SYNTHESIS AND REACTIONS OF NEW PYRAZOLE DERIVATIVES

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Chemical transformation of 3-amino-5-hydroxy-4-phenylazo-1H-pyrazole (1) provided a series of new pyrazol derivatives such as N-(4-(2-phenyldiazenyl)-2,5-dihydro-3-hydroxy-1H-pyrazol-5-yl)-2 chloroacetamide (**2**) obtained in the reaction of **1** with chloroacetyl chloride. Reaction of 2 with malononitrile and ammonium isothiocyanate gave the corresponding 1-(4-(2-phenyldiazenyl)-5-hydroxy-1H-pyrazol-3-yl)-2-amino-4,5-dihydro-5-oxo-1H-pyrrol-3-carbonitrile (**3**) and 3-(2-phenyldiazenyl)-7-amino-2-hydroxypyrazolo[1,5-a]pyrimidin-5(1H)-one (**4**). Reaction of **1** with P_2S_5 gave the corresponding 3-amino-5-mercapto-4-phenylazo-1H-pyrazole **5**. The reaction of compound 5 with chloroacetic acid, ethyl chloroacetate, tetrahydrofuran, 3-hydroxybenzaldehyde, phenacylbromide and ninhydrine gave the corresponding N-substituted derivatives (**6, 7, 8, 9, 10, 11, 12, 13**), respectively. The reaction of compound **7** with hydrazine hydrate and a consecutive cyclization in the presence of glacial acetic acid and sulfuric acid mixture afforded **12**. 1-(4-(2-Phenyldiazenyl)-5-mercapto-1H-pyrazol-3-yl)-3- phenylthiourea **14** was obtained from reaction of **5** with phenyl isothiocyanate, which was transformed into pyrazolothiadiazole **15** and pyrazolotriazole **16** derivatives with bromine in different solvents. 3-Amino-5-hydrazino-4-phenylazo-1H-pyrazole **17** was obtained from reaction **5** with hydrazine hydrate. Cyclization of compound **17** by reacting it with ethyl acetoacetate, acetylacetone, phthalic anhydride and phenacyl bromide gave the corresponding N-pyrazolylpyrazoles (**18** and **19**), pyrazol-2,3-dihydrophthalazine-1,4-dione (**20**) and pyrazolotriazine (**21**), respectively. Reaction of 17 with sodium nitrite in the presence acetic acid, ethyl pyruvate and carbon disulfide gave the corresponding pyrazolotetrazole (**22**), imidazolopyrazole (**23**) and pyrazolotriazole derivatives (**26**).

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Introduction

Pyrazoles and their substituted derivatives are interesting as potential pharmaceuticals, and intermediates in dye industry. Despite the enormous number of substituted pyrazoles reported in the literature only a limited number of bispyrazole derivatives have so for been reported. Our interest in synthesis and reactivity of the parent compounds arises from promise medicinal chemistry[1-3] and organometallic complex reactivity. The present investigation is in continuation of our previous work on 3-amino-5-hydroxy-4-phenylazo-1H-pyrazole (**1**) and all analysis is agreement with the structure.[4]

Experimental

Melting points were recorded using SMP30 Melting Point Apparatus (Stuart) and are uncorrected. The IR spectra were record on KBr discs using a FTIR 600 series spectrophotometer (JASCO) and ^{1}H NMR spectra (δ ppm) were recorded on a Varian 300 MHZ spectrometer using CDCl3 as solvent.

N-(4-(2-Phenyldiazenyl)-2,5-dihydro-3-hydroxy-1*H*-pyrazol-5-yl)-2-chloroacetamide (2).

To a solution of compound **1** (0.21 g, 1 mmol) in dioxane (30 mL), chloroacetyl chloride (0.09 g, 1 mmol) was added drop wise with stirring at room temperature. The reaction mixture was refluxed for 30 min. at 60 °C, the solution was concentrated to a small volume, poured into ice-cold water and recrystallized from ethonal, yield 60 %. M. p.210 °C. IR (KBr): 3425 (O-H), 3335 (N-H), 1700 (C=O) cm^{-1}. 1H-NMR($CDCl_3$): 2.8 (s, 2H, CH_2), 5.0 (s, 1H, NH), 6.8-7.8 (m, 5H, Ar-H), 9.0 (s, 1H, NH), 12.33 (br, 1H, OH). Anal. Calcd. for $C_{11}H_{10}N_5O_2Cl$: C: 47.24 %; H: 3.60 %; N: 25.04 %; Cl: 12.67 %; Found : C: 47.21 %; H: 3.61 %; N: 25.05 %; Cl: 12.68 %.

1-(4-(2-Phenyldiazenyl)-5-hydroxy-1*H*-pyrazol-3-yl)-2-amino-4,5-dihydro-5-oxo-1*H*-pyrrol-3-carbonitrile (3).

