

Development of Newer Tetrahydroquinolines

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ABSTRACT

Different quinoline derivatives have attracted the interest of researchers due to their immensely attractive medicinal activity profile. Among quinolines derivatives, tetrahydroquinolines are an important scaffold widely present in various natural products and many synthetic tetrahydroquinoline derivatives have displayed promising wide spectrum biological activity as well.

The present paper covers a brief report of newer tetrahydroquinoline derivatives.

Keywords: Quinolines, Tetrahydroquinolines.

I. INTRODUCTION

Quinoline is a heterocyclic scaffold of tremendous medicinal importance. Number of natural or synthetic quinoline derivatives have displayed remarkable biological activity profile and many quinoline derivatives are clinically prescribed as effective medicines for many diseases.

In view of this, researchers have always been attracted towards development of new quinoline derivatives in order to explore their bioactivity profile. Tetrahydroquinoline derivatives have drawn attention due to their attractive bioactivity profile since decades. Number of researchers have explored the preparation and biological evaluation of various functionalized tetrahydroquinoline derivatives [1, 2].

The present paper reports brief overview of development of newer tetrahydroquinolines.

II. ADVANCES IN DEVELOPMENT OF TETRAHYDROQUINOLINES

Khan et al. have studied one protocol to prepare the derivatives of tetrahydroquinolines by utilising Pavarov reaction [3].

For the preparation of fused pyrano- and furano-fused tetrahydroquinolines, ferrous sulphate was found to be acting as efficient catalyst in one pot multiple component method.

This reaction involved three component reaction of aryl amines, aldehydes and enoethers. This study has claimed to be appropriate in terms of green chemistry, as this protocol was characterized with lower cost and less hazardous chemicals.

Katayama, S. et al. have developed a new resolution process using enzymes for obtaining highly pure optically active tetrahydroquinoline derivatives [4].

The tetrahydroquinolines thus obtained are useful in preparation of novel quinoxaline derivatives.

Enantiopure carboxylate containing tetrahydroquinoline derivatives were obtained by resolution in almost more than 95% ee.

Resolution of fluorinated tetrahydroquinolines was studied in detail by Bálint, J. et al. [5]. Tartaric acid was used as agent for resolution. The investigation on kinetics and effect of solvent was carried out.

An investigation was done by research group for preparation of novel tetrahydroquinolines starting from optically active aziridines [6].

The preparation was achieved with high amount of optical purity using palladium catalyzed reaction. The process has a good prospect for enhancing the enantiomeric purity of tetrahydroquinolines.

Chabert, J. et al. have submitted a new protocol initiating from substituted benzo[b]thiophene used for the preparation of not so common type of heterocycles including tetrahydroquinolines [7]. The preparation involved reduction followed by desulfurization to give diversely substituted tetrahydroquinolines.

Mellor J. et al. have reported one study for the multicomponent preparation to give tetrahydroquinolines [8].

The preparation involved reaction of arylamines, alkenes and methanal. The separation of byproducts such as alcohols was carried out and the mechanism was proved to be nonconcerted one.

By using Thrope Ingold effect, preparation of tetrahydroquinolines have been carried out by Taylor, E. et al. [9].

The preparation involved intramolecular inverse reactions of the starting triazines which were then assisted by Diels-Alder type reaction. The reaction was first time reported for the preparation of 5,6,7,8-tetrahydroquinolines.

L. vivier et al. have submitted one report the comparable study was being done with respect to aluminate type of catalyst in a flow microreactor with certain type of reaction conditions to prepare the

derivatives of isoquinoline and tetrahydroquinoline [10].

Reed, J. N et al. have reported one study over the importance of lithiation reaction to prepare the novel tetrahydroquinoline scaffolds [11]. During the study the preparation was being done by taking approach of one pot multiple component method.

In this approach, N-Boc protected anilines were transformed into their corresponding tetrahydroquinolines based derivatives.

This preparation involved lithiation followed by reaction with 1,3-dihalopropane. Thus a novel method to furnish quinolines moieties was reported .

