

활성화된 비산회 촉매를 이용하여 간단히 수행된 1,2,4,5-Tetrazines의 One-pot 합성

M. Gopalakrishnan*, J. Thanusu, and V. Kanagarajan

Synthetic Organic Chemistry Laboratory, Department of Chemistry, Annamalai University,
Annamalainagar-608 002, Tamil Nadu, India
(2007. 7. 17 접수)

Easy-to-execute 'One-pot' Synthesis of 1,2,4,5-Tetrazines Catalyzed by Activated Fly Ash

M. Gopalakrishnan*, J. Thanusu, and V. Kanagarajan

Synthetic Organic Chemistry Laboratory, Department of Chemistry, Annamalai University,
Annamalainagar-608 002, Tamil Nadu, India
(Received July 17, 2007)

요 약. Thiourea/urea, 다양한 aromatic aldehydes, ammonium acetate의 세가지 요소를 가지고 마이크로파의 조사하에서 무수조건으로 활성화된 비산화재를 촉매로 사용하여 높은 수율의 6-aryl-1,2,4,5-tetrazinan-3-thiones/ones를 얻었다. 6-aryl-1,2,4,5-tetrazinan-3-thiones/ones의 구조는 녹는점, MS, IR, ¹H NMR, D₂O 교환, ¹³C NMR, 이차원의 NMR 스펙트럼(HOMOCOR, HSQC)을 바탕으로 증명되었다.

주제어: 활성화된 비산화, 6-aryl-1,2,4,5-tetrazinan-3-thiones/ones, one-pot 합성, 다성분 반응, 무수조건

ABSTRACT. Three-component coupling of thiourea/urea, various structurally diverse aromatic aldehydes and ammonium acetate is catalyzed by activated fly ash in dry media under microwave irradiation to give 6-aryl-1,2,4,5-tetrazinan-3-thiones/ones in good yields. The structure of 6-aryl-1,2,4,5-tetrazinan-3-thiones/ones have been elucidated on the basis of their melting points, elemental analysis, MS, IR, ¹H NMR, D₂O exchange, ¹³C NMR and two dimensional NMR spectral studies including Homonuclear Correlation (HOMOCOR) and Heteronuclear Single Quantum Correlation (HSQC) spectra.

Keywords: Activated Fly Ash, 6-aryl-1,2,4,5-tetrazinan-3-thiones/ones, 'one-pot' Synthesis, Multicomponent Reaction, Dry Media

INTRODUCTION

Organic compounds with a high-nitrogen content currently attract significant attention from many researchers, due to their novel energetic properties.^{1,2} 1,2,4,5-Tetrazines have, however, been very widely utilized for the highly effective synthesis of natural products, bioactive compounds, ligands, highly energetic materials, building blocks, diazocines, imidazoles, alkylidene-/arylidene-malonalde-

hydes, acrylic acid derivatives, pyrazoles and polycyclic aromatic compounds.³ Since the formation of N-N bond is relatively difficult, 1,2,4,5-tetrazines were generally prepared from hydrazine derivatives or from nitrilimines. A number of monohydrazones of simple aldehydes and ketone with thiocarbonylhydrazide and 6-alkylhexahydro-1,2,4,5-tetrazinan-3-thiones have been reported.⁴ In this report, only aliphatic aldehydes gave 1,2,4,5-tetrazines. But benzaldehyde gave only true monohy-

drazone with thiocarbohydrazide.

It has been about 70 years to research and use fly ash. With its application, the action mechanism of fly ash had been recognized. During the initial stage, only its pozzolanic activity is paid attention.^{5,6} Many researchers devoted themselves to the research of the potential activity of fly ash and the hydration process of Fly ash cement.⁷ Recently activated fly ash is used to catalyze Knoevenagel condensation, 'One-Pot' conversions of ketones to amides via Beckmann rearrangement, Schiff Bases formation, Biginelli and Hantzsch reactions.⁸ Owing to our interest in solid-state reactions,⁹ we attempted to use activated fly ash to catalyze three-component coupling of thiourea/urea, various structurally diverse aromatic aldehydes and ammonium acetate to form 6-aryl-1,2,4,5-tetrazinan-3-thiones/ones, which possess antimicrobial activity.¹⁰

RESULTS AND DISCUSSION

The fly ash collected from Neyveli Lignite Corporation, Neyveli, Tamil Nadu, India was utilized for catalyzing the reactions. The physical properties, such as specific gravity and specific surface area, of fly ash used were 1.9 and 127 m²/g, respectively. The chemical compositions (%) of fly ash [7a] used were SiO₂, Fe₂O₃, Al₂O₃, CaO, MgO, loss of ignition, insoluble residue in the ratio 64.03, 6.50, 15.50, 4.62, 3.00, 4.35, 2.00 respectively.

