Support Catalyst and Microwave Irradiation in Eco-Friendly Organic Synthesis

by

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HISAR – 125 004

2005

..... To my parents

CERTIFICATE – I

This is to certify that this thesis entitled, **Support Catalyst and Microwave Irradiation in Eco-friendly Organic Synthesis,** submitted for the degree of **Master of science** in the subject of Chemistry to CCS Haryana Agricultural University, is a bonafide research work cited out by **Ms. Lalita Yadav** under my supervision and that no part of this thesis has been submitted for any other degree.

The assistance and help received during the course of investigation have been fully acknowledged.

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CERTIFICATE – II

This is to certify that this thesis entitled, **Support Catalyst and Microwave Irradiation in Eco-friendly Organic Synthesis,** submitted by **Ms. Lalita Yadav** to the CCS Haryana Agricultural University in partial fulfilment of the requirements for the degree of **Master of science** in the subject of Chemistry, has been approved by the studentôs advisory committee after an oral examination on the same.

HEAD OF THE DEPARTMENT **MAJOR ADVISOR**

DEAN, POST-GRADUATE STUDIES

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(LALITA YADAV)

Date:SEPTEMBER 2005

CONTENTS

Abbreviation

cm	Centimeter
DMF	Dimethyl formamide
DMSO	Dimethyl sulphoxide
g	Gram(s)
hr.	Hour
min.	Minutes
ml	Milliliter(s)
mol	Mole(s)
MW	Microwave
^{O}C	Degree centigrade
Hz	Hertz
IR	Infrared
Mg	Milligram

m.p	Melting point
m.m.p.	mixed melting point
TLC	Thin Layer Chromatography
MHz	Mega Hertz
GHz	Giga Hertz
R.F	Radio frequency

CHAPTER-I

INTRODUCTION

Industrial chemistry in the new millennium is adopting the concept of *green chemistry* to meet the fundamental scientific challenges of protecting the human health and environment while maintaining commercial viability. The emerging area of *green chemistry* envisages minimum hazard as the performance criteria while designing new chemical processes to explore alternative reaction conditions and reaction media to accomplish the derived chemical transformation with minimized by-products or waste. Among the important tools, the use of microwave as alternative energy source is becoming an attractive alternative. This expeditious solvent-free approach involves the exposure of neat reactants to microwave (MW) irradiation in conjunctions with the use of supported reagents or catalysts, which are primarily of mineral origin. The salient feature of these high yield protocols is the enhanced reaction rates, greater selectivity and the experimental ease of manipulation.

Microwave heating has been found to be a very conventional thermal source not only in kitchen but also in chemical laboratory. A wide range of chemical process can be promoted by microwave irradiation and this technique offers much promise. Most of the reported reactions have been carried out either in sealed vessels or in the solid phase, though a few reports of the use of unmodified domestic microwave ovens have also appeared for carried out organic synthesis in open vessels using organic solvents such as ethanol, N,N-dimethylformamide (DMF), *o*-dichlorobenzene, 1,2-dichloroethane as energy transfer media. It was found that a number of organic reactions could be performed by microwave irradiation. Microwave irradiation is used in sealed or open containers either in the presence or absence of catalyst or solid support under solvent free dry conditions for carrying out common organic reaction. Thus, the problem associated with the disposal of waste solvents or use of excess chemicals is avoided or minimized. Since the solid support catalyst is used in the solvent free conditions the product obtained are highly pure, reaction times are drastically reduced and solid support can be recycled or regenerated. The short reaction time and the expanded reaction range that are offered by microwave-assisted organic synthesis are well suited to increased demands in industry. While microwave ovens has been used to heat food-stuff for over 50 years, in inorganic chemistry, microwave irradiation has been used since the late 1970s while it has been only implanted in organic chemistry since mid 1980s. Microwave heating had been used for a wide variety of purpose such as moisture analysis, the wet ashing of biological and dissolution of geological materials, regeneration of activated carbon, and preparation of activated carbon from carbonaceous material, treatment of sewage, sewage sludge and drying spaghetti.

Microwaves are electromagnetic waves, which are associated with electric as well as magnetic field. The electric field applies a force on a charged particle causing energy explosion at dielectric site. The microwave activation of polar sites, which are capable of dielectric loss, in the molecule and generate *hot spots* that facilitates the bond breaking and making process and new molecules are formed. The presence of solid support catalyst enhances the reaction rate and the products, thus obtained, are in good yield and relatively more pure. Support reagents constitute a major change in the traditional synthetic methods and clay mediated synthesis is of high significance. The clay not only acts as adsorbate to bring the molecule close enough but also are used as a heterogeneous catalyst after impregnation with suitable reagent. These solid supports e.g. oxides (silica, alumina) neither absorb nor inhibit the passage of microwave irradiation through them. Heterogeneous reactions are affected by the reagents immobilized on the solid supports and have the advantage over the conventional solution phase reactions because of the good dispersion of active reagent site, associated selectivity and easier workup. The recyclability of some of these solid supports renders these processes into truly eco-friendly *green protocols*.

Microwave energy has been used for heating food materials for almost half century and now it has been realized that this technique may find potential useful application in chemical technology. These include acceleration of chemical reaction such as aqueous emulsion polymerization of butyl acrylate, acrylic acid and methacrylic acid using pulse electromagnetic radiation. The polymerization reactions have been found to be faster than those observed under conventional conditions, emulsion polymerization. Microwave energy is also used for alkane decomposition, polymer technology, drug release and ceramics. Microwave-assisted organic synthesis (MAOS) has been extensively used in the field of polymer sciences thiophene oligomers, with application as biological florescent markers, have been synthesized. Utilization of this microwave technique to solid-state organic synthesis and to inorganic chemistry has shown significant advantage. This methodology has also been found to be useful in wide range of decomposition process including hydrolysis of protein and peptides.

When, microwave dielectric heating is used, the energy is introduced into the chemical reactor remotely and there is no direct contact between the energy source and reaction mixture as compared to conventional heating which involve the direct heating of reaction mixture through the walls of vessel and may result in decomposition of product due to over heating. Furthermore, the lack of direct contact between the energy sources and the sample facilitates reaction optimization by enabling immediate changes to reaction conditions without the need to wait for the heat source to recalibrate.

The solid support catalysis in organic chemistry can be compared to conventional methods, which involve the use of large amount of the solvents, which are often not recycled but add to the pollution. The solid-support catalysis after due to exploration and standardization can help in developing new techniques, which will be environmentally friendly.

During microwave irradiation of reactions under dry conditions the organic compound are adsorbed on the surface of inorganic oxides, such as alumina, silica and clay, or ódopedô reagents absorbs microwave whereas solid supports does not absorb or restrict, the transmission of microwaves. The bulk temperature is relatively low in such solventï free reactions although higher localized temperature may reached during MW irradiation. These solvent-free microwave-assisted reactions provide an opportunity to work with the open vessels thus avoiding the risk of high-pressure development and increasing the potential of such reaction to up-scale. Consequently, such support reagents efficiently induce reactions under safe and simple conditions with the domestic MW oven instead of specialized commercial microwave system that require sealed Teflon bomb.

Conventional synthesis of industrially significant compounds and intermediates is carried out using toxic solvents and reagents which are seldom recycled whereas microwave irradiation involves the usage of no solvent and catalytic amount of doped metal salt onto inert adsorbent as reagent. Hence, due to growing concern about the environment protection, there is need of chemical conserving technique and one such approach is microwave assisted organic synthesis (MAOS). Keeping this point in view, the present research work is proposed with following objectives:

1) To study the role of support catalysts and microwave irradiation in organic synthesis.
2) To compare the traditional methods of synthesis with eco-friendly methods in terms of ease of synthesis, purity of product and time of reaction.

CHAPTER-II

REVIEW OF LITERATURE

High-speed microwave organic synthesis has attracted a considerable amount of attention in recent years. Specially, an explosive growth has been witnessed in organic synthesis where the chemical reactions are accelerated because of selective absorption of microwave energy by polar molecules and non-polar molecule being inert to the microwave irradiation. Of special interest is the environmentally friendly solvent-free approaches that often involve exposure of neat reactant to microwave irradiation or employ supported reagents on recyclable inorganic oxide or catalysts and have been adequately demonstrated in several microwave-assisted condensation, deprotection, rearrangement, cyclization, and reduction and oxidation reactions. Very recently, the rapid heating capability of the microwave oven has been exploited to heat mixtures of ore samples and acid in sealed vessels leading to considerable saving in dissolution times.

The microwave region of electromagnetic spectrum lies between infrared radiation and radio frequencies and correspond to wavelength between 1cm to 1m (Frequencies of 30GHz to 300 MHz respectively). In order to avoid interference with RADAR, domestic and industrial microwave reactor of chemical use operates at 2.45 GHz frequency. In case of microwave, the energy transfer does not occur by conduction or convection as in conventional heating but by dielectric loss. The rapid one-pot preparation of heterocyclic compounds from *in situ* generated reactive intermediate and the general application to multicomponent reactions that are adaptable for building a library of compounds has been accomplished using microwave technique. More recently, the strategy has been extended to combinational chemistry and the synthesis of newer class of solvents, ionic liquids that are essentially molten salts with barely measurable vapor pressure. The salient features of this method are high yields, selectivity, experimental ease of manipulation and enhanced reaction rates.

Microwave energy has been used for heating food materials for almost half a century (Buffler, 1993) and now it has been realized that this technique may find potential useful applications in chemical technology. These include acceleration of chemical reactions (Varma, 2000; Varma, 2002*a*; Varma, 1999a; Varma, 1997; Varma *et. al.,* 2002*b*) polymer technology (Fujiimatsu *et. al*., 1990), applications in waste treatment, alkanes decomposition (Tse *et. al*., 1990), ceramics and preparation of samples for analysis (Aysola *et. al.,* 1988). Utilization of this technique for reactions appears to occur at relatively low bulk temperature although higher localized temperature may be reached during microwave irradiation (Mingos and Baghurst, 1991). This methodology has also been found to useful in wide range of decomposition process including hydrolysis of protein and peptides (Chen *et. al*., 1987).

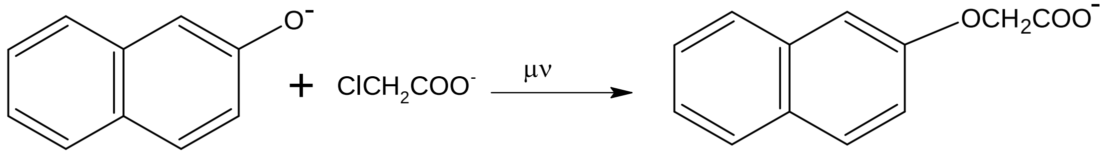
Since then explosive growth has been witnessed in organic synthesis where in chemical reactions are accelerated because of selective absorption of microwave energy by polar molecules and non-polar molecule being inert to the microwave dielectric loss (Gabriel *et. al*., 1998). Probably, the first recorded application of microwave energy in organic synthesis is the aqueous emulsion polymerization of butyl acrylate, acrylic acid and meta acrylic acid using pulsed electromagnetic radiation where polymerization rates obtained were substantially higher than those observed under conventional polymerization. Not much attention seen to have been paid to this publications for it was not until 1986 that the first report of applications of commercial kitchen microwave oven for the synthesis of small organic molecule appeared (Gigure *et. al.,* 1987; Gedye *et. al.,* 1986).

The first report of the surface mediated chemical transformation dates back to 1924 (Brit Pat, 1924), but it was not until almost half a century later that the technique received widespread attention as attested by several book reviews and accounts articles (Posner, 1978; Cornelis, 1985). Initial reports on the application of microwave for the chemical synthesis in polar solvents (Gigure *et. al.,* 1987; Gedye, *et. al.,* 1986). Another major factor responsible for their popularity is the ready availability of inexpensive household microwave ovens that can be safely used for solvents-less reaction and an opportunity to work with open vessels, thus avoiding the risk of development of high-pressure.

An explosive growth in the application of microwave energy in organic synthesis was ignited by publication in 1986 by Gedye and Coworkers (Gedye *et. al.*, 1986) which reported 113 to 1240 fold rates in increase in variety of reactions in sealed Teflon vessels as compared to same reactions being carried out under reflux conditions. These reactions are aqueous acid-catalyzed hydrolysis, esterification, formation of benzophenone oxime, and SN_2 etherification of 4-cyanophenoxide ions with benzyl chloride to give the product.

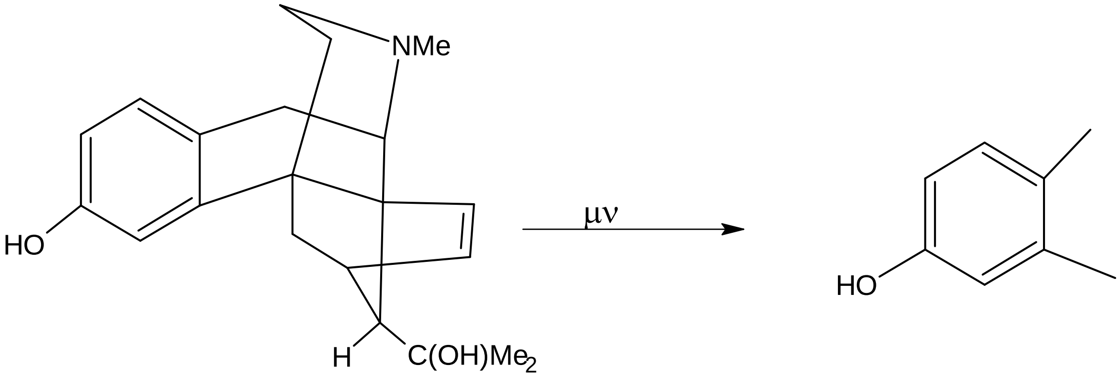
$$NCC_6H_4O^- + PhCH_2Cl \xrightarrow[MW]{MeOH} NCC_6H_4OCH_2Ph + Cl^-$$

2-Naphthoxide with sodium chloroacetate gave 2-napthoxy acetic acid.

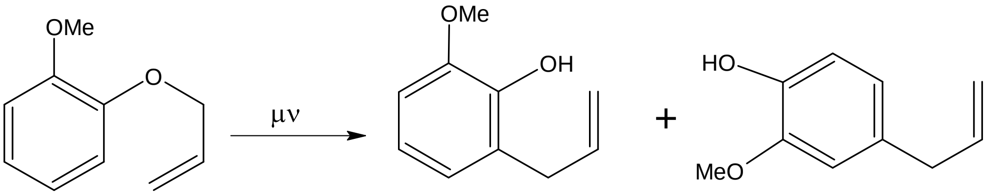


Similar result on much larger scale has been reported using a continuous flow microwave system by Chen *et. al.*, 1990.

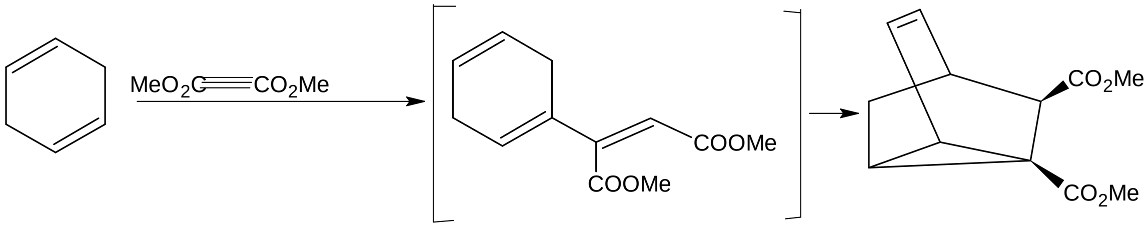
An example of alkyl ether cleavage to the corresponding phenol has been reported. (Linders *et. al.*, 1988). Dearylation using KOH in glycol gave the desired phenol under microwave irradiation conditions.



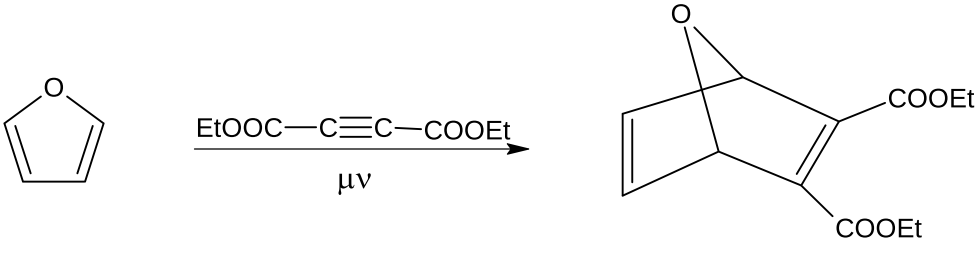
Gigure *et. al.*, (1986) observed the rearrangement of allyl ether to ortho-and para-products in 12 minute (71%) as compared to conventional heating for 12 hours. In DMF solution, an 87% yield was obtained in 90 seconds upon microwave irradiation.



