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Research Article

GREEN SYNTHESIS OF TETRA-AZEPINES USING MICROWAVE ASSISTED METHOD

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ABSTRACT
Synthesis of tetra-azepines has been achieved by environmentally benign methods. In this dihydroformazan has been reacted with oxalic acid, ethylene glycol, chloro acetic acid etc. in microwave oven for about 1 to 2 minutes to yield tetra-azepines. All the products have been purified by crystallization and these have been acetylated and benzoylated by using acetic anhydride and benzoyl chloride to yield acetylated and benzoylated products respectively. Thestructure of all these synthesized compound have been established on the basis of elemental analysis and spectral data.

Keywords: Tetraazepines, Microwave, Dihydroformazan.

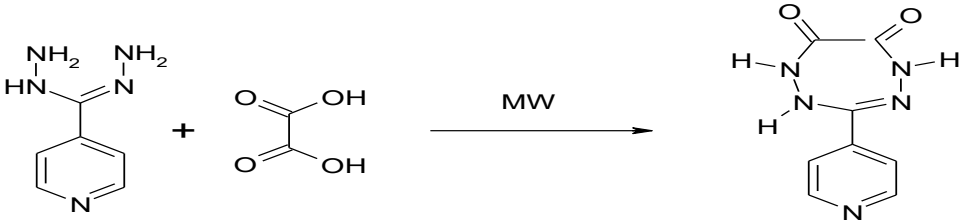
1. INTRODUCTION
Green amalgamation is an arising region in the field of science and gives monetary and natural advantages as an option in contrast to substance and actual strategies. In this, microwave helped technique is utilized to perform response.

Green science manages union strategies as per its 12 vital standards without or possibly with diminished adverse consequences [1, 2] on human wellbeing and climate. These standards, to be successful, should be applied at the same time [3]. A totally Green amalgamation doesn't exist: as another option, a Greener combination is a more honest definition. These standards of green science were portrayed in the primary exemplary book [4] around here and Internet assets [5, 6].

These standards are helpful and basic [7], Green science, additionally called reasonable science, is a space of science and synthetic designing zeroed in on the plan of items and cycles that limit or dispose of the utilization and age of perilous substances.[8] While ecological science centers around the impacts of contaminating synthetics on nature, green science centers around the natural effect of science, including lessening utilization of nonrenewable assets and innovative methodologies for forestalling pollution.[9-14]. Azepines are seven-membered nitrogen heterocycles discovered comprehensively in the two drugs and regular items as center skeletal parts and as practical limbs.

2. EXPERIMENTAL
Melting points were determined on open capillary apparatus and are uncorrected. IR spectra were recorded on Perkin Elmar spectrophotometer and 1H, NMR spectra on Bruker advanced II 400 spectrometer.

In the synthesis of Tetra-azepines Dihydroformazan is reacted with Carbonyl/Dihydroxy compounds. Dihydroformazan prepared by using a mixture of isoniazid (0.01 mole) and hydrazine hydrate (0.01 mole) in 15 ml ethanol was refluxed for 1.5 hour on a water bath a solid white crystalline residue was obtained. It was crystallized from ethanol to yield dihydroformazan.



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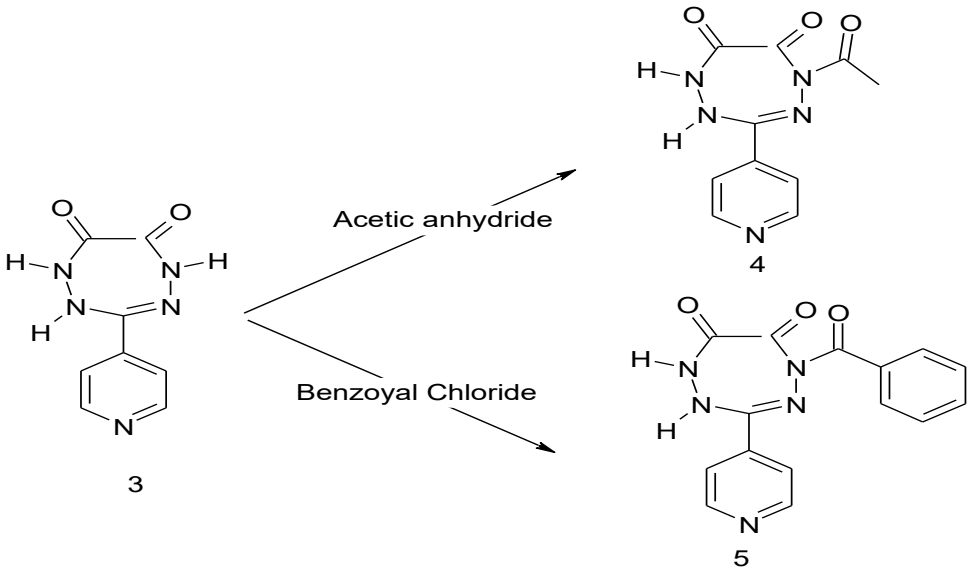

Reaction Scheme

Where,

1. *Dihydroformazan*
2. *Oxalic Acid*
3. *1H,4H,5H-3-pyrid-4yl-6,7-dioxo-1,2,4,5-tetra-azepine*
4. *4H,5H,1-acetyl-3-(pyrid-4yl)-6,7dioxo-1,2,4,5-tetra-azepine*
5. *4H,5H,1-benzoyal-3-(pyrid-4-yl)-6,7-dioxo-1,2,4,5-tetra-azepine*

2.1. Synthesis of 1H,4H,5H-3Pyrid-4yl-6,7-substituted 1,2,4,5-tetra-azepines. (Microwave Method)

A mixture of dihydroformazan (0.01 mole) and oxalic acid (0.01 mole) were thoroughly mixed in a 50 ml beaker and ethanol (4 drops) was added to it to moisten the mixture. The beaker was covered with a watch glass and irradiated in a microwave oven for 2 minutes. After completion of reaction the beaker was removed from the oven and mixture was cooled to room temperature. The product was crystallized by hot water.

The spectral analysis of compound 1H,4H,5H-3-pyrid-4yl- 6,7-dioxo-1,2,4,5-tetra-azepines was recorded IR spectral analysis indicated absorption band at 3429 cm^{-1} (N-H stretching), 1681 cm^{-1} (C=O stretching), 1660 cm^{-1} (C=O stretching), 1303 cm^{-1} (C-N stretching), 1226 cm^{-1} (N-N stretching), 1H NMR spectrum 7.39 (s, 1-NH), 10.69 (s, 1-NH), 7.85-7.87 (d, 2H pyridyl), 8.768.78 (d, 2H pyridyl).

The spectral analysis of compound 1H, 4H,5H-3(pyrid-4yl)- 1,2,4,5-tetra-azepines was recorded IR spectral analysis indicated absorption band at 3302cm^{-1}(N-H stretching), 1335 cm^{-1} (C-N stretching), 1220 cm^{-1} (N-N stretching) 1H NMR spectrum 2.17-2.64 (d, 4H-CH_2-CH_2-), 7.6 (s, 1H-NH), 9.99 (s, 1H-NH), 7.65 .7.76 (d, 2H-pyrid-H), 8.69.8.76 (d, 2H- pyrid H).

The spectral analysis of compound 1H,4H,5H-3 (pyrid-yl)-6,7-oxo-1,2,4,5-tetra- azepines was recorded IR spectral analysis indicated absorption band at 3431 cm^{-1} (N-H stretching), 1680 cm^{-1} (C-O stretching), 1340 cm^{-1} (C-N stretching), 1210 cm^{-1} (N-N stretching), 1H NMR spectrum 2.4 (s, 2H-CH2-), 9.09 (s, 1H -NH), 7.70 (s, 1H –NH), 10.21 (s, 1H-NH), 6.44-6.88 (dd, Ar-H), 7.29-7.26 (dd, Ar-H).

The spectral analysis of compound 1H,4H,5H-3(pyrid-4yl)-6-oxo-1,2,4,5-tetra- azepines was recorded IR spectral analysis indicated absorption band at 3429 cm^{-1} (N-H stretching), 1660 cm^{-1} (C-O stretching), 1303 cm^{-1} (C-N stretching), 1226 cm^{-1} (N-N stretching), 1H NMR spectrum 2.03 (s, 2H-CH2-), 7.30 (s, 1H-NH), 10.69 (s, 1H-NH), 8.30 (s, 1H-NH), 7.85-7.90 (d d, para substituted Ar-H), 8.86-8.98 (d d, para substituted Ar-H).

The spectral analysis of compound 4H-3(pyrid-4yl)-1,2,4,5-tetra-azepines was recorded IR spectral analysis indicated absorption band at 1336 cm^{-1}(C-N stretching), 1670, 1630 cm^{-1} (C=N stretching), 1203,1211 cm^{-1} (N-N stretching), 1451, 1491 cm^{-1} (Aromatic C=C), 1H NMR spectrum 2.9 (d, 1H-CH-), 2.5 (d, 1H-CH), 6.50-6.66 (dd, 1H-ArH), 7.35-7.43 (d d, 1H- ArH).

2.2. Synthesis of 1H, 4H, 5H -3Pyrid-4yl-6,7-substituted 1,2,4,5-tetra-azepines. (Conventional Heating Method)

A mixture of dihydroformazan (0.01 mole) and oxalic acid (0.01 mole) were taken in a 50 ml round bottom flask and 15 ml ethanol was added to it. It was then heated for three hours. After completion of reaction the mixture was cooled and product recrystallized by using ethanol.

3. RESULTS

Table 1: Microwave heating method (tetra-azepines)

S. N.	Carbonyl/ Dihydroxy compound	Name of Product	Yield %	Time (min)	Melting Point (°C)	Benzoyalazepines Melting Point (°C)	Acetylazepine melting point (°C)
1	Oxalic Acid	1H,4H,5H-3-pyrid-4yl-6,7-dioxo-1,2,4,5-tetra-azepines.	73	2	252	80	202
2	Ethylene Glycol	1H, 4H,5H-3(pyrid-4yl)-1,2,4,5-tetra-azepines.	67	1.5	115	92	175
3	Chloro acetic acid	1H,4H,5H-3(pyrid-yl)-oxo-1,2,4,5-tetra-azepines	69	1.5	185	158	133
4	Glycolic acid	1H,4H,5H-3(pyrid-4yl)-6-oxo-1,2,4,5-tetra-azepines.	71	1.5	262	201	198
5	Glyoxal	4H-3(pyrid-4yl)-1,2,4,5-tetra-azepines.	82	0.5	248	182	142

Table 2: Conventional heating method (tetra-azepines)

S. N.	Carbonyl/ Dihydroxy compound	Name of Product	Yield %	Time (hrs)	Melting Point (°C)	Benzoyalazepines Melting Point (°C)	Acetylazepine meltingpoint (°C)
1	Oxalic Acid	1H,4H,5H-3-pyrid-4yl-6,7-dioxo-1,2,4,5-tetra-azepines.	50	3hrs	250	79	200
2	EthyleneGlycol	1H, 4H,5H-3(pyrid-4yl)-1,2,4,5-tetra-azepines.	53	3hrs	114	90	171
3	Chloro acetic acid	1H,4H,5H-3(pyrid-yl)-6,7-oxo-1,2,4,5-tetra-azepines	49	3hrs	184	155	131
4	Glycolic acid	1H,4H,5H-3(pyrid-4yl)-6-oxo-1,2,4,5-tetra-azepines.	62	3hrs	259	200	196
5	Glyoxal	4H-3(pyrid-4yl)-1,2,4,5-tetra-azepines.	74	3hrs	246	181	141

4. CONCLUSION

In this synthesis of tetrazepines using microwave heating methods offer advantages over conventional heating methods such as, microwave heating method required less time than using conventional heating method. The yield of compound was very good by using microwave heating method. Observing melting points from both methods it is concluded that using microwave heating method compounds found better purity than using conventional heating methods.

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