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Short Review on the Synthesis and Applications of Heterocyclic Quinones

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Abstract:- This review explores the synthesis and diverse applications of heterocyclic quinones, highlighting versatile methods such as Diels-Alder reactions. Heterocyclic quinones impact electrochemistry, batteries, textiles, and medicine, particularly in cancer treatment. Their antioxidant properties, exemplified by ubiquinone, are crucial for cellular protection. Quinones play essential roles in photography, organic synthesis, polymer chemistry, and enhancing conductivity. They act as catalysts, indicators, and probes in various chemical and analytical processes. The review emphasizes their potential in cancer therapy, enzyme inhibition, antibacterial, antifungal, and cytotoxic activities. Serving as a valuable resource, it concludes by acknowledging the significant contributions of heterocyclic quinones to scientific, industrial, and creative advancements.

Keywords:- *Heterocyclic Quinones; Synthesis; Applications; Anticancer, Antioxidant.*

I. INTRODUCTION

Quinones and their derivatives exhibit exceptional versatility, finding applications across a spectrum of fields due to their unique chemical properties. In the field of Energy, there is a crucial role in the flow of batteries and other energy storage systems. Their ability to undergo reversible reduction and oxidation reactions makes them indispensable for efficient energy storage [1-7].

These compounds also leave a significant imprint in the domain of dyes and pigments, particularly in the textile industry. Their conjugated structure imparts vibrant and stable coloration to fabrics and various materials [8-11]. Moving into the domain of medicine and pharmaceuticals, certain quinone derivatives, exemplified by anthracycline antibiotics like doxorubicin, demonstrate valuable contributions. The incorporation of a quinone moiety enhances their efficacy, particularly in cancer treatment [12]. Quinone derivatives showcase notable properties as antioxidants, safeguarding cells against oxidative stress. Ubiquinone (Coenzyme Q10), for instance, stands out as a cellular antioxidant with a crucial role in the electron transport chain [13-18]. In the field of photography, quinones play an integral role in the development process of black and white films. Their involvement in dye formation during film development underscores their significance in this creative domain [19-26].

Quinones also emerge as versatile building blocks in the realm of organic synthesis, participating in diverse reactions such as Diels-Alder reactions and Michael additions. This versatility facilitates the synthesis of intricate organic molecules [27]. Their impact extends into polymer chemistry, where quinones enhance the conductivity and electrochemical properties of polymers. This contribution is vital in the creation of conductive polymers used in sensors and electronic devices [28]. As catalysts in various chemical reactions, quinones contribute to the field of catalysis, leveraging their redox properties to promote oxidation and reduction reactions in the presence of other reactants [29]. In the field of analytical chemistry, quinone derivatives act as indicators and probes. Their ability to undergo color changes or fluorescence modulation in the presence of specific analytes facilitates the detection of various substances [30]. Furthermore, quinones find their place in natural products and the food industry. They are integral to various natural products, including essential vitamins like vitamin K. Additionally, their antimicrobial properties make them valuable in the food industry as additives and preservatives [31].

Finally, the diverse applications of quinones underscore their significance in advancing scientific, industrial, and creative pursuits across a wide range of disciplines. One key aspect of the review might be the elucidation of the diverse applications of these heterocyclic quinones. These compounds often exhibit intriguing properties that make them valuable in a range of fields. Potential applications could include their role in medicinal chemistry, where they may display pharmacological activities, or their use in materials science for creating functional materials with unique properties [32-34].

Herein, the review highlights any recent advancements or innovations in the field, emphasizing the potential impact of these developments on both academic research and practical applications. The significance of heterocyclic quinones in contemporary scientific endeavors is likely underscored, showcasing their relevance and potential for

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future advancements. In summary, synthesis, and applications of heterocyclic quinones appears to be a valuable resource for those interested in the synthesis and diverse applications of these intriguing compounds, offering a nuanced understanding of their role in organic chemistry and beyond.

II. APPLICATIONS OF HETEROCYCLIC QUINONES

A number of studies highlight the intriguing biological properties of quinones and their derivatives, particularly those that include fused heterocyclic rings [35-40]. Therefore, it has been discovered that naphtho-quinones, a kind of quinones, exhibit potent fungicidal [41-44] and antimalarial properties [45]. However, quinones that are combined with oxazole or thiazole nuclei have demonstrated strong bactericidal properties. The intriguing characteristics of these compounds have motivated the current research to synthesize thiazoloquinolinediones and oxazoloquinolinediones that have not been reported before. It is possible that some or all of these compounds may possess noteworthy biological features.

The enzymatic activation of quinones into potent anticancer agents holds significant promise in cancer therapy. Numerous nitrogen-containing quinoid heterocycles have demonstrated antitumor effects, with a primary focus on their potential to induce tumor-selective toxicity. This selectivity is attributed to variations in oxygen tension between normal and tumor tissues and the presence of activating enzymes at distinct levels. This review provides a concise overview of the most noteworthy heterocyclic quinones [46-48].

Cancer, currently the second leading cause of global mortality, is characterized by cell cycle deregulation, leading to a progressive loss of cellular differentiation and uncontrolled cellular growth. Despite advancements in medicine, cancer remains a major life-threatening pathology, necessitating the development of novel therapies grounded in current knowledge of cancer biology and leveraging the distinct phenotype of cancer cells, as described by [49].

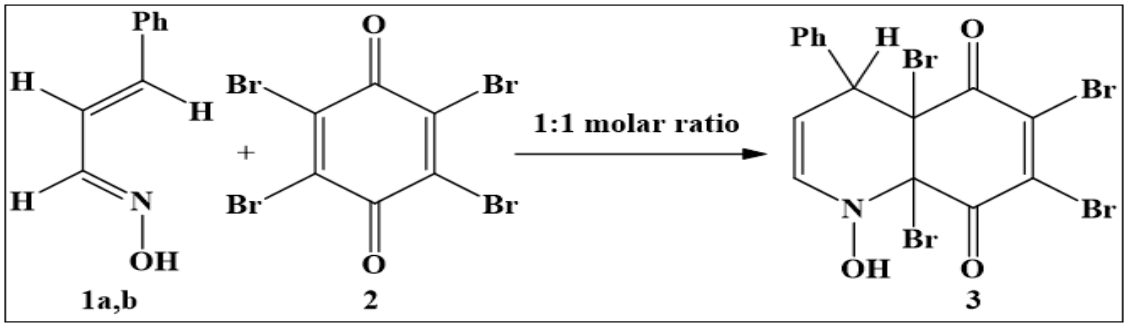
Quinones, prevalent in nature, are integral components of various drugs, including anthracyclines, daunorubicin, doxorubicin, mitomycin, mitoxantrones, and saintopin, widely used in the clinical therapy of solid cancers. The cytotoxic effects of these quinones primarily stem from the inhibition of DNA topoisomerase-II [50-53]. However, the intricate structure of most antitumor quinonoid compounds often complicates the separation of chemical reactivity contributions and the impact of diverse metabolic pathways on overall biological activity.