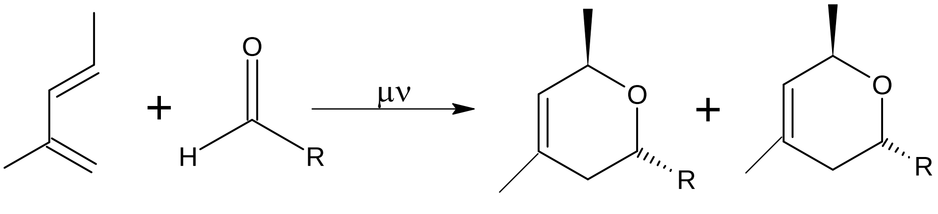
Giguere *et. al.,* (1987) reported tandem ñeneò/ intramolecular Diels-Alder reactions of 1,4-cyclohexadiene and mono-and diactivated acetylenes. Analogous reaction with disubstitued bicyclohexa-1,4-dienes regioselectivity produced highly functionalized tetra cyclicadducts.



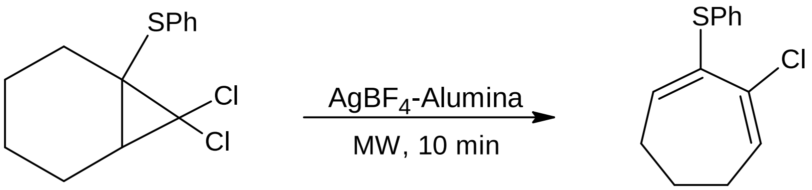
Stambouli *et. al.,* (1991) reported that the Diels-Alder reaction has proceeded much more rapidly using microwave heating. The reaction of furan and diphenyl acetylene dicaroxylate gave the product in 86% yields. The reaction time is 12 times faster than the conventional heating.



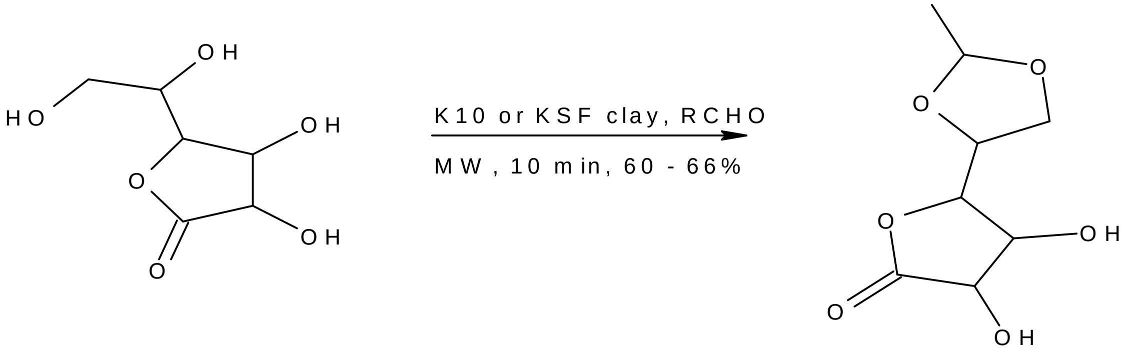
The [4+2] cycloaddition of glyoxal derivatives to 2-methylï 1,3-pentadiens using 72 Watt of microwave power took place faster than under control conditions (Stambouli *et. al.,* 1991).



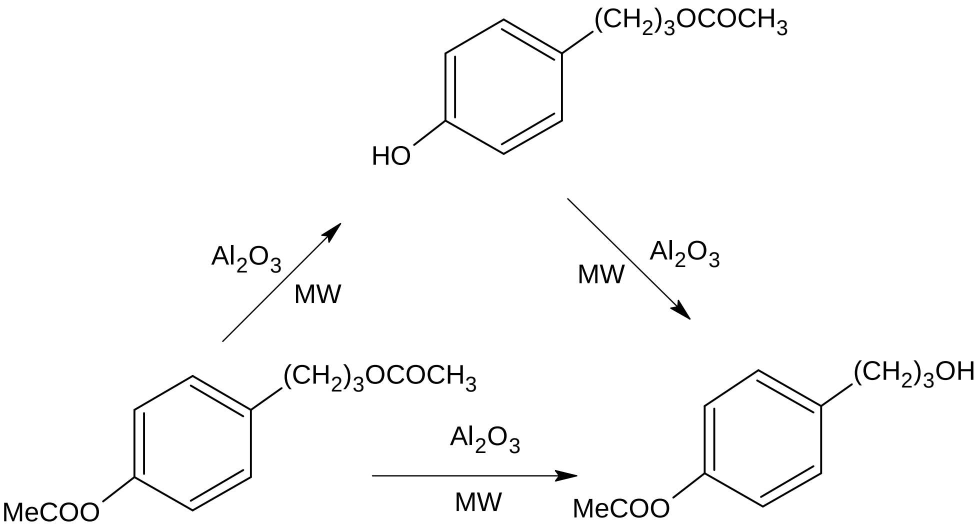
An efficient method of ring expansion transformation is described by Villeman and Labiad (1992) under solvent-less conditions. Solvent-free microwave protocol is superior to the reactions conducted in conventional methanolic solution.



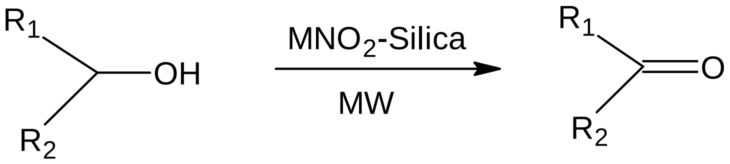
Csiba *et. al* (1993) have efficiently prepared acetals of 1-galactono-1,4-lactone in excellent yields by adsorbing the lactone and aldehyde on montmorillonite K10 or KSF clay followed by exposing the reaction mixture to microwave irradiation.



Varma *et. al.*, (1993*a*) have described the utility of recyclable alumina as viable support surface for deacylation reactions where in the deprotection of alcohols is possible under solvent-free condition on neutral alumina using microwave irradiation. Chemeselectivity between alcoholic and phenolic groups in the same molecule is achievable simply by changing the reaction time; the phenolic acetates are deacetytated quicker than their alcoholic analogues.

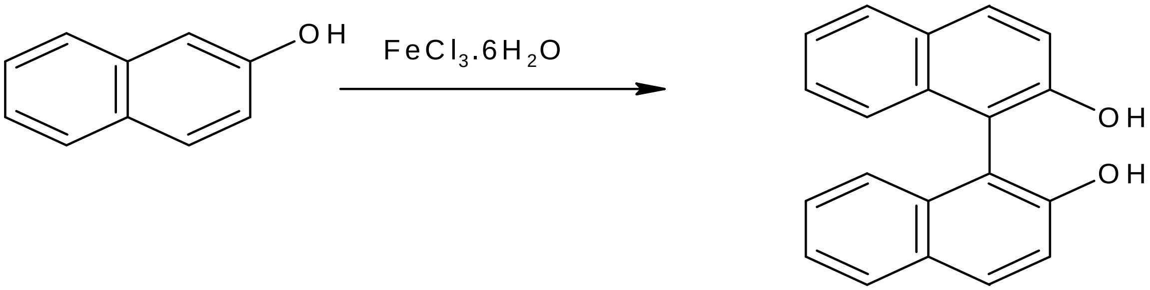


Various reagents involving metal salts have been extensively used as oxidative reagents in organic synthesis e.g. potassium permanganate, manganese dioxide, and chromium trioxide, potassium dichromate and potassium chromate. These reagents adsorbed on solid support such as silica, clay (bentonite) or alumina have been used for the oxidation of alcohol to carbonyl compounds (Gomez-Lara *et. al*., 2000; Ousaid *et. al.,* 1994)

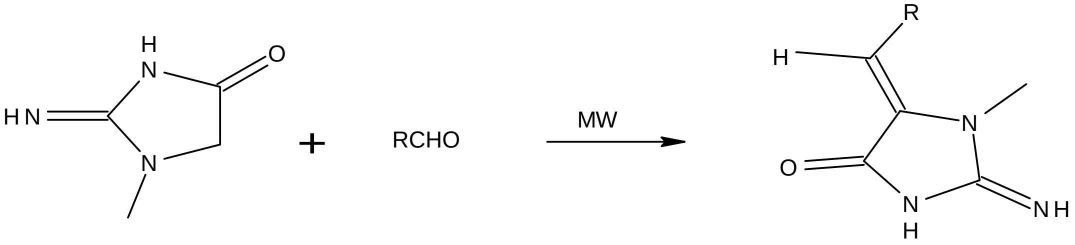


. Ammonium formate has been used for alliylic reduction (Bose *et. al*., 1994) and the protocol has subsequently been adapted for the reduction of imines and in halogenation of aryl halide in presence of 10% Pd/C.

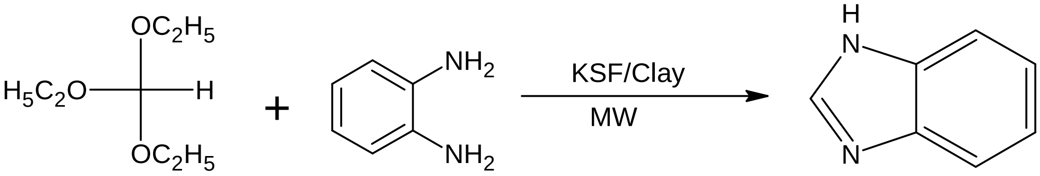
Villemin and Sauvaget (1994) reported that the β-napthols undergo a quick and efficient method of self-coupling reactions in the presence of iron (II) chloride, $FeCl_3.6H_2O$, under focused microwave irradiation in solvent free conditions when compared to classical heating mode.



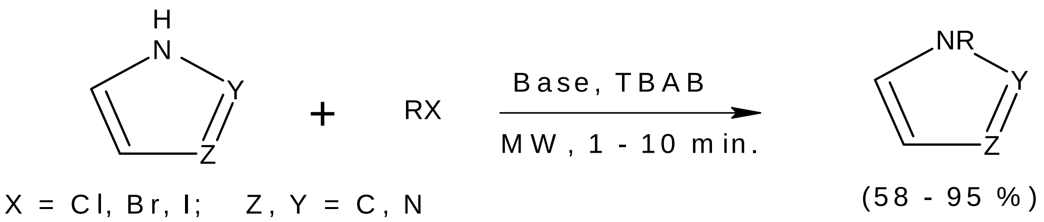
Villemin and Martin (1995) reported the expeditious Knoevenagel condensation of creatinine, with aldehyde has been achieved using focused microwave irradiation (40-60 W) under solvent-free conditions at 160-170 ^{O}C.



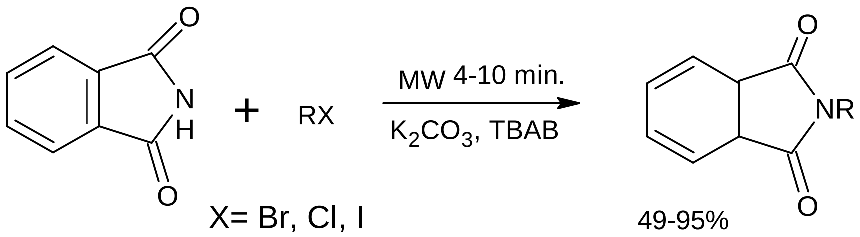
Villiemin *et. al.,* (1996) reported the condensation reaction of *o*-phenylenediamine with ortho esters in the presence of KSF clay under either refluxing conditions in the toluene or solvent free conditions using MW irradiation to afford corresponding benzimidazoles.



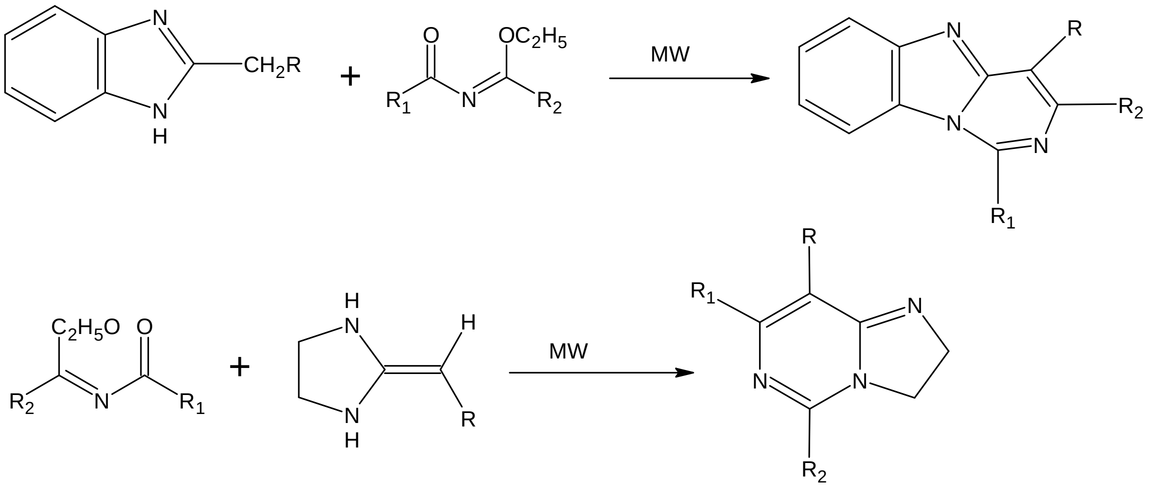
Bogdal and coworkers (1997) reported solvent free N-alkylation reactions, which involve the use of phase transfer reagent, tetrabutylammonium bromide (TBAB), under microwave irradiation conditions. Subsequently, the approach has been extended to a variety of hetrocycles e.g. carbazoles, azaheterocycles.



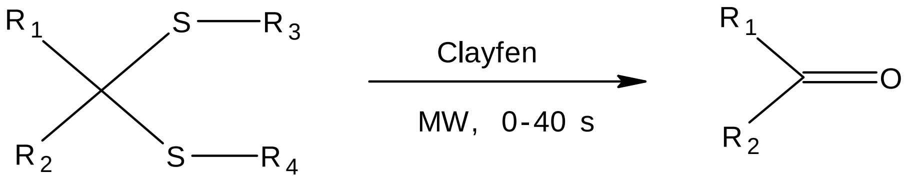
Bogdal and coworkers (1996) reported a new method of synthesis of N-alkylphthalimides *via* alkylation of phthalimide in dry media under microwave irradiation. The reactions were carried out with high yield (49- 95 %) by simple mixing of phthalimide with an alkyl halide, which adsorbed on potassium carbonate.



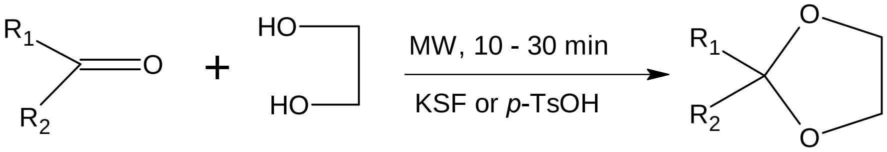
A rapid microwave assisted one pot synthesis of pyrimidino [1,6-*a*] benzimidazoles or imidadzoles and 2,3-dihydroimidazo [1,2-*c*] pyrimidinien from N-acylimidates and activated 2-benzimidazoles or imidazolines, ketene aminals respectively have been achieved in enhanced yields (Rahmouni *et . al.*, 1996).



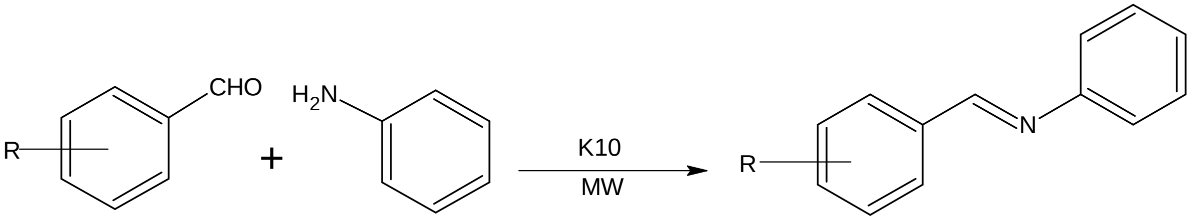
Varma and Saini (1997*a*) reported the processes for the regeneration of carbonyl compounds, the cleavage of acid and base stable thioacetals and thioketals using clayfen as adsorbent in high yields whereas conventionally it require heavy metals such as Hg^{2+}, Ag^{2+}, Cd^{2+}, Ti^{2+} and reagents such as benzeneseleninic anhydride.

