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Title: **Synthesis and Applications of 1, 2-Diketones**

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Synthesis and Applications of 1, 2-Diketones

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ABSTRACT

This review article outlines the published data on the synthesis of 1, 2-diketones and its applications. Significantly, 1, 2-diketones play a vital role as an intermediate in the pharmaceutical field. They are mostly used in the production of medicine-related components. The derivatives of 1, 2-diketones are used as photoinitiators in material science. In this review article, efficient procedures and applications are primarily focused on the synthesis of 1, 2-diketones.

Keywords: applications, derivatives, synthesis, 1,2-diketones

INTRODUCTION

Chemistry plays a vital role in ensuring that the upcoming generation of materials, chemicals, and electricity is more stable than the present generation. It is significant for the development of cost-effective and new approaches to reduce pollution, fulfill required needs for chemical products, and to produce friendly environment. Wherever practicable, it must build synthetic methods to use and produce chemicals that do not compromise the environment and human health [1]. Chemists around the world are acting regularly to design novel synthetic techniques to assemble the industry for the production of significant intermediates [2].

In synthetic organic chemistry 1, 2-diketones, intermediates plays a vital role in the generation of medicine-related components like heterocycles, pyrazines, imidazoles, and quinoxaline. In material chemistry and many metal complexes, they also act as ligands [3].

Harries and Temme prepared special conditions for the monomeric glyoxal and identified it as an odour-like yellow liquid formaldehyde with a sweetish taste afterwards [4]. It is present in many foodstuffs like wine, roasted coffee, dairy products, and in the manufacturing of microwave popcorn because of its buttery aroma and flavour. Diacetyl [2, 3-butanedione) is among those foods which is classified by the United States

Food and Drug Administration (U.S. FDA) as GRAS. It is often used in alcohol-free beverages, mostly to give aroma [5].

One can synthesize imidazole, which is an organic compound from 1, 2-diketones. Aryl, alkyl, and heteroaryl imidazoles are produced under microwave irradiation. Acetoin and diacetyl are present in cigarette smoke, waste vapours, liquid and solid animal waste vapours, petroleum-based fuel exhaust emissions, mouldy building vapours, and in charcoal processing, which also act as chemical reagents [6].

The elevated octane rating of 2, 3-butanedione makes it a suitable fuel for the air transport. Accumulation of 2, 3-butanedione were also identified in various bacteria, including organisms, Klebsiella and Paenibacillus, as well as in several Enterobacter, Serratia, and Serratia bacteria [7].

1,2-diketones are among the most important precursors which are considered versatile building blocks in organic synthesis, because of their easy conversion into various useful compounds like 1,2,4-triazines, quinolinyl, cycloheptanes, imidazoles, oligopyridines, pyridopyrazine, and quinoxaline with an extended conjugation [8].

2. BACKGROUND

Throughout the past decades, several protocols have been published for synthesizing 1, 2-diketones: via Sonogashira coupling, since internal alkynes could be readily accessible as starting material through direct oxidation of internal alkynes, in which one of the most basic methods is 1,2-dicarbonyl derivatives. Chi and Yusubov proposed the oxidation of alkynes in DMSO that was PdCl2 catalyzed oxidation. Meanwhile, Wan's group proposed the synthesis of 1, 2-diketones under alkynes oxidation and oxygen used as an oxidant. After this, Li and his co-workers reported Ag/Au- a catalyzed process using diphenyl sulfoxide as an oxidant [9]. 1, 2-diketones' derivative, camphor quinone was represented as (CQ) sensitive to blue light used as a dental material [10].

3. SCOPE OF THE REVIEW

The current review article aims to review the increasing need for 1, 2-diketones and their synthesis to make more reliable, economical, and greener. Environmental safety and hazards are also a major concern of the current review. Therefore, performing chemical reactions in the presence of a suitable catalyst that provides a high yield in a short time under mild conditions.

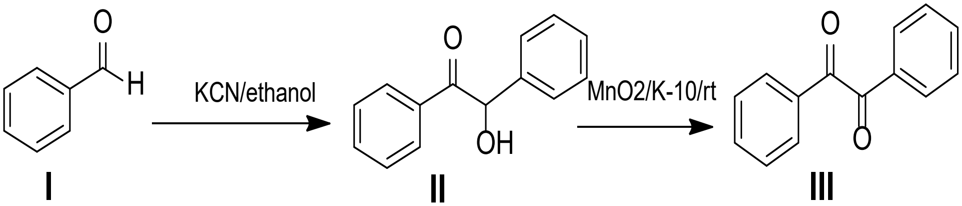
The development of such economic and eco-friendly methodologies is the prime focus of green and sustainable chemistry. 1, 2-diketones are major precursors for various organic synthesis in today's chemistry which is quite significant. It is a conventional thought that 1, 2-diketone can make azacyclic compounds [11].

4. SYNTHESIS OF 1,2-DIKETONES

Many methods have been reported for the synthesis of 1, 2-diketones. A few of them are mentioned below:

4.1. Oxidation of Benzoin

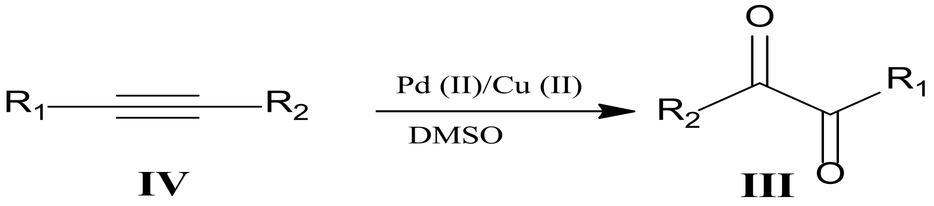
Scheme 1 shows a new oxidative procedure in a solvent-free domestic microwave oven for the formation of benzil [1,2-diketone) from heterogeneous benzoin [12].



Scheme 1. Oxidation of Benzoin

4.2. Oxidation of Alkynes

The Wacker-type oxidation of alkynes IV catalyzed by Pd(II), Cu (II)in the presence of DMSO and water is a convenient procedure for the synthesis of 1,2-diketone (**Scheme 2**). The reaction occurs under neutral conditions with high efficiency [13].

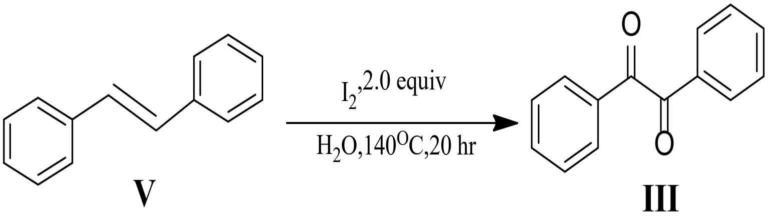


Scheme 2. Oxidation of alkynes

4.3. Oxidation of Stilbene

Green chemistry's two key principles are eradication of solvents in chemical processes or the substitution of dangerous solvents and substitution of eco-friendly metal with organic catalysts. In the world, water is the most eco-friendly media and in many fields, the use of benzil has prompted a lot of interest in the development of new techniques for their synthesis in water. Chemists have described molecular iodine as an important agent for both the oxidation of alkenes to diols and alcohols to aldehydes or ketones in water [14].

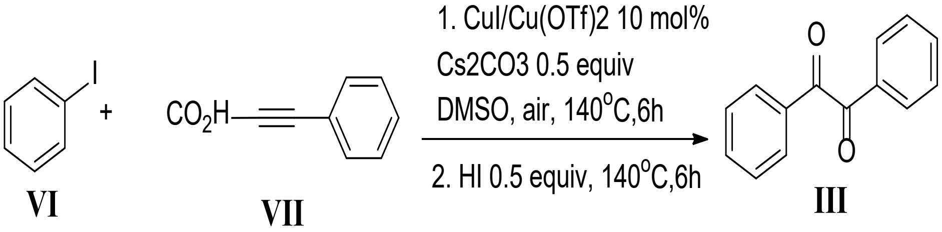
In this ongoing effort towards the conversion of alkenes, chemists wished to build a fast and highly chemo-selective system, without the addition of an acid, water oxidizes stilbenes V to benzil III (**Scheme 3**) under air or metal [15].



Scheme 3. Oxidation of Stilbene to Benzil

4.4. Synthesis of Benzil from Phenylpropynoic Acid and Aryl Iodides

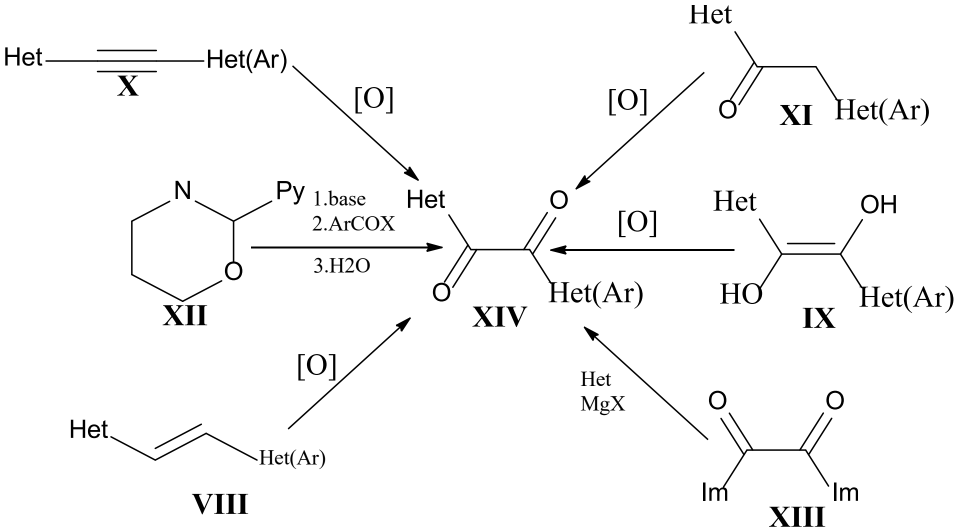
Scheme 4 showed the composition of $Cu(OTf)_2$ and CuI which was successful for the synthesis of 1,2-diketones from phenylpropanoic acid VII and aryl iodides VI. Production of benzil III was a decarboxylation coupling catalyzed by CuI/$Cu(OTf)_2$ [16].



Scheme 4. Synthesis of Benzil from Phenylpropynoic Acid and Aryl Iodides

4.5. Synthesis of Heteroaryl 1,2-Diketone

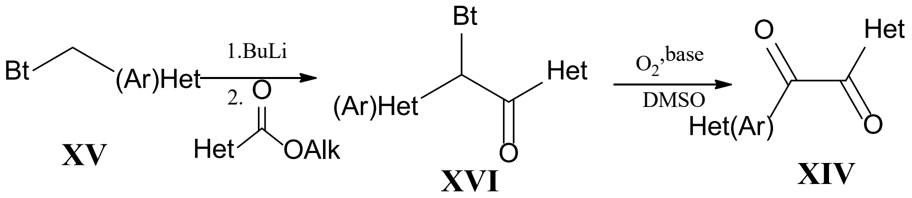
Synthesis of famous hetero aryl/ aryl 1, 2-diketone XIV (**Scheme 5**) involved oxidation of olefins VIII, oxidation of alpha-hydroxyketones IX, oxidation of acetylenesX, oxidation of methylene ketones XI. Additionally, it can also be synthesized by the reaction of 2-(pyridine-4-yl)-1, 3-oxazine XII lithiated in the presence of ester and chloride acid and by Grignard reagent substitution of imidazolyl group in 1,2-di(imidazole-1-yl) glyoxal [17].



