine a useful redox window and higher chemical stability[3]. The tetrasubstituted catalysts have shown catalytic performance comparable to that of [Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6) in the decarboxylative conjugate addition of Cbz-proline to dimethyl maleate in the presence of acetonitrile when irradiated in the presence of blue light for 20 h gave 88% yield[3].

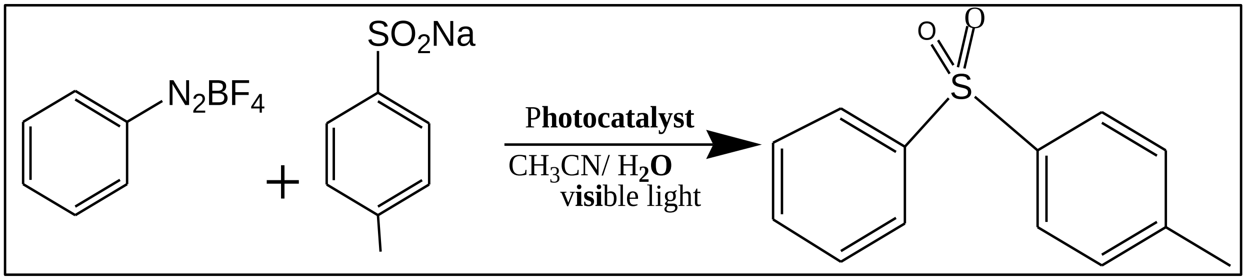
9. Alkoxylation of Benzene with 3-Cyano-1-methylquinolinium ion ($QuCN^+$)



In 2012, Kei Ohkubo et al. reported photocatalytic alkoxylation of benzene to phenol. Photoirradiation of an oxygen-saturated MeCN solution containing $QuCN^+$, benzene and methanol (MeOH) was done with a xenon lamp (500 W, $\lambda > 290$ nm) to yield methoxybenzene and H_2O_2[10].The yield of methoxybenzene after 4 h of photoirradiation was 26%. When methanol was replaced by ethanol, isopropanol and tert-butanol, the photocatalytic alkoxylation of benzene occurred to yield the corresponding alkoxybenzenes[11].

Result and Discussions

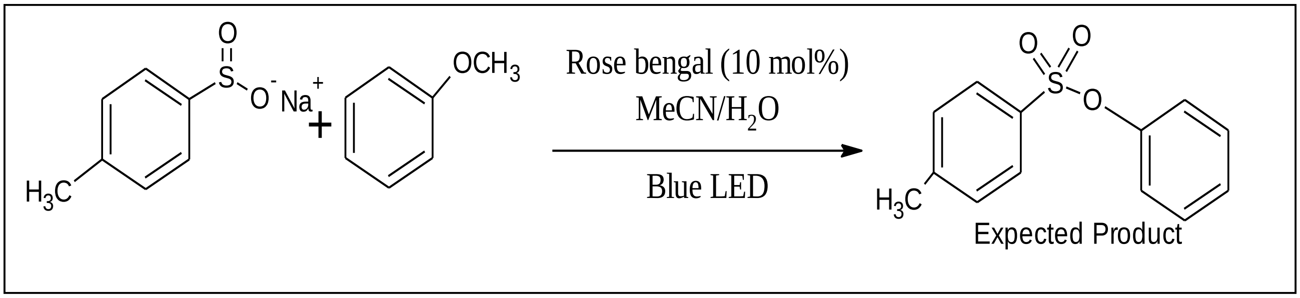
1. Reaction Methodologies involving dyes as Photoredox Catalyst

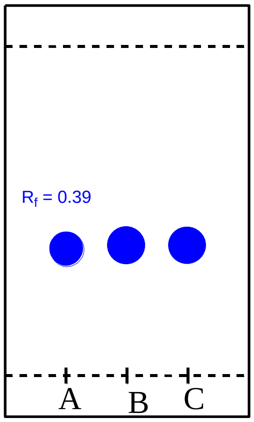


Above reaction is reported using rose bengal as photocatalyst. Utilization of p-toluenesulfinate with reactants undergoes coupling reactions to give interesting bond formation. Therefore using similar reaction conditions, sodium p-toluenesulfinate was reacted with anisole, phenol and cyclohexene. We also wanted to check the reactivity using some other dye as catalyst, therefore methylene blue was used. Reactivity of 1-hexane sulfonic acid salt was also studied by carrying out reactions under similar reaction conditions using blue light irradiation.

i. Reactions Using Sodium p-toluenesulfinate

a) With anisole and rose bengal as the photocatalyst

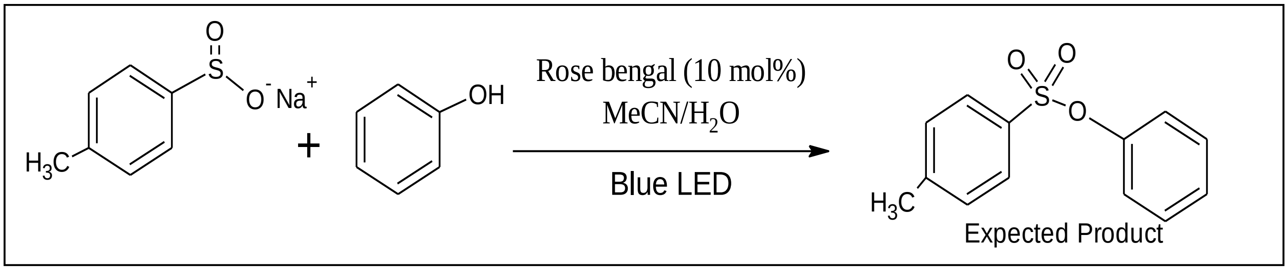


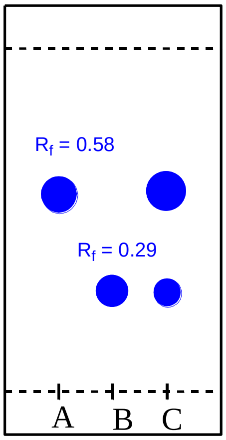


A	Anisole
B	Reaction mixture
C	Co

No product was obtained with anisole and Sodium p-toluene sulfinate even after the long hours of irradiation with Blue LEDs in presence of Rose Bengal as a photo catalyst.