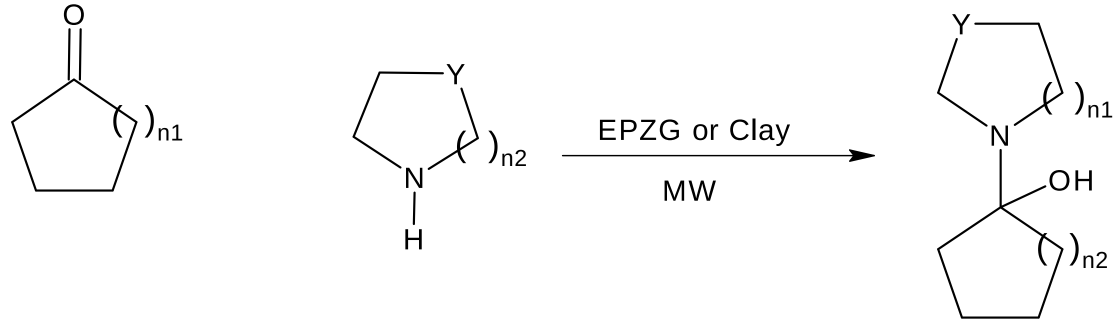


Perio *et. al*., (1997) prepared the acetals and dioxolane derivatives of aldehyde and ketones using orthoformates, 1,2-ethanedithol or 2,2-dimethyl-1,3-dioxolane in acid catalyzed reactions that proceed in the presence of p-toluenesulfonic acid (p-TsOH) or KSF clay under solvent free condition, the yield obtained with microwave method are better than those obtained using conventional heating in an open bath.

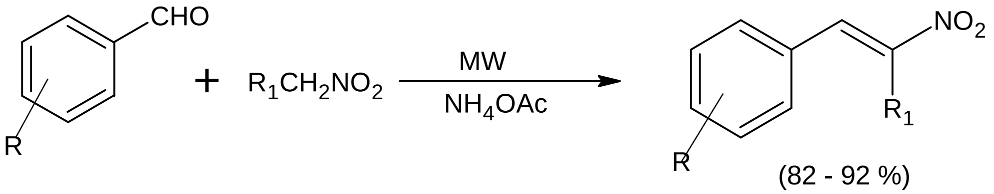


Varma *et. al*., (1997*b*) reported the rapid synthesis of imines and enamines *via* the reaction of primary and secondary amines with aldehyde and ketones, respectively using montmorillonite K10 clay or EPZG R as adsorbent. The formation of polar transition state intermediates is proposed to be responsible for rapid synthesis.

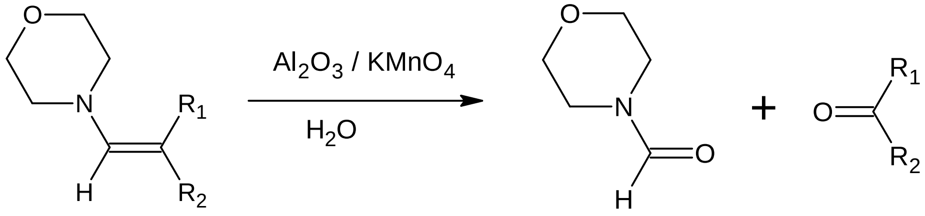




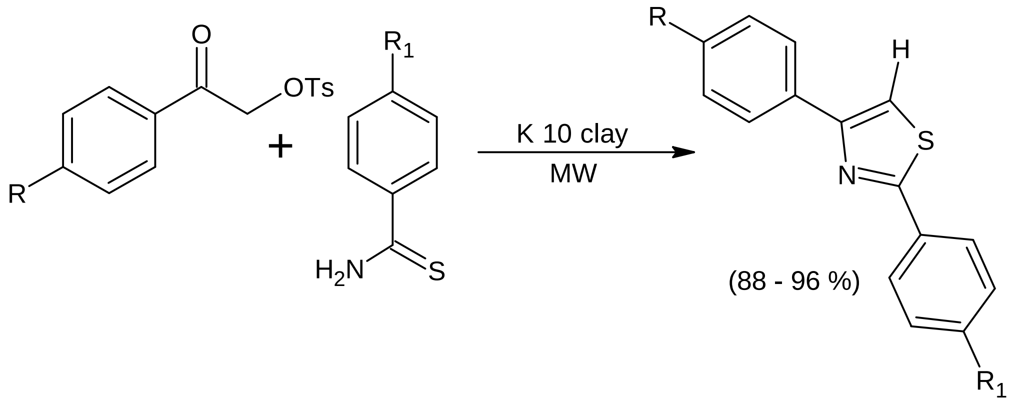
Varma and co-workers (1997*c*) studied the Henry reaction, which involve the condentation of nitroalkanes usage of large amount of polluting nitrohydrocarbons, which are normally used in reactions such as cycloaddition, reduction and oxidation. The Ŭ, ɓ-unsaturated nitroalkenes have been used for the synthesis of vast array of functional groups such as nitroalkanes, N-substituted hydroxylamines, amines ketones, oximes and Ŭ-substituted oximes and ketones (Varma, 1986; Kabalka, 1987, Kabalka, 1990).



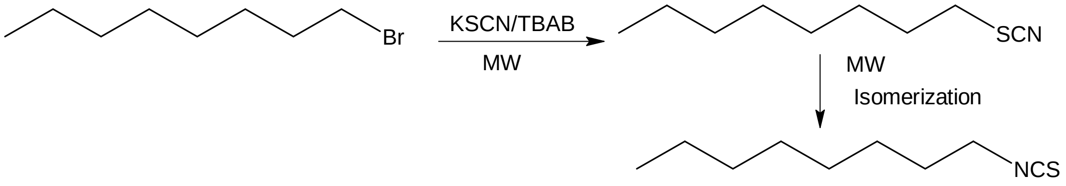
Under solvent-free conditions, Benhaliliba group (Benhaliliba *et. al.*, 1998) has successfully oxidized Ŭ,ɓ-disubstituted enamines into carbonyl compounds with $KMnO_4$-Al_2O_3 in domestic (225 W, 82 ^{O}C) as well as in focused (330 W, 140 ^{O}C) microwave ovens. The yields are better in the latter case whereas no ketone formation is observed when the same reactions are conducted on oil bath at 140 ^{O}C.



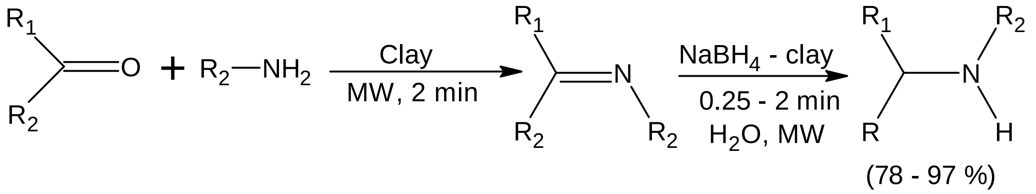
Thiazole and its derivatives are simply obtained by the reaction of Ŭ-tosyloxyketones, which are generated *in situ* from aryl methyl ketones and [hydroxyl (tosyloxy) iodo] benzene (HTIB) with thioamides in the presence of K10 clay using microwave irradiation in the process that is solvent-free. (Varma *et. al.*, 1999*d*)



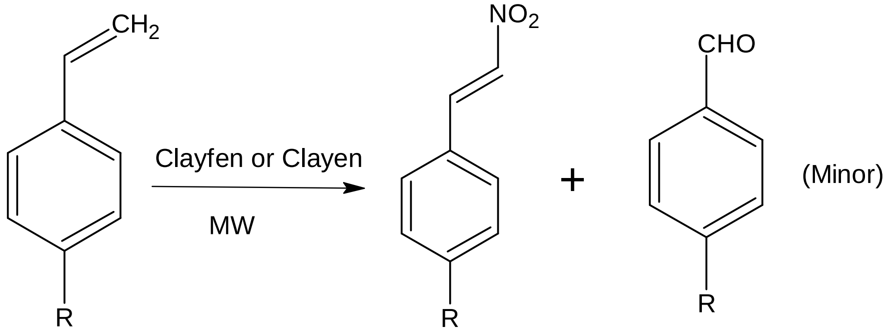
Vass and coworkers (1998) have explained the utility of non-traditional support, which are chemically inactive and couple poorly with microwave. In the presence of a phase transfer catalyst, tetrabutyl ammonium bromide (TBAB) on sodium chloride surface, octyl bromide undergoes thiocyanation reaction with potassium thiocyanide and further isomerizes to isothiocynate under microwave irradiation in excellent yields.



Varma and Dahiya (1998*a*) reported the reductive amination of carbonyl compounds using solvent-free reductive amination procedure for carbonyl compounds employing wet montmorilonite K10 clay supported sodium borohydride facilitated by microwave irradiation. The yields obtained were high as compared to the conventional method, which involve the use of sodium cyanoborohydride, sodium triacetoxy borohydride or $NaBH_4$ coupled with sulphuric acids. These reagents either produced waste stream or involve the use of corrosive acids.

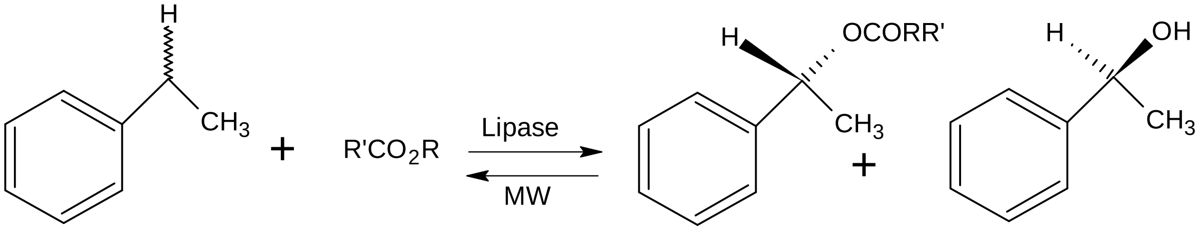


Varma and coworkers (1998*b*) have developed a solid-state synthesis of β-nitrostyrenes using readily available styrene and its substituted derivatives and inexpensive clay supported nitrate salts, clayfen and clayan. In the case of clayan intermediate heating for 30 sec. is responsible for fast reaction.

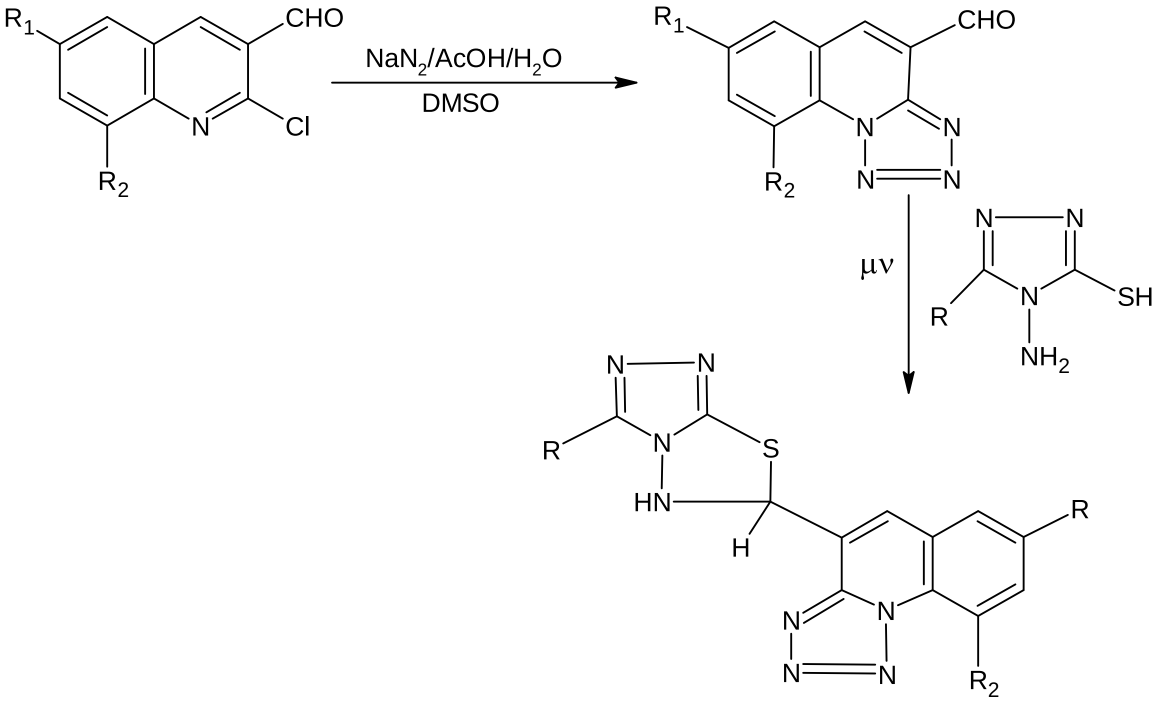


In traditional synthetic transformation, enzymes are normally used in organic or aqueous solvent at moderate temperature to preserve the activity of enzymes, these reactions that require a longer time. In view of the newer development that immobilizes enzymes on solid supports, they are now amenable to operate at relatively higher temperature reaction with adequate p^H control. The application of microwave irradiation has been investigated with two enzymes system namely *Pseudomonas lipase* dispersed in Hyplo super cell that essentially consist of diatomeous silica around p^H (8.5-9.0) and commercially available SP 435 Novozym (*Candida antarctica* lipase grafted on an acrylic resin).

A comparison of the microwave assisted reaction with conventional heating revealed enhanced enantioselectivity for the former presumably due to efficient removal of low molecular weight alcohols or water upon exposure to microwave or alternatively an etropic effect due to dipolar polarization which induces a previous organization of the system. Thermostable enzymes such as crude homogenate of *Sulfolobus solfactaricus* and recombinant β-glucosidase from *Pyrococus furiosus* have been successfully applied to transglycosylation reaction where recycling of the biocatalyst is feasible (Gelo-pijic *et. al.,* 1996)



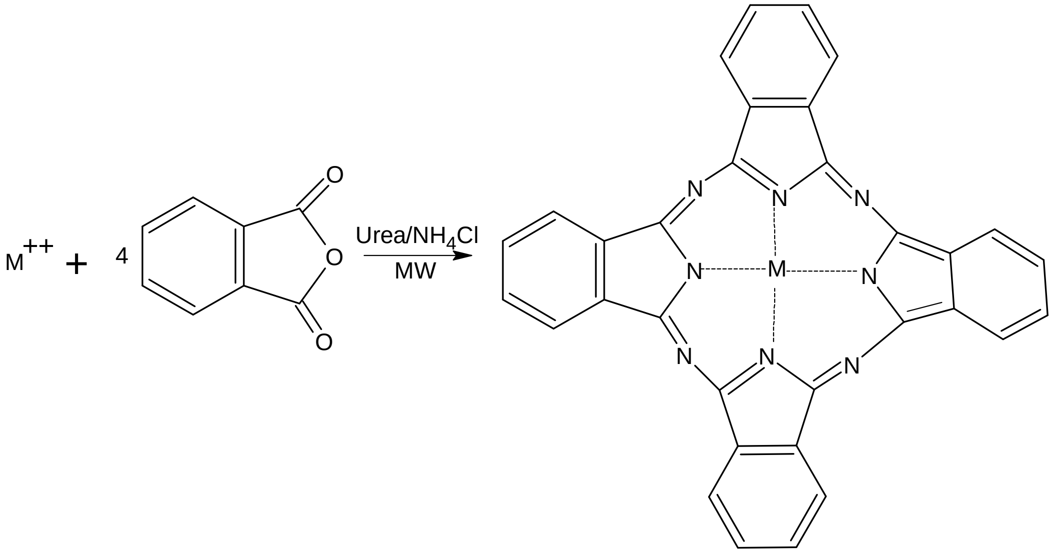
Gupta *et. al*., (2000) synthesized a series of Novel 7/9-substituted-4(3-alkyl/aryl-5,6-dihydro-*s*-triazolo[3,4-*b*][1,3,4]thiadiazolo[1,5-*a*]quinolines by the condensation of 7/9-substituted-4-formyltetrazolo[1,5-*a*] quinolines with 5-substituted 4-amino-3-mercapto-1,2,4-triazoles under microwave irradiation using basic alumina as solid support. The synthesized compound have been characterized and screened for their antifungal, antibacterial and antinflammatory activities.