To a solution of compound **2** (0.27 g, 1 mmol) in dioxane (30 mL) a catalytic amount of TEA (triethylamine) (0.5 mL), malononitrile (0.06 mL, 1 mmol) was added. The reaction mixture was refluxed for 4 h, cooled, poured onto cold water and neutralized with dilute HCl, the precipitate was collected, filtered off, dried and recrystallized from dioxane. Yield 54 %, M. p. 300 °C. IR (KBr): 3540 (O-H), 3375 (NH_2), 3280 (N-H), 3050 ($CH_{aromatic}$), 2240 (CN), 1690 (C=O) cm^{-1} . ^{1}H-NMR($CDCl_3$): 2.3 (s, 2H, CH_2), 5.2(s, 2H, NH_2), 7.1-8.9 (m, 5H, Ar-H), 9.2(s, 2H, NH), 12.3(br, 1H, OH). Anal. Calcd. for $C_{14}H_{11}N_7O_2$: C: 54.36 %; H: 3.58 %; N: 31.70 %; Found: C:54.34 %; H: 3.59 %; N: 31.71 %.

3-(2-Phenyldiazenyl)-7-amino-2-hydroxy pyrazolo[1,5-*a*] pyrimidin-5(1*H*)-one (4).

To a solution of compound **2** (0.27 g, 1 mmol) in absolute ethanol (30 mL) containing sodium ethoxide (0.01 g, 1 mmol), ammonium isothiocyanate (0.07 g, 1 mmol) was added. The reaction mixture was refluxed for 5 h. The solid product was collected and recrystallized from ethanol. Yield 69 %. M. p.140 °C. IR (KBr): 3550 (O-H), 3443 (NH_2), 3275 (N-H), 3058 ($CH_{aromatic}$), 1680 (C=O) cm^{-1}. ^{1}H-NMR

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($CDCl_3$): 5.8 (s, 2H, NH_2), 6.8-7.8 (m, 6H, Ar-H and pyrimidine-H), 8.9 (s, 1H, NH), 12.0 (br, 1H, OH). Anal. Calcd. for $C_{16}H_{11}N_7O_3$: C: 53.13 %; H: 4.08 %; N: 30.98 %; Found: C: 53.11 %; H: 4.09 %; N: 30.99 %.

3-Amino-5-mercapto-4-phenylazo-1*H*-pyrazole (5)

A solution of compound **1** (0.2 g, 1 mmol) was heated at reflux temperature in dry pyridine (20 mL) containing phosphorus pentasulfide (0.2 g, 1 mmol) for 5 h. The solution was acidified with dil. HCl and the solid precipitate was filtered off, washed several times with water, dried and recrystallized from dimethylformamide. Yield 75 %, M. p. 200 °C. IR (KBr): 3432 (NH_2), 3375 (NH), 2560 (SH) cm^{-1}. ^{1}H-NMR ($CDCl_3$): 6.3 (s, 1H, NH), 6.8-7.6 (m, 5H, Ar-H), 8.5 (s, 2H, NH_2), 13.04 (s, 1H, SH). Anal. Calcd. for $C_9H_9N_5S$: C: 49.29 %; H: 4.14 %; N: 31.49 %; S: 14.62 %; Found: C: 49.28 %; H: 4.15 %; N: 31.48 %; S: 14.63 %.

2-(4-(2-Phenyldiazenyl)-5-mercapto-1*H*-pyrazol-3-ylamino)-acetic acid (6)

A solution of compound **5** (0.21 g, 1 mmol), chloro acetic acid (0.08 g, 1 mmol) and sodium acetate (0.07 g, 1 mmol) was heated at reflux temperature for 3 h in absolute ethanol (20 mL), the precipitate was collected and recrystallized from ethanol. Yield 75 %. M. p. 256 °C. IR (KBr): 3300 (OH), 3260 (NH), 2641 (SH), 1700 (C=O) cm^{-1} ^{1}H-NMR ($CDCl_3$): 2.8(s, 2H, CH_2), 5.8 (s, 1H, NH), 7.0-7.8 (m, 5H, Ar-H), 8.9 (s, 1H, NH), 12.0 (s, 1H, OH), 13.2 (s, 1H, SH). Anal. Calcd. for $C_{11}H_{11}N_5O_2S$: C: 47.64; H: 3.99; N: 25.25; S: 11.56 %; Found: C: 47.263; H: 3.98; N:25.28; S: 11.55 %.

Ethyl 2-(4-(2-phenyldiazenyl)-5-mercapto-1*H*-pyrazol-3-yl)aminoacetate (7)

A solution of compound **5** (0.21 g, 1 mmol), ethyl chloroacetate (0.11 g, 1 mmol) and sodium acetate (0.07 g, 1 mmol) in absolute ethanol (20 mL) were heated at reflux temperature for 3 h. After cooling to room temperature, the precipitate was filtered off, dried and recrystallized from ethanol. Yield 70 %. M. p. 246 °C. IR (KBr): 3480 (NH), 2650 (SH), 1710 (C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$):1.26(t, 3H, CH_3), 2.8(s, 2H, CH_2), 4.2 (q, 2H, CH_2), 5.8 (s, 1H, NH), 7.0-7.8 (m, 5H, Ar-H), 8.9 (s, 1H, NH), 12.9 (s, 1H, SH). Anal. Calcd. for $C_{13}H_{15}N_5O_2S$: C: 51.13; H:4.95; N: 22.93; S: 10.50 %; Found: C: 51.14; H: 4.94; N:22.91; S: 10.52 %.