Scheme 5. Heteroaryl 1, 2-Diketone Synthesis

4.6. With Heteroaryl Esters Reaction of Lithium Heteroaryl-(or aryl-) Methylbenzotriazoles to Give Ketones R-Benzotriazolyl

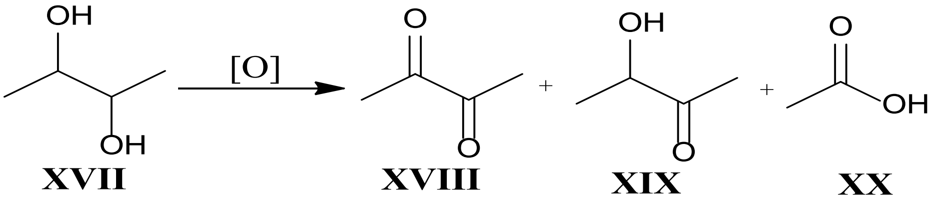
Lithiation of methylbenzotriazoles XV to aryl- (or heteroaryl-) methylbenzotriazoles intermediate XVI. Oxidation by metallization followed three main steps. As shown in **Scheme 6**. First, the metallization reaction with sodium or hydrogen peroxide occurred [18]. Then occurrence of a foundation equivalent to oxidative decyanizationdiaryl-acetonitriles takes place by reacting molecular oxygen with hydrogen peroxide. Lastly, the reaction of diarylacetonitriles in the presence of DMSO and base must provide heteroaryl or aryl diketone XIV (**Scheme 6**) [19].



Scheme 6. Reaction of Lithium Heteroaryl Methylbenzotriazoles with Heteroaryl (or aryl) Esters to give Ketones R-Benzotriazolyl

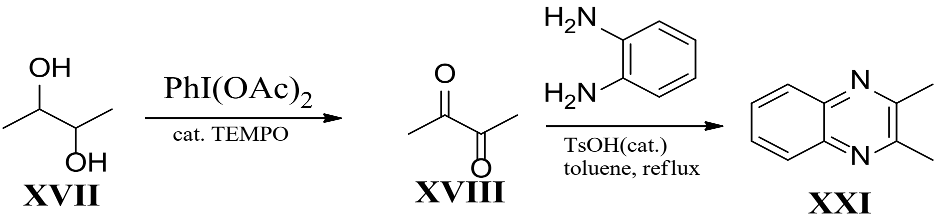
4.7. Oxidation of 2,3-Butanediol

Oxidation of 2, 3-butanediol XVII results in the formation of major product 3-hydroxy-2-butanone XIX and 2,3-butanedione XVIII(**Scheme7, 8**) [20].



Scheme 7. Oxidation of 2, 3-Butanediol

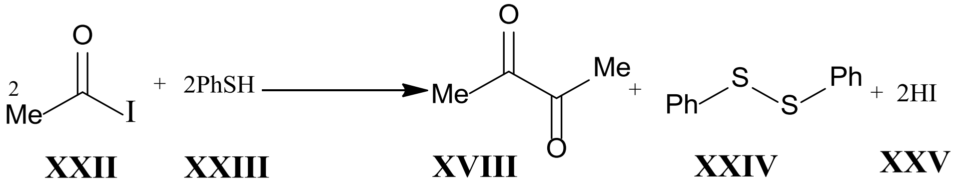
Alcohol oxidation into carbonyl compounds plays an essential role in organic chemistry. Using chromium-based reagents such as manganese dioxides, which traditionally enabled and accomplished the transformation, as Collins' reagent, or processes known as Swern or Parikh–Doering oxidation [21].



Scheme 8. Oxidation of Alcohol

4.8. Reaction of Acetyl Iodide with Thiols

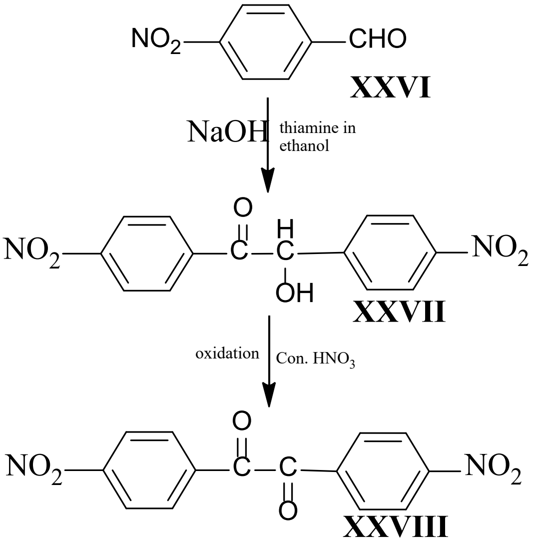
Scheme 9 shows the reaction of acetyl iodide XXII with diphenyl disulfide XXIII, condensation-generated iodide or elemental iodine for butane-2,3-dione XVIII of acetyl iodide [22].



Scheme 9. The reaction of Acetyl Iodide with Thiols

4.9. Synthesis of Dinitro Benzil

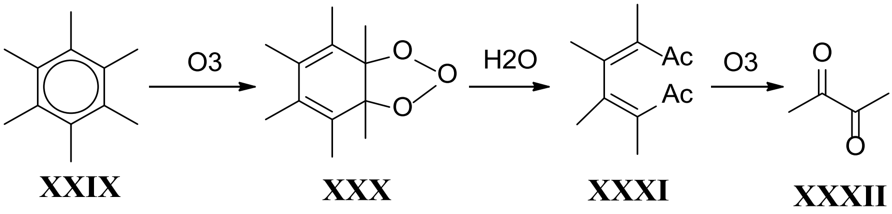
Scheme10 shows the oxidation of Dinitro benzoin XXVII to produce dinitro benzil XXVII [23].



Scheme 10. Synthesis of Dinitro Benzil

4.10. Reaction of Hexamethyl Benzene

Scheme 11 explains the attack on hexamethyl benzene XXIX resulting in a primary ozonide XXX that binds to carbonyl-oxide. This planned combination of two functions does not occurred but the feature of carbonyl oxide reacts to ozonide, with water on the support present hydroxy results in hydroperoxide, which breaks down to H_2O_2 and derivative of diacetyl XXXI. The ozonolysis tends to 2,3-butanedione that results from additional ozonolysis of the derivative of diacetyl [24].

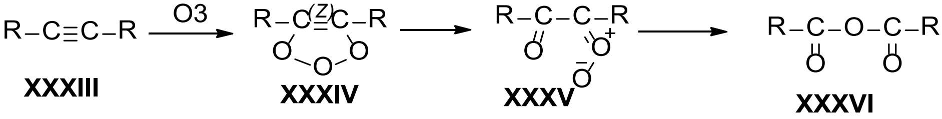


XXIX XXX XXXI XXXII

Scheme 11. Reaction of Hexamethyl Benzene

4.11. 2-Diazo-3-Butanone Oxygenation

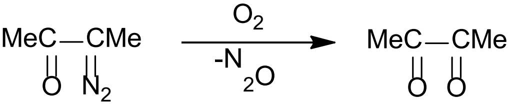
Oxygenation of olefin, 4-membered ring peroxides binding to heterocyclic ring continue hypothetical intermediate detailed investigations of 1,2-dioxetanes. Ozonation of diphenyl acetylene XXXIII and trioxabicyclo XXXIV at low temperature is done to generate benzoic anhydride XXXVI (**Scheme 12**) [25]. Such a dioxetane is likely to occur from carbonyl oxide intramolecular cycling to the adjacent ketone. Diazo compounds and carbonyl oxide photosensitized oxygenation have documented in particular, alpha-carbonyl oxide exhibits strong oxenoid characteristics [26].



XXXIII XXXIV XXXV XXXVI

Scheme 12.2-Diazo-3-Butanone Oxygenation

After oxygenation, 2-diazo-3-butanone, diphenyl sulfide were added to the mixture, and diacetyl (**Scheme 13**) got with acetic anhydride [25].



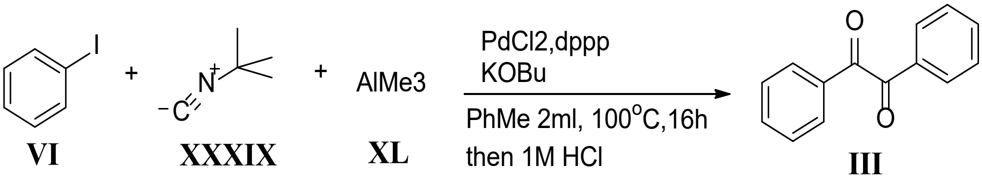
$$\underset{O}{\overset{\|}{\text{MeC}}}-\underset{N_2}{\overset{\|}{\text{CMe}}} \xrightarrow[-N_2O]{O_2} \underset{O}{\overset{\|}{\text{MeC}}}-\underset{O}{\overset{\|}{\text{CMe}}}$$

XXXVII XXXVIII

Scheme 13. 2-Diazo-3-Butanone Oxygenation

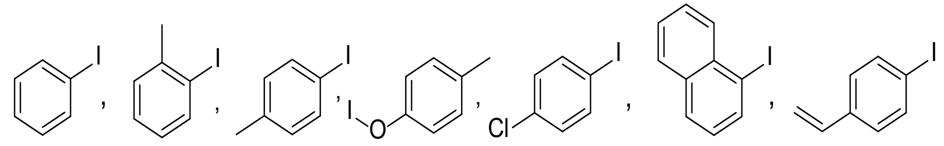
4.12. From Aryl Halides Synthesis of Palladium-Catalyzed 1,2-Diketone

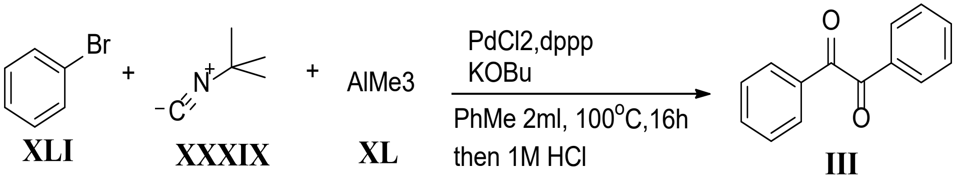
The substituent of iodobenzenes at various positions enhances the excellent yields for desired products. The reaction also continued smoothly with 1-iodonaphthalene 75% yield and gave the goal product. As shown in **Scheme 14, 15** I the yield of 75% [27].



Scheme 14. Synthesis of 1, 2-Diketone from Aryl Iodides

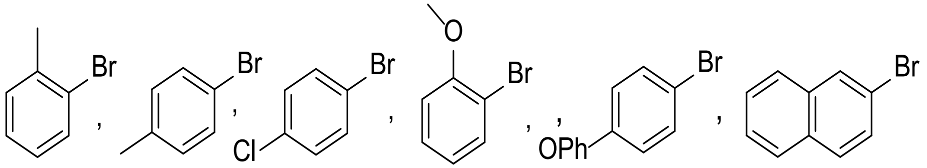
Various aryl iodides that are used:





Scheme 15.1, 2-Diketone from Aryl Bromides Synthesis

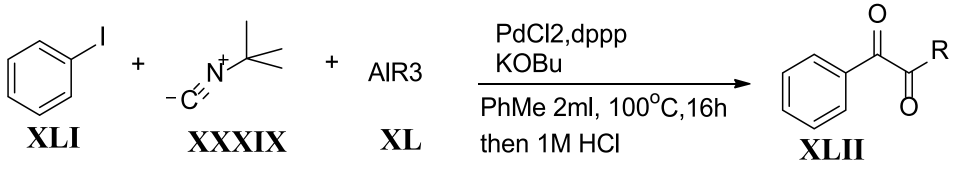
Various aryl bromides that are used:



4.13. Variations of Organoaluminum

The attractiveness of organoaluminum reagents is because of their high coupling pairs in synthetic chemistry, low cost, low toxicity, and fast availability of toxic products metal aluminium [28]. The very first study, which indicated the use of organoaluminum was a cross-coupling metal-catalyzed reaction in transition-traced reverse to 1976 by Negishi and co-workers. With organoaluminum many examples of cross-coupling reactions were recorded [29].