b) With Phenol and Rose bengal as photocatalyst

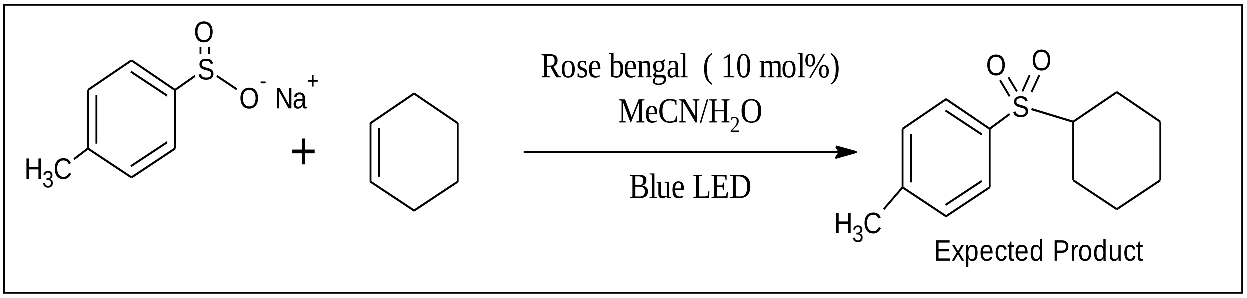


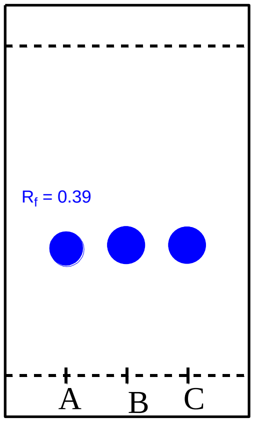


A	Phenol
B	Reaction mixture
C	Co

Silica gel plate and 20 % ethylacetate was used as the development solvent. As observed from the TLC, reaction mixture gave a new spot which indicates the formation of product. This product was extracted and purified using column chromatography. Visualization techniques used were UV light and iodine vapours.

c) With Cyclohexene and Rose bengal as photocatalyst





A	Cyclohexene
B	Reaction mixture
C	Co

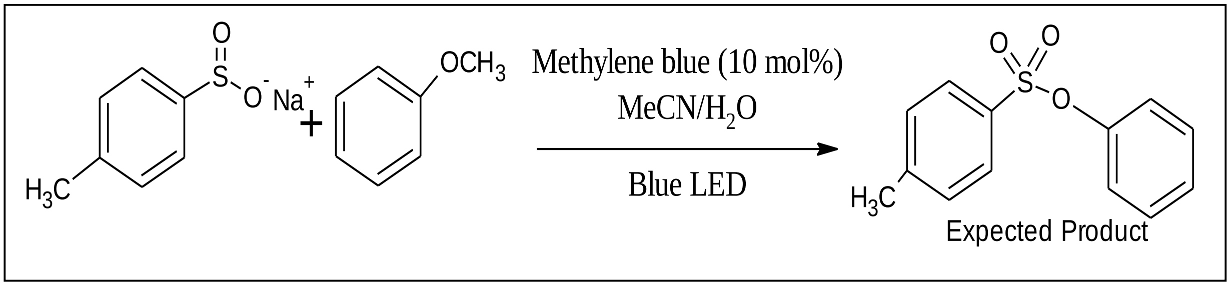
Using a silica plate and 20% ethylacetate as the development solvent, cyclohexene, reaction mixture and Co when spotted side by side gave spot for cyclohexene and no other spot was observed for reaction mixture which concluded that there is no formation of product in this reaction. Visualization techniques used were UV light and iodine vapours.

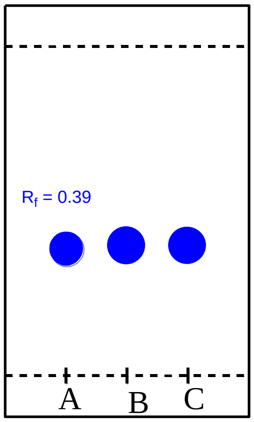
Combine results of all three reactions of Sodium p-toluene sulfinate with Rose bengal as photocatalyst are depicted in table 1.

TABLE 1.

Substrate	Light source	λ (nm)	Solvent	Time	Yield (%)
Anisole	Blue LED	455	MeCN/ H_2O	24h	n.r.
Phenol	Blue LED	455	MeCN/ H_2O	24h	25%
Cyclohexene	Blue LED	455	MeCN/ H_2O	24h	n.r.

d) With Anisole and Methylene blue as photocatalyst

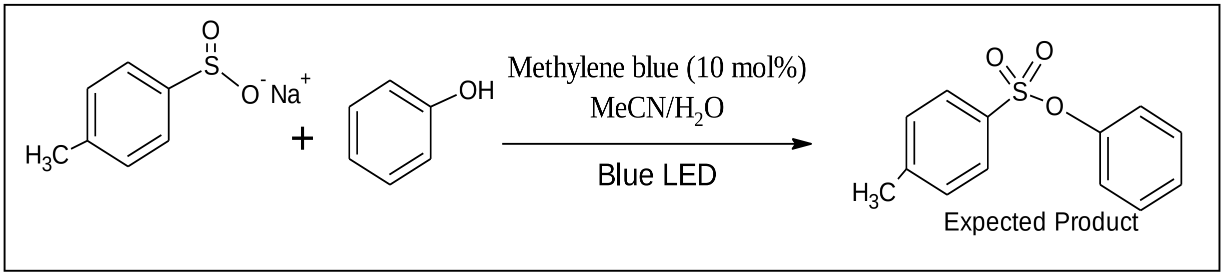


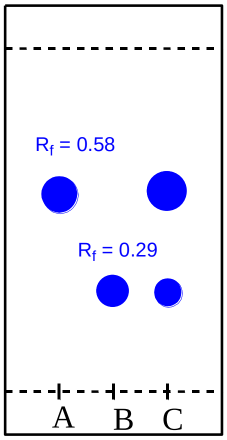


A	Anisole
B	Reaction mixture
C	Co

No product was obtained with anisole and p-Toluene sulfinate salt even after the long hours of irradiation with blue LEDs in presence of methylene blue as a photo catalyst.