2-(4-(2-Phenyldiazenyl) -5-mercapto-1*H*- pyrazol -3ylamino)-acetohydrazide (8)

A solution of compound **7** (0.3 g, 1 mmol) was mixed with a solution containing absolute ethanol (15 mL) and hydrazine hydrate (0.05 g, 1 mmol) and the reaction mixture was heated at reflux temperature for 2 h, left standing overnight at 25 °C, the precipitate formed was filtered off, washed with methanol and light petroleum, dried and recrystallized from diluted acetic acid or water. Yield 70 %. M. p. 100 °C. IR (KBr): 3400 (NH_2), 3381 (NH), ($CH_{aromatic}$), 2850 (CH-aliphatic), 2650 (SH), 1686 (C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): 4.4 (s, 2H, NH_2), 7.1-7.8 (m, 5H, Ar-H), 9.6 (s, 1H, NH), 9.8 (s, 1H, NH), 13.3 (s, 1H, SH). Anal. Calcd. for $C_{11}H_{13}N_7OS$: C: 45.35; H: 4.49; N:33.65; S: 11.00 %; Found: C: 45.38; H: 46; N: 33.63; S: 11.02 %.

4-(2-Phenyldiazenyl)-3-(pyrrolidin-1-yl)-1*H*-pyrazol-5-thiol (9).

A solution of compound **5** (0.21 g, 1 mmol) and tetrahydrofuran (0.06 g, 1 mmol) in glacial acetic acid (15 mL) were heated at reflux temperature for 8 h. The solvent was reduced to one third of its volume under reduced pressure and after cooling the precipitate formed was collected and recrystallized from ethanol. Yield 52 %. M. p. 190 °C. IR (KBr): 3450 (NH), 3055 ($CH_{aromatic}$), 2645 (SH) cm^{-1}. ^{1}H NMR ($CDCl_3$): 1.4 (m, 4H, $2CH_2$), 2.9 (m, 4H, $2CH_2$), 5.9 (s, 1H, NH), 7.0-7.8 (m, 5H, Ar-H), 13.2 (s, 1H, SH). Anal. Calcd. for $C_{13}H_7N_5S$: C: 58.85; H: 2.65; N: 26.39; S: 12.08 %; Found: C:58.84; H:2.66; N: 26.38; S: 12.09 %.

3-((-4-(2-Phenyl diazenyl) 5-mercapto-1*H*- pyrazol -3-yl imino) methyl)phenol (10).

A solution of compound **5** (0.21 g, 1 mmol) and 3-hydroxybenzaldhyde (0.12 g, 1 mmol) in absolute ethanol (15 mL) was heated at reflux temperature for 7 h, cooling to room temperature, the precipitate formed was filtered off, dried and recrystallized from ethanol. Yield 80 %. M. p. 244 °C. IR (KBr): 3560 (OH), 3450 (NH), 3060 ($CH_{aromatic}$), 2590 (SH), 1634 (C=N) cm^{-1}. ^{1}H-NMR ($CDCl_3$): 7.0-7.8 (m, 9H, Ar-H), 8.6 (s, 1H, N=CH), 9.8 (s, 1H, NH), 12.0 (S,1H,OH), 13.4 (s,1H,SH). Anal. Calcd. for $C_{16}H_9N_5OS$: C: 60.17; H: 2.84; N: 21.93; S: 10.04 %; Found: C: 60.18; H: 2.85; N: 21.94; S: 10.03 %.

2-(4-(2-Phenyldiazenyl) 3-amino-1*H*- pyrazol -5-yl thio) 1-phenylethanone (11).

A solution of compound **5** (0.21 g, 1 mmol), phenacyl bromide (0.19 g, 1 mmol) and sodium acetate (0.07 g, 1 mmol) were heated at reflux in ethanol (15 mL) for 3 h. The precipitate formed was filtered off, washed with water several times, dried and recrystallized from ethanol. Yield 50 %. M. p. 240 °C. IR (KBr): 3450(NH2), 3325 (NH), 1700 (C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): 2.5 (s, 2H, CH_2), 5.8 (s, 1H, NH), 7.0-7.8 (m, 10H, Ar-H), 8.9 (s, 2H, NH_2). Anal. Calcd. for $C_{16}H_{15}N_5OS$: C:59.05; H: 4.65; N: 21.52; S: 9.82 %; Found: C: 59.02; H: 4.68; N: 21.53; S: 9.84 %.

***N*-4,5-Diphenylpyrazolo[3,4-*b*][1,4]thiazine-3,4(1*H*)-diamine (12).**

To a solution of compound **11** (0.3 g, 1 mmol) in a glacial acetic acid:sulphuric acid mixture (5 mL:1 mL) were heated on water bath for 5 h. The reaction mixture was allowed to cool, neutralized by sodium carbonate solution (10 %). The precipitate formed was collected and recrystallized from acetic acid. Yield 55 %. M. p. 300 °C. IR (KBr): 3450 (NH_2), 3380 (NH), 3050 ($CH_{aromatic}$) cm^{-1}. ^{1}H-NMR ($CDCl_3$): 5.8 (s, 1H, NH) , 7.0-7.8 (m, 11H, Ar-H and thiazine-H), 8.9 (s, 1H, NH), 9.2(s, 2H, NH_2). Anal. Calcd. for $C_{17}H_{14}N_5S$: C: 63.73; H: 4.40; N: 21.85; S: 10.00 %; Found : C: 63.72; H: 4.41; N: 21.84; S: 10.01 %.