Organoaluminum reagents commonly used Grignard reagent or reagent of organolithium and aluminium trichloride, which can easily be prepared. The reaction with Tri-isobutylaluminum and under Tri-butylaluminum normal reaction conditions are going well and the ideal conditions are working well (**Scheme16**).



Scheme 16. From Organoaluminum 1,2-Diketone Synthesis

The organoaluminum used in these are:

$$Al(n\text{-}Bu)_3, AlPh_3, Al(i\text{-}Bu)_3$$

4.14. Synthesis of Benzil

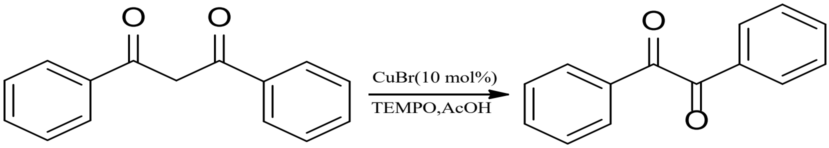
In the acetic acid solution, 1,3-diphenylpropane-1,3-dioneXLIII (0.5mmol), CuBr, and TEMPO were added, then at 100ºC mixture was heated for 2 hours. After this, the reaction was thoroughly checked through TLC. After the reaction cooled down, neutralized with NaHCO3 aqueous solution, and extracted with DCM, dried over anhydrous magnesium sulfate. To obtain pure benzil the product was purified through column chromatography.

With the addition scavenger BHT and III significantly inhibited the reaction and this reaction was only 13% yield (**Scheme 17**), a radical pathway involved [30]. Then hypothesized TEMPO could remove an atom of hydrogen from alpha-methylene and alpha-methylene.

To make our speculation confirmed by carrying the reaction, substrates XLIV and XLV were selected under normal terms. Substrate XLIV converted into III yields obtained was 69 % (**Scheme 18**).

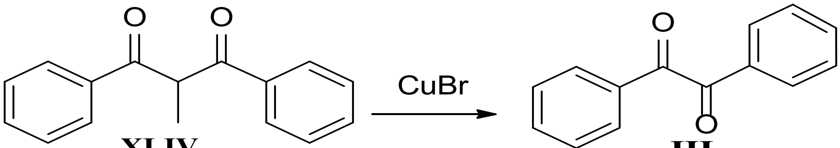
Yet there was no product transformed (**Scheme 19**) into substrate XLV. Then intermediate prepared triketone XLVI and found that XLVI could easily produce III yield 81% (**Scheme 20**) under regular or even CuBr conditions used only. The formation of progress based on these experimental results to find out, main intermediate XLVI was required [31].

The experimental findings proved that a radical pathway could generate compound XLVII and then create compound XLVII (**Scheme 21**) to triketone XLVI converted.



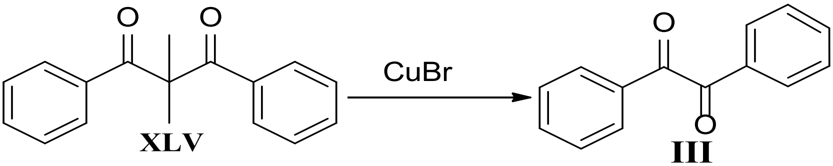
XLIII **III**

Scheme 17. Benzil synthesis 13% yield



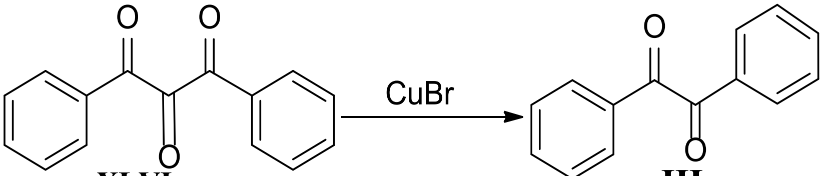
XLIV **III**

Scheme 18. Benzil synthesis 69% yield



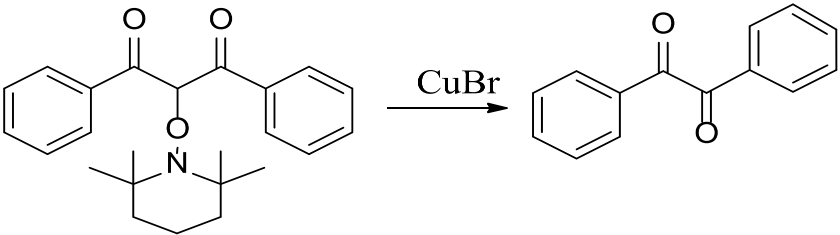
XLV **III**

Scheme 19. Benzil synthesis 0% yield



XLVI **III**

Scheme 20. Benzil synthesis 81% yield

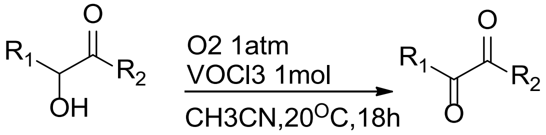


XLVII **III**

Scheme 21. Benzil synthesis 78% yield

4.15. Fatty 1,2-Diketone Synthesis

There are many procedures for the synthesis of fatty 1,2-diketone. One is the unsaturated fatty acids oxidation by using $KMnO_4$ leads to 1,2-diketone formation. Another method is using epoxides in the existence of $Bi(OTf)_3$, DMSO acts as an oxidant. One major method is the conversion of fatty 1,2-diols into 1,2-diketone using pyridine in CCl_4 and NBS that acts as an oxidant. Keeping in mind that two green approaches were recently created for fatty alpha-hydroxyketone XLVIII in preparation, these primary intermediates for fatty 1,2-diketoneXLIXsynthesis(**Scheme 22**) [32].

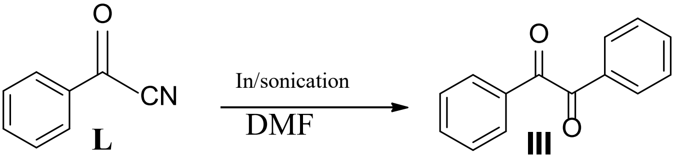


XLVIII XLIX

Scheme 22. From Alpha Hydroxyl Ketones formation of 1,2-Diketone

4.16. Reductive Coupling of Acyl Cyanide

The carbonyl derivatives reductive coupling is a useful technique for the formation of carbon-carbon bonds. Recently, it has found the transformation of aromatic aldehydes and aldimines into pinacols and neighboring diamines, with indium, respectively. The coupling reduction of acid chlorides or acyl cyanides combining by SmI2 leads to the formation of 1,2-diketone(**Scheme 23**) [33].



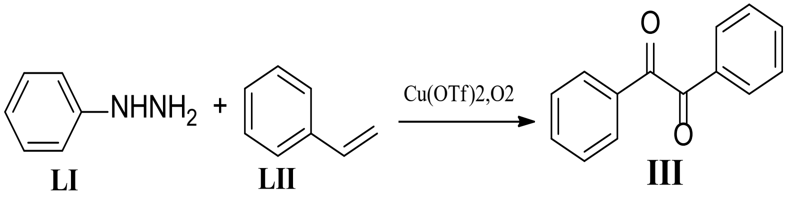
L III

Scheme 23. Reductive coupling of Acyl Cyanide

4.17. Synthesis of 1,2-Diketone by Different Routes

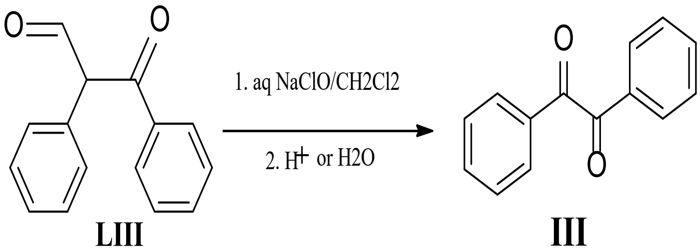
The copper-catalyzed formation of 1,2-diketonedeveloped by Jiao and co-workers (**Scheme 24**) by coupling of cascade using olefins and hydrazines, oxygenation response. In the presence of NaClO and using beta ketoaldehydes Yang and Tang et al. synthesized 1,2-diketone(**Scheme 25**) [34].

4.17.1. Jiao's Work



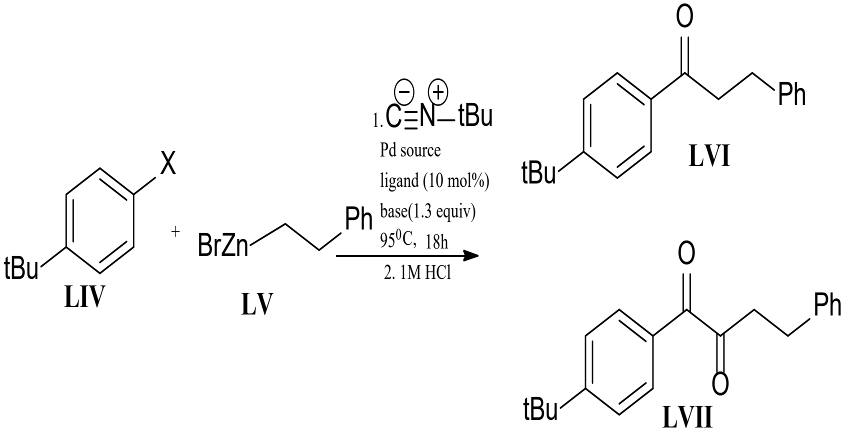
Scheme 24. 1,2-Diketone formation

4.17.2. Yang and Tang's Work

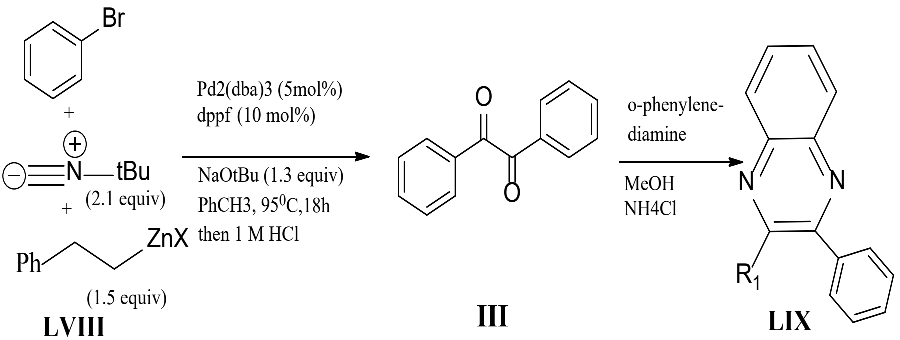


Scheme 25. Synthesis of 1,2-Diketone using Beta Ketoaldehyde

1-bromo-4-(tert-butyl)benzene combined with phenethyl zinc bromide and tert-butyl isocyanide used, with a desire for monoketone LVI production along with a diketone LVII (**Scheme 26**, **27**) that is a byproduct [35].



