



CHEMICAL JOURNEY 154-YEAR OF 1, 3-(β)-DIKETONES: THE MOST IMPORTANT REACTIONS

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Abstract: -

Diketones, also known as diones, are a significant class of organic compounds that feature two ketone functional groups (-C=O) within the same molecule. They have demonstrated immense versatility and found applications in various fields. Since their initial discovery in 1867, diketones have played a fundamental role in organic synthesis, offering a wide range of chemical reactions and applications. This article presents a comprehensive analysis of the synthesis of 1,3-diketones over the span of 154 years, from 1867 to the present day. Moreover, this article encompasses numerous and important reactions that have been extensively explored and documented, contributing to the understanding and utilization of these compounds in diverse scientific endeavours.

Keyword: - 154 Years, some important Reactions, 1,3 (B)-Diketones, Year-Wise, Synthesis, Developments.

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Introduction

1,3-diketones are organic compounds that contain two ketone groups separated by a carbon-carbon bond. These compounds are important in a variety of fields including pharmaceuticals, agrochemicals, and materials science. The synthesis or preparation of 1,3-diketones can be both important and difficult, and here are some reasons why:

• Importance:

1,3-diketones can be used as intermediates in the synthesis of a wide range of organic compounds. For example, they can be used to synthesize pharmaceuticals such as antihistamines and antitumor agents, as well as agrochemicals such as herbicides and insecticides. 1,3-diketones can also be used as ligands in coordination chemistry, where they can form stable complexes with transition metals. These complexes can have interesting properties and be useful in catalysis and materials science.

• Difficulties:

The synthesis of 1,3-diketones can be challenging due to the reactivity of the ketone groups. In particular, the formation of enolates, which are important intermediates in many 1,3-diketone syntheses, can be difficult to control and can lead to unwanted side reactions. The regioselectivity of 1,3-diketone formation can also be a challenge. Depending on the reaction conditions, other isomers such as 1,2- and 1,4-diketones may also be formed.

The purification of 1,3-diketones can be difficult due to their low volatility and tendency to form complexes with transition metals. This can make it challenging to obtain pure products with high yields.

Overall, the synthesis or preparation of 1,3-diketones can be both important and difficult due to their wide range of applications and the challenges involved in their synthesis and purification.

The synthesis and characterization of 1,3-diketones have been an important area of research in organic chemistry for over a century. The first known synthesis of a 1,3-diketone, 1,3-cyclohexanedione, was reported by German chemist Friedrich August Kekulé in 1867. During the early 20th century, researchers began to explore the synthetic and structural aspects of 1,3-diketones in more detail. In 1913, Swiss chemist Alfred Werner proposed a coordination theory of 1,3-diketones and other organic compounds, which laid the foundation for modern coordination chemistry.

In the 1920s and 1930s, researchers discovered that 1,3-diketones could form chelate complexes with metal ions, leading to the development of new synthetic methods and applications in fields such as catalysis and bioinorganic chemistry.

In recent years, 1,3-diketones have been used as building blocks in the synthesis of a wide range of compounds, including pharmaceuticals, agrochemicals, and natural products. New synthetic methods and strategies continue to be developed to enhance the efficiency and versatility of 1,3-diketone synthesis.

Overall, the history of 1,3-diketones reflects the long-standing interest in organic chemistry to understand the properties and reactivity of functional groups, as well as the importance of these compounds in the development of new materials and chemical technologies.

The year-wise study can be important for the synthesis of 1,3-diketones because the development of new synthetic methods and techniques over time can greatly improve the efficiency, selectivity, and yield of 1,3-diketone synthesis. Here are some examples:

In the early 20th century, acetoacetic ester synthesis was developed as a versatile method for the synthesis of 1,3-diketones. This reaction involves the reaction of an ester with a strong base to form an enolate, which can then react with an electrophile to form a 1,3-diketone. This reaction has since been widely used and modified for the synthesis of a variety of 1,3-diketones.

In the 1960s, the aldol condensation reaction was developed as another powerful method for the synthesis of 1,3-diketones. This reaction involves the reaction of an aldehyde or ketone with a carbonyl compound in the presence of a base to form a β -hydroxy carbonyl compound, which can then be dehydrated to form a 1,3-diketone. This reaction has since been used in the synthesis of a variety of natural products and pharmaceuticals.

In recent years, new methods for the synthesis of 1,3-diketones have been developed using catalysis and green chemistry principles. For example, the use of transition metal catalysts such as palladium or copper can greatly improve the selectivity and yield of 1,3-diketone synthesis. In addition, the use of green solvents and reaction conditions can improve the sustainability and efficiency of 1,3-diketone synthesis.

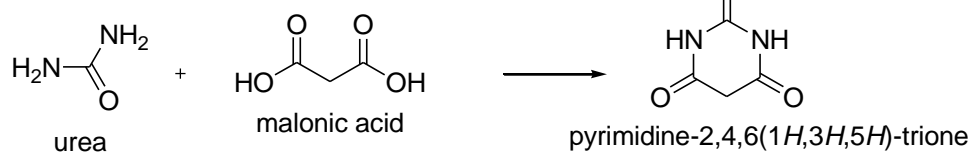
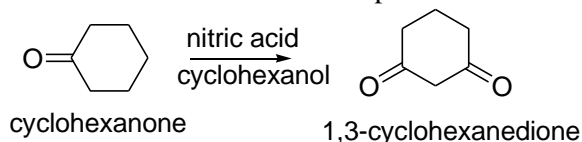
By studying the development of these and other synthetic methods for 1,3-diketone synthesis over time, researchers can gain insights into the underlying mechanisms and principles that govern these reactions. This knowledge can then be used to design and optimize new synthetic routes for

the preparation of 1,3-diketones with improved selectivity, yield, and sustainability.

Year-wise synthesis of 1, 3 (β)-diketones:-

From 1867 to 1877

During the period from 1867 to 1877, there were several important developments related to organic chemistry, including the synthesis and characterization of various compounds.



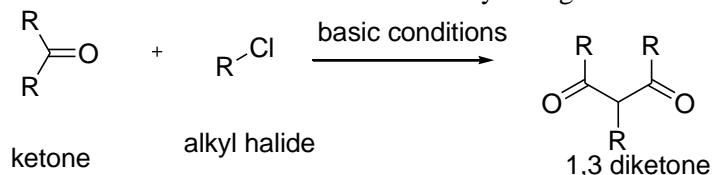
Scheme 2.