Robl, J. A. et al. have submitted one study in which the preparation of fused azepino- heterocycles can be performed by utilisation of tetrahydroquinolines [12].

A report submitted by research group has explored tertiary-amino effect in the preparation of spiro-tetrahydroquinolines Tverdokhlebov et al. [13]. One type of interaction was found to be reaction of cyclohexyl-substituted arylaldehydes and acetonitriles having various types of substitution.

This interaction leads to the formation of alkylated tetrahydroquinone-spiro derivatives having carbonitrile substitution at third place. The mechanism involved Knoevenagel reaction later followed the tertiary amino pathway for the cyclization.

Ghashghaei, O. et al. have reviewed applications of multi-component Povarov reaction in the development of different biologically active tetrahydroquinolines [14].

The multiple component method involves reaction of arylamines, activated alkenes and substituted-aldehydes to form diversely substituted tetrahydroquinoline derivatives.

The review includes reports which used Povarov method for the formation of tetrahydroquinolines and the bioactivity screening of the resulting tetrahydroquinolines.

It was concluded that Povarov method has been successful in generating diversely substituted tetrahydroquinolines which have been screened for broad spectrum of biological activities.

Ma, X. et al. have reported preparation of tetrahydroquinoline derivatives which involves formation of new carbon-carbon bonds and cyclization by the reaction between the glycein esters and enols catalysed by Tris(4-bromophenyl)ammoniumyl hexachloroantimonate [15]. The developed approach has given rise to novel one pot multiple component approach to generate novel tetrahydroquinolines.

Jin, G. et al. have carried reported the preparation of fluoro-substituted tetrahydroquinolines in the presence of iodine [16].

The study involved the assessment of catalytic impact of iodine for the two preparation routes for fluoro-substituted tetrahydroquinolines.

One route involved the reaction between fluoro-substituted arylimines with enolethers. The other route yielded the same fluoro-substituted tetrahydroquinolines using one pot multicomponent reaction of fluoro-substituted arylaldehydes, arylamines and enolethers.

Both the protocols offered mixture of geometrical isomers in good yields. Iodine was found to be beneficial as catalyst because it was economic and required mild conditions.

Moss, T. A. et al. have carried out research on ring closing approach [17]. The study reported preparation of quinolino-fused azepines.

The preparation was achieved by the reaction involving ring closing approach by metathesis protocol. The reaction was catalyzed by ruthenium based catalyst to give diversely substituted tetrahydroquinolines.

Kamal, A. et al. have carried out one study to explore the easy approach for preparation of pyrano-fused tetrahydroquinoline type of scaffolds [18].

So with the aim to investigate an easy protocol to form fused tetrahydroquinolines, the reaction between aromatic azides and dihydro-pyran in the presence of catalytic amount of sodium iodide and ferric chloride was performed. Moreover this type of reaction offered the regio-selectivity, as most of the time ring-closure resulted into cis form.

Sakai, N. et al. have submitted a report for novel process of preparation of tetrahydroquinolines [19].

The novel protocol involved the reaction of tertiary arylamines with unsaturated compounds like olefins or cyclic imides. The reaction involving cyclic imides gave fused tetrahydroquinolines.

The cyclization involved cobalt as a catalyst and the reaction protocol could be applied to electron-poor as well as electron-rich olefins and generated diversely substituted as well as fused tetrahydro- and polyhydro-quinolines in good yield.

Qin, L. et al. have carried out one study regarding resolution of tetrahydroquinolines [20].

The application of bacterial strain *P. monteilii* was studied. The researched bacterial strain found to be performing the conversion upto fifty percent to give the optically active tetrahydroquinoline derivatives in good ee% of more than 98%. The bacteria-mediated resolution was found to be an attractive protocol for future investigations.

Yadav, A. et al. have done study on the Carbon – Hydrogen activation. In that study they have prepared derivatives of tetrahydroquinolines [21]. A new approach which is free from the use of metal have been applied by the team for the synthesis.

The synthesis involves cyclization reaction of N-methylarylamines with electron deficient cyclic imides. The approach is a lower cost protocol, handling potassium persulphate is easy and the activation of carbon – hydrogen bond can be done easily at the normal reaction conditions.