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2-(4-(2-Phenyldiazenyl)-5-mercapto-1*H*-pyrazol-3-yl imino)-2*H*-indene-1,3-dione (13)

A solution of compound **5** (0.12 g, 1 mmol) and ninhydrine (0.17 g, 1 mmol) in absolute ethanol (25 mL) was stirred for 2 h, then the precipitate formed was collected and recrystallized from ethanol. Yield 80 %. M. p. 130 °C. IR (KBr): 3453 (NH), 3058 ($CH_{aromatic}$), 2590 (SH), 1688, 1628 (2C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): 5.8 (s, 1H, NH), 7.0-7.9 (m, 9H, Ar-H), 13.0 (s, 1H, SH). Anal. Calcd. for $C_{18}H_{11}N_5O_2S$: C: 59.82; H: 3.06; N: 19.38; S: 8.87 %. Found: C: 59.81; H: 3.07; N: 19.39; S: 8.86 %.

1-(4-(2-Phenyldiazenyl)-5-mercapto-1*H*-pyrazol-3-yl)-3-phenyl-thiourea (14)

A solution of compound **5** (0.21 g, 1 mmol) and phenylisothiocyanate (0.15 g, 1 mmol) was heated at reflux temperature for 7 h in absolute ethanol (30 mL), the precipitate was collected and recrystallized from ethanol. Yield 57 %. M. p. 100 °C. IR (KBr): 3500 (NH), 3055 ($CH_{aromatic}$), 2600 (SH), 1335 (C=S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): 6.8 (s, 1H, NH), 7.0-7.8 (m, 10H, Ar-H), 9.2 (s, 1H, NH), 9.8 (s, 1H, NH) and 13.0 (s, 1H, SH). Anal. Calcd for $C_{16}H_{14}N_6S_2$: C: 54.21; H: 3.98; N: 23.71; S: 18.09 %. Found: C: 54.23; H: 3.96; N: 23.72; S: 18.08 %.

7-(2-Phenyldiazenyl)-2-(phenylamino)pyrazolo[1,5-*b*][1,2,4]-thiadiazol-1-yl-6-thiol (15)

To a solution of compound **14** (0.12 g, 1 mmol) in pyridine (20 mL), bromine (0.15 g, 1 mmol) in pyridine (5 mL) was added dropwise at room temperature. The reaction mixture were heated under reflux for 1 h. The mixture was cooled, poured into water with stirring, the solid precipitated was collected, filtered off, washed with water, dried and recrystallized from ethanol. Yield 57 %. M. p. 90 °C. IR (KBr): 3450 (NH), 3055 ($CH_{aromatic}$), 2680 (SH)cm^{-1}. ^{1}H-NMR ($CDCl_3$): 5.8 (s, 1H, NH) , 7.0-7.9 (m, 10H, Ar-H), 13.0 (s, 1H, SH).Anal. Calcd for $C_{16}H_{12}N_6S_2$: C: 54.52; H: 3.43; N: 23.85; S: 18.19 %. Found: C: 59.53; H: 3.42; N: 23.86; S: 18.18 %.

3-Phenyl-7-(phenyldiazenyl)-3*H*-pyrazolo[1,5-*b*][1,2,4]triazol-2,6-dithiol (16)

To a solution of compound **14** (0.21 g, 1 mmol) in a glacial acetic acid (20 mL), bromine(0.15 g, 1 mmol) in a glacial acetic acid (5 mL) was added dropwise at room temperature. The reaction mixture were heated under reflux for 1 h, cooled, poured into water with stirring. The solid precipitated was filtered off, washed with water, dried and recrystallized from ethanol. Yield 66 %. M. p. 110 °C. IR (KBr): 3065 (CH-aromatic), 2600, 2590 (2SH) cm^{-1} . ^{1}H-NMR ($CDCl_3$): 7.0-7.9 (m, 10H, 2Ar-H), 12.9(s, 1H, SH), 13.2 (s, 1H, SH). Anal. Calcd. for $C_{10}H_{13}N_6S_2$:C: 42.68; H: 4.65; N: 29.86; S: 22.79 %. Found : C: 42.69; H: 4.64; N: 29.87; S: 22.78 %.

3-Amino-5-hydrazino-4-phenylazo-1*H*-pyrazole (17)

Hydrazine hydrate (0.05 g, 1 mmol) was added to a solution of compound **5** (0.2 g, 1 mmol) in absolute ethanol (15 mL), the reaction mixture was heated under reflux for 6 h or until the evolution of H_2S ceased, the solid precipitated was filtered off, dried and recrystallized from ethyl acetate. Yield 75 %. M. p. 270 °C. IR (KBr): 3438 (NH2), 3382 (N-H), 3055 ($CH_{aromatic}$) cm^{-1}. ^{1}H-NMR ($CDCl_3$): 4.5 (s, 1H, NH), δ4.9 (s, 2H, NH_2), δ5.6 (s, 2H, NH_2), δ6.9-7.3 (m, 5H, Ar-H) and at δ8.4 (s, 1H, NH). Anal. Calcd. For $C_9H_{11}N_7$: C: 49.75; H: 5.10; N: 45.14 %. Found: C: 49.76; H: 5.11; N: 45.12 %.