The purpose of the present investigation is to activate the as-received fly ash by physical method followed by thermal method (Fig. 1) and to study the influence of activated fly ash to catalyze three-component coupling of thiourea/urea, various structurally diverse aromatic aldehydes and ammonium acetate to form 6-aryl-1,2,4,5-tetrazinan-3-thiones/ones. Activated fly ash was shown to be one of the most efficient MW absorbers with a very high specificity to MW heating. It was able to reach a temperature of 135 °C after 6 minutes of irradiation in domestic oven. (P-320 W). During the course of reaction, the catalyst assists in the release of hydrogen molecules. The amount of hydrogen molecule released is in very low concentration. Since all the

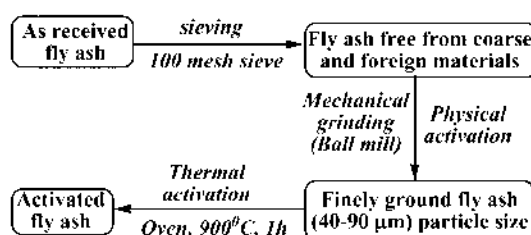


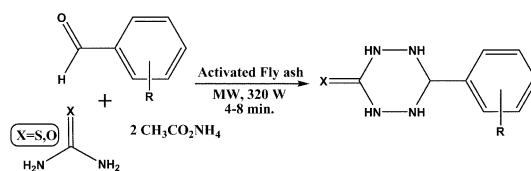
Fig. 1. Flow chart for the preparation of activated fly ash.

reactions are conducted in open vessels, the released hydrogen molecule escapes. Moreover, the catalyst assists in the removal of water molecules. Thus activated Fly ash catalyst assists for dehydrogenation and dehydration.

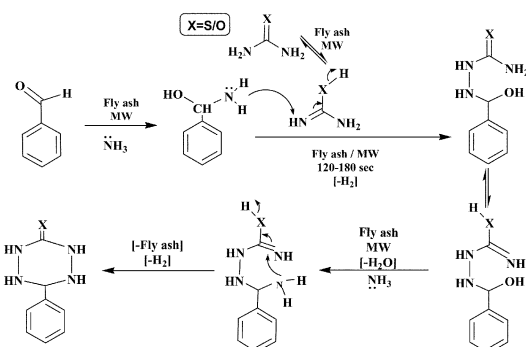
'One-pot' multicomponent cyclocondensation reaction of one mole of thiourea/urea, one mole of substituted benzaldehyde and two moles of ammonium acetate in the presence of activated fly ash yields 6-aryl-1,2,4,5-tetrazinan-3-thiones/ones in dry media under microwave irradiation (Scheme 1).

The structure of 6-aryl-1,2,4,5-tetrazinan-3-thiones/ones have been elucidated on the basis of their melting points, elemental analysis, MS, IR, ¹H NMR, D₂O exchange, ¹³C NMR and two dimensional NMR spectral studies including Homonuclear Correlation (HOMOCOR) and Heteronuclear Single Quantum Correlation (HSQC) spectra. The mechanistic pathway is given in Scheme 2.

Spectral analysis reveals the existence of two isomeric structures of 6-aryl-1,2,4,5-tetrazinan-3-thiones/ones, which is due to different conformations in solution. Unlike carbocyclic six membered systems, the tetrazines, which have four nitrogen atoms including four lone pairs, expected to exist in non-chair conformations due to lone pair-lone pair interactions. Among these conformations, the phenyl group occupies axial like or equatorial like orientation. Due to



Scheme 1. Synthesis of 6-aryl-1,2,4,5-tetrazinan-3-thiones/ones catalyzed by activated fly ash.