The protocol can offer various diversely substituted tetrahydroquinoline and good quantity of products.

Hao, Y. et al. have prepared a novel sequence of tetrahydroquinoline derivatives [22].

They have investigated their application as dye-sensitizers. In the prepared tetrahydroquinolines, the tetrahydroquinoline nucleus and nitrile-carboxylic acid fragments were linked using thiophenyl linker group.

The prepared scaffolds showed high sensitizing abilities compared to previously reported sensitizers of the same class of compounds. The sensitizing abilities were remarkable when evaluated with reference to sensitized solar cells.

With the aim to develop the reusable catalyst for preparation of 4-anilino substituted tetrahydroquinolines, research group have reported one study [23]. In this report, they have tried to explore preparation and application of halide salt of halogenated-aniline based polymer as the catalyst.

It was concluded that the newly developed catalyst can efficiently catalyze the preparation of diversely substituted tetrahydroquinolines in such a way that the use of catalyst can be minimized. This catalyst is economic, less toxic, easily handled during the preparation.

The preparation can be achieved in good yields using the catalyst by the reaction between arylamines and lactams bearing vinylic substitution. Moreover, the preparation was found to be regioselective, as the resulting tetrahydroquinolines were of the trans-type.

Babu, T. H. et al. have reported a novel catalyst-free method for the preparation of tetrahydroquinolines [24].

They have developed the protocol in which, without the use of catalyst, tetrahydroquinolines can be prepared in outstanding yield by one pot multiple component reaction between quinolines, different halides and Hantzsch DHP esters. The report claimed to furnish tetrahydroquinolines with N-substitution using very mild reaction conditions without the use of catalyst.

Chen, W. et al. have reported preparation of tetrahydroquinolines bearing substituted phenyl fragment at the three position [25]. The preparation involved cyclization of 2-nitrophenylacetonitrile derivatives to furnish the desired tetrahydroquinolines.

The cyclization involved the reductive closure in presence of Palladium which furnished the tetrahydroquinolines in high yield and the approach could be extended to diverse acetonitriles hence showing the versatility and ease of approach.

Wilson, J. et al. have reported an approach to diastereoselectively prepare the tetrahydroquinolines [26]. The preparation involved palladium catalyzed reaction of boronic acid and ortho-halophenyl olefins. The reaction offered products with 40 and 30 types of stereocenters. The possible mechanism pathways and the impacts of ligands on the preparation were discussed thoroughly.

Kim, S. et al. have reported novel preparation of diversely substituted optically active tetrahydroquinolines [27].

The preparation involved aza Michael reaction and furnished the products with good stereoselectivity. The compounds were furnished by the reaction of nitroolefins and aminophenyl bearing carbonyls.

The protocol gives an easy access to optically active and highly functionalized tetrahydroquinolines which cannot be synthesized by existing traditional methodologies.

Filatova, E. V. et al. have tried to explore the same protocol involving reaction of nitroolefins and aminophenyl bearing carbonyls in presence of *sc*-CO₂ [28]. The reaction was conducted using a tertamine based catalyst.

It was concluded that the use of *sc*-CO₂ and tertamine catalyst was proved to be an efficient protocol in furnishing optically active tetrahydroquinolines in good yield and high stereoselectivity.

Jia, X. D. et al. have done investigation on one-pot preparation of tetrahydroquinolines [29].

The disubstituted derivatives were prepared by performing domino reaction starting from enols in the presence of Tris(4-bromophenyl)ammoniumyl hexachloroantimonate as a catalyst.

The enols used were mainly acyclic and served as the substitute of methanal in the reaction. The protocol successfully furnished 2-alkyl- tetrahydroquinolines having anilino-substitution at the fourth position.

Rong, Z. et al. have carried out one interesting research for the preparation of trisubstituted tetrahydroquinolines [30].

They have developed a protocol in such a manner that the preparation can be performed in reagent and catalyst free condition by simply heating in appropriate solvent.