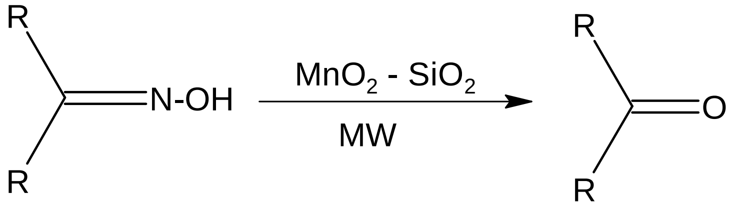
Kappe *et. al*., (2000) have prepared monastrol, the kinesis EG5 inhibitor, under microwave dielectric heating. The inhibitor was synthesized *via* microwave assisted

Bignelli reaction, and was obtained in a higher yield and improved purity compared to traditional heating.

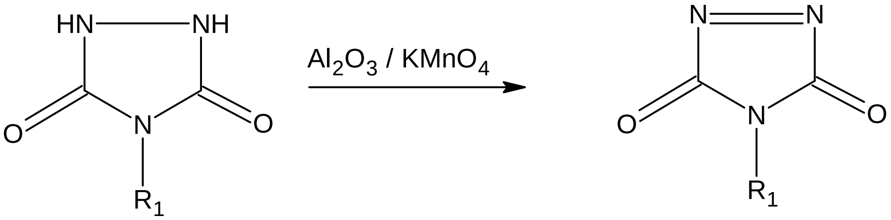
The phthalocyanine complex of Ru, Rh,Cl, Pt and Pd are prepared by Shaabani *et. al.,* (2001) from phthalic anhydride and the corresponding metal salts by exposing to microwave radiation under solvent-free conditions. The reaction time was found to be reduced dramatically and 12-15 % yields of the product were obtained.



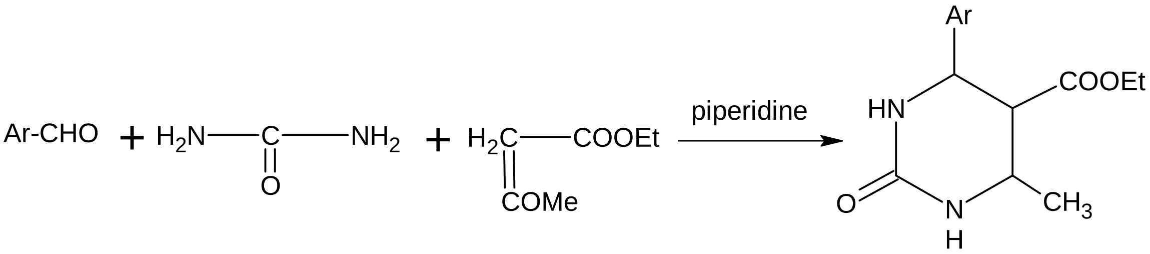
Khadilkar and Madyar (2002) reported an efficient and convenient method for solvent free dry state conversion of oximes to corresponding carbonyl compounds using silica supported MnO_2 under microwave irradiation.



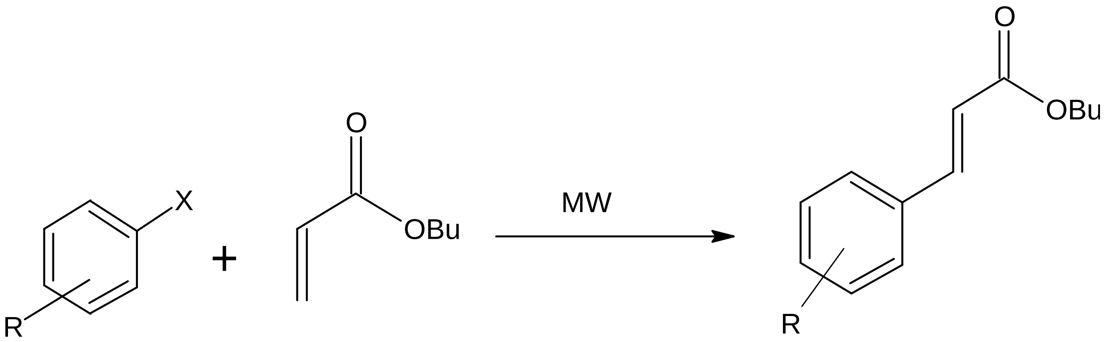
Hajipour *et. al*., (2002) reported the oxidation of urazole to trizolinediones under solvent free conditions using permanganate and alumina-supported permanganate. Treatments of urazoles with $KMnO_4$ led to a simple and mild oxidation to triazolinediones. When $KMnO_4$ was used doped on Al_2O_3, the reaction rate increased and higher yield of product were obtained.



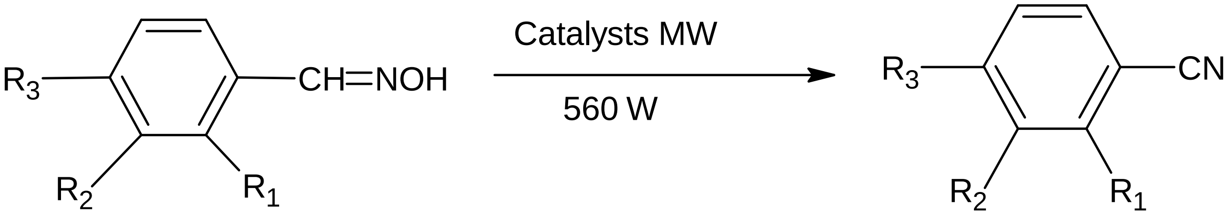
Kumar *et. a*l., (2002) reported the synthesis of 6-methyl-4-substituted phenyl-2-oxo-1,2,3,4-tetrahydropyrimidin-5-carboxilic acid ethyl ester by the reaction of aromatic aldehydes, urea and ethyl acetoacetate in presence of piperidine as catalyst. Methyl-4-substitutedphenyl-2-thioxoï 1,2,3,4-tetrahydropyridin-5-carboxlic acid ethyl ester was also prepared substituting urea with thiourea under microwave irradiation. Potent Ca^{2+}channel antagonistic activity has been evaluated.



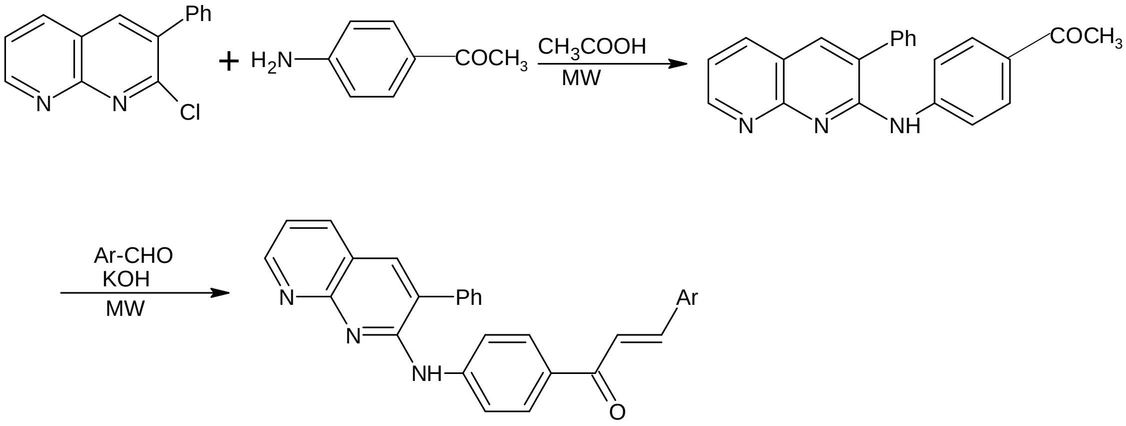
Larhead *et. al.,* (2002) reported the first palladium catalyzed Heck arylations in ($[BMIM]^+[PF_6]^-$). The couplings were performed in sealed tubes within 5-45 minutes of heating. The phosphine free ionic liquid catalyst phase could be recycled in five successive 20 min reactions at 180 ^{O}C without significant reduction in yield.



Microwave assisted synthesis of nitriles by dehydration of aldoximes over heterogeneous environmentally benign Na_2SO_4 (anhyd.) and $MgSO_4$ (anhyd.) catalyst in dry media under MW irradiation in very short times was reported by Dewan *et. al*., (2002).

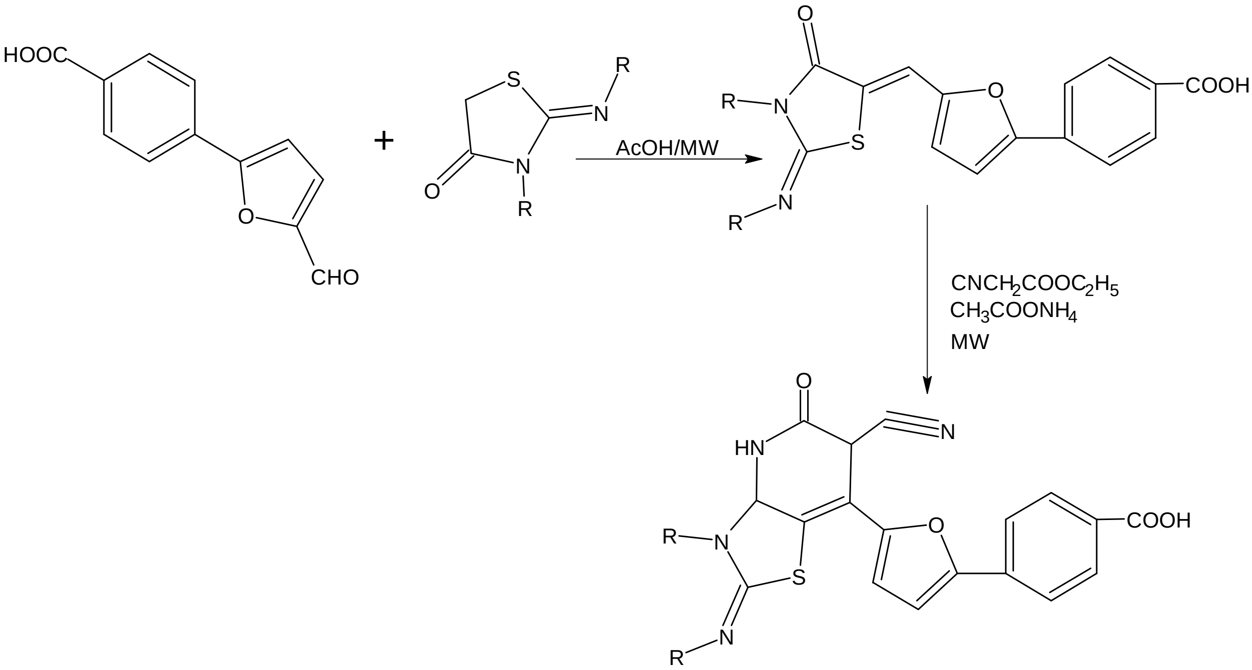


Mogilaiah and Kankaiah (2002a) reported the fast method of Claisen-Schmidt condensation of 2-(4-acetylphenylamino)-3-phenyl-1,8-napthyridin with various aromatic aldehydes under MW irradiation using solid KOH in the absence of any solvent.

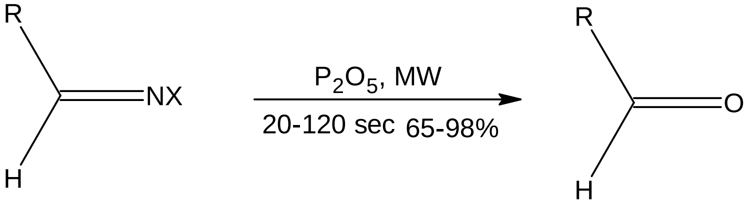


Zhang A and Neumeyer *et. al.,* (2003) have described the use of microwave synthesis in the highly efficient preparation of 3-cyano-3-desoxy-10-ketomorphinans, an important precursor for a series of opioid receptor agonists. Wide ranges of 3-cyano-3-desoxy-10-ketomorphinans were obtained from their triflate precursor in 86-94% yield after 15 minutes at 200 ^{O}C in the presence of $Zn(CN)_2$ and palladium tetrakistriphenylphosphine in DMF.

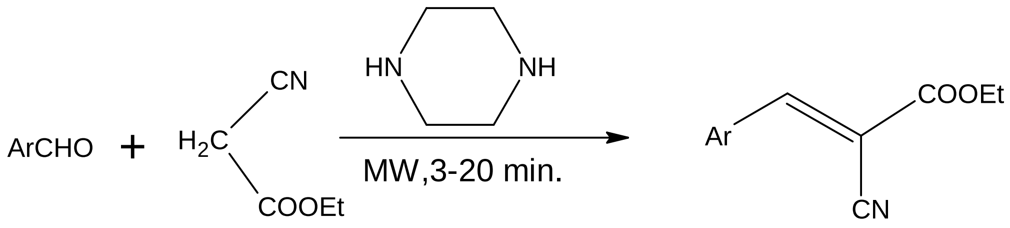
Sodha *et. al.*, (2003) reported the reaction of *p*-(5-formylfuran-2-yl) benzoic acid with substituted thiozolidinones followed by condensation with ethyl cynoacetate in the presence of NH_4OAc leading to the formation of 4-[5-(6-cyano-oxo-3-phenyl-2-phenylimino-2,3,4,5,6,7-hexahydrothiazolo(4,5-*b*)pyridine-7-yl)furan-2-yl] benzoic acids using microwave irradiation and conventional heating. The reaction rate was found to be enhanced 120 times and better yields when using microwave irradiation as compared to classical heating.Antimicrobial activity of there thiazolidinanones also reported.



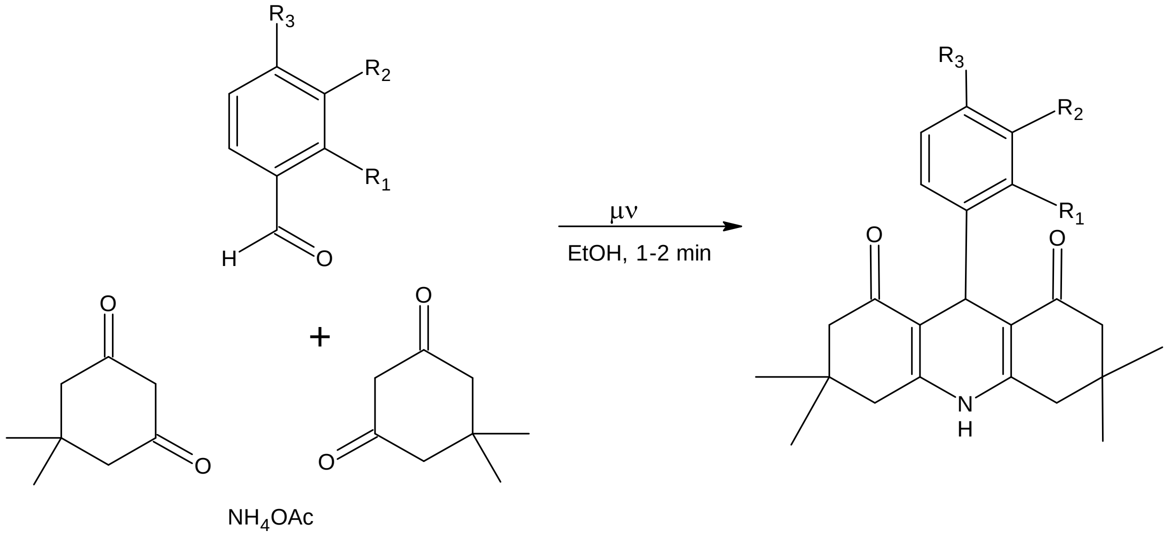
Banerjee and Mitra (2003) reported the regeneration of aldehydes from oximes, semicarbazones, and phenylhydrazones using phosphorous pentaoxide in solvent free condition using microwave irradiation.