Enzymatic reduction of quinoid anticancer agents, involving one or two electrons, yields the corresponding semiquinone radical or hydroquinone. Under aerobic conditions, the semiquinone radical anion can transfer its extra electron to molecular oxygen, producing the parent quinone and superoxide radical anion. This redox-cycling process, initiated by bioreduction and followed by oxidation, persists until the system becomes anaerobic. The hydroquinone formed through a two-electron reduction may be excreted in a detoxification pathway or undergo a comproportionation reaction with the parent quinone, generating the semiquinone radical anion. Both the semiquinone and the superoxide radical anion can generate hydroxyl radicals, leading to DNA strand breaks [54-59].

The molecular framework of several naturally occurring anti-tumor agents includes an aminoquinonoid moiety as a key structural component (e.g., mitomycin C, cribrostatin 3, streptonigrin) [60-62]. This structural motif has inspired the synthesis of novel compounds with cytotoxic activity against human cancer cell lines [63-66]. The quinone moiety participates in various biochemical processes such as electron transport and oxidative phosphorylation [67]. Quinones and quinone derivatives exhibit diverse biological properties, including enzyme inhibition, antibacterial, antifungal, and anticancer activities [68-75]. Heterocyclic quinones, featuring nitrogen atoms, have demonstrated antibacterial [76-78], antifungal [79-81], and cytotoxic activities [82-85]. The incorporation of nitrogen or sulfur atoms into five- or six-membered heterocyclic rings while retaining the 'core' chromophore has been a cornerstone of structural and chemical modifications within this compound class [86-96].

III. SYNTHESIS OF HETEROCYCLIC QUINONES

The 4a,6,7,8a-tetrabromo-1-hydroxy-4-phenyl-1,4,4a,8a-tetrahydroquinoline-5,8-dione **3** was synthesized through the Diels-Alder reaction. This reaction involved the reaction of *syn* (or *anti*) cinnamaldehydeoxime (**1a** or **1b**) with bromanil **2** in a 1:1 molar ratio. The synthesis took place in boiling dry xylene over a period of 30 hours, resulting in the desired product (**Scheme 1)** [97].



Scheme 1 Synthesis of 4a,6,7,8a-tetrabromo-1-hydroxy-4-phenyl-1,4,4a,8a-tetrahydroquinoline-5,8-dione 3

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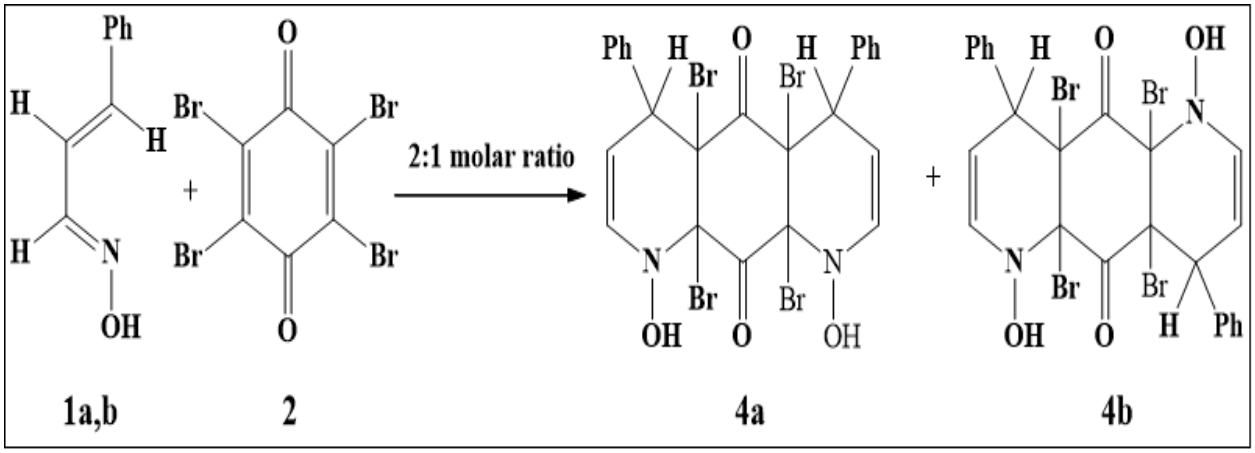
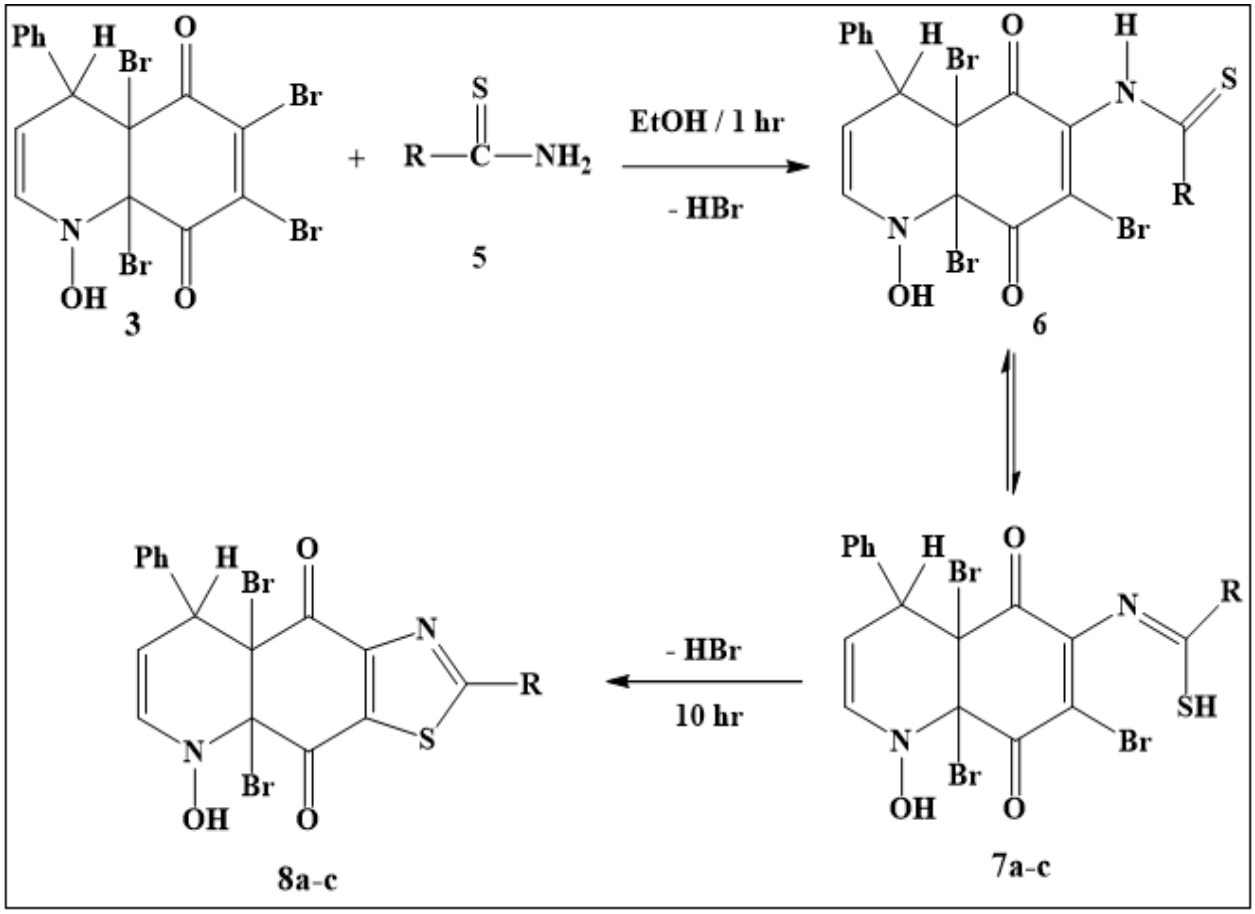
Conducting the reaction between diene 1 and bromanil **2** in a 2:1 molar ratio resulted in the facile formation of two isomeric products, namely 5a,9a-dibromo-1,9-dihydroxy-4,6-diphenyl-5a,6,9,9a-tetrahydropyrido[3,2-g]quinoline-5,10(1H,4H)-dione **4a** and 5a,9a-dibromo-1,6-dihydroxy-4,9-diphenyl-5a,6,9,9a-tetrahydropyrido[2,3-g]quinoline-5,10(1H, 4H)-dione **4b**.