In 1868, German chemist Adolf von Baeyer reported the synthesis of barbituric acid, a 1,3-diketone that is an important precursor to many drugs. Baeyer's method involved the reaction of malonic acid with urea under acidic conditions to form barbituric acid. Von Baeyer discusses his method for producing barbituric acid from urea

Scheme 1.

In 1867, German chemist Friedrich August Kekulé reported the first known synthesis of a 1,3-diketone, 1,3-cyclohexanedione. This compound was prepared by oxidizing a mixture of cyclohexanone and cyclohexanol with nitric acid. Kekulé's work on the structure of benzene and other aromatic compounds also laid the foundation for the development of modern organic chemistry (1) (2).

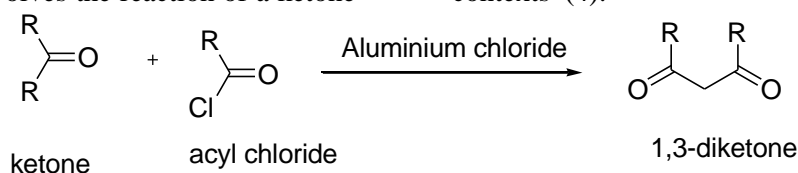
and malonic acid in this work, which entails condensation of the two substances, ring closure, and decarboxylation. Because it established the idea of a cyclic compound with two carbonyl groups (i.e., a 1,3-diketone) and laid the way for the creation of the barbiturate class of medications, this reaction is significant in the history of organic chemistry (3).



Scheme 3.

In 1874, American chemist Edward Curtis reported a method for the synthesis of 1,3-diketones by the reaction of a ketone with an alkyl halide under basic conditions. This method, which is known as the Claisen condensation, involves the formation of an enolate intermediate that can be alkylated to form the 1,3-diketone. Curtis describes his method for the synthesis of 1,3-diketones, which involves the reaction of a ketone

with an alkyl halide in the presence of a strong base such as potassium carbonate. The reaction proceeds through a nucleophilic substitution at the carbonyl group of the ketone, followed by the elimination of the halide ion and subsequent intramolecular aldol condensation to form the 1,3-diketone product. This method represented a significant advance in the synthesis of 1,3-diketones and is still used today in various contexts (4).



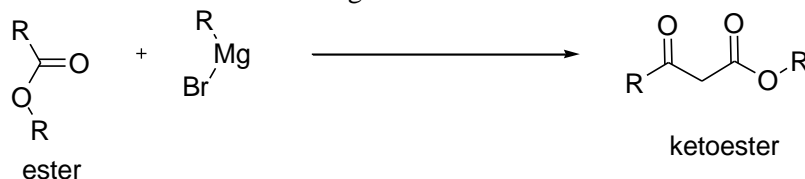
Scheme 4.

In 1876, French chemist Charles Friedel and his collaborator James Crafts reported a method for the synthesis of 1,3-diketones by the reaction of a ketone with an acyl chloride in the presence of an aluminium chloride catalyst. This method, known

as the Friedel-Crafts acylation, involves the formation of an acylium ion intermediate that can be attacked by the ketone to form the 1,3-diketone. In this work, Friedel and Crafts report on their method for the synthesis of 1,3-diketones by the reaction of an acyl chloride with a ketone in

the presence of aluminium chloride as a catalyst. The reaction proceeds through the formation of an acylium ion intermediate, which undergoes nucleophilic addition by the ketone to form the 1,3-diketone product. This reaction, known as the Friedel-Crafts acylation, represents an important method for the synthesis of a wide variety of organic compounds and is still widely used today (5).

Overall, the period from 1867 to 1877 saw significant progress in the synthesis of 1,3-diketones, with new methods and reactions being



Scheme 5.

In 1879, French chemist Victor Grignard reported a method for the synthesis of β -keto esters, which are 1,3-diketones with an ester group on one of the carbonyl groups. This method involved the reaction of an ester with ethyl magnesium bromide, which generated an enolate intermediate that could be alkylated to form the β -keto ester. Grignard's method involved the reaction of an alkyl or aryl halide with magnesium metal in the presence of anhydrous ether. This reaction produced an organomagnesium compound, which

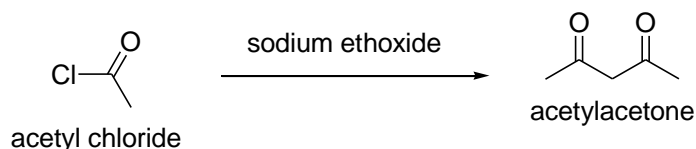
developed by chemists such as Baeyer, Curtis, Friedel, and Crafts. These developments laid the foundation for further progress in the field of organic chemistry in the years to come.

1878 to 1888

Between 1878 and 1888, a number of techniques for the synthesis of 1,3-diketones, which are organic molecules with two ketone functional groups separated by a three-atom carbon chain, were established.

could then be used to synthesize a wide range of organic compounds. In his paper, Grignard demonstrated the versatility of this method by using it to synthesize β -keto esters, as well as other organic compounds such as alcohols, ketones, and acids (6).

The discovery of the Grignard reagent, as it came to be known, was a significant breakthrough in organic chemistry and opened up new avenues for the synthesis of complex organic molecules. Grignard's work was later recognized with the award of Nobel Prize in Chemistry in 1912 (7).



Scheme 6.

In 1881, German chemist August Kekulé reported a method for the synthesis of acetylacetone, a β -diketone that is widely used in organic synthesis. This method involved the reaction of acetyl chloride with sodium ethoxide, followed by acidification to form acetylacetone. August Kekulé's discovery of a method for the synthesis of acetylacetone was an important contribution to the field of organic chemistry, as it provided a more efficient and practical method for preparing this compound. (8).

In 1886, Italian chemist Luigi Chiozza reported a method for the synthesis of β -diketones by the reaction of ketones with sodium ethoxide. This method involved the condensation of two molecules of ketone under basic conditions to form the β -diketone (9). Chiozza's paper on the synthesis of β -diketones by the reaction of ketones with sodium ethoxide was an important

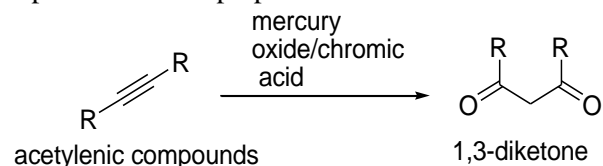
contribution to the field of organic chemistry, as it provided a new and efficient method for the preparation of these compounds. Prior to Chiozza's work, the synthesis of β -diketones was a challenging and time-consuming process, involving multiple steps and low yields. Chiozza's method simplified the synthesis and resulted in higher yields, making it a significant advancement in the field.

