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Synthesis of 1,5- Benzodiazepines: A Review

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ABSTRACT
Benzodiazepines are bicyclic heterocycles having medicinal importance. As a result several greener procedures have been developed using mild conditions and recyclable catalysts, easy work up good yields, multi component reactions less wastage and solvent less synthesis.

KEYWORDS: *1,5- benzodiazepines. o-phenylenediamine, ketones*

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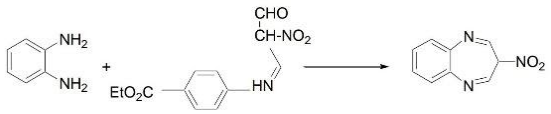
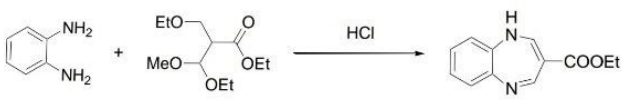
INTRODUCTION
The benzodiazepines[1] are bicyclic heterocycles; benzene nucleus being fused to a seven membered hetero ring having two nitrogen atoms. The benzodiazepines are a class of drugs with hypnotic, anxiolytic, anticonvulsant, amnestic and muscle relaxant properties. They serve as cholecystokinin A and B antagonists, opioid receptor ligands, platelet-activating factor antagonists, HIV inhibitors, farnesyltransferase inhibitors and as somatoform disorder.

Synthesis of 1,5- benzodiazepines:

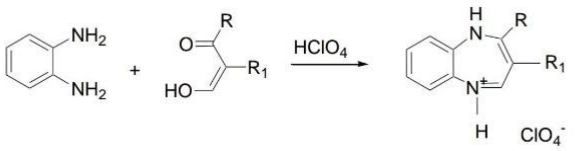
Thiele and Stemming **in [1907]** [2] The first synthesis of 1,5-benzodiazepines 2,4-dimethyl derivatives was reported in 1907 by Thiele and Stemming by the condensation of *o*-phenylenediamine with acetyl acetone in ethanol and acetic acid. Addition of perchloric acid precipitated the purple hydrochloride.3-Nitrobenzodiazepine can also be prepared by the reaction of schiff's base from ethyl-*p*-aminobenzoate and nitromaloandialdehyde with *o*-phenylenediamine.



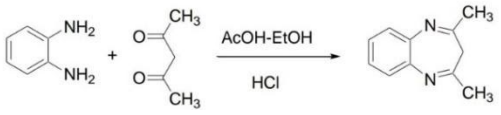
Takamizawa et.al **in [1967]**[3] They patented 3-ethoxycarbonylbenzodiazepine obtained by the condensation of *o*-phenylenediamine with ethyl 2-ethoxymethoxymethyl-3-ethoxypropronate.



M. Weissenfels et.al **in [1965]**[4] 1,5-Benzodiazepines can be synthesized by reacting *o*-phenylenediamine with hydroxymethylene ketone in alcoholic perchloric acid.

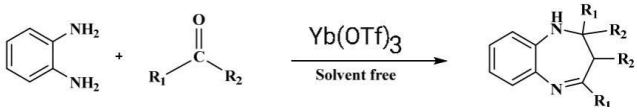


D.Lloyd et.al in **[1965]**[5] reported *pH* dependence synthesis of benzodiazepines; *pH* being 4-6.

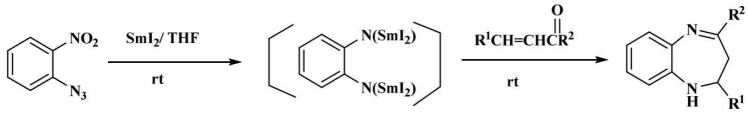


Baakrishna and Kaboudin in **[2001]** [6] introduced the solvent free method for the synthesis of Benzodiazepines that had an operationally simple procedure. A mixture of o-phenylenediamine, magnesia/phosphorus oxychloride and ketone were reacted under solvent-free conditions was capable of producing high yields of 2,3-dihydro-2,2,*4-trimethyl-1H*-1,5-benzodiazepines by condensation of *o*-phenylenediamine with acetone under mild reaction conditions with 90% yield.

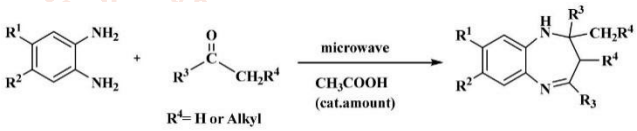
Curini et.al **in [2001]** [7]**,** synthesized 2, 3-Dihydro-1*H*-1, 5 benzodiazepines in very good yield in solvent-free conditions from *o*-phenylendiamine and ketones in the presence of Ytterbium (III) trifluoromethanesulfonate as catalyst. The method is applicable to both cyclic and acyclic ketones.



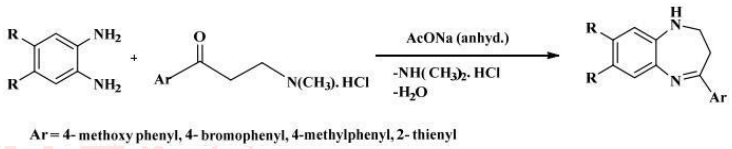
Chen et.al **in [2001]** [8] introduced applications of samarium diiodide (SmI_2) as a mild, neutral, selective and versatile single-electron transfer reducing and coupling reagent in organic synthesis which has grown significantly in the last decade. When *o*-nitrophenylazide was treated with SmI_2 at room temperature, the simultaneous reduction of nitro group and azide group resulted in the formation of trivalent samarium species.



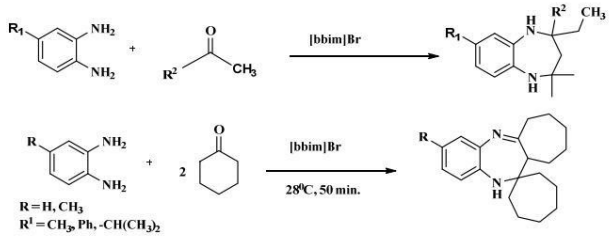
Pozarentzi et.al **in [2002]**[9]**,** reported a simple reaction for the synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepines by condensation of ketones with *o*-phenylenediamines by application of microwave irradiation without using solvent.



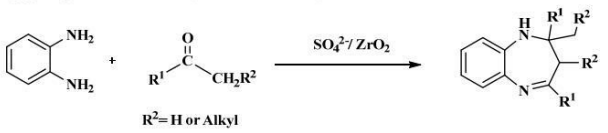
Roman et.al **in [2002]**[10]**,** synthesized 4-aryl-2,3-dihydro-1*H*-1,5-benzodiazepines by cyclocondensation of ketonic Mannich bases hydrochlorides with o-arylenediamines and reactions proceeded smoothly in ethanol in the presence of anhydrous sodium acetate which led to fused diazepines.



Jarikote et.al **in [2003]**[11], introduced the reaction of *o*-phenylenediamines with both acyclic and cyclic Ketones in 1,3-di-n-butylimidazolium bromide as anionic liquid to afford 1,5-benzodiazepines in excellent isolated yields in the absence of a catalyst at ambient temperature.



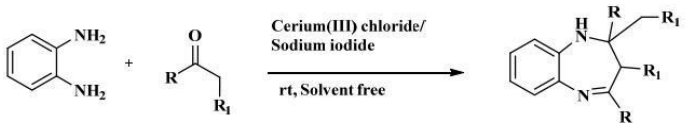
Reddy et.al **in [2003]**[12] synthesized 2, 3-dihydro-*1H*-1,5-benzodiazepines by taking a 1:2.5 mole ratio mixture of *o*-phenylenediamine and the ketone along with a catalytic amount of sulfated zirconia in a round bottom flask and stirred it at the ambient temperature for appropriate time.