Scheme 2 Synthesis of 4a,5a,9a,10a-tetrabromo-1,9-dihydroxy-4,6-diphenyl-1,4,4a,5a,6,9,9a,10a-octahydropyrido[3,2-g]quinoline-5,10-dione 4a and 5a,9a-dibromo-1,6-dihydroxy-4,9-diphenyl-5a,6,9,9a-tetrahydropyrido[2,3-g] quinoline-5,10(1H,4H)-dione 4b

The monoadduct **3** reacted with thioamides **5** in absolute ethanol, producing dark colored solids within a time frame of 9-11 hours from the start of the reaction. The yield of the reaction ranged from 50% to 75%. The solids were identified as dibromotetrahydroquinolino[2,3-d]thiazolediones 8a-c. Using the reaction of compound 3 with thioacetamide as an illustration, product **7a** was obtained after a brief duration of 1 hour. Subsequently, product **7a** was further converted into compound 8a by subjecting it to reflux in ethanol for an extended length of 10 hours. Thus, it can be proposed that N-(4a,7,8a-tribromo-1-hydroxy-5,8-dioxo-4-phenyl-1,4,4a,5,8,8a-hexahydroquinolin-6-yl)ethanimidothioic acid **7a** serves as an intermediary in the production of **8a** (**Scheme 3**) **[**97**].**



Scheme 3 Synthesis of dibromotetrahydroquinolino[2,3-*d*] thiazolediones 8a-c. where 8a, R=CH_3, 8b, R= NH_2, 8c, R=NHPh

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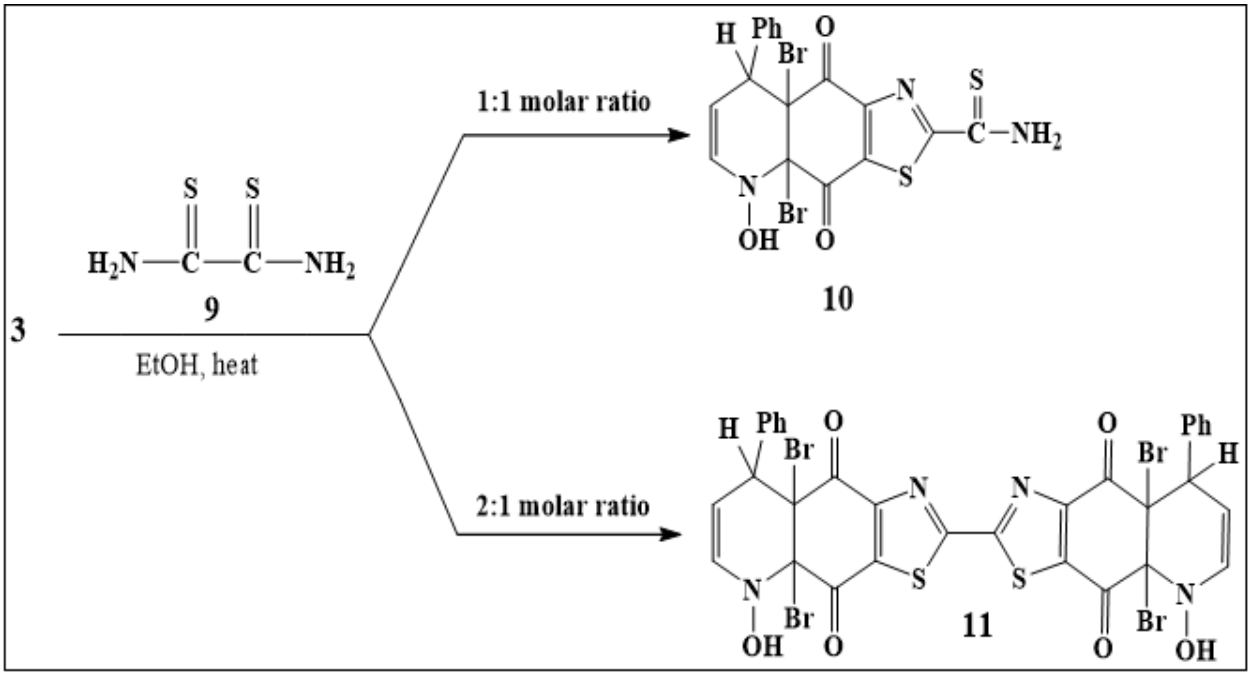
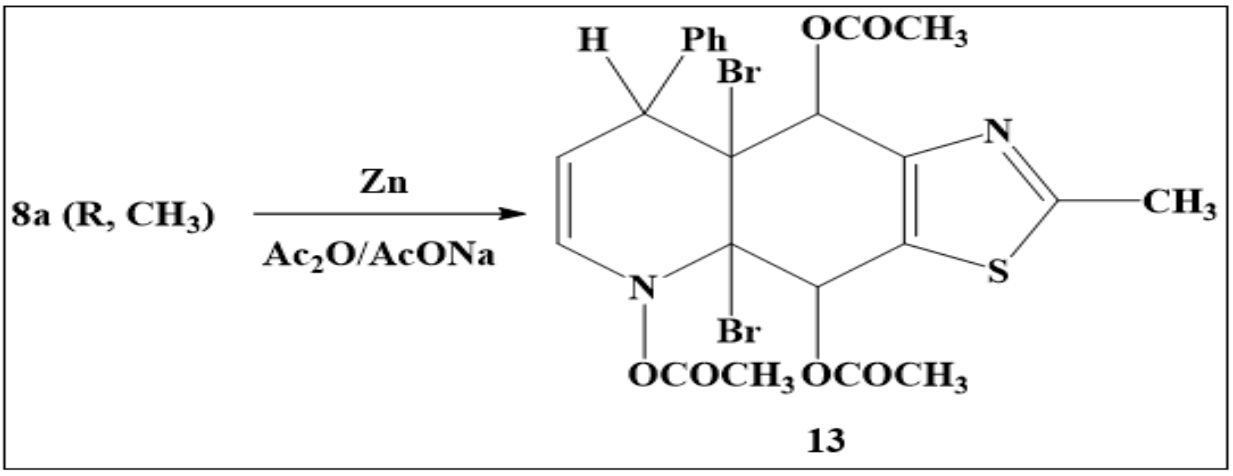
Dithioxamide, having two thioamido groups **9**, also reacted readily with the monoadduct **3** in a 1 : 1 molar ratio to give 4α,8α-dibromo-8-hydroxy-4α,5,8,8α-tetrahydro-4,9-dioxy-5-phenylthio-quinolino[2,3-*d*]thiazole-2-carboxamide **10**, and in a 1 : 2 molar ratio to give 2,2'-bis(4α,8α-dibromo-8-hydroxy-4α,5,9,8α-tetrahydro-5-phenylquinolino[2,3-*d*]thiazole-4,9-dione **11 (Scheme 4)**. **[**97**]**