Scheme 2. Mechanistic pathway for the formation of 6-phenyl-1,2,4,5-tetrazinan-3-ones/thiones.

nitrogen quadrupole effect, it is difficult to calculate the coupling constant between the protons attached to nitrogen atoms. The coupling constant of proton attached to nitrogens and H-6 is only measurable, we expected triplet or double-doublet for H-6 protons. But only two separate doublets are observed. This clearly indicates that N-1 proton or N-5 proton is coupled with H-6 proton. The phenyl group, which occupies equatorial like orientation, has N-5 proton couple with H-6 proton, but N-1 proton does not couple with H-6 proton (the dihedral angle is nearly 90°). The phenyl group, which occupies axial like orientation, have N-5 proton does not couple but N-1 proton couple with H-6 proton. The above spectral analysis reveals that existence of two isomers. Between the two isomers, one isomer with phenyl ring in equatorial like is major and phenyl ring in axial like orientation is minor.

EXPERIMENTAL

General Remarks

All the organic reagents used were pure commercial products. Performing TLC assessed the reactions and the purity of the products. All the reported melting points were taken in open capillaries and were uncorrected. IR spectra were recorded in KBr (pellet forms) on a Nicolet-Avatar-330 FT-IR spectrophotometer and note worthy absorption values (cm^{-1}) alone are listed. ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz respectively on Bruker AMX 400 NMR spectrometer

using DMSO as solvent. Homonuclear Correlation (HOMOCOR) Spectrum and Heteronuclear Single Quantum Correlation (HSQC) spectrum were recorded on Bruker DRX 500 NMR spectrometer using standard parameters. The ESI +ve MS spectra were recorded on a Bruker Daltonics LC-MS spectrometer. Satisfactory microanalysis was obtained on Carlo Erba 1106 CHN analyzer. A conventional (*unmodified*) domestic microwave oven equipped with a turntable (LG, MG-395 WA, 230V~50 Hz, 760 W) was used for the irradiation.

General experimental procedure for the 'one pot' synthesis of 6-aryl-1,2,4,5-tetrazinan-3-thiones/ones catalyzed by activated fly ash under microwave irradiation (entries 1-14): A mixture containing thiourea/urea (10 mmol), substituted benzaldehyde (10mmol), ammonium acetate (20 mmol) and activated fly ash (150 mg) was added in an alumina bath and mixed properly with the aid of glass rod (10s) and then irradiated in a microwave oven for the appropriate period of time as mentioned in Table 1 at 320W (monitored by TLC). After completion of the reaction, the reaction mixture was extracted with ethyl acetate (3×10 mL). The catalyst was removed by filtration. The combined organic layer was washed with water three times and then dried over anhydrous Na_2SO_4 . The organic layer was concentrated in vacuo to furnish the products, which were purified by column chromatography using ethyl acetate: petroleum ether (40:60) [2:8] as eluent.

6-Phenyl-1,2,4,5-tetrazinan-3-thione (1): IR (KBr) (cm^{-1}): 3398, 3211, 3162, 3033, 2896, 1521, 1450, 1178, 700; ^1H NMR (δ ppm): 3.90 [3.22] (t, 2H, $\text{H}_{1,6a}$), 8.6 [8.46] (s, 2H, $\text{H}_{2,6d}$), 4.96, $J=8.61\text{Hz}$, [5.42, $J=10.71\text{Hz}$] (d, 1H, H_6), 7.30-7.44 9 (m, 5H, H_{arom}). ^{13}C NMR (δ ppm): 64.9 [68.8] - C_6 , 176.0 [177.6] - C-S , 140.1 -*ipso* C, 126.9, 127.2, 128.3, 128.5 - C_{arom} . [The values in parentheses [], represent the minor isomer. Moreover, to confirm the NH proton signals, ^1H NMR spectrum is recorded after adding D_2O . The signals observed at 3.22, 3.90, 8.46 and 8.6 ppm are exchanged with D_2O . In order to confirm the assignment of signals, HOMOCOR is also recorded for 6-phenyl-1,2,4,5-tetrazinan-3-thione. The sig-

Table 1. Physical and analytical data of 6-aryl-1,2,4,5-tetrazinan-3-thiones/ones