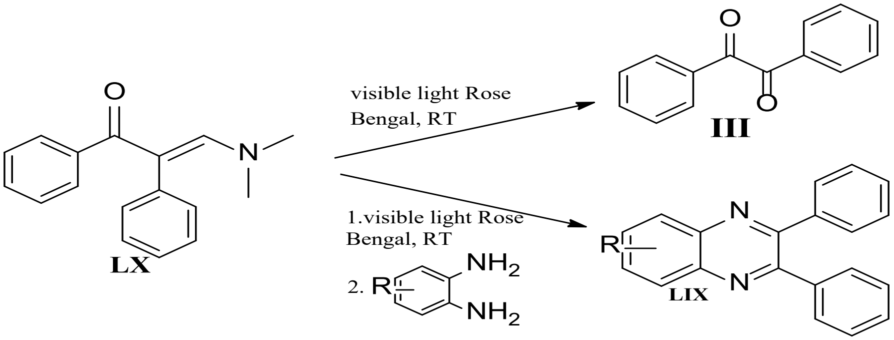
Scheme 26. 1,2-Diketone synthesis



Scheme 27. 1, 2-Diketone synthesis and its substrate scope

4.18. Photocatalytic1,2-Diketone and Quinoxaline Formation

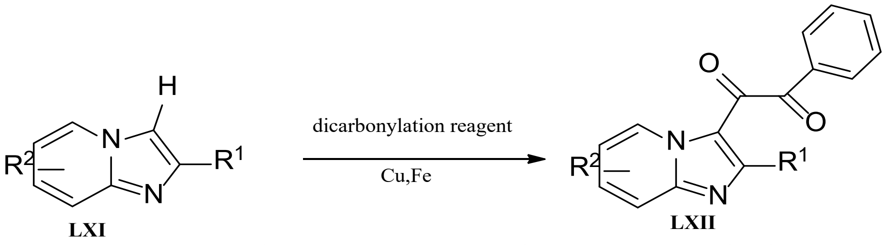
Enaminones detected by bond cleavage C=C under atmospheric conditions by catalysis of visible light in Rose Bengal's involvement. It contributes to the formation of a family of 1,2-diketonewith no metal catalyst. Also, the one-pot synthesis of quinoxaline LIX was under equal photocatalytic conditions, 1,2-diketone III produced in situ as intermediates (**Scheme 28**) [36].



Scheme 28. 1, 2-Diketone and Quinoxaline photocatalytic synthesis

4.19. Synthesis of 1,2-Dicarbonyl Imidazoheterocycle under Metal-Catalyzed and Metal-free and Catalyst-free

Cao *et al.* worked on the synthesis of derivatives of 1,2-dicarbonyl imidazopyridine that are copper-catalyzed with methyl ketone(**Scheme 29**) [37].



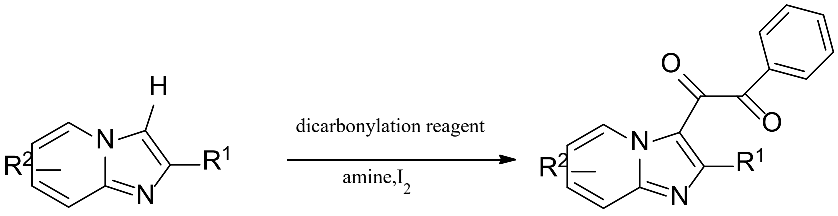
LXI

LXII

dicarbonylation reagent=aryl acetaldehyde, methyl ketones, oxaldehyde

Scheme 29. 1,2-Dicarbonyl Imidazoheterocycle formation

Wu et al. identified pyrrolidine/I2indoles cross-coupling with methyl ketone whereas, containing many indoles decarbonylation of C-3 [38]. Kamal et al. documented decarbonylation of I2-mediated styrenesimidazoheterocycles (**Scheme 30**) [39].



LXI

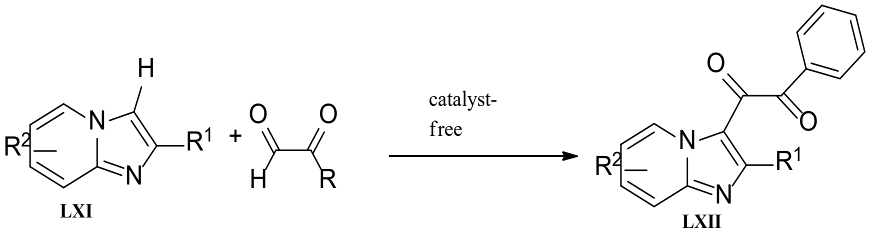
LXII

dicarbonylation reagent= methyl ketones,styrenes

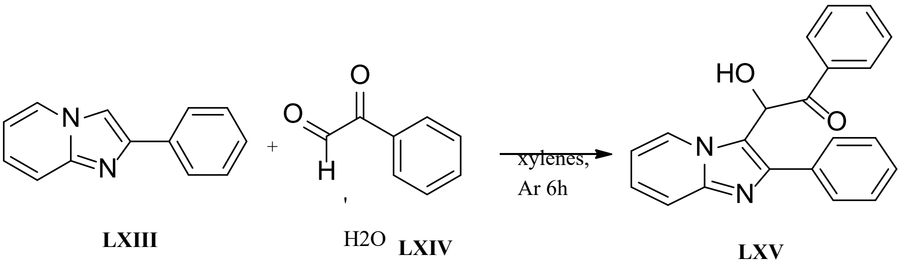
Scheme 30. Metal-free synthesis of 1, 2-Dicarbonyl Imidazoheterocycle

For 1,2-dicarbonyl synthesis imidazo heterocycle, cross-dehydrogenative coupling of healthy yields of imidazoheterocycle by glyoxal hydrates occurred, and no catalyst was required (**Scheme 31**) [40]. When this reaction was carried out under an argon atmosphere, only 1,2-dicarbonylimidazo[1,2-a] pyridine found with alpha hydroxyl ketone got a compound LXV(**Scheme 32**). This obtained compound was sensitive to air. When this reaction proceeded under air, a mixture of 1,2-diketone and alpha hydroxyl ketone was obtained. So by carrying this reaction, a plausible mechanism was proposed.

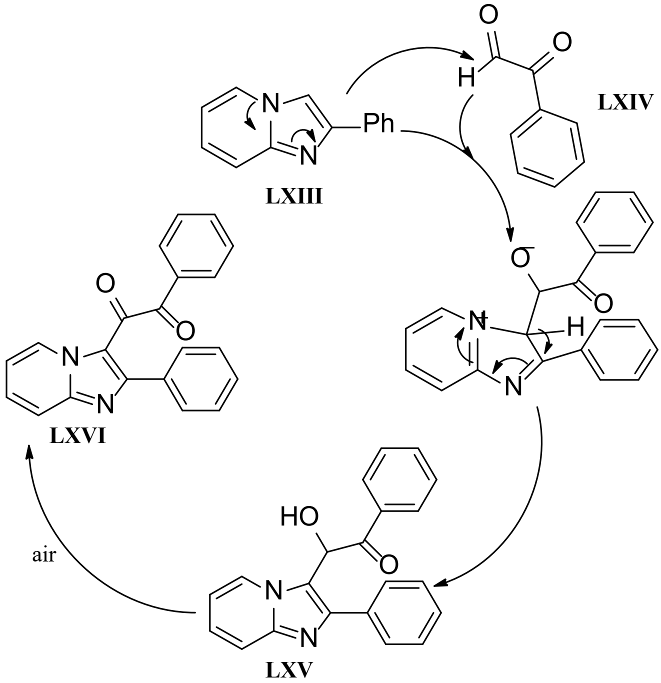
The reaction started with the nucleophilic attack of phenyl glyoxal hydrates and finally; the compound LXV (**Scheme 33**) converted into 1,2-dicarbonyl imidazopyridine [41].



Scheme 31. Catalyst-free synthesis of 1,2-Diketone

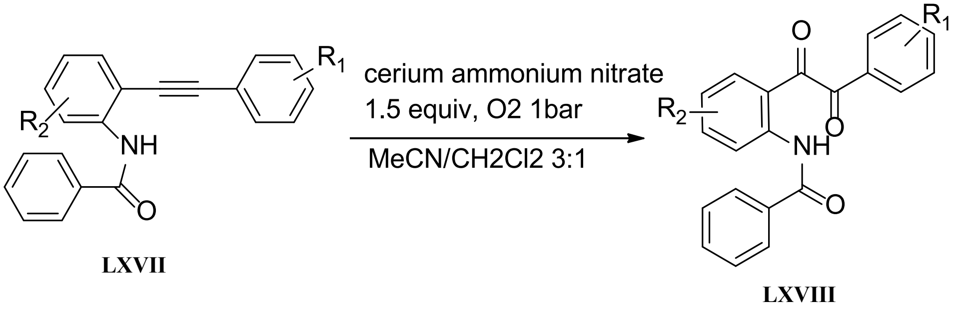


Scheme 32. Imidazohetero cycle coupling

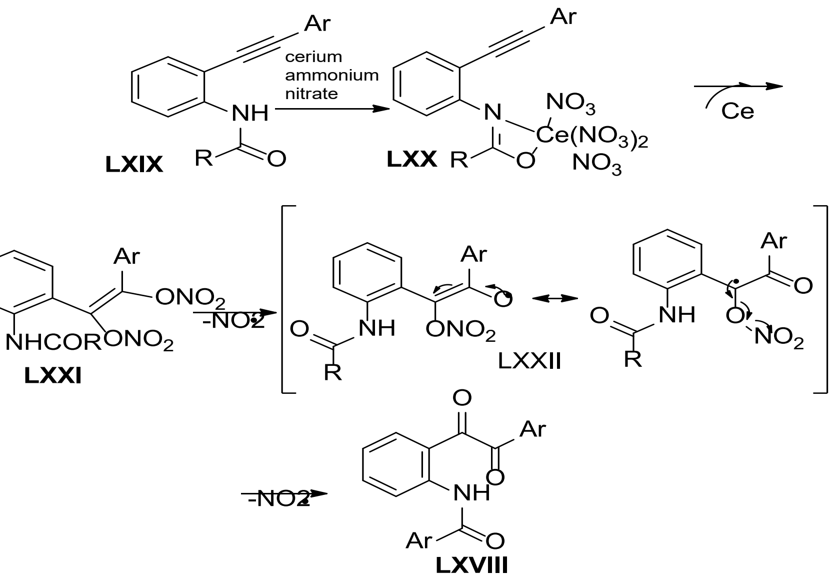


Scheme 33. Reaction Mechanism of Heteroaryl 1,2-Diketone synthesis

In 2012, Wang and his coworkers defined that diaryl alkyne oxidation, which contained ortho amide function as a phenyl ring. In the presence of CeF4 which acts as an oxidant, the 1,2-diketone yield was about 30%. The level rises to about 51% in the presence of KMnO4, and with the cerium ammonium nitrate, yield increases to about 62%. When this reaction was carried out with cerium ammonium nitrate 1.5 equivalent to CH2Cl2 in the presence of oxygen, various diaryl alkynes that contained different substituents on aromatic rings have been known (**Scheme 34**, **35**) [42].



