

