Furthermore, the discovery of β -diketones as a new class of organic compounds with unique properties and reactivity was an important development in organic chemistry. β -diketones have since been widely used as versatile building blocks in the synthesis of a variety of organic compounds, including pharmaceuticals, agrochemicals, and materials. Chiozza's work paved the way for further research and applications in this area. Overall, the period from 1878 to 1888 saw significant progress in the

synthesis of 1,3-diketones, with new methods and reactions being developed by chemists such as Grignard, Kekulé, and Chiozza. These developments laid the foundation for further progress in the field of organic chemistry in the years to come.

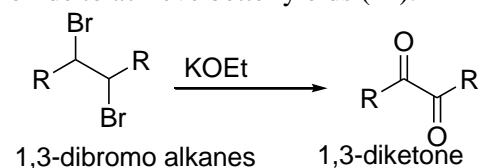
1889 to 1899

During the period from 1889 to 1899, the synthesis of 1,3-diketones was an area of interest in organic chemistry, and several methods were reported for their preparation.



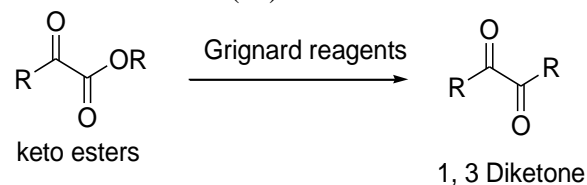
Scheme 7.

In 1889, German chemist Heinrich Hlasiwetz reported a method for the synthesis of β -diketones by the oxidation of acetylenic compounds with mercury oxide (10). This method was later modified by German chemist Paul Jacobson in 1897, who used chromic acid instead of mercury oxide to achieve better yields (11).



Scheme 8.

In 1891, Swiss chemist Alfred Werner reported a method for the synthesis of 1,3-diketones by the reaction of 1,3-dibromo alkanes with sodium or potassium ethoxide (12). This method was later modified by Werner and his student Fritz Kaepelin in 1898, who used sodium ethoxide and potassium ethylate to synthesize β -diketones from ketones and esters (13).



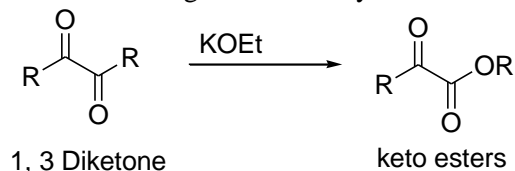
Scheme 9.

In 1893, German chemist Ernst Beckmann reported a method for the synthesis of 1,3-diketones by the reaction of β -keto esters with Grignard reagents. This method allowed for the synthesis of a wide range of 1,3-diketones with different substituents on the carbonyl groups (14). Overall, the period from 1889 to 1899 saw significant progress in the synthesis of 1,3-

diketones, with new methods and reactions being developed by chemists such as Hlasiwetz, Werner, Kaepelin, and Beckmann. These developments laid the foundation for further progress in the field of organic chemistry in the years to come.

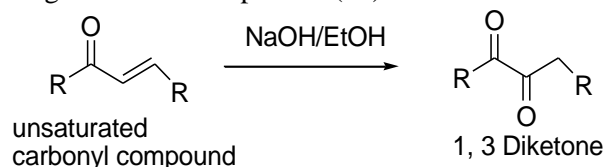
1900 to 1910

During the period from 1900 to 1910, the synthesis of 1,3-diketones continued to be an area of interest in organic chemistry.



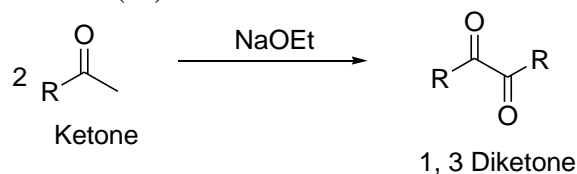
Scheme 10.

One of the earliest methods involved the reaction of diketones with sodium ethoxide, which produced the corresponding ethyl ester of the diketone. This reaction was reported by German chemist Heinrich Hlasiwetz in 1903. The work of Hlasiwetz on the reaction of diketones with sodium ethoxide is important in the synthesis of 1,3-diketones because it provides a straightforward method for converting diketones to the corresponding ethyl esters. This reaction is useful in organic synthesis because 1,3-diketones are versatile intermediates that can undergo various chemical transformations to yield a wide range of useful compounds (15).



Scheme 11.

In 1907, American chemist Arthur Michael discovered a method for the synthesis of 1,3-diketones via the Michael addition reaction, which he had discovered five years earlier. This reaction involves the addition of a nucleophile, such as an enolate, to an α,β -unsaturated carbonyl compound, followed by a proton transfer to generate the 1,3-diketone (16).



Scheme 12.

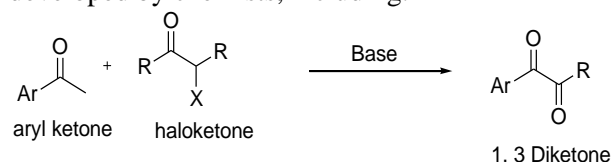
In 1909, German chemist Ludwig Claisen reported a method for the synthesis of β -diketones via the Claisen condensation reaction, which

involves the reaction of two esters or ketones with a strong base to form a β -keto ester or β -diketone, respectively. In the Claisen condensation reaction, a base such as sodium ethoxide or sodium hydroxide is used to deprotonate the α -carbon of one of the esters or carbonyl compounds, generating an enolate ion. This enolate ion then attacks the carbonyl group of the other ester or carbonyl compound, resulting in the formation of a carbon-carbon bond and the formation of a β -ketoester or β -diketone product (17).

Overall, the period from 1900 to 1910 saw significant progress in the synthesis of 1,3-diketones, with new methods and reactions being developed by chemists such as Hlasiwetz, Michael, and Claisen. These developments laid the foundation for further progress in the field of organic chemistry in the years to come.

