CYCLOKETONES AS PRECURSOR FOR CONVENIENT SYNTHESIS OF AZOLOPYRIMIDINES AND 5-ARYLAZOTHIAZOLES

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Keywords: hydrazonoyl halides; aminopyrazoles; pyrazolo[1,5-*a*]pyrimidines; pyrazolo[1,5-*a*]quinazolines; imidazo[1,2-*a*]cycloal-ka[*e*]pyrimidine; hydrazine-carbothioamide; arylazothiazoles

Condensation of sodium (3-oxocycloalkylidene)methenolate with several heterocyclic amines afforded pyrazolo[1,5-*a*]pyrimidine and pyrazolo[1,5-*a*]quinazoline derivatives. Also, 2-(2-cycloalkylidenehydrazinyl)-4-substituted-5-(phenyldiazenyl)-thiazole derivatives were synthesized via reaction of hydrazonoyl halides with 2-cycloalkylidene-hydrazinecarbothioamide. Structures of the newly synthesized compounds were elucidated by elemental analysis, spectral data, alternative synthethic routes and chemical transformation whenver possible.

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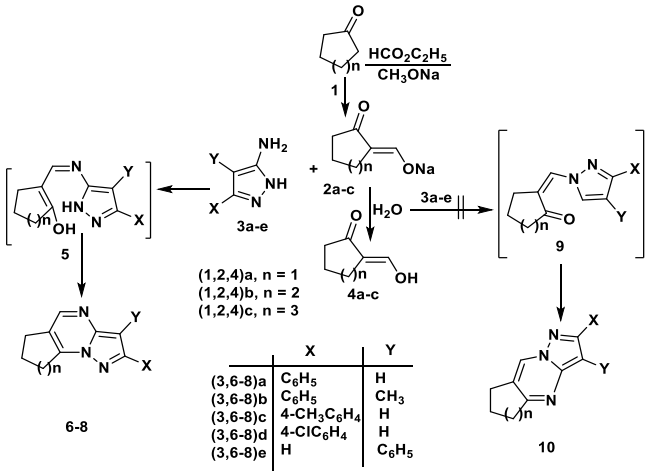
Introduction

Compounds containing the pyrimidine nucleus are of significant biological importance and are used as antibacterial,[1-5] antifungal,[6,7] antitumour [8,9], antiviral [9-13], anti-inflammatory [14,15] and antihypertensive [16-18] agents. Also, thiazole derivatives have been reported to posse's broad spectrum of pharmacological activities like anticancer [19], antidiabetic [20], CNS depressant [21], analgesic [22], antifilarial [23], antifungal and antibacterial [24], anthelmintic and antitumoral [25] activities. Mostly thiazole derivatives are known to posse's interesting biological properties that show anticancer [26] and antimicrobial activities. In this work, we synthesized some new pyrazolo[1,5-*a*]pyrimidine and 5-arylazothiazole derivatives.

Results and discussion

Treatment of 3-amino-5-phenyl-1*H*-pyrazole (**3a**) with sodium (2-oxocyclopentylidine)methenolate [27] (**2a**) in acetic acid containing piperidinum acetate afforded a product that may be 2-phenyl-7,8-dihydro-6*H*-cyclopenta[*e*]pyrazolo[1,5-*a*]pyrimidine (**6a**) or isomeric 2-phenyl-6,7-dihydro-5*H*-cyclopenta[*d*]pyrazolo[1,5-*a*]pyrimidine (**10a**) (Scheme 1). The structure **6a** was confirmed by elemental analysis, spectral data. IR (cm^{-1}) spectrum of the product revealed bands at 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C). Its ^1H NMR spectrum showed signals at δ = 2.57 (m, 2H, CH_2), 2.87-2.92 (m, 4H, $2CH_2$), 6.51 (s, 1H, pyrazole H-4), 7.34-7.89 (m, 5H, ArH's), 8.23 (s, 1H, pyrimidine H-4). The reaction seems to occur *via* the initial formation of the intermediate **5** followed by dehydration cyclization to give of the **6a** as end product (Scheme 1).

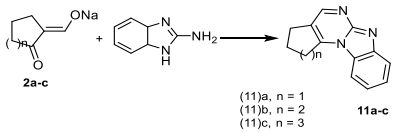


Scheme 1: Synthesis of pyrazol[1,5-a]pyrimidines (6-8)a-e

The suggestion of the formation of the alternative isomeric product **9** is based on the initial attack of the pyrazole NH group at the formyl group **4a.** This suggestion is excluded due to the higher nucleophilicity of the exocyclic primary amino group than the endocyclic NH group. Similarly, treatment of the appropriate **3b-e** were reacted with each of **2a-c** to give the tetrahydrocyclopenta- **5b-e**, tetrahydrocyclohexa- **6a-e**, and tetrahydrocycloheptapyrazolo[1,5-*a*]pyrimidine derivatives **7a-e**, respectively.

Analogously, the reaction of 2-aminobenzimidazole with each of **2a-c** in piperidinum acetate gave 2,3-dihydro-1*H*-benzo[4,5]imidazo[1,2-*a*]cyclopenta[*e*]pyrimidine (**11a**),

1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]quinazoline (**11b**) and 2,3,4,5-tetrahydro-*1*H-benzo[4,5]imidazo[1,2-*a*]cyclohepta[*e*]pyrimidine (**11c**), respectively (Scheme 2).



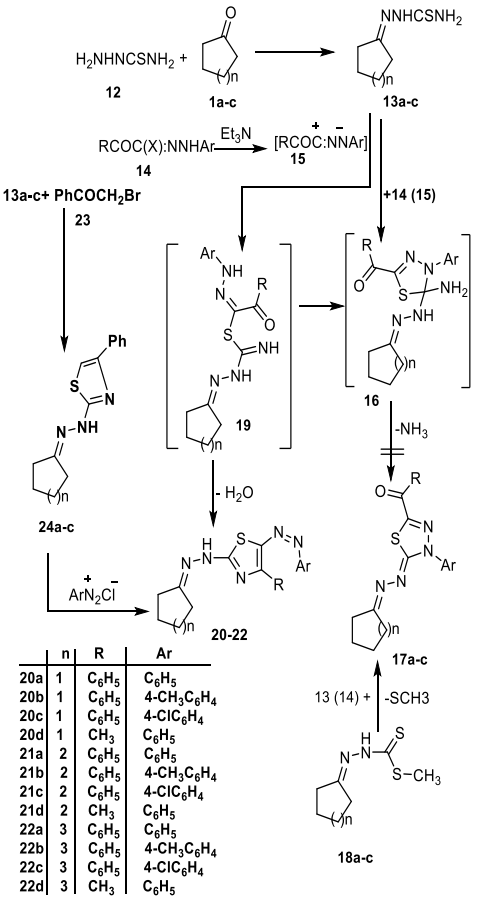
Scheme 2. Imidazo[1,2-a]cyclopenta[*e*]pyrimidine **11a**, imidazo[1,2-a]quinazoline **11b** and imidazo[1,2-*a*]cyclohepta[*e*]pyrimidine **11c**.