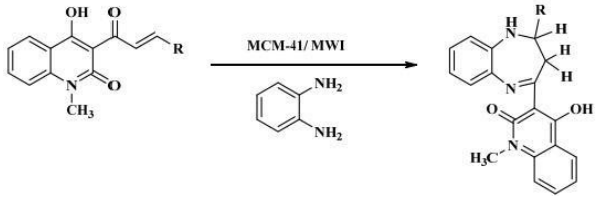
Yadav et.al **in [2004]**[13], introduced a new approach for the synthesis of benzodiazepines in which treatment of *o*-phenylenediamine with ketone in the presence of 10 mol% indium (III) bromide as Lewis acid for 1.5 h afforded 2, 3-dihydro-2,2,4-trimethyl-1*H*-1,5-benzo [b] [1,4]-diazepine in 95% yield. This method was effective for preparation of benzodiazepines from electron deficient *o*-phenylenediamines. The reactions proceeded well at room temperature under solvent free conditions but $InBr_3$ was found to be superior in terms of conversion and reaction rates.

***Sivamurugan et.al* in [2004]**[14], carried out the synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepines by mixing *o*-phenylenediamine with ketones in the presence of a catalytic amount of $[Proline]_2Zn$

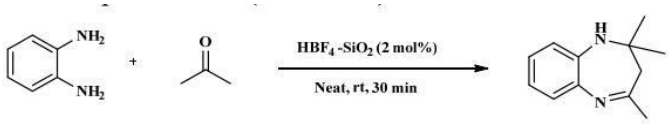
***Gowravaram et.al* in [2004]**[15], introduced a novel and green approach for the synthesis of 2, 3-dihydro-1*H*-1,5-benzodiazepines from *o*-phenylenediamines and ketones using Cerium (III) chloride/ Sodium iodide under mild and heterogeneous conditions.



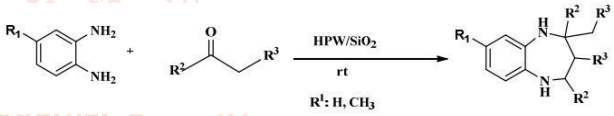
***Sucheta and Rao* in [2005]**[16], described an effective and operationally simple method for the synthesis of 1,5-benzodiazepine compounds under microwave irradiation versus conventional thermal cyclisation for comparative purposes. The procedure consists of reacting an intimately ground equimolar proportion of *o*-phenylenediamine and α, β-unsaturated enones with silica gel in the presence of catalytic amount of mesoporous zeolite MCM-41 with 90-98% yield.



***Bandgar et.al* in [2006]**[17], introduced the reaction which was very slow and low yielding in the absence of catalyst. In the presence of silica as a catalyst yields were poor at 25°C. After doing the optimization of the quantity of the catalyst at room temperature under solvent free conditions and it was observed that the use of just 2 mol% of HBF_4-SiO_2 was sufficient to give the desired products in excellent yields.

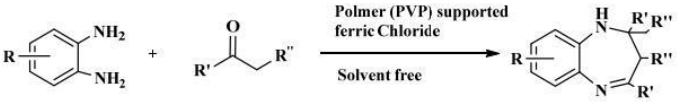


***Alibeck et.al* in [2006]**[18] introduced the application of silica supported 12-tungstophosphoric acid (HPW/SiO_2) as solid acid catalyst for the synthesis of 1,5-benzodiazepines by reaction of *o*-phenylenediamines with ketones.



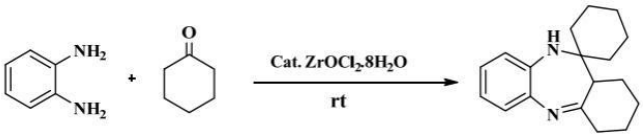
***De and Gibbs* in [2005]**[19] introduced the reaction which were carried out in neat at room temperature for 3 h by taking a 1:2.2 mol ratio mixture of *o*-phenylenediamine and the ketone in the presence of 5mol% Scandium (III) triflate Sc $OTf)_3$ to give the desired products in excellent yield.

***Chari and Syamsundar* in [2005]**[20] introduced a new procedure in which polymer (PVP) supported ferric chloride catalyzed efficiently the condensation of *o*-phenylenediamines with ketones under solvent free conditions to afford the corresponding 1,5-benzodiazepine derivatives in high yields. The reaction proceeded efficiently under ambient conditions giving excellent yields (85–96%)

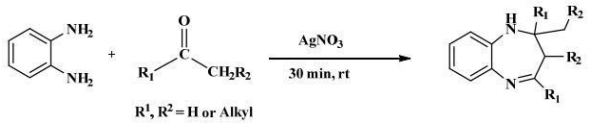


***Tajbakhsh et.al* in [2006]**[21] They reported organic synthesis using solid acid heterogeneous catalyzes as a synthetic route for synthesis of 2,2,4-trimethyl-2,3-dihydro-1,5-benzodiazepine from acetone and *o*-phenylenediamine (4:1) in acetonitrile or dichloromethane using Zeolite as a catalyst.

***Nagawade and Shinde*in [2006]**[22] *o*-phenylenediamines undergo rapid condensation with ketones having hydrogens at the α-position in the presence of 10 mol% zirconyl (IV) chloride under extremely mild reaction conditions to afford the corresponding 1,5-benzodiazepines in excellent yields with high selectivity. This method works well for both electron-rich as well as electron-deficient *o*-phenylenediamines. Zirconyl (IV) chloride is moisture stable, readily available and inexpensive oxy salt of zirconium and versatile lewis acid catalyst.

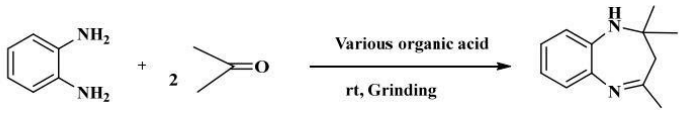


***Chandra et.al* in [2006]**[23] introduced the reactions which were carried out by treating a 1: 2.5 molar ratio mixture of *o*-phenylenediamine and the ketone with a catalytic amount of silver nitrate.



***Wu* in [2006]**[24] introduced Ytterbium trichloride catalyzed condensation of *o*-phenylenediamines and cyclic and acyclic ketones under solvent-free conditions afforded 1,5-benzodiazepine derivatives in excellent yields.

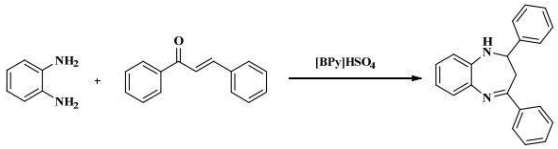
***Thakuria et.al* in [2006]**[25] introduced one pot method for the synthesis of a 2, 3-dihydro-1,5-benzodiazepines by the condensation of acetone with *o*-phenylenediamine using an organic acid as the catalyst under solvent-free conditions at room temperature using 1,3,5-benzene-tri-carboxylic acid (Trimesic acid) as catalyst.



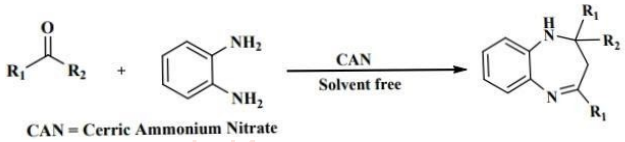
***Pasha and Jayashankara* in [2006]**[26] reported synthesis of 2,3-dihydro-1H-1,5-benzodiazepines by the condensation of *o*-phenylenediamine with cyclic/ acyclic ketones in the presence of *p*-toluenesulfonic acid (*p*-TSA) as catalyst at 80-85°C temperature.

***Kuo et.al* in [2006]**[27] introduced the reaction which was performed by reacting *o*-phenylenediamine and acetone in the presence of 2 mol% NBS as a catalyst without any solvent at room temperature. Under these conditions, 1,5-benzodiazepine was obtained.

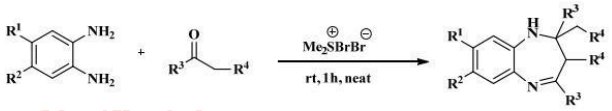
***Yuying et.al* in [2006]**[28] introduced a novel and simple ionic liquid methodology for the synthesis of 1,5-benzodiazepines. 1-Butylpyridinium hydrogen sulphate ([BPy]HSO4), an acidic room-temperature ionic liquid, as a novel and efficient catalyst, was synthesized and used in the preparation of a series of 1,5-benzodiazepine derivatives by the reaction of *o*-phenylenediamine with chalcones under mild conditions.



