RJC
http://www.rasayanjournal.com

RASĀYAN *J. Chem.*
Vol.3, No.4 (2010), 693-696
ISSN: 0974-1496
CODEN: RJCABP

MICROWAVE PROMPTED RAPID REACTION FOR THE SYNTHESIS OF SOME TRIAZOLO-BENZOTHIAZOLES, NAPHTHATHIAZOLES AND TO STUDY THEIR ANTIBACTERIAL ACTIVITY

D.K.Swamy[1],* and M.V. Deshmukh[2]
[1]Department of Chemistry, Pratibha Niketan College, Nanded, (M.S.) India
[2]Post graduate department of Chemistry, Science College, Nanded
*E-mail: swamy_deelip@rediffmail.com

ABSTRACT

Earlier methods for the ring closure of aza heteryl hydrazones were by the use of acidic cyclo dehydrating agents like nitrobenzene, bromine acetic acid, $FeCl_3$ and some such reagents. These methods were tedious. The use of microwave irradiation reduces substantial time and yields are also better.

Key words: s-triazolo-benzothiazoles and naphthathiazoles, microwave irradiation and antibacterial activity.

INTRODUCTION

Oxidative cyclizations were carried out by different workers[1,2] using nitrobenzene, ferric chloride, bromine acetic acid, manganese dioxide and potassium ferricyanide. Time required for the completion of reaction ranges from 4 to 6 hours[3], with LTA[4] results somewhat better but it causes formation of acetoxylated product as impurity. Therefore author tried to prepare the cyclised products using these hydrazones and subjected them to microwave induced cyclization (scheme-1). Most of the reactions are carried out in unaltered domestic microwave oven.

EXPERIMENTAL

Melting points were determined in open capillaries and are found uncorrected. IR spectra (KBr discs) were recorded on FTIR- SCHIMADZU 84005 Spectrophotometer and absorption was expressed in cm^{-1}. NMR spectra were recorded on Gemini 200 MHz spectrometer with TMS as an internal standard. Chemical shift values were mentioned in δ ppm. Microwave irradiation was done by domestic microwave oven. The progress of the reactions was monitored by TLC on 2x5 cm pre coated silica gel. The compounds were analyzed for C, H and N and the values were found within ±0.4% of the calculated values.

Preparation of 2-hydrazino benzothiazole

2-Chloro benzothiazole (1.5 g) in ethanol (10 ml) was treated with 80% (w/v; 2ml) of hydrazine hydrate and heated to reflux on water bath. Within 20-25 minutes solid separated. The content was cooled and precipitate of 2-hydrazinobenzothiazole (1.0 gm; 67%) was collected and recrystallized from ethanol; m.p. 192°C.

General preparation for 2-substituted benzothiazolyl hydrazone

A mixture of 2-hydrazinobenzothiazole (1.01 mole) prepared as above, required (0.01 mole) aldehyde and ethanol (25 ml) was taken in a flask. The mixture was refluxed for 1.5 to 2 hours. The contents were cooled and ethanol was removed. Product obtained on recrystallization gave 2-substituted benzothiazolylhydrazone.

Microwave induced synthesis

Benzothiazolyl/naphthathiazolyl hydrazone (0.52 gm, 0.002 mole), potassium permanganate (0.2 gm) and acetone (40 ml) and subjected to microwave irradiation in domestic microwave oven, in pulses (800W, 10

seconds) for a total irradiation time ranging between 50-60 seconds. The reaction was monitored by TLC after each pulse. The mass was cooled to room temperature, and filtered. The contents were decolorized with sulphur dioxide. The solid separated was recrystallized with benzene.

Authentication of the products obtained by microwave irradiation was done by thermal oxidative cyclization using acetone/$KMnO_4$.

Thermal oxidative cyclization

Hydrazone (0.0013 mole) potassium permanganate (0.2 g) and acetone (50 ml) was refluxed on water bath for 3 hrs. Contents were cooled and filtered. The filtrate was decolorized by SO_2 gas. The solid obtained was recrystallized from benzene. Analytical and spectral data tallies with the data from microwave irradiation (Table-1 and Table-2).