Next, we studied the reactions of hydrazonoyl halides with 2-cycloalkylidene-hydrazinecarbothioamide [28] **13a-c**. Thus, reaction of compound **13a** reacted with 2-oxo-*N'*, 2-diphenylacetohydrazonoyl bromide (**14a**) in ethanol in presence of catalytically amount of triethylamine gave one isolable product evidenced by *tlc* that proved to be 2-(2-cyclopentylidenehydrazinyl)-4-phenyl-5-(phenyldiazenyl)-thiazole (**20a**) (Scheme 3). Structure of **20a** was confirmed by elemental analysis, spectral data and alternative synthesis. For example, IR spectrum its exhibit revealed band at 3320 (NH), it show no of any CO group. ^{1}H NMR showed signals at δ 1.56-1.60 (m, 4H, $2CH_2$), 2.13-2.25 (m, 4H, $2CH_2$), 7.33-7.98 (m, 10H, ArH's) and 9.08 (s, br., 1H, NH). Moreover, **24a** [29], which was prepared via reaction of ω-bromoacetophenone (**23**) with **13a** in ethanol, was reacted with benzendiazonium chloride in ethanolic sodium acetate at 0 °C afforded product identical in all aspect (mp., mixed mp. and spectra) with **20a** (Scheme 3).

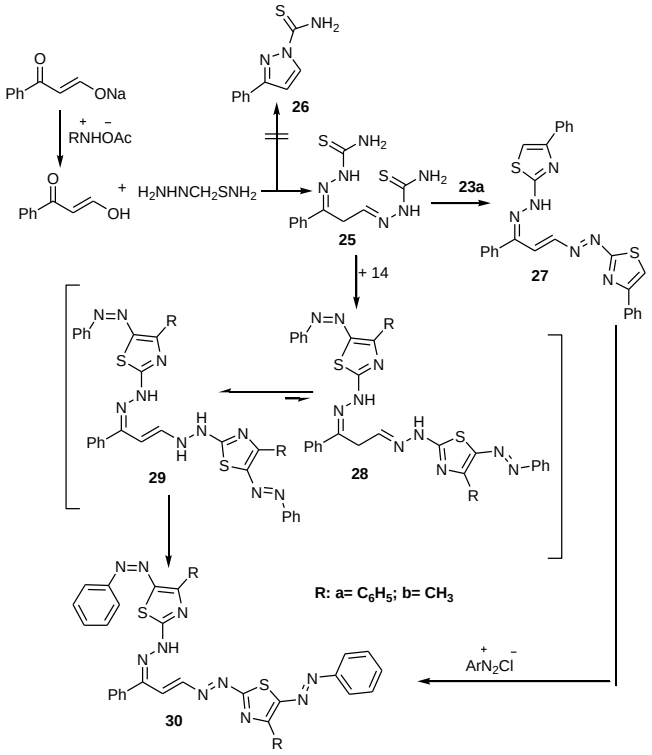
Two possible pathways can account for the formation **20a** via 1,3-addition of the thiol tautomer of **13** to the nitriliimine **15**, (generated in situ from hydrazonoyl halide **14a** and triethylamine), to form the thiohydrazonate ester **19a**, which undergoes dehydrative cyclization to yield **20a**. The formations of **19** and **20** are similar to the reaction of hydrazonoyl chloride with 1-phenyl-1,4-dihydrotetrazole-5-thione [30] and 5-phenyl-1,3,4-thiadiazole-2(3*H*)-thione [31] or 1,3-cycloaddition of nitrilimine **15** to C=S double bond of **13a** can give directly **16**. The latter intermediate **16** was converted to **17a,** by loss one molecule of ammonia (Scheme 3). The latter pathway was ruled out on the base of IR, ^{1}H NMR and alternative synthetic route.[32]

Similarly, the appropriate **13a-c** reacted with each of hydrazonoyl halides **14a,b** and ω-bromoacetophenone in ethanol gave **(20-22)a-d** and **24a-c** (Scheme 3).

Finally, reaction of sodium 3-oxo-3-phenylprop-1-en-1-olate was reacted with thiosemicarbazide (**12**) in acetic acid containing piperidinum acetate afforded 2,2'-(1-phenylpropane-1,3-diylidene)bis(hydrazinecarbothioamide) (**25**) and not 3-phenyl-1*H*-pyrazole-1-carbothioamide (**26**) according to mp. and reaction of benzoylacetaldehyde with thiosemicarbazide [33]. Treatment of compound **25** was reacted with the appropriate hydrazonoyl halides afforded 4-phenyl-2-(2-(1-phenyl-3-(4-phenyl-5-(phenyldiazenyl)thiazol-2-yl)diazenyl)allylidene)-hydrazinyl)-5-(phenyldiazenyl)-thiazole (**30a**) (Scheme 4).



Scheme 3: 2-(2-Cycloalkylidenehydrazinyl)-4,5-disubstituted thiazoles (20-22)a-d



Scheme 4: Synthesis of thiazoles **30a** and **30b**

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Structure of **30a** was confirmed by elemental analysis, spectral data and alternative synthetic route. Thus, treatment of 4-phenyl-2-(2-(-1-phenyl-3-(4-phenyl-5-phenylthiazol-2-yl)diazenyl)allylidene)hydrazin-yl)thiazole (**27a**), which obtained by reaction of **25** with ω-bromoacetophenone, with benzenediazonium chloride ethanolic sodium acetate solution at 0-5 ºC afforded product identical in all aspect (mp., mixed mp. and spectra) with **30a**.

Experimental

All melting points were determined on an electrothermal apparatus and are uncorrected. IR spectra were recorded (KBr discs) on a Shimadzu FT-IR 8201 PC spectrophotometer. NMR spectra were recorded in $CDCl_3$ and $(CD_3)_2SO$ solutions on a JNM-LA 400 FT-NMR system and a Varian Gemini 300 MHz spectrometer and chemical shifts are expressed in δ ppm units using TMS as an internal reference. Mass spectra were recorded on a GC-MS QP1000 EX Shimadzu. Elemental analyses were carried out at the Microanalytical Center of Cairo University. Sodium (2-oxocycloalkylidine)methenolate [27] (**2a-c**), 2-cycloalklidenehydrazinecarbothioamide [28] **13a-c**, and hydrazonoyl halides [34,35] **14,** methyl 2-cyclopentylidenehydrazine-1-carbodithioate **(18)** [36] were synthesized as previously reported.