***Varala et.al* in [2006]**[29] introduced ceric ammonium nitrate (CAN) as an efficient reagent for the preparation of 1,5-benzodiazepine derivatives of a wide range of substituted *o*-phenylenediamines and electronically divergent ketones in moderate to excellent isolated yields (60-98%) under mild conditions using methanol as solvent at ambient temperature.

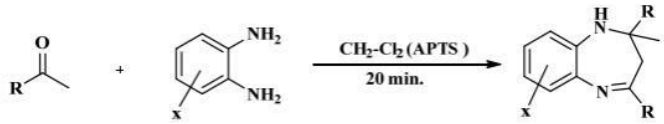


***Das et.al* in [2006]**[30] reported an efficient solvent-free synthesis of 1,5-benzodiazepines by condensation of *o*-phenylenediamines with ketones in the presence of catalytic amount of bromodimethyl sulfonium bromide.

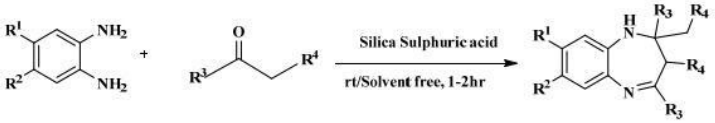


***Heravi et.al* in [2006]**[31] synthesized 2, 3-dihydro-1*H*-1,5-benzodiazepines by condensation of *o*-phenylendiamine and various ketones in the presence of ferric per chlorate ($Fe(ClO_4)_3$) under solvent free conditions.

***Guzen et.al* in [2006]**[32] reported a new method for the synthesis of 1,5-benzodiazepines which were synthesized by a reaction of *o*-phenylenediamines with a diketone or ketone series by ultrasound irradiation in presence of APTS. The condensation occurred in a mild condition with good to excellent yields.



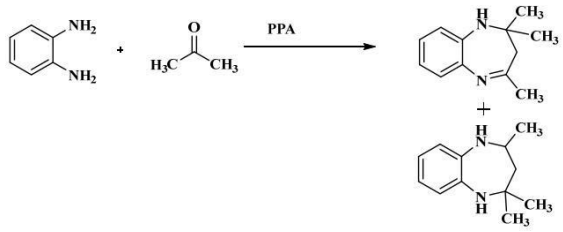
***Shaabani and Maleki* in [2007]** [33] introduced the new approach for both the linear and cyclic ketones that react with the diamines containing both electron donating and electron-withdrawing groups on aromatic rings, without any significant difference, gave the corresponding 1,5-benzodiazepine derivatives in quantitative yields under solvent-free conditions. A mixture of *o*-phenylenediamine (1 mmol) and acetophenone (2.1 mmol) was stirred at room temperature in the presence of silica sulfuric acid (0.05 g) for 1.2 h to afford 93% pure compound.



***Pandit et.al* in [2007]**[34] reported reaction between *o*-phenylenediamine and aliphatic, aromatic and cyclic ketones in the presence of $LaCl_3.7H_2O$.

***Reddy et.al* in [2007]**[35] reported the catalytic activity of zirconium (IV) tetrachloride for the cyclo-condensation reaction of *o*-phenylenediamine and a ketone in refluxing 1,2-dichloroethane to afford the corresponding 2, 3-dihydro-1*H*-1,5-benzodiazepine in high yield.

***Jung et.al* in [2007]**[36] reported the synthesis of 1*H*-1,5-benzodiazepine derivatives with heteroaromatic ketone (2-acetylfuran, 2-acetylthiophene, 2-acetylpyridine, 3-acetylpyridine, 4-acetylpyridine) by using conc. HCl, SiO_2, or polyphosphoric acid (PPA).



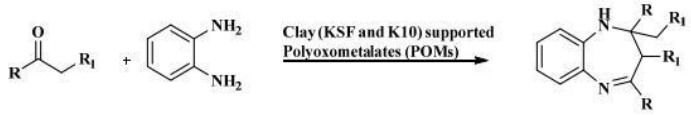
***Zhenjiang et.al* in [2007]**[37] synthesized 2, 3-dihydro-1*H*-1,5-benzodiazepines in good to excellent yield from direct condensation of *o*-phenylenediamines with ketones promoted by sulfamic acid at room temperature under neat condition or in acetonitrile.

***Varala et.al* in [2007]**[38] introduced *p*-nitrobenzoic acid promoted synthesis of 1,5-benzodiazepines by taking a mixture of *o*-phenylenediamine and cyclic and acyclic ketones.

***Sangshetti et.al* in [2007]**[39] reported the synthesis of 1,5-benzodiazepines using o-phenylenediamine and the ketone substrates and varying the mol% of sulfanilic acid. Among the results obtained, using 10 mol% sulfanilic acid gave better yield (97%) for the synthesis.

***Heravi et.al* in [2007]**[40] reported a new method in which mixture of ketone, *o*-phenylenediamine derivative and $H_{14}[NaP_5W_{30}O_{110}]$ (0.1 mol %) was refluxed in ethanol at 78°C. But in the case of cyclohexanone as a cyclic ketone the reaction times were longer than others, it may be because of the steric effect of cyclic ketones.

***Fazaeli and Aliyan* in [2007]**[41] introduced aluminium dodeca tungsto phosphate promoted synthesis of 1,5 benzodiazepine derivatives under solvent free conditions.

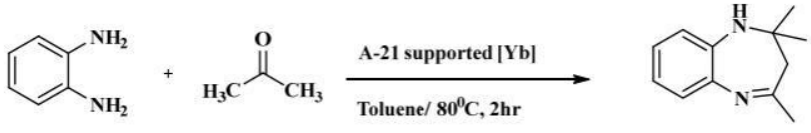


***Fazaeli and Aliyan* in [2007]**[42] introduced a simple and versatile method for the synthesis of 1,5-benzodiazepines via condensation of 1,2-phenylenediamines and ketones in the presence of catalytic amount of clay (K10 and KSF montmorillonite)-supported polyoxometalates (POMs). The method was applicable to both cyclic and acyclicketones without significant differences.

***Sharma et.al* in [2007]**[43] introduced a simple, efficient, mild and green method which has been developed for the synthesis of 1,5-benzodiazepines employing dodecyl sulfonic acid (DSA) as an excellent surfactant-type Bronsted acid catalyst in aqueous media at room temperature.

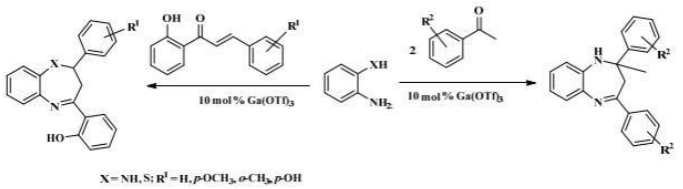
***Gholap et.al* in [2008]**[44] described a clean solvent free synthesis of 2, 3-dihydro-*(1H)*-1,5-benzodizepines by condensation of ketones possessing at least one α-hydrogen with o-phenylenediamine was mixed, heated and stirred at 80°C temperature catalyzed by silica supported perchloric acid ($HClO_4$-SiO_2).

***Tao and Yi* in [2008]**[45] introduced a method in which Amberlyst-21, a kind of well-known and cheap polymeric material, was treated with ytterbium perfluorooctanesulfonate [Yb $(OPf)_3$] giving a reagent with ytterbium loading of 1.34 (wt%). The polymer-supported fluorous ytterbium catalyzed the highly efficient synthesis of 1,5-benzodiazepine derivatives. The catalyst was recovered by simple filtration under fluorous-solvent-free conditions and used again without a significant loss of catalytic activity. Amberlyst A-21-Yb $(OPf)_3$ was very tolerant and stable to water. The robustness of the catalyst for recycling may partly be attributed to the water repellent nature of the perfluoroalkane chain "(-CF2-CF2-)n"of$Yb(OPf)_3$ which refuses the approach of water molecules to the central metal cation, thus maintaining its high catalytic activity.