Scheme 4 Synthesis of 4α,8α-dibromo-8-hydroxy-4α,5,8,8α-tetrahydro-4,9-dioxy-5-phenylthio-quinolino[2,3-*d*]thiazole-2-carboxamide 10, and in a 1 : 2 molar ratio to give 2,2'-bis(4α,8α-dibromo-8-hydroxy-4α,5,9,8α-tetrahydro-5-phenylquinolino [2,3-*d*]thiazole-4,9-dione 11

The reductive acetylation of compound **8a** (where R=CH_3) was carried out employing a mixture of zinc dust, acetic anhydride, and fused sodium acetate. This reaction resulted in the formation of the triacetate derivative, namely, 4α,8α-dibromo-8-hydroxy-4α,5,8,8α-tetrahydro-2-methyl-5-phenylquinolino[2,3-d]-thiazole-4,9-dione **13** (**Scheme 5**) [97].



Scheme 5 Synthesis of 4α,8α-dibromo-8-hydroxy-4α,5,8,8α-tetrahydro-2-methyl-5-phenylquinolino[2,3-*d*]- thiazole-4,9-dione 13

Oxazoloquinolinediones **17a-e** were synthesized through the interaction of compound 3 with acid amides **14**. The synthesis was conducted in boiling ethylene glycol in the presence of bicarbonate and refluxing for 8-10 hours was employed.

The proposed mechanism for the formation of compounds 17a-c suggests a nucleophilic attack by the amide at position 2 of the adduct 3. This leads to the formation of intermediate *N*-(3,4α,8α-tribromo-5-hydroxy-4α,5,8,8α-tetrahydro-1,4-dioxo-8-phenyl-2-quinolinyl)amide derivatives **16a-e**. Subsequently, under the influence of the basic effect of bicarbonate and the high energy of the reaction medium, these intermediates undergo dehydrobromination, resulting in the final mesoionic product 2-Substituted-8-oxy-5-phenylquinolino[2,3-d]oxazole-4,9-dione **17a-e** (**Scheme 6**) [97].

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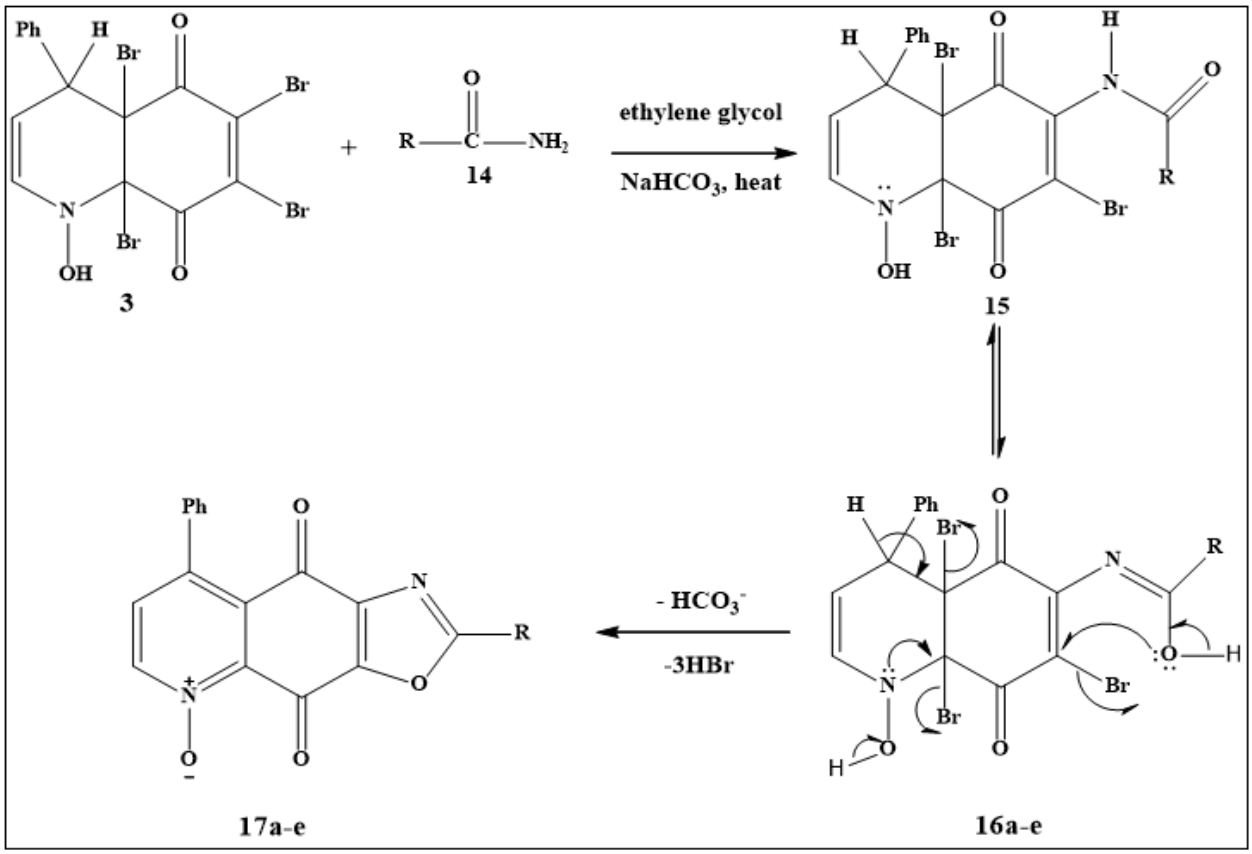
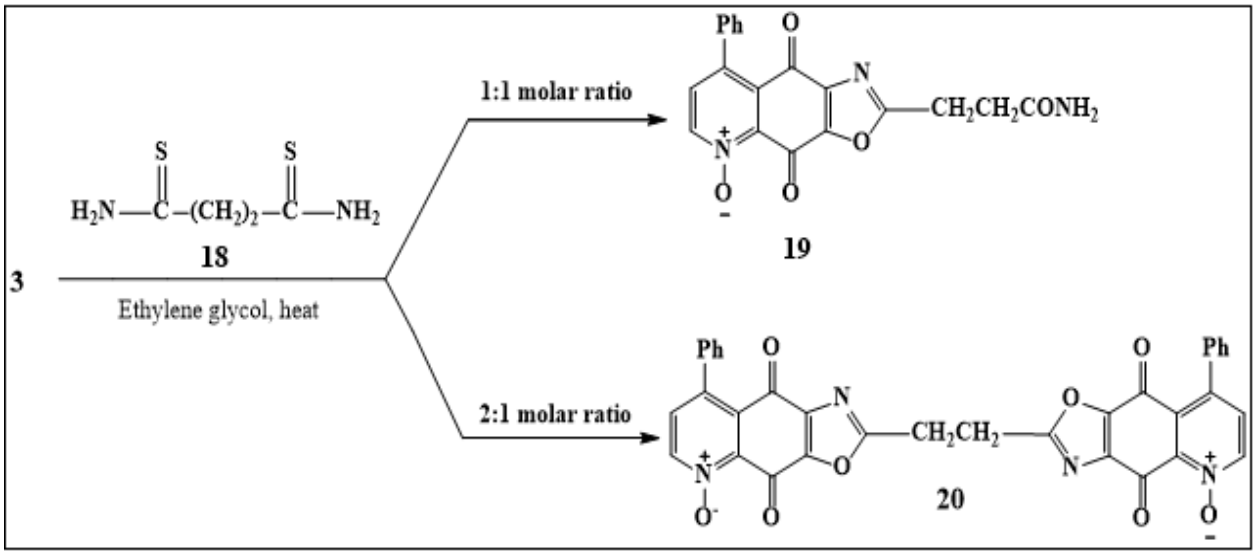


