Short communication

Reactions of 1,3-Diphenyl-2-pyrazolin-5-one and 4-Amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one. Synthesis of Some New Pyrazoles and Pyrazolones

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Abstract

1,3-Diphenyl-2-pyrazolin-5-one **1** was converted to 5-azido-4-formylpyrazolone **3** which is used as the key starting compounds of some new pyrazole derivatives **4**–**9**. Also, 4-amino-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one **10** is coupled with some diazonium salts to give coloured products **11**, and reacted with isocyanates and isothiocyanates to give pyrazolylurea and thiourea derivatives which are then reacted with organohalogen compounds under PTC conditions to give **13**,**14** while with some active methylene compounds yielded **15** via Michael 1,4-addition reaction.

Keywords: Azidoformylpyrazole, pyrazolotriazine, pyrazolopyridinone, antipyrene, pyrazolyl phenyl thiourea, hexahydropyrrolo[3,2-*c*]pyrazoles.

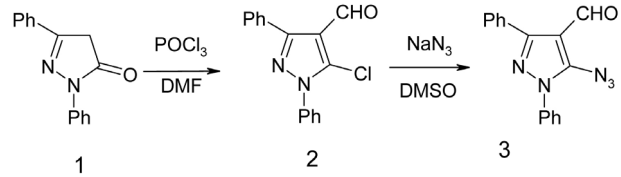
1. Introduction

Pyrazoles and pyrazolones are very important class of heterocycles due to their biological and pharmacological activities,[1,2] which exhibit an anti-inflammatory[3] herbicidal,[4] fungicidal,[5] bactericidal,[5] plant growth regulating properties,[4] antipyretic[6] and protein kinase inhibitors.[7] Also, they are used as key starting material for the synthesis of commercial aryl/heteroary1pyrazolone dyes.[8–11] Some arylidenepyrazolones are used as anti-fungal agents[12–15] or antidepressant agents,[16] while others are used as photographic dyes or as intermediates in pharmaceuticals[17–20] and antioxidants.[21]

The approach reported here deals with the synthesis of some new pyrazoles and pyrazolones starting from 2-pyrazolin-5-one **1** and aminopyrazolone **10** as key starting compounds. The new products might possess novel biological activity and may be used as commercial dyes.

2. Results and Discussion

2-Pyrazolin-5-one **1** has been synthesized by treating a mixture of ethyl benzoylacetate and phenylhydrazine in boiling acetic acid as reported.[22] Vilsmeier–Haack formylation of pyrazolone **1** by DMF/$POCl_3$ yielded pyrazole-4-carbaldehyde **2** as reported in the literature,[23,24] which was treated with sodium azide in DMSO to give azidoformylpyrazole **3**.[25] (Scheme 1)

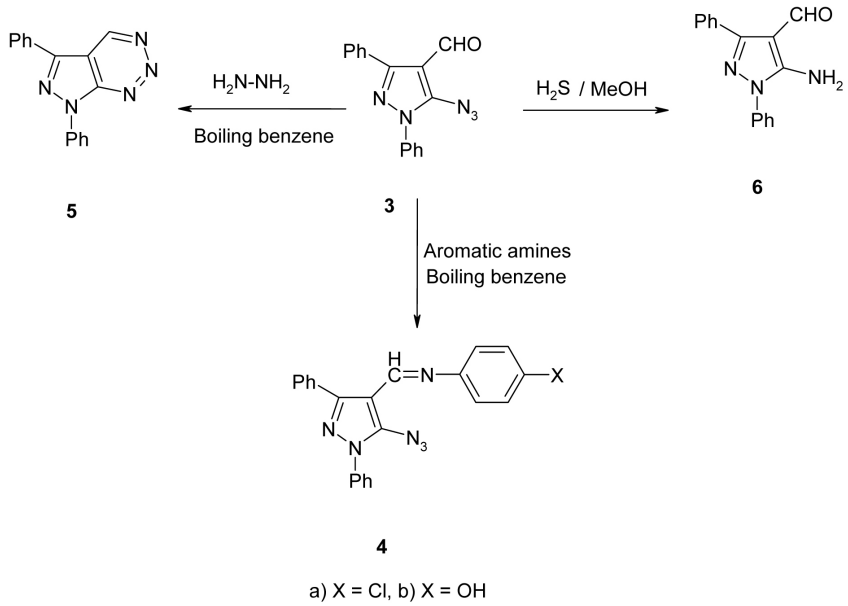


1 2 3

Scheme 1

Treatment of azidoformylpyrazole **3** with 4-chloroaniline and 4-hydroxyaniline afforded the corresponding Schiff's bases **4a** and **4b**, respectively. Azidoformylpyrazole **3** also reacted with hydrazine hydrate to give pyrazolo[3,4-*d*][1,2,3]triazine **5**.[26] (Scheme 2)