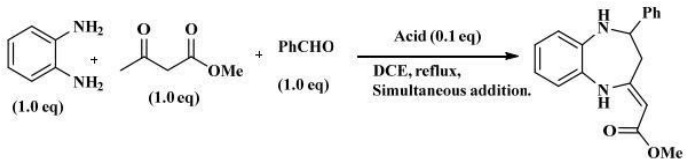
***Pan et.al* in [2008]**[46] reported the condensation reactions of *o*-phenylenediamine and two equivalents of acetophenone under Gallium (III) triflate catalysis which produced biaryl substituted 1,5-benzodiazepines. Similar reactions of *o*-phenylenediamine or *o*-aminothiophenol and *o*-hydroxychalcones lead to formation of

functionalized 1,5-benzodiazepines and 1,5-benzothiazepines in good to excellent yields. The *o*-hydoxy group of chalcones is crucial for this unprecedented condensation process.



***Kumar and Shandhu* in [2008]**[47] introduced the use of Gallium (III) chloride for the synthesis of 1,5-benzodiazepines from *o*-phenylenediamine and α-methylene ketones. Diamines with electron releasing and *o*-naphthylenediamine reacted smoothly with ketones to afford products in excellent yields. $GaCl_3$ is an established water scavenger and seems to help both in the formation of imines and the cyclisation step.

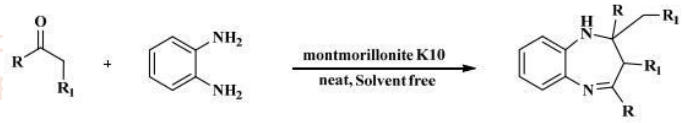
***Murai et.al* in [2008]**[48] reported the novel three component reaction of aromatic aldehydes, ethylenediamine, and β-keto esters producing seven membered 1,4-azepane compounds. This reaction was very unique because β-keto esters reacted at the generally unreactive γ-positions.



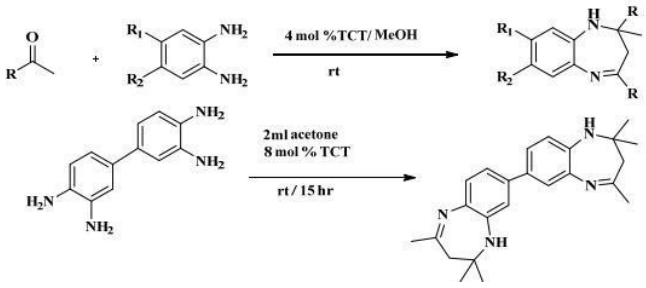
***D. Mahajan et.al* in [2008]**[49] introduced the synthesis of 1,5-benzodiazepine from the condensation of 1 mole of *o*-phenylenediamine with 2 moles of ketone under solvent-free conditions catalyzed by alum $[KAl(SO_4)_2{\cdot}12H_2O]$ which was found to be an efficient, non-toxic, cheap, and environmentally benign and gave good to excellent yields.

***Heravi et.al* in [2008]**[50] reported a simple method for the condensation of *o*-phenylenediamines (*o*-PDA) with 1,3-diketones using catalytic amounts of different types of HPAs including $H_{14}[NaP_5W_{30}O_{110}]$, $H_5[PMo_{10}V_2O_{40}]$ and $H_6[P_2W_{18}O_{62}]$ as the catalyst to synthesize 3*H*-1,5-benzodiazepines.

***Li-Tao et.al* in [2008]** [51] introduced the synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepines which have been synthesized under solvent-free conditions in good yields from *o*-phenylenediamine and ketones catalyzed by montmorillonite K10.

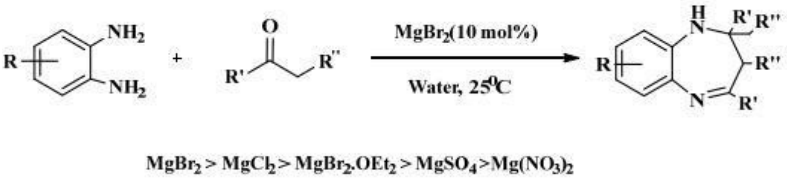


***Kuo et.al* in [2008]** [52] introduced 2,4,6-trichloro-1,3,5-triazine (TCT) efficiently catalyzed the condensation reactions between 1,2-diamines and various enolizable ketones to afford 1,5-benzodiazepines in good to excellent yields.

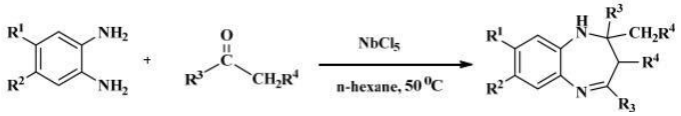


***Prakash et.al* in [2009]** [53] introduced the synthesis of 1,5-benzodiazepine derivatives by the condensation of *o*-phenylenediamines and ketones in the presence of Gallium (III) triflate in catalytic amount.

***Pawar et.al* in [2009]** [54] reported the reaction of *o*-phenylenediamine (1 mmol) and ketone (1.2 mmol)) in water which was carried in the presence of $MgBr_2$, stirred with respective time at room temperature to afford the corresponding 2,3-dihydro-2,2,4-trimethyl-1*H*-1,5-benzodiazepine in good yield. The reaction proceeds rapidly at ambient temperature with 10 mol% of catalyst.

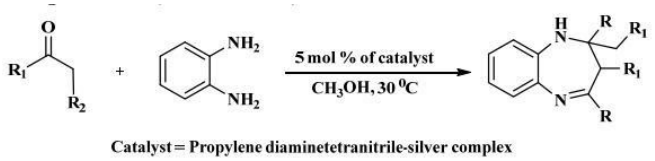


***Gao et.al* in [2009]**[55] introduced the synthesis of 1,5-benzodiazepine derivatives in moderate to excellent isolated yields by the condensation reactions of *o*-phenylenediamine and



ketones catalyzed by Niobium pentachloride ($NbCl_5$) under mild conditions using n-hexane as solvent at 50°C.

***Gopala krishanapanicker et.al* in [2009]**[56] reported a method in which tetranitrile silver complex was prepared and used as homogeneous catalyst for one pot thee component. Mannich reaction and benzodiazepine synthesis from *o*-phenylenediamine and various ketones.



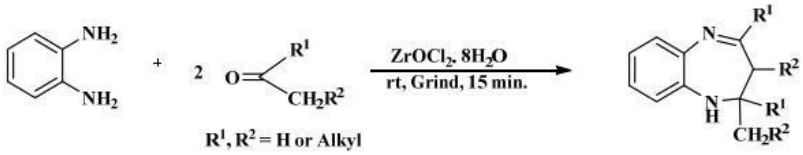
Catalyst = Propylene diaminetetranitrile-silver complex

***Vijayashankar et.al* in [2010]**[57] introduced a facile method for the synthesis of 1,5-benzodiazepines by the condensation of *o*-phenylenediamine with ketones with an amorphous mesoporous iron aluminophosphate (Fe-AIP) catalyst in the presence of a solvent and under solvent-free conditions heated with stirring in a temperature-controlled oil bath at 80°C.

***Shi et.al* in [2010]**[58], described an efficient and clean method for the synthesis of 1,5-benzodiazepines from *o*-phenylenediamine and ketones catalyzed by sodium tetrachloroaurate(III) dihydrate under mild conditions.

***Parveen et.al* in [2011]**[59] described the synthesis of 2, 3-dihydro-1*H*-1,5-benzodiazepine by taking a solution of OPD/substituted OPD and the ketone in I_2 (10 mol%) by adding 3-4 drops of ethanol for well mixing and stirred at ambient temperature for appropriate time.

***Baseer and Khan* in [2011]**[60] introduced a method in which zirconium oxychloride efficiently catalyzed the condensation of ketones (cyclic and acyclic) with *o*-phenylenediamine at room temperature, under solvent free conditions, in short reaction time with excellent yield of the product. OPD, ketones and zirconium oxychloride (catalytic amount) were ground well using mortar and pestle at room temperature.

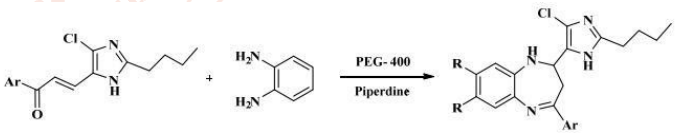


R¹, R² = H or Alkyl

***Sharma et.al* in [2011]**[61] designed the synthesis of benzodiazepines using anhydrous tin (II) chloride as efficient catalyst in which substituted ketone (20 mmoles), *o*-phenylenediamine (10 mmoles), and tin (II) chloride anhydrous (0.5 mmoles) were ground well using mortar and pestle and transferred to a 50 ml round bottomed flask and heated at 80-85°C for 40 min to 1H.