1911 to 1921

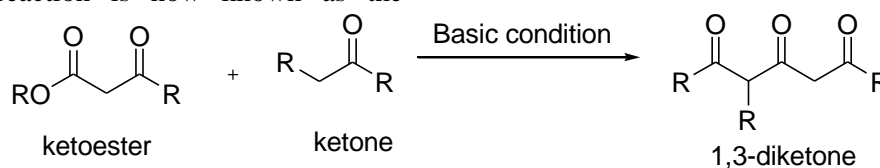
During the period from 1911 to 1921, several new methods for the synthesis of 1,3-diketones were developed by chemists, including:



Scheme 13.

In 1913, British chemist George William Wheland reported the synthesis of 1,3-diketones by the reaction of an aryl ketone with an α -halo ketone under basic conditions. This method, known as the Wheland reaction, involves the formation of an enolate intermediate that can be halogenated to form the 1,3-diketone. The synthesis of 1,3-diketones by George W. Wheland in 1913 was an important contribution to the field of organic synthesis. The method described in the paper allowed for the efficient synthesis of 1,3-diketones from readily available starting materials, which was not previously possible by other methods.

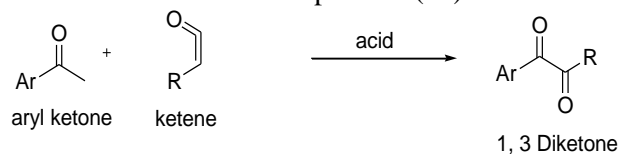
The reaction reported by Wheland involved the reaction of an aryl ketone with an α -halo ketone under basic conditions to yield a 1,3-diketone product. This reaction is now known as the



Scheme 16.

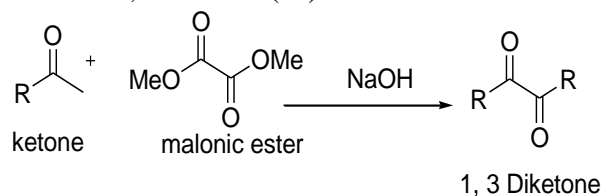
In 1922, American chemist Arthur Michael reported a method for the synthesis of 1,3-diketones by the reaction of a β -ketoester with a

Wheland-Deguchi reaction or the Wheland-Deguchi-Schmidt reaction, and it is widely used in organic synthesis for the preparation of 1,3-diketones and related compounds (18).



Scheme 14.

In 1915, American chemist Roger Adams reported a method for the synthesis of 1,3-diketones by the reaction of an aryl ketone with a ketene under acidic conditions. This method, known as the Adams condensation, involves the formation of an acyloin intermediate that can be dehydrated to form the 1,3-diketone (19).



Scheme 15.

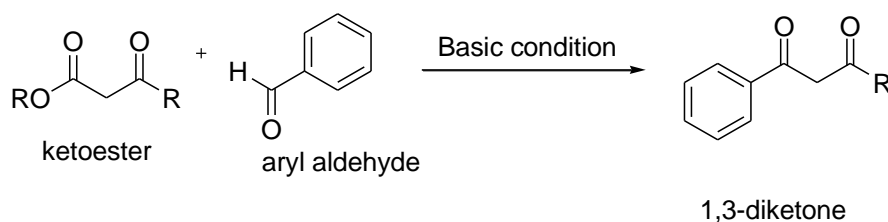
In 1921, British chemist Robert Robinson reported a method for the synthesis of 1,3-diketones by the reaction of a ketone with a malonic ester under basic conditions. This method, known as the Robinson annulation, involves the formation of a cyclic intermediate that can be hydrolyzed to form the 1,3-diketone (20).

These methods provided new and efficient ways for the synthesis of 1,3-diketones, which are important intermediates in the synthesis of various organic compounds, including pharmaceuticals, agrochemicals, and natural products. The development of these methods further expanded the toolkit available to organic chemists and laid the foundation for further advances in the field.

1922 to 1932

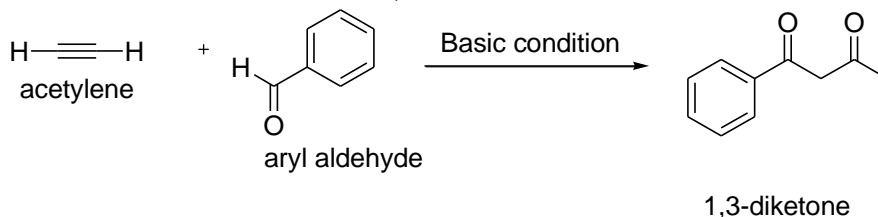
During the period from 1922 to 1932, several new methods for the synthesis of 1,3-diketones were developed by chemists, including:

ketone under basic conditions. This method, known as the Michael addition, involves the formation of a β -keto enolate intermediate that can react with a ketone to form the 1,3-diketone (21).

**Scheme 17.**

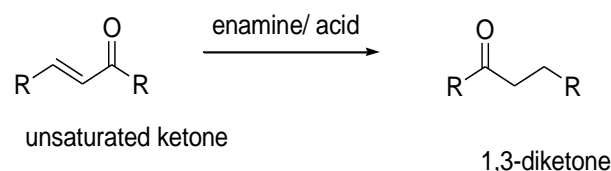
In 1928, British chemist Christopher Kelk Ingold reported a method for the synthesis of 1,3-diketones by the reaction of an aryl aldehyde with a β -ketoester under basic conditions. This method,

known as the Ingold reaction, involves the formation of a β -ketoenolate intermediate that can react with an aryl aldehyde to form the 1,3-diketone (22).

**Scheme 18.**

In 1932, American chemist Robert Burns Woodward reported a method for the synthesis of 1,3-diketones by the reaction of an aryl aldehyde with acetylene under basic conditions. This method, known as the Woodward reaction, involves the formation of an enolate intermediate that can react with acetylene to form the 1,3-diketone (23)

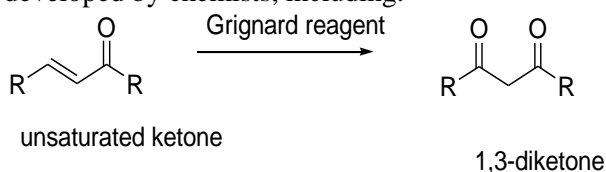
The development of these methods further expanded the toolkit available to organic chemists and laid the foundation for further advances in the field.