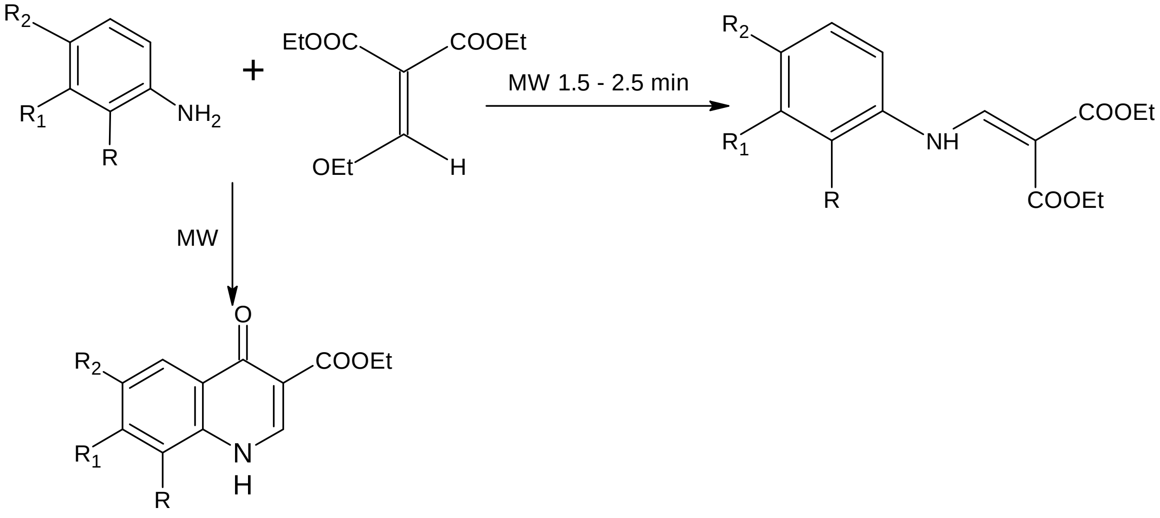
Mitra *et. al.*, (2003) reported the Knovenagel condensation of ethyl cyanoacetate and aromatic aldehyde by using piperazine as a catalyst with rate enhancement by microwave irradiation under solvent free condition.



Nandagopal *et. al.*, (2003) reported microwave-assisted one pot synthesis of 9-aryl-3,3,6,6ï tetramethylï 3,4,6,7,9,10-hexahydro-1,8 (2*H*,5*H*)- acridinedione.

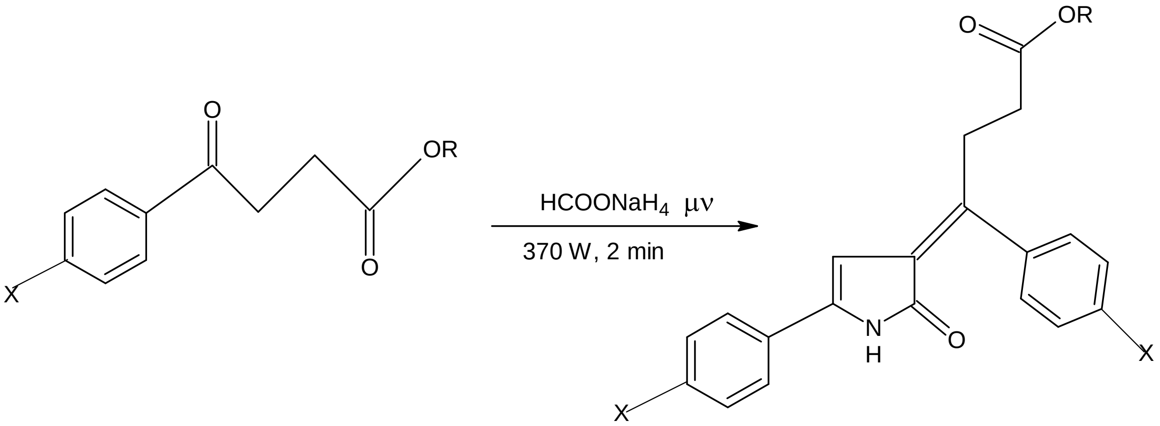


A single step Gould-Jacob reaction between aromatic amines and diethyl ethoxy methylene malonates (EMME) for the synthesis 4-quinolines under solvent free microwave irradiation has been carried and compared with classical heating by Dave and Joshipura (2002). The authors observed that 15 to 16 times faster reaction rate and 80-98% yields.

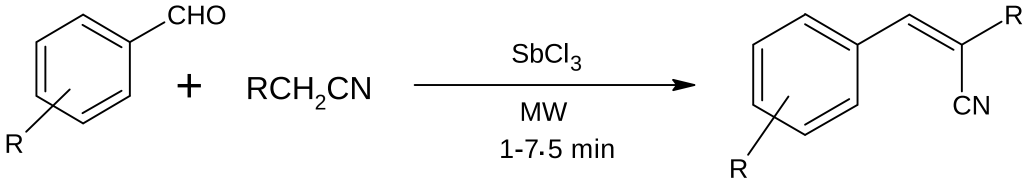


Fisher-indole synthesis in less then 30 seconds has been reported by Sridhar (1996) using microwave irradiation.

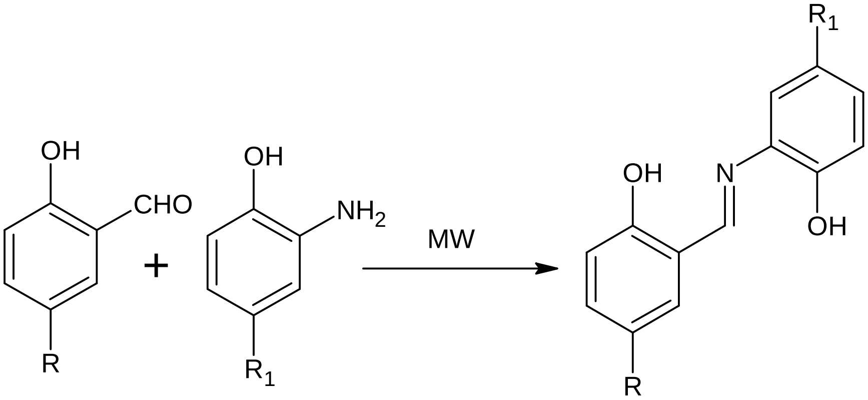
Rao and Senthilkumar (2004) reported the Microwave-mediated three component condensation of 4-aryl-4-oxobutanoates with ammonium formate furnishing 3-methylidene-5-phenyl-2,3-dihydropyrrolidones in good yield with in 2 min. The pyrrolidone products were characterized on the basis of spectral data and X-ray crystal structure analysis.



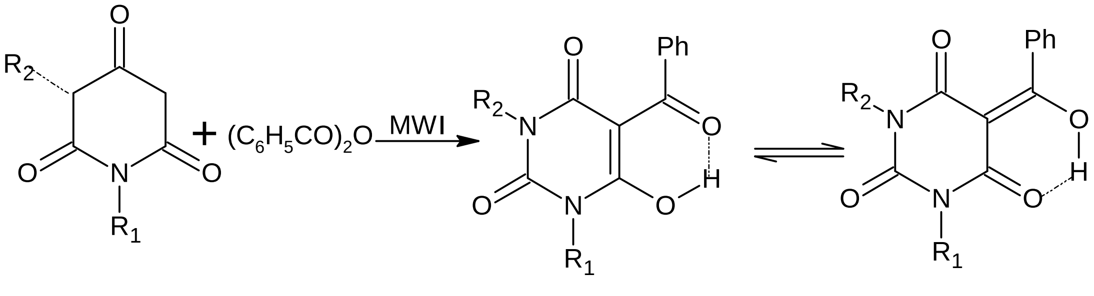
Mitra *et. al.,* (2005) reported rapid microwave assisted Knoevenagel condensation exploiting antimony trichloride under solvent free condition. Several aromatic aldehydes condensed with malononitrite and ethyl cyanacetate with in a few minute in high yields.



Sridharan *et. al.,* (2005) reported microwave assisted synthesis of 4-alkyl-2-([5-substituted-2-hydroxyphenyl]-iminomethyl) benzenols in excellent yields from corresponding aldehyde and amines by microwave irradiation. The resultant Schiff bases have been characterized by spectral data.



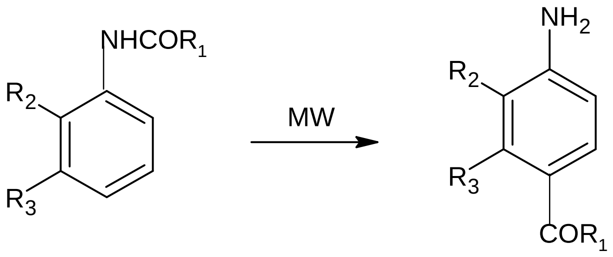
Singh and Paul (2005) reported the synthesis of N-mono-substituted and N,N`-disubstituted barbituric acid on treatment with benzene anhydride /acetic anhydride under microwave irradiation without using any solvent. This provided a convenient methodology for the synthesis of 5-benzoyl/acylbarbituric acids in moderate high yields.



R_1= H, CH_3, $-CH_2CH_3$, - C_6H_{11}, Ph, CH_2Ph, -CH (CH_3) Ph

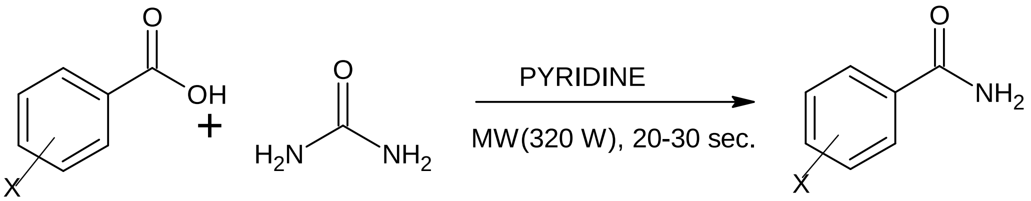
R_2=H, CH_3,

Easwaramurthy *et. al.,* (2005) developed a rapid, cleaner, cost effective and eco-friendly method for the synthesis of- 4-aminoaryl ketones and- 4-aminoaryl amides in solvent-free conditions using solid supports under microwave irradiation.



R_1=CH_3, Ph, NH_2; R_2=H, CH_3, Cl; R_3=H, NO_2, Cl, OH

A very rapid and efficient procedure for the synthesis of primary amides from carboxylic acids and urea in the presence of pyridine under microwave irradiation is described by Pasha and Jayashankara (2005). Various amides were prepared with in 20-30s and in excellent yields.



X= CH3, Cl, OH, NO_2, OCH_3

CHAPTER-III

MATERIAL AND METHODS

The present research work has been carried out with the objective to prove the superiority of microwave-assisted organic synthesis over traditional methods of organic synthesis of different organic compounds. The details of materials and methods are presented in this chapter.

3.1 SOLVENTS AND CHEMICALS

The solvents *viz.* methonal (GR, Merk), acetone (Qualigens), hexane (Qualigens), dehydrated alcohol (Bengal Chemicals and Pharmaceuticals), ethyl acetate (Qualigens) and dichloromethane (SRL) were used as supplied. Double distilled water was used through out the study for washing. Chemicals viz. hydrazine hydrate (Qualigens), thionyl chloride (Spectrochem), 4-cresol (Merck), potassium thiocyanate (BDH), ethylinediamine (SRL), benzaldehyde (E.Merck), 2-nitrobenzaldehyde (SDH), 4-hydroxybenzaldehyde (Qualigens), 4-chlorobenzaldehyde (SDH), 4-methoxybenzaldehyde (SRL), 2-hydroxybenzaldehyde (SRL), 4-N,N-dimethylaminobenzaldehyde (NICE), 4-chlorobenzoic acid (Qualigens), acetophenone (Merck), 4-methoxyacetophenone (SDH), 4-chloroacetophenone (BDH), 3,4-dimethoxybenzaldehyde (SRL), hydroxylamine hydrochloride (Qualigens), formaldehyde solution (BDH), sodium hydroxide (Qualigens), silica gel for column chromatography (SRL), silica gel for Thin Layer Chromatography (Qualigens), Alumina (acidic, basic, neutral (SRL) were used as supplied.

3.2 MICROWAVE DEVICE

Unmodified Kitchen microwave (BPL-Sanyo Utilities and Appliances Ltd., Model BMO: 700T) was used throughout the course of present research work. The magnetron operates at 2.45 GHz frequency and the instrument has a control for time of irradiation.

3.3 SYNTHESIS OF ARYLIDENE HYDRAZINES

3.3.1 Synthesis of benzoyl hydrazine

Equimolar quantities of ethyl benzoate (1.50 g, 0.01mol) and hydrazine hydrate (0.50 g, 0.01mol) were dissolved in methanol (3 ml). To this solution was added neutral alumina (3 g) so that whole of the solution is adsorbed on it. The adsorbed material was dried in air and irradiated in a microwave oven for 4 min. in intervals of 30 sec. The progress of reaction was monitored with the help of TLC. After the completion of reaction, alumina was washed with diethyl ether. The product, thus obtained, was purified by crystallization from ethanol. m.p. 112-3 ^{O}C (Lit. m.p. 112.5 ^{O}C, Heilborn and Bunberry, 1965), yield 1.86 g, 93 %.

3.3.2 Synthesis of N-benzylidene-N'-benzoylhydrazine:

Benzoyl hydrazine (1.36 g, 0.01 mol) and benzaldehyde (1.06 g, 0.01 mol) were dissolved in methanol (3 ml) in equimolar quantity. Acidic alumina (3 g) was added to this solution so that whole of solution was adsorbed on it. The adsorbed material was dried in air and irradiated in microwave oven for 2 min. in intervals of 30 sec. The progress of reaction was monitored by TLC. After the completion of the reaction, alumina was washed with methanol. The product, thus obtained, was purified by crystallization from ethanol. m.p. 205-6 ^{O}C (Lit m.p. 205 ^{O}C, Charonnat and Boime 1953), yield 2.1 g, 93%.

3.3.3 Synthesis of N-(2'-Nitrobezylidene)-N'-Benzoylhydrazine

Equimolar quantities of benzoyl hydrazine (1.36 g, 0.01mol) and 2-nitrobenzaldehyde (1.51 g, 0.01 mol) were dissolved in methanol (3 ml). In this solution, acidic alumina (3 g) was added so that whole of the solution was adsorbed on it. The adsorbed material was dried in air and irradiated in a microwave oven for 5 min. in intervals of 30 sec. The progress of the reaction was monitored by TLC. After the completion of the reaction, alumina was washed with methanol. The product, thus obtained, was crystallized from ethanol. m.p. 190-1 ^{O}C (Lit m.p. 190 ^{O}C, Charonnat and Boime 1953), yield 2.5 g, 92 %.

3.3.4 Synthesis of N-(4'-methoxybenzylidene)-N'-benzoyl hydrazine

Benzoyl hydrazine (1.36 g, 0.01mol) and 4-methoxybenzaldehyde (1.36 g, 0.01 mole) were dissolved in methanol (3 ml). Acidic alumina (3 ml) was added to this solution for adsorption. The adsorbed material was dried in air and irradiated in microwave oven for 4 min. in intervals of 30 sec. The progress of reaction was monitored with the help of TLC. After the completion of reaction, alumina was washed with methanol. The product, thus obtained, was crystallized from ethanol. m.p. 147 ^{O}C (Lit m.p. 147 ^{O}C, Aggarwal *et. al.*, 1929) yield 2.3 g, 90%.

3.3.5 Synthesis of N-(4'-hydroxybenzylidene)-N'-benzoyl hydrazine

Equimolar quantity of benzoyl hydrazine (1.36 g, 0.01mol) and 4-hydroxybenzaldehyde (1.22 g, 0.01mol) were dissolved in methanol (3 ml). Acidic alumina (3 g) was added to this solution so that whole of solution was adsorbed on it. The adsorbed material was dried in air and irradiated in microwave oven for 5 min in intervals of 30 sec. The progress of the reaction was monitored by TLC. After the completion of reaction alumina was washed with methanol. The product, thus obtained, was purified by crystallization from ethanol. m.p. 204 ^{O}C, yield 2.4 g, 90%.

Similarly N-(4-N,N-dimethylbenzylidine)-Nôbenzoyl hydrazine was prepared by using method used above. m.p. 177-8 ^{O}C (Lit m.p. 177 ^{O}C, Charonnat and Boime 1953). The physical data is tabulated below.