Entry	R	X	Reaction conditions		Yield (%)	m.p° C	Elemental analysis (%)			m/z (M ⁻) Molecular formula	Amounts Major (Minor)
			MW (W)	Time (min)			C Found (calculated)	H Found (calculated)	N Found (calculated)		
1	H	S	320	4	60	186-188	49.50 (49.48)	5.12 (5.15)	28.88 (28.86)	(195) C ₈ H ₁₀ N ₄ S	80.88 (19.12)
2	<i>p</i> -Cl	S	320	5	52	171-172	42.04 (42.01)	3.93 (3.97)	24.48 (24.50)	(229) C ₈ H ₉ N ₄ ClS	74.62 (25.38)
3	<i>o</i> -Cl	S	320	5	50	157-160	-	-	-	(229) C ₈ H ₉ N ₄ ClS	73.45 (26.55)
4	<i>p</i> -F	S	320	4	65	169-172	45.29 (45.27)	4.25 (4.27)	26.41 (26.40)	(213) C ₈ H ₉ N ₄ FS	100
5	<i>p</i> -CH ₃	S	320	6	60	146-148	51.88 (51.90)	5.79 (5.81)	26.89 (26.90)	(209) C ₉ H ₁₂ N ₄ S	100
6	<i>p</i> -OCH ₃	S	320	6	55	170-174	48.19 (48.20)	5.37 (5.39)	24.96 (24.98)	(225) C ₉ H ₁₂ N ₄ OS	76.75 (23.25)
7	<i>o</i> -CH ₃	S	320	7	40	160-164	-	-	-	(209) C ₉ H ₁₂ N ₄ S	100
8	<i>m</i> - OC ₆ H ₅	S	320	8	35	148-151	58.69 (28.72)	4.92 (4.93)	19.56 (19.57)	(287) C ₁₃ H ₁₃ N ₄ OS	71.10 (28.90)
9	C ₆ H ₅	O	320	5	50	191-193	53.96 (53.93)	5.60 (5.61)	31.48 (31.46)	(179) C ₈ H ₁₀ N ₄ O	83.63 (16.37)
10	<i>p</i> -Cl	O	320	6	55	180-182	45.16 (45.19)	4.24 (4.27)	16.65 (16.67)	(213) C ₈ H ₉ N ₄ ClO	78.67 (21.33)
11	<i>p</i> -F	O	320	5	60	150-153	48.95 (48.98)	4.61 (4.62)	28.55 (28.56)	(197) C ₈ H ₉ N ₄ FO	68.70 (31.30)
12	<i>p</i> -CH ₃	O	320	7	55	177-179	58.28 (56.25)	6.22 (6.25)	29.19 (29.16)	(193) C ₉ H ₁₂ N ₄ O	67.17 (32.83)
13	<i>p</i> -OCH ₃	O	320	7	60	160-162	51.95 (51.92)	5.26 (5.28)	26.95 (26.92)	(209) C ₉ H ₁₂ N ₄ O ₂	94.03 (05.97)
14	<i>m</i> -NO ₂	O	320	6	40	186-189	43.03 (43.05)	4.04 (4.06)	31.36 (31.38)	(224) C ₈ H ₉ N ₄ O ₂	55.63 (44.37)

nal at 4.96 ppm shows cross peaks with signals at 3.90 and 8.67 ppm. The cross peak signal at 3.90 ppm is having two protons.

6-(4-Chlorophenyl)-1,2,4,5-tetrazinan-3-thione (2): IR (KBr) (cm⁻¹): 3388,3228, 3180,3054, 2967,1593, 1489,1166, 821; ¹H NMR (δ ppm): 4.04 [3.65] (t, 2H, H_{1&5}), 8.8 [8.64] (s, 2H, H_{2&4}), 4.95, J=8.4Hz, [5.40, J=9.8Hz] (d, 1H, H₆), 7.32-7.47 (m, 4H, H_{arom}). ¹³C NMR (δ ppm): 64.0 [67.3] -C₆, 176.1 [177.1] -C=S, 132.6, 138.2 -*ipso* C, 128.8, 129.0, 129.2, 129.3 -C_{arom}.

6-(2-Chlorophenyl)-1,2,4,5-tetrazinan-3-thione (3): IR (KBr) (cm⁻¹): 3368,3240, 3186,3058, 2968, 1588, 1480,818; ¹H NMR (δ ppm): 4.10 [3.61] (t, 2H, H_{1&5}), 8.82 [8.67] (s, 2H, H_{2&4}), 4.94, J=8.4Hz, [5.47, J=9.8Hz] (d, 1H, H₆), 7.32-7.47 (m, 4H, H_{arom}). ¹³C NMR (δ ppm): 61.9 [65.6] -C₆, 176.9 [177.6] -C=S,

135.5, 136.6 -*ipso* C, 125.9, 126.7, 127.7, 130.5 -C_{arom}.