Synthesis of pyrazolo[1,5-*a*]pyrimidines (6-8)a-e, benzo[4,5]imidazo[1,2-*a*]cyclopenta[*e*]pyrimidine 11a, benzo[4,5]imidazo-[1,2-*a*]quinazoline 11b and benzo[4,5]imidazo[1,2-*a*]cyclohepta[*e*]pyrimidine 11c.

A solution of sodium salt of (2-oxocycloalkylidine)-methanolates **2a-c (**0.01 mol), aminopyrazoles, 2-aminobenzimidazole (0.01 mol) and piperidine acetate (1 ml) in H_2O (3 ml) was refluxed for 15 minutes. Acetic acid (1.5 ml) was added to the hot solution. The solid product was filtered off and recrystallized from ethanol to give **(5-7)a-e, 11a, 11b and 11c.**

2-Phenyl-7,8-dihydro-6*H*-cyclopenta[*e*]pyrazolo[1,5-*a*]pyrimidine (6a)

This compound was obtained as yellow solid (78 %). m.p. 185-86 °C. IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 235 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.57 (m, 2H, CH_2), 2.87-2.92 (m, 4H, $2CH_2$), 6.51 (s, 1H, pyrazole H-4), 7.34-7.89 (m, 5H, ArH's), 8.23 (s, 1H, pyrimidine H-4). ^{13}C NMR δ = 21.87, 28.74, 30.62, 100.45, 118.77, 127.62, 128.23, 130.19, 133.18, 143.57, 144.47, 150.75, 154.66. Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86 Found: C, 76.47; H, 5.53; N, 17.93

3-Methyl-2-phenyl-7,8-dihydro-6*H*-cyclopenta[*e*]pyrazolo[1,5-*a*]pyrimidine (6b)

This compound was obtained as yellow solid (72 %). m.p. 165-66 °C. IR (KBr): 3080 (CH, aromatic), 2987 (CH, aliphatic), 1620 (C=N), 1595 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 249 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.20 (s, 3H, CH_3), 2.57 (m, 2H, CH_2), 2.87-2.92 (m, 4H, $2CH_2$), 7.34-7.89 (m, 5H, ArH's), 8.23 (s, 1H, pyrimidine H-4). ^{13}C NMR δ = 8.12, 21.43, 28.74, 30.62, 106.27, 118.86, 128.67, 128.75, 128.99, 132.12, 135.23, 143.90, 148.57, 152.34. Anal. Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85. Found: $C_{16}H_{15}N_3$ (249.31); C, 77.15; H, 6.20; N, 16.97

2-(p-Tolyl)-7,8-dihydro-6*H*-cyclopenta[*e*]pyrazolo[1,5-*a*]pyrimidine (6c)

This compound was obtained as yellow solid (77 %). m.p. 190-92 °C. IR (KBr): 3057 (CH, aromatic), 2984 (CH, aliphatic), 1618 (C=N), 1595 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 249 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.30 (s, 3H, CH_3), 2.64-2.69 (m, 2H, CH_2), 3.16-3.18 (t, 2H, *J* = 4 Hz, CH_2), 3.62-3.68 (m, 2H, CH_2), 6.47 (s, 1H, pyrazole H-4), 7.34-7.36 (d, 2H, *J* = 4 Hz, ArH's), 7.81-7.83 (d, 2H, *J* = 4 Hz, ArH's), 8.34 (s, 1H, pyrimidine H-4); ^{13}C NMR δ = 21.43, 21.77, 28.74, 30.48, 100.42, 118.44, 128.27, 130.56, 132.27, 136.20, 142.27, 143.45, 149.99, 152.14. Anal. Calcd for $C_{16}H_{15}N_3$; C, 77.08; H, 6.06; N, 16.85. Found: C, 77.11; H, 6.17; N, 17.00.

2-(p-Chlorophenyl)-7,8-dihydro-6*H*-cyclopenta[*e*]pyrazolo[1,5-*a*]pyrimidine (6d)

This compound was obtained as yellow solid (72 %). m.p. 175-77 °C. IR (KBr): 3069 (CH, aromatic), 2985 (CH, aliphatic), 1620 (C=N), 1600 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 269 (M+), 271 (M+2). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.64-2.69 (m, 2H, CH_2), 3.16-3.18 (t, 2H, *J* = 4 Hz, CH_2), 3.62-3.68 (m, 2H, CH_2), 6.47 (s, 1H, pyrazole H-4), 7.54-7.56 (d, 2H, *J* = 4 Hz, ArH's), 7.80-7.82 (d, 2H, *J* = 4 Hz, ArH's), 8.30 (s, 1H, pyrimidine H-4); ^{13}C NMR δ = 21.43, 28.57, 30.42, 100.32, 118.48, 128.75, 130.95, 132.11, 133.89, 142.45, 143.49, 150.12, 152.24. Anal. Calcd for $C_{15}H_{12}ClN_3$: C, 66.79; H, 4.48; N, 15.58. Found: C, 66.67; H, 4.39; N, 15.48.

3-Phenyl-7,8-dihydro-6*H*-cyclopenta[*e*]pyrazolo[1,5-*a*]pyrimidine (6e)

This compound was obtained as yellow solid (82 %). m.p. 170-72 °C. IR (KBr): 3072 (CH, aromatic), 2983 (CH, aliphatic), 1615 (C=N), 1598 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 235 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.64-2.69 (m, 2H, CH_2), 3.16-3.18 (t, 2H, *J* = 4 Hz, CH_2), 3.62-3.68 (m, 2H, CH_2), 6.93-6.95 (d, 2H, J = 4 Hz, ArH's), 7.54-7.62 (m, 3H, ArH's), 8.22 (s, 1H, pyrimidine H-4), 8.34 (s, 1H, pyrazole H-3); ^{13}C NMR δ = 21.42, 28.48, 30.67, 113.45, 118.62, 126.65, 128.22, 128.74, 130.76, 143.28, 144.18, 144.78, 149.52. Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.67; H, 5.49; N, 17.78.