Aldehyde	**m.p(^{O}C)**	**Yield (%)**	**Time MW (min.)**	**Conventional Time (hr.)**
Benzaldehyde	205-6	93	2	3
4-methoxybenzaldehyde	147	92	4	3
2-nitrobenzaldehyde	190-1	90	5	3
4N,N-dimethylbenzaldehyde	177-8	80	4	3
4-hydroxy benzaldehyde	204	90	5	3

3.3.6 Synthesis of 4-Chlorobenzoyl Hydrazine

Equimolar quantities of 4-chloro ethylbenzoate (1.59 g, 0.01 mol) and hydrazine hydrate (0.50 g, 0.01 mole) were dissolved in methanol (3 ml). This solution was added neutral alumina (3.5 g) so that whole of the solution was adsorbed. The adsorbed material was dried in air and irradiated in a microwave oven for 4 min. in intervals of 30 sec. After the completion of reaction alumina was washed with diethyl ether. The product, thus obtained, was purified by crystallization from methanol. m.p. 210-11 ^{O}C (210 ^{O}C, Heilborn and Bunberry, 1965), yield 91%.

3.3.7 Synthesis of N-benzylidene-N`-4-Chlorobenzoyl hydrazine

A mixture of 4-chlorobenzoyl hydrazine (1.70 g, 0.01 mol) and benzaldehyde (1.06 g, 0.01 mol) was dissolved in a methanol (3 ml). Acidic alumina (3 g) was added to this solution so that the whole of solution was adsorbed on it. The adsorbed material was dried in air and irradiated in microwave oven for 3 min. in intervals of 30 sec. The progress of reaction was monitored by TLC. After the completion of reaction the alumina was washed with methanol. The product, thus obtained, was purified by crystallization from ethanol. m.p. 224-6 ^{O}C (Lit m.p.226 ^{O}C, Dave *et. al.*, 1984), yield 2.55 g, 92%.

3.3.8 Synthesis of N-(4'-methoxybenzylidene)-N'-4-Chlorobenzoyl hydrazine

Using 4-chlorobenzoyl hydrazine (1.70 g, 0.01 mol) and 4-methoxybenzaldehyde (1.36 g, 0.01 mol) and following similar procedure as mentioned in section 3.3.7 gave the desired product. m.p.198 ^{O}C, yield 2.85 g, 93%.

3.3.9 Synthesis of N-(2-nitrobenzylidene)-N'-4-Chlorobenzoyl hydrazine

Reaction of 4-chlorobenzoyl hydrazine (1.70 g, 0.01 mol) and 2-nitrobenzaldehyde (1.51 g, 0.01 mol) and following similar procedure used above gave the desired product. m.p. 212-5 ^{O}C, yield 2.82 g, 95%.

The authenticity of the synthesized compound was established by comparison with authentic samples which were prepared by heating corresponding aldehyde with benzoyl hydrazine in presence of sodium acetate in ethanol or acetic acid used as solvent.

The reaction time and yields obtained have been compared with the standard reaction times and yields reported earlier.

A comparison of conventional heating and microwave heating method is presented here. The physical data is tabulated below:

Aldehyde	**m.p.(^{O}C)**	**Yield (%)**	**Time MW (min.)**	**Conventional Time (hr.)**
Benzaldehyde	224-6	92	3	3
4- methoxybenzaldehyde	198	93	5	3
2-nitrobenzaldehyde	212-5	95	5	3

3.4 PROTECTION OF CARBONYL COMPOUNDS AS OXIMES

3.4.1 Synthesis of Acetophenone oxime

A solution of acetophenone (2.4 g, 0.02 mole) and hydroxylamine hydrochloride (1.0 g) in water was added to silica supported Na_2CO_3 as adsorbent. The adsorbed material was dried in air and irradiated in a microwave oven for 6 min. in intervals of 30 sec. The progress of reaction was monitored by TLC. After the completion of reaction Na_2CO_3-silica was washed with methanol. The product, thus obtained, was purified by crystallization from ethanol. m.p 58 ^{O}C (Lit m.p. 59 ^{O}C, Mitra *et. al.*, 1999*a*), yield 2.23 g, 92 %.

3.4.2 Synthesis of 4-methoxy acetaphenone oxime

A solution of 4-methoxy acetophenone (3.00 g, 0.02 mole) and hydroxylamine hydrochloride (1.0 g) in water was added to silica supported Na_2CO_3 as adsorbent. The adsorbed material was dried in air and irradiated in a microwave oven for 5 min. in intervals of 30 sec. The progress of reaction was monitored by TLC. After the completion of reaction Na_2CO_3-silica was washed with methanol. The product, thus obtained, was purified by crystallization from ethanol. m.p. 86-7 ^{O}C (Lit m.p. 87 ^{O}C, Mitra *et. al.*, 1999*a*) yield 2.75 g, 91%.

3.4.3 Synthesis of benzaldoxime

A solution of benzaldehyde (2.1 g, 0.02 mole) and hydroxylamine hydrochloride (1.0 g) in water was added to Na_2CO_3-silica as adsorbent. The adsorbed material was dried in air and irradiated in microwave oven 4-5 min in intervals of 30 sec. After the completion of reaction Na_2CO_3-silica was washed with methanol and product, thus obtained, was crystallized by ethanol m.p. 127-8 ^{O} C (Lit m.p. 128 ^{O} C, Smolkova *et. al*., 1980), yield 1.95 g, 93%.

3.4.4 Synthesis of 4-hydroxy benzaldoxime

A solution of 4-hydroxybenzaldehyde (2.4 g, 0.02 mole) and hydroxylamine hydrochloride (1.0 g) in water was added to Na_2CO_3-silica as adsorbent. The adsorbed material was dried in air and irradiated in microwave oven 4 min in intervals of 30 sec. After the completion of reaction Na_2CO_3-silica was washed with methanol and product thus obtained was crystallized by ethanol. m.p. 71-2 ^{O} C (Lit m.p. 72 ^{O}C, Dewan and Singh 2002), yield 2.30 g, 94%.

The authenticity of the products was established by comparison with authentic samples prepared by conventional method (Vogel, 1978) and the physical data is tabulated below:

Oxime	**m.p (^{O}C)**	**Yield (%)**	**Time MW (min.)**	**Conventional Time (hr.)**
Acetaphenone oxime	58	92	6	2
4-methoxy acetaphenonoxime	86-7	91	5	2
Benzaldoxime	127-8	93	5	2
4-hydroxybenzaldehyde	71-2	94	4	2

3.5 OXIDATION USING ALUMINA AND $KMnO_4$

Preparation of 2,6-diformyl-4-methyphenol

Equimolar quantities of alumina (4 g) and $KMnO_4$ (5 %, 3 g) were mixed in water and dried in air. 4-cresol (1.08 g, 0.01 mole) and formaldehyde (40 %) solution sodium hydroxide (0.40 g, 0.01 mole) were mixed and kept overnight. Alumina-$KMnO_4$ was add to it and irradiated in microwave oven for 4 min. in intervals of 30 sec. The progress of reaction was monitored by TLC. After the completion of the reaction Aluminaï $KMnO_4$ was washed with methanol. The product, thus obtained, was purified by crystallization from ethanol. m.p. 133 ^{O}C (Lit m.p.133 ^{O}C, Gagne *et.al.,* 1981), yield 1.52 g, 92%.

Using alumina doped with $KMnO_4$, 4-Chlorophenol used methylated and oxidized to 2,6ï diformyl-4-Chlorophenol following similar method as discussed above. m.p.126 ^{O}C (Lit m.p. 126 ^{O}C, Weast *et al*, 1964), yield 1.56g, 91 %. By conventional method 2,6-diformyl-4-methyl phenol is prepared.

4-cresol (4.32 g, 0.04 mole) was added to a solution of NaOH (2.0 g) in water (10 ml) and after stirring it for 10 min. formaldehyde solution (8.6 g) was added. The mixture was further stirred and allowed to stand overnight at the room temperature (Lederer-Manarse reaction). The granular 2,6-dimenthylol-4-methylphenol, thus formed, was collected by filtration and washed with saturated sodium chloride (2×40ml) solution. To this product was added water (40 ml) and 33% sodium hydroxide solution (3 ml). The mixture was stirred with an overhead stirrer for 30 min. and *p*-toluenesulfonyl chloride (10 g) dissolved in toluene (15 ml) was added slowly, and the solution was allowed to stir for 20 hr. The mixture was cooled in ice water and toulene (10 ml) was added with tirring after 10 min, additional toulene (20 ml) was added the reaction mixture was stirred for 15 min. and the white solid tosylated derivative was collected by filtration, washed with toluene (20 ml) and dried for 12 hr. The white solid was weighted; acetic acid (14 mol/mol of the tosylated phenol) and sodium dichromate (1 mol/mol of the tosylated phenol) were used for the oxidation. Approximately one fourth of the acetic acid was added to the tosylated phenol. The mixture was heated to reflux with stirring (110-116 ^{O}C) the dichromate acid solution was added drop wise with stirring to the tosylated phenol over 30 min. After the addition was completed, stirring at reflux was continued for 10 minute solution was then allowed to cool slowly to temperature the crystal, thus formed, were collected by filtration and washed with water until most of the green colour was gone. The dry tosylated dialdehyde (5.6 g) was added slowly to concentrated sulphuric acid (5 ml) and the solution was stirred for 1 hr. Ice water slurry was added to the acid solution until the total volume reached 100 ml. After all the ice melted, the precipitate was collected by vaccum filtration washed with water a dried over night. The crude product was recrystallized from toluene; yielding pale yellow needles melting point 133 ^{O}C, yield 1.8 g, 27%.

2,6-diformyl-4-methylphenol prepared by microwave irradiation method was formed to be identical with this product. m.m.p. 132-3 ^{O}C.

3.6 CYCLIZATION REACTIONS – SYNTHESIS OF BRIDGEHEAD NITROGEN HETEROCYCLES

3.6.1 Preparation of bezoyl thiosemcarbazide

A mixture of benzoyl hydrazine (4.1 g, 0.03 mol) and potassium thiocyanate (4.86 g, 0.06 mol), concentrated HCl (5 ml) and water (20 ml) was heated, under reflux, for about 1 hour. The reaction mixture was cooled and white solid, thus separated and crystallized from ethanol m.p. 180 ^{O}C (Lit. m.p. 180-1 ^{O}C, Vogel, 1978) yield, 3.9 g.

Similarly *p*-chlorobenzoyl thiosemicarbazide is prepared. m.p. 200 ^{O}C, yield, 3.5 g.

3.6.2 Synthesis of 3-phenyl-*s*-triazolyl-5-thione

Benzoyl thiosemicarbazide (3.56 g, 0.02 mol) and potassium hydroxide (2.0 g) in ethanol (10 ml) was heated under reflux for 3 hr. The reaction mixture was filtered to remove impurities and diluted with water and acidify with dilute acetic acid. The solid, thus separated, was filtered, washed with water and crystallized from ethanol. m.p. 201-2 ^{O}C (Ali *et. al.*, 1976), yield 3.2 g.

Similarly 3-*p*-chlorophenyl-*s*-triazolyl-5-thione was prepared by following the similiar procedure used above.

3.6.3 Synthesis of 2-phenyl-5,6-dihydrothiazolo[3,2-*b*]-*s*-triazole

Phenyl-*s*-traizolyl thione (1.6 g, 0.01 mol) and 1,2-dichloro ethane (0.98 g, 0.01 mol) was dissolved in a methanol (2 ml). Acidic alumina (3 g) was added to this solution so that the whole of solution was adsorbed on it. The adsorbed material was dried in air and irradiated in microwave oven for 6 min. in intervals of 30 sec. The progress of reaction was monitored by TLC. After the completion of reaction the alumina was washed with methanol. The product, thus obtained, was purified by crystallization from ethanol. m.p. 270-2 ^{O}C (Ali *et. al.*, 1976), yield 2.35 g, 90%.

Similarly 2-*p*-chlorophenyl-5,6-dihydrothiazolo[3,2-*b*]-*s*-triazole prepared by following the procedure used above. m.p. 250 ^{O}C, yield 1.94 g, 92 %. The physical data is tabulated below.

R	**m.p. (^{O}C)**	**Yield (%)**	**Time MW (min.)**	**Conventional Time (hr.)**
C_6H_5	270-2	90	6	3
4-Cl C_6H_4	250	92	5	3

3.6.4 Synthesis of 2-phenyl -5,6,7-trihydrothiazino[3,2-*b*]-*s*-triazole

3-Phenyl-*s*-triazolyl-5-thione (1.6 g, 0.01 mol) and 1,3-dibromopropane (2.01 g, 0.01 mol) was dissolved in a methanol (2 ml). Acidic alumina (3 g) was added to this solution so that the solution was adsorbed on it. The adsorbed material was dried in air and irradiated in microwave oven for 5 min. in intervals of 30 sec. The progress of reaction was monitored by TLC. After the completion of reaction the alumina was washed with methanol. The product, thus obtained, was purified and crystallized from ethanol. m.p.195-6 ^{O}C (Ali *et. al.*, 1976), yield 2.98 g, 82%.

Similarly 2-*p*-chlorophenyl-5,6,7-trihydrothiazino[3,2-*b*]-*s*-triazole was prepared by following the procedure used above. m.p. 208-9 ^{O}C, yield 3.65 g, 93%. The physical data is tabulated below.

R	m.p. (^{O}C)	Yield (%)	Time MW (min.)	Conventional Time (hr.)
C_6H_5	195-6	82	5	3
4-Cl C_6H_4	208-9	93	5	3

3.6.5 Synthesis of 3-phenyl-*s*-triazolyl-5-thiolacetic acid

A mixture of phenyl-*s*-triazolyl-5-thione (1.6 g, 0.01 mol) and chloro acetic acid (0.94 g, 0.01 mol) was dissolved in methanol (3 ml). Silica gel (3 g) was added to this solution so that the whole of solution was adsorbed on it. The adsorbed material was dried in air and irradiated in microwave oven for 7 min. in intervals of 30 sec. The progress of reaction was monitored by TLC. After the completion of reaction the alumina was washed with methanol. The product, thus obtained, was purified and crystallized from ethanol. m.p. 210 ^{O}C (Ali *et. al.*, 1976), yield 2.3 g, 91%.

Similarly 3-*p*-chlorophenyl-*s*-triazolyl-5-thiolacetic acid is prepared by following the procedure used above. m.p. 203 ^{O}C, yield 3.2 g 91%. The physical data is tabulated below.

R	m.p. (^{O}C)	Yield (%)	Time MW (min.)	Conventional Time (hr.)
C_6H_5	210	91	7	3
4-Cl C_6H_4	203	91	5	3

3.6.6 Synthesis of 2-phenylthiazolo[3,2-*b*]-*s*-triazol-5-(6*H*)-one

A mixture of 3-phenyl-*s*-triazolyl-5-thiolacetic acid (2.2 g, 0.01 mol) was dissolved in a methanol (3 ml) and acidic alumina (3 g) was added to this solution so that the whole solution was adsorbed on it. The adsorbed material was dried in air and irradiated in microwave oven for 6 min. in intervals of 30 sec. The progress of reaction was monitored by TLC. After the completion of reaction the alumina was washed with methanol. The product, thus obtained, was purified by crystallization from ethanol. m.p. 184-5 ^{O}C (Ali *et. al.*, 1976), yield 2.05 g, 93%.

Similarly 2-*p*-chlorophenyl thiazolo[3,2-*b*]-*s*-triazolo-5-(6*H*)-one was prepared by following the procedure used above. m.p. 215 ^{O}C, yield 2.3 g, 92%. The physical data is tabulated below.

R	**m.p. (^{O}C)**	**Yield (%)**	**Time MW (min.)**	**Conventional Time (hr.)**
C_6H_5	184-5	93	6	3
4-Cl C_6H_4	215	92	5	3

3.7 CONDENSATION REACTIONS

3.7.1 Synthesis of α,α'-dibenzylidene cyclohexanone

Benzaldehyde (2.02 g, 0.02 mol) and cyclohexanone (0.98 g, 0.01 mol) were taken in methanol (3 ml). Acid Alumina was added to it. Adsorbed material was dried in air and irradiated in microwave oven for 5 min. in intervals of 30 sec. The progress of reaction was monitored with the help of TLC. After the completion of reaction, the alumina was washed with methanol and product, thus obtained, was purified by crystallization from ethanol. m.p. 116-7 ^{O}C (Lit m.p. 117 ^{O}C, Gupta *et. al.*, 1995*a*), yield.1.99 g, 97%.