6-(4-Fluorophenyl)-1,2,4,5-tetrazinan-3-thione (4): IR (KBr) (cm⁻¹): 3380, 3245, 3199, 3067, 2920, 1541, 1450, 1178, 779; ¹H NMR (δ ppm): 4.02 (t, 2H, H_{1&5}), 8.71(s, 2H, H_{2&4}), 4.92, J=8.2Hz, (d, 1H, H₆), 7.22-7.41 (m, 4H, H_{arom}). ¹³C NMR (δ ppm): 64.0 [67.5] -C₆, 175.9 [173.3] -C=S, 135.8, 162.7 -*ipso* C, 128.3, 128.8, 128.9, 129.1 -C_{arom}.

6-(4-Methylphenyl)-1,2,4,5-tetrazinan-3-thione (5): IR (KBr) (cm⁻¹): 3368, 3198, 3166, 3065, 2920, 1538, 1460, 1175, 768; ¹H NMR (δ ppm): 2.31 (s, 3H, CH₃), 3.85 [2.31] (t, 2H, H_{1&5}), 8.64 [8.42] (s, 2H, H_{2&4}), 4.91, J=8.2Hz, (d, 1H, H₆), 7.13-7.26 (m, 4H, H_{arom}). ¹³C NMR (δ ppm): 21.0 -CH₃, 64.5 -C₆, 175.9 -C=S, 137.1,137.3 -*ipso* C, 126.9, 127.5, 128.0, 128.7 -C_{arom}.

6-(4-Methoxyphenyl)-1,2,4,5-tetrazinan-3-thione (6): IR (KBr) (cm^{-1}): 3316, 3211, 3168, 3071, 2933, 1510, 1463, 1174, 835; ^1H NMR (δ ppm): 3.81 (s, 3H, OCH_3), 3.83 [3.10] (t, 2H, $\text{H}_{1,\&3}$), 8.61 [8.36] (s, 2H, $\text{H}_{2,\&4}$), 4.88, $J=8.2\text{Hz}$, [5.34, $J=10.8\text{Hz}$] (d, 1H, H_6), 7.11-7.37 (m, 4H, H_{arom}). ^{13}C NMR (δ ppm): 55.05 ($-\text{OCH}_3$), 63.9 [66.8] $-\text{C}_6$, 175.9 [173.3] $-\text{C}=\text{S}$, 130.8, 157.9 $-\text{ipso}$ C, 114.0, 128.5, 128.8, 129.8 $-\text{C}_{\text{arom}}$.

6-(2-Methylphenyl)-1,2,4,5-tetrazinan-3-thione (7): IR (KBr) (cm^{-1}): 3320, 3216, 3153, 3065, 2920, 1538, 1463, 1175, 760; ^1H NMR (δ ppm): 2.09 (s, 3H, CH_3), 3.61 (t, 2H, $\text{H}_{1,\&3}$), 8.58 (s, 2H, $\text{H}_{2,\&4}$), 5.08, $J=8.5\text{Hz}$, (d, 1H, H_6), 7.15-7.33 (m, 4H, H_{arom}). ^{13}C NMR (δ ppm): 17.71 $-\text{OCH}_3$, 62.2 $-\text{C}_6$, 176.9 $-\text{C}=\text{S}$, 135.6, 137.6 $-\text{ipso}$ C, 125.4, 126.2, 127.8, 130.3 $-\text{C}_{\text{arom}}$.

6-(3-Phenoxyphenyl)-1,2,4,5-tetrazinan-3-thione (8): IR (KBr) (cm^{-1}): 3407, 3171, 3039, 2902, 1543, 1450, 1248, 783; ^1H NMR (δ ppm): 3.68 [3.98] (t, 2H, $\text{H}_{1,\&3}$), 8.65 [8.80] (s, 2H, $\text{H}_{2,\&4}$), 5.35, $J=8.3\text{Hz}$, [4.92, $J=9.7\text{Hz}$] (d, 1H, H_6), 6.92-7.45 (m, 9H, H_{arom}). ^{13}C NMR (δ ppm): 67.4 [64.2] $-\text{C}_6$, 177.0 [176.0] $-\text{C}=\text{S}$, 160.0, 157.4 $-\text{ipso}$ C, 122.9, 123.1, 123.9, 124.1, 124.4, 129.1, 129.6, 129.9, 130.6, 137.8 $-\text{C}_{\text{arom}}$.