***Konda et.al* in [2011]**[62] described a new method in which a mixture of substituted chalcone (1 mmol), *o*-phenylenediamine (1.5 mmol) and piperidine (1 ml) in polyethylene glycol (PEG-400) (15 mL) was heated at 60°C.

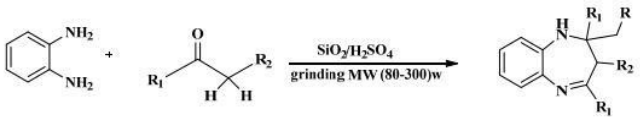
***Chaskar et.al* [2011]**[63] reported bismuth (III) salts catalyzed synthesis of 2,3-dihydro-1H-1,5-benzodiazepine from *o*-phenylenediamine and acyclic and cyclic and aromatic ketones in mild conditions.



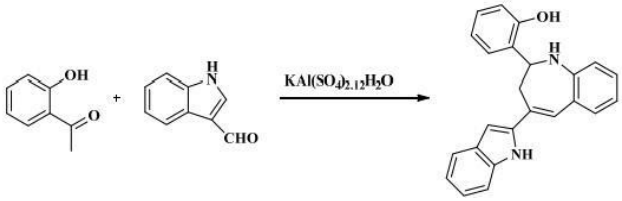
***Majid et.al* in [2012]**[64] reported a simple and versatile method for the synthesis of 1,5-benzodiazepines is via condensation of *o*-phenylenediamines and ketones in the presence of catalytic amount of H-MCM-22 using acetonitrile as solvent at room temperature.

***Makone and Vayavahare*in [2012]**[65]introduced sodium perchlorate as an efficient agent for the preparation of 2,3-dihydro-1H-1,5-benzodiazepine derivatives by the condensation of *o*-phenylenediamine and various ketones in the presence of stoichiometric amount of $NaClO_4$ in an aqueous media.

***Shushizadeh and Dalband*in [2012]**[66] introduced a green method for the synthesis of 1,5-benzodiazepines by the application of silica resin with acid functional moieties, during which they found that SiO_2/H_2SO_4 mixture was a simple and efficient catalyst for this method under microwave irradiation.



***Singla et.al* in [2012]**[67] reported a simple and versatile method for the synthesis of 1,5-benzodiazepines via condensation of o-phenylenediamines and ketones in the presence of catalytic amount of potassium aluminium sulfate dodecahydrate ($KAl(SO_4)_2.12H_2O$) as a non-toxic and cheap catalyst.



***Sandhar and Singh* in [2012]**[68] introduced a rapid and efficient environment friendly multicomponent one-pot synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepines catalyzed by tannic acid under solvent free condition by simple condensation of *o*-phenylenediamine with different ketones.

***Munoz et.al* in [2012]**[69] explored the catalytic activity of Argentinean bentonite as catalysts for the synthesis of 1,5-benzodiazepines though a condensation reaction between *o*-phenylenediamine and excess of acetone as reactive and solvent at room temperature.

Based on the work of ***Munoz et.al , Kurane et.al* in [2013]**[70] designed an ionic liquid film of [Bmim]Cl containing an organometallic catalyst (Cp_2ZrCl_2) has been anchored on the porous matrix of an aerogel by adsorption interactions and successfully used for the synthesis of medicinally relevant 1,5-benzodiazepines.

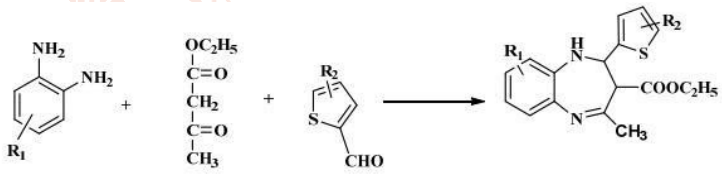
***Ilango et.al* in [2013]**[71] described the synthesis of (4-methyl-1,5-dihydro-1,5 benzodiazepine-2-ylidene)-aryl-amines using *o*-phenylenediamine and acetoacetanilide catalyzed by $CdCl_2$ under thermal and microwave irradiation.

***Alinezhad et.al* in [2013]**[72] described the synthesis of 1,5-benzodizepinederivative using (2-MPyH)OTf as a catalyst. They reported a method for synthesis of 1,5-benzodizapine.

***Sajadiffer and Rezayati* in [2013]**[73] described the synthesis of 1,5-benzodizepine derivatives using boron sulfonic acid

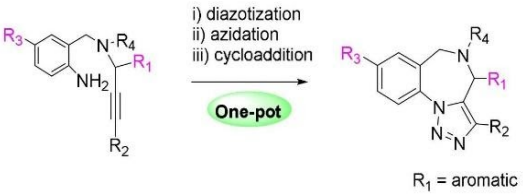
***Goswami et.al* in [2013]**[74] introduced the synthesis of 1,5-benzodizepine via condensation of o-phenylenediamine with ketone in the presence of catalytic amount of phenylboronic acid in acetonitrile solvent under reflux condition.

***Li and Wang* in [2014]**[75] introduced the one pot synthesis of 1, 5 benzodizepine derivative containing thiophene and $COOCH_2CH_3$ groups. The reaction preceded by the component condensation of substituted thiophenecarboxaldehyde, *o*-phenylenediamine and ethylacetoacetate in ethanol at 0°C.

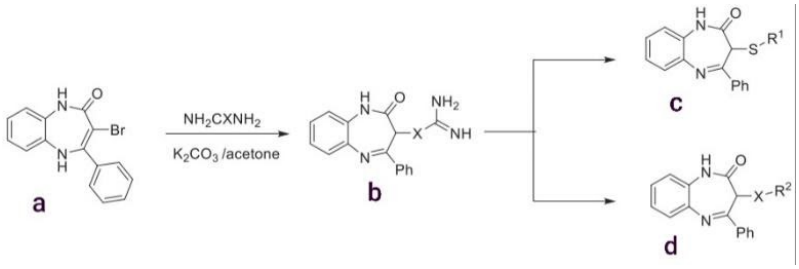


***Zhao et.al* in [2014]**[76] described the one-pot three-components condensation reaction of **o**-phenylenediamines with α,β-unsaturated carbonyl compounds to form a derivatives of 1,5-benzodiazepines by using TFA (trifluoroacetic acid) as a catalyst.

N. Sudhapriya et.al [2015][77] An efficient diversity oriented synthesis of [1,2,3]triazolo[1,5-a][1,4]benzodiazepines has been developed by sequential diazotization, azidation and cycloaddition reactions in a one-pot fashion.

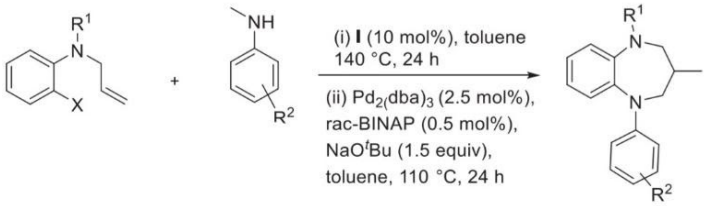


Khodairy et al [2016][77] reported the synthesis of new 3-pyrimidinyl- and imidazolyl-1,5-benzodiazepines from 3-bromo-4-phenyl-1H-[1,5]benzodiazepin-2-one **(a)** as a substrate. They synthesized 2-oxo-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-3-ylimidothiocarbamate **(b)** and 1-(2-oxo-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-3-yl)guanidine **(c)** by reacting with thiourea or guanidine in the presence of potassium carbonate. Intermediate upon reaction withnitriles, diethyl malonate or mixture of an aldehyde and β-keto esters or acetylacetone in the presence of ceric ammonium nitrate provided pyrimidyl thiobenzodiazepines **(d)** in good to excellent yields. On the other hand, intermediate **(b)** upon reaction with α-haloesters, nitriles, and/or ketones yielded new imidazole in moderate to good yield.