2-Phenyl-6,7,8,9-tetrahydropyrazolo[1,5-*a*]quinazoline (7a)

This compound was obtained as yellow solid (76 %). m.p. 190-92 °C. IR (KBr): 3072 (CH, aromatic), 2980 (CH, aliphatic), 1612 (C=N), 1600 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 249 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.58-1.66 (m, 2H, CH_2), 1.80-190 (m, 2H, CH_2), 2.62-2.68 (m, 2H, CH_2), 3.15-3.17 (t, 2H, J = 4 Hz, CH_2), 6.50 (s, 1H, pyrazole

H-4), 7.45-7.82 (m, 5H, ArH's), 8.32 (s, 1H, pyrimidine H-4), ^{13}C NMR δ = 21.67, 23.20, 24.56, 38.63, 100.12, 115.23, 127.40, 128.15, 130.21, 132.98, 142.52, 150.97, 153.27. Anal. Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85. Found: C, 76.87; H, 5.96; N, 16.78.

3-Methyl-2-phenyl-6,7,8,9-tetrahydropyrazolo[1,5-*a*]quinazoline

This compound was obtained as yellow solid (76 %). m.p. 160-61 °C. IR (KBr): 3057 (CH, aromatic), 2982 (CH, aliphatic), 1615 (C=N), 1594 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 263 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.58-1.66 (m, 2H, CH_2), 1.80-190 (m, 2H, CH_2), 2.47 (s, 3H, CH_3), 2.62-2.68 (m, 2H, CH_2), 3.15-3.17 (t, 2H, J = 4 Hz, CH_2), 7.24-7.36 (m, 3H, ArH's), 7.81-7.83 (d, 2H, J= 4 Hz, ArH's), 8.25 (s, 1H, Pyrimidine H-4), ^{13}C NMR δ = 8.12, 21.67, 23.21, 24.56, 38.63, 105.18, 115.23, 128.75, 128.89, 131.79, 135.23, 146.12, 149.31, 153.45. Anal. Calcd for $C_{17}H_{17}N_3$ (263.31): C, 77.54; H, 6.51; N, 15.96. Found: C, 77.67; H, 6.45; N, 15.78.

2-(p-Tolyl)-6,7,8,9-tetrahydropyrazolo[1,5-*a*]quinazoline (7c)

This compound was obtained as yellow solid (76 %). m.p. 170-72 °C. IR (KBr): 3057 (CH, aromatic), 2982 (CH, aliphatic), 1615 (C=N), 1594 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 263 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.58-1.66 (m, 2H, CH_2), 1.80-190 (m, 2H, CH_2), 2.28 (s, 3H, CH_3), 2.62-2.68 (m, 2H, CH_2), 3.15-3.17 (t, 2H, J = 4 Hz, CH_2), 6.48 (s, 1H, pyrazole H-4), 7.34-7.36 (d, 2H, ArH's), 7.81-7.83 (d, 2H, J= 4 Hz, ArH's), 8.35 (s, 1H, pyrimidine H-4), ^{13}C NMR δ = 21.67, 21.88, 23.32, 24.67, 38.63, 100.20, 115.32, 128.26, 130.65, 132.24, 135.19, 124.52, 145.37, 150.97, 153.18. Anal. Calcd for $C_{17}H_{17}N_3$ (263.31): C, 77.54; H, 6.51; N, 15.96. Found: C, 77.59; H, 6.57; N, 15.89.

2-(4-Chlorophenyl)-6,7,8,9-tetrahydropyrazolo[1,5-*a*]quinazoline (7d)

This compound was obtained as yellow solid (76 %). m.p. 180-82 °C. IR (KBr): 3057 (CH, aromatic), 2982 (CH, aliphatic), 1615 (C=N), 1594 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 283 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.58-1.66 (m, 2H, CH_2), 1.80-190 (m, 2H, CH_2), 2.62-2.68 (m, 2H, CH_2), 3.15-3.17 (t, 2H, J = 4 Hz, CH_2), 6.48 (s, 1H, pyrazole H-4), 7.64-7.66 (d, 2H, ArH's), 7.80-7.82 (d, 2H, J= 4 Hz, ArH's), 8.32 (s, 1H, Pyrimidine H-4), ^{13}C NMR δ = 21.67, 23.30, 24.56, 38.63, 100.20, 115.32, 128.57, 130.64, 131.98, 133.76, 142.28, 145.13, 150.78, 153.27. Anal. Calcd for $C_{16}H_{14}ClN_3$: 283.76: C, 67.72; H, 4.97; N, 14.81. Found: C, 67.65; H, 5.00; N, 14.76.

3-Phenyl-6,7,8,9-tetrahydropyrazolo[1,5-*a*]quinazoline (7e)

This compound was obtained as yellow solid (76 %). m.p. 170-72 °C. IR (KBr): 3057 (CH, aromatic), 2982 (CH, aliphatic), 1615 (C=N), 1594 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 249 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.58-1.66 (m, 2H, CH_2), 1.80-190 (m, 2H, CH_2), 2.62-2.68 (m, 2H, CH_2), 3.15-3.17 (t, 2H, J = 4 Hz, CH_2), 7.64-7.82 (m, 5H, ArH's), 8.32 (s, 1H, pyrimidine H-4), 8.34 (s, 1H, pyrazole H-3), ^{13}C NMR δ = 21.67, 23.45, 24.56, 38.63, 100.20, 115.32, 123.25, 127.42, 128.78, 131.26, 131.75, 133.27, 137.27, 149.68, 143.38, 145.13, 150.87, 152.35. Anal. Calcd for $C_{16}H_{15}N_3$: 249.14: C, 77.08; H, 6.06; N, 16.85. Found: C, 77.15; H, 5.89; N, 16.76.

2-Phenyl-7,8,9,10-tetrahydro-6*H*-cyclohepta[*e*]pyrazolo[1,5-*a*]-pyrimidine (8a)

This compound was obtained as yellow solid (76 %). m.p. 155-56 °C. IR (KBr): 3057 (CH, aromatic), 2982 (CH, aliphatic), 1615 (C=N), 1594 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 263 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.60-1.90 (m, 4H, CH_2), 2.70-2.80 (d, 1H, *J* = 6 Hz, CH_2), 2.85 (t, 2H, *J* = 6 Hz, CH_2), 3.15 (d, 1H, CH), 3.5 (t, 2H, *J* = 6 Hz, CH_2), 6.50 (s, 1H, pyrazole H-4), 7.45-7.82 (m, 5H, ArH's), 8.30 (d, 1H, *J* = 6Hz, pyrimidine H-4). ^{13}C NMRδ = 23.12, 26.58, 28.13, 28.42, 29.15, 100.20, 115.12, 127.38, 128.27, 130.19, 133.25, 142.52, 145.35, 145.65, 151.78, 154.56. Anal. Calcd for $C_{17}H_{17}N_3$: 263.34: C, 77.54; H, 6.51; N, 15.96. Found: C, 77.45; H, 6.38; N, 16.10.