Reduction of azidoformylpyrazole **3** by hydrogen sulphide in methanol gave aminoformylpyrazole **6** (Scheme 2),[27] which was fused with ethyl acetoacetate

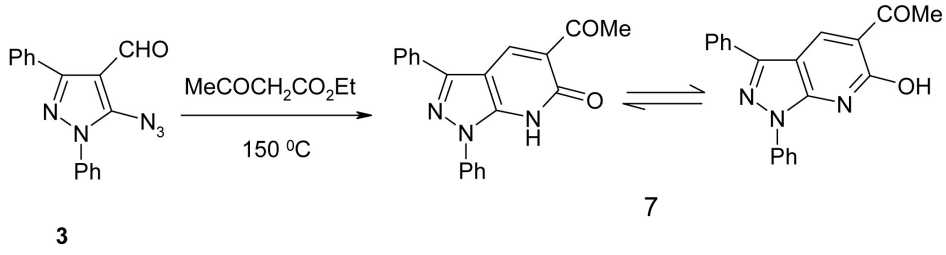


Scheme 2

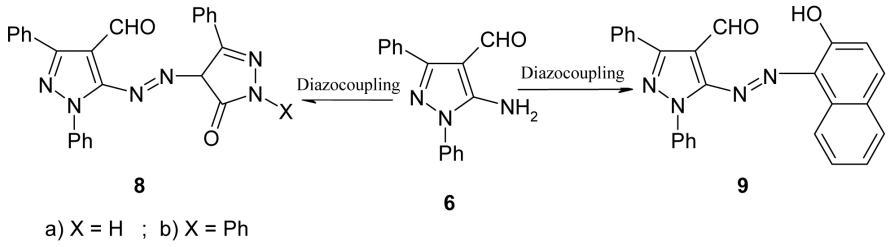
at 150 °C to give pyrazolo[3,4-*b*]pyridinone **7**, which exists in keto-enol forms and was crystallized from ethanol/DMF as yellow crystals, m.p. 108–110 °C. (Scheme 3)

Diazotization of aminopyrazole **6** which was coupled in pyridine with 3-phenyl-2-pyrazolin-5-one, 1,3-diphenyl-2-pyrazolin-5-one and 2-naphthol gave the corresponding coloured azo-dyes **8a**,**b** and **9**, respectively.

rated cyclic ketone. Treatment of a solution of aminopyrazolone **10** with sodium nitrite and conc. HCl at low temperature gives the corresponding diazonium salt which is coupled in water (in the presence of AlCl3 as catalyst)[28,29] with 3-phenyl-1*H*-pyrazol-2-en-5-one, 3-(3-pyridyl)-1*H*-pyrazol-2-en-3-one and 1,3-diphenyl-2-pyrazolin-5-one to give the corresponding azo-dyes **11a-c** in good yields as orange to red crystals. (Scheme 5).



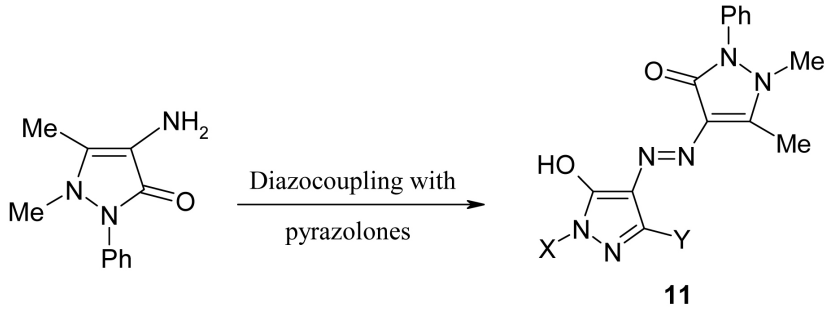
Scheme 3



Scheme 4

On the other hand, the aminopyrazolone **10** can also be used as a key starting material in this approach, as it might behave as an aromatic amine and as an α,β-unsatu-

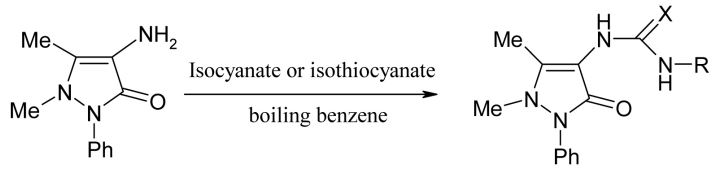
It is reported that treatment of aminopyrazolone **10** with ethyl isothiocyanate, phenylisothiocyanate or phenyl isocyanate in boiling benzene gives the corresponding