e) With Phenol and Methylene blue as photocatalyst

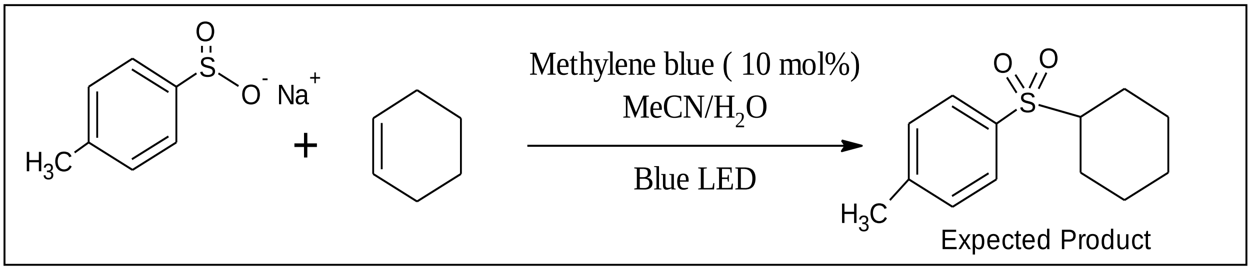


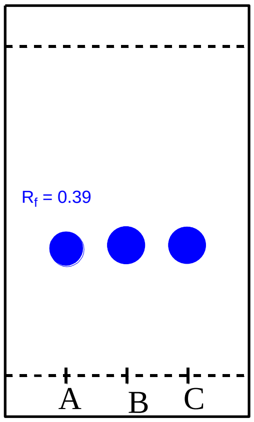


A	Phenol
B	Reaction mixture
C	Co

Silica gel plate and 20 % ethylacetate was used as the development solvent. As observed from the TLC, reaction mixture gave a new spot which indicates the formation of product. This product was extracted and purified using column chromatography. Visualization techniques used were UV light and iodine vapours.

f) With Cyclohexene and Methylene blue as photocatalyst





A	Cyclohexene
B	Reaction mixture
C	Co

No product was obtained with cyclohexene and p-Toluene sulfinate salt even after the long hours of irradiation with blue LEDs in presence of methylene blue as a photo catalyst.

Combine results of all three reactions of Sodium p-toluene sulfinate with Methylene blue as photocatalyst are depicted in table 2.

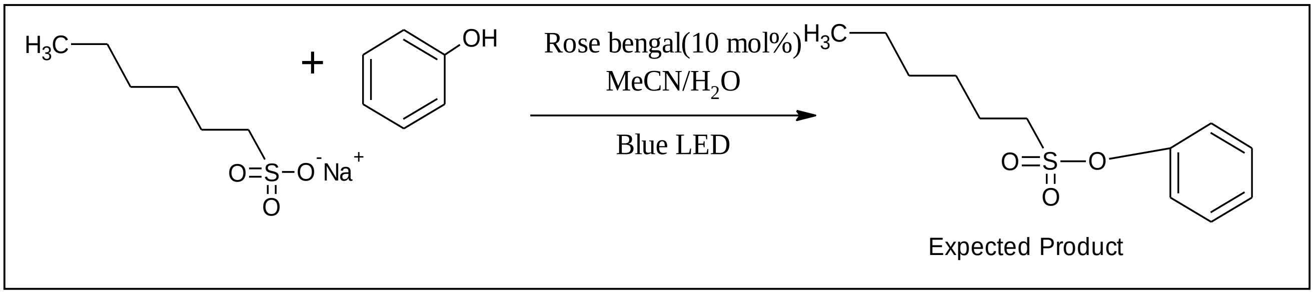
TABLE 2.

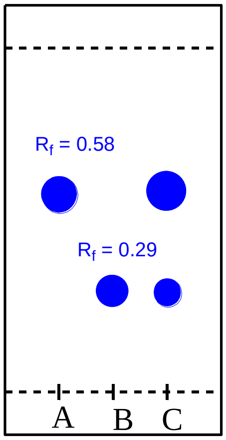
Substrate	Light source	λ (nm)	Solvent	Time	Yield (%)
Anisole	Blue LED	455	MeCN/H_2O	34h	n.r.
Phenol	Blue LED	455	MeCN/H_2O	24h	24%
Cyclohexene	Blue LED	455	MeCN/H_2O	24h	n.r.

As seen above sodium p-toluene sulfinate when reacted with phenol in presence of rose bengal and methylene blue both cases resulted in the formation of product, therefore following reactions were carried out using 1-hexane sulfonic acid sodium salt and phenol in presence of rose bengal and methylene blue as photocatalyst.

ii. Reactions using 1-Hexane sulfonic acid sodium salt

a) Using Phenol and Rose bengal as photocatalyst

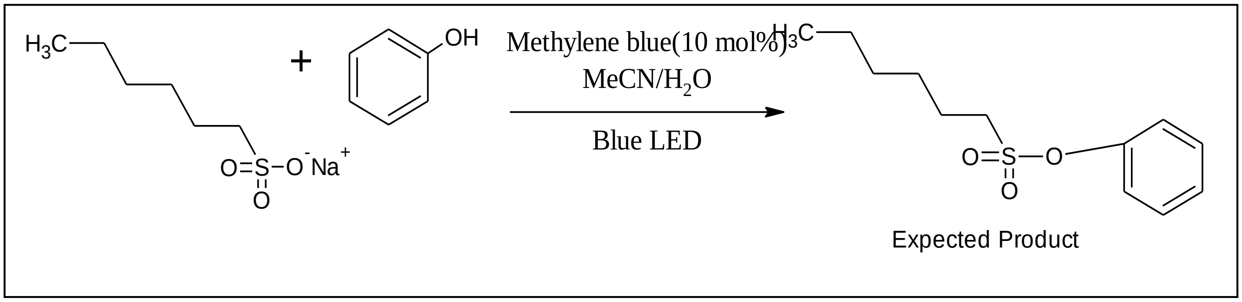


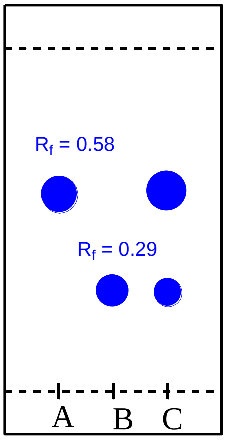


A	Phenol
B	Reaction mixture
C	Co

Silica gel plate and 20 % ethylacetate was used as the development solvent. As observed from the TLC, reaction mixture gave a new spot which indicates the formation of product. This product was extracted and purified using column chromatography. Visualization techniques used were UV light and iodine vapours.

b) Using Phenol and Methylene blue as photocatalyst





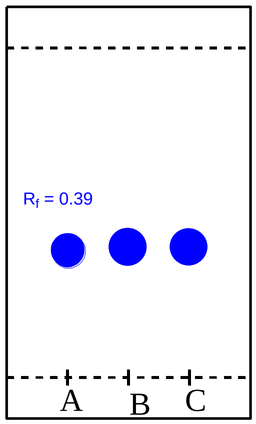
A	Phenol
B	Reaction mixture
C	Co

Silica gel plate and 20 % ethylacetate was used as the development solvent. As observed from the TLC, reaction mixture gave a new spot which indicates the formation of product. This product was extracted and purified using column chromatography. Visualization techniques used were UV light and iodine vapours.

Combine results of the above two reactions of 1-Hexane Sulphonic acid Sodium Salt are depicted in table 3.

TABLE 3.