3-Methyl-2-phenyl-7,8,9,10-tetrahydro-6*H*-cyclohepta[*e*]pyrazolo[1,5-*a*]pyrimidine (8b)

This compound was obtained as yellow solid (76 %). m.p. 149-150 °C. IR (KBr): 3057 (CH, aromatic), 2982 (CH, aliphatic), 1615 (C=N), 1594 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 277 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.60-1.90 (m, 4H, CH_2), 2.20 (s, 3H, CH_3), 2.70-2.80 (d, 1H, *J* = 6 Hz, CH_2), 2.85 (t, 2H, *J* = 6 Hz, CH_2), 3.15 (d, 1H, CH), 3.5 (t, 2H, *J* = 6 Hz, CH_2), 7.45-7.82 (m, 5H, ArH's), 8.30 (s, 1H, pyrimidine H-4). ^{13}C NMR δ = 8.24, 23.11, 26.59, 28.23, 29.18, 105.27, 115.23, 126.76, 128.79, 129.Anal. Calcd for $C_{18}H_{19}N_3$: 277.16: C, 77.95; H, 6.90; N, 15.15. Found: C, 78.10; H, 6.78; N, 15.29.

2-(p-Tolyl)-7,8,9,10-tetrahydro-6*H*-cyclohepta[*e*]pyrazolo[1,5-*a*]pyrimidine (8c)

This compound was obtained as yellow solid (76 %). m.p. 160-61 °C. IR (KBr): 3057 (CH, aromatic), 2982 (CH, aliphatic), 1615 (C=N), 1594 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 277 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.60-1.90 (m, 4H, CH_2), 2.20 (s, 3H, CH_3), 2.70-2.80 (d, 1H, *J* = 6 Hz, CH_2), 2.85 (t, 2H, *J* = 6 Hz, CH_2), 3.15 (d, 1H, CH), 3.5 (t, 2H, *J* = 6 Hz, CH_2), 6.48 (s, 1H, pyrazole H-4), 7.34-7.36 (d, 2H, ArH's), 7.81-7.83 (d, 2H, J= 4 Hz, ArH's), 8.35 (s, 1H, pyrimidine H-4), ^{13}C NMR δ = 21.77, 23.11, 26.57, 28.23, 29.18, 100.24, 115.31, 128.27, 130.65, 132.23, 138.30, 242.34, 145.30, 151.13, 154.65. Anal. Calcd for $C_{18}H_{19}N_3$ (277.36): C, 77.95; H, 6.90; N, 15.15. Found: C, 77.84; H, 7.10; N, 14.98.

2-(4-Chlorophenyl)-7,8,9,10-tetrahydro-6*H*-cyclohepta[*e*]pyrazolo[1,5-*a*]pyrimidine (8d)

This compound was obtained as yellow solid (76 %). m.p. 160-61 °C. IR (KBr): 3057 (CH, aromatic), 2982 (CH, aliphatic), 1615 (C=N), 1594 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 297 (M^+), 299 (M+2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60-1.90 (m, 4H, CH_2), 2.70-2.80 (d, 1H, *J* = 6 Hz, CH_2),

2.85 (t, 2H, *J* = 6 Hz, CH_2), 3.15 (d, 1H, CH), 3.5 (t, 2H, *J* = 6 Hz, CH_2), 6.48 (s, 1H, pyrazole H-4), 7.64-7.66 (d, 2H, ArH's), 7.80-7.82 (d, 2H, J= 4 Hz, ArH's), 8.32 (s, 1H, pyrimidine H-4), ^{13}C NMR δ = 23.11, 26.63, 28.12, 28.48, 29.13, 100.32, 115.23, 128.84, 136.57, 131.92, 133.80, 142.35, 145.30, 151.52, 154.75. Anal. Calcd for $C_{17}H_{16}ClN_3$ (297.78): C, 68.57; H, 5.42; N, 14.11. Found: C, 68.75; H, 5.35; N, 14.24

2-Phenyl-6,7,8,9-tetrahydro-5*H*-cyclohepta[*d*]pyrazolo[1,5-*a*]-pyrimidine (8e)

This compound was obtained as yellow solid (76 %). m.p. 170-72 °C. IR (KBr): 3057 (CH, aromatic), 2982 (CH, aliphatic), 1615 (C=N), 1594 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 263 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60-1.90 (m, 4H, CH_2), 2.70-2.80 (d, 1H, *J* = 6 Hz, CH_2), 2.85 (t, 2H, *J* = 6 Hz, CH_2), 3.15 (d, 1H, CH), 3.5 (t, 2H, *J* = 6 Hz, CH_2), 7.64-7.82 (m, 5H, ArH's), 8.32 (s, 1H, pyrimidine H-4), 8.34 (s, 1H, pyrazole H-3), ^{13}C NMR δ = 23.12, 26.62, 28.13, 28.42, 29.13, 100.20, 111.23, 126.68, 126.14, 128.74, 130.81, 144.72, 145.29, 147.29, 150.90. Anal. Calcd for $C_{17}H_{17}N_3$: 263.34: C, 77.54; H, 6.51; N, 15.96. Found: C, 77.45; H, 6.37; N, 16.12

2,3-Dihydro-1*H*-benzo[4,5]imidazo[1,2-*a*]cyclopenta[*e*]pyri-midine (11a)

This compound was obtained as yellow solid (78 %). m.p. 185-87 °C. IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 209 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.57 (m, 2H, CH_2), 2.87-2.92 (m, 4H, $2CH_2$), 7.21-7.54 (m, 4H, ArH's), 8.33 (s, 1H, pyrimidine H-4). ^{13}C NMR δ = 21.65, 30.98, 32.16, 113.46, 117.87, 118.42, 121.49, 123.79, 129.28, 145.62, 156.72, 158.44, 166.27. Anal. Calcd for $C_{13}H_{11}N_3$: C, 74.62; H, 5.30; N, 20.08. Found: C, 74.62; H, 5.29; N, 20.18

1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]quinazoline (11b)

This compound was obtained as yellow solid (75 %). m.p. 202-204 °C. IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 223 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.85-2.22 (m, 4H, $2CH_2$), 2.85-2.95 (m, 2H, CH_2), 3.15-3.24 (m, 2H, CH_2), 7.21-7.54 (m, 4H, ArH's), 8.21 (s, 1H, pyrimidine H-4). ^{13}C NMR δ = 22.76, 23.40, 24.90, 38.65, 113.43, 114.65, 118.33, 121.49, 123.79, 128.94, 145.61, 147.51, 159.24, 160.27. Anal. Calcd for $C_{14}H_{13}N_3$: C, 75.31; H, 5.87; N, 18.82. Found: C, 75.28; H, 5.78; N, 18.68.