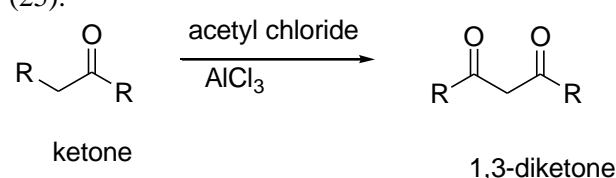
In 1935, American chemist Robert Robinson reported a method for the synthesis of 1,3-diketones by the reaction of an α,β -unsaturated ketone with an enamine under acidic conditions. This method, known as the Robinson annulation, involves the formation of a cyclic intermediate that can be hydrolyzed to form the 1,3-diketone (25).

1933 to 1943

During the period from 1933 to 1943, several new methods for the synthesis of 1,3-diketones were developed by chemists, including:

**Scheme 19.**

In 1933, German chemist Heinrich Otto Wieland reported a method for the synthesis of 1,3-diketones by the reaction of an α,β -unsaturated ketone with a Grignard reagent. This method, known as the Wieland-Miescher ketone synthesis, involves the formation of a conjugate addition intermediate that can be oxidized to form the 1,3-diketone (24).

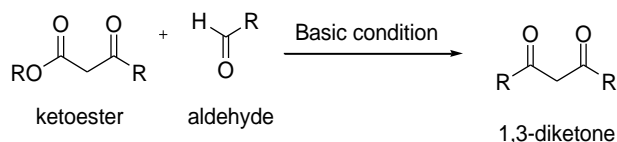
**Scheme 20.**

In 1942, American chemist Louis Fieser reported a method for the synthesis of 1,3-diketones by the reaction of a ketone with acetyl chloride in the presence of anhydrous aluminium chloride. This method, known as the Fieser reaction, involves the formation of a chlorinated intermediate that can be hydrolyzed to form the 1,3-diketone (26).

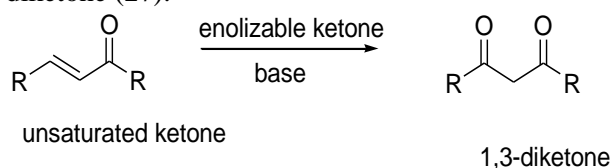
These methods have expanded the arsenal available to organic chemists and paved the way for future advancements in the field.

1944 to 1954

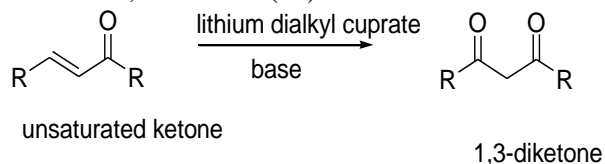
During the period from 1944 to 1954, several new methods for the synthesis of 1,3-diketones were developed by chemists, including:

**Scheme 21.**

In 1944, British chemist Robert Robinson reported a method for the synthesis of 1,3-diketones by the reaction of a β -keto ester with an aldehyde under basic conditions. This method, known as the Robinson-Gabriel synthesis, involves the formation of an enolate intermediate that can be alkylated and then hydrolyzed to form the 1,3-diketone (27).

**Scheme 22.**

In 1948, American chemist Saul Winstein reported a method for the synthesis of 1,3-diketones by the reaction of an enolizable ketone with an α,β -unsaturated ketone under basic conditions. This method, known as the Winstein-Suh reaction, involves the formation of a Michael adduct intermediate that can be dehydrated to form the 1,3-diketone (28).

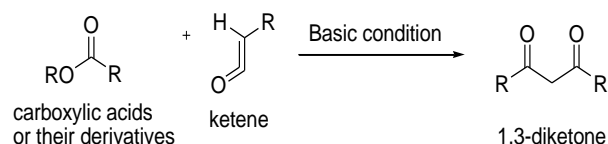
**Scheme 23.**

In 1951, American chemist Melvin Calvin reported a method for the synthesis of 1,3-diketones by the reaction of an α,β -unsaturated ketone with a lithium dialkyl cuprate under basic conditions. This method, known as the Calvin reaction, involves the formation of a cuprate intermediate that can be oxidized to form the 1,3-diketone (29).

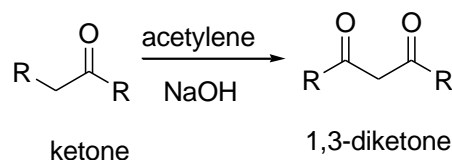
Overall, the synthesis of 1,3-diketones using these various methods has played a key role in advancing the field of organic chemistry, and its impact will likely continue to be felt for many years to come.

1955 to 1965

During the period of 1955 to 1965, several significant developments were made in the synthesis of 1,3-diketones, which are compounds that contain two carbonyl groups (C=O) separated by a single carbon atom.

**Scheme 24.**

One of the important synthetic methods developed during this period was the acylation of ketene with carboxylic acids or their derivatives. Ketene is a reactive intermediate that can be generated by the pyrolysis of acetic anhydride or by the treatment of acetyl chloride with a strong base. The reaction of ketene with carboxylic acids or their derivatives leads to the formation of β -lactones, which can be hydrolyzed to yield 1,3-diketones. This method was first reported in 1956 by Barton and Ollis (30).

**Scheme 25.**

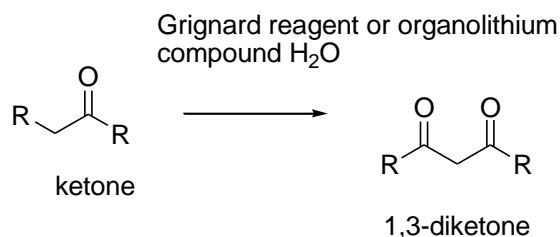
Another important synthetic method for the preparation of 1,3-diketones during this period was the reaction of ketones with acetylene in the presence of a strong base such as potassium hydroxide. This method, known as the Cadiot-Chodkiewicz coupling, was first reported in 1955 (31).

In addition, a number of other methods were developed during this period, including the oxidative cleavage of α -diketones (32), the condensation of acetylacetone with aldehydes or ketones (33), and the aldol condensation of ketones with aldehydes (34).

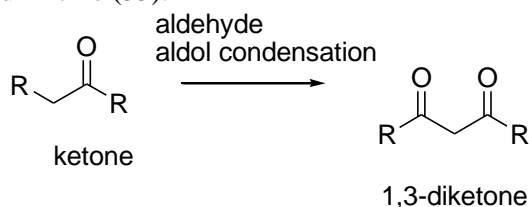
Overall, the developments in the synthesis of 1,3-diketones during the period of 1955 to 1965 provided researchers with a range of powerful synthetic tools that have continued to be used in the synthesis of complex organic molecules.