6-phenyl-1,2,4,5-tetrazinan-3-one (9): IR (KBr) (cm^{-1}): 3444, 3212, 3061, 2920, 1684, 1493, 1451, 697; ^1H NMR (δ ppm): 2.77 [3.68] (t, 2H, $\text{H}_{1,\&3}$), 6.82 [7.01] (s, 2H, $\text{H}_{2,\&4}$), 5.39 ($J=11.22\text{ Hz}$) [4.99, ($J=8.26\text{ Hz}$)] (d, 1H, H_6), 7.31-7.52 (m, 5H, H_{arom}). ^{13}C NMR (δ ppm): 68.7 [64.5] $-\text{C}_6$, 156.2 [155.1] $-\text{C}=\text{O}$, 140.4 $-\text{ipso}$ C, 127.4, 127.5, 127.6, 128.0, 128.3 $-\text{C}_{\text{arom}}$. The D_2O exchange spectrum was also recorded to confirm the $-\text{NH}$ proton signals. The signals 2.77, 3.68, 6.82, 7.01 ppm are exchanged with D_2O . In order to confirm the assignment of signals, HSQC spectrum is also recorded. The signals at 5.39 and 4.99 ppm show cross peaks with signals at 68.7 and 64.5 ppm. The above spectral analysis reveals that existences of two isomers. Between the two isomers, one isomer with phenyl ring in equatorial like is the major isomer and phenyl ring in axial like orientation is the minor isomer.

6-(4-chlorophenyl)-1,2,4,5-tetrazinan-3-one (10): IR (KBr) (cm^{-1}): 3386, 3220, 3068, 2965, 1596, 1486, 1450, 820; ^1H NMR (δ ppm): 2.90 [3.12] (t, 2H, $\text{H}_{1,\&3}$), 6.39 [6.57] (s, 2H, $\text{H}_{2,\&4}$), 5.52 ($J=11.21$

Hz), [4.94 ($J=8.42\text{ Hz}$)] (d, 1H, H_6), 7.60-7.76 (m, 4H, H_{arom}). ^{13}C NMR (δ ppm): 64.0 [67.3] $-\text{C}_6$, 155.3 [156.1] $-\text{C}=\text{O}$, 132.4, 138.2 $-\text{ipso}$ C, 128.2-129.3 $-\text{C}_{\text{arom}}$.

6-(4-fluorophenyl)-1,2,4,5-tetrazinan-3-one (11): IR (KBr) (cm^{-1}): 3392, 3216, 3026, 2960, 1586, 1484, 1451, 780; ^1H NMR (δ ppm): 2.98 [3.74] (t, 2H, $\text{H}_{1,\&3}$), 6.85 [6.88] (s, 2H, $\text{H}_{2,\&4}$), 5.36 ($J=11.21\text{ Hz}$), [4.95, ($J=8.41\text{ Hz}$)] (d, 1H, H_6), 7.12-7.51 (m, 4H, H_{arom}). ^{13}C NMR (δ ppm): 67.8 [63.8] $-\text{C}_6$, 156.1 [154.9] $-\text{C}=\text{O}$, 136.6, 162.8 $-\text{ipso}$ C, 128.7, 128.7, 129.0, 129.2 $-\text{C}_{\text{arom}}$.

6-(4-methylphenyl)-1,2,4,5-tetrazinan-3-one (12): IR (KBr) (cm^{-1}): 3328, 3209, 3057, 2920, 1679, 1512, 1446, 813; ^1H NMR (δ ppm): 2.28 (s, 3H, CH_3), 2.49 [3.52] (t, 2H, $\text{H}_{1,\&3}$), 6.88 [6.83] (s, 2H, $\text{H}_{2,\&4}$), 4.92 ($J=12.30\text{ Hz}$), [5.40, ($J=8.33\text{ Hz}$)] (d, 1H, H_6), 7.11-7.35 (m, 4H, H_{arom}). ^{13}C NMR (δ ppm): 20.5 $-\text{CH}_3$, 64.2 [63.9] $-\text{C}_6$, 155.0 [154.9] $-\text{C}=\text{O}$, 136.6, 138.6 $-\text{ipso}$ C, 126.5, 126.8, 128.1, 128.5 $-\text{C}_{\text{arom}}$.