2,3,4,5-tetrahydro-1*H*-benzo[4,5]imidazo[1,2-*a*]cyclohepta[*e*]-pyrimidine (11c)

This compound was obtained as yellow solid (75 %). m.p 220-22 °C. IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 237 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.60-1.90 (m, 4H, CH_2), 2.70-2.80 (d, 1H, *J* = 6 Hz, CH_2), 2.85 (t, 2H, *J* = 6 Hz, CH_2), 3.15 (d, 1H, CH), 3.5 (t, 2H, *J* = 6 Hz, CH_2), 7.21-7.54 (m, 4H, ArH's), 8.28 (s, 1H, pyrimidine H-4). ^{13}C NMR δ = 22.99, 26.52, 28.62, 28.58, 36.03, 113.42, 114.56, 121.49, 123.79, 128.58, 145.59, 145.59, 147.40, 160.11, 160.47. Anal. Calcd for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; N, 17.71. Found: C, 76.12; H, 6.29; N, 17.82.

Synthesis of 5-arylthiazole derivatives (20-22)a-d

Method A: A mixture of thiosemicarbazide **13a-c** (5 mmol) and the appropriate hydrazonoyl halides **14a-c** (5 mmol) in ethanol (20 mL) containing triethylamine (5 mmol, 0.75 mL) was refluxed for 4h, allowed to cool and the solid formed was filtered off, dried and recrystallized from acetic acid to give **(20-22)a-d**.

Method B: To a appropriate of **24a-c** (5 mmol) in ethanol (30 mL) was added sodium acetate trihydrate (1.3 g, 5 mmol), and the mixture was cooled to 0-5 C in an ice bath. To the resulting cold solution was added portionwise a cold solution of arenediazonium chloride [prepared by diazotizing the appropriate of aniline, 4-methylaniline, 4-chloroaniline (5 mmol) dissolved in hydrochloric acid (6 M, 3 mL) with a solution of sodium nitrite (0.35 g, 5 mmol) in water (3 mL)]. After complete addition of the diazonium chloride, the reaction mixture was stirred for a further 30 min in an ice bath. The solid that separated was filtered off, washed with water and finally recrystallized from ethanol to give proved to be identical in all aspects (mp, mixed mp and spectra) with compound **(20-22)a-d** which obtained from method A.

2-(2-Cyclopentylidenehydrazinyl)-4-phenyl-5-(phenyldiaze-nyl)thiazole (20a)

This compound was obtained as brown solid (75 %). m.p. 190-93 °C. IR (KBr): 3320 (NH), 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 361 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.83-1.97 (m, 4H, $2CH_2$), 2.53 (t, 2H, *J* = 4 Hz, CH_2), 2.66 (t, 2H, CH_2), 7.21-8.12 (m, 10H, ArH's), 12.21 (s, br., 1H, NH). ^{13}C NMR δ = 24.90, 24.92, 30.10, 32.26, 107.70, 121.47, 126.89, 128.83, 129.14, 129.15, 130.41, 133.95, 136.75, 155.37, 173.78, 174.12, Anal. Calcd for $C_{20}H_{19}N_5S$: C, 66.46; H, 5.30; N, 19.37; S, 8.87. Found: C, 66.54; H, 5.18; N, 19.29; S, 8.78

2-(2-Cyclopentylidenehydrazinyl)-5-(phenyldiazenyl)-4-(p-to-lyl)thiazole (20b)

This compound was obtained as brown solid (82 %). m.p. 176-78 °C. IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 375 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.83-1.97 (m, 4H, $2CH_2$), 2.34 (s, 3H, CH_3), 2.53 (t, 2H, *J* = 4 Hz, CH_2), 2.66 (t, 2H, CH_2), 7.38-8.15 (m, 9H, ArH's), 12.21 (s, br., 1H, NH). ^{13}C NMR δ = 21.41, 24.90, 24.92, 30.11, 32.26, 107.70, 121.67, 126.97, 128.88, 129.14, 129.18, 133.94, 136.76, 137.11, 152.46, 173.82, 174.12, Anal. Calcd for $C_{21}H_{21}N_5S$: C, 67.17; H, 5.64; N, 18.65; S, 8.54. Found: C, 67.17; H, 5.49; N, 18.56; S, 8.45

4-(4-Chlorophenyl)-2-(2-cyclopentylidenehydrazinyl)-5-(phenyldiazenyl)thiazole (20c)

This compound was obtained as brown solid (77 %). m.p. 180-81 °C. IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 395 (M+), 397 (M+2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83-1.97 (m, 4H, $2CH_2$), 2.53 (t, 2H, *J* = 4 Hz, CH_2), 2.66 (t, 2H, CH_2), 7.38-8.15 (m, 9H, ArH's), 12.21 (s, br., 1H, NH). Anal. Calcd for $C_{20}H_{18}ClN_5S$ (395.91); C, 60.67; H, 4.58; N, 17.69; S, 8.10. Found: C, 60.72; H, 4.49; N, 17.75; S, 8.22

2-(2-Cyclopentylidenehydrazinyl)-4-methyl-5-(phenyldiazenyl)-thiazole (20d)

This compound was obtained as brown solid (72 %). m.p. 205-207 °C. IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 299 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.83-1.97 (m, 4H, $2CH_2$), 2.50 (s, 3H, CH_3), 2.53 (t, 2H, *J* = 4 Hz, CH_2), 2.66 (t, 2H, CH_2), 7.38-8.15 (m, 5H, ArH's), 12.21 (s, br., 1H, NH). ^{13}C NMR δ = 12.84, 24.90, 24.92, 30.11, 32.26, 114.40, 121.72, 129.15, 129.65, 130.23, 154.90, 166.98, 173.85, Anal. Calcd for $C_{15}H_{17}N_5S$: C, 60.18; H, 5.72; N, 23.39; S, 10.71. Found: C, 60.18; H, 5.72; N, 23.39; S, 10.71

2-(2-Cyclohexylidenehydrazinyl)-4-phenyl-5-(phenyldiazenyl)-thiazole (21a)