Substrate	**Light source**	**Photocatalyst**	**λ (nm)**	**Solvent**	**Time**	**Yield (%)**
Phenol	Blue LED	Rose bengal	455	MeCN/H_2O	36h	21%
Phenol	Blue LED	Methylene blue	455	MeCN/H_2O	36h	20%



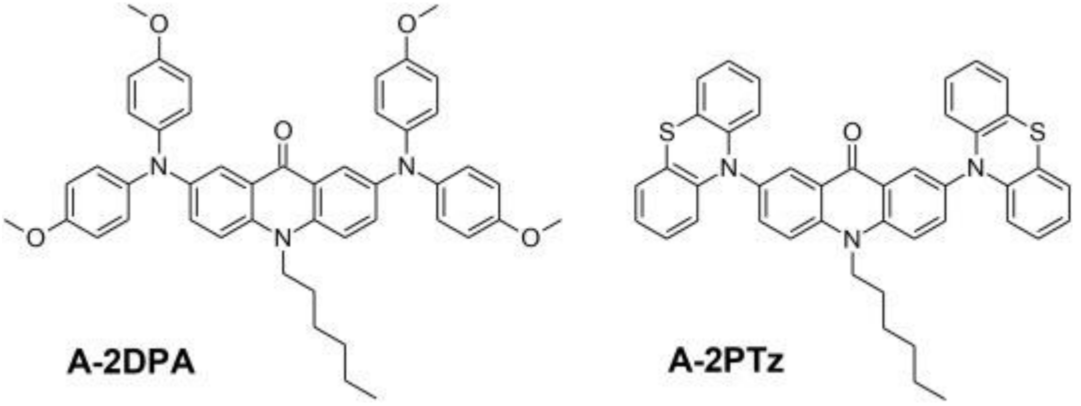
A	1-Hexane sulfonic acid sodium salt with phenol in presence of rose bengal
B	1-Hexane sulfonic acid sodium salt with phenol in presence of methylene blue
C	Co

It was found that the new spot formed for both the above reactions appeared at the same R_f value. This indicates that the product formed in both the reactions is same.

2. Synthesis of Photoredox Catalyst

Fluorescent heterocyclic compounds are point of interest in many disciplines such as emitters for electroluminescence devices, molecular probes for biochemical research but also as dyes in traditional textile and polymer fields, fluorescent whitening agents and photo conducting materials[1]. Acridones and their derivatives are well-known fluorescent compounds with high quantum yields and have attracted much attention owing to their potential high technology applications including fluorescence probes in chemosensors[1].

Previously, acridone has been reported as a photoinitiator for free radical polymerization (FRP) under UV light or in combination with a photoactive component such as Cl_2 or Br_2 under visible light for the polymerization of methyl methacrylate (MMA). However, the latter study requires a heating temperature up to 40°C, and it is carried out in a highly toxic solvent such as CCl_4[1].



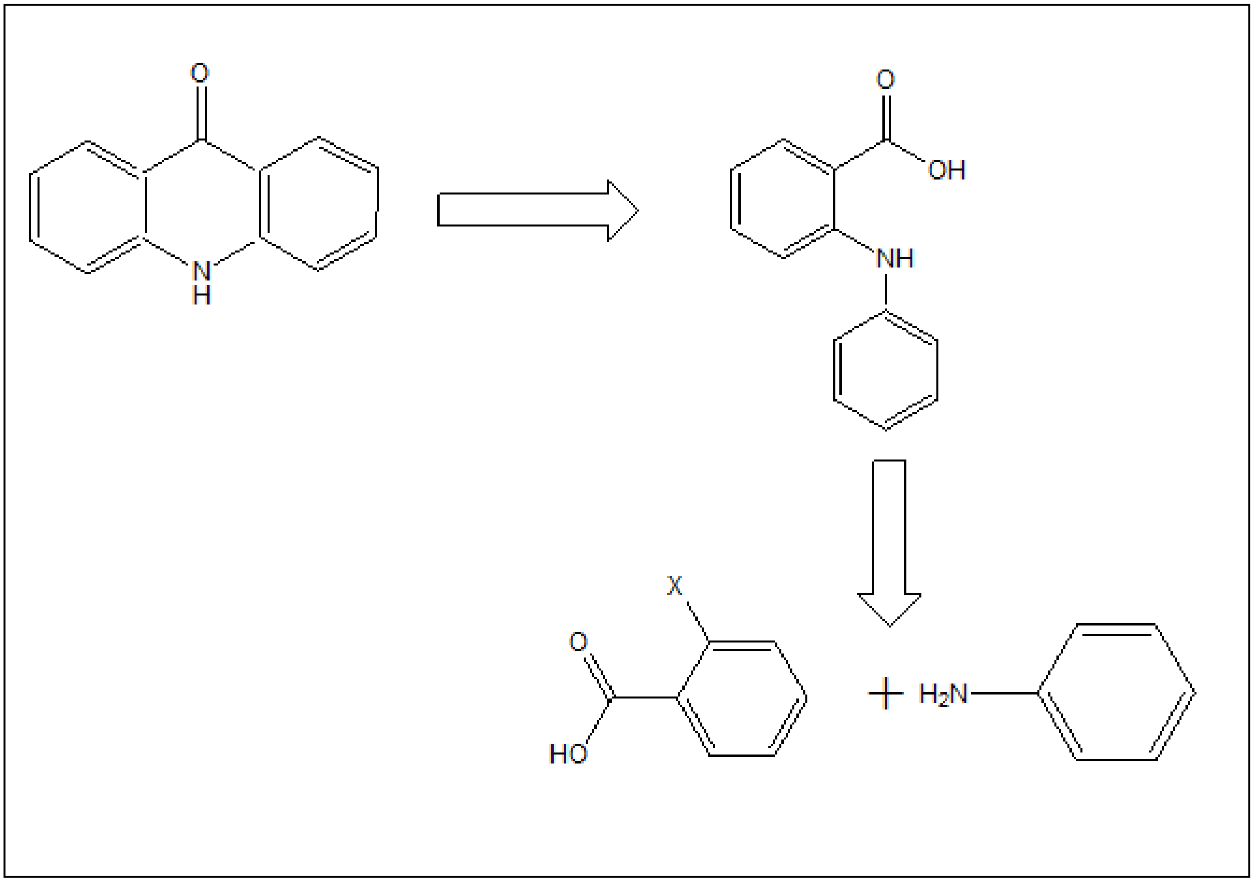
A-2DPA

A-2PTz

Two new acridone derivatives (A-2DPA & A-2PTz) were developed as photo initiators for the cationic polymerization of epoxides and the free radical polymerization of (meth) acrylates upon near-UV or visible LEDs. These new initiating systems have found an interesting applications in 3D printing and also for low migration resins[1].