10 **11**

a) X = H, Y = Ph
b) X = H, Y = 3-pyridyl
c) X = Y = Ph

Scheme 5



10 **12**

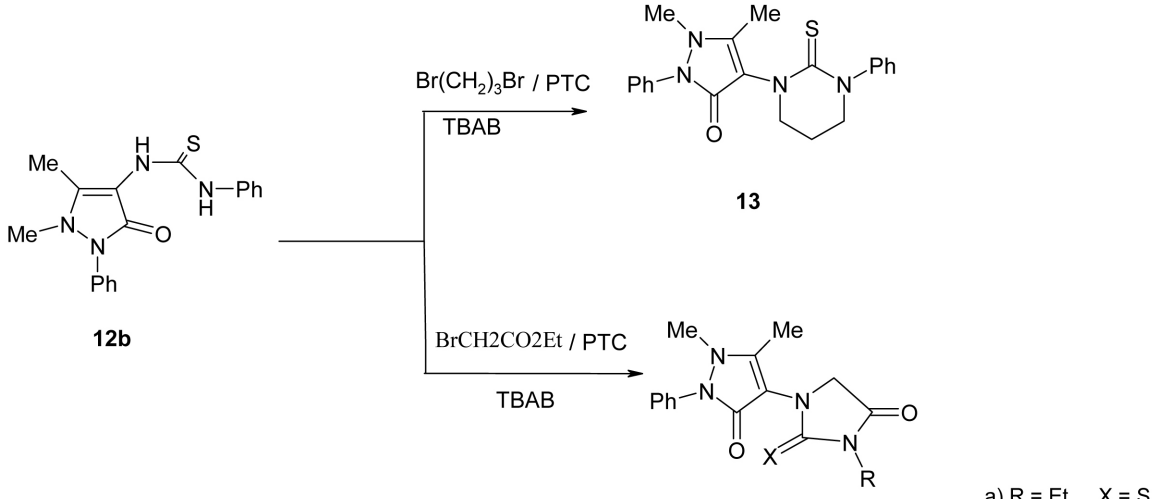
a) R = Et, X = S ; b) R = Ph, X = S; c) R = Ph, X = O

Scheme 6

well known thiourea or urea derivatives **12a**–**c**, possessing ethyl or phenyl substituent,[30–34] respectively. (Scheme 6)

Treatment of the thiourea **12b** with 1,3-dibromopropane under phase-transfer catalysis condition using tetrabutylammonium bromide (TBAB) as catalyst in benzene/anhydrous K_2CO_3 as liquid/solid phases gives thioxotetrahydropyrimidine **13**, while under the same PTC-condition, ethyl bromoacetate reacts with ureas **14a**–**c** with ring closure to give imidazolidinediones **14a**–**c**. (Scheme 7)

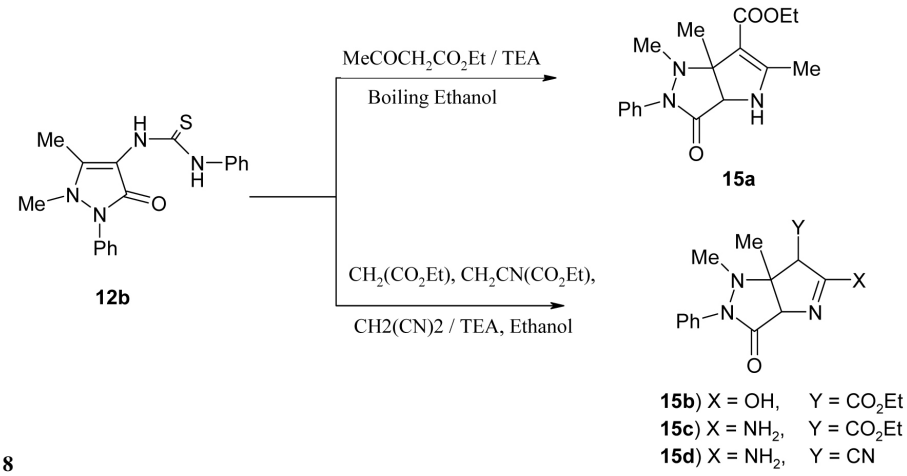
On the other hand, base-catalyzed cycloaddition of some active methylene compounds such as ethyl acetoacetate, diethyl malonate, ethyl cyanoacetate or malononitrile on pyrazolylphenylthiourea **12b** proceeds via Michael addition to cyclic α,β-unsaturated ketone followed with ring closure with subsequent elimination of phenyl isothiocyanate to give pyrrolo[3,2-*c*]pyrazoles **15a**–**d**. (Scheme 8)



12b **13** **14**

a) R = Et, X = S
b) R = Ph, X = S
c) R = Ph, X = O

Scheme 7



Scheme 8

3. Conclusion

Compounds **3** and **10** are used as key starting materials for the synthesis of a set of annulated heterocyclic products containing pyrazole moiety. The new synthesized azo-dyes have been prepared in aqueous medium as environmental friendly solvent. It is expected that these new products might have biological and pharmacological activities.