This compound was obtained as orange solid (76 %). m.p. 178-80 °C. IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 375 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69-1.80 (m, 6H, $3CH_2$), 2.41 (t, 2H, *J* = 4 Hz, CH_2), 2.65 (t, 2H, CH_2), 7.12-8.15 (m, 10H, ArH's), 12.21 (s, br., 1H, NH). ^{13}C NMR δ = 26.99, 27.15, 27.95, 31.11, 31.76, 107.70, 121.47, 126.89, 128.83, 129.14, 129.15, 130.41, 133.94, 136.78, 155.37, 173.97, 196.65, Anal. Calcd for $C_{21}H_{21}N_5S$: C, 67.17; H, 5.64; N, 18.65; S, 8.54. Found: C, 67.04; H, 5.52; N, 18.57; S, 8.47

2-(2-Cyclohexylidenehydrazinyl)-5-(phenyldiazenyl)-4-(p-tolyl)thiazole (21b)

This compound was obtained as brown solid (79 %). m.p. 165-67 °C. IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 389 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.69-1.80 (m, 6H, $3CH_2$), 2.45 (s, 3H, CH_3), 2.41 (t, 2H, *J* = 4 Hz, CH_2), 2.65 (t, 2H, CH_2), 7.12-8.15 (m, 9H, ArH's), 12.10 (s, br., 1H, NH). ^{13}C NMR δ = 21.41, 25.99, 27.15, 27.98, 31.11, 31.76, 107.70, 121.87, 126.97, 128.83, 129.14, 129.17, 133.98, 136.76, 137.12, 152.46, 174.12, 196.65, Anal. Calcd for $C_{22}H_{23}N_5S$: C, 67.84; H, 5.95; N, 17.98; S, 8.23. Found: C, 67.76; H, 6.10; N, 18.08; S, 8.32

4-(4-Chlorophenyl)-2-(2-cyclohexylidenehydrazinyl)-5-(phenyldiazenyl)thiazole (21c)

This compound was obtained as brown solid (79 %). m.p. 171-74 °C. IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 409 (M+), 411 (M+2). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.69-1.80 (m, 6H, $3CH_2$), 2.41 (t, 2H, *J* = 4 Hz, CH_2), 2.65 (t, 2H, CH_2), 7.12-8.15 (m, 9H, ArH's), 12.10 (s, br., 1H, NH). ^{13}C NMR δ = 26.12, 27.15, 27.98, 31.11, 31.75, 107.70, 125.99, 126.97, 127.12, 128.79, 129.15, 133.94, 136.76, 138.99, 155.14, 174.12, 196.65, Anal. Calcd for $C_{21}H_{20}ClN_5S$ (409.93); C, 61.53; H, 4.92; N, 17.08; S, 7.82. Found: 409.93: C, 61.46; H, 4.86; N, 17.12; S, 7.78

2-(2-Cyclohexylidenehydrazinyl)-4-methyl-5-(phenyldiazenyl)thiazole (21d)

This compound was obtained as orange solid (79 %). m.p. 185-88 °C. IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 313 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.69-1.80 (m, 6H, $3CH_2$), 2.41 (t, 2H, *J* = 4 Hz, CH_2), 2.49 (s, 3H, CH_3), 2.65 (t, 2H, CH_2), 7.12-7.38 (m, 5H, ArH's), 12.00 (s, br., 1H, NH). ^{13}C NMR δ = 12.94, 26.14, 27.15, 27.98, 31.11, 31.76, 114.40, 121.71, 129.15, 129.56, 130.41, 154.90, 167.12, 196.65, Anal. Calcd for $C_{16}H_{19}N_5S$ (313.42): C, 61.31; H, 6.11; N, 22.34; S, 10.23. Found: C, 61.21; H, 6.00; N, 22.45; S, 10.19

2-(2-Cycloheptylidenehydrazinyl)-4-phenyl-5-(phenyldiazenyl)thiazole (22a)

This compound was obtained as orange solid (82 %). m.p. 178-80 °C. IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 389 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.50-1.54 (m, 4H, $2CH_2$), 1.68-1.69 (m, 2H, CH_2), 2.17-2.18 (m, 2H, CH_2), 2.24-2.26 (m, 2H, CH_2), 2.45-2.48 (m, 2H, CH_2), 7.12-8.22 (m, 10H, ArH's), 12.00 (s, br., 1H, NH). ^{13}C NMR δ = 22.25, 28.99, 29.80, 37.30, 107.40, 121.41, 126.87, 128.82, 129.14, 129.15, 130.41, 133.94, 136.76, 155.38, 173.99, 186.89, Anal. Calcd for $C_{22}H_{23}N_5S$ (389.52): C, 67.84; H, 5.95; N, 17.98; S, 8.23. Found: C, 67.78; H, 6.05; N, 18.10; S, 8.32

2-(2-Cycloheptylidenehydrazinyl)-5-(phenyldiazenyl)-4-(*p*-tolyl)thiazole (22b)

This compound was obtained as orange solid (82 %). m.p. 176-78 °C. IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 403 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.50-1.54 (m, 4H, $2CH_2$), 1.68-1.69 (m, 2H, CH_2), 2.17-2.18 (m, 2H, CH_2), 2.24-2.26 (m, 2H, CH_2), 2.45-2.48 (m, 2H, CH_2), 7.12-8.23 (m, 9H, ArH's), 12.00 (s, br., 1H, NH). ^{13}C NMR δ = 21.23, 22.25, 28.99, 29.80, 37.30, 107.60, 121.67, 126.89, 129.83, 129.14, 129.17, 133.94, 136.76, 137.15, 152.46, 174.12, 186.97, Anal. Calcd for $C_{23}H_{25}N_5S$: 68.46; H, 6.24; N, 17.35; S, 7.95. Found: C, 68.38; H, 6.30; N, 17.51; S, 7.86

4-(4-Chlorophenyl)-2-(2-cycloheptylidenehydrazinyl)-5-(phenyldiazenyl)thiazole (22c)

This compound was obtained as orange solid (82 %). m.p. 185-88 °C. IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 423 (M+), 425 (M+2). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.50-1.54 (m, 4H, $2CH_2$), 1.68-1.69 (m, 2H, CH_2), 2.17-2.18 (m, 2H, CH_2), 2.24-2.26 (m, 2H, CH_2), 2.45-2.48 (m, 2H, CH_2), 7.12-8.23 (m, 9H, ArH's), 12.00 (s, br., 1H, NH). ^{13}C NMR δ = 22.25, 29.11, 29.80, 37.30, 107.70, 125.99, 126.89, 127.11, 128.83, 129.14, 133.93, 136.67, 138.98, 155.14, 173.99, 186.89, Anal. Calcd. for $C_{22}H_{22}ClN_5S$: C, 62.33; H, 5.23; 16.52; S, 7.56. Found: C, 62.41; H, 5.32; 16.48; S, 7.65

2-(2-Cycloheptylidenehydrazinyl)-4-methyl-5-(phenyldiazenyl)thiazole (22d)