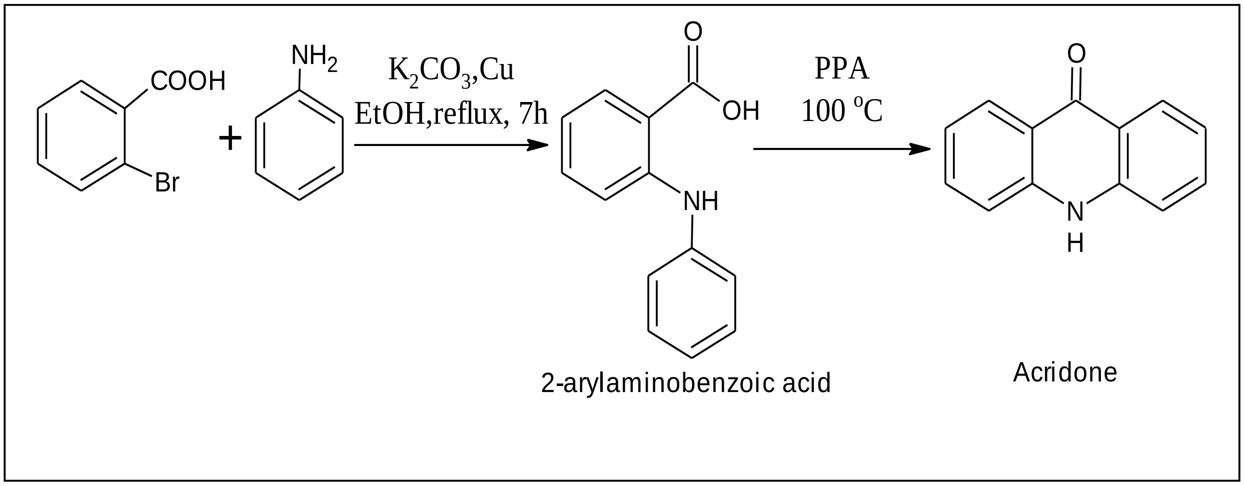
Owing to the knowledge, we gave a retrosynthetic pathway for acridone via 2-arylaminobenzoic acid.

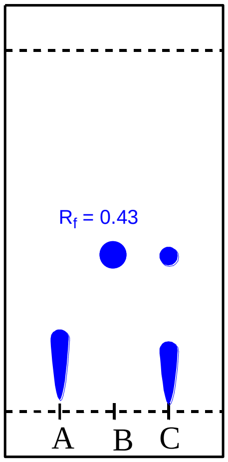
Retrosynthetic Pathway



On the basis of retrosynthetic pathway, a scheme was proposed using 2-bromobenzoic acid and aniline.

i. Synthesis of Acridone





A	2-Bromobenzoic acid
B	Acridone
C	Co

The reaction was monitored by TLC using 50% ethylacetate

Yield: 75%

Nature: Pale yellow

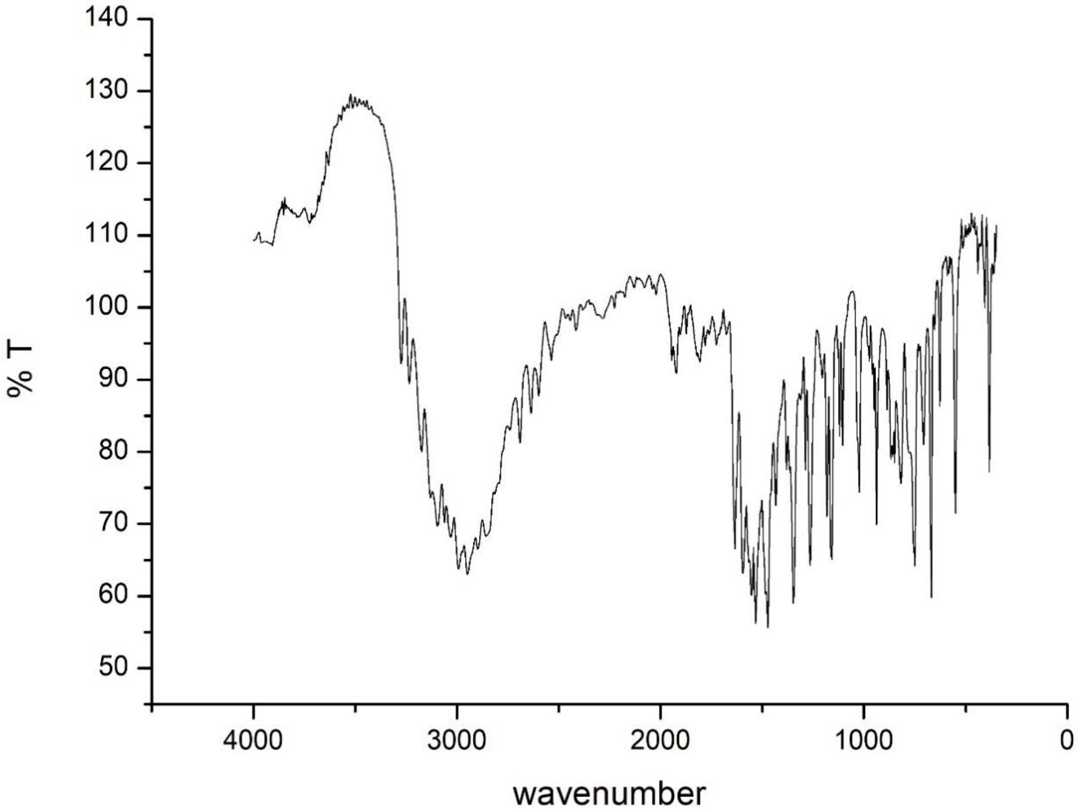
Melting point: 345°C

IR spectra details (KBr), cm^{-1}: N-H Stretch: 3250 cm^{-1}

C=O Stretch: 1675 cm^{-1}

IR DATA TABLE:

IR of Acridone:

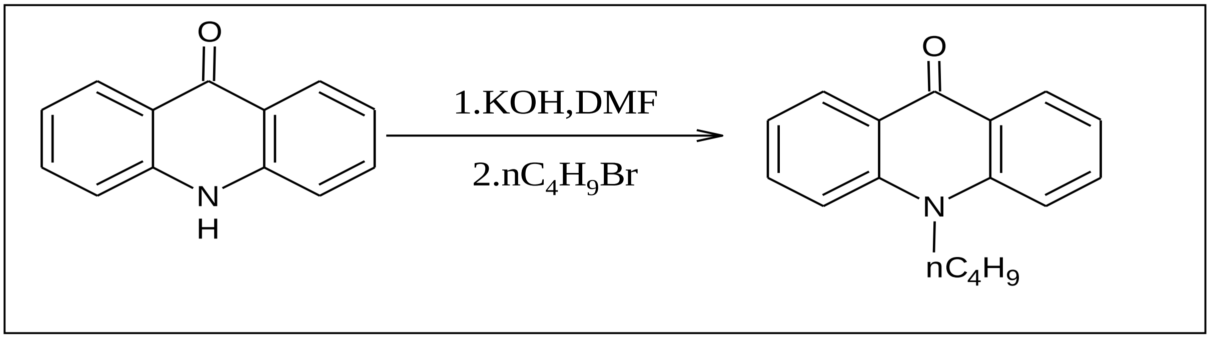


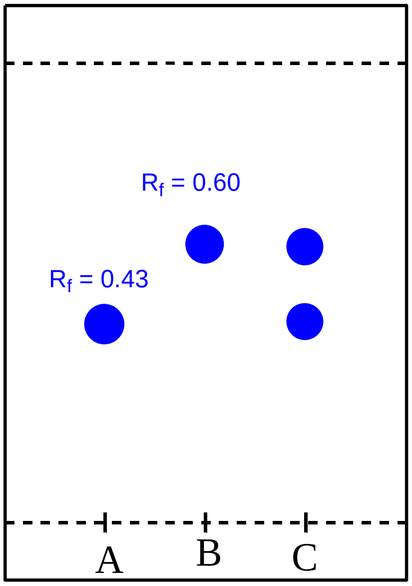
N-H Stretch: 3250 cm^{-1}

C=O Stretch: 1675 cm^{-1}

Band at 1675 cm^{-1} for carbonyl frequency and 3250 cm^{-1} for N-H confirms the formation of acridone. Once the acridone was synthesized the next step towards photoredox catalyst was N-alkylation. For N-alkylation we chose n-butylbromide in alkaline condition. The results of the reaction are depicted below.

ii. N-alkylation of acridone





A	Acridone
B	N-alkylated Acridone
C	Co

The reaction was monitored by TLC 50% ethyl acetate.

Yield: 70%

Nature: Pale yellow

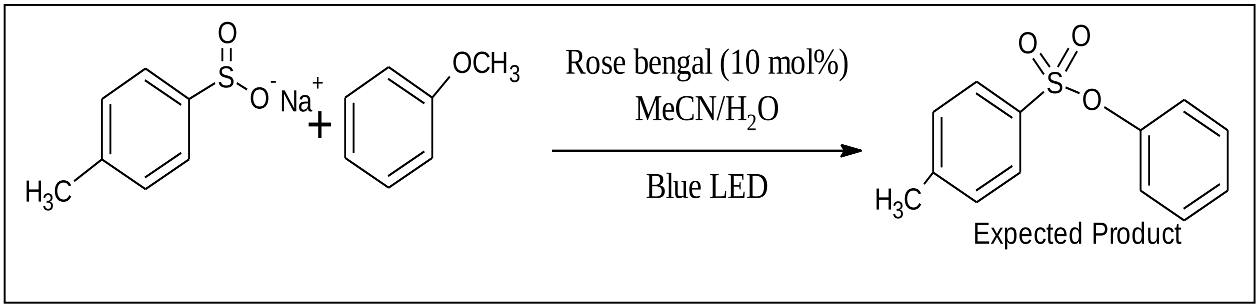
Melting Point: 100°C

Experimental work

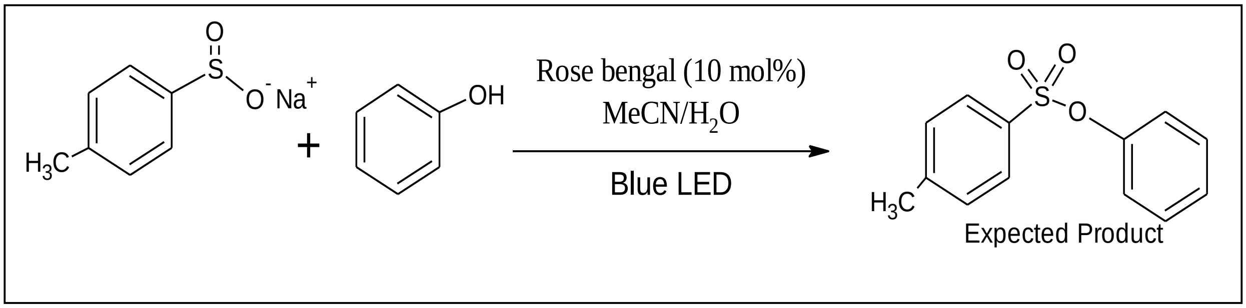
1. Reaction Methodologies involving dyes as Photoredox Catalyst

i. Reactions Using Sodium p-toluenesulfinate

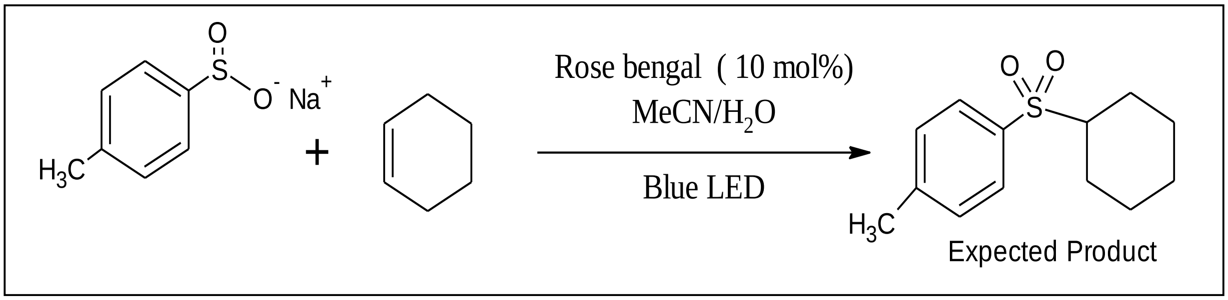
a) With anisole and rose bengal as the photocatalyst



b) With phenol and rose bengal as photocatalyst



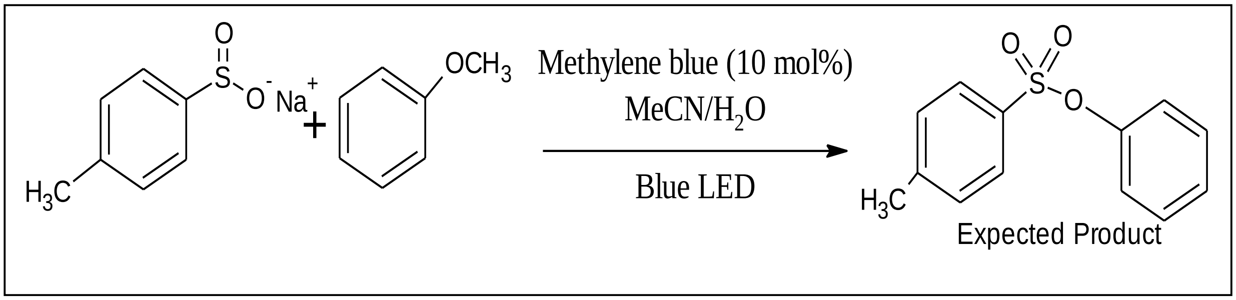
c) With cyclohexene and rose bengal as photocatalyst