4. Experimental

Melting points reported are uncorrected. IR spectra were recorded on Perkin Elmer's Spectrum RXIFT-IR spectrophotometer (ν in cm^{-1}), ^{1}H NMR spectra were recorded in $CDCl_3$ on Bruker Avance DPX400, ^{13}C NMR spectra were recorded on Varian Gemini 300 MHz spectrometers using TMS as internal standard (chemical shifts in ä values in ppm). Mass spectra were measured on GC-MS QP1000 EX Shimadzu. Elemental analyses were preformed by Perkin–Elmer 2400, Series II micro-analyzer. Light petroleum (b.p. 60–80 °C) used was as supplied. 4-Amino-2,3-dimethyl-1-phenyl-1*H*-pyrazol-3-en-5-one (**10**) is an Aldrich product and was used without any further purification.

General procedure for preparation of 4 and 5. A solution of **3** (1.45 g, 0.005 mol) and 4-chloroaniline or 4-hydoxyaniline or hydrazine hydrate (0.005 mol) in benzene (50 mL) was refluxed for 4 h. After evaporation the solid residue was crystallized from light petroleum to give **4a** (65% yield) and **4b** (68% yield) as white crystals or **5** (56% yield) as yellow crystals.

***N*-[(5-Azido-1,3-diphenyl-1*H*-pyrazol-4-yl)methylidene]-4-chloroaniline (4a)**. mp 175–176 °C. IR (KBr, ν_{max}/cm^{-1}) 1573 (C=C, C=N), 3061, 3187 (Ar-H). ^{1}H NMR δ 6.01 (s, 1H, CH=), 6.94–8.07 (m, 14H, Ar-H). ^{13}C NMR δ 108.2, 123.5, 124.5, 128.8, 130.4, 133.6, 135.3, 140.3, 144.7, 152.4, 162.3. Anal. Calcd. for $C_{22}H_{15}ClN_6$ (398.1): C, 66.25; H, 3.79; N, 21.07%. Found: C, 66.38; H, 3.64; N, 20.93%.

***N*-[(5-Azido-1,3-diphenyl-1*H*-pyrazol-4-yl)methylene]-4-hydroxyaniline (4b)**. mp 160–162 °C. IR (KBr, ν_{max}/cm^{-1}) 1598 (C=C, C=N), 3059, 3134 (Ar-H), 3428 (OH). ^{1}H NMR δ 5.98 (s, 1H, CH=), 6.62–7.99 (m, 15H, Ar-H, OH). ^{13}C NMR δ 107.5, 118.8, 125.4, 127.8, 130.3, 134.7, 139.7, 141.7, 142.3, 151.4, 158.7, 161.2. Anal. Calcd. for $C_{22}H_{16}N_6O$ (380.1): C, 69.46; H, 4.24; N, 22.09%. Found: C, 69.37; H, 4.13; N, 21.88%.

5,7-Diphenyl-7*H*-pyrazolo[3,4-*d*][1,2,3]triazine (5). mp 132 °C. IR (KBr, ν_{max}/cm^{-1}) 1597 (C=C, C=N), 3054, 3132 (Ar-H). ^{1}H NMR δ 7.30–8.41 (m, 11H, Ar-H). ^{13}C NMR δ 107.2, 120.4, 127.2, 127.9, 130.2, 133.6, 140.2, 146.3. Anal. Calcd. for $C_{16}H_{11}N_5$ (273.1): C, 70.32; H, 4.06; N, 25.63%. Found: C, 70.45; H, 3.97; N, 25.51%.

5-Acetyl-1,3-diphenyl-1*H*-pyrazolo-[3,4-*b*]pyridine-6(7*H*)-one (7). A mixture of **6** (1.3 g, 0.005 mol), ethyl acetoacetate (0.006 mol) and few drops of piperidine was heated at 150 C for 4 h. The solid product was crystallized from ethanol to give pyrazolopyridinone **7** (64% yield) as yellow crystals. mp 112–114 °C. IR (KBr, ν_{max}/cm^{-1}) 1591 (C=C, C=N), 1667 (C=O acetyl), 3326 (OH). ^{1}H NMR δ 2.13 (s, 3H, CH_3), 7.22–7.67 (m, 11H, Ar-H), 9.61 (s, 1H, OH). ^{13}C NMR δ 30.3, 98.7, 124.2, 126.6, 128.3, 129.0, 134.8, 138.5, 149.7, 162.3, 198.5. Anal. Calcd. for $C_{20}H_{15}N_3O_2$ (329.4): C, 72.94; H, 4.59; N, 12.76%. Found: C, 72.63; H, 4.47; N, 12.50%.