1-(4-(2-Phenyldiazenyl)-3-amino-1*H*-pyrazol-5-yl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (18)

Ethyl acetoacetate (0.1 g,1 mmol) was added to a solution of compound **17** (0.21 g, 1 mmol) in absolute ethanol (20 mL), the reaction mixture was heated under reflux for 10 h. The solution was concentrated and cooled, the solid precipitated was filtered off, dried and recrystallized from benzene. Yield 65 %. M. p. 250 °C. IR (KBr): 3450 (NH_2), 3395 (NH), 3045 ($CH_{aromatic}$), 1688 (C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$):2.3 (s, 2H, CH_3), 5.8(s, 2H, CH_2 of pyrazolone), 7.2-8.0 (m, 5H, Ar-H), 8.9(s, 2H, NH_2), 12.5 (s, 1H, NH). Anal. Calcd for $C_{13}H_{11}N_7O$: C: 55.51; H: 3.94; N; 34.85 %. Found: C: 55.50; H: 3.93; N: 34.87 %.

4-(2-Phenyldiazenyl)-5-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1*H*-pyrazol-3-amine (19)

Acetyl acetone (0.1 g, 1 mmol) was added to a solution of compound **17** (0.21 g, 1 mmol) in absolute ethanol (20 mL), the reaction mixture was heated under reflux for 10 h. The mixture was concentrated and cooled, the solid precipitated were collected by filtration, dried and recrystallized from benzene. Yield 77 %. M. p. 210 °C. IR (KBr): 3445 (NH_2), 3390 (NH), 3055 ($CH_{aromatic}$) cm^{-1} . ^{1}H-NMR ($CDCl_3$): 1.5 (s, 6H, $2CH_3$), 6.0 (s, 2H, CH_2 of pyrazolone), 7.0-7.8 (m, 5H, Ar-H), 8.4 (s, 2H, NH_2), 13 (s, 1H, NH). Anal. Calcd for $C_{14}H_{13}N_7$: C: 60.20; H: 4.69; N: 35.11 %. Found: C: 60.22; H: 4.68; N: 35.10 %.

2-(4-(2-Phenyldiazenyl)-3-amino-1*H*-pyrazol-5-yl)-2,3-dihydro-phthalazine-1,4-dione (20)

Phthalic anhydride (0.14 g, 1 mmol) was dissolved in a solution of compound **17** (0.21 g, 1 mmol) in acetic acid (30 mL), the reaction mixture was heated under reflux for 10 h. The mixture was concentrated, cooled, poured onto crushed ice, the solid precipitated was collected by filtration, dried and recrystallized from chloroform. Yield 80 %. M. p. 256 °C. IR (KBr): 3445 (NH_2), 3368 (NH), 3095 ($CH_{aromatic}$), 1670, 1685 (2C=O) cm^{-1} . ^{1}H-NMR ($CDCl_3$):5.8 (s, 1H, NH), 6.2(s, 1H, NH), 7.0-7.8 (m, 9H, Ar-H), 8.9(s, 2H, NH_2). Anal. Calcd. for $C_{17}H_9N_7O_2$: C: 59.47; H: 2.64; N: 28.56 %. Found : C: 59.45; H: 2.65; N: 28.57 % .

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(3-Amino-4-(phenylamino)-4,5-dihydro-1*H*-pyrazolo[4,3-*e*]-[1,2,4]triazin-5-yl)(phenyl)methanone (21)

A solution of compound **17** (0.21 g, 1 mmol) and phenacyl bromide (0.1 g, 1 mmol) in absolute ethanol (30 mL) was refluxed for 5 h, the precipitate formed was filtered off, dried and recrystallized from chloroform. Yield 60 %. M. p. 70 °C. IR (KBr): 3468 (NH_2), 3378 (N-H), 3055 ($CH_{aromatic}$), 1703 (C=O) cm^{-1} . ^1H NMR($CDCl_3$): 5.8(s, H, NH), 7.0-7.9 (m, 10H, 2Ar-H), 8.3(s, 1H, NH), 9.2 (s, 1H, NH_2). Anal. Calcd for $C_{17}H_{15}N_7O$: C: 58.84; H: 4.33; N: 28.06 %. Found : C: 58.82; H: 4.34; N: 28.05 %.

6-((Acetoxy)diazenyl)-7-(phenyldiazenyl)-3*H*-pyrazolo[1,5-*d*]tetrazole (22)

A solution of sodium nitrite (0.13 g, 1 mmol) in water (10 mL) was added to a cold solution of **17** (0.21 g, 1 mmol) in acetic acid (20 mL). After completion of addition, the ice bath was removed and srirring was continued for 1 h. The precipitate was filtered off, dried and recrystallized from ethanol. Yield 58 %. M. p. 130 °C. IR (KBr): 3440 (N-H), 3055 ($CH_{aromatic}$), 2120 (N_2), 1703 (C=O) cm^{-1} . ^1H-NMR ($CDCl_3$): 7.0-7.9 (m, 5H, Ar-H), 13.0(s, 1H, NH). Anal. Calcd for $C_{11}H_{11}N_9O_2$: C: 39.63; H: 3.32; N: 37.81 %. Found: C: 39.60; H: 3.33; N: 37.83 %.