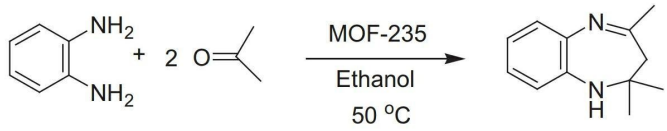


Weers et al [2016][78] developed a novel and alternative one-pot efficient methodology for the synthesis of pharmacologically relevant 1,5-benzodiazepines from N-allyl-2-bromoanilines.

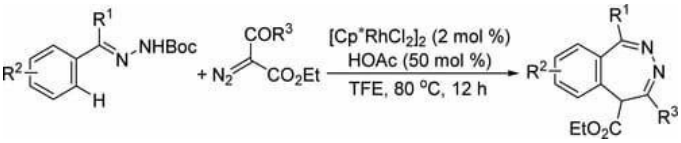
T.D. Le et.al [2016][79] did cyclocondensation of 1,2-phenylenediamine with acetone to form 2,3-dihydro-2,2,4-trimethyl-1H-1,5-benzodiazepine using MOF-235 as catalyst.



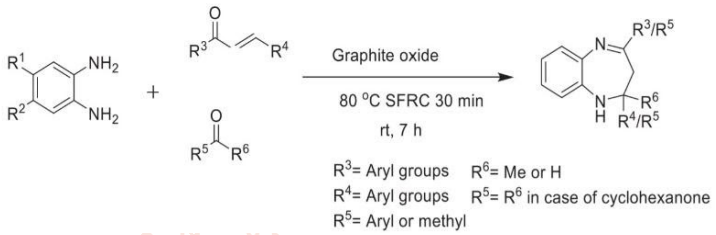
J. Wang et.al [2017][80] efficient Rh(III)-catalyzed C–H activation protocol has been developed for the synthesis of 2,3-benzodiazepines with use of N-Boc hydrazones and diazoketoesters as substrates.



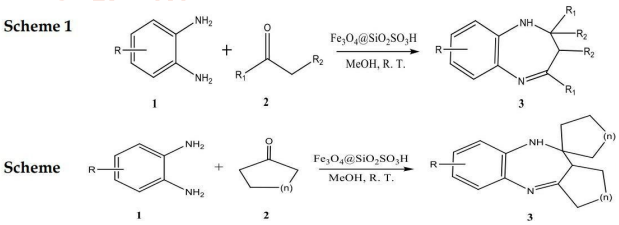
Indalkar et al [2017][81] developed environmentally benign one-pot solvent-free procedure for the synthesis of 4-substituted 1,5-benzodiazepines via three-component reaction of *o*-phenylenediamine, dimedone and aldehyde catalyzed by sulphated polyborate.



Jamatia et al [2017][82] developed a green synthetic protocol for the synthesis of 1,5-benzodiazepines *via* condensation of α,β-unsaturated ketone or aryl ketone with various diamines using graphite oxide (GO) as a catalyst.



B.P. Sathe et.al [2018][83] did reactions between various substituted o-phenylenediamines (10 mmol) and ketones (20 mmol) in presence of Fe3O4@SiO2SO3H (20 mol%) in methanol (Scheme 1 & 2).



V.I. Isaeva et.al [2018][84] synthesized physiologically active 1,5-benzodiazepines from 1,2-phenylenediamine and ketones (acetone, acetophenone, methyl ethyl ketone). Catalytic properties of MIL/K-SO3H and MIL/Ks-CN composites

A.Savari et al.[2019][85] reacted o-phenylenediamine (1 mmol), dimedone (1 mmol), and 4-chlorobenzaldehyde(1 mmol) in the presence of CoFe2O4@SiO2@NH-NH2-PCuW as a catalyst.

Physical properties and Spectral Details

2,2,4-trimethyl-2,3-dihydro-1*H*-1,5-benzodiazepine

Yellow crystals; m.p. Found 137-38ºC, Reported:136-38ºC

IR (KBr): 3343, 1657, 1610 cm^{-1}

^1H NMR $CDCl_3$): δ 1.35 (s, 6H), 2.20(s, 2H), 2.35 (s, 3H), 2.95 (br s, 1H, NH), 6.65-7.3 (m, 4H)

^{13}C NMR ($CDCl_3$): δ 29.7, 30.4, 45.0, 67.8, 121.6, 122.0, 125.4, 126.7, 137.8, 140.6, 171.8; MS: m/z 188 (M+).

2,4-Diethyl-2-methyl-2,3-dihydro-1*H*-1,5-benzodiazepine.

Yellow solid; m.p. Found 138ºC, Reported 137-39ºC

IR (KBr): 3335, 1648, 1605 cm^{-1}

^1H NMR ($CDCl_3$): δ 0.99 (t, 3H, J = 6.9 Hz), 1.25 (t, 3H, J = 7.0 Hz), 1.70 (q, 2H, J=6.9 Hz), 2.15 (m, 2H), 2.35 (s, 3H), 2.69 (q, 2H, J= 7.0 Hz), 3.25 (br s, 1H, NH), 6.78-7.35 (m, 4H)

^{13}C NMR ($CDCl_3$): δ 8.7, 10.8, 26.9, 35.5, 35.7, 42.1, 70.5, 121.8, 125.4, 126.2, 127.0, 137.9, 140.8, 175.6; MS: m/z 216 (M+).

2,2,4-triethyl-3-methyl-2,3-dihydro-1*H*-1,5-benzodiazepine
Colorless solid; m.p. Found 142- 44ºC, Reported 143-44ºC;

IR (KBr): 3325, 1640, 1610 cm^{-1};

^1H NMR ($CDCl_3$): δ 0.75-1.05 (m, 10H), 1.20-1.38 (m, 4H), 1.50-1.65 (m, 2H), 2.40-2.60 (m, 2H),

2.87 (q,1H, J = 6.9 Hz), 3.75 (br s,1H, NH), 6.57 (d, 1H, J = 8.0 Hz), 6.65 (t, 1H, J = 8.0 Hz), 6.90 (t, 1H, J = 8.0 Hz), 7.38 (d, 1H, J =8.0 Hz);

^{13}C NMR ($CDCl_3$): δ 7.5, 7.9, 11.5, 12.3, 28.0, 28.4, 35.6, 46.2, 68.6, 117.5, 118.0, 126.6, 132.8, 139.0, 142.4, 173.4; MS: m/z 244 (M+).

2-Methyl-2,4-diisobutyl-2,3-dihydro-1*H*-1,5-benzodiazepine
Yellow solid; m.p. Found 119ºC, Reported 118-20ºC

IR (KBr): 3335, 1645, 1600 cm^{-1}

^1H NMR ($CDCl_3$): δ 0.95-1.05(m, 12H), 1.32 (s, 3H), 1.49-1.52 (m, 2H), 1.65-1.75 (m, 1H), 2.05-2.25 (m, 3H), 2.24 (d, 2H, J = 12.7Hz), 6.60-6.65 (m, 1H), 6.85-6.95 (m, 2H), 7.05-7.15 (m, 1H);

^{13}C NMR ($CDCl_3$): δ 22.5, 22.7, 24.2, 24.9, 25.0, 26.3, 28.1, 43.5, 51.7, 51.9, 70.8, 121.4, 121.5, 125.2, 127.2, 137.8, 140.4, 173.9; MS: m/z 272 (M+).

2-Methyl-2, 4-diphenyl-2, 3-dihydro-1*H*-1, 5-benzodiazepine
Yellow solid; m.p. Found 150-52ºC, Reported 151-52ºC;

IR (KBr): 3345, 1635 cm^{-1};

^1H NMR ($CDCl_3$): δ 1.80 (s, 3H), 2.95 (d, 1H, J = 12.8 Hz), 3.15 (d, 1H, J = 12.8 Hz) 3.45 (br s, NH), 6.55-7.0 (m, 3H), 7.15-7.35 (m, 7H), 7.55-7.65 (m, 4H);

^{13}C NMR ($CDCl_3$): δ 167.5, 146.6, 140.1, 139.5, 138.2, 129.8, 128.6,128.4, 121.1, 127.1, 126.4, 125.5, 121.7, 121.5, 73.9, 43.2, 29.9; MS: m/z 312 (M+).