Diazoformylpyrazole Derivatives 8 and 9. A solution of sodium nitrite (1.0 g, 0.014 mol) in water (10 mL) was added to a mixture of **6** (1.3 g, 0.005 mol) and conc. HCl (1.0 mL) at 0 C with stirring. The mixture was added to a

cold alkaline solution of 3-phenyl-2-pyrazolin-5-one, 1,3-diphenyl-2-pyrazolin-5-one or 2-naphthol (0.005 mol) in NaOH (5 mL, 10% aqueous alcoholic solution). The precipitated coloured products were filtered, washed with water (3 × 10 mL), dried and crystallized from ethanol/DMF mixture to give **8a** (58% yield) as orange red crystals, **8b** (65% yield) as deep red crystals, and **9** (78% yield) as red crystals.

5-[(5-Oxo-1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-4-yl) diazenyl]-1,3-diphenyl-1*H*-pyrazole-4-carbaldelhyde (8a). mp 237–239 °C. IR (KBr, ν_{max}/cm^{-1}) 1603 (C=C, C=N), 1650, 2523 (CHO), 2836 (Aliph-CH), 3187 (Ar-H), 3376 (OH, or NH). ^{1}H NMR δ 2.42 (s, 1H, CH), 7.08–8.07 (m, 16H, Ar-H, OH), 9.75 (s, 1H, CH=O). ^{13}C NMR δ 72.7, 108.4, 125.4, 128.2, 129.9, 130.5, 132.3, 133.7, 135.9, 141.5, 151.3, 157.4, 174.6, 190.3. Anal. Calcd. for $C_{25}H_{18}N_6O_2$ (434.2): C, 69.11; H, 4.18; N, 19.34%. Found: C, 69.03; H, 4.09; N, 19.21%.

5-[(5-Oxo-1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-4-yl) diazenyl]-1,3-diphenyl-1*H*-pyrazole-4-carbaldehyde (8b). mp 208–210 °C. IR (KBr, ν_{max}/cm^{-1}) 1605 (C=C, C=N), 1658, 2493 (CHO), 3706 (Ar-H), 3341 (NH_2 or OH). ^{1}H NMR δ 7.19–8.13 (m, 21H, Ar-H, OH enolic), 9.72 (s, 1H, CH=O). ^{13}C NMR δ 68.4, 108.2, 124.3, 126.8, 129.5, 131.6, 133.9, 139.4, 151.2, 156.7, 169.5, 192.2. Anal. Calcd. for $C_{31}H_{22}N_6O_2$ (510.2): C, 72.93; H, 4.34; N, 16.46%. Found: C, 73.07; H, 4.29; N, 16.28%.

5-[(2-Hydroxylnaphthalen-1-yl)diazenyl]-1,3-diphenyl-1*H*-pyrazole-4-carbaldehyde (9). mp 222–224 °C. IR (KBr, ν_{max}/cm^{-1}) 1602 (C=C, C=N), 1653, 2437 (CHO), 3098–3113 (Ar-H), 3420 (OH). ^{1}H NMR δ 7.03–8.17 (m, 16H, Ar-H), 9.77 (s, 1H, CH=O), 10.97 (s, 1H, OH). ^{13}C NMR δ 108.5, 124.7, 125.3, 126.8, 128.2, 129.4, 130.4, 132.3, 133.7, 144.3, 161.6, 190.3. Anal. Calcd. for $C_{26}H_{18}N_4O_2$ (418.1): C, 74.63; H, 4.34; N, 13.39%. Found: C, 74.50; H, 4.27; N, 13.12%.

Coupling of diazonium salt of aminopyrazolone 10 A solution of **10** (2.03 g, 0.01 mol) in concentrated hydrochloric acid (2 mL), diluted by water (20 mL) was cooled at 0–5 C in an ice-bath. An aqueous cold solution of sodium nitrite (0.69 g, 0.01 mol in 1.0 mL H_2O) at 0 °C was added to the prepared aminopyrazolone hydrochloride to give the desired diazonium chloride solution. The latter solution was added drop-wise with stirring for 30 min in an ice-bath to a cold suspension of pyrazolones (0.01 mol) in water (50 mL) containing $AlCl_3$ (3.0 g). The pH of the reaction mixture was adjusted to 8–8.5 by adding drop-wise sodium hydroxide solution (10%). The coloured precipitated azo-dye was filtered, washed with water (3 × 20 mL), dried and crystallized from benzene/ethanol mixture to give **11a** (66% yield) as red crystals, while **11b** (61% yield) crystallized from ethanol/DMF mixture as orange crystals and **11c** (66% yield) from benzene as red crystals.

4-[(5-Hydroxy-3-phenyl-1*H*-pyrazol-4-yl)diazenyl]-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (11a). mp 234 °C. IR (KBr, ν_{max}/cm^{-1}) 1594 (C=C, C=N), 1671 (C=O), 2807–2886 (Aliph-CH), 3088–3106 (Ar-H), 3465, 3537 (NH, OH). ^{1}H NMR δ 2.60 (s, 3H, C-CH_3), 3.16 (s, 3H, N-CH_3), 7.2–8.18 (m, 10H, Ar-H), 10.03 (s, 1H, OH), 11.43 (s, 1H, NH). ^{13}C NMR δ 13.5, 34.2, 97.3, 106.7, 123.3, 124.7, 128.7, 129.2, 136.5, 153.7, 164.4. Anal. Calcd. for $C_{20}H_{18}N_6O_2$ (374.2): C, 64.16; H, 4.85; N, 22.45%. Found: C, 64.03; H, 4.80; N, 22.27%.