Scheme 6 Synthesis of 2- Substituted-8-oxy-5-phenylquinolino[2,3-*d*]oxazole-4,9-dione 17a-e where 17a, R=H, 17b, R=CH_3, 17c, R= Ph, 17d, R=CH_2Ph, 17e, R=NH_2

The interaction between butanebis(thioamide) **18** and 4a,6,7,8a-tetrabromo-1-hydroxy-4-phenyl-1,4,4a,8a-tetrahydroquinoline-5,8-dione 3 resulted in the formation of two products: 8-oxy-5-phenylquinolino[2,3-d]oxazole-4,9-dione-2-carbo-succinamide **19** and 1,2-bis[8-oxy-5-phenylquinolino[2,3-d]oxazole-4,9-dione]-ethane **20**. The specific product obtained was influenced by the molar ratios of the reactants used **(Scheme 7)** [97].



Scheme 7 Synthesis of 8-oxy-5-phenylquinolino[2,3-*d*]oxazole-4,9-dione-2-carbo-succinamide 19 and 1,2-bis[8-oxy-5-phenylquinolino[2,3-*d*]oxazole-4,9-dione]- ethane 20.

The synthesis of aminopyrimido[4,5-c]isoquinolinequinone derivatives **25a-ad** was accomplished through the amination reaction of quinones **23** with various primary and secondary amines **24**. This reaction was conducted in ethanol in the presence of 5% mol of $CeCl_3.7H_2O$ and under aerobic conditions. Due to the unsuccessful nucleophilic substitution on quinone **23** with *p*-nitroaniline, the nitrophenyl derivative **26** was prepared, albeit in low yields, using microwave irradiation (MWI) of the precursors loaded on the acid clay montmorillonite KSF (**Scheme 8)** [98-101].

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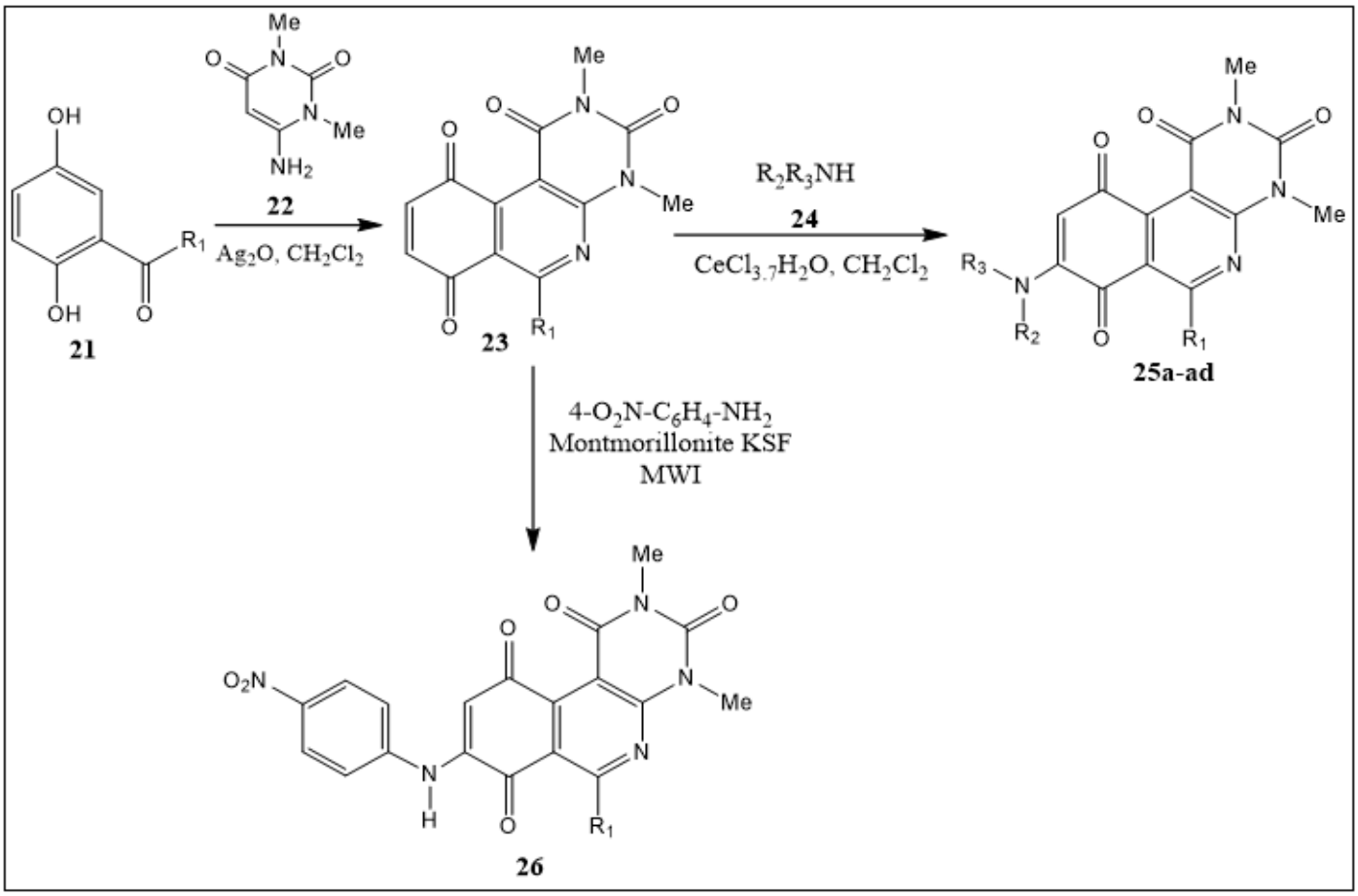
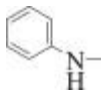
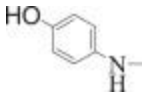
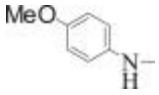
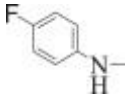
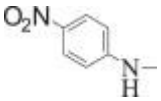
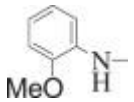