Antibacterial activity

The synthesized compounds were tested for their antimicrobial activity by paper disc method against *Xanthomonas, Erwinia* and *E-Coli* (gram–ve) using *ampicillin* as a standard antibacterial compound for comparison. The antibacterial screening data of the compounds have been incorporated in Table-3.

Dimethyl formamide was used as a control solvent. The compounds exhibited zone of inhibition of 15-13-18 mm in diameter where as standard ampicilin exhibited zone of inhibition of 18-16-08 mm in diameter against *Xanthomonas, Erwinia* and *E-Coli* respectively. Amongst the compounds tested 3-(4'-Pyridyl)-1,2,4-triazolo(3,4-*b*) benzothiazole showed higher zone of inhibition against *Xanthomonas, Erwinia* and *E-Coli* respectively.

RESULTS AND DISCUSSION

The spectacular reduction in time under microwave induced reaction starting from 2-hydrazinobenzothiazole and permanganate solution. The residual product was found to be 3-substituted 1,2,4-triazolobenzothiazole/naphthathiazole in good yields ranging from 63-77%.

To authenticate the above products another experiment was set up in which benzothiazolyl hydrazones were subjected to thermal oxidation using potassium permanganate in organic solvent like acetone yielded the title compounds. The yields are good and products are having sharp melting. The melting points of 3-substituted triazolobenzothiazoles are identical with the products isolated from microwave induced cyclizations. When comparison was done, the yields obtained from microwave cyclization were better than thermal oxidative results. Time required is very short. We are the first to report both the reactions of heteryl/aryl benzothiazolyl hydrazones to triazolo benzothiazoles by microwave induced reaction an expedious transformation so also thermal oxidative cyclization using acetone and potassium permanganate.

Even naphthathiazolyl hydrazones when subjected to microwave irradiation and thermal oxidative cyclization, triazolonaphthathiazole were obtained in good yield. The biological importance of bridge nitrogen and sulphur heterocycles[5,6,7] and our recent work on benzothiazole moiety encouraged us to synthesize the title compounds.

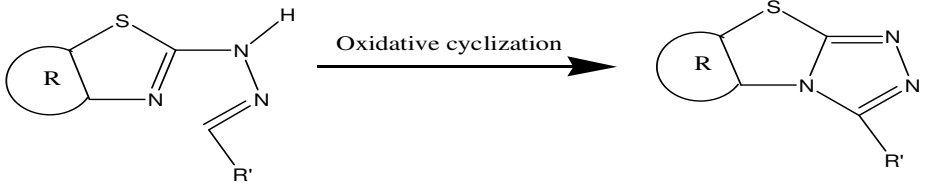
ACKNOWLEDGEMENTS

Authors are thankful to Dr.G.M.Kalamse Principal Science College Nanded, and Mr.R.K.Pathak, Pratibha Niketan College, Nanded for encouragement Thanks are due to Dr. M.M.V. Baig for antibacterial screening.

REFERENCES

1. L.G. S. Brooker and E. T. Vanlare, *Chem. Abstr.,* **51**, 9385 (1957).
2. J. D. Bower, and F. P. Doyle, *J. Chem. Soc.,* **80**, 727 (1957).
3. G.A. Reynolds and J. A. Van Allen, *J. Org. Chem.*, **24**, 200, (1964).
4. D.S. Deshpande, *J.I.C.S.*, Vol. LVI 742 (1979).
5. M.V. Deshmukh, *Ind. J. Chem.* **37**, 921 (1998).
6. A.K. Kamal, M.N. Reddy and Y.N. Srikanth, Chemical Biology and Drug Design Black Well Synergy (2008).