4-{[5-Hydroxy-3-(3-pyridyl)-1*H*-pyrazol-4-yl]diazenyl}-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (11b). mp 251–253 °C. IR (KBr, ν_{max}/cm^{-1}) 1574 (C=C, C=N), 1685, 1716 (C=O), 2895 (Aliph CH), 3010 (Ar-CH), 3416–3438 (OH, NH). ^{1}H NMR δ 2.48 (s, 3H, C-CH_3), 3.31 (s, 3H, N-CH_3), 7.08–9.32 (m, 9H, Ar-H), 10.32 (s, 1H, OH), 11.34 (s, 1H, NH). ^{13}C NMR δ 14.7, 35.3, 106.5, 123.5, 124.3, 125.7, 134.4, 135.9, 138.4, 151.2, 156.8, 161.7, 162.7. Anal. Calcd. for $C_{19}H_{17}N_7O_2$ (375.4): C, 60.78; H, 4.57; N, 26.13%. Found: C, 60.83; H, 4.50; N. 25.88%.

4-[(5-Hydroxy-1,3-diphenyl-1*H*-pyrazol-4-yl)diazenyl]-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (11c). mp 230–231 °C. IR (KBr, ν_{max}/cm^{-1}) 1583 (C=C, C=N), 1698, 1712 (C=O), 2904 (Aliph-CH), 3107 (Ar-CH), 3483–3497 (OH, NH). ^{1}H NMR δ 2.60 (s, 3H, C-CH_3), 3.16 (s, 3H, N-CH_3), 7.26–8.20 (m, 15H, Ar-H), 12.03 (s, 1H, OH). ^{13}C NMR δ 14.7, 35.2, 98.9, 106.6, 123.2, 124.4, 125.2, 134.7, 135.7, 138.3, 151.8, 156.4, 161.7, 162.7. Anal. Calcd. for $C_{26}H_{22}N_6O_2$ (450.5): C, 69.32; H, 4.92; N, 18.65%. Found: C, 69.11; H, 4.82; N, 18.50%.

Synthesis of pyrazolylurea and thiourea 12a-c:[32–34]
A solution of **10** (0.005 mol) in benzene (28 mL) and phenylisocyanate or ethyl, or phenyl isothiocyonate (0.005 mol) was refluxed for 3 h. The solid products which are separated after concentration and cooling was filtered and crystallized from benzene/ethanol mixture to give the corresponding ureas **12a–c** as white crystals.[32–34]

PTC-alkylation of pyrazolylphenylthiourea 12b. Formation of 13 and 14. A solution of 1,3-dibromopropane or ethyl bromoacetate (0.006 mol) in THF (20 mL) was added to a stirred solution of **12** (1.7 g, 0.005 mol) and anhydrous potassium carbonate (2.7 g, 0.02 mol) in tetrahydrofuran (THF, 50 mL). The reaction mixture was kept at room temperature with stirring for 48 h. K_2CO_3 was removed by filtration and the solution was evaporated. The solid residue was triturated with light petroleum, filtered and crystallized from light petroleum to give **13** (71%

yield) as yellow crystals or **14a** (43% yield) as white crystals, whereas **14b** (58% yield) crystallized from benzene as white crystals, while **14c** (41% yield) crystallized from ethanol as white crystals.

1,5-Dimethyl-2-phenyl-4-(3-phenyl-2-thioxotetrahydropyrimidin-1(2*H*)-yl)-1,2-dihydro-3*H*-pyrazol-3-one (13). mp 173–175 °C. IR (KBr, ν_{max}/cm^{-1}) 1574 (C=C), 1422 (C=S), 1669 (C=O), 2830–2920 (Aliph-CH), 3080 (Ar-H). ^{1}H NMR δ 1.83 (m, 2H, CH_2), 2.28 (s, 3H, C-CH_3), 3.23 (s, 3H, N-CH_3), 4.14 (m, 2H, CH_2), 4.82 (m, 2H, CH_2), 6.73–7.48 (m, 10H, Ar-H). ^{13}C NMR δ 13.8, 20.3, 35.1, 55.5, 57.2, 117.3, 123.4, 124.7, 128.3, 129.5, 131.9, 133.6, 134.5, 141.0, 161.3, 178.2. Anal. Calcd. for $C_{21}H_{22}N_4OS$ (378.2): C, 66.64; H, 5.86; N, 14.80%. Found: C, 66.42; H, 5.77; N, 14.63%.