Scheme 8 Synthesis of the aminopyrimido[4,5-c]isoquinolinequinones derivatives 25a-ad and nitrophenyl derivative 26

Table 1 Synthesis of the aminopyrimido[4,5-c]isoquinolinequinones derivatives 25a-ad and nitrophenyl derivative 26

R^3R^2N	Compound	R^1	Yield (%)	Compound	R^1	Yield (%)
	**25a**	H	99	**25n**	Me	99
	**25b**	H	40	**25o**	Me	46
	**25c**	H	99	**25p**	Me	99
	**25d**	H	91	**25q**	Me	72
	–	–	–	**25r**	Me	39
	**25e**	H	95	**25s**	Me	95
	**25f**	H	74	**25t**	Me	65

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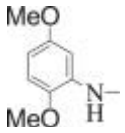
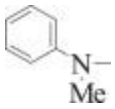
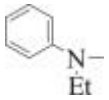
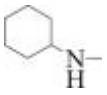
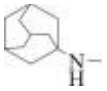
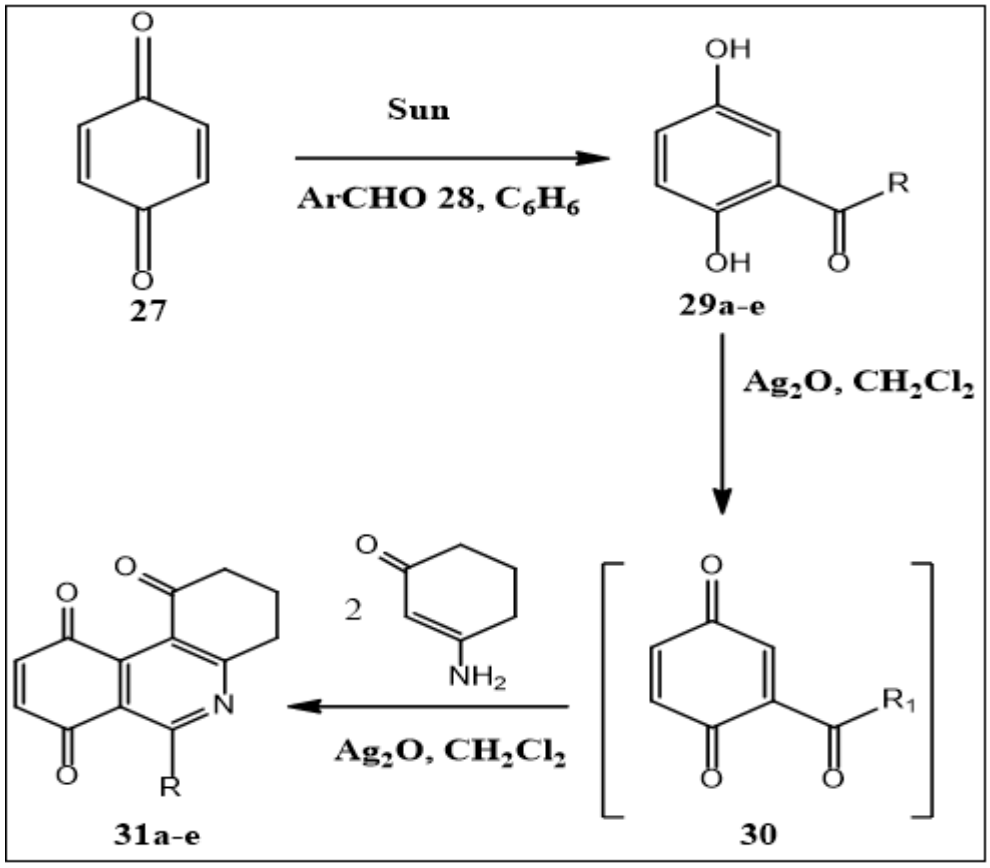
R^3R^2N	Compound	R^1	Yield (%)	Compound	R^1	Yield (%)
	**25g**	H	81	**25y**	Me	79
	**25h**	H	61	**25w**	Me	63
	**25i**	H	55	**25z**	Me	58
nC$_4$H$_9$NH–	**25j**	H	75	**25aa**	Me	75
	**25k**	H	74	**25ab**	Me	78
	**25l**	H	49	**25ac**	Me	65
	**25m**	H	6	**25ad**	Me	16

The synthesis of phenanthridine-7,10-quinones **31a-e** was carried out through solar-chemical photo-Friedel-Crafts acylation of 1,4-benzoquinone **27** with benzaldehyde, furan-2-carbaldehyde, and thiophene-3-carbaldehyde. This process, conducted in accordance with a recently reported procedure [101, 102], yielded intermediate products **29a-e**. Subsequently, these intermediates were subjected to a reaction with two moles of 3-aminocyclohex-2-enone in the presence of silver oxide, resulting in the desired derivatives **31a-e** (**Scheme 9)**.



Scheme 9 Synthesis of phenanthridine-7,10-quinones 31a-e. Where 31a, R= H; 31b, R= Me, 31c; R= phenyl; 31d, R= furan-2-yl; 31e, R= thiophen-3-yl