6-(4-methoxyphenyl)-1,2,4,5-tetrazinan-3-one (13): IR (KBr) (cm^{-1}): 3443, 3216, 3000, 2918, 1662, 1512, 1459, 834; ^1H NMR (δ ppm): 3.87 (s, 3H, OCH_3), 2.70 [3.87] (t, 2H, $\text{H}_{1,\&3}$), 6.92 [6.86] (s, 2H, $\text{H}_{2,\&4}$), 4.95 ($J=12.02\text{ Hz}$), [5.35, ($J=8.35\text{ Hz}$)] (d, 1H, H_6), 7.12-7.33 (m, 4H, H_{arom}). ^{13}C NMR (δ ppm): 55.0 $-\text{OCH}_3$, 63.9 [66.8] $-\text{C}_6$, 157.9 [158.7] $-\text{C}=\text{O}$, 130.8, 160.3 $-\text{ipso}$ C, 128.5, 128.8, 129.8, 130.8 $-\text{C}_{\text{arom}}$.

6-(3-nitrophenyl)-1,2,4,5-tetrazinan-3-one (14): IR (KBr) (cm^{-1}): 3445, 3213, 3061, 2916, 1689, 1493, 1453, 754; ^1H NMR (δ ppm): 3.81 [4.18] (t, 2H, $\text{H}_{1,\&3}$), 7.19 [7.31] (s, 2H, $\text{H}_{2,\&4}$), 5.53 ($J=10.05\text{ Hz}$), [5.12 ($J=8.47\text{ Hz}$)] (d, 1H, H_6), 7.53-7.89 (m, 9H, H_{arom}). ^{13}C NMR (δ ppm): 67.15 [66.85] $-\text{C}_6$, 155.6 [154.6] $-\text{C}=\text{O}$, 134.1, 147.3 $-\text{ipso}$ C, 121.8, 122.6, 129.3, 129.8 $-\text{C}_{\text{arom}}$.

CONCLUSION

The eye-catching features of this synthetic procedure are the mild reaction conditions, high conversions, cleaner reaction profiles, solvent-free reaction conditions, operational simplicity and inexpensive and readily available Fly ash, an industrial waste (pollutant), which act as a catalyst will make it a

useful strategy for the preparation of novel 6-aryl-1,2,4,5-tetrazinan-3-thiones/ones. Developments of further works are in progress in these directions.

REFERENCES

1. Benson, F. R. *The High Nitrogen Compounds*; Wiley-Interscience: New York, NY, **1984**.
2. Kerth, J.; Lobbecke, S. *Propellants, Explos., Pyrotech.* **2002**, *27*, 111.
3. Saracoglu, N. *Tetrahedron*, **2007**, *63*, 4199.
4. Lamon, R. W. *J. Org. Chem.*, **1969**, *34*, 756.
5. Watt, J. D.; Throne, D. J. *J. Appl. Chem.* **1965**, *15*, 595.
6. Throne, D. J.; Watt, J. D. *J. Appl. Chem.* **1966**, *16*, 33.
7. (a) Saraswathy, V.; Muralidharan, S.; Thangavel, K.; Srinivasan, S. *Cement Concr. Res.* **2003**, *25*, 673. (b) Yueming, F.; Suhong, Y.; Zhiyun, W.; Jingyu, Z. *Cement Concr. Res.* **1999**, *29*, 467. (c) Caijunshi, *Cement Concr. Res.* **1996**, *26*, 1351.
8. Gopalakrishnan, M.; Sureshkumar, P.; Kanagarajan, V.; Thanusu, J.; Govindaraju, R. *Arkivoc* **2006**, *13*, 1.
9. (a) Gopalakrishnan, M.; Sureshkumar, P.; Kanagarajan, V.; Thanusu, J.; Govindaraju, R. *J. Chem. Res.* **2005**, *5*, 299. (b) Gopalakrishnan, M.; Sureshkumar, P.; Kanagarajan, V.; Thanusu, J. *Lett. Org. Chem.* **2005**, *2*, 444. (c) Gopalakrishnan, M.; Sureshkumar, P.; Kanagarajan, V.; Thanusu, J. *Catal. Communications* **2005**, *6*, 753-756. Gopalakrishnan, M.; Sureshkumar, P.; Thanusu, J.; Kanagarajan, V.; Prabhu, C. *J. Chem. Res.* **2007**, *2*, 80.
10. Gopalakrishnan, M.; Sureshkumar, P.; Thanusu, J.; Kanagarajan, V. *J. Erz. Inhib. Med. Chem.* **2007** (in press).