7-(2-Phenyldiazenyl)-6-hydrazinyl-2-methyl-5*H*-imidazo[1,2-*b*]pyrazol-3-ol (23)

A solution of compound **17** (0.21 g, 1 mmol) was refluxed in absolute ethanol (20 mL) containing ethyl pyruvate (0.11 g, 1 mmol) for 5 h. The precipitate formed was filtered off, washed several times with water, dried and recrystallized from dioxane. Yield 55 %. M. p. 180 °C. IR (KBr): 3529 (O-H), 3430 (NH_2), 3358 (N-H), 3030 ($CH_{aromatic}$) cm^{-1} . ^1H-NMR ($CDCl_3$):2.8 (s, 3H, CH_3), 4.8(s, 2H, NH_2), 5.8(s, 1H, NH), 7.0-7.8 (m, 5H, Ar-H), 9.6(s, 1H, NH), 12.1 (s, 1H, OH). Anal. Calcd for $C_{12}H_{13}N_7O$: C: 50.15; H: 4.56; N: 34.12 %. Found: C: 50.16; H: 4.57; N: 34.10 %.

Potassium 5-hydrazinyl-4-(phenyldiazenyl)-1H-pyrazol-3 yl-carbamodithioate (24)

To a warmed ethoxide solution prepared by dissolving potassium hydroxide (0.011 g, 1 mmol) in absolute ethanol (30 mL), compound **17** (0.21 g, 1 mmol) and CS_2 (0.07 g, 1 mmol) were added. The reaction mixture wase heated under reflux for 2 h in a water bath. After cooling, the mixture was poured onto crushed ice, neutralized by diluted acetic acid and the solid precipitated was collected by filtration, dried and recrystallized from ethanol. Yield 60 %. M. p. 240 °C. IR (KBr): 3355 (NH_2), 3250 (N-H), 3055 ($CH_{aromatic}$), 1334 (C=S) cm^{-1} . Anal. Calcd for $C_{10}H_{11}N_7S_2$: C: 40.93; H: 3.77; N: 33.42; S: 21.85 %. Found : C: 40.94; H: 3.76; N: 33.43; S: 21.84 %.

***N*-[5-(hydrazino)4-(phenyldiazenyl)-1*H*-pyrazol-3yl]hydrazine-carbothioamide (25):**

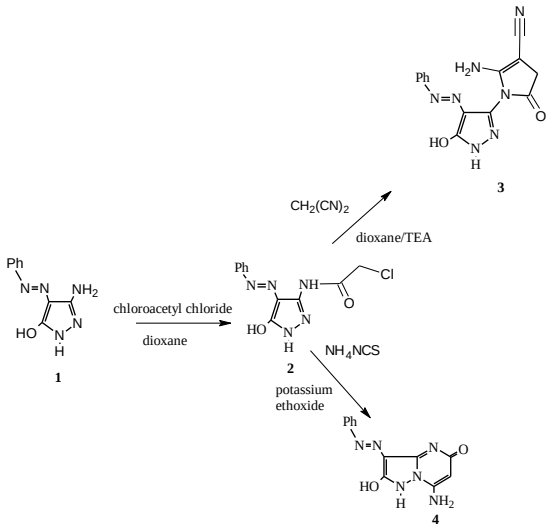
A mixture of compound **24** (0.29 g, 1 mmol) and hydrazine hydrate (0.05 g, 1 mmol) was heated in absolute ethanol (15 mL) under reflux for 10-12 h. The solids precipitated was collected, filtered off, dried and recrystallized from chloroform. Yield 55 %. M. p. 265 °C. IR (KBr): 3375 (NH_2), 3280 (N-H), 3050 ($CH_{aromatic}$), 1335(C=S) cm^{-1} .Anal. Calcd for $C_{10}H_8N_9S$: C: 41.95; H: 2.81; N: 44.03; S: 11.20 %. Found : C: 41.94; H: 2.82; N: 44.02; S: 11.21 %.

4-(5-Hydrazinyl-4-phenyldiazenyl-1*H*-pyrazol-3yl)3-phenyl-1*H*[1,2,4]triazole-5(4*H*)-thione (26)

Benzoylchloride (0.12 g, 1 mmol) was added dropwise to a cold solution of thiosemicarbazide derivative **25** (0.29 g, 1 mmol) in dry pyridine (15 mL), the reaction mixture was heated under reflux for 5 h. The solid precipitated was collected by filtration, washed with water several times, dried and recrystallized from ethanol. Yield 55 %. M. p. 300 °C. IR (KBr): 3540 (O-H), 3375 (NH_2), 3280 (N-H), 3050 ($CH_{aromatic}$), 2240 (CN), 1690 (C=O) cm^{-1}. ^1H-NMR ($CDCl_3$): 5.8 (s ,1H, NH), 4.4(s, 2H, NH_2), 7.0-7.8 (m, 10H, Ar-H), 8.6(s, 1H, NH), 12.0 (s,1H, NH). Anal. Calcd. for $C_{14}H_{11}N_7O_2$: C: 54.36; H: 3.58; N: 31.70 %; Found : C: 54.34; H: 3.59; N: 31 %.

RESULTS AND DISCUSSION

3-Amino-5-hydroxy-4-phenylazo-1H-pyrazole **1** was prepared and was allowed to react with chloroacetyl chloride in dioxane at room temperature with formation of the acylated product, namely *N*-(4-(2-phenyldiazenyl)-2,5-dihydro-3-hydroxy-1*H*-pyrazol-5-yl)-2-chloroacetamide **2**. The IR spectra revealed the presence of (C=O) at 1700 cm^{-1} and the absorption bands characteristic for NH_2 group were disappeared completely. The cyclization of compound **2** with malononitrile or ammonium isothiocyanate in various solvents gave the corresponding pyrazolopyrrol-3-carbonitrile **3** and pyrazolo[1,5-*a*]pyrimidine 4 derivatives (Scheme 1).