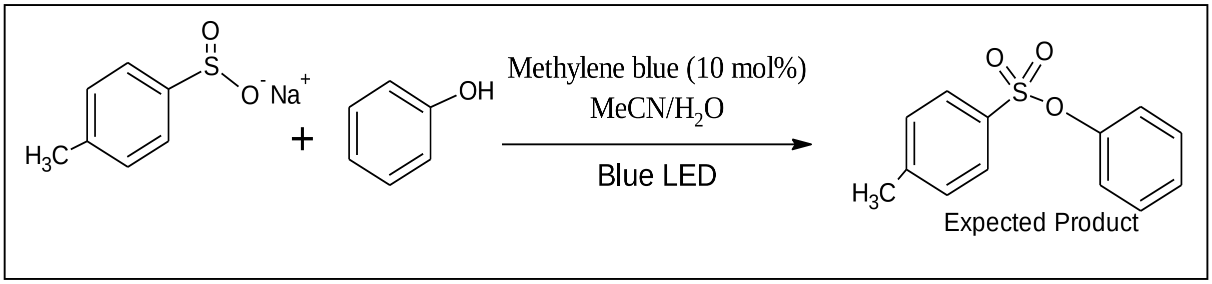
Sodium p-toluene sulfinate (1mmol) was taken in a clean round bottom flask .To this the reactant (anisole or phenol or cyclohexene) (1.3 mmol) was added using pipette. To the same acetonitrile/ water (10:1) was added as a solvent, followed by the addition of an organic dye rose bengal (10 mol %) as a photocatalyst. The reaction mixture was stirred for 24 hours in presence of blue

LEDs.The progress of the reaction was monitored using TLCs and after the completion of the reaction the product was extracted using ethyl acetate and water.

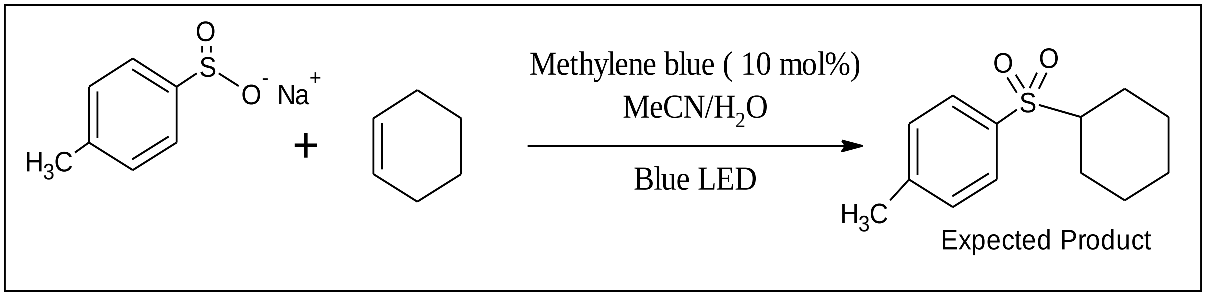
d) With anisole and methylene blue as photocatalyst



e) With phenol and methylene blue as photocatalyst



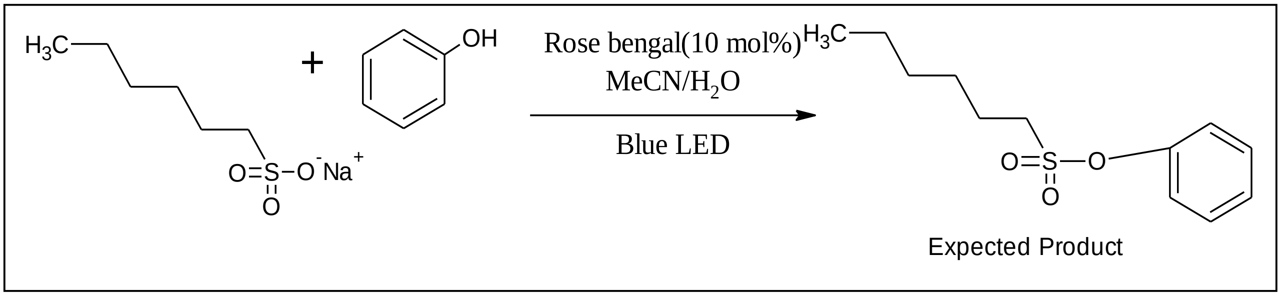
f) With cyclohexene and methylene blue as photocatalyst



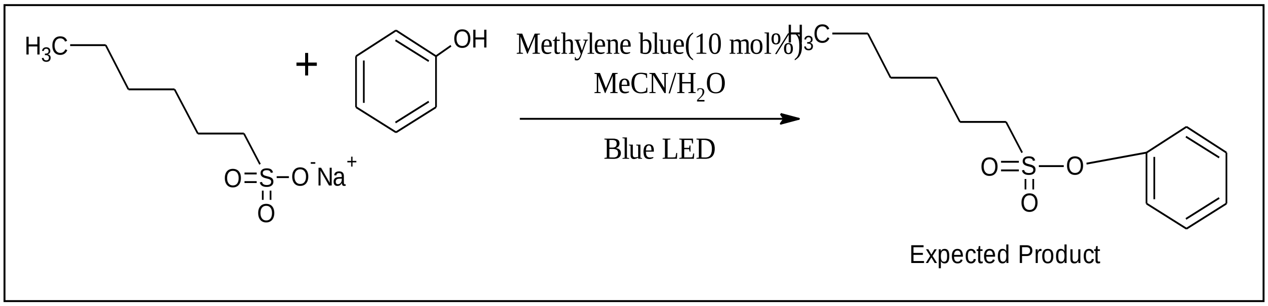
Sodium p-toluene sulfinate (1mmol) was taken in a clean round bottom flask .To this the reactant (anisole or phenol or cyclohexene) (1.3 mmol) was added using pipette. To the same acetonitrile/ water (10:1) was added as a solvent, followed by the addition of an organic dye methylene blue (10 mol %) as a photocatalyst. The reaction mixture was stirred for 24 hours in presence of blue LEDs.The progress of the reaction was monitored using TLCs and after the completion of the reaction the product was extracted using ethyl acetate and water.

