GREEN SYNTHESIS OF 1H, 2H, 5H-3(PYRID-4YL)- 6-PHENYLIMINO-1,2,4,5-TETRAZINES

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ABSTRACT

Synthesis of various tetrazines has been achieved by environmentally benign method. In this dihydroformazan have been reacted with Phenyl immino-isocynodichloride, o-tolyl imino-isocynodichloride etc. in microwave oven to yield tetrazines. The synthesis of tetrazines is achieved by the reaction of dihyroformazan and cynodichloride in microwave oven. All these 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 product respectively. The structure of all these synthesized compound have been established on the basis of elemental analysis and spectral data.

Keywords: *dihydroformazan, tetrazines.*

Introduction

Green synthesis using Microwave irradiations have been successfully applied in organic synthesis. Microwave heating has emerged as a powerful technique to promote a variety of chemical reaction. Microwave chemistry is the science of applying microwave radiation to chemical reactions. [1-5] Microwaves act as high frequency electric fields and will generally heat any material containing mobile electric charges, such as polar molecules in a solvent or conducting ions in a solid. Polar solvents are heated as their component molecules are forced to rotate with the field and lose energy in collisions. Semiconducting and conducting samples heat when ions or electrons within them form an electric current and energy is lost due to the electrical resistance of the material. Microwave heating can have certain benefits over conventional ovens:

- reaction rate acceleration
- milder reaction conditions
- higher chemical yield
- lower energy usage
- different reaction selectivity

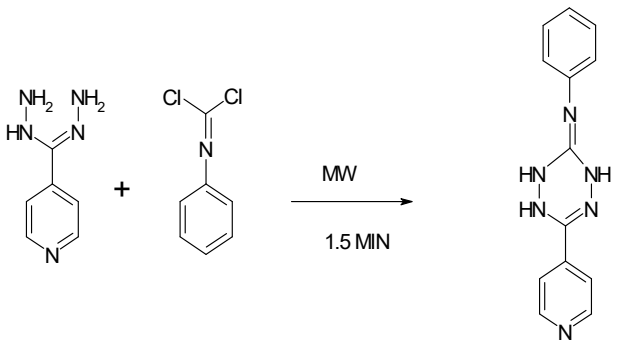
Microwave chemistry is applied to organic chemistry [6] and to inorganic chemistry.[7-11]

Results and Discussion

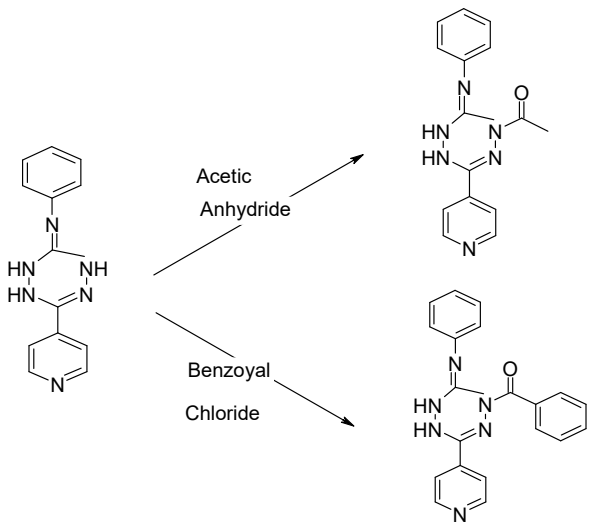
The compound 1H, 2H, 5H-3(pyrid-4yl)-6-phenylimino-1,2,4,5-tetrazine was prepared by the reaction of dihydroformazan (0.01mole) and phenylimino-isocynodichloride (0.01 mole). They were thoroughly mixed in a 50 ml beaker and ethanol (3 drops) was added to it to moisten the mixture. The beaker was covered with a watch glass and irradiated in a microwave oven for 1.5 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 and melting point is found to be 222^0C. The product has been acetylated and benzoyalted by using acetic anhydride and benzoyl chloride.

IR spectra of compound was found to be 3429 cm^{-1} (N-H starching), 1303 cm^{-1} (C-N starching) , 1226 cm^{-1} (N-N starching) also NMR spectra of compound was found to be δ 7.39(s, 1H, N-H), δ 10.69 (s, 1H, N-H), δ 7.85-7.87 (d, 2H, Ar H), δ 8.768.78 (d, 2H, Ar-H).