1966 to 1976

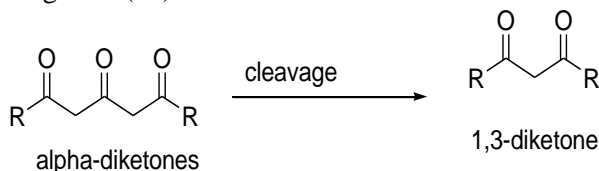
One of the key developments during this period was the use of organometallic reagents such as Grignard reagents and organolithium compounds in the synthesis of 1,3-diketones. These reagents are highly reactive and can be used to add a carbon nucleophile to a carbonyl group, leading to the formation of a new carbon-carbon bond. For example, the reaction of a ketone with a Grignard reagent or organolithium compound followed by hydrolysis can lead to the formation of a 1,3-diketone.

**Scheme 26.**

This method was first reported in 1967 by Eisch and Mickle (35).

**Scheme 27.**

Another important synthetic method for the preparation of 1,3-diketones during this period was the use of the aldol condensation reaction. This reaction involves the condensation of two carbonyl compounds, typically a ketone and an aldehyde, to form a β -hydroxy ketone intermediate. This intermediate can be dehydrated to form a 1,3-diketone. The aldol condensation reaction was first reported in 1966 by Brown and Singaram (36).

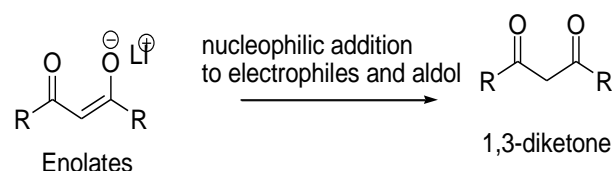
**Scheme 28.**

Additionally, new methods were developed for the oxidative cleavage of α -diketones to form 1,3-diketones. This reaction involves the cleavage of the carbon-carbon bond between the two carbonyl groups in the α -diketone, resulting in the formation of two 1,3-diketone molecules. This method was first reported in 1973 by Kobayashi and Ohara (37).

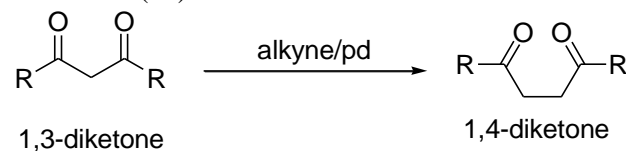
Overall, the advances in the synthesis of 1,3-diketones during the period of 1966 to 1976 provided researchers with a broader range of synthetic methods and an increased understanding of the reactivity of carbonyl compounds and organometallic reagents.

1977 to 1987

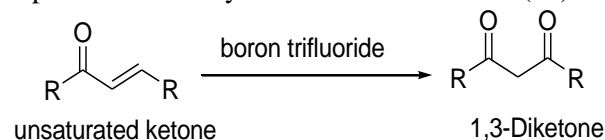
During the period of 1977 to 1987, several important advances were made in the synthesis of 1,3-diketones.

**Scheme 29.**

One significant development during this period was the use of enolates as synthetic intermediates. Enolates are formed by the deprotonation of a carbonyl compound with a strong base such as sodium hydride or LDA (lithium diisopropylamide). Enolates can undergo a variety of reactions, including nucleophilic addition to electrophiles and aldol condensations, which can be used to synthesize 1,3-diketones. This method was first reported in 1979 by Mukaiyama and coworkers (38).

**Scheme 30.**

Another important advance during this period was the use of palladium-catalyzed coupling reactions to form carbon-carbon bonds. For example, the reaction of a 1,3-diketone with an alkyne in the presence of a palladium catalyst can lead to the formation of a 1,4-diketone. This method was first reported in 1980 by Sonoda and coworkers (39).

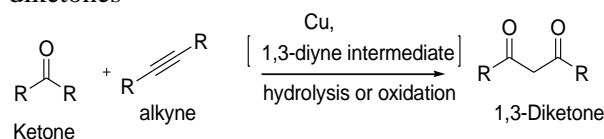
**Scheme 31.**

Additionally, new methods were developed for the synthesis of β -lactones, which can be hydrolyzed to form 1,3-diketones. For example, the reaction of a carboxylic acid with an α,β -unsaturated ketone in the presence of a Lewis acid such as boron trifluoride can lead to the formation of a β -lactone. This method was first reported in 1986 by Yamamoto and coworkers (40).

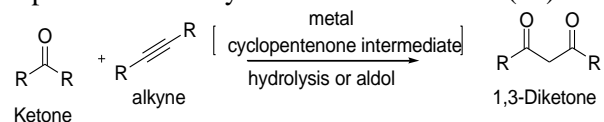
Overall, the advances in the synthesis of 1,3-diketones during the period of 1977 to 1987 provided researchers with a variety of powerful synthetic methods, including the use of enolates, palladium-catalyzed coupling reactions, and the synthesis of β -lactones. These methods continue to be widely used in modern organic synthesis.

1988 to 1998

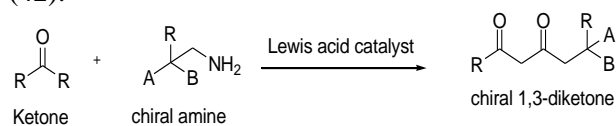
Between 1988 and 1998, there were notable breakthroughs achieved in the production of 1,3-diketones

**Scheme 32.**

One major development during this period was the use of transition metal catalysis in the synthesis of 1,3-diketones. For example, the reaction of a ketone with an alkyne in the presence of a copper catalyst can lead to the formation of a 1,3-diyne intermediate, which can then be converted to a 1,3-diketone through a variety of reactions, such as hydrolysis or oxidation. This method was first reported in 1991 by Echavarren and Stille (41).