Scheme 1. Synthesis of compounds **1-4**.

IR spectrum of compound **3** unambiguously confirmed the presence of NH_2 group vibrations at 3375 and CN group bands at 2240 cm^{-1}. Treatment of compound **1** with P_2S_5 in dry pyridine gave the corresponding 3-amino-5-mercapto-4-phenylazo-1H-pyrazole (**5).**

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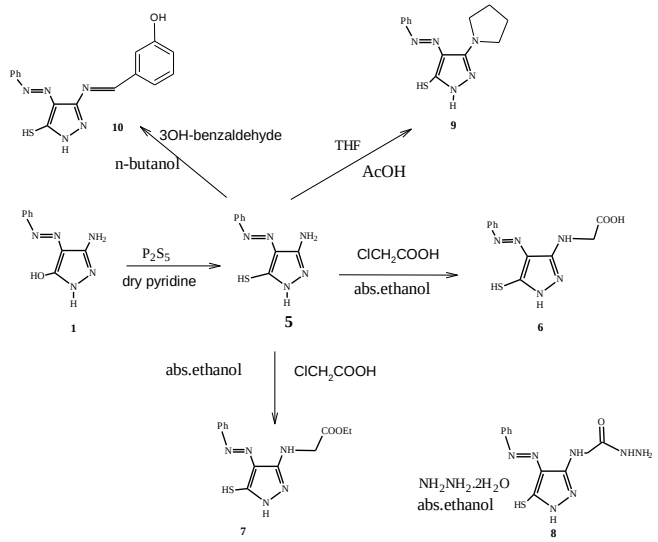
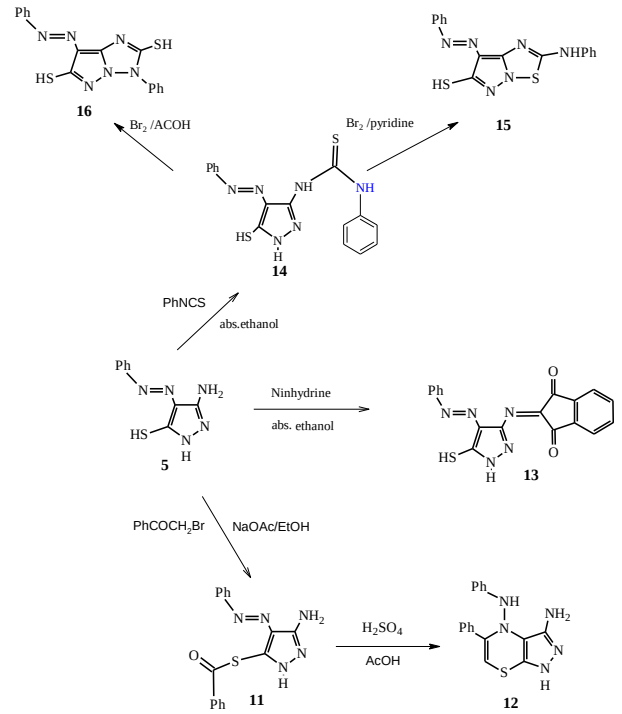
Treatment of compound **5** with chloroacetic acid, tetrahydrofuran, 3-hydroxybenzaldhyde, phenacyl bromide and ninhydrine gave the corresponding N-alkylation or condensation products (**6, 7, 9** and **10**, respectively). Reaction of the compound **7** with hydrazine hydrate afforded compound **8**. (Scheme 2). Treatment of compound **5** with phenacyl bromide and ninhydrine gave the corresponding N-alkylation or condensation products **11** and **13**, respectively.



Scheme 2. Synthesis of compounds **5-10.**

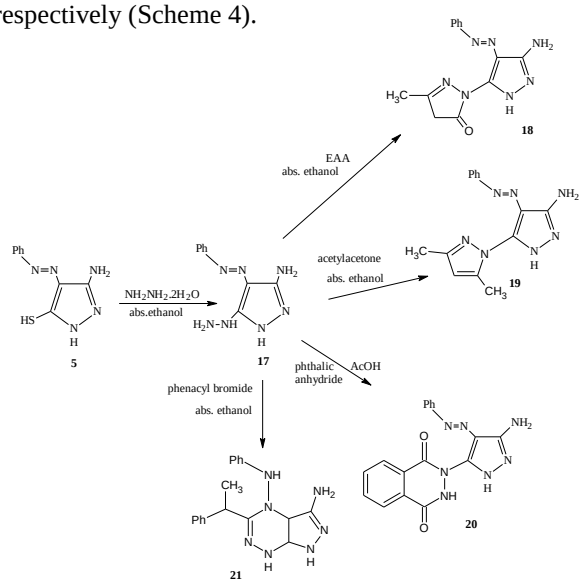
In the IR spectrum of compound **13** the bands appear at 1688 and 1682 cm^{-1}, respectively, are characteristic for the C=O groups. The ring closure of compound **11** in the presence of sulphuric acid and acetic acid mixture gave the pyrazolothiazine **12.**