This compound was obtained as orange solid (82 %). m.p. 142-44 °C. IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 427 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.50-1.54 (m, 4H, $2CH_2$), 1.68-1.69 (m, 2H, CH_2), 2.17-2.18 (m, 2H, CH_2), 2.24-2.26 (m, 2H, CH_2), 2.34 (s, 3H, CH3), 2.44-2.47 (m, 2H, CH_2), 7.12-8.23 (m, 5H, ArH's), 12.00 (s, br., 1H, NH). ^{13}C NMR δ = 12.92, 22.25, 29.12, 29.81, 37.30, 114.48, 121.72, 129.15, 129.65, 130.39, 154.88, 186.97, Anal. Calcd. for $C_{17}H_{21}N_5S$ (327.45): C, 62.36; H, 6.46; N, 21.39; S, 9.79. Found: C, 62.28; H, 6.37; N, 21.52; S, 9.68

2,2'-(1-phenylpropane-1,3-diylidene)bis(hydrazine-1-carbothioamide) (25).

A mixture of sodium 3-oxo-3-phenylprop-1-en-1-olate (1.7 g, 10 mmol) thiosemicarbazide (0.91 g, 10 mmol) and piperidine acetate (1 ml) in H_2O (3 ml) was refluxed for 15 minutes. Acetic acid (1.5 ml) was added to the hot solution. The solid product was filtered off and recrystallized from ethanol to give product identical in all aspect (mp., mixed mp., and spectra) with 2,2'-(1-phenylpropane-1,3-diylidene)bis(hydrazine-1-carbothioamide) (**25**) which prepared via reaction of thiosemicarbazide with 3-oxo-3-phenylpropanal.[33]

4-Phenyl-2-(2-(1-phenyl-3-((4-phenylthiazol-2-yl)diazenyl)allylidene)hydrazinyl)-thiazole (27), 4-phenyl-2-(2-(1-phenyl-3-(4-phenyl-5-(phenyldiazenyl)thiazol-2-yl)diazenyl)allylidene)hydrazinyl)-5-(phenyldiazenyl)thiazole (30a) and 4-methyl-2-(2-(3-((4-methyl-5-(phenyldiazenyl)thiazol-2-yl)diazenyl)-1-phenyl-allylidene)-hydrazinyl)-5-(phenyldiazenyl)thiazole (30b).

A mixture of 2,2'-(1-phenylpropane-1,3-diylidene)bis(hydrazine-1-carbothioamide) (**25**) (1.47 g, 5 mmol), the appropriate of ω-bromoacetophenone, 2-oxo-N,2-diphenylacetohydrazonoyl bromide or 2-oxo-N-phenylpropanehydrazonoyl chloride and triethylamine (5 mmol) in ethanol (15 mL) was refluxed for 2 h. The solid which precipitated after cooling was collected and recrystallized from proper solvent afforded **27**, **30a** and **30b**, respectively.

4-Phenyl-2-(2-(1-phenyl-3-((4-phenylthiazol-2-yl)diazenyl)-allylidene)hydrazinyl)-thiazole (27)

This compound was obtained as pale brown solid (77 %). m.p. 175-787 °C (from ethanol). IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 492 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.31 (d, 1H, CH=CH), 5.85 (d, 1H, CH=CH), 7.27-7.98 (m, 17H, (3x 5) ArH's and 2 thiazole H-5) and 12.15 (s, br, 1H, NH). ^{13}C NMR δ = 105.34, 110.12, 116.71, 126.48, 127.45, 127.60, 127.91, 128.20, 128.30, 128.87, 135.45, 135.68, 136.47, 152.67, 155.28, 156.75, 167.53, 170.24, 171.32, Anal. Calcd. for $C_{27}H_{20}N_6S_2$: C, 65.83; H, 4.09; N, 17.06; S, 13.02. Found: C, 65.72; H, 4.17; N, 16.89; S, 13.00

4-Phenyl-2-(2-(1-phenyl-3-(4-phenyl-5-(phenyldiazenyl)thiazol-2-yl)diazenyl)-allylidene)hydrazinyl)-5-(phenyldiazenyl)-thiazole (30a)

This compound was obtained as orange solid (69 %). m.p. 208-209 °C (from acetic acid). IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 700 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.31 (d, 1H, CH=CH), 5.85 (d, 1H, CH=CH), 7.17-7.88 (m, 25H, (5x 5) ArH's and 12.10 (s, br, 1H, NH). ^{13}C NMR δ = 106.54, 110.42, 112.76, 116.71, 119.98, 121.46, 126.88, 127.45, 127.86, 128.30, 128.83, 129.89, 130.41, 133.18, 134.43, 136.77, 137.00, 138.54, 155.20, 155.28, 158.37, 167.53, 171.33, 172.39, Anal. Calcd for $C_{39}H_{28}N_{10}S_2$: C, 66.84; H, 4.03; N, 19.99; S, 9.15. Found: C, 66.68; H, 4.12; N, 20.14; S, 9.28

4-Methyl-2-(2-(3-((4-methyl-5-(phenyldiazenyl)thiazol-2-yl)-diazenyl)-1-phenyl-allylidene)-hydrazinyl)-5-(phenyldiazenyl)-thiazole (30b)

This compound was obtained as orange solid (70 %). m.p. 220-22 °C (from acetic acid). IR (KBr): 3085 (CH, aromatic), 2986 (CH, aliphatic), 1615 (C=N), 1597 (C=C) cm^{-1}. MS (EI, 70 eV) *m/z*: 576 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.45 (s, 6H, $2CH_3$), 5.31 (d, 1H, CH=CH), 5.85 (d, 1H, CH=CH), 7.17-7.88 (m, 15H, (3x 5) ArH's and 12.10 (s, br, 1H, NH). ^{13}C NMR δ = 12.94, 113.23, 112.99, 116.71, 119.79, 121.72, 127.91, 127.45, 128.30, 128.43, 129.15, 130.41, 138.44, 154.73, 154.90, 155.28, 164.34, 165.40, 167.53, Anal. Calcd for $C_{29}H_{24}N_{10}S_2$: C, 60.40; H, 4.19; N, 24.29; S, 11.12. Found: C, 60.40; H, 4.19; N, 24.29; S, 11.12

Conclusion

In conclusion, compounds of type 2 proved to be useful precursors for synthesis of various fused pyrimidines via their reactions with heterocyclic amines. Also, 2 reacted with thiosemicarbazones then with hydrazonoyl halides gave thiazole derivatives in good yields. The structures of the newly synthesized compounds were confirmed by spectral data and elemental analyses.

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