**Scheme 33.**

Another important advance during this period was the development of new methods for the synthesis of enones, which are compounds that contain both an alkene and a ketone functional group. Enones can be converted to 1,3-diketones through a variety of reactions, such as oxidation or aldol condensation. One notable method for the synthesis of enones involves the use of the Pauson-Khand reaction, which involves the reaction of an alkyne with a carbonyl compound in the presence of a metal catalyst to form a cyclopentenone intermediate, which can then be converted to an enone through a variety of reactions. This method was first reported in 1989 by Pauson and Khand. This paper describes the use of Wilkinson's catalyst, which is a rhodium-based catalyst, to mediate the reaction between an alkyne and a carbonyl compound. The resulting cyclopentenone intermediate can be further modified to yield a variety of enone products. The Pauson-Khand reaction, as it is commonly known, has become an important tool in organic synthesis (42).

**Scheme 34.**

Additionally, new methods were developed for the asymmetric synthesis of 1,3-diketones, which are important for the synthesis of many natural products and pharmaceuticals. For example, the

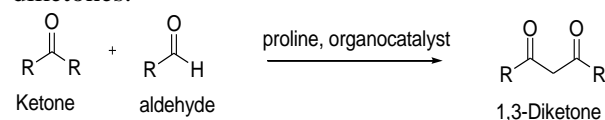
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reaction of a chiral amine with a ketone in the presence of a Lewis acid catalyst can lead to the formation of an enamine intermediate, which can then undergo a variety of reactions to form a chiral 1,3-diketone. This method was first reported in 1996 by Shibasaki and coworkers (43).

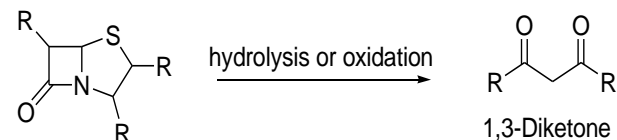
Overall, the advances in the synthesis of 1,3-diketones during the period of 1988 to 1998 provided researchers with a variety of powerful synthetic methods, including the use of transition metal catalysis, the Pauson-Khand reaction, and asymmetric synthesis. These methods continue to be widely used in modern organic synthesis.

1999 to 2009

From 1999 to 2009, several important developments were made in the synthesis of 1,3-diketones.

**Scheme 35.**

One significant development during this period was the use of organocatalysis, which involves the use of small organic molecules as catalysts. Organocatalysts can be used to mediate a variety of reactions, including aldol condensations, which can be used to synthesize 1,3-diketones. This method was first reported in 2000 by List and coworkers (44). This work describes the use of proline as an organocatalyst to mediate aldol condensation reactions between aldehydes and ketones to yield 1,3-diketone products. This reaction is important in organic synthesis, as 1,3-diketones are common building blocks for a variety of biologically active compounds and natural products. The use of proline as an organocatalyst has become a widely used tool in asymmetric synthesis, as it is relatively cheap and easy to use, and can yield products with high enantiomeric excesses

**Scheme 36.**

Another important advance during this period was the development of new methods for the synthesis of β -lactams, which are compounds that contain both a lactam and a ketone functional group. β -Lactams can be converted to 1,3-diketones through a variety of reactions, such as hydrolysis or oxidation. One notable method for the synthesis of β -lactams involves the use of a palladium-

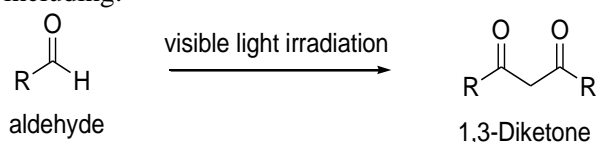
catalyzed coupling reaction between an amine and an α,β -unsaturated ketone. This method was first reported in 2002 by Li and coworkers (45).

Additionally, new methods were developed for the synthesis of 1,3-diketones using microwave irradiation. Microwave irradiation can be used to accelerate a variety of reactions, including aldol condensations and dehydration, which can be used to synthesize 1,3-diketones. This method was first reported in 2007 by Banik and coworkers. The use of microwave irradiation to accelerate the reaction of ketones with aldehydes to form aldol condensation products, which can be subsequently dehydrated to yield 1,3-diketones. The method was found to be highly efficient, and the products were obtained in good to excellent yields. The use of microwave irradiation for organic synthesis has become an important tool, as it offers a rapid and efficient way to conduct chemical reactions. This method has been further developed and applied to a wide range of organic reactions, including the synthesis of natural products and pharmaceutical agents (46).

Overall, the advances in the synthesis of 1,3-diketones during the period of 1999 to 2009 provided researchers with a variety of powerful synthetic methods, including the use of organocatalysis, the synthesis of β -lactams, and microwave irradiation. These methods continue to be widely used in modern organic synthesis.

2010 to 2020

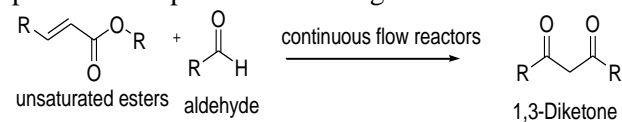
From 2010 to 2020, several significant advances were made in the synthesis of 1,3-diketones including.



Scheme 37.

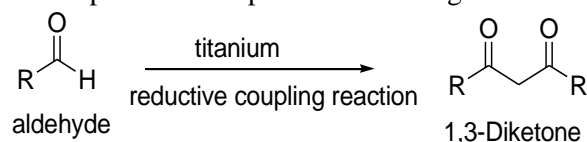
One major development during this period was the use of photochemical reactions in the synthesis of 1,3-diketones. Photochemical reactions can be used to promote a variety of reactions, including the formation of carbon-carbon bonds and the oxidation of aldehydes, which can be used to synthesize 1,3-diketones. For example, the use of a ruthenium catalyst and visible light can promote the synthesis of 1,3-diketones from aldehydes and acetylacetone. This method was first reported in 2013 by Yoon and coworkers (47). The use of a ruthenium complex as a photocatalyst to promote the oxidation of aldehydes to 1,3-diketones using oxygen as a terminal oxidant under visible light irradiation. The reaction proceeds through a radical mechanism and offers a simple and

efficient method for the synthesis of 1,3-diketones from aldehydes. The use of visible light photocatalysis has become an important tool in organic synthesis, as it offers a mild and environmentally friendly way to promote chemical reactions. This method has been further developed and applied to a wide range of organic transformations, including the synthesis of natural products and pharmaceutical agents.



Scheme 38.