4-(3-Ethyl-4-oxo-2-thioxoimidazolidin-1-y1)-1,5-dimethy1-2-pheny1-1,2-dihydro-3*H*-pyrazo1-3-one (14a). mp 182–183 °C. IR (KBr, ν_{max}/cm^{-1}) 1603 (C=C), 1661 (C=O), 1708 (C=O), 2870 (Aliph-CH), 3050 (Ar-OH). ^{1}H NMR δ 1.27 (m, 3H, CH_3), 2.19 (s, 3H, N-CH_3), 3.04 (s, 3H, N-CH_3), 3.83 (m, 2H, CH_2), 3.91 (m, 2H, CH_2), 7.26–7.45 (m, 5H, Ar-H). ^{13}C NMR δ 13.4, 15.1, 39.7, 45.2, 58.3, 124.3, 125.7, 130.8, 135.6, 156.3, 162.8, 174.2. Anal. Calcd. for $C_{16}H_{18}N_4O_2S$ (330.1): C, 58.16; H, 5.49; N, 16.96%. Found: C, 58.27; H, 5.36; N, 16.80%.

1,5-Dimethy1-4-(4-oxo-3-phenyl-2-thioxoimidazolidin-1-y1)-2-pheny1-1,2-dihydro-3*H*-pyrazo1-3-one (14b). mp 235 °C. IR (KBr, ν_{max}/cm^{-1}) 1593 (C=C), 1658, 1687 (C=O), 2803 (Aliph-CH), 2978–3093 (Ar-CH). ^{1}H NMR δ 2.32 (s, 3H, C-CH_3), 3.27 (s, 3H, N-CH_3), 3.93–4.10 (m, 2H, CH_2), 6.97–7.53 (m, 10H, Ar-H). ^{13}C NMR δ 15.3, 35.6, 58.4, 118.0, 123.7, 124.2, 128.7, 129.2, 134.6, 142.8, 162.5, 175.6, 176.4. MS (*m/z*): 378 (100%), 379 (32%), 380 (7.3%). Anal. Calcd. for $C_{20}H_{18}N_4O_2S$ (378.12): C, 63.47; H, 4.79; N, 14.80%. Found: C, 63.63; H, 4.66; N, 14.68%.

1-(1,5-Dimethy1-3-oxo-2-pheny1-2,3-dilydro-1*H*-pyrazol-4-yl)-3-phenylimidazolidine-2,4-dione (14c). mp 132–134 °C. IR (KBr, ν_{max}/cm^{-1}) 1603 (C=C), 1648, 1690 (C=O), 2853 (Aliph-CH), 2946 (Ar-CH). ^{1}H NMR δ 2.33 (s, 3H, C-CH_3) 3.19 (s, 3H, N-CH_3), 4.61 (m, 2H, CH_2), 7.27–7.53 (m, 10H, Ar-H). ^{13}C NMR δ 13.2, 35.3, 49.7, 124.2, 125.5, 129.5, 130.4, 135.5, 137.1, 138.7, 154.6, 157.9, 162.3, 173.7. Anal. Calcd. for $C_{20}H_{18}N_4O_3$ (362.1): C, 66.29; H, 5.01; N, 15.46%. Found: C, 66.43; H, 4.87; N, 15.23%.

Base-catalyzed cycloaddition of active methylene compounds to pyrazolylphenylthiourea (3b). Formation of Cyclic Michael Adduct 15a–d. A solution of **3b** (1.7 g, 0.05 mol), ethyl acetoacetate, diethyl malonate, ethyl cyanoacetate or malononitrile (0.06 mol) and few drops of triethylamine in ethanol (30 mL) was refluxed for 4 h. The solvent was evaporated and the residue was triturated with light petroleum, dried and crystallized from light petroleum to give **15a** (48% yield) as white crystals and **15b** (53% yield) crystallized from benzene/light petroleum as white crystals, whereas **14c,d** (57%, 47% yield, respectively) crystallized from benzene as white crystals.

Ethy1 1,5,6a-trimethy1-3-oxo-2-phenyl-1,2,3,3a,4,6a-hexahydropyrrolo[3,2-*c*]pyrazole-6-carboxylate (15a). mp 170–171 °C. IR (KBr, ν_{max}/cm^{-1}) 1585 (C=C, C=N), 1673, 1725 (C=O), 2833 (Aliph-CH), 2994–3017 (Ar-CH), 3320 (br, NH). ^{1}H NMR δ 1.30 (m, 3H, CH_3), 1.47 (s, 3H, CH_3), 2.19 (s, 3H, C-CH_3), 3.08 (s, 3H, N-CH_3), 3.78 (d, 1H, CH), 4.44 (q, 2H, CH_2), 7.22–7.45 (m, 5H, Ar-H), 8.78 (s, 1H, NH). ^{13}C NMR δ 15.2, 20.6, 42.7, 53.6, 58.2, 63.5, 113.3, 128.7, 129.2, 133.4, 158.9, 169.1, 170.6. MS (*m/z*): 315 (100%), 316 (23.5%). Anal. Calcd. for $C_{17}H_{21}N_3O_3$ (315.16): C, 64.74; H, 6.71; N, 13.32%. Found: C, 64.85; H, 6.57; N, 13.22%.