Scheme 34. Cerium Ammonium Nitrate and O2 promoted Diarylalkyne Oxidation

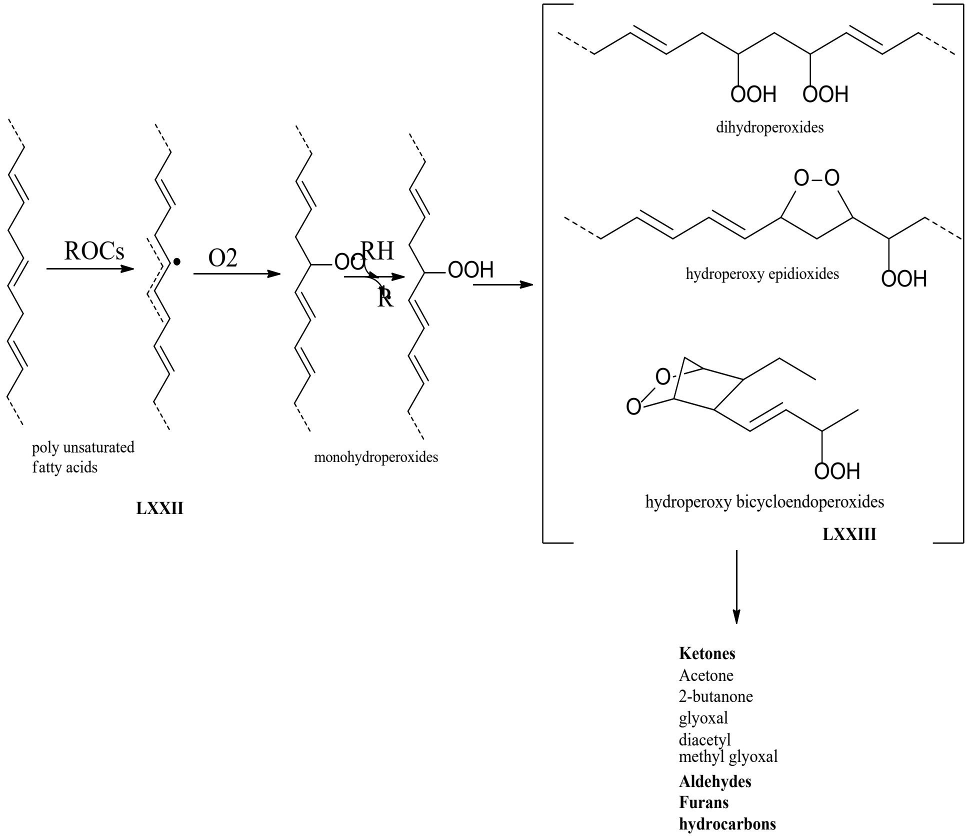


Scheme 35. Mechanism of Cerium Ammonium Nitrate promoted oxidation of Diarylalkyne

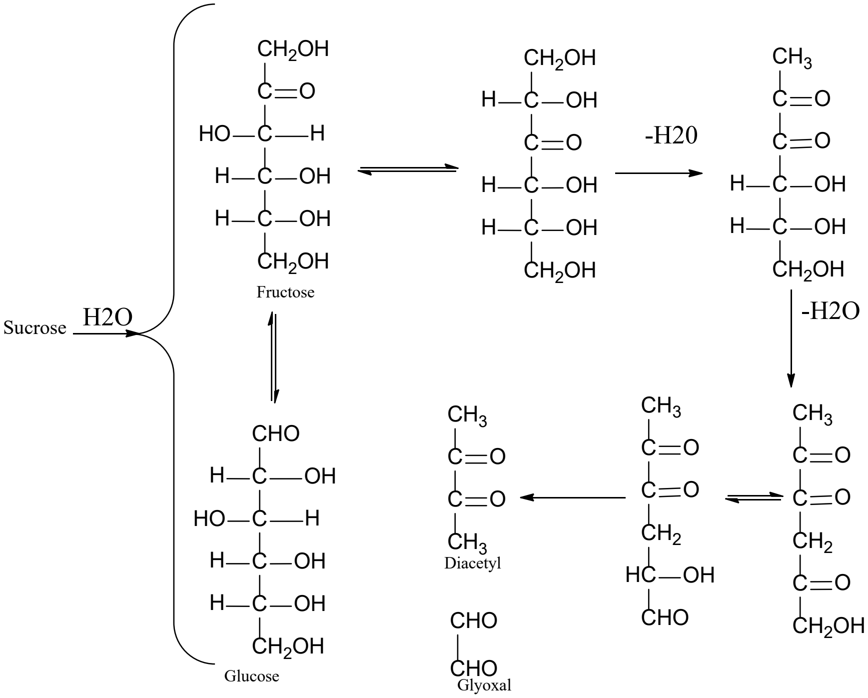
4.20. Formation of Diacetyl from Sucrose and Lipids

Sugar or lipid leads to the formation of many radicals having the low molecular weight when radicals are joined, the formation of diacetyl occurred [43]. In (**Scheme 36**), tautomerization occurred in the first step, sugar-free group, and at keto-enol bonding in alkaline or acidic solutions cleavage occurred.

It can synthesize diacetyl higher level from sugars (**Scheme 37**) in basic or acidic solutions rather than neutral solutions. In 1980, the synthesis of carbonyl compounds from lipids was recorded. Some recognize that sugars mortify into carbonyl compounds, having low molecular compounds that also containing diacetyl [44].



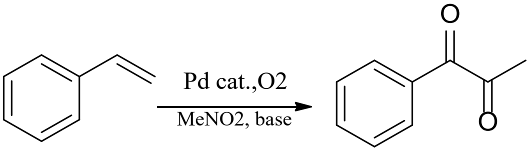
Scheme 36. Formation of carbonyl compounds from lipids



Scheme 37. Synthesis of Diacetyl from Sucrose

4.21. Diketonization of Terminal Aromatic Alkenes for 1,2-Diketone Synthesis

From the reaction of nitro alkanes with aromatic terminal alkenes, 1,2-diketone was prepared. In (**Scheme 38**), the synthesis of 1, 2-diketone occurred when styrene reacts with the MeNO2. It was also observed that the formation of 1, 2-diketone occurred in the presence of NaOAc or KOAc in the presence of catalyst PdCl2 [45].

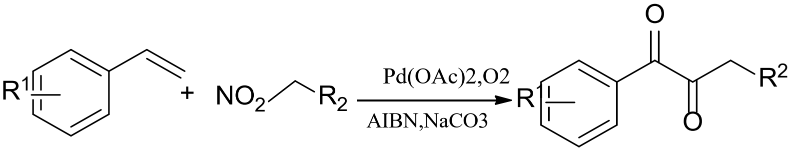


Scheme 38. Diketonization of Styrene

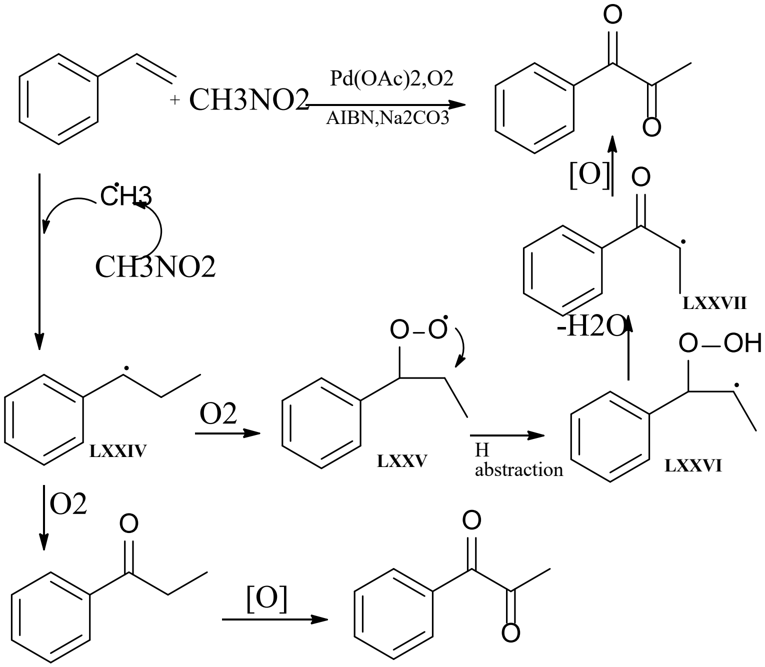
The reaction of styrene with nitromethane is showed in **Scheme 39**. In the first step, from nitromethane radical of methyl generated and in the occurrence of Na2CO3 and Pd(OAc)2, and intermediate LXXIV is formed.

Then this intermediate reacts with oxygen and a superoxide radical LXXV was formed [46].

This intermediate leads to the formation of hydroperoxide LXXVI, which converted into ketone radical LXXVII (**Scheme 40**).

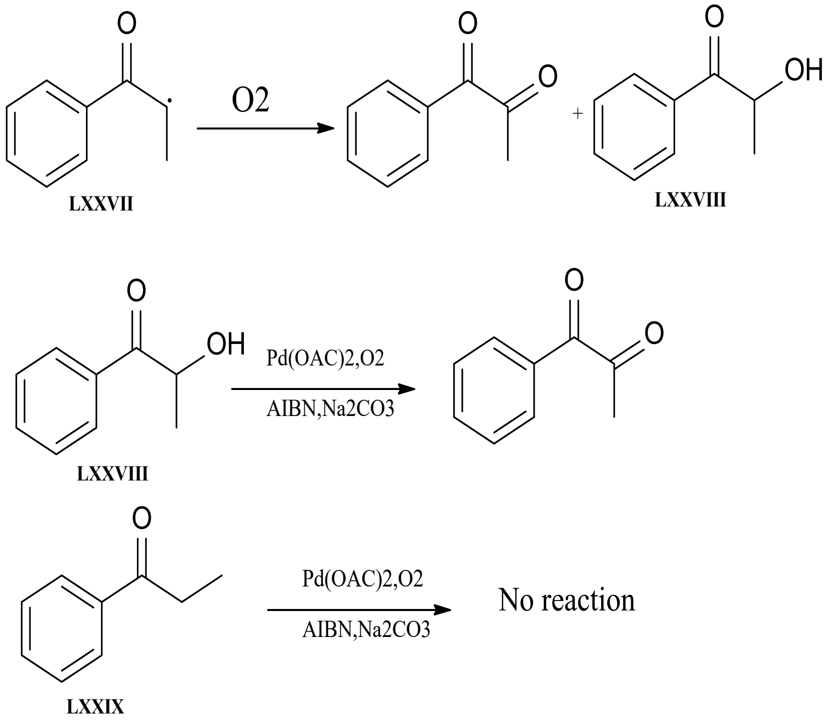


Scheme 39. Terminal alkenes diketonization with nitro alkane



Scheme 40. Plausible reaction pathway

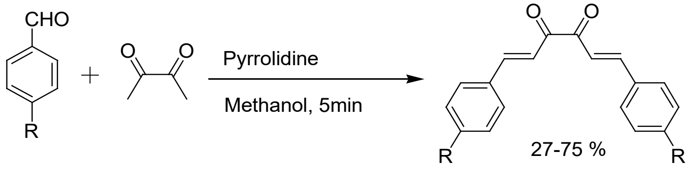
In Russell mechanism (**Scheme 41**) [47] ketone radical LXXVII oxidation leads to 1,2-diketone and R-hydroxy ketone LXXVIII formation. R-hydroxy ketone further converts the oxidation of propiophenone LXXIX into 1,2-diketone,while in that reaction no product was obtained [48].