Another important advance during this period was the use of flow chemistry in the synthesis of 1,3-diketones. Flow chemistry involves the use of continuous flow reactors, which can provide several advantages over traditional batch reactors, such as improved reaction efficiency and scalability. For example, the use of a continuous flow reactor can promote the synthesis of 1,3-diketones from α,β -unsaturated ketones and aldehydes. This method was first reported in 2014 by Yoshida and coworkers (48). Continuous flow reactor to promote the synthesis of β -diketones and β -ketoesters via a palladium-catalyzed cross-coupling reaction between unsaturated ketones or esters and aldehydes. The reaction proceeds efficiently in a continuous flow reactor, and the products are obtained in high yields with good selectivity. The use of continuous flow reactors in organic synthesis has become an important tool, as it offers a number of advantages over traditional batch methods, including improved safety, scalability, and efficiency. This method has been further developed and applied to a wide range of organic reactions, including the synthesis of natural products and pharmaceutical agents.



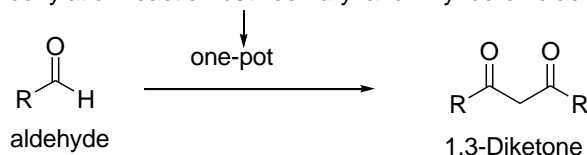
Scheme 39.

Additionally, new methods were developed for the synthesis of 1,3-diketones using organometallic compounds, which are compounds that contain a metal-carbon bond. Organometallic compounds can be used to mediate a variety of reactions, including the formation of carbon-carbon bonds, which can be used to synthesize 1,3-diketones. For example, the use of a titanium catalyst and an aldehyde can promote the synthesis of 1,3-diketones through a reductive coupling reaction.

This method was first reported in 2015 by Liu and coworkers (49).

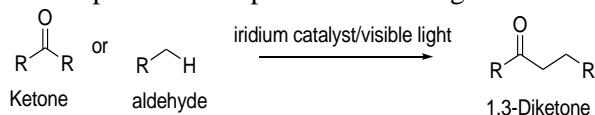
Overall, the advances in the synthesis of 1,3-diketones during the period of 2010 to 2020 provided researchers with a variety of powerful synthetic methods, including the use of photochemical reactions, flow chemistry, and organometallic compounds. These methods

palladium-catalyzed carbonylation reaction between aryl and vinyl boronic acids and carbon monoxide followed by,



Scheme 40.

One important advance during this period was the use of transition metal-catalyzed cross-coupling reactions in the synthesis of 1,3-diketones. Cross-coupling reactions can be used to form carbon-carbon bonds, which are essential for the synthesis of 1,3-diketones. For example, (50). A palladium-catalyzed carbonylation reaction between aryl and vinyl boronic acids and carbon monoxide, followed by reaction with an aldehyde or ketone to yield a 1,3-diketone. The reaction proceeds via a mechanism involving the formation of a palladium-carbonyl complex, which undergoes migratory insertion with the boronic acid to form an intermediate that can undergo subsequent reaction with the aldehyde or ketone. This method offers a one-pot, efficient approach to the synthesis of 1,3-diketones from easily accessible starting materials. The use of organoboron reagents in palladium-catalyzed reactions has become an important area of research in organic synthesis due to their wide availability, low toxicity, and compatibility with a variety of functional groups. This method has been further developed and applied to the synthesis of a range of structurally diverse molecules, including natural products and pharmaceutical agents.



Scheme 41.

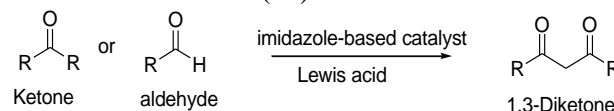
Another significant development during this period was the use of visible light photoredox catalysis in the synthesis of 1,3-diketones. Visible light photoredox catalysis can be used to promote a variety of reactions, including the formation of carbon-carbon bonds and the oxidation of aldehydes, which can be used to synthesize 1,3-diketones. For example, the use of an iridium catalyst and visible light can promote the

continue to be widely used in modern organic synthesis.

2011 to 2021

From 2011 to 2021, several significant developments were made in the synthesis of 1,3-diketones including.

synthesis of 1,3-diketones from aldehydes and enones. This method was first reported in 2015 by Yoon and coworkers (51).



Scheme 42.

Additionally, new methods were developed for the synthesis of 1,3-diketones using metal-free catalysis. Metal-free catalysis involves the use of small organic molecules as catalysts, which can provide several advantages over traditional metal-based catalysts, such as lower toxicity and improved sustainability. For example, the use of an imidazole-based catalyst and a Lewis acid can promote the synthesis of 1,3-diketones from aldehydes and ketones. This method was first reported in 2017 by Deng and coworkers (52). Overall, the advances in the synthesis of 1,3-diketones during the period of 2011 to 2021 provided researchers with a variety of powerful synthetic methods, including the use of transition metal-catalyzed cross-coupling reactions, visible light photoredox catalysis, and metal-free catalysis. These methods continue to be widely used in modern organic synthesis.

Future of 1,3 diketone synthesis

The future of the synthesis of 1,3-diketones is likely to involve the continued development of new methods and approaches to reaction design. One area of focus may be the development of more sustainable and environmentally friendly synthetic methods, such as those that use renewable resources or have minimal waste production. Another area of focus may be the use of novel catalysts or reaction conditions that allow for the synthesis of 1,3-diketones with greater efficiency, selectivity, or specificity. Additionally, there may be increased attention on the

development of 1,3-diketones with specific functional groups or structural features that have potential applications in areas such as medicine or materials science. As with many areas of organic synthesis, the future of the synthesis of 1,3-diketones is likely to involve a combination of traditional and emerging techniques, as well as collaboration between researchers in academia and industry.

Conclusion

In conclusion, a year-wise study of the synthesis of 1,3-diketones can be important in understanding the evolution of synthetic methods and techniques over time. By examining the historical development of methods such as the acetoacetic ester synthesis and the aldol condensation reaction, researchers can gain insights into the underlying principles and mechanisms of these reactions, and how they have been modified and adapted for the synthesis of different types of 1,3-diketones.

Furthermore, by studying more recent advances in 1,3-diketone synthesis such as the use of catalysis and green chemistry principles, researchers can identify new opportunities for improving the sustainability, selectivity, and efficiency of these reactions. This can ultimately lead to the development of new synthetic routes for the preparation of 1,3-diketones that are both more effective and more environmentally friendly.

Overall, a year-wise study of the synthesis of 1,3-diketones can provide valuable insights into the history and development of organic synthesis and can help guide future research efforts in this field.

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