2-Methyl-2,4-bis(3-methoxyphenyl)-2,3-dihydro-1*H*-1,5-benzodiazepine
Viscous oil.

^1H NMR ($CDCl_3$, 300 MHz) δ: 7.5 - 6.5 (12H, m), 4.1 (1H, br s), 3.9 – 3.7 (6H, s), 3.2 (2H, s), 1.8 (3H, s).

IR(KBr)ν_{max}/cm^{-1}: 3325, 2980, 1640, 1530.

ESI-MS m/z = 395 $(M+Na)^+$.

*Anal Calcd.*for $C_{22}H_{24}N_2O_2$:C, 77.42, H, 6.54, N, 7.62. Found: C, 77.76, H, 6.88, N, 7.96.

2-Methyl-2,4-bis(4-chlorophenyl)-2,3-dihydro-1*H*-1,5-benzodiazepine
Dark yellow solid, M.pt. 162 - 163 ^oC.

^1H NMR ($CDCl_3$, 300 MHz) δ: 7.5 - 6.8 (12H, m), 4.1 (1H, br s), 2.9 (2H, s), 1.7 (3H, s).

IR(KBr)ν_{max}/cm^{-1}: 3330, 2980, 1625, 1535.

ESI-MS m/z = 382 (100) $(M+H)^+$, 384 (30) $(M+H)^+$.

*Anal Calcd.*for $C_{22}H_{18}Cl_2N_2$:C, 69.40, H, 4.76, N, 7.40. Found: C, 69.78, H, 5.08, N, 7.74.

2-Methyl-2,4-bis(4-hydroxyphenyl)-2,3-dihydro-1*H*-1,5-benzodiazepine
Yellow solid, M.pt. 140- 141 ^oC.

^1H NMR ($CDCl_3$, 300 MHz) δ: 7.4 - 6.9 (12H, m), 4.2 (1H, br s), 2.9 (2H, s), 1.6 (3H, s).

IR(KBr)ν_{max}/cm^{-1}: 3345, 3310, 2980, 1635, 1530.

ESI-MS m/z = 367 $(M+Na)^+$.

*Anal Calcd.*for $C_{22}H_{20}N_2O_2$:C, 76.62, H, 5.85, N, 8.10. Found: C, 76.97, H, 6.22, N, 8.46.

References

[1] J. K. Landquist, A. R. Katritzky, C. W. Rees, *Comprehensive Heterocyclic Chemistry*, *Vol. IPergamon, Oxford,* **1984**, 166.

[2] J. Thiele, G. Steimming, Ber., 1907, 40, 955.

[3] A. Takamizawa, K. Hirai, Japanese patent 18, 950, Chem. Abstr., 1967, 66, 37969.

[4] M. Weissenfels, R. Kanche, W. Krauter, J. Prakt. Chem., 1965, 35, 166.

[5] D. Lloyd, R. H. Mc. Dougall, D. R. Marshall, J. Chem. Soc., 1965, 3785.

[6] M. S. Balakrishna, B. A Kaboudin, Tetrahedron Lett. 42(2001) 1127-1129.

[7] M. Curini, F. Epifano, M. C. Marcotullio, O. Rosati, TetrahedronLett. 42 (2001) 3193-3195.

[8] X. Y. Chen, W. H. Zhong, Y. M. Zhang, Chin. Chem. Lett. 12 (2001) 5–6.

[9] M. Pozarentzi, J. S. Stephanatou, C. A. Tsoleridis, 43 (2002) 1755-1758.

[10] G. Roman, E. Comanita, B. Comanita, ActaChim. Slov. 49 (2002) 575–585.

[11] D. V. Jarikote, S. A. Siddiqui, R. Rajagopal, T. Daniel, R. J. Lahoti, K. V. Srinivasan, Tetrahedron Lett. 44 (2003) 1835-1838.

[12] B. M. Reddy, P. M. Sreekanth, Tetrahedron Lett. 44 (2003) 4447–4449.

[13] J. S. Yadav, B. V. S. Reddy, S. P. Kumar, K. Nagaiah, Synthesis 36 (2005) 480-484.

[14] V. Sivamurugan, K. Deepa, M. Palanichamy, V. Murugesan, Synth. Commun. 34 (2004) 3833-3846.

[15] S. Gowravaram, G. S. K. K. Reddy, K. B. Reddy, N. M. Reddy, J. S. Yadav, Adv. Syn. Catal. 346 (2004) 921–923.

[16] K. Sucheta, B. V. Rao, Ind. J. Chem. 44(B) (2005) 2152-2154.

[17] B. P Bandgar, A. V. Patil, O. S. Chavan, J. Mol. Catal. A: Chem. 256 (2006) 99–105.

[18] M. A. Alibeik, Z. Zaghaghi, I. M. Baltork, J. Chinese Chem. Soc. 55 (2008) 1-4.

[19] S. K. De, R. A. Gibbs, Tetrahedron Lett. 46 (2005)1811–1813.

[20] M. A. Chari, K. Syamasundar, Catal. Commun. 6 (2005) 67-70.

[21] M. Tajbakhsh, M. M. Heravi, B. Mohajerani, A. N. Ahmadi, J. Mol. Catal. A: Chem. 247 (2006) 213–215.

[22] R. R. Nagawade, D. B. Shinde, Mendeleev Commun. 16 (2006) 113–115.

[23] R. Chandra, R. Kumar, P. Choudhary, S. Nimesh, A. K. Verma, Green Chem. 8 (2006) 519–521.

[24] J. Wu, F. Xu, Z. Zhou, Q. Shen, Synth. Commun. 36 (2006) 457-464.

[25] H. Thakuria, A. Pramanik, B. M. Borah, G. Das, Tetrahedron Lett. 47 (2006) 3135–3138.

[26] M. A. Pasha, V. P. Jayashankara, J. Pharmacol. Toxicol. 1 (2006) 573-578

[27] C. W. Kuo, S. V. More, C. F. Yao, Tetrahedron Lett. 47 (2006) 8523–8528.

[28] D. Yuying, F. Tian, W. Zhao, Synth. Commun. 36 (2006) 1661-1669.

[29] R. Varala, R. Enugala, S. R. Adapa, S. Nuvula, Synlett. 17 (2006)1009-1014.

[30] B. Das, R. Ramu, B. Ravikanth, V. S. Reddy. J. Mol. Catal. A: Chem. 246 (2006) 76-78.

[31] M. M. Heravi, V. Zadsirjan, F. K. Behbahani, H. A. Oskooie, J. Mol. Catal. A: Chem. 259 (2006) 201-204.

[32] K. P Guzen, R. Cella, H. A. Stefani, Tetrahedron Lett. 47 (2006) 8133-8136.

[33] A. Shaabani, A. Maleki, Iran. J. Chem. Chem. Eng. 26 (2007) 93-97.

[34] S. S. Pandit, B. D. Vikhe, G. D. Shelke, J. Chem. Sci. 119 (2007) 295–297.

[35] K. S. Reddy, C. V. Reddy, M. Mahesh, K. R. Reddy, P. V. K. Raju, V. V. N. Z. Reddy, Can. J. Chem. 85 (2007) 184-188.

[36] D. I. Jung, J. H. Song, Y. H. Kim, D. H. Lee, Y. G. Lee, Y. M. Park, S. K. Choi, J. T Hahn. Bull. Korean Chem. Soc. 28 (2007) 1877-1880.

[37] L. Zhenjiang, S. Yingjie, R. Xinghua, L. Weisi, S. Yuhu, O. Pingkai, Synth. Commun. 37 (2007) 1609-1615.

[38] R. Varala, R. Enugala, S. R. Adapa, J. Braz. Chem. Soc. 18 (2007) 291-296.

[39] J. N. Sangshetti, N. D. Kokare, D. B Shinde, Chin. Chem. Lett. 18 (2007) 1305–1308.

[40] M. M. Heravi, F. Derikvand, L. Ranjbar, F. F. Bamoharramb, J. Mol. Catal. A: Chem. 261 (2007) 156–159.

[41] R. Fazaeli, H. Aliyan, Heterocycles 71 (2007) 805-814.

[42] R. Fazaeli, H. Aliyan, App. Catal. A: Gen. 331 (2007)78-83.