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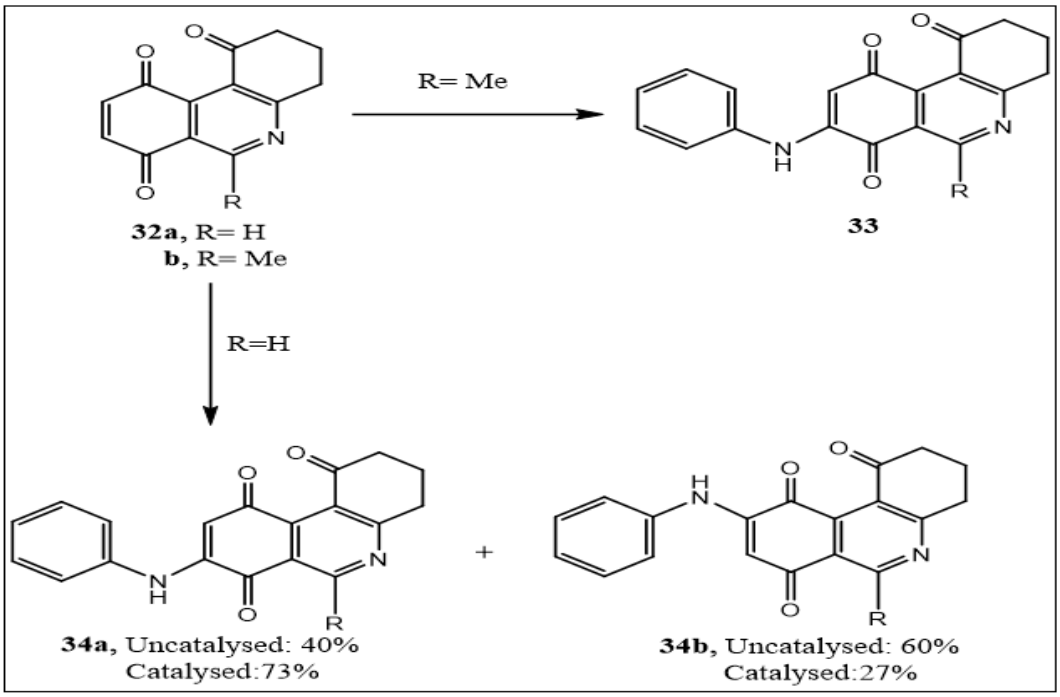
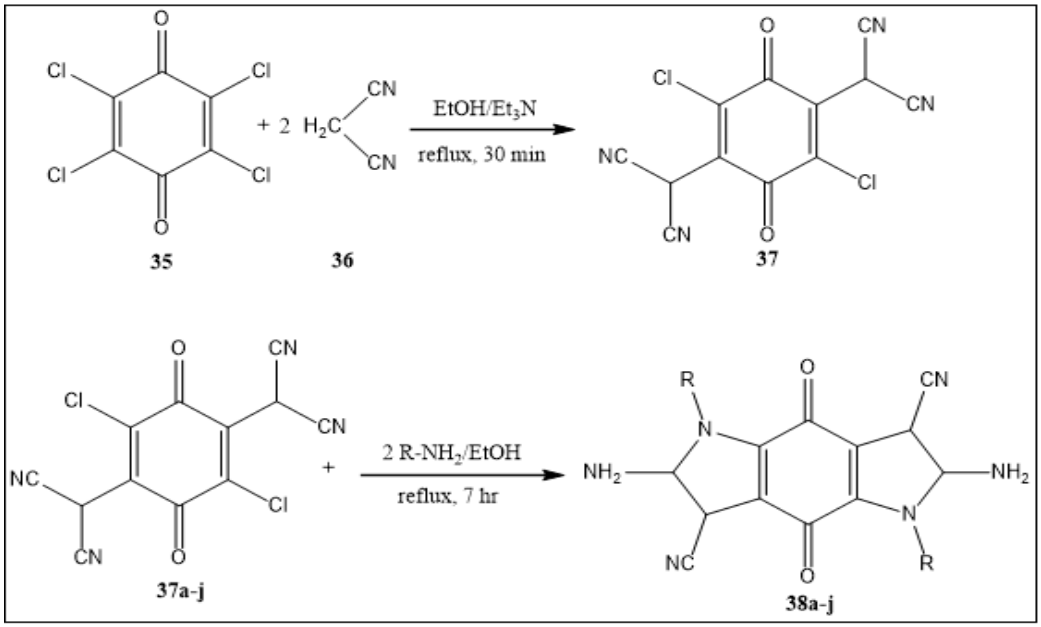
Recent observations concerning the interaction of phenanthridine-7,10-quinones **32a** and **32b** with aniline reveal that, under ambient conditions in ethanol, **32a** undergoes a reaction with aniline, yielding a mixture of regioisomers 8- and 9-Phenylamino-3,4-dihydrophenanthridine-1,7,10(2H)-trione (34a, 34b) in a 40:60 ratio, with a moderate overall yield. The introduction of $CeCl_3.7H_2O$ in this reaction leads to a change in regioselectivity and an enhancement in the yield of the amination reaction. In the case of the reaction between 32b and aniline, the isolation of aminoquinone 8-(Phenylamino)-6-methyl-3,4-dihydrophenanthridine1,7,10(2H)-trione **33** is achieved with a low yield; however, the use of the $CeCl_3.7H_2O$ catalyst improves the yield of the amination reaction without altering the regioselectivity (**Scheme 10)** [101, 103].



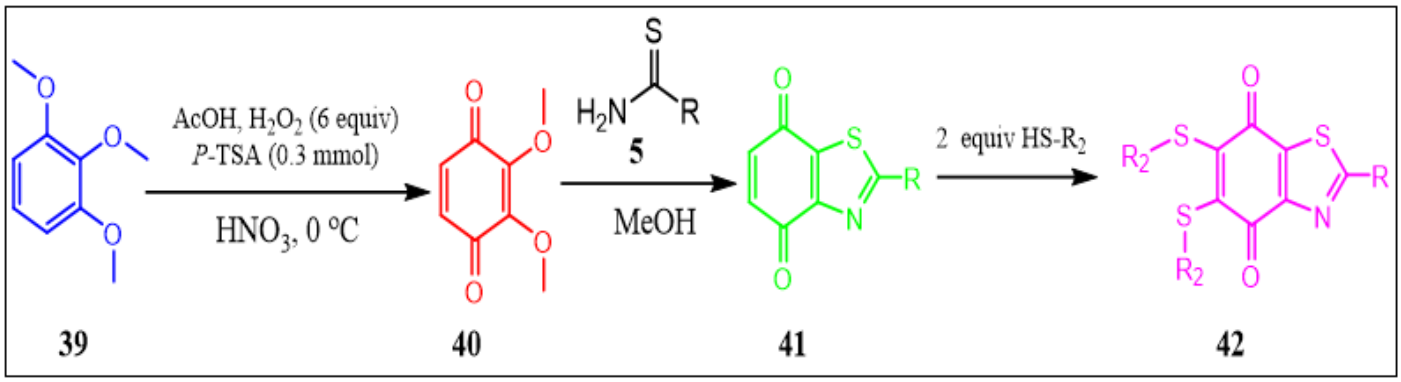
Scheme 10 Reactions of 32a (R=H) and 32b (R=CH_3) with aniline

Derivatives of 2,6-diamino-4,8-dioxo-1,4,5,8-tetrahydropyrrolo[2,3-f]indole-3,7-dicarbonitrile **38a-j** were synthesized through the reaction of chloranil **35** with two equivalents of malononitrile **36** in the presence of a basic catalyst, yielding the dimalononitrile derivative **37a-j**. Subsequently, the latter undergoes a reaction with two equivalents of various primary aromatic or aliphatic amines with diverse substituents in the para position (**Scheme 11)** [104].