Scheme 41. Russell mechanism

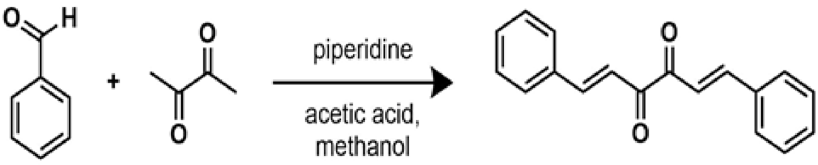
4.22. Synthesis of Cinnamils (1,6-di(phenyl)hexa-1,5-diene-3,4-dione)

Gillani*et al* reported the synthesis of cinnamils by using pyrrolidine as a catalyst (**Scheme 42**). In comparison to Sorenson protocol (**Scheme 43**) reported that previously, they produced high yields within short reaction time by using stoichiometric quantities of aldehydes [49].



R= -CH3, -OCH3, -X, NO2…….

Scheme 42. Synthesis of derivatives of 1,6-di(phenyl)hexa-1,5-diene-3,4-dione [Cinnamil]

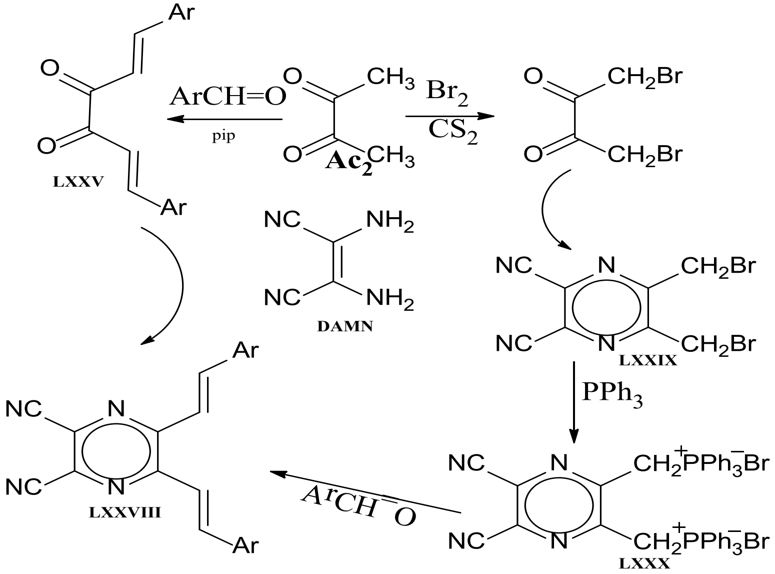


Scheme 43. Synthesis of 1,6-di(phenyl)hexa-1,5-diene-3,4-dione [83, 84]

4.23. Dinitrile Precursors Synthesis

For the synthesis of porphyrazines with an annulated heterocycle, heterocyclic ortho-dinitriles was considered as the most appropriate precursors [50]. 5, 6-distyryl-2,3-pyrazinedicarbonitriles LXXVIII primary precursors for the synthesis of octastyryltetrapyrazinoporphyrazines [St8PyzPzM] have been prepared in two stages, beginning with readily available arylaldehyde ArCH=O, diacetyl (Ac2), and diaminomaleodinitrile (DAMN).

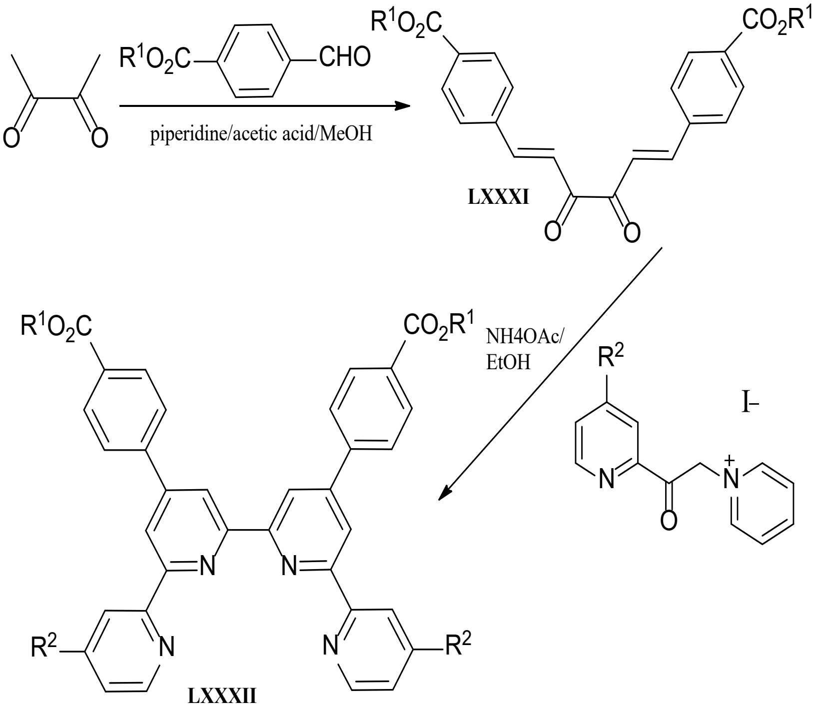
In the first step, Crotone-type condensation of diacetyl and arylaldehyde in piperidine/acetic acid mixture yields styryl-substituted 1,2-diketone (cinnamils) LXXVin 10–15% yields occurred (**Scheme 44**). Below, summarize dinitriles resulted from the reaction of cinnamil with DAMN with a yield of about 90% [51].



Scheme 44. Dinitrile Precursor's synthesis

4.24. Quarter Pyridine Synthesis

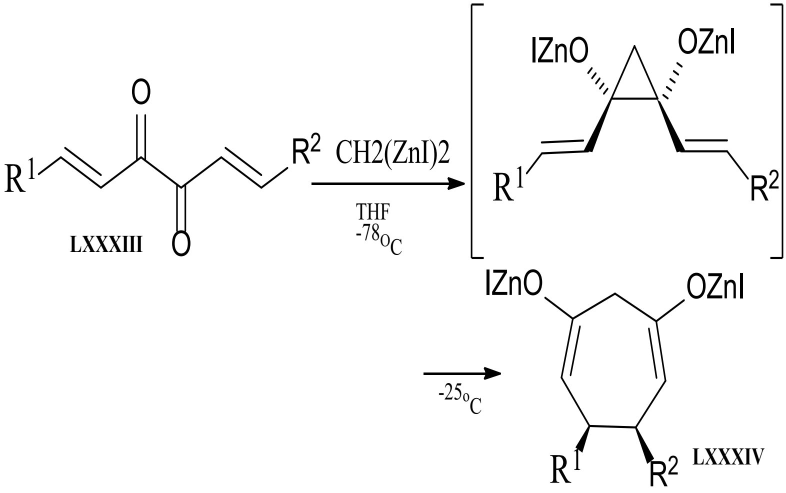
The 2,3-butanedione reacted with methyl 4-formyl-benzoate in methanol which leads to the formation of cinnamil LXXXI 20-25% yield. Then cinnamil in the presence of ammonium acetate with reagent Krohnke's reagent leads to the formation of quarter pyridine LXXXII (**Scheme 45**) [52].



Scheme 45. Quarterpyridines synthesis

4.25. Synthesis of Cycloheptane Ring

At room temperature, zinc alkoxides of cis-5,6-dialkylcyclohepta-3,7-diene-1,3-diol LXXXIV was obtained by treating 1,6-dialkylhexa-1,5-diene-3,4-diones LXXXIII with bis(iodozincio)methane (**Scheme 46**) [53]. The reaction took place with high stereospecificity. The diketone transformed by bis(iodozincio)methane stereoselectively into the cis-divinylcyclopropane-1,2-diol; this diol was then converted into related cycloheptane [49].



Scheme 46. Synthesis of Cycloheptane Ring from 1,2-Diketone

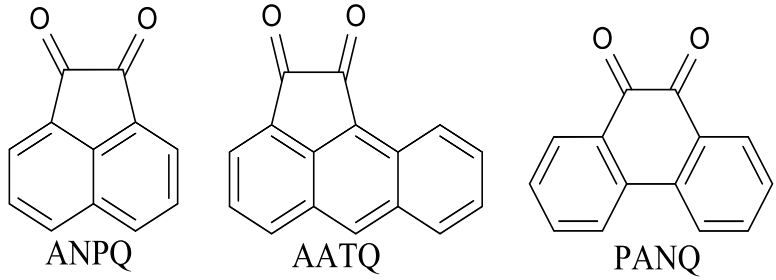
5. APPLICATIONS OF 1,2-DIKETONES

5.1. 1,2-Diketone as Photoinitiators

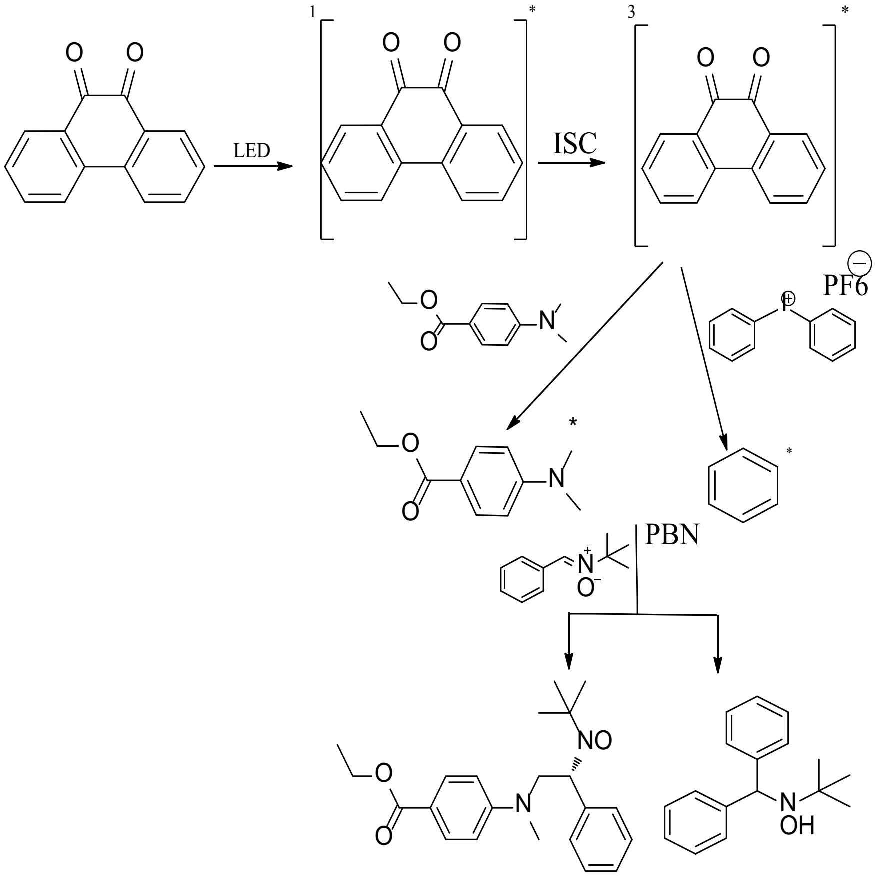
The skills of three 1, 2-diketone for photoinitiation is sub-categorized, Acenaphthenequinone (ANPQ) =L, Aceanthrenequinone (AATQ**)** LI**,** and 9,10-phenanthrenequinone (PANQ)LII**,** with additives such as N-vinylcarbazole, iodonium salt (NVK), tertiary amine, and cationic phenacyl bromide (R-Br) photopolymerization of free-radicals light-emitting diode (LED) bulbs investigated for irradiation. The generation of radical photochemical processes from 1, 2-diketone based on PISs tested and compliant with the corresponding efficiency of photopolymerization (**Scheme 47**) [54].