[43] S. D. Sharma, P. Gogoi, D. Konwar, Green Chem. 9 (2007)153-157.

[44] S. S. Gholap, S. C. Chaskar, C. H. Gill, Rasayan J. Chem. 1 (2008) 331-336.

[45] F. Tao, W-B Yi, ChemInform. 5 (2008) 655-658.

[46] G. K. S. Prakash, H. Vaghoo, A. Venkat, C. Panja, S. Chacko, T. Mathew, G. A. Olah, Fut. Med. Chem. 1 (2009) 909-920.

[47] S. Kumar, J. S. Sandhu, Ind. J. Chem. 47(B) (2008) 1463-1466.

[48] K. Murai, R. Nakatani, Y. Kita, H. Fujioka, Tetrahedron 64 (2008) 11034–11040.

[49] D. Mahajan, T. Naqvi, R. L. Sharma, K. K. Kapoor, Aus. J. Chem. 61 (2008) 159-162.

[50] M. M. Heravi, S. Sadjadi, H. A. Oskooie, R. Hekmatshoar, F. F. Bamoharram, J. Chin. Chem. Soc. 55 (2008) 842-845.

[51] Li-T. An, F-Q Ding, J-P Zou, X-H Lu, Synth. Commun. 38 (2008) 1259–1267.

[52] C. W. Kuo, C. C. Wang, V. Kavala, C. F. Yao, Molecules 13 (2008) 2313-2325.

[53] G. K. S. Prakash, H. Vaghoo, A. Venkat, C. Panja, S. Chacko, T. Mathew, G. A. Olah, Fut. Med. Chem. 1(2009) 909-920.

[54] S. S. Pawar, M. S. Shingare, S. N. Thore, Chin. Chem. Lett. 20 (2009) 32–36.

[55] S. T. Gao, W. H. Liu, J. J. Ma, C. Wang, Q. Liang, Syn. Commun. 39 (2009) 3278-3284.

[56] R. K. Gopalakrishnapanicker, S. Radhakrishnan, S. Krishna Pillai, Lett. Org. Chem. 6 (2009) 17-21.

[57] A. V. Vijayasankar, B. R. Venugopal, N. Nagaraju, Chin. J. Catal. 31 (2010) 1321-1327.

[58] R. X. Shi, Y. K. Liu, Z. Y. Xu, J. Zhejiang University 11 (2010) 102-108.

[59] A. Parveen, V. A. Patil, M. A. Baseer, S. K. Ahmed, Int. J. Ind. Chem. 2 (2011) 144-153.

[60] M. A. Baseer, A. J. Khan, Der ChemicaSinica 2 (2011) 84-87.

[61] S. Sharma, D. N. Prasad, R. K. Singh, J. Chem. Pharm. Res. 3 (2011) 382-389.

[62] S. G. Konda, B. M. Shaikh, S. A. Chavan, B. S. Dawane, Chin. Chem. Lett. 22 (2011) 65–68.

[63] A. Chaskar, L. Patil, K. Phatangare, V. Padalkar, S. Takale, International Scholarly Research Network, ISRN Organic Chemistry(2011) 1-4.

[64] S. A. Majid, W. A. Khanday, R. J. Tomar, J. Biomed. Biotechnology. (2012) 1-6.

[65] S. S. Makone, D. B. Vyawahare, Der ChemicaSinica 3 (2012) 1369-1373.

[66] M. R. Shushizadeh, N. Dalband, J. Jundishapur, Nat. Pharm. Prod. 7 (2012) 61-64.

[67] R. K. Singla, G. V. Bhat, G. G. Shenoy, B. S. Jayashee, S. G. Kini, A. Joseph, R. S. Jeyeprakash, S. D. Vachala, J. E. Mathew, N. Udupa, J. O. Igoli, Indo Global J. Pharm. Sci. 2 (2012) 279-285.

[68] A. Sandhar, R. K. Singh, Asian J. Chem. 24 (2012) 5643-5645.

[69] M. Munoz, G. Sathicq, G. Romanelli, S. Hernandez, C. I. Cabello, I. L. Botto, M. Capron, J. Porous Mat. 20 (2012) 65-73.

[70] R. Kurane, J. Jadhav, S. Khanapur, R. Salunkhe, G. R. Rashinkar, Green Chem. 15 (2013) 1849-1856.

[71] S. S. Ilango, P. V. Remya, S. Ponnuswamy, Indian J. Chem. 52B (2013) 136-140.

[72] H. Alinezhad, M. Tejbakhsh, M. Norouzi, S. Baghery, World Appl. Sci. J. 22 (2013) 1711-1717.

[73] S. Sajjadifar, S. Rezayati, Int. J. Chem. Tech. Res. 5 (2013) 1964-1968.

[74] V. S. Goswami, P. B. Thorat, S. R. Bhusare, J. Chem. Sci. 125 (2013) 745-749.

[75] X. Q. Li, L. Z. Wang, Chin. Chem. Lett. 25 (2014) 327-332.

[76] Y. Zhao, S. Sharma, M. Huang, A. Sandhar, R. K. Singh, Y. Ma, Asian J. Chem. 26 (2014) 5116- 5120.

[77] N. Sudhapriya, A. Nandakumar, Y. Arun, P. T. Perumal, C. Balachandran, N. Emi, An expedient route to highly diversified [1, 2, 3]triazolo[1, 5-a][1, 4]benzodiazepines and their evaluation for antimicrobial, antiproliferative and in silico studies, RSC Adv. 5 (2015)

[78] E. A. Khodairy, H. A. Ahmed, Ghany, hetaryl-1, 5 benzodiazepines-Part I: synthesis of 3-pyrimidinyl- and imidazolyl-1, 5-benzodiazepines, J. Het. Chem. 54 (2016)

[79] M. Weers, L. H. Lühning, V. Lührs, C. Brahms, S. Doye, One-pot procedure for the synthesis of 1, 5-benzodiazepines from N-Allyl-2-bromoanilines, Chem. - A Eur. J. 23 (2016)

[80] T. D. Le, K. D. Nguyen, V. T. Nguyen, T. Truong, N. T. S. Phan, 1, 5-Benzodiazepine synthesis via cyclocondensation of 1, 2-diamines with ketones using iron based metal-organic framework MOF-235 as an efficient heterogeneous catalyst, J. Catal. 333 (2016)

[81] J. Wang, L. Wang, S. Guo, S. Zha, J. Zhu, Synthesis of 2, 3-benzodiazepines via Rh(III)-catalyzed C-H functionalization of N-Boc hydrazones with diazoketoesters, Org. Lett. 19 (2017) 3640–3643,

[82] K. S. Indalkar, M. S. Patil, G. U. Chaturbhuj, An efficient, environmentally benign, and solvent-free protocol for the synthesis of 4-substituted 1, 5-benzodiazepines catalyzed by reusable sulfated polyborate, Tet Lett. 58 (2017) 4496–4502

[83] R. Jamatia, A. Gupta, B. Dam, M. Saha, A. K. Pal, Graphite oxide: a metal free highly efficient carbocatalyst for the synthesis of 1, 5-benzodiazepines under room temperature and solvent free heating conditions, Green Chem. 19 (2017)

[84] B. P. Sathe, P. S. Phatak, V. S. Dalve, A. B. Rote, R. M. Tigote, K. P. Haval, Synthesis of 1, 5-benzodiazepines by using Fe3O4@ SiO2SO3H nanocatalyst, Int. Res. J. Sci. (2018) 93–92.

[85] V. I. Isaeva, M. N. Timofeeva, V. N. Panchenko, I. A. Lukoyanov, V. V. Chernyshev G. I. Kapustin, Design of novel catalysts for synthesis of 1, 5-benzodiazepines from 1, 2-phenylenediamine and ketones: NH2-MIL-101(Al) as integrated structural scaffold for catalytic materials based on calix[4]arenes, J. Catal.

[86] A. Savari, F. Heidarizadeh, N. Pourreza, Synthesis and characterization of CoFe2O4@SiO2@NH-NH2-PCuW as an acidic nano catalyst for the synthesis of 1, 4-benzodiazepines and a powerful dye remover, Polyhedron 166 (2019)