Similarly, other Ŭ,Ŭô-diarylidene cyclohexanones were prepared from 4-methoxybenzaldehyde and 3,4-dimethoxy benzaldehyde with cyclohexanone. The physical data is given in Table below:

Aldehyde	**m.p. (^{O}C)**	**Yield (%)**	**Time MW (min.)**	**Conventional Time (hr.)**
CHO	116-7	97	5	2
4-OCH_3 C_6H_4CHO	161-2	96	5	2
3,4-$(OCH_3)_2$ C_6H_3	156-8	92	6	2

All compounds synthesized by microwave irradiation method were compared with authentic samples prepared by known procedures (discussed in Chapter-4) and their authenticity was established by their co-TLCs, m.p. and m.m.p.

CHAPTER-IV

RESULT AND DISCUSSION

Chemical reaction, performed using microwave irradiation techniques are rapid as the reactions are performed at higher temperature than their conventional methods. The modern microwave based synthesizers can achieve temperature of up to 250 ^{O}C and pressure of up to 20 bars allowing reaction to be carried out at higher temperature than their reflux procedure. Under microwave irradiation at atmospheric pressure the boiling point of solvents can be raised up to 26 ^{O}C above their conventional value. Microwave is a collective term for electromagnetic irradiation with frequency in the range of 0.3-300 GHz, frequencies that appliances used for heating purposes is at 2.45 GHz.

In case of microwaves, the energy transfer does not occur by conduction or convection as in conventional heating but by dielectric loss. Material dissipates microwave energy by dipole rotation, ionic conduction. Energy in the form of microwave can be generated by magnetron, led into the chamber and transferred to substances that are present in the beam line of the microwave radiation. Absorption of energy occurs when dipolar molecule rotate to align themselves with the fluctuating electric field component of the radiation or when ion move back and forth by the same phenomena. When molecules rotate or move back and forth in a matrix, they generate heat by friction. The amount of heat generated by a given reaction mixture is a complex function of its dielectric property, volume, geometry, concentration, viscosity and temperature (Galema, 1997).

The advent of commercial microwave reactors incorporating magnetic stirring, temperature and pressure regulation and with ability to process sealed reaction vials obviate the problems of solvent loss and cross contamination due to bumping. Microwave irradiation was used under solvent-free dry conditions, which allows reactions to occur on a preparative scale in open vessels (avoiding the risk of high pressure and explosions).

The principle features of kitchen microwave oven (700W, 2.45GHz Magnetron) are shown below in Fig.1 microwave technology is used in advanced microwave oven for the organic reactions, which prevent the formation of hot *and cold spots* with in the sample, resulting in a uniform heating pattern. This allows for higher reproducibility and predictability of results as well as optimization of yields, which are usually more difficult when using domestic microwave oven.

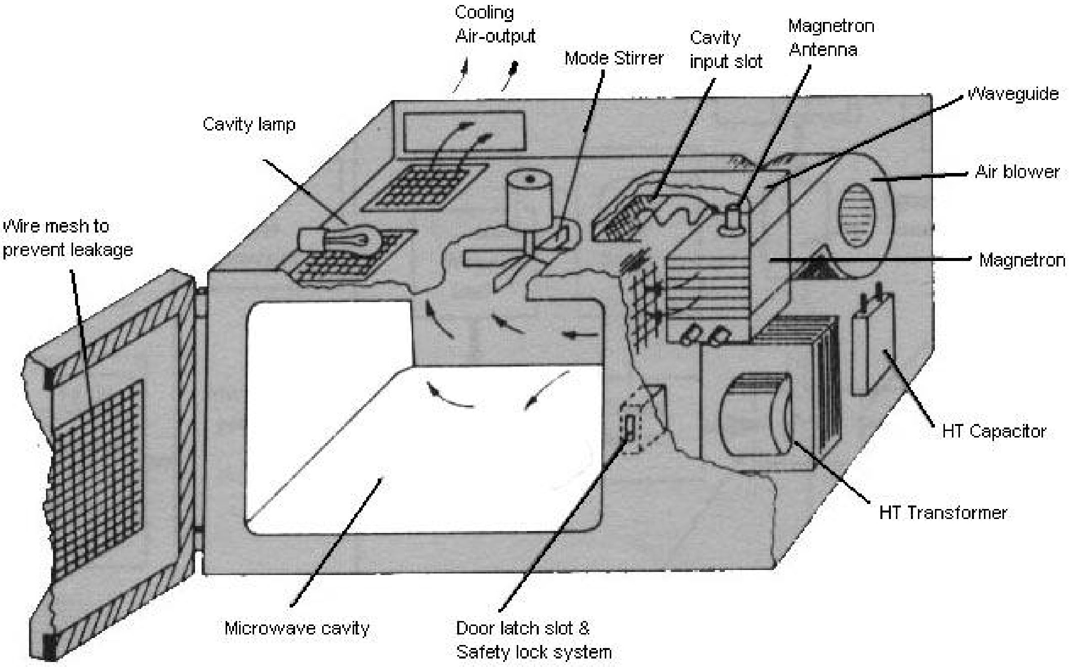


Fig.-1 Major features of domestic microwave oven

Microwave irradiation in solvent-free condition offers a clean, cheap and convenient method of heating which often results in higher yield and shorter reaction times and which is superior and advantageous over the conventional heating method. Four series of experiments were carried out using suitable support catalysts and *doped* supports. The detailed results are presented and discussed below.

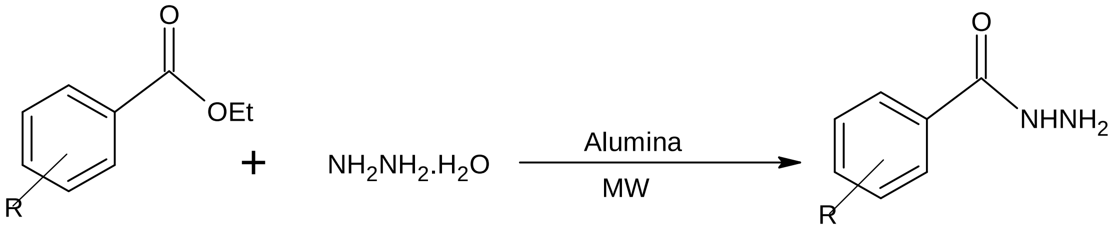
4.1 SYNTHESIS OF ARYLIDENE HYDRAZINES

Conventionally, benzoyl hydrazine is prepared by heating ethyl benzoate and hydrazine hydrate in absolute ethanol for 3-6 hours of refluxing (Kumar *et .al.,* 1991).

Similarly 4-chlorobenzoyl hydrazine is also prepared conventionally by heating the corresponding ester with hydrazine.

In the present investigation, benzoyl hydrazine was prepared by the reaction **(Scheme-1)** of ethyl benzoate with the hydrazine hydrate adsorbed on neutral alumina in 4 min. Usual workup gave 93% yield of benzoyl hydrazine, which was 78 % in conventional heating method. Similarly 4-chlorobenzoyl hydrazine has been prepared (**Scheme-1**) using neutral alumina and silica as adsorbent. Usual workup gave 91% yield of 4-chlorobenzoyl hydrazine, which was 75% in conventional method.

Scheme-1

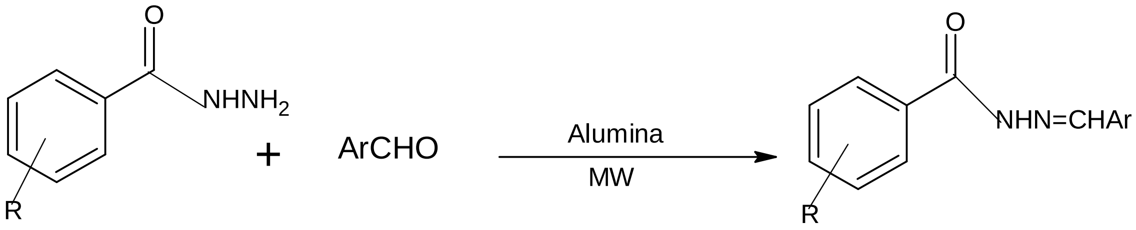


R= 4-Cl, H

Both the hydrazide were compared with their authentic samples prepared by conventional method by co-TLC and m.m.p.

Nucleophillic addition reactions can occur in carbonyl compounds with the elimination of water in mild basic acidic medium. However, here this reaction is accomplished by using benzoyl hydrazine and aromatic aldehyde adsorbed on acidic alumina and irradiating with microwaves in 2-5 min. **(Scheme-2).** Same reaction is done with 4-chlorobenzoyl hydrazine in place of benzoyl hydrazine. Usual workup of the reaction gave product in very pure state and high yields as compared to traditional method of preparation. Hence, no reagent i.e. sodium acetate and solvent was used. The results are given in Table-2 (a) and 2(b).

Scheme-2



R= H , 4-Cl

Ar = C_6H_5
= 2-NO_2 C_6H_4
= 4-MeO C_6H_4
= 4-N,N $(CH_3)_2$ C_6H_3
= 4-OH C_6H_4

Similarly, other substituted arylidenearoyl hydrazines were prepared using 4-methoxybenzaldehyde and 2-nitrobenzaldehyde with both p-chlorobenzoyl hydrazine and benzoyl hydrazine but 4-hydroxybenzaldehyde and N,N-dimethylaminobenzaldehyde was treated with only benzoyl hydrazine. All the compounds were compared with authentic samples prepared by conventional method by co-TLC and m.m.p. The physical data is tabulated in Table 2(a) and 2(b).

Table-2(a): Physical data of N-benzylidene-N`-benzoyl hydrazine

Ar	**m.p.(Lit, m.p. ^{O}C)**	**Yield (%)**	**Time MW (min.)**	**Conventional Time (hr.)**
C_6H_5	205-6 (205) [a]	93	2	3
2NO_2 C_6H_4	190-1(190) [a]	92	5	3
4-MeO C_6H_4	147 (147) [b]	90	4	3
4-OH C_6H_4	204	90	5	3
4-N(CH3)$_2$ C_6H_3	177-8(177) [a]	80	4	3

[a] Charonnat and Boime (1953) ; [b] Aggarwal *et. al., (*1929)

Table-2(b): Physical data of N-benzylidene-N`-4-Chlorobenzoyl hydrazine

Ar	m.p. (Lit, m.p.^{O}C)	Yield (%)	Time MW (min.)	Conventional Time (hr.)
C_6H_5	224-6 (226) [a]	92	3	3
4-OMe C_6H_4	198	93	5	3
2-NO_2 C_6H_4	212-5	95	5	3

[a] Dave *et. al*., (1984)

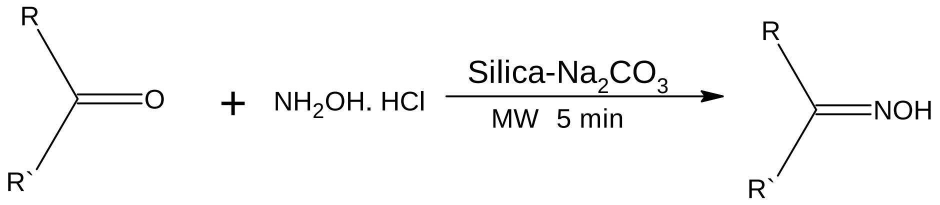
4.2 PROTECTION OF CARBONYL COMPOUNDS AS OXIMES

Oximes are very useful in protecting the aldehyde or ketone group in organic synthesis (Greene and Wuts, 1991). Oximes are readily prepared, highly stable and used for purification and characterization of carbonyl compound and in the conversion of amides *via* Beckmann rearrangement (Donaruma *et. al*., 1960).

Oximes are prepared conventionally by heating the corresponding ketones and aldehyde with hydroxylamine hydrochloride in presence of pyridine as solvent (Vogel, 1978). This method involves the use of reagents and solvent which led to wastage and is environmental hazard.

In the present work, method involves in which the conventional heating is replaced by microwave irradiation. A mixture of acetophenone and hydroxylamine hydrochloride was adsorbed on silica-supported Na_2Co_3 and irradiated in microwave for 5 min. to afford acetophenone oximes **(Scheme-3)**. The yield was found to be 92% .The product obtained by microwave method has been found to be same as that obtained by conventional method (m.m.p. 59 ^{O}C, Mitra *et. al*., 1999).

Scheme-3



R = C_6H_5 R` = CH_3
= 4-MeO C_6H_4 = CH_3
= C_6H_5 = H
= 4-OH C_6H_4 = H

Similarly, other subsitituted oximes were prepared using 4-chloroacetophenone, 4-methoxyacetophenone and benzaldehyde with hydroxylamine hydrochloride following same procedure used as above. All the compounds were compared with authentic samples prepared by conventional method by co-TLC and m.m.p. The physical data is tabulated in Table-3.

TABLE-3: Physical data of oximes

R	**R`**	**m.p. (^{O}C, Lit. m.p.)**	**Yield (%)**	**Time MW (min.)**	**Conventional Time (hr.)**
C_6H_5	CH_3	58 (59) [a]	92	6	2
4-MeO C_6H_4	CH_3	86-7 (87) [a]	91	5	2
C_6H_5	H	127-8 (128) [b]	93	5	2
4-OH C_6H_4	H	71-2 (72) [c]	94	4	2

[a] Mitra *et. al.*, 1999; [b] Smolkova *et. al.*, 1980; [c] Dewan and Singh, 2002.

4.3 OXIDATION USING ALUMINA AND $KMnO_4$

Oxidation reactions involve the use of toxic reagents hence their utility in oxidation is compromised due to potential danger in handling and waste disposal problems. Immobilization of metallic reagents on solid supports has addressed some of these limitations in organic synthesis because of selectivity and prevention of leaching of metals into environment.

In present investigation, oxidation has been carried using alumina doped with $KMnO_4$ (Fatiadi, 1986; Trost, 1991) for which 5% $KMnO_4$ solution was adsorbed on alumina and dried in air. Hence alumina-supported KMnO4 is used as reagent which is easy to store, if need be. However, during the present course of investigation, the doped reagent was prepared a fresh in all reaction.

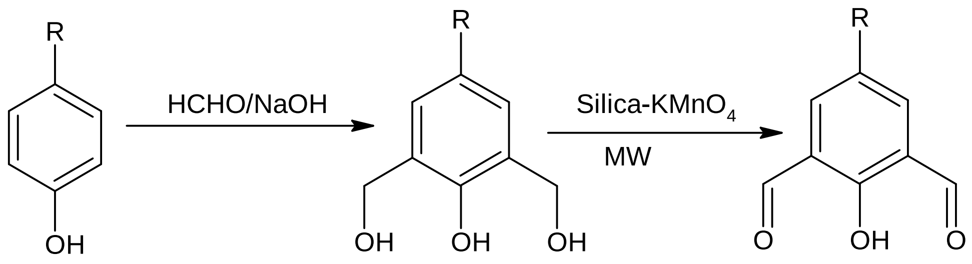
Preparation of 2,6 diformyl-4-methylphenol

Binucleating ligand complexes involve the use of 2,6-diformyl-4-methylphenol as a starting material. This diformyl-derivative is predominantly synthesized by two methods (Gagne. *et. al.,* 1981; Okawa *et. al*., 1972). Both these methods are long, use highly toxic reagents and yields are very poor.

2,6-dimethylol-4-phenyl phenol was oxidized to 2,6-diformyl-4-methylphenol by using $KMnO_4$ doped alumina **(Scheme-4)** 2,6-dimethylol-4-methyl phenol was prepared by treating 4-cresol with formaldehyde solution in basic medium at room temperature over night and was adsorbed on preformed alumina doped $KMnO_4$ catalyst. This material was irradiated in microwave oven for 4 min. afforded the desire formyl product. The diformyl compound, thus obtained, was compared with the authentic samples by co-TLC and m.m.p and was found to be same. Hence microwave method is better in terms of reduced time (4 min.) and higher yields (92%) as compared to conventional methods.

The earlier methods were long (2-3 days) and used highly acidic reagents (polyphosphoric acid) wherever alumina-$KMnO_4$ microwave method is very benign.

Scheme- 4



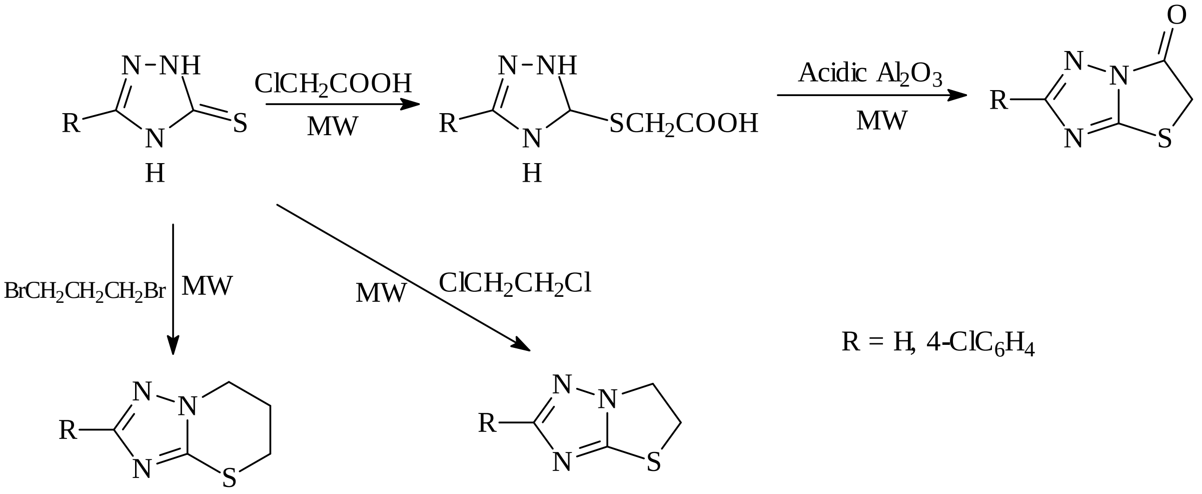
R = $CH_{3,}$ Cl

Using alumina doped with $KMnO_4$, 4-chloro phenol was comered to 2,6-dimethylol-4-chlorophenol and oxidized to 2,6-diformyl-4-chlorophenol following similar method as discussed above. m.p. 120 ^{O}C (Lit m.p. 126 ^{O}C , Weast *et. al.*, 1964), yield 1.56 g. 91%.

4.4. CYCLIZATION REACTIONS – SYNTHESIS OF BRIDGEHEAD NITROGEN HETEROCYCLES

3-phenyl-*s*-triazolyl-5-thione was prepared by the cyclization of benzoyl thiosemicarbazide in 10% KOH-EtOH medium under reflux (**Scheme 5)** (Kumar *et. al.*, 1991). The benzoyl thiosemicarbazide was prepared by the reaction of benzoyl hydrazine (**Section 3.3.1**) with KSCN following the already reported procedure (Vogel, 1978).

Scheme- 5



3-phenyl-*s*-triazolyl-5-thione was condensed with chloroacetic acid by dissolving in methanol and adsorbing on silica gel followed by microwave irradiation for 7 min. to afford 3-phenyl-*s*-triazolyl-5-thiolacetic acid. The progress of the reaction was monitored by TLC. The recrystallized product was found to be identical with the reported acid (Ali *et. al.,* 1976). The presence of the carboxyl functional group in the product was another indication that the condensation reaction has indeed taken place.

3-phenyl-*s*-triazolyl-5-thiolacetic acid was cyclized to afford a bridgehead nitrogen heterocycle namely 2-phenylthiazolo[3,2-*b*]-*s*-triazol-5-(6*H*)-one by adsorbing the acid on acidic alumina and irradiating in microwave for 6 min. The absence of a carboxyl group and presence of a carbonyl functional group is an indication that cyclization has taken place. Furthermore, the comparison with authentic sample (Ali *et. al.,* 1976) by co-TLC and m.m.p. supported the proposed structure of the triazolo-thiazolidinone (**Scheme 5**).

Microwave assisted cyclization of 3-phenyl-*s*-triazolyl-5-thione was accomplished using 1,2-dichloroethane and 1,3-dibromopropane in presence of acidic alumina to afford 2-phenyl-5,6-dihydrothiazolo[3,2-*b*]-*s*-triazole and 2-phenyl -5,6,7-trihydrothiazino[3,2-*b*]-*s*-triazole, respectively in 5 min. The structures of the cyclized products were proposed on the basis of their co-TLC and m.m.p. on comparision with authentic samples (Kumar, 1990).

By following similar procedures, the 4-chloro- analogues were prepared using 3-(4-chloro)phenyl-*s*-triazolyl-5-thione in place of 3-Phenyl-*s*-triazolyl-5-thione (**Scheme 5**). The structures of all compounds have been proposed on the basis of their comparison with already known compounds by co-TLC and m.m.p.

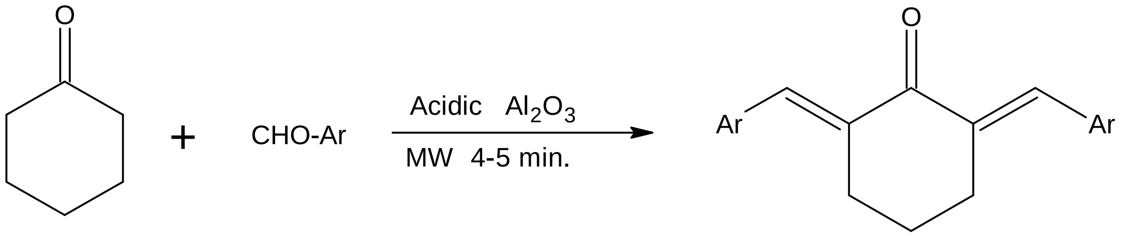
The cyclization reaction of 3-phenyl/(4-chloro)phenyl-*s*-triazolyl-5-thione with chloroacetic acid, 1,2-dichloroethane and 1,3-dibromopropane have been carried out using acidic alumina/silica in 3-7 min. duration without using any solvent and/or reagents whereas in conventional methods (Ali *et. al.,*, 1976; Kumar, 1990), large excess of solvents, reagents like acetic anhydride and pyridine have been used. Moreover, the present microwave assisted reaction gave better yields (>80%) while in the conventional methods, the yields were 40-65% only.

4.5 CONDENSATION REACTIONS

Condensation reactions generally involve the usage of large amount of solvent e.g. condensation of 1-tetralone with various aldehydes requires excess of solvent (Hassner and Norman, 1958) and the disadvantage of these methods is the long reaction time (Sinha A.K and Rastogi, 1991). The Ŭ,Ŭ̀-diarylidene cyclohexanones were prepared by the condensation of cyclohexonone and aromatic aldehyde in solvent-free *dry* conditions

The synthesis has been carried out by mixing cyclohexanone with benzaldehyde **(Scheme- 6)** in methanol. The mixture was adsorbed on acidic alumina and irradiated in a domestic microwave oven for 4 min. in intervals of 30 sec. Usual workup of the reaction gave product in very pure state and high yields as compared to traditional method of preparation. The products, thus obtained, by both the methods were found to have same m.p. and m.m.p. (117 ^{O}C, Gupta *et. al.,* 1995).

Scheme-6



Ar = C_6H_5
= 4-OCH_3 C_6H_4
= 3,4-$(OCH_3)_2$ C_6 H_3

Theoratically, the monoarylidene derivative is also a feasibility which was ruled out from the m.p. data as reported by Gupta *et. al.*, 1995. Similarly, cyclohexonone was condensed with 4-methoxybenzaldehyde, and 3,4-dimethoxybenzaldehyde. The results are tabulated in Table-5.

Table-5: Physical data of α,α`-diarylidene cyclohexonones.

Ar	m.p (Lit, m.p. ^{O}C)	Time MW (min)	Yield (%)	Conventional Time (hr.)
C_6H_5	116-7 (117)[a]	5	97	2
4-OCH_3 C_6H_4	161-2 (157-62)[a]	5	96	2
3,4-$(OCH_3)_2$ C_6H_3	156-8 (155-57)[a]	6	92	2

[a] Gupta *et. al*., (1995)

These four different series of experiments under solvent-free conditions using microwave irradiation involved the use of inorganic oxides, solid supports and doped catalysts and indicated that microwave-assisted organic synthesis (MAOS) method is easier, faster, cleaner and environmentally benign. Various type of starting materials intermediate etc. can be now prepared by this method.

CHAPTER-V

SUMMARY

Industrial chemistry in the new millennium is widely adopting the concept of *green chemistry* because of the awareness regarding environment and its conservation and to meet the fundamental scientific challenges of protecting the human health. The emerging area of *green chemistry* envisages minimum hazards as the performance criteria while designing new chemical process. One of the thrust areas for achieving this target is to explore alternative reaction conditions and reaction media that are friendlier to the environment and to accomplish the desired chemical transformation with minimized by-product or waste as well as eliminating the use of conventional organic solvent, if possible. Among the important tools, the use of microwave (MW) as alternative energy source is becoming an attractive alternative. This approach has been getting considerable attention since last two decades and is now termed as *green chemistry***.**

Normally, the reaction carried out by conventional methods require large amount of volatile, toxic solvent which are hazardeous to the health and generally cannot be recycled but discharged to the surrounding. Thus, there is need for chemical conserving techniques which can eliminate or minimize the generation of associated pollutants and are friendlier to the environment. One such approach is microwave-assisted organic synthesis in which reaction can be carried out either in the presence or absence of catalysts or solid support under solvent-free dry conditions. Thus, the problem associated with disposable of solvent is minimized or reduced. Solid-state reaction (or solvent-free reaction) has many advantages such as reduced pollution, low cost and simplicity in process and handling. Keeping in view the need of the hour about developing environmentally benign synthetic methods, the present research work is planned for the following objectives:

1) To study the role of Support Catalysts and microwave irradiation in organic synthesis.
2) To compare the traditional method of synthesis with eco-friendly methods in terms of ease of synthesis, purity of product, time of reaction.

Five series of different reactions were carried out using microwave irradiation as the source of energy in solvent-less dry state and using doped catalysts.In the first series, a remarkable fast synthesis of arylidene hydrazines in solvent-free dry conditions under microwave irradiation has been achieved. The synthesis has been carried out by mixing benzaldehyde, 2-nitrobenzaldehyde, 4-methoxybenzaldehyde with both benzoyl hydrazine and 4-chlorobenzoyl hydrazine but 4-hydroxy benzaldehyde and 4-N,N-dimethylamino benzaldehyde with only benzoyl hydrazine by microwave irradiation adsorbed on alumina and silica. Carbonyl compounds are known to undergo nucleophilic addition reactions followed by elimination of water in mild basic acidic. However, this reaction is achieved here using benzoyl hydrazine and / or 4-chlorobenzoyl hydrazine and aromatic aldehyde adsorbed on neutral alumina and irradiating with microwave in 2-5 min. Usual workup of the reaction gave product in very pure state and high yields (80-95%) as compared to traditional method of preparation. moreover, no reagent *i.e.* sodium acetate and solvent has been used.

In the second series, various oximes were prepared in solvent-free dry conditions using microwave irradiation. The synthesis has been carried out by mixing acetophenone with hydroxylamine hydrochloride and adsorbing it on silica-supported Na_2CO_3 followed by its irradiation in a domestic microwave oven for 4-5 min. in intervals of 30 sec., a usual workup, after the completion of reaction gave pure acetophenone oxime. Acetophenone oxime was also prepared by reaction of acetophenone with hydroxylamine hydrochloride in presence of pyridine as solvent by conventional method in 2 hr. and compared with one prepared by microwave method. Other substituted oximes were prepared by reacting hydroxylamine hydrochloride with 4-methoxyacetophenone, 4-hydroxybenzaldehyde and benzaldehyde in 4-6 min. with 91-94 % yields. The present method has definitely eliminated the usage of pyridine and longer reaction times.

Oxidation reactions involve the use of highly toxic reagent hence their utility is compromised due to potential danger in handling and waste disposal problems. These toxic reagents can not be recycled and also create environment pollution. In the third series, oxidation reactions have been carried out using alumina doped with $KMnO_4$.This method using alumina-supported $KMnO_4$ is quick and cleaner as compared to the conventional methods which are time consuming and very untidy and the reagent is easy to store, if need be. 2,6-diformyl-4-methyl(or chloro) phenol was prepared by oxidation of 2,6-dimethylol-4-methyl(or chloro)phenol using alumina-supported $KMnO_4$ in excellent yields and in 5-7 min.

In the fourth series, bridgehead nitrogen heterocycles were prepared in solvent-free dry conditions. Benzoyl hydrazine, obtained from ethyl benzoate and hydrazine hydrate, on reaction with potassium thiocyanate gave benzoyl thiosemicarbazide which in boiling sodium hydroxide yielded 3-phenyl-*s*-triazolyl-5-thione. This thione on reaction with chloroacetic acid in the presence of acidic alumina afforded 3-phenyl-*s*-triazolyl-5-thiolacetic acid which was cyclized to the desired , 2-phenylthiazolo[3,2-*b*]-*s*-triazol-5-(6*H*)-one. Microwave assisted cyclization reaction of 3-phenyl-*s*-triazolyl-5-thione was accomplished using 1,2-dichloroethane and 1,3-dibromopropane in presence of acidic alumina to afford 2-phenyl-5,6-dihydrothiazolo[3,2-*b*]-*s*-triazole and 2-phenyl-5,6,7-trihydrothiazino[3,2-*b*]-*s*-triazole, respectively in 5 min. The structures of the cyclized products were proposed on the basis of their co-TLC and m.m.p. on comparision with authentic samples.

By following similar procedures, the 4-chloro- analogues were prepared using 3-(4-chloro)phenyl-*s*-triazolyl-5-thione in place of 3-Phenyl-*s*-triazolyl-5-thione. The structures of all compounds have been proposed on the basis of their comparison with already known compounds by co-TLC and m.m.p.

In the fifth series, Condensation reaction for the preparation of substituted Ŭ,Ŭ̀-dibenzylidene cyclohexanone was carried out. A mixture of cyclohexanone with substituted aromatic aldehydes including benzaldehyde, 4-methoxybenzaldehyde and 3,4-dimethoxybenzaldehyde was adsorbed on acidic alumina and irradiating with microwave for 4-6 min. to afford Ŭ,Ŭ̀-diarylidene cyclohexanone in 95% yield.

The microwave-assisted reaction under these conditions provided an eco-friendly organic synthesis and is a promising alternative to conventional polluting reactions. Solid state reactions (solvent free reactions) have been found to be very fast, clean, giving higher yields, reduced pollution, low cost, simplicity in process and handling as compared to conventional methods. Hence microwave-assisted reactions are superior and environmentally benign than conventional methods.

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ABSTRACT

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ABSTRACT

(An abstract of the thesis submitted in partial fulfillment of the requirement for the degree of M.Sc. in subject of Chemistry of the CCS Haryana Agriculture University, Hisar)

Key Words: Microwave, Green chemistry, solvent-free synthesis

The present study reports an eco-friendly organic synthesis for the preparation of organic compound using support catalyst and microwave irradiation. This method has been found to be cheaper, cleaner, faster, and gave higher yields of the products. Substituted arylidene benzoyl hydrazine were prepared by using benzaldehyde, 4-hydroxybenzaldehyde, 2-nitrobenzaldehyde, 4-

methoxybenzaldehyde, and 4-N,N-dimethoxybenzaldehyde with benzoyl hydrazine and arylidene 4-chlorobenzoyl hydrazines were prepared by using aldehydes with 4-chlorobenzoyl hydrazine by microwave irradiation and adsorbed on alumina. The product obtained have yield 90-95 % which is better than conventional method. Oximes of carbonyl compounds has been prepared by the microwave assisted reaction of ketones and hydroxylamine hydrochloride adsorbed on silica supported Na_2Co_3 in 4-6 minutes with 91-94 % yield.

Alumna supported $KMnO_4$ has been found as a very efficient and clean reagent for the oxidation of primary alcohols to aldehydes. 2,6-diformyl-4-methyl/chlorophenol was prepared by the oxidation of 2,6-dimethylol-4-methyl/chlorophenol using $KMnO_4$ doped alumina. Bridgehead nitrogen heterocycles namely 2-phenyl/(4-chlorophenyl)thiazolo[3,2-*b*]-*s*-triazol-5-(6*H*)-one, 2-phenyl-5,6-dihydrothiazolo[3,2-*b*]-*s*-triazole and 2-phenyl-5,6,7-trihydrothiazino[3,2-*b*]-*s*-triazole were prepared by the microwave irradiation of 3-phenyl/(4-chlorophenyl)-*s*-triazolyl-5-thione and chloroacetic acid, 1,2-dichloroethane and 1,3-dibromopropane, respectively. The reactants were adsorbed on acidic alumina/silica. Cyclohexanone has been condensed with various substituent aromatic aldehydes in presence of acidic alumina and microwave irradiation to afford Ŭ,Ŭ`-diarylidene cyclohexanone in 90-96% yields. The structures of all compounds have been proposed on the basis of their comparison with the known structures.

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