Ethyl 1,6a-Dimethy1-3,5-dioxo-2-phenyloctahydropyrrolo[3,2-*c*]pyrazole-6-carb-oxylate (15b). mp 168–170 °C. IR (KBr, ν_{max}/cm^{-1}) 1605 (C=C, C=N), 1665, 1730 (C=O), 2808 (Aliph-CH), 3107 (Ar-CH), 3380 (br, CH or MH). ^{1}H NMR δ 1.37 (m, 3H, CH_3), 2.23 (s, 3H, C-CH_3), 3.11 (s, 1H, CH), 3.22 (s, 3H, N-CH_3), 4.54 (m, 2H, CH_2), 7.28–7.51 (m, 5H, Ar-H), 8.32 (br s, 1H, OH or NH), 5.67 (br s, 1H, OH). ^{13}C NMR δ 15.3, 24.6, 38.8, 42.7, 58.3, 63.7, 128.4, 129.2, 133.9, 136.3, 157.1, 170.4, 170.9. MS (*m/z*): 317 (100%), 318 (28.4%). Anal. Calcd. for $C_{16}H_{19}N_3O_4$ (317.14): C, 60.56; H, 6.03; N, 13.24%. Found: C, 60.68; H, 5.79; N, 13.12%.

Ethyl 5-Amino-1,6a-dimethy1-3-oxo-2-pheny1-1,2,3,3a,6,6a-hexahydropyrrolo[3,2-*c*]pyrazole-6-carboxylate (15c). mp 158–160 °C. IR (KBr, ν_{max}/cm^{-1}) 1585 (C=C, C=N), 1648, 1723 (C=O), 2905 (Aliph-CH), 2990–3108 (Ar-CH), 3435 (NH_2). ^{1}H NMR δ 1.38 (m, 3H, CH_3), 1.93 (s, 1H, CH), 2.31 (s, 3H, C-CH_3), 3.07 (s, 1H, CH), 3.21 (s, 3H, CH_3), 4.53 (m, 2H, CH_2), 7.29–7.50 (m, 5H, Ar-H), 9.07 (br s, 2H, NH_2). ^{13}C NMR δ 15.7, 25.2, 39.4, 42.3, 58.3, 64.4, 128.7, 129.3, 133.5, 156.1, 166.7, 171.3, 171.7. Anal. Calcd. for $C_{16}H_{20}N_4O_3$ (316.15): C, 60.75; H, 6.37; N, 17.71%. Found: C, 60.56; H, 6.23; N, 17.83%.

5-Amino-1,6a-dimethy1-3-oxo-2-phenyl-1,2,3,3a,6,6a-hexahydropyrrolo[3,2-*c*]pyrazole-6-carbonitrile (15d). mp 190 °C. IR (KBr, ν_{max}/cm^{-1}) 1603 (C=C, C=N), 1665 (C=O), 2227 (CN), 2875–2904 (Aliph-CH), 2998–3107 (Ar-CH), 3433 (NH_2). ^{1}H NMR δ 2.29 (s, 3H, C-CH_3), 2.54 (s, 1H, CH), 2.73 (s, 1H, CH), 3.17 (s, 3H, N-CH_3), 4.53 (br s, 2H, NH_2), 7.29–7.49 (m, 5H, Ar-H). ^{13}C NMR δ 25.4, 39.7, 40.9, 43.2, 63.2, 118.1, 128.7, 129.3, 133.6, 135.7, 167.2, 171.4. Anal. Calcd. for $C_{14}H_{15}N_5O$ (269.13):

C, 62.44; H, 5.61; N, 26.01%. Found: C, 62.73; H, 5.50; N, 25.87%.

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Povzetek

1,3-Difenil-2-pirazolin-5-on **1** smo pretvorili v 5-azido-4-formilpirazolon **3**, ki smo ga uporabili kot ključno izhodno spojino za pripravo nekaterih novih pirazolskih derivatov **4**–**9**. 4-Amino-2-fenil-1,5-dimetil-1*H*-pirazol-3(2*H*)-on **10** smo pripojili z nekaterimi diazonijevimi solmi in dobili obarvane produkte **11**; reagirali z izocianati in izotiocianati do derivatov pirazolilsečnin in tiosečnine, ki smo jih nato reagirali z organohalogeni pod PTC pogoji do spojin **13**,**14**; z nekaterimi spojinami, ki vsebujejo aktivne metilenske skupine, smo z Michaelovo 1,4-adicijo pripravili produkte **15**.