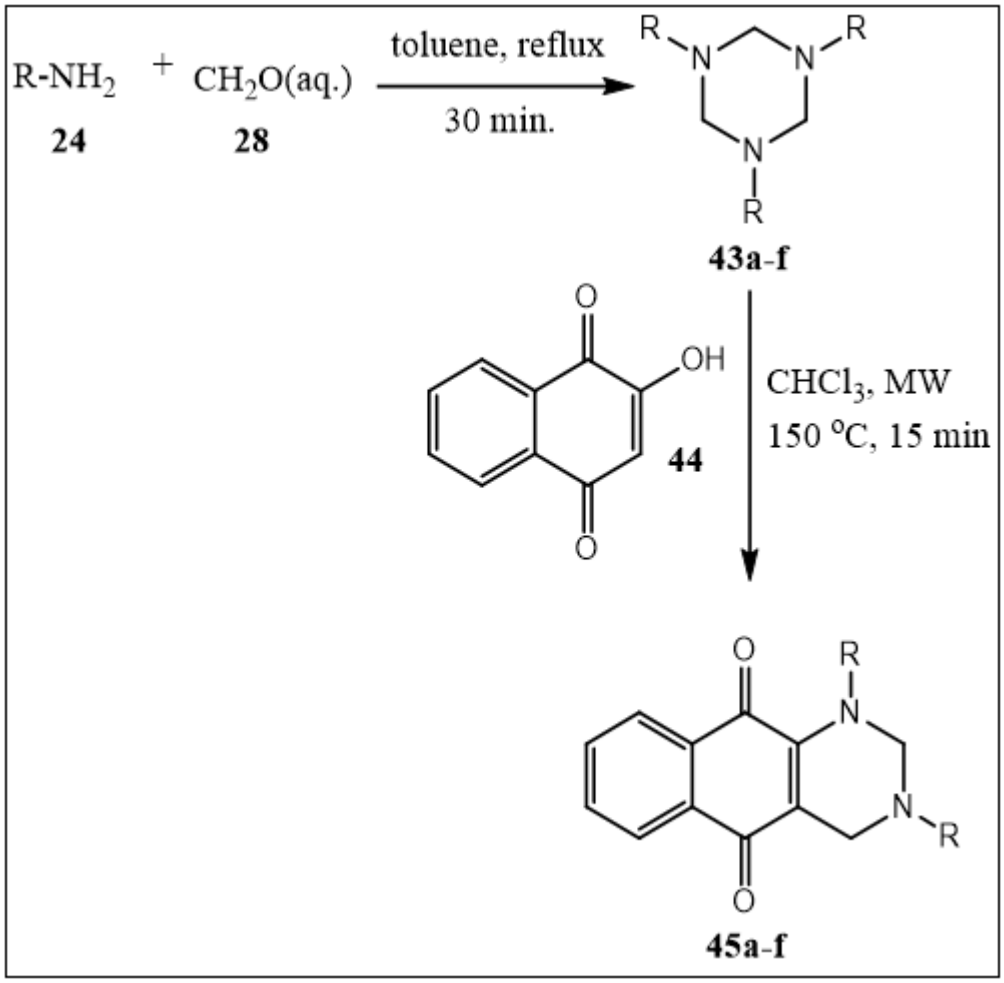
Scheme 11. Synthesis of pyrolo[2,3-F]indole-3,7-dicarbonitriles 38a-j. where 38a, R= C_6H_5, 38b, R= *P*-OH-C_6H_4, 38c, R=*p*-COOH-C_6H_4, 38d, R= *p*-Cl-C_6H_4, 38e, R= *p*-OCH_3-C_6H_4, 38f = *p*-CH_3-C_6H_4, 38g, R= *p*-NO_2-C_6H_4, 38h, R=H, 38i, R=CH_3, 38j, R=CH_2CH_3.

Recently, a systematic synthesis of 2-Alkyl-5,6-bis(alkylthio)benzo[d]thiazole-4,7-dione **42** was initiated. The process commenced with the production of 2,3-dimethoxy-1,4-benzoquinone **40**, achieved through the reaction of 1,2,3-trimethoxybenzene **39** and acetic acid in the presence of a nitrogen gas bubbler and mineral oil to maintain an open system for the exothermic reaction. Subsequently, p-toluene sulfonic acid monohydrate and hydrogen peroxide were introduced to yield 2,3-dimethoxy-1,4-benzoquinone **40**. This compound then reacted with thioacetamide and thiobenzamide, resulting in the formation of 2-substituted benzo[d]thiazole-4,7-dione **41**. Further treatment of **41** with alkylthio reagents led to the synthesis of 2-Alkyl-5,6-bis(alkylthio)benzo[d]thiazole-4,7-dione **42** (**Scheme 12)** [105].



Scheme 12 Synthesis of 2-Alkyl-5,6-bis(alkylthio)benzo [d]thiazole-4,7-dione 42a,b where 42a, R=H, 42b, R=CH_3

Recently, high yields of hexahydropyrimidine-fused 1,4-naphthoquinones **45a-f** were obtained through the sequential reaction of readily available 1,3,5-triazinanes **43a-f** with 2-hydroxy-1,4-naphthoquinone **44** under microwave irradiation (**Scheme 13**) [106-123].



Scheme 13 Synthesis of hexahydropyrimidine-fused 1,4-naphthoquinones 45a-f in high yields. Where 45a, R= butyl, 75%; 45b, R= pentyl, 89%; 45c, R= decyl, 70%; 45d, R=4-chlorobenzyl, 85%; 45e, R=2,4-dichlorobenzyl, 88%

IV. CONCLUSION

Finally, this comprehensive review study explores the synthesis and numerous applications of heterocyclic quinones, shining light on their unique functions in a variety of scientific, industrial, and creative disciplines. The synthesis of these molecules, as demonstrated by methods such as the Diels-Alder reaction, is thoroughly investigated, providing useful insights for researchers and organic chemistry aficionados. Heterocyclic quinones' versatility is demonstrated by their use in electrochemistry, batteries, textiles, medicine, and other fields. In the field of medicine, the review stresses their promising function in cancer therapy, demonstrating the enzymatic activation of quinones into anticancer drugs. Their role in inhibiting DNA topoisomerase-II and their potential for tumor-selective toxicity highlight their significance in tackling the challenges posed by cancer, a primary cause of death. Beyond medicine, heterocyclic quinones have applications in photography, organic synthesis, polymer chemistry, catalysis, and analytical chemistry. Their contributions to the production of black and white films, the increase of conductivity in polymers, and the use as catalysts and probes highlight their adaptability across a wide range of applications. The review also looks at the synthesis of heterocyclic quinones, highlighting the many reactions and processes that lead to the creation of these molecules. The insertion of nitrogen or sulfur atoms in five- or six-membered heterocyclic rings expands their structural and chemical alterations, resulting in compounds having antibacterial, antifungal, and cytotoxic properties. Furthermore, the study discusses current advances in the subject, recognizing the fluid nature of research and its potential impact on both academic and practical applications. The importance of heterocyclic quinones in scientific, industrial, and artistic breakthroughs is highlighted, placing them as vital resources for current and future initiatives. To summarize, this review provides a thorough and important resource for understanding the synthesis and different applications of heterocyclic quinones, providing a nuanced perspective on their critical role in promoting knowledge and innovation across multiple fields.

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