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Microwave Assisted Organic Reactions In Dry Media - A Review

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ABSTRACT

This review highlights the recent advances made in the realm of microwave supported reaction in dry media. The mechanism of microwave heating is explained and the focus is on the protection-deprotection reactions and synthesis of heterocycles. The advantages and the disadvantages of using microwave assisted synthesis are also described.

INTRODUCTION

Microwave irradiation has changed synthetic strategies in the field of organic synthesis[1-7]. The initial reactions were carried out in solvents with high dielectric constants but recent developments are largely in the field of solid-state reactions assisted by microwave irradiation. A new method adopted should be able to cover many aspects like waste minimization, reduction in energy usage while not shifting from the main goal of high synthetic utility.

Microwaves are electromagnetic waves. The electric field applies a force on charged particles that results in the rotation or migration of the particle leading to further polarization. The applied field is alternating and the molecules are unable to align with the applied field so rapidly that the friction results in heat. The properties ε' and ε" are associated with the material regarding the extent of heating that may take place in a dielectric field. The rate of heating in an applied dielectric field is given by the equation,

$$\text{Tan } \delta = \varepsilon' / \varepsilon''$$

Where,

Tan δ is the dielectric loss tangent and defines the ability of the material to convert electromagnetic energy to heat at a particular frequency and temperature,

ε' is the relative permittivity and

ε" is the dielectric loss that is indicative of the ability of the medium to convert dielectric energy to heat.

The value of tanδ of an assembly of molecules depends on, (i) frequency of the electromagnetic waves (ii) temperature and (iii) physical state or composition of the mixture. Dielectric heating is direct and effective when the matrix has a sufficiently large dielectric loss tangent. Polar solids may be used and hence the use of solvent is not mandatory for the conduction of heat. Although, these are applicable and can explain the liquid phase reactions, the exact mechanism of thermal effect of microwaves on solid state reactions has not been explained. It is believed that the microwave radiation affects the particle at the atomic level and excites the particle to higher energy levels that results in rate acceleration of the reactions. Microwaves are found to cause surface defects in solids and these help in increasing the excitation levels of the ions. However, this proposed theory is still a contentious issue.

The main goal in devising novel synthetic pathways is that they should account for high atom efficiency. Highly efficient methods that reduce steps with environmentally benign protocols during synthesis are mostly sought[8,9]. Solventless techniques lead the way in eco-friendly sustainable chemical technologies. Of these, ionic liquids, supercritical CO_2 and dry media reactions are predominant. Although ionic liquids are recyclable during some reactions, they are expensive and often require tedious procedures. Supercritical CO_2 may not be easy to handle in many reactions. Most reactions require heat activation and this can be provided very efficiently through microwave irradiation.

Microwave radiation is largely seen as an alternate to heat transfer techniques such as heating jackets and oil baths. The conventional heating equipments suffer from (i) loss of excess energy (ii) unidirectional heating and (iii) time consumption. However microwave offers an excellent method to heat the reaction mixture without dissipation of heat to the reaction vessel. The reactant molecules absorb the irradiation and undergo the reaction with increase in their energies. The ability to absorb the energy is based on the dielectric property of the reactant molecule and the media. When the medium or the solvent has a high dielectric constant, it aligns itself with the applied electromagnetic field and is heated rapidly. This process is known as "super heating" and the media thus transfers its excess heat energy to the reactant molecule thereby accelerating the reaction. However, this has some inherent disadvantages. The possibility of runaway reactions cannot be ruled out as the reaction mixture is rapidly heated to very high temperatures in a very short span of a minute or two. The decomposition of the reactants and products also pose a challenge to this approach. Further, solvents are corrosive and their vapours cause damage to the reactor. Therefore, there was a need to maximize the utility of the microwave oven while minimizing the use of solvents.

Before carrying out a reaction in solventless media, many issues need to be addressed. First and fore-

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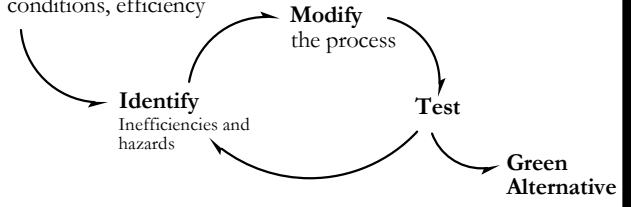


Figure 1: Steps involved in introducing a new alternative

most is the fact that solvents help to supply the heat to a reaction as well as dissipate the excess heat of the reaction[10]. The choice should be made after a thorough investigation of the factors like selectivity, stereochemistry, yield, wastage, recyclability, power inputs, ease in isolation of products and heat of the reaction (Figure 1). Solventless reactions have a head start in some of the factors like product isolation and purification, recyclability and time consumption. Solvent evaporation and pressure buildup during the course of reactions is avoided. It is believed that for a reaction where the equilibrium of the reaction may be shifted by the evaporation of one of the products, microwave irradiation in dry media offers a promising alternative. These inherent advantages need to be carried further while devising reactions.

The control of energy input plays an important role in reaching the predefined reaction conditions for the treatment of reaction mixtures in organic chemistry. The temperature control methods that are generally adopted are (i) control of power output, (ii) dilution of power output, (iii) allowing the reaction mixture to be at reflux conditions, (iv) setting a pressure limit (in closed systems with pressure release) and (v) allow for adequate mixing in the reaction vessel in conjunction with control of power output.

Although solids had been identified as supports for conducting microwave assisted reactions even when the process was at an early stage, not many syntheses had been carried out. The method was popular with material chemists for obtaining materials with high crystallinity that were unheard of while using the conventional thermal conditions. It is only in the recent years that microwave coupled with dry media is becoming popular judging by the amount of publications in various journals.

Solid catalysts can be easily separated from the reaction products by simple filtration and quantitatively recovered in the active form[11]. They can be recycled, making less expensive the preparation of sophisticated fine chemicals and at the same time avoiding contamination of products. Most supports that are used in microwave reactions are those that had been studied earlier as heterogeneous catalysts. Polar adsorbents like silica and alumina are found to catalyse a wide range of reactions. Further, these act as perfect supports for reagents that may be impregnated by simple procedures. Some reagents like alkali metal carbonates and sulphates, may be used as supports. Zeolites, mesoporous materials and many types of clay are used as such. When the acidity of these materials is found insufficient, they are modified by treatment with Lewis acids or protic acids to increase their catalytic activity. Ion exchange resins and molecular sieves have also been identified as support reagents in microwave assisted reactions. Polymeric supports having immobilized surface active sites are also gaining interest.

Nearly all the reactions that are used by organic chemists have been attempted with the microwave oven since the first attempt by Gedye and Giguere in 1986. Our interest in microwave assisted organic synthesis has been in both reactions carried out in the presence of a solvent as well as in dry conditions [12-16]. We have attempted protection-deprotection, Diels-Alder reactions and some synthesis of alkyl dicarbonyl compounds. We noted that the Diels-Alder reactions of cycloalkenones and cyclic dienes were endoselective and rapid in the presence of microwave with chlorobenzene as the solvent.

A comprehensive view of the reactions that are being carried out in the recent years have been compiled in this review. We shall be focused on the protection-deprotection reactions, cycloaddition and reactions concerning the synthesis of heterocycles.

1. Protection -deprotection reactions

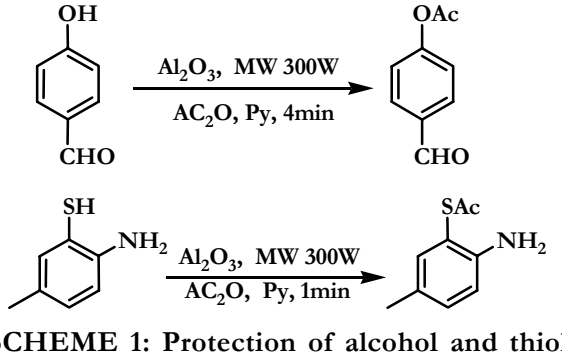
Protecting groups are one of the main aspects of synthetic organic chemistry.[17] The steps involved

in a total synthesis invariably contain several protection-deprotection steps. High selectivity with simplicity and mildness is a prerequisite for these kinds of reactions. The reaction should be swift leading to ease in isolation of products. Many substrates are labile, and therefore, quenching and separation may cause degradation.

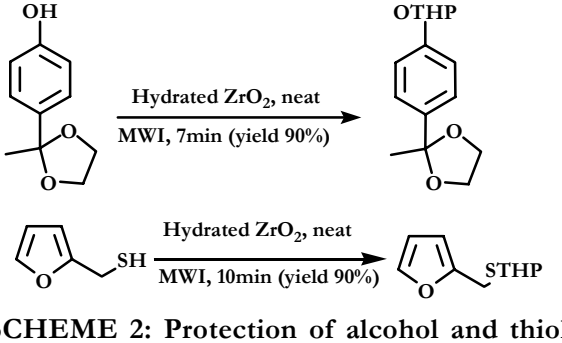
1.1. Protection of hydroxyl and thiol groups

Hydroxyl groups are present in many substrates in synthetic transformations. They are highly reactive and there is a great need for their protection during the course of other reactions. The procedures for hydroxyl groups are often used for the protection of thiols as well.

Acetylation is frequently used for derivatisation and characterization of alcohols as well as for further transformations. Conventionally these reactions were carried out with bases such as triethylamine and pyridine. Microwave irradiation has been employed for the acetylation of phenols and thiophenols in basic alumina under solventless conditions. The acetic acid remains adsorbed in alumina (SCHEME 1)[18] .



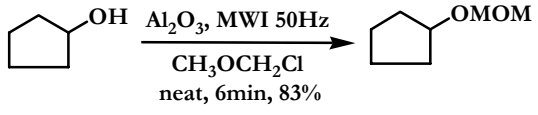
SCHEME 1: Protection of alcohol and thiol groups as esters



SCHEME 2: Protection of alcohol and thiol groups as tetrahydropyranyl ethers

Microwave coupled with hydrated zirconia has been reported to catalyse the protection of allylic and acetylenic alcohols without the isomerisation of double and triple bonds. Phenols containing a dioxolane protecting group could be converted to THP ethers in high yield (SCHEME 2)[19].

Alcohols are also protected as alkoxy ethers that are quite stable and the other functional groups in the substrate may be made to undergo synthetic transformations (SCHEME 3)[20].

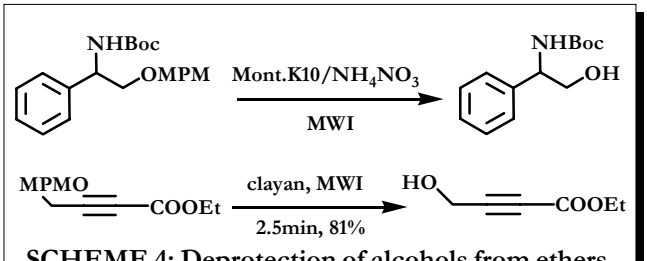


SCHEME 3: Protection of alcohol as methylmethoxy ethers

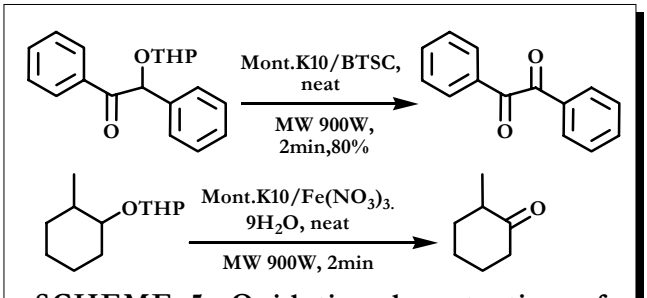
1.2. Deprotection of alcohols

Regeneration of alcohols from their esters and ethers can be carried out under heterogeneous conditions by using solid catalysts. Deprotection of alcohols is carried out in almost all major multistep processes. Reagents that are very selective and mild are used. Yadav et al., has performed the selective deprotection of methoxy phenylethers in montmorillite supported ammonia nitrate (SCHEME 4)[21].

Oxidative deprotection of tetrahydropyranyl



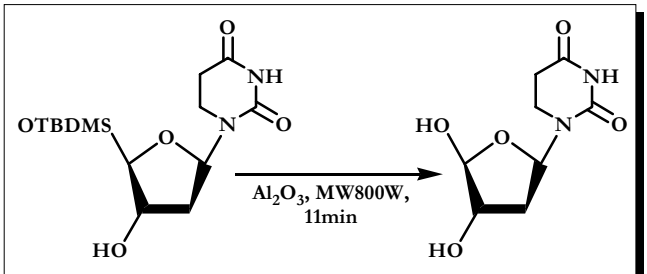
SCHEME 4: Deprotection of alcohols from ethers



SCHEME 5: Oxidative deprotection of alcohols from THP ethers

ethers have been carried out in BTSC (Bis trimethylsilyl Chromate) and hydrated ferric nitrate supported on montmorrilite (SCHEME 5)[22].

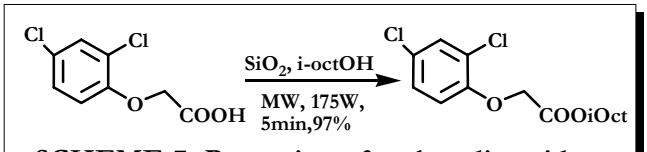
Deprotection of silyl ethers have also been carried out in the presence of microwave irradiation (SCHEME 6)[23].



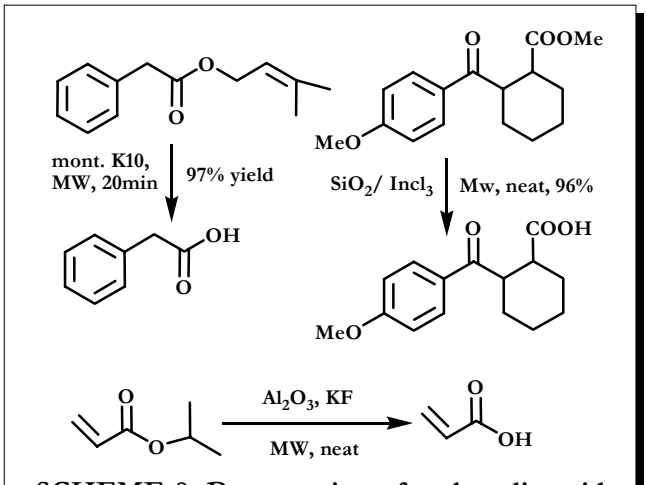
SCHEME 6: Deprotection of alcohols from silyl ethers

1.3. Carboxyl protecting groups

The carboxyl groups are often protected as their esters during organic synthesis. Conversion to esters although simple, does not generally proceed to completion due to the effect of water. Dry media is an excellent alternative for the synthesis of esters (SCHEME7)[24].



SCHEME 7: Protection of carboxylic acids as esters



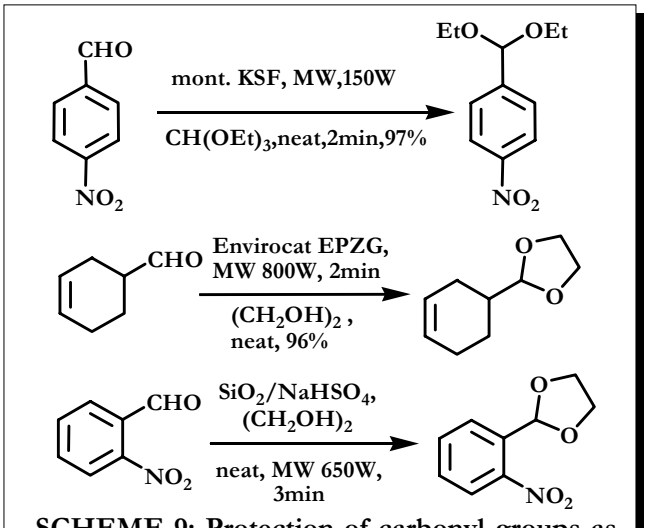
SCHEME 8: Deprotection of carboxylic acids from esters

1.4. Deprotection of carboxyl esters

Hydrolysis of esters is generally accomplished in moderate yields under acidic or basic conditions. Deprotection of the carboxyl esters is achieved in very high yields using solid catalysts like K-10, indium chloride impregnated silica and KF/alumina in the presence of microwave irradiation (SCHEME 8)[25].

1.5. Protection of carbonyl groups

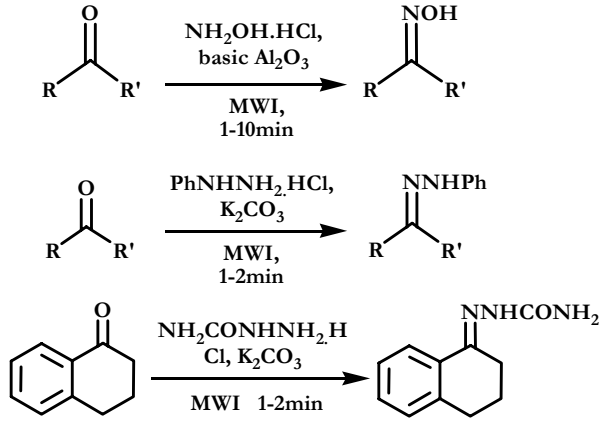
The carbonyl group is versatile as it has both electrophilic and nucleophilic centers. The protection of a carbonyl group from nucleophilic attack assumes importance. Acetals, ketals, 1,1-diacetates and nitrogenous derivatives have been used extensively for this purpose. Microwave irradiation has been proven to accelerate these reactions[26]. Envirocat EPZG and sodium bisulphate supported on silica were found to catalyse the formation of acetals (SCHEME 9)[27,28].



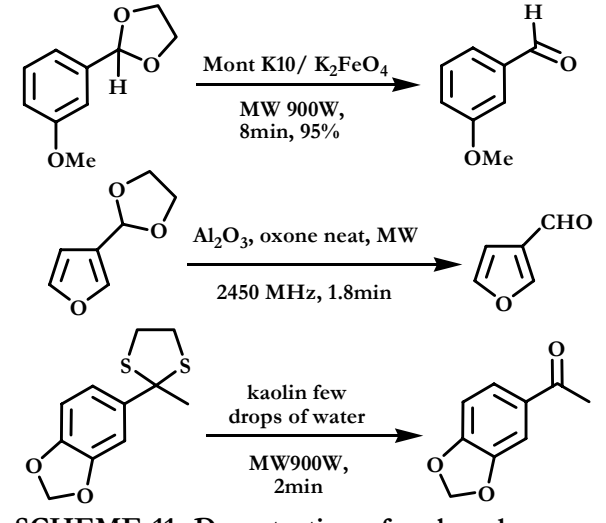
SCHEME 9: Protection of carbonyl groups as acetals

Protection of carbonyl compounds as their nitrogenous derivatives is not a simple protection process. These derivatives themselves are further used as precursors for the synthesis of carbazoles, lactams and other interesting heterocycles. Synthesis of oximes in basic alumina had been reported by Kad *et al* in 2001[29]. We have performed stereo selective synthesis of oximes using potassium carbonate in conjunction with microwave irradiation that yields the E isomer[16]. This procedure also yields semicarba-

zones and phenyl hydrazones in good yields (SCHEME 10).



SCHEME 10: Protection of carbonyl groups as nitrogenous derivatives



SCHEME 11: Deprotection of carbonyl groups

1.6. Deprotection of carbonyl groups

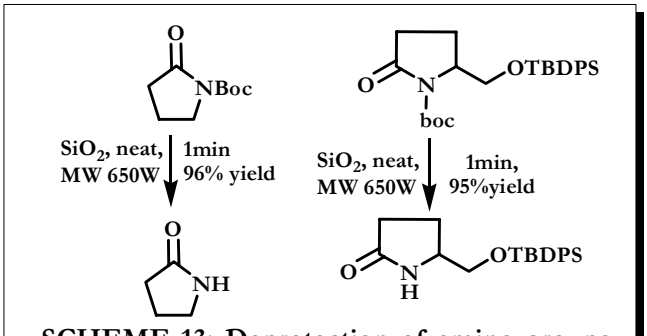
Deprotection of carbonyl groups has been generally performed under acidic conditions. Acetals have been deprotected to their parent aldehydes by the use of clay/potassium ferrate and Bose *et al*, has shown that deprotection also occurs in alumina[30, 31]. Selective deprotection of thioacetals has been reported in the presence of hydrated kaolin under microwave conditions (SCHEME 11)[32].

1.7 Amino protecting groups

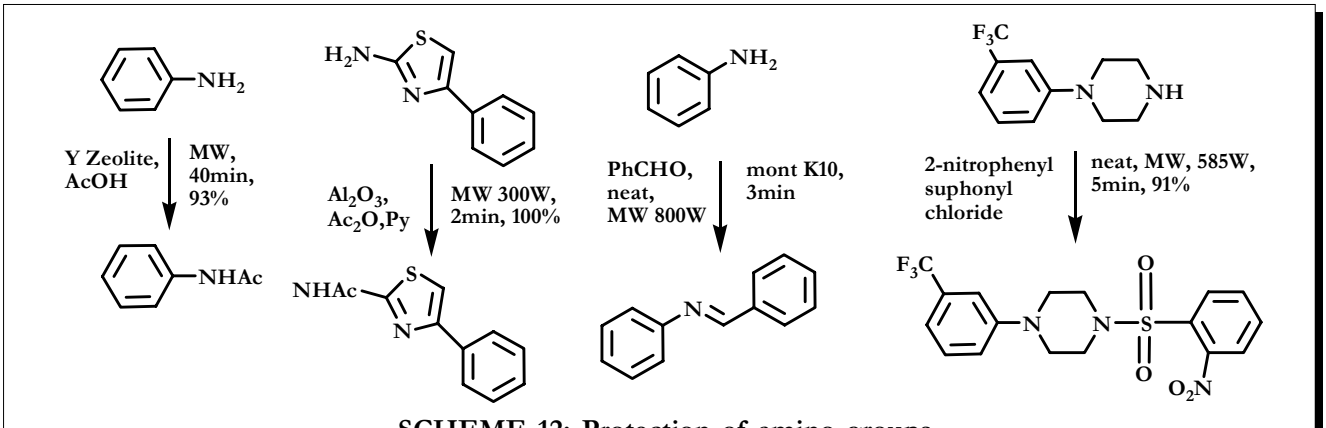
Amines are protected as amides on treatment with acetic acid in the presence of zeolites[33]. Treating the amine with acetic anhydride in alumina also gives amides[18]. Amines are protected as imines[34]. Imines by themselves are synthons for further transformations. Further, amines are protected as sulphonamides [35] which also have biological activity (SCHEME 12).

1.8. Deprotection of amines

Amines are generally protected as their Boc derivatives. Selective deprotection of Boc esters have been carried out under microwave conditions without affecting the silyl group (SCHEME 13). [37]



SCHEME 13: Deprotection of amino groups



SCHEME 12: Protection of amino groups

Microreview

Cyclization reactions in heterocyclic synthesis

Heterocycles form by far the largest of the classical divisions of organic chemistry and are of immense importance biologically and industrially. Heterocycle synthesis is the backbone of pharmaceutical and bioactive agrochemical industry. Nearly all the medicines that are consumed are heterocycles and thus their synthesis assumes high significance. In addition, hetrocyclic compounds also find use as additives and modifiers in cosmetics, reprography information storage and plastics. Methodologies are constantly updated to give high yields with high atom efficiency[38].

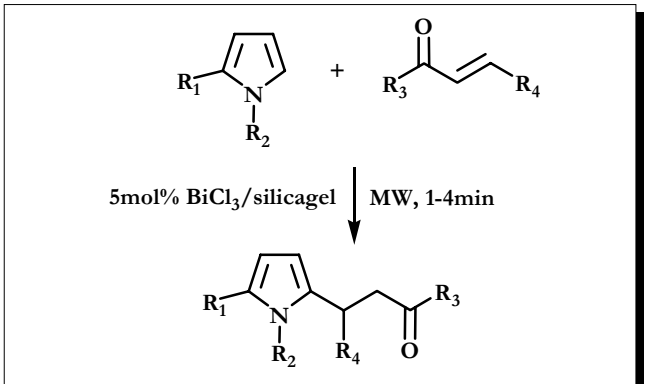
Heterocycles may be broadly divided into nitrogen, oxygen and sulphur containing compounds. Of these, the most abundant heterocyclic compounds are found to be nitrogen containing rings.

Nitrogen containing heterocycles

1. Heterocycles containing one nitrogen atom

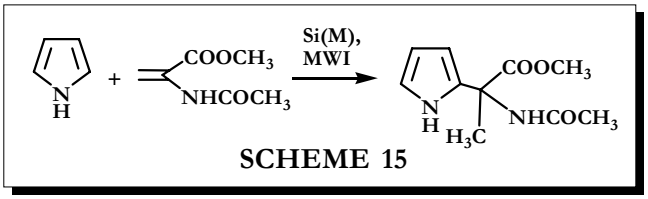
1.1 Pyrroles

Substituted pyrroles are synthesized by Michael addition of N-alkyl pyrroles to α, β-unsaturated ketones under MWI conditions in silica gel supported with bismuthtrichloride (SCHEME14)[39].

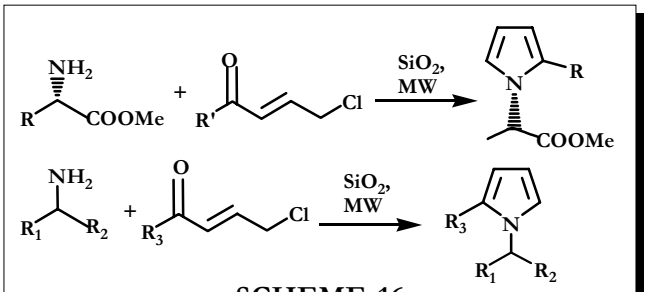


SCHEME 14

Recently, 2-substituted chiral pyrrole derivatives have been synthesized from amines and aminoacid esters (SCHEME 15)[40].



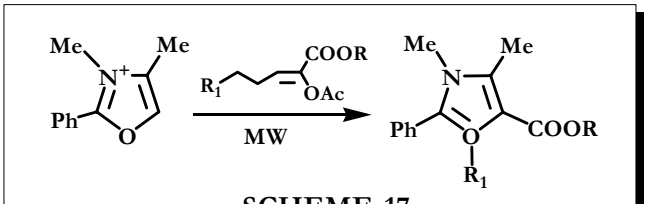
SCHEME 15



SCHEME 16

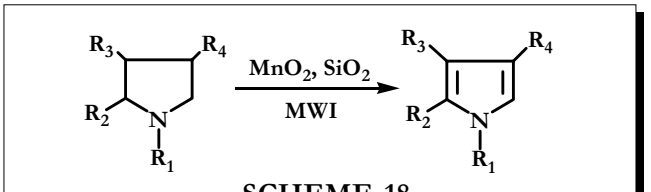
The amines and beta unsaturated chloroketones when subjected to microwave irradiation with silica as the support yielded the chiral pyrroles (SCHEME 16)[41].

Synthesis of 3-carboxylate pyrroles using microwave irradiation[42] from N-methyl oxazolinium salt and electron rich alkene has been very recently achieved by Grassi and coworkers (SCHEME 17).



SCHEME 17

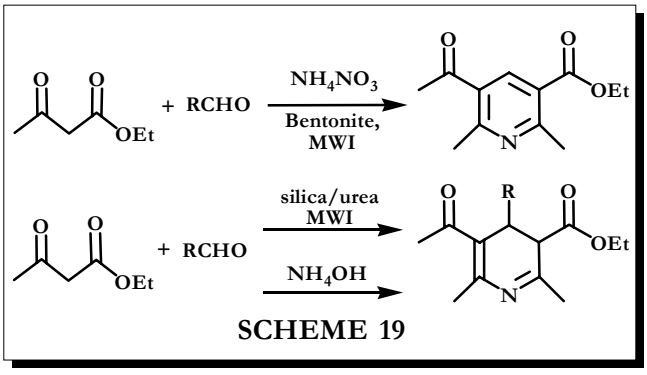
Often the heterocycles that are formed are in their reduced state. Microwave irradiation has also been found to accelerate the oxidation reactions of heterocycles without affecting the ring or any substituents. MnO_2 mixed with silica gel was found to catalyse the oxidation of tetrahydropyrroles to pyrrole (SCHEME 18)[43].



SCHEME 18

1.2 Pyridines

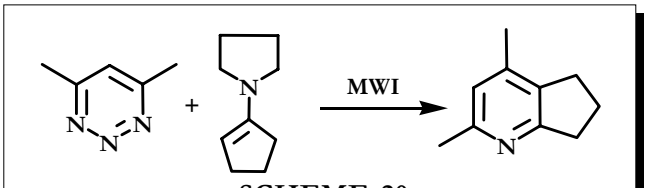
Synthesis of pyridines from beta ketoesters has been achieved in ammonium nitrate supported bentonite clay under microwave conditions[44]. Microwave irradiation in conjunction with acidic clay decomposes the ammonium nitrate to ammonia and nitric acid. These species initiate the cyclisation and



SCHEME 19

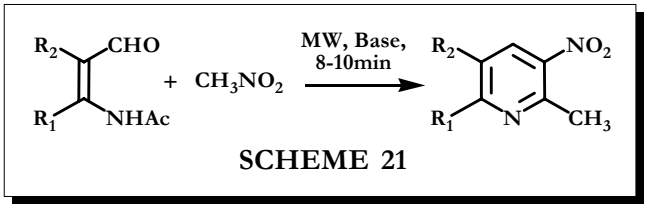
insitu oxidation (SCHEME 19). Urea and hydroxylamine have also been used as nitrogen sources[45]. When a Smith synthesizer was used, where one could control temperature and pressures further improvements were noted[46].

Microwave irradiation generates pyridine from triazine and enamine by cheleotropic Diels-Alder reaction by the elimination of a molecule of nitrogen (SCHEME 20)[47].

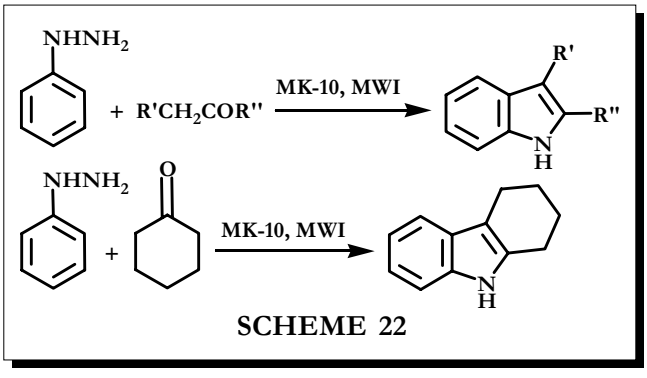


SCHEME 20

Base catalysed solid phase condensation of β-formyl enamides with nitromethane in MWI conditions afforded substituted pyridines in good yields (SCHEME 21)[48].



SCHEME 21

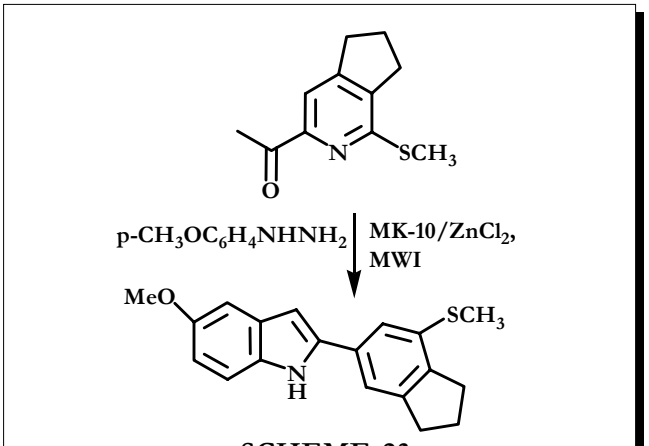


SCHEME 22

1.3 Indoles and carbazoles

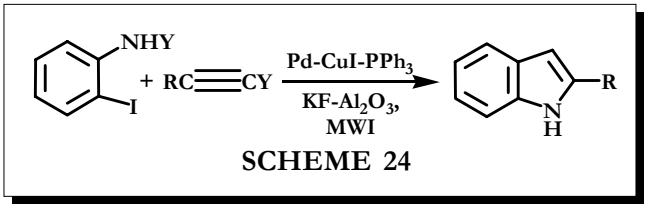
Indoles and carbazoles have been synthesized under microwave irradiation in montmorrilite K-10 clay by Fischer-Indole synthesis (SCHEME 22)[49].

Synthesis of quinolizine alkaloids, methoxy analogues of the semperverine alkaloid has been achieved in zinc chloride supported on K-10 (SCHEME 23)[50].



SCHEME 23

Sonogashira coupling cyclisation reactions of *o*-iodoanilines with terminal alkynes have been carried out with Palladium-phosphine catalyst supported on potassium fluoride alumina under solventless microwave conditions to yield indoles (SCHEME 24)[51].

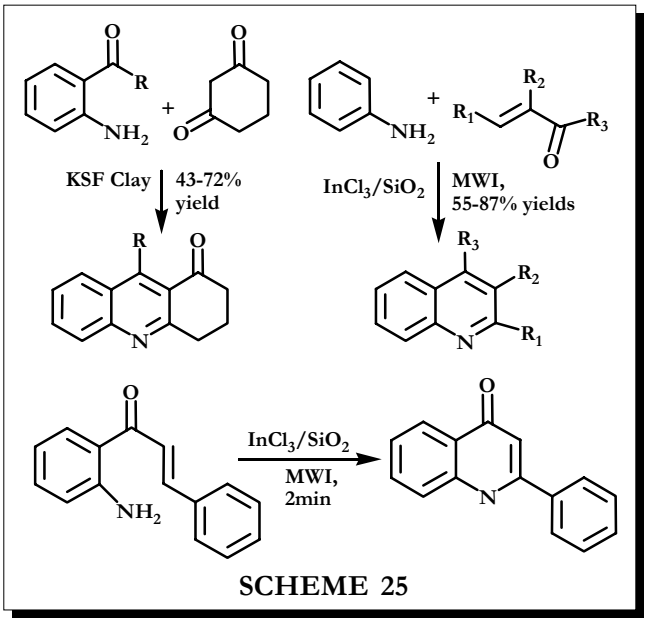


SCHEME 24

1.4 Quinolines

Quinolines and substituted quinolines have been synthesized using solid state microwave reactions (SCHEME 25). Amino ketones when reacted with 1,3-dicarbonyl compounds gave quinolinones[52]. Substituted quinolines were generated from chalcones and anilines under microwave conditions[53]. Hemanth Kumar *etal*, further improved the synthesis of dihydroquinolinones by rapid cyclisation of 2-aminochalcones[54].

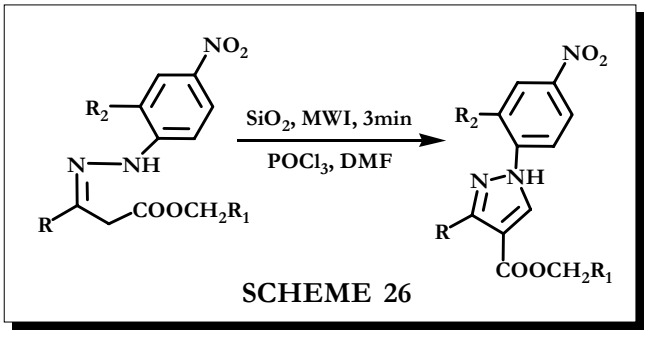
Microreview



SCHEME 25

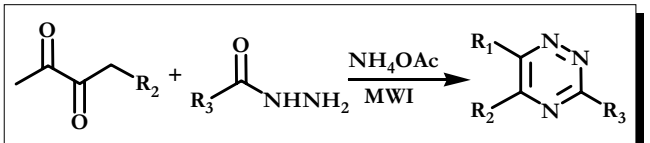
Heterocycles with more than one nitrogen atom pyrrazoles, imidazoles, triazines, azaquinolines

Oxidative cyclization was also performed by Sridar *etal* for the synthesis of pyrrazoles (SCHEME 26)[43].



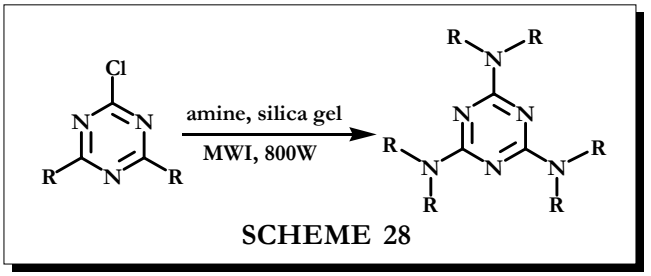
SCHEME 26

Microwave irradiation has been extended to the preparation of triazines from 1,2-dicarbonyl compounds. (SCHEME 27)[55].



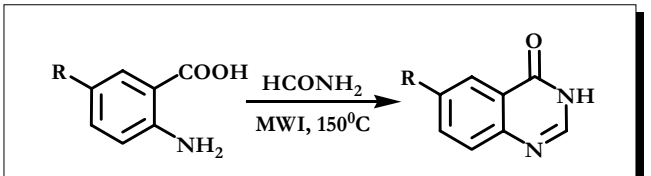
SCHEME 27

Kurteva *etal*, has reported the synthesis of melamines including ones with a wide range of biological activities using cyanuric chloride[56]. It was found to be highly effective and interestingly, when moderately bulk amines were used there was a considerable rate enhancement. The by-product of the reaction, hydrogen chloride, is quenched as ammonium salts, preventing its release into the environment (SCHEME 28).



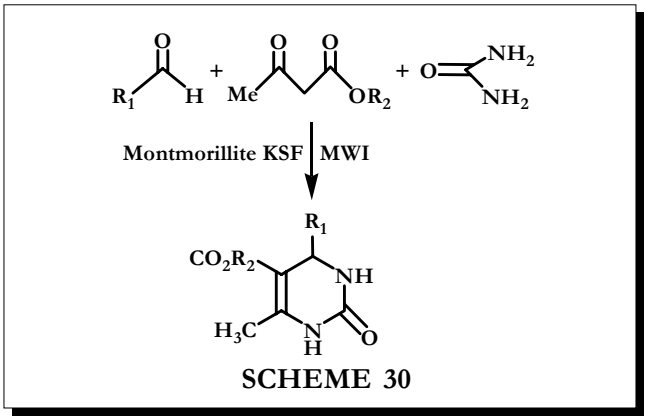
SCHEME 28

1-amino aromatic acids have been converted to azaquinolinones by reaction with formamide in neat conditions (SCHEME 29)[57].



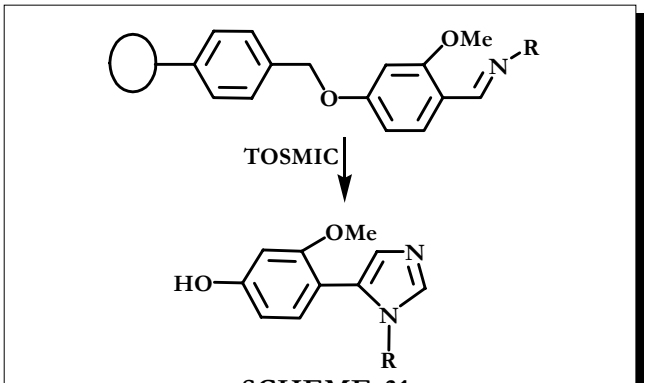
SCHEME 29

One pot synthesis of 3-4-dihydropyrimidin-2-(1H)ones from beta ketoesters, urea and various aliphatic and aromatic aldehydes using KSF clay under MWI (SCHEME 30). The catalyst may be recycled and the yields obtained are in the range of 80-97%[58].



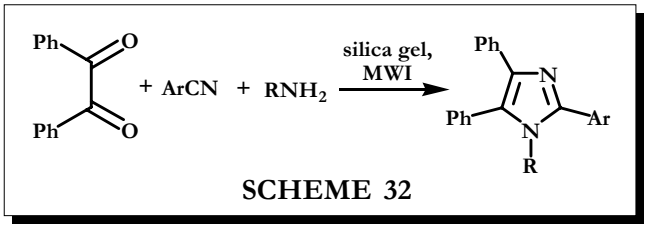
SCHEME 30

Imidazoles have been synthesized using microwave assisted reactions. 1,5-disubstituted imidazoles has been synthesized on a polymer support using base promoted 1,3-dipolar cycloaddition reactions of p-toluenesulfonylmethylisocyanide (TOSMIC) with immobilized imines under microwave irradiation (SCHEME 31)[59].



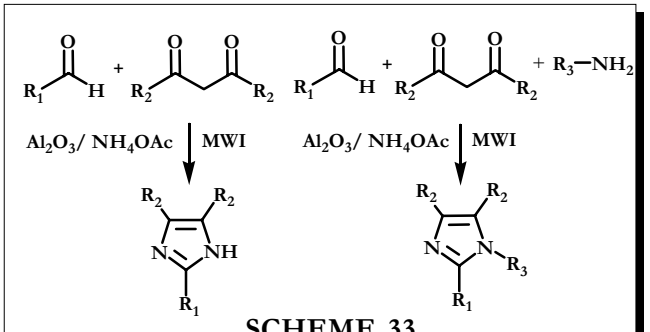
SCHEME 31

One pot condensation of benzil, benzonitrile derivatives and primary amines on the surface of silica gel under solventfree conditions and MW irradiation provided tetra substituted imidazoles in high yields (SCHEME 32)[60].



SCHEME 32

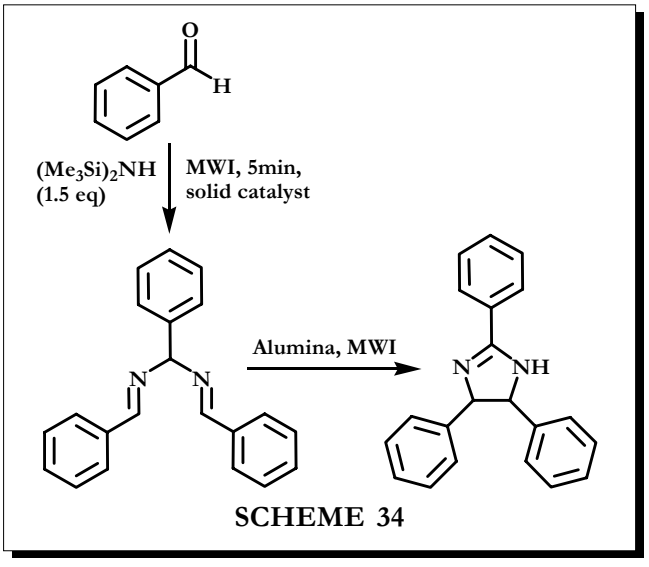
2,4,5-substituted and 1,2,4,5-substituted imidazoles are obtained by condensation of 1,2-dicarbonyl compounds with an aldehyde and an amine using acidic alumina impregnated with ammoniumacetate as solid support (SCHEME 33)[61].



SCHEME 33

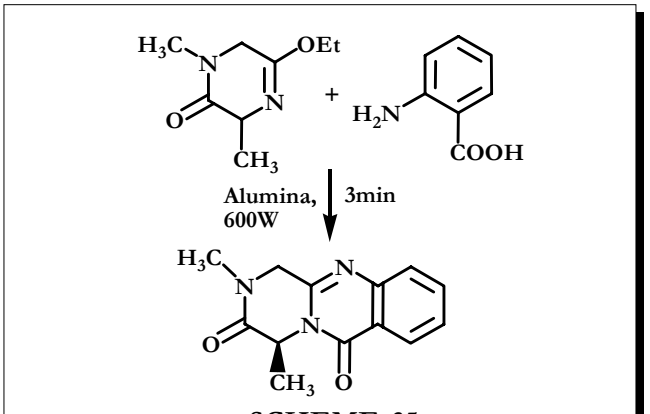
A one-pot selective synthesis of cis and trans imidazolines from aromatic aldehyde and hexamethyldisilazone in the presence of alumina has been achieved under MWI and solvent free conditions (SCHEME 34)[62].

MWI increases the yields of cyclocondensation between anthranilic acid and lactim ethers derived



SCHEME 34

from 2,5-piperazine diones leading to pyrazino[2,1-*b*]quinazoline-3,6-diones (SCHEME 35)[63].

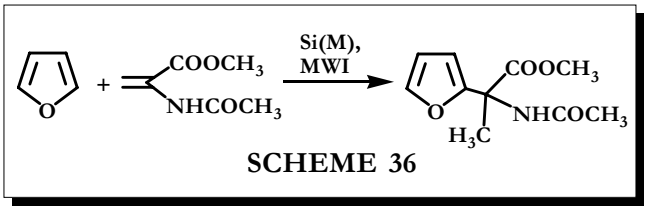


SCHEME 35

Oxygen containing heterocycles

1. Furans

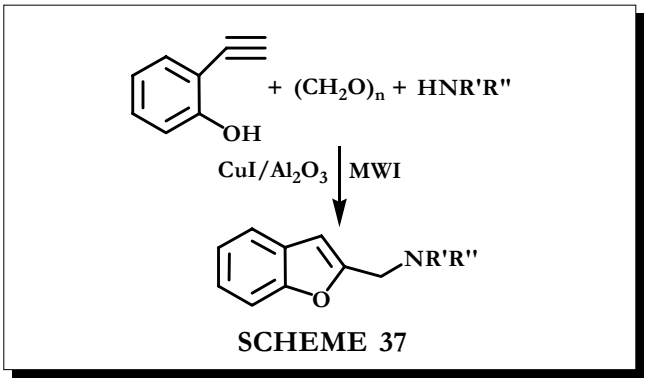
Aminoacid substituted furans have been synthesized using silica supported metal Lewis acid catalysts in conjunction with microwave irradiation for the synthesis of alanine derivatives (SCHEME 36)[40].



SCHEME 36

Substituted benzofurans are synthesized using the Mannich condensation-cyclisation sequence. 2-ethynylphenol condenses with secondary amine and

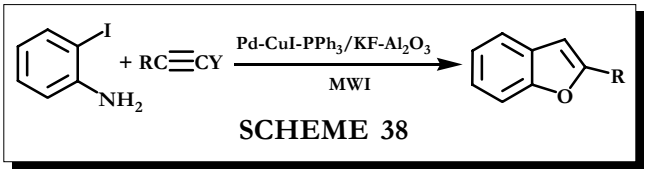
Microreview



SCHEME 37

paraformaldehyde on copper iodide doped alumina to give 2-dialkylaminomethylbenzofurans in good yields (SCHEME 37)[64].

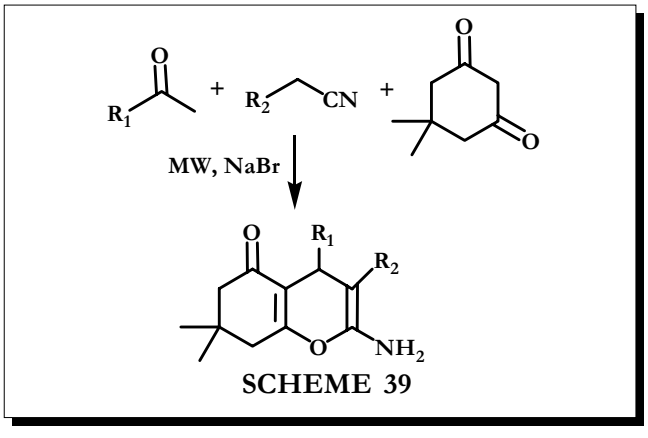
Sonogashira coupling cyclisation of o-iodophenol with terminal alkynes in solventless microwave conditions yields 2-substituted benzofurans (SCHEME 38)[51].



SCHEME 38

2. Pyrans, chromenones and flavones

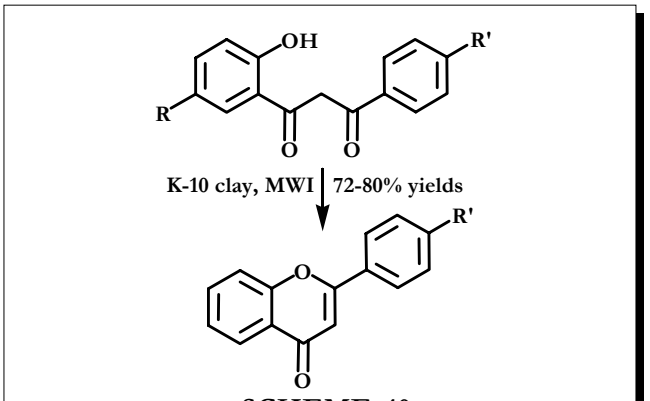
Fused pyrans have been synthesized through condensation of cyclic dicarbonyl compounds with aldehydes and nitriles in sodium bromide under MWI conditions (SCHEME 39)[65].



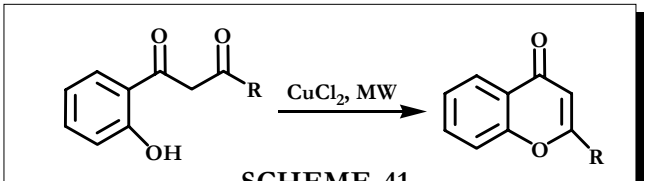
SCHEME 39

Cyclisation reactions have been carried out for diaryl diketones for the synthesis of heterocyclic compounds such as chromenones and flavones under solventless microwave irradiation (SCHEME 40)[66].

Functionalized flavones and chromones have been synthesized using copper chloride as the catalyst under neat conditions (SCHEME 41)[67].



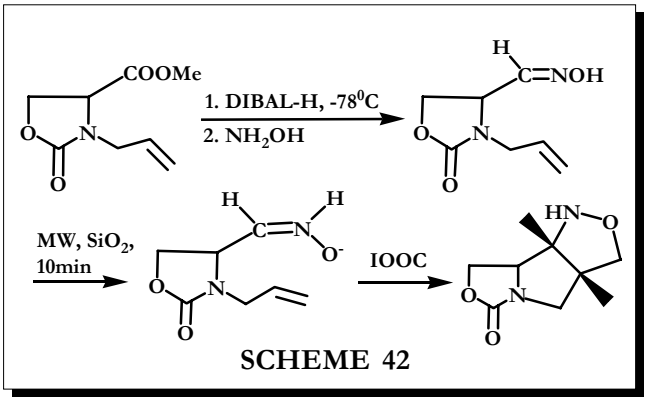
SCHEME 40



SCHEME 41

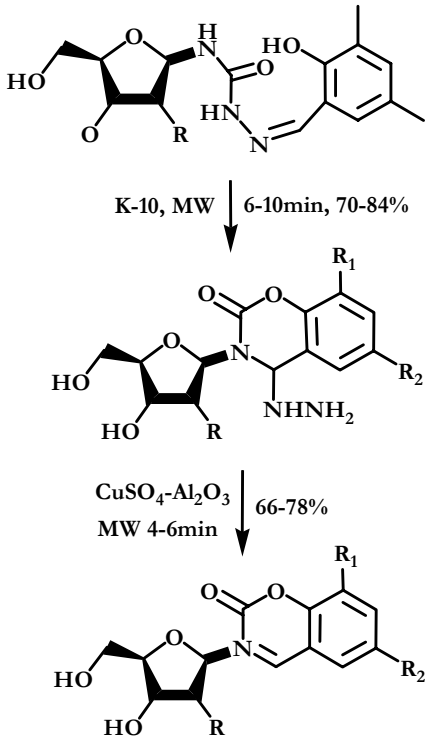
Heterocycles with different atoms

Qian Cheng *et al*, have studied that, 1,3-dipolar intramolecular cycloadditions of N-substituted oximes, nitrones and azomethine ylides were found to be induced under microwave conditions[68]. They follow the intramolecular oxime olefin cycloaddtion mechanism and these are largely used for the synthesis of chiral functionalised heterocycles (SCHEME 42).



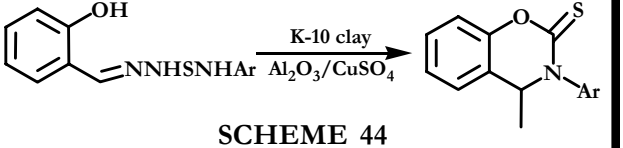
SCHEME 42

Synthesis of biologically important benzoxazinone nucleosides have been carried out by Yadav *etal*.[69] under microwave conditions in a two step procedure (SCHEME 43)



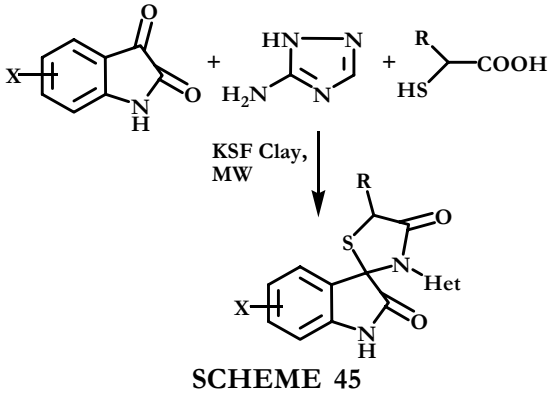
SCHEME 43

They have also synthesized benzoxazine-2-thiones using alumina supported copper sulphate in K-10 clay (SCHEME 44)[70].



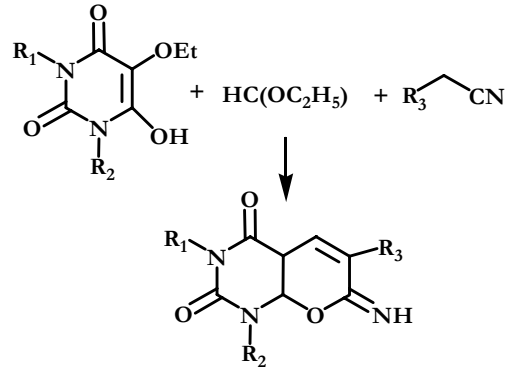
SCHEME 44

Antifungal agents like benzimidazoyl and triazoyl spiro indole-thiazolidones have been synthesized under irradiation in KSF clay (SCHEME 45)[71].



SCHEME 45

Three component cyclic condensation of barbituric acid, triethylorthoformate and alkylnitriles in acetic anhydride gives pyrano[2,3-*d*] pyrimidines (SCHEME 46)[72].



SCHEME 46

CONCLUSIONS

Microwave assisted organic synthesis is an environment friendly method for the synthesis of many compounds. The technique has been well established for the laboratory scale preparation of organic compounds. This has lead to the design of many microwave synthesizers that are available in the market. The catalytic effect of using a microwave oven arises from the rapid heating thermal effects although some chemists argue about the special microwave effect. While the existence of a special microwave effect cannot be completely ruled out, the effect appears to be a rarity and of marginal synthetic importance.

The reactions carried out in dry media are favoured mainly because the procedure satisfies the three R's of green chemistry namely, (i) recovery (ii) reuse/recycling and (iii) regeneration. Recovery of products and reagents is made simple following completion. The supports may be reused without purification and sometimes recycled with minimal effort. The reagents are mostly regenerated.

However, there are some inherent disadvantages of conducting reactions in dry media assisted by microwave irradiation. For a technique to be wholeheartedly appreciated, it should be reproducible. Most reactions have been studied in domestic microwave ovens where the control of temperature is not very effective. The up-scaling of reactions that

have been studied poses a mammoth task that needs the expertise of chemists, chemical engineers and best brains in instrumentation. But, given the benefits associated with the procedure, the prize would be worth the effort.

ACKNOWLEDGEMENTS

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