7. Y. Hu, Z.G. Lee and Q. Zheng, *Synthetic communication*, (2004).



R= aryl or naphtha R'=substituted

i. 2'-Thienyl
ii. 3'-pyridyl
iii. 4'-pyridyl
iv. 4'-chlorophenyl
v. 2',4'-dichlorophenyl
vi. 4'-hydroxyphenyl
vii. 4'-methoxyphenyl

Scheme-1

Table-1: Physical and analytical data of synthesized compounds

Compound No.	Compounds Formula Wt.	Reaction time		% Yield		M.P. ^{0}C	Found (Calculated) %		
		A Seconds	B Hours	A	B		C	H	N
1	$C_{12}H_7N_3S_2$ 257	50	2.5	68	55	171	56.00 (56.01)	2.53 (2.74)	16.13 (16.33)
2	$C_{13}H_8N_4S$ 252	65	2	77	58	211	61.35 (61.89)	3.12 (3.20)	22.10 (22.21)
3	$C_{13}H_8N_4S$ 252	75	3	73	61	230	61.30 (61.89)	3.14 (3.20)	22.12 (22.21)
4	$C_{14}H_8N_3SCl$ 285	65	2	75	65	142	58.52 (58.84)	2.63 (2.82)	14.47 (14.71)
5	$C_{14}H_7N_3SCl_2$ 320	68	1.5	63	58	Above 350	52.03 (52.51)	2.00 (2.20)	12.78 (13.12)
6	$C_{18}H_{11}N_3OS$ 317	55	2.25	68	60	340	68.02 (68.13)	3.41 (3.47)	13.13 (13.24)
7	$C_{19}H_{13}N_3OS$ 331	65	2.5	72	63	173	68.80 (68.86)	3.58 (3.95)	12.59 (12.68)

Where A= Microwave induced cyclization B= Thermal oxidative cyclization

Table-2: Characterization data of synthesized compounds

Compound No.	IR (KBR) vibrations in cm^{-1}	1H NMR, $CDCl_3$ (δ ppm)
1	1440 cm^{-1}(C-N stretch); 1681 cm^{-1}(C=N stretch); 1580 cm^{-1}(N=N stretch)	7.0-8.2 (Aromatic protons)
2	1303 cm^{-1}(C-N stretch); 1697 cm^{-1}(C=N stretch); 1595 cm^{-1}(N=N stretch)	7.4-8.8 (Aromatic protons)
3	1317 cm^{-1}(C-N stretch); 1681 cm^{-1}(C=N stretch); 1595 cm^{-1}(N=N stretch)	7.2-8.7 (Aromatic protons)
4	1400 cm^{-1}(C-N stretch);1597cm^{-1} (N=N stretch); 752 cm^{-1}(C-Cl stretch)	7.3-8.2 (Aromatic protons)
5	1423 cm^{-1}(C-N stretch); 1578 cm^{-1} (N=N stretch); 747 cm^{-1}(C-Cl stretch)	7.0-8.4 (Aromatic protons)
6	1443 cm^{-1} (C-N stretch); 1507 cm^{-1}(C=N stretch); 1602 cm^{-1}(N=N stretch); 3203 cm^{-1}(broad, -O-H stretch)	6.8-8.2 (Aromatic protons); 5.0 (Hydroxyl protons)
7	1442 cm^{-1}(C-N stretch);1500 cm^{-1} (C=N stretch); 1606 cm^{-1}(N=N stretch)	3.9 (-OCH_3 protons); 6.9-8.0 (Aromatic protons).

Table-3: Evaluation of antibacterial activity

Sr. No.	Compound	Antimicrobial Activity (Zone of inhibition in mm)		
		Xanthomonas	Erwinia	E-Coli
1.	3(2'-Thielyl)-1,2,4-triazolo(3,4-*b*) benzothiazole	15	12	08
2.	3(3'-Pyridyl)-1,2,4-triazolo(3,4-*b*) benzothiazole	13	NA	18
3.	3-(4'-Pyridyl)-1,2,4-triazolo(3,4-*b*) benzothiazole	14	13	17
4.	3(4'-Chlorophenyl)-1,2,4-triazolo(3,4-*b*) benzothiazole	12	08	18
5	Standard (Ampicilin) 1mg/ml	18	16	08

NA=No Activity

[RJC- 671/2010]