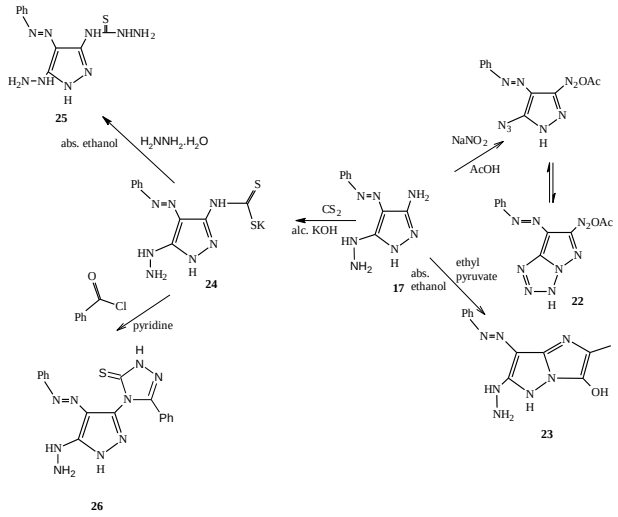
Scheme 3. Synthesis of compounds **11**-**16**.

Reaction of compound **5** with phenyl isothiocyanate gives a pyrazolothiourea derivative (**14**). The compounds pyrazolothiadiazole **15** and pyrazolotriazole **16** were obtained by the reaction of **14** with bromine in different solvent. In the IR spectrum of compound **16** the bands appear at 2600 and 2590 cm^{-1} are characteristic for (SH)groups. (Scheme 3).

3-Amino-5-hydrazino-4-phenylazo-1H-pyrazole **17** was obtained by the reaction of **5** with hydrazine hydrate in the abs. ethanol. Condensation of hydrazinopyrazole **17** with ethyl acetoacetate, acetylacetone, phthalic anhydride and phenacyl bromide in different solvents gave the corresponding N-pyrazolylpyrazole derivatives **18** and **19**, N-alkylated pyrazole **20**, and pyrazolotriazine **21**, respectively (Scheme 4).



Scheme 4. Synthesis of compounds **17**-**21**.



Scheme 5. Synthesis of compounds **22**-**26**.

Diazotization of compound **17** with sodium nitrite and acetic acid led obtain pyrazolo[1,5-*d*]tetrazole derivative **(22).** Cyclization of compound **17** with ethyl pyruvate yielded imidazolo[1,2-*b*]pyrazole **(23).** The structure of compound **23** has assigned on basis of its spectroscopic data.

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The IR revealed the presence of (OH) at 3529 cm-1 moreover, reaction of **17** with carbon disulfide yielded the corresponding pyrazolocarbamodithioate **24**. Hydrazonolysis of compound 17 in the presence hydrazine hydrate afforded pyrazolohydrazinecarbothioamide **25** which underwent further cyclization with benzoylchloride in pyridine afforded pyrazolotriazole **26 (**Scheme 5**).** The structures of all these compounds were elucidated from its spectral and elemental analysis data.

Conclusion

3-Amino-5-hydroxy-4-phenylazo-1H-pyrazole **1** was effectively used as precursor in the preparation of various pyrazole derivatives. N-(4-(2-Phenyldiazenyl)-2,5-dihydro-3-hydroxy-1H-pyrazol-5-yl)-2 chloroacetamide **2** was obtained from reaction of **1** with chloroacetyl chloride, and the further reaction of **2** with malononitrile and ammonium isothiocyanate gave the corresponding 1-(4-(2-phenyldiazenyl)-5-hydroxy-1H-pyrazol-3-yl)-2-amino-4,5-dihydro-5-oxo-1H-pyrrol-3-carbonitrile **3** and 3-(2-phenyldiazenyl)-7-amino-2-hydroxypyrazolo[1,5-*a*]pyrimidin-5(1H)-one **4**.

Thiation of **1** with P_2S_5 gave the corresponding 3-amino-5-mercapto-4-phenylazo-1H-pyrazole **5**. The reaction of compound **5** with chloroacetic acid, ethyl chloroacetate, tetrahydrofuran, 3-hydroxybenzaldehyde, phenacyl bromide and ninhydrine gave the corresponding N-substituted substituted pyrazoles (**6**, **7**, **8**, **9**, **10**, **11**, **12**, **13**), respectively. Hydrazenolysis of **7** in the presence of hydrazine hydrate afforded **8** and cyclization of **11** in the presence glacial acetic acid and sulfuric acid mixture afforded the compound **12**.

The 1-(4-(2-Phenyldiazenyl)-5-mercapto-1H-pyrazol-3-yl)-3-phenylthiourea **14** was obtained from reaction of **5** with phenyl isothiocyanate. Pyrazolothiadiazole **15** and pyrazolotriazole **16** were obtained by the reaction of **14** with bromine in different solvents.

3-Amino-5-hydrazino-4-phenylazo-1H-pyrazole **17** could be obtained from reaction **5** with hydrazine hydrate.

Cyclization of compound **17** by reacting it with ethyl acetoacetate, acetylacetone, phthalic anhydride and phenacyl bromide gave the corresponding N-pyrazolylpyrazole derivatives **18** and **19,** pyrazol-2,3-dihydrophthalazine-1,4-dione **20** and pyrazolotriazine **21**, respectively.

Reaction of **17** with sodium nitrite in the presence acetic acid, ethyl pyruvate and carbon disulfide gave the corresponding pyrazolotetrazole **22**, imidazolopyrazole **23** and pyrazolotriazole derivatives **26**.

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