This protocol involves the reaction between arylaldehydes and arylamines. The protocol is an easy one pot method which can be extended for the formal synthesis of few natural alkaloids as well.

Han, W. Y. et al. have reported preparation of amine containing tetrahydroquinoline derivatives using scandium triflate as the catalyst [31].

The preparation method can be useful for preparing the wide range of tetrahydroquinolines with ease which cannot be achieved by traditional reported methods.

The preparation method was useful for the synthesis of polycyclic, spiro- as well as optically active tetrahydroquinolines. The mechanism involved the transfer of Hydride and the annulation steps. The mechanism was also proved by derivatization studies.

Jiang, F. et al. have reported the preparation of haloalkyl-substituted tetrahydroquinolines using the palladium catalyst [32].

The cyclization was oxidative type from the starting ortho-amido alkenes. The process gave the fine amount of yield and had the ease of approach to get the tetrahydroquinolines with the haloalkyl substituents.

Kouznetsov, V. et al. have given new approach for the preparation of the novel alkyl- and dialkyl-substituted derivatives of tetrahydroquinolines [33].

One pot preparation was achieved by using multicomponent approach using bismuth chloride as a catalyst. So the alkylated quinolines and tetrahydroquinolines could be generated with ease.

It was demonstrated that both quinolines and hydrogenated quinolines could be prepared by using the reaction of non-aromatic aldehydes, arylamines and olefinic amides.

Kamble, V. T. et al. have submitted one report describing the preparation of tetrahydroquinoline derivatives using perchloric acid as a catalyst [34].

In this protocol catalyst adsorbed on silica support was applied for the successful execution of the reaction. The one pot multicomponent approach was a mild protocol and did not require special reaction conditions.

The catalyst was successful in enhancing the rate of reaction between arylaldehydes, arylamines and different types of activated dienophiles.

The studies on the preparation of fused tetrahydroquinolines derivatives have been carried out [35]. Novel furano-fused tetrahydroquinolines were prepared using the Sm(NO₃)₃ catalyst.

The preparation was carried out using one-pot multicomponent approach involving the reaction between anilines and dihydrofurans. This protocol yielded mixture of geometrical isomers-cis and trans. The product amount as outcome was found to be moderate level.

The activity of the liquidified catalyst was found to be unaltered during the reaction, furthermore, it can be recycled from the mixture as well. The different geometrical forms of these scaffolds were found to be good agents for DNA photolytic cleavage.

New tetrahydroquinolines based dyes have been reported [36].

The aryl-substituted tetrahydroquinoline dyes were synthesized using very simple condition without the requirement of environment free of oxygen.

Different properties were found to be based on different structural features. Also, the prepared tetrahydroquinoline based dyes were used in preparation of sensitized solar cells.

Ramesh, E. et al. have reported one study for the preparation of polycyclic fused tetrahydroquinoline derivatives [37].

The preparation involved the aza diels alder approach. Cyclizations of imines derived from pyrrolopyrimidines and arylamines gave the desired annulated tetrahydroquinoline derivatives.

Different catalysts were studied to carry out the cyclization but Indium chloride was found to be the most effective for the cyclization. Good yields of the annulated tetrahydroquinolines were obtained using the protocol. The protocol can be extended for desining other diverse heterocycle annulated tetrahydroquinolines.

Kumar, A. et al. have reported preparation of optically active tetrahydroquinolne derivatives [38].

In this investigation, novel supramolcular carbohydrates were used as the catalyst.

Different polysaccharides were converted in their sulphonic acid derivatives and used as the supramolecular catalysts.

The protocol involved the reaction between enolethers and arylamines. The products were obtained in good purity with excellent ee%.

The supramolecular catalysts were found to be having superior catalytic properties for the stereoselective conversions.

III. CONCLUSION

Owing to greatly diverse and promising bioactivity profile of tetrahydroquinolines, newer facile and effective protocols have been developed to synthesize diversely functionalized tetrahydroquinolines. Also,

newly developed tetrahydroquinolines have shown promising potential with their wide spectrum of biological activities.

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