ii. Reactions using 1-Hexane sulphonic acid sodium salt

a) With phenol and rose bengal as photocatalyst



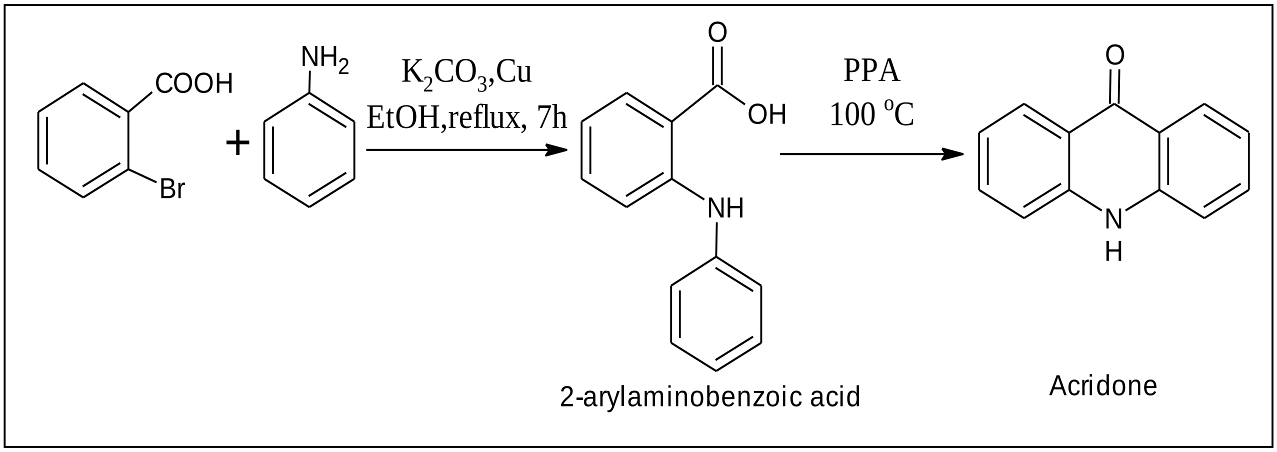
b) With phenol and methylene blue as photocatalyst



1-Hexane Sulphonic acid sodium salt (1mmol) was taken in a clean round bottom flask .To this phenol (1.3 mmol) was added using pipette. To the same acetonitrile/ water (10:1) was added as a solvent, followed by the addition of an organic dye (rose bengal/methylene blue) (10 mol %) as photocatalyst. The reaction mixture was stirred for 36 hours in presence of blue LEDs.The progress of the reaction was monitored using TLCs and after the completion of the reaction the product was extracted using ethyl acetate and water.

2. Synthesis of Photoredox Catalyst

i. Synthesis of acridone



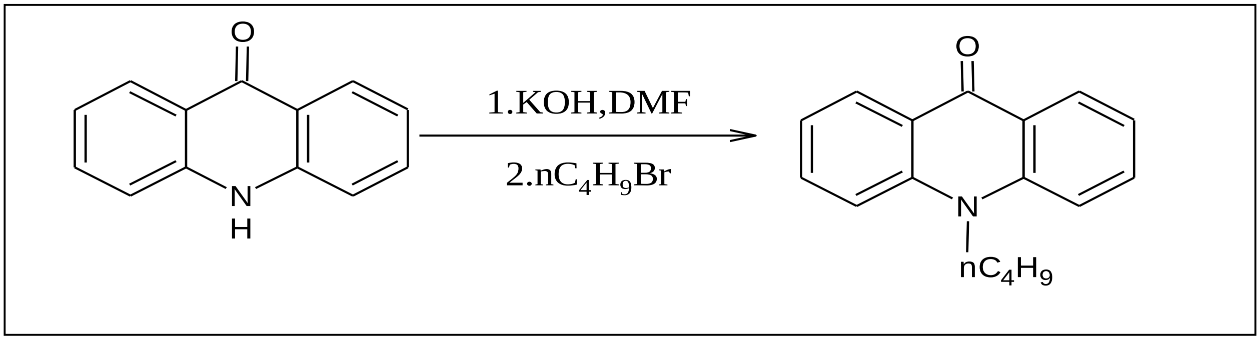
General procedure for the synthesis of 2-arylaminobenzoic acids

A solution of 2-bromobenzoic acid (8.5 mmol), aniline (159.0 mmol), copper powder (4.7 mmol), and potassium carbonate (119.0 mmol) in ethanol (80 ml) was heated under reflux for 7 h. After completion of reaction (checked by TLC), the reaction mixture was cooled down to room temperature, poured into hot water and boiled in the presence of activated charcoal for 15 min. Then, it was filtered through celite and the filtrate was acidified with HCl to obtain precipitated product which was purified using recrystallization from ethanol to obtain pure products.

General procedure for the synthesis of acridone

A mixture of 2-arylaminobenzoic acid (1 mmol) and polyphosphoric acid (PPA) (10mmol) was heated at 100 °C for 3 h. Upon completion, the reaction mixture was poured into hot water (50 ml). After cooling to room temperature, the mixture was made alkaline by ammonia solution. The obtained yellow precipitates were filtered off, washed with hot water, and purified using recrystallization from acetic acid to obtain the pure products.

ii. N-alkylation of acridone



General procedure for N-alkylation of acridone

The acridone (1mmol) and powdered potassium hydroxide (1.1mmol) were boiled in 20-30 ml DMF for 10 min, and the mixture was distilled azeotropically until removal of water was complete. N-butyl bromide (1.1mmol) was added under stirring to the cooled solution. The mixture was refluxed for 10-30 minutes, and then poured over ice-water mixture. The filtered precipitate was dried and extracted twice with chloroform. Thereafter, the solvent was evaporated and the product was recrystallized from methanol.

Conclusion

Our aim was to use organic photocatalysts to carry out reactions as they are cheap, readily available and easy to handle.

Therefore using dyes like rose bengal and methylene blue as photocatalyst and blue LED’s as the source of light, series of reactions were carried out using different reagents and solvent conditions. We came to the conclusion, sodium p-toluene sulfinate and 1-hexane sulfonic acid salt when reacted with phenol using acetonitrile/ water (10:1) as solvent resulted in product. But due to the lack of time we were not able to characterize the product and therefore needs further studies.

However no product was formed when sodium p-toluene sulfinate and 1-hexane sulfonic acid salt was reacted with anisole and cyclohexene.

We were successful in synthesizing n-alkylated acridone using 2-bromobenzoic acid and aniline. We were supposed to use this n-alkylated acridone as photocatalyst to carry out organic transformations using suitable reagents and solvent conditions but due to lack of time we were not able to do so and therefore it needs further studies.

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