5.2. Synthesis of Triazines and Pyrazinones from 1,2-Diketone

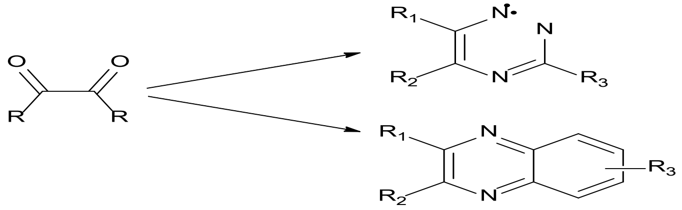
Protocols that are effective for the preparing heterocyclic substituted freshly revealed theoretically high-yielding conditions in the microwave for the synthesis of triazines and pyrazinones from 1,2-diketone (**Scheme 48**) [55, 56]. These situations (microwave, 5 min) show a significant improvement over typical thermal heating (8-24 h) and allow 1,2-diketone to a point of diversification in biological routes heterocycles that are active.



Chemical Structures of ANPQ, AATQ, PANQ 1,2-Diketone

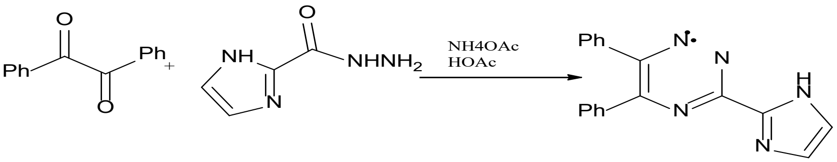


Scheme 47. Amechanism for Theradical generation of LED exposure from 1,2-Diketone PANQ/Iod system



Scheme 48. Synthesis of Triazines and Pyrazinones from 1,2-Diketone

5.3. Synthesis of 1,2,4-Triazine from 1,2-Diketone

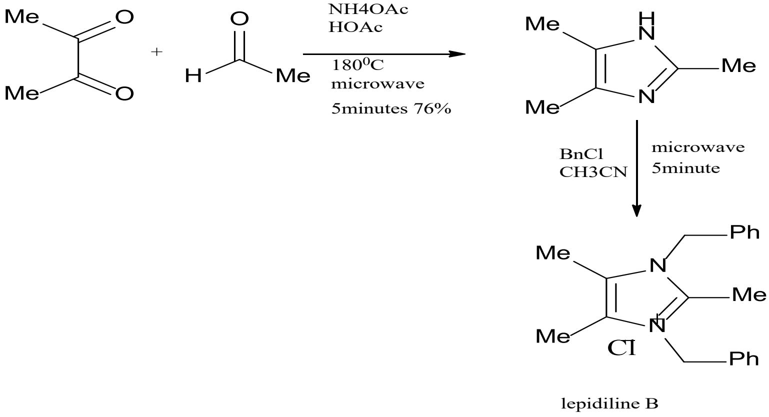


Scheme 49. Synthesis of 1,2,4-Triazine

5.4. Synthesis of Lepidiline B from 2,3-Butanedione

Lepidilines A and B were collected from the extraction of root *Lepidiummeyenii*. This root was collected from the Andes mountain during the research on natural products, which were biologically active [57].

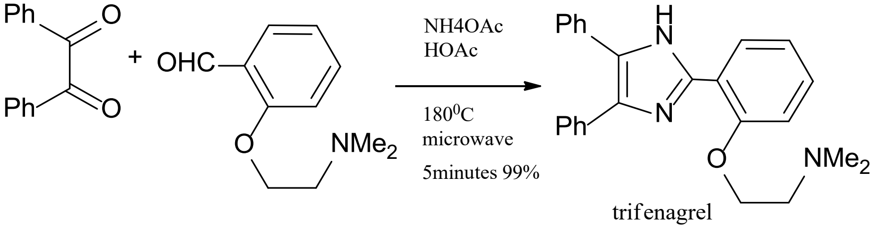
The lepidiline was synthesized from acetaldehyde and 2, 3-butanedione. It is a two-step process, and both steps occurred under the microwave. The formation of 2,4,5-trimethyl imidazole in the first step was a faster and high yield route(**Scheme 50**) [58].



Scheme 50. Synthesis of Lepidiline B from 2,3-Butanedione

5.5. Synthesis of Trifenagrel(drug) from 1,2- Diketone

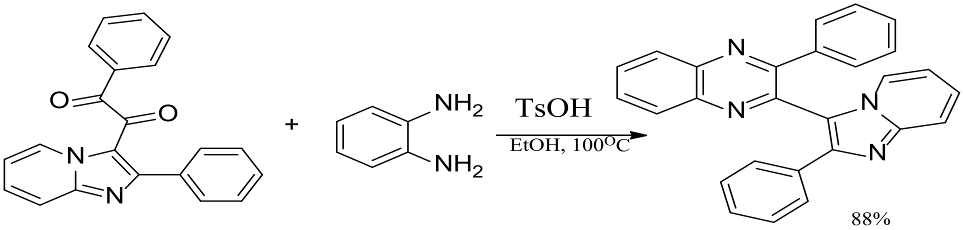
A drug trifenagrel synthesized from aldehyde and 1, 2-diketone (**Scheme 51**) under microwave conditions. The condensation of aldehyde, 1, 2-diketone, leads to the formation of trifenagrel [59].



Scheme 51. Synthesis of Trifenagrel (drug) from 1,2-Diketone

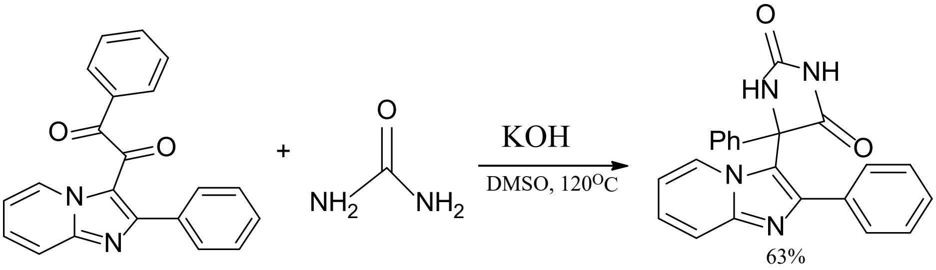
5.6. 1,2-Dicarbonyl Imidazoheterocycles Synthetic Applications

When 1, 2-dicarbonyl imidazoheterocycle reacts with ortho-phenylenediamine, a product is obtained containing nitrogen heterocycles with 88% yield (**Scheme 52**).



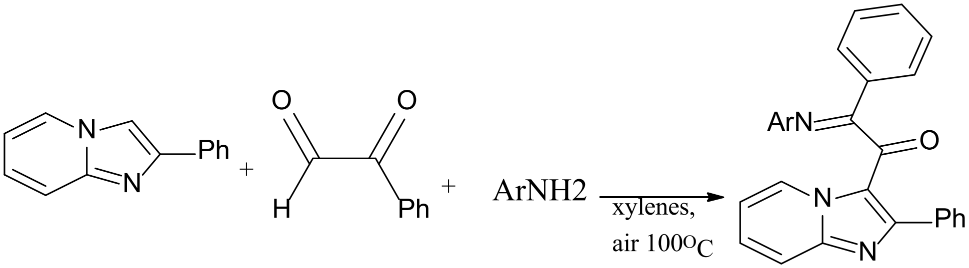
Scheme 52. Synthetic applications of 1,2-Diketone

When urea and 1, 2-diketone are combined as a product, 63% yield was obtained (**Scheme 53**).



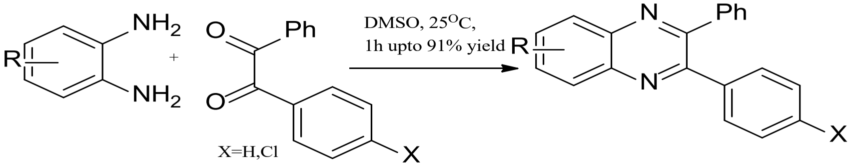
Scheme 53. 1,2-dicarbonyl Imidazoheterocycles synthetic applications

Phenyl glyoxal hydrates and imidazopyridine when reacted with aromatic amines in the presence of air at 100°C product got alpha-keto ketamines(**Scheme 54**) [40, 60]. Alpha keto ketamines are used in some natural products and pharmaceuticals.



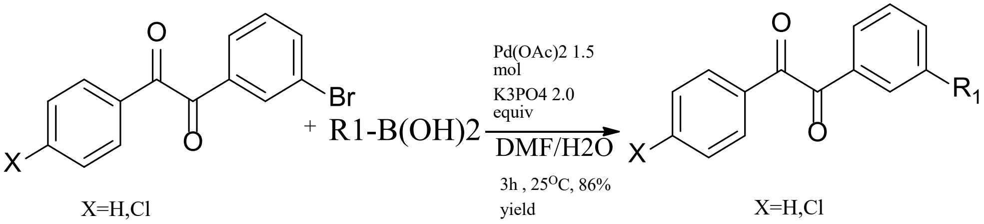
Scheme 54. Synthesis of Alpha-Keto Ketamines from 1,2-Diketone

1, 2-diketone and ortho phenylenediamine reacted together 2,3-diaryl quinoxalinegot. The reaction was carried out at 25°C for 1 hour at continuously stirring of 1,2-diketone, ortho phenylenediamine, and the product from this contained a good yield of 91%(**Scheme 55**) [2].



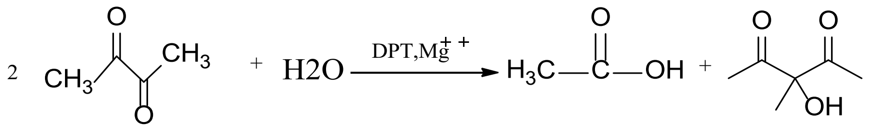
Scheme 55. Quinoxaline synthesis from 1,2-Diketone

When 2,3-diaryl quinoxaline are combined together then halogen-substituted 1,2-diketone with palladium-catalyzed Suzuki-Miyaura [61] cross-coupling reactions formed aromatic rings of 1,2-diketone. 1,2-diketone with aryl boronic acid, which leads to higher analogous 1,2-diketone (**Scheme 56**).



Scheme 56. Higher analogous 1,2-Diketone synthesis

Juni and Hevm, in 1956 confirmed that microorganisms were able to use acetylmethylcarbinol and 2,3-butanediol as a source of energy for growth and the formation of cyclic pathway that converted these into acetic acid. Diacetyl undergoes diphosphothiamin acyloin condensations that lead to the formation of acetic acid and diacetylmethylcarbinol(**Scheme 57**) [62].

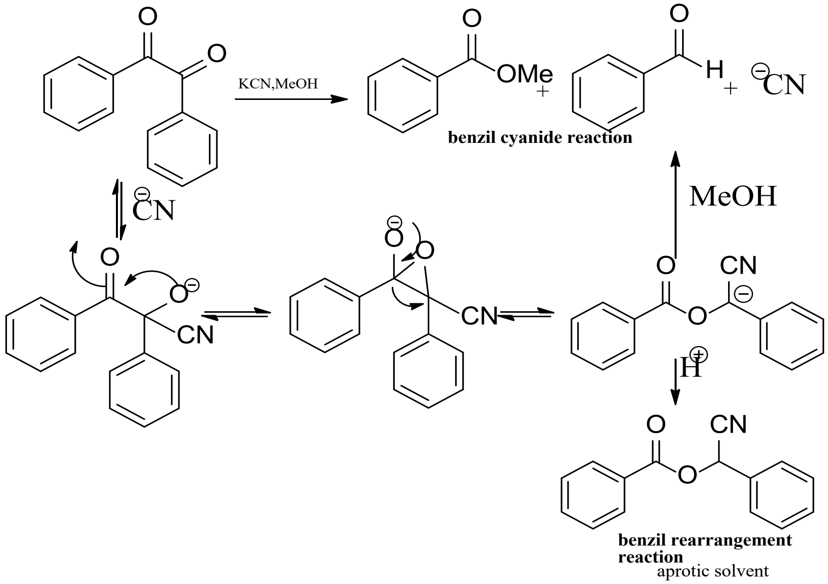


Scheme 57. Synthesis of Diacetylmethylcarbinol from Diacetyl

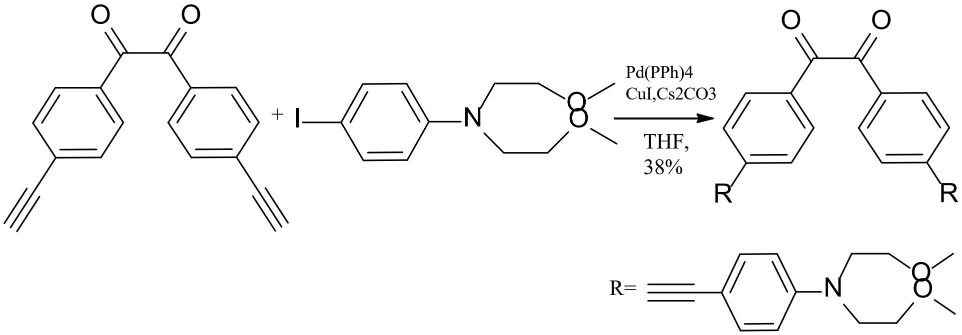
5.7. Applications of Benzil Cyanide Reaction

A cyanide-specific reaction is the benzil cyanide reaction, and used it in the formation of a colourimetric indicator, which is used for the toxic anion.

Benzil derivatives cleavage leads to the formation of benzoate esters in methanol and derivatives of benzaldehyde. For this reaction, only the cyanide catalytic amount is essentially required. This reaction also leads to the formation of cleavage of a bond. The benzil cyanide reaction shows the benzyl-based rearrangement and isused for the detection of cyanide anion (**Scheme 58**, **59**) [63, 64].

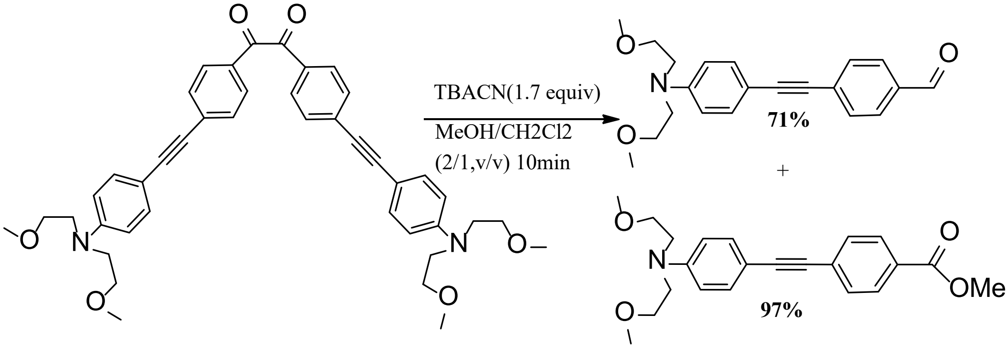


Scheme 58. Benzil-Cyanide reaction



Scheme 59. Synthetic scheme of Benzil Cyanide reaction

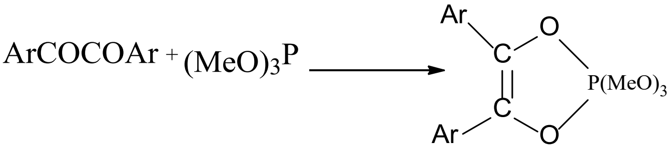
When benzil cyanide reaction takes place under MeOH/CH2Cl2, by thin-layer chromatography it separates two compounds with 71% and 97% yields (**Scheme 60**).



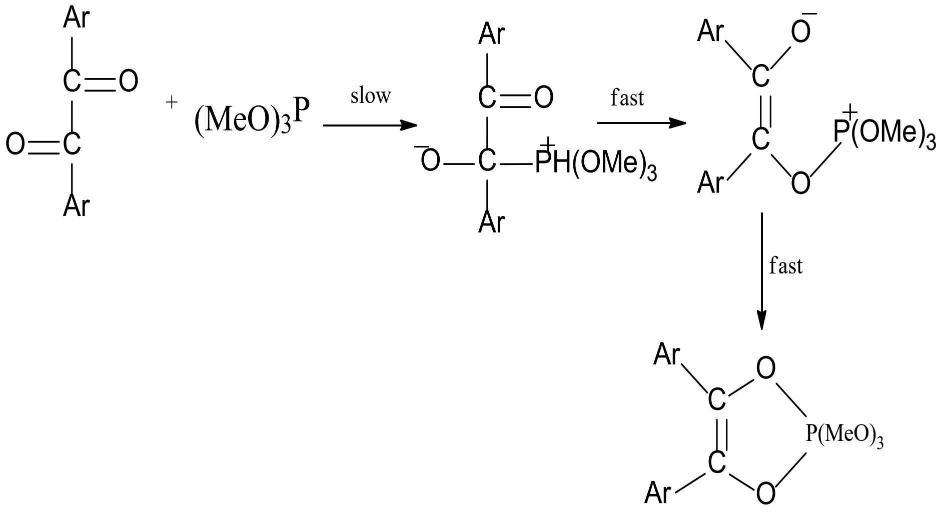
Scheme 60. Benzil Cyanide Reaction Under MeOH/CH$_2$Cl$_2$

5.8. Reaction of Benzil with Trimethyl Phosphate

In 1958, alpha diketone with trimethyl phosphate were considered as the first time reaction. The reaction of benzil with trimethyl phosphite occurred at room temperature, and the product obtained from these two was 2, 2, 2-trimethoxy-4, 5-diaryl-1,3,2 dioxaphosphole(**Scheme 61**) [65].



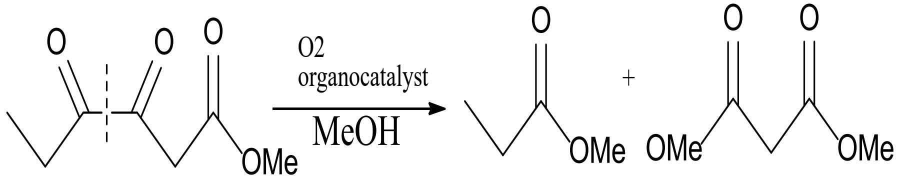
Scheme 61. Benzil with Trimethyl Phosphate



Scheme 62. Mechanism of the reaction of Benzil with Trimethyl Phosphite

5.9. Fatty 1,2-Diketone Cleavage

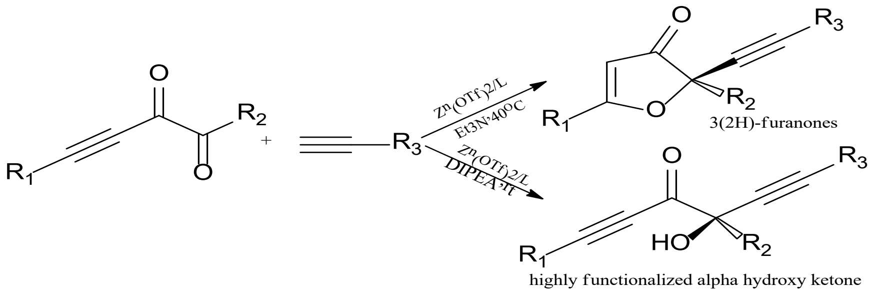
1,2-diketone cleavage through methyl oleate into the desiring esters, which is dimethyl azelate and methyl nonanoic, by using oxygen as an oxidant, were studied by organocatalysis (**Scheme 63**). It was discovered that oxidative cleavage leads to the creation of a 1:1 mixture of potassium carboxylates and esters [66].



Scheme 63. 1,2-diketone cleavage

5.10. Formation of 3(2H)-Furanone and Alpha Hydroxyl Ketones from Alkynyl 1,2-Diketone

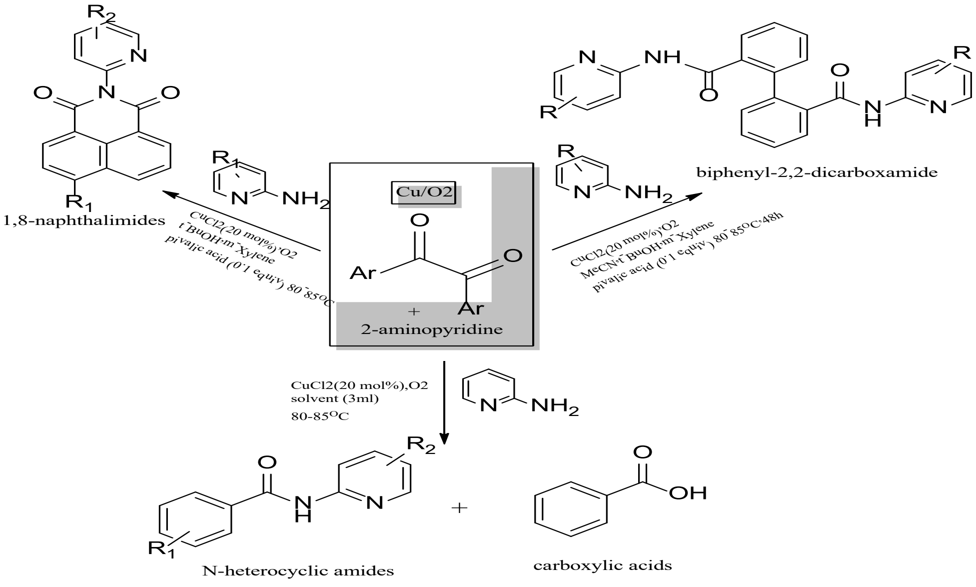
Under Lewis acid catalysis reported that enantioselective and highly region alkynylation of alkynyl 1,2-diketone, conducting to high values of biologically relevant 3(2H)-furanone (**Scheme 64**). Highly functionalized alpha-hydroxy ketones were generated by a slight change in the reaction conditions [67].



Scheme 64. Alkynylation of Alkynyl 1,2-Diketone

5.11. C-C Bond Cleavage of 1,2-Diketone

Copper-catalyzed C-C bond cleavage of 1,2-diketone with 2-amino heterocycles leads to the synthesis of biphenyl-2,2-dicarboxamides, cyclic imides, and N-heterocyclic amides. In **Scheme 65**, first acenaphthoquinones and 2-aminopyridines lead to the formation of 1,8naphthalimides under copper-catalyzed oxidative C-C bond cleavage. In the second policy formation of biphenyl-2, 2-dicarboxamides from 2-aminopyridines and 9,10-phenanthrenequinone and the third one from 1,2-diketone formation of carboxylic acids and n heterocyclic amides occur [68].



Scheme 65. C-C Bond cleavage of 1,2-Diketone

6. CONCLUSION

This review article highlighted different organic synthesis facilitated by 1,2-diketones. The discussion section uncovered that organic transformations mediated by 1,2-diketones could also be facilitated by the use of other diketones compounds. Different reagents were found to have different reactivity profiles, and the selectivity of 1,2-diketone was controlled by choosing an appropriate diketone compound.

1,2-diketone intermediates play a vital role in many fields. 1,2-diketone are among the most significant precursors and versatile building blocks in organic synthesis that set the future horizon for the synthesis of polymers.

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