Reaction Scheme



Dihydroformazan Phenyl imino-iso Tetrazine cynodichloride



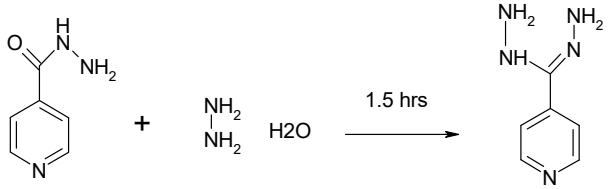
Tetrazine Acetylated, Benzoylated Derivatives

The reaction of dihydroformazan was extended to other cynodichloride compounds like o-tolylimino-isocynodichloride, m-tolylimino-isocynodichloride, p-tolylimino-isocynodichloride and related 1,2,4,5-tetrazines have been isolated in good yield. They were converted to their acetyl and benzoyl derivatives.

Experimental

The melting points of all synthesized compounds ware recorded using paraffin bath and are uncorrected. The IR spectra ware recorded on a Perkin Elmer spectrophotometer in the frequency range 4000-400 cm^{-1}. ^1H NMR spectra ware recorded on Brukar advanced 400 spectrometer with TMS as internal standard using $CDCl_3$ and DMSO-d6 as solvent. Synthesis of dihydroformazan and phenyl isocynodichloride:-

A mixture of isoniazid (0.01mole) and hydrazine hydrate (0.0mole) in ethanol (15 ml) was refluxed for 1.5 hr on a water bath a solid white crystalline residue was obtained. It was crystallized from ethanol to yield dihydroformazan.



Isoniazid hydrazine hydrate Dihydroformazan

Though a chloroform solution of phenyl isothiocynate (1.3 ml + 12 ml chloroform) Chlorine (generated from 3.2 gm KmnO4 and 12 ml concentrated HCl) was passed. After the addition of chlorine has been completed yellow colored mixture is formed. The solvent was removed by evaporation; phenyl isocynodichloride in the form of oily solid was collected.

Phenyl isothiocynate **Chlorine** **Phenyl iso-cynodichloride**

Conventional Heating Method

S.N.	Cynodi-chloride compounds	Name of Product	Time	Yield	Melting Point	Acetylated Derivative M.P.	Benzoylated Derivative M.P.
1	Phenyl imio-isocynodichloride	1H,2H,5H-3(pyrid-4yl)-6-phenylimino-1,2,4,5-tetrazine.	3hrs	52%	222	110	128
2	o-tolylimio-isocynodichloride	1H,2H,5H-3(pyrid-4yl)-6-o-tolyl-imino-1,2,4,5-tetrazine	3hrs	64%	195	200	208
3	m-tolyliminoisocynodichloride	1H,2H,5H-3(pyrid-4yl)-6-m-tolyl-imino-1,2,4,5-tetrazine	3hrs	59%	166	173	96
4	p-tolylimino-isocynodichloride	1H,2H,5H-3(pyrid-4yl)-6-p-tolyl-imino-1,2,4,5-tetrazine	3hrs	66%	134	96	112

Microwave Heating Method

S.N.	Cynodi-chloride compounds	Name of Product	Time	Yield	Melting Point	Acetylated Derivative M.P.	Benzoylated Derivative M.P.
1	Phenyl imio-isocynodichloride	1H,2H,5-H-3(pyrid-4yl)-6-phenylimino-1,2,4,5-tetrazine.	90 Sec	72%	218	112	128
2	o-tolylimio-isocynodichloride	1H,2H,5H-3(pyrid-4yl)-6-o-tolyl-imino-1,2,4,5-tetrazine	60 Sec	76%	193	201	211
3	m-tolylimino-isocynodichloride	1H,2H,5H-3(pyrid-4yl)-6-m-tolyl-imino-1,2,4,5-tetrazine	90 Sec	79%	165	178	98
4	p-tolylimino-isocynodichloride	1H,2H,5H-3(pyrid-4yl)-6-p-tolyl-imino-1,2,4,5-tetrazine	90 Sec	80%	132	95	115

Conclusion

In this synthesis of tetrazines using microwave heating method offer advantages over conventional heating method 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 point from both methods it is concluded that using microwave heating method compound found better purity than using conventional heating method.

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