



Review Article

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Green Techniques in Synthesis of Some Thiazolidinones

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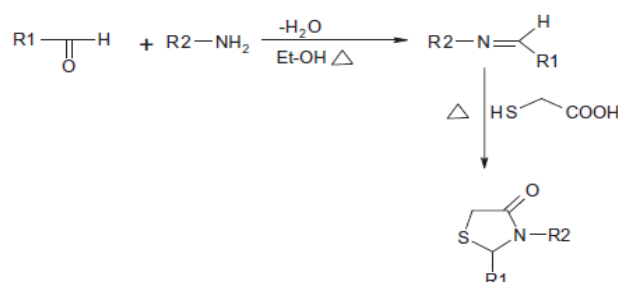
ABSTRACT

A survey of synthesis of thiazolidine derivatives has revealed that the thiazolidine nucleus has fascinated the chemists, pharmacologist and the researchers because of the biological responses exhibited by these compounds. This has led to designing the synthesis of a variety of such derivatives that are of high interest from the point of view of their bioactivity. Attempts were made by the researchers to synthesize these derivatives both by conventional methods as well as greener approach. Present study on the literature survey of thiazolidine derivatives emphasizes only eco-friendly methods of producing these derivatives. Purpose of this study is to create an enthusiasm among medicinal chemists, biochemists and the researchers to design synthesis of potential bioactive agents in a greener way.

Keywords: Green Synthesis, thiazolidines, microwave irradiation, ultrasonication.

INTRODUCTION

4-thiazolidinones are derivatives of thiazolidine which belong to an important group of heterocyclic compounds containing sulfur and nitrogen in a five member ring. The nucleus is also known as wonder nucleus because it gives out different derivatives as substitution is possible at position numbers 2, 3 and 5. These derivatives belong to the most frequently studied moieties of medicinal interest as the presence of thiazolidine in penicillin was the first recognition of its occurrence in nature. Several methods for the synthesis of 4-thiazolidinones are widely reported in the literature. These involve conventional one pot, two pot synthesis and microwave irradiation method. The main synthetic route to thiazolidin-4-ones involves three components viz. an amines, a carbonyl compounds and a mercapto-acetic acid.



The aim of this review is generalization of the data published on the synthesis of thiazolidine derivatives. It has been noticed so far, that the modifications on thiazolidine moiety displayed valuable biological activities and these modifications can be made by operationally simple, inexpensive, efficient and environmental benign methods of synthesis viz. Microwave irradiation, Ultrasonication etc. So we have decided to review briefly on novel green synthetic methodologies of thiazolidine derivatives and expect that this effort will be beneficial to researchers interested in heterocyclic chemistry.

The data is collected on synthesis of thiazolidine derivatives especially by using International Journals

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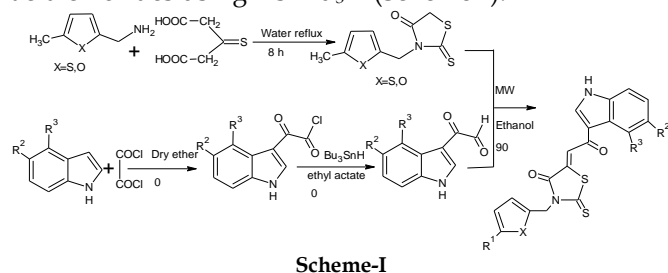
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such as Int. J. of Pharmaceutical Sciences, Tetrahedron Letters, Organic Communication, Journal of Catalysis, Montasch Chem, J. Med. Chem., J. Iran Chem, Org. Lett., Int. J. Res. Pharm. Sci., Bio. Org. Med. Chem., Bull. Org. Medicinal Chem. etc. Synthetic methods selected are related to green approach, viz. Microwave assisted reactions and ultra sonic conditions.

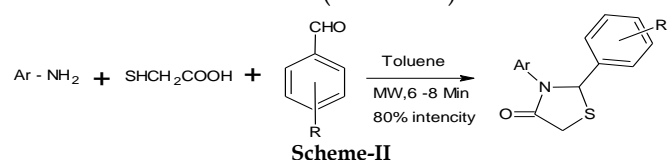
Brief Review on Thiazolidine Derivatives

Sukanta Kamila *et al.*, (Z)-5-(2-(1H-Indol-3-yl)-2-oxoethylidene)-3-(aryl/alkyl-2-ylmethyl)-2-thioxothiazolidin-4-ones have been synthesized by the Knoevenagel condensation reaction of 3-(aryl/alkyl-2-ylmethyl)-2-thioxothiazolidin-4-ones with suitably substituted 2-(1H-indol-3-yl)-2-oxoacetaldehydes *under microwave conditions*. The thioxothiazolidin-4-ones were prepared from the corresponding aryl/alkyl amines and di-(carboxymethyl)-trithiocarbonyl. The aldehydes were synthesized from the corresponding acid chlorides using HsnBu_3 [1] (Scheme-I).



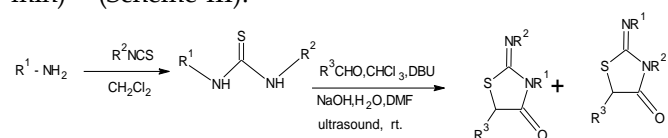
Scheme-I

Sriram *et al.*, have synthesized series of 1,3-thiazolidin-4-ones bearing variously unsubstituted diaryl ring at C-2 and N-3 positions and evaluated them for their anti-YFV activity. The synthesis of the 2,3-diaryl-1,3-thiazolidin-4-ones (15) was done by reacting substituted benzaldehyde with equimolar amount of an appropriate substituted aromatic amine in the presence of an excess of mercaptoacetic acid in toluene utilizing *microwave irradiation*. [2] (Scheme-II).



Scheme-II

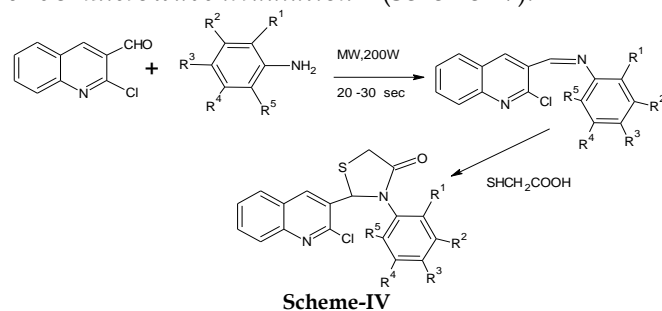
Manouchehr Mamaghani *et al.*, A convenient one-pot protocol was developed for the synthesis of 2-imino-1,3-thiazolidin-4-ones by the reaction of amines, isocyanates, aldehydes, and chloroform in the presence of sodium hydroxide *under ultrasonic conditions* in high yields (75-91%) and shorter reaction times (12-15 min) [3] (Scheme-III).



Scheme-III

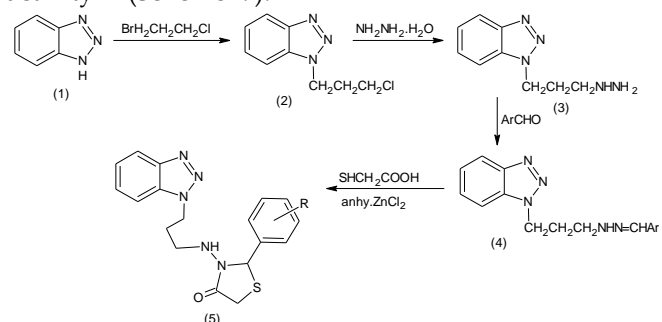
Vandana Tiwari *et al.*, used Zeolite 5A° for the synthesis of 2-(2-chloroquinoline-3-yl)-3-substituted

phenyl thiazolidin-4-ones starting from N-aryl-2-chloroquinolin-3-yl-azomethine and thioglycolic acid under *microwave irradiation* [4] (Scheme-IV).



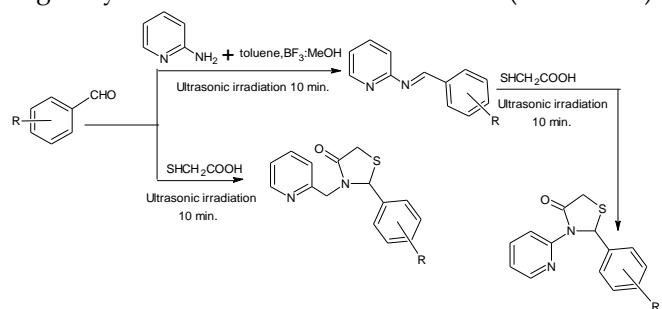
Scheme-IV

Adesh Dubey *et al.*, Some new kinds of thiazolidine derivatives of benzotriazole were prepared. Thereaction was carried out by both conventional and *microwave* methods. All the synthesized compounds were screened for their antimicrobial activity against some selected microorganism. Unexpectedly, some thiazolidine derivatives of benzotriazole showed better activity [5] (Scheme-V).



Scheme-V

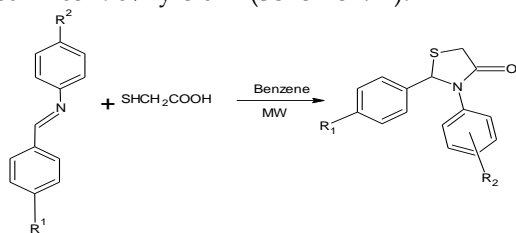
Daniela P. Gouve *et al.*, Synthesized efficient multicomponent thiazolidinones from the reaction of arenealdehydes, mercaptoacetic acid and 2-picolilamine or 2-aminopyridine under *ultrasound irradiation* are reported. The reaction with 2-aminopyridine needs a Lewis acid catalysis to afford the corresponding 2-aryl-3-(pyridin-2-yl)-1,3-thiazolidin-4-ones. All novel compounds were identified and characterized by ^1H and ^{13}C NMR spectra. Applying the sonochemical methodology, two series of heterocyclic thiazolidinones were synthesized in good yields after short reaction times [6] (Scheme-VI).



Scheme-VI

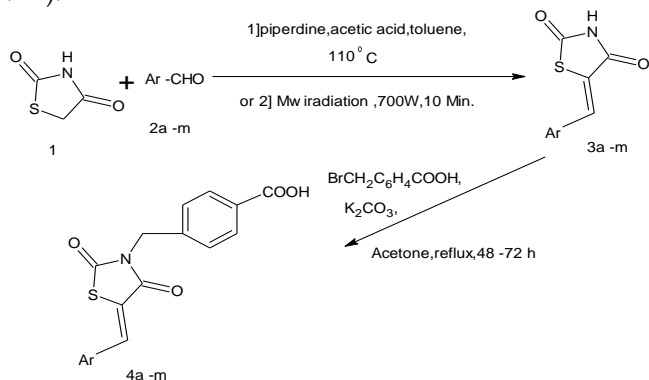
Bolognese *et al.*, prepared a range of 1,3-thiazolidin-4-one derivatives by the *microwave-assisted* reaction between benzylidene-anilines and mercaptoacetic acid

in benzene at 30°C for 10 min. After purification by chromatography, the 1,3-thiazolidin-4-ones are isolated in 65-90% yield [7] (Scheme-VII).



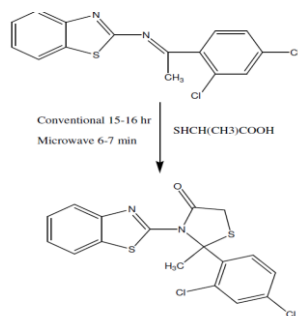
Scheme-VII

Shankar G. Alegaon *et al.*, have prepared New (Z)-5-substituted-2,4-thiazolidinediones (3a-m) by the condensation of thiazolidine-2,4-dione (1) with suitable aldehydes (2a-m) via *microwave irradiation* technique. The reaction between (Z)-5-substituted-2,4-thiazolidinediones and 4-(bromomethyl) benzoic acid, followed by a workup in acidic medium provided 4-(((Z)-5-substituted-2,4-dioxothiazolidin-3-yl)methyl) benzoic acid derivatives (4a-m). The structures of the newly synthesized compounds were confirmed by IR, ¹H NMR, ¹³C NMR spectral studies, and elemental analysis. All compounds were evaluated for their in vitro antimicrobial and cytotoxic activities [8] (Scheme-VIII).



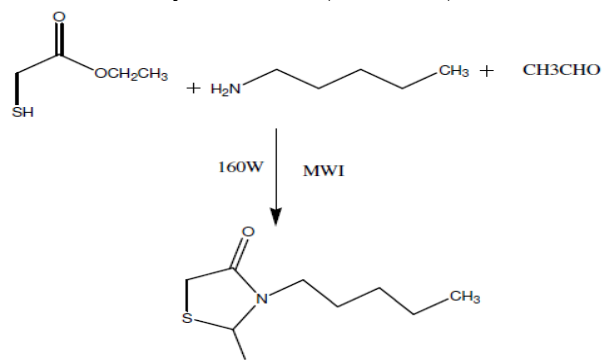
Scheme-VIII

Desai KR *et al* has carried out themicrowave assisted synthesis ofthiazolidinone from the Schiff's bases by using thiolactic acid. Theproducts were synthesized byconventional and *microwave* synthesisand the yield were compared with each other. They concluded that the percent yield with the microwave irradiatedsynthesis was better than the conventional [9] (Scheme-IX).



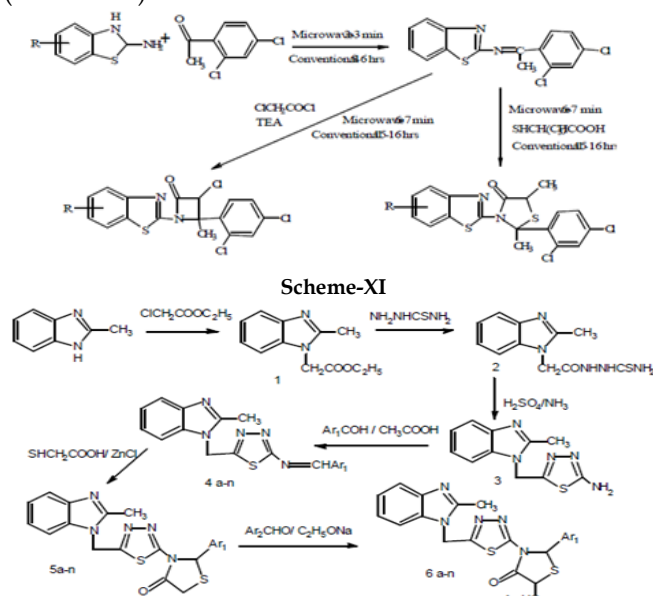
Scheme-IX

Pawelczyk A and Zaprutko L have synthesized the 4-thiazolidinone derivatives by *microwave method* as a new fragrant substances and unsaturated analogs of jasmynes91. The npentylamine was mixed with acetaldehyde. The mixture was stirred at room temperature under condenser. After 1 h ethyl thioglycolate (or thioglycolic acid) was added. Reagentswere irradiated for 5 min with 160 W by microwaves in a flask with condenser and further treated with ethyl acetate [10] (Scheme-X).



Scheme-X

Ketan *et al.*, synthesized new series of compounds namely 3-chloro-4-(2',4'-dichlorophenyl) -4-methyl-1-(substituted-1',3'-benzothiazol-2'yl)-azetidin-2- ones and 2-(2',4'-dichlorophenyl) -2,5-dimethyl-3-(substituted-1',3'-benzothiazol- 2'-yl)-1,3-thiazolidin-4- ones by the reaction of schiff base derivatives with chloroacetyl chloride in presence of triethylamine thiolactic acid respectively by *microwave method* [11] (Scheme-XI).



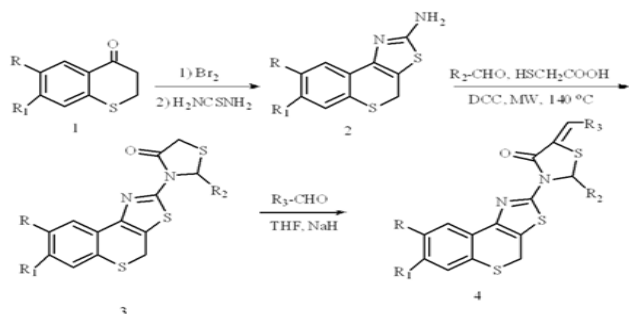
Scheme-XI

6b= Ar₁=2-Cl C₆H₄, Ar₂=2-Cl C₆H₄; 6c= Ar₁=3-Cl C₆H₄, Ar₂=3-Cl C₆H₄;
6d= Ar₁=4-Cl C₆H₄, Ar₂=4-Cl C₆H₄; 6e= Ar₁=2-Br C₆H₄, Ar₂=2-Br C₆H₄;
6f= Ar₁=3-Br C₆H₄, Ar₂=3-Br C₆H₄; 6g= Ar₁=4-Br C₆H₄, Ar₂=4-Br C₆H₄.

Rajiv *et al* synthesized some new N1-[2'-{2-substituted-phenyl-5-substitutedbenzylidene-1,3-thiazolidine-4-one}-5'-methylene-1',3',4'-thiadiazole] -2-methyl-benzimidazoles, 6(a-n) conventional and *green*

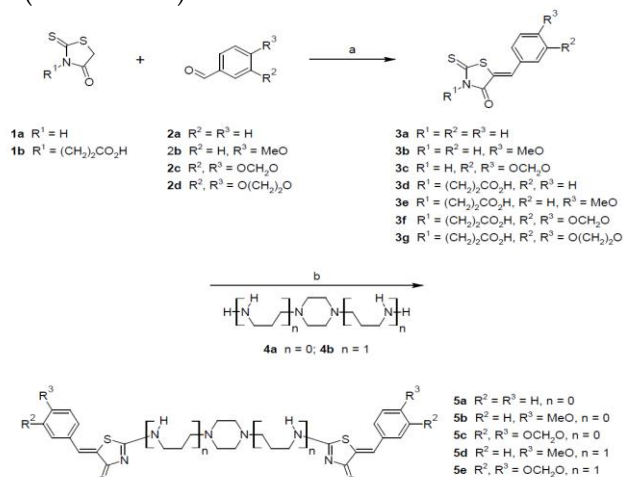
approach methods in terms to yield and reaction time along with antimicrobial activity against *Bacillus subtilis*, *Escherichia coli*, *Klebsiella pneumoniae* and *Streptococcus aureus* bacteria and *Aspergillus niger*, *Aspergillus flavus*, *Fusarium oxysporium* and *Trichoderma viride* fungi *in vitro* at 50 and 100 ppm concentrations [12] (Scheme-XII).

Zhengyue Ma and Xinghua Zhang carried out **Microwave-assisted synthesis** of New 1,3-thiazolidin-4-ones for evaluation of their Anticancer Efficacy [13] (Scheme-XIII).



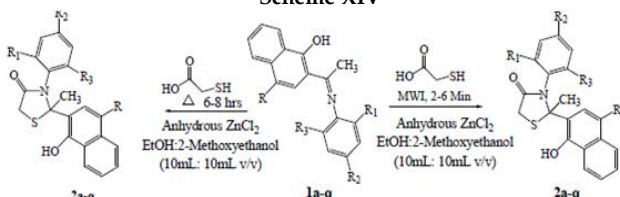
Scheme-XIII

W. K. Coulibaly *et al.* synthesised New N,N'-Bis(5-arylidene-4-oxo-4,5-dihydrothiazolin-2-yl)piperazine Derivatives Under Microwave Irradiation [14] (Scheme-XIV).



Sch. 1. a) for 3a-c: MeOH, AcONa 3 eq., MWI, 65°C, 10 min. and for 3d-g: MWI, 130°C, 10 min. b) MWI, 80-120°C, 30 min.

Scheme-XIV

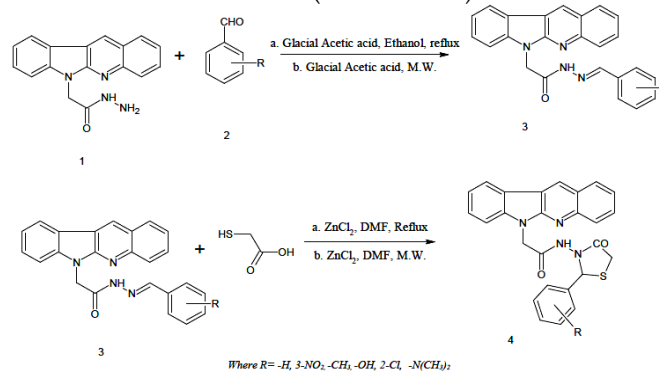


Scheme-XV

Sainath B Zangade *et al.*, **Microwave Assisted Synthesis** of Some Novel Series of 4-Thiazolidinone Derivatives as Potent Antimicrobial Analogs [15] (Scheme-XV).

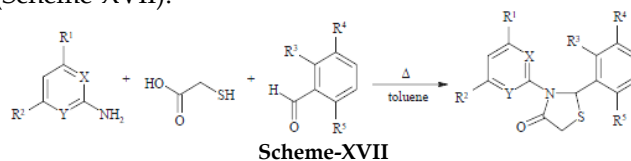
Krishnakant T. Waghmode- Indolo[2,3-b]quinoxalin-1-yl-N(4-oxo-2-phenyl-1,3-thiazolidin-3-yl)acetamide

derivatives were synthesized from N'-benzylidene-2-(6H-indolo [2,3-b] quinoxalin-6-yl) acetohydrazide derivatives by conventional method and under **microwave irradiation** [16] (Scheme-XVI).



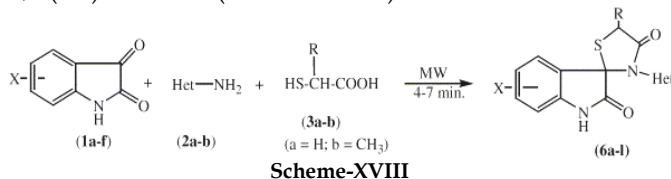
Where R = -H, 3-NO2, -CH3, -OH, 2-Cl, -N(CH3)2
Scheme-XVI

Angela Rao *et al.*, carried out **microwave-assisted synthesis** of benzimidazole and thiazolidinone derivatives as HIV-1 RT inhibitors [17] (Scheme-XVII).



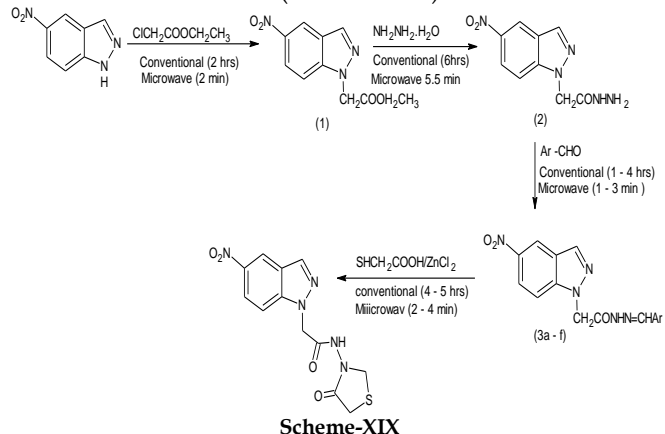
Scheme-XVII

Anshu Dandia *et al.*, carried out efficient **microwave enhanced regioselective synthesis** of a series of benzimidazolyl/triazolyl spiro [indole-thiazolidinones] as potent antifungal agents and crystal structure of spiro[3H-indole-3,2'-thiazolidine]-3'-(1,2,4-triazol-3-yl)-2,4'(1H)-dione [18] (Scheme-XVIII).



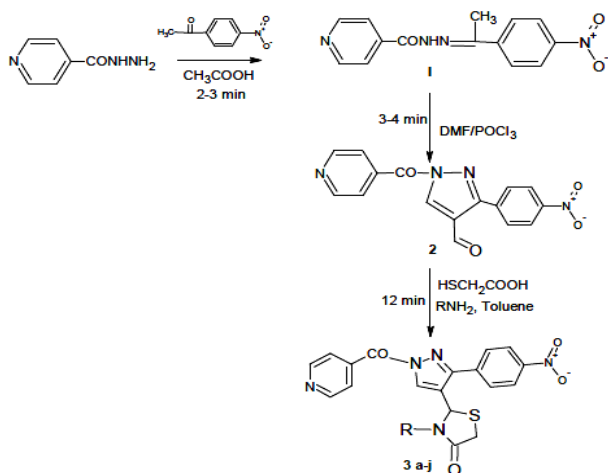
Scheme-XVIII

Several new N-[(4-oxo-2-substituted aryl-1, 3-thiazolidine)-acetamidyl]-5-nitroimidazoles were synthesized by Upadhyay A. *et al* from N-(arylidene amino acetamidyl)-5- nitroindazoles. The reactions were carried out by both conventional as well as **microwave method** [19] (Scheme-XIX).



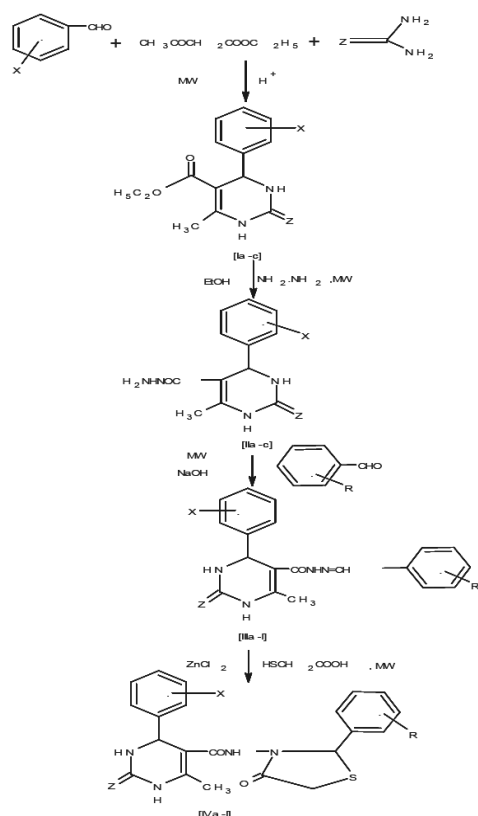
Scheme-XIX

Microwave induced synthesis of some new 3-substituted-1, 3-thiazolidin-4-ones for their anti microbial and antitubercular activities was carried out by D.Visagaperumal [20] (Scheme-XX).



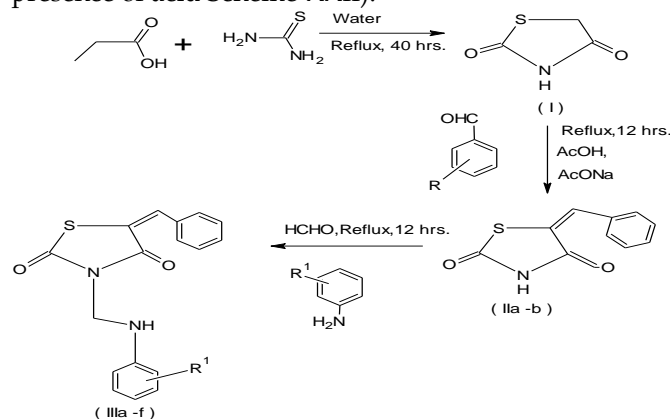
Scheme-XX

Pravina piste *et al.*, synthesized 6-methyl-4-(Sub.)Phenyl-2-Oxo/Thioxo-1,2,3,4-Tetrahydro pyrimidine -5-(2-Sub.Phenyl,3-Amido)thiazolidine -4-ones (IVa-1) was achieved from corresponding Mannich Base (IIIa-1) by reaction with mercapto acetic acid and anhydrous zinc chloride for 2-3 minutes in **Microwave irradiation**. The synthesized compounds have been screened in vitro for their antimicrobial activity against *S. aureus* and *E.coli*. Some of the compounds displayed pronounced biological activity [21] (Scheme-XXI).



Scheme-XXI

Kanase *et al.*, developed simple and efficient method in synthesis of some derivatives of thiazolidine by using easily available reagents. The Synthesis of 5-(4-substituted benzylidene)-3-[(anilino) methyl]-1, 3-thiazolidene-2,4-diones has been carried out from Synthesis of thiazolidene-2, 4-dione by using the reaction of chloro acetic acid and thiourea in presence of green and **universal solvent** i.e. water followed by reaction with substituted benzaldehyde and sodium acetate in presence of acid afforded 5-(substituted benzylidene)-1,3-thiazolidene-2,4-dione (IIa-b) which further treatment with formaldehyde in ethanol in presence of acid Scheme-XXII). [22]



Scheme-XXII

Microwave irradiation process is the fastest synthetic procedure for thiazolidine-4-ones. The literature reveals that easy synthetic routes for thiazolidine-4-one derivatives have taken attention of the chemists, pharmacologists and researchers to produce these chemicals. It is also noticed that attachment of other moieties to thiazolidine nucleus at positions 2, 3 and 5 are possible and such an endeavour results in enhanced biological responses of it. Further we conclude that more interest may be shown by the chemists, pharmacologists and researchers to devise more number of environmentally benign synthetic routes to produce many other derivatives of thiazolidine and explore their biologically activities. We hope that, our brief review will assist all those interested in this promising field of heterocyclic chemistry to reach decisions in the choice of targets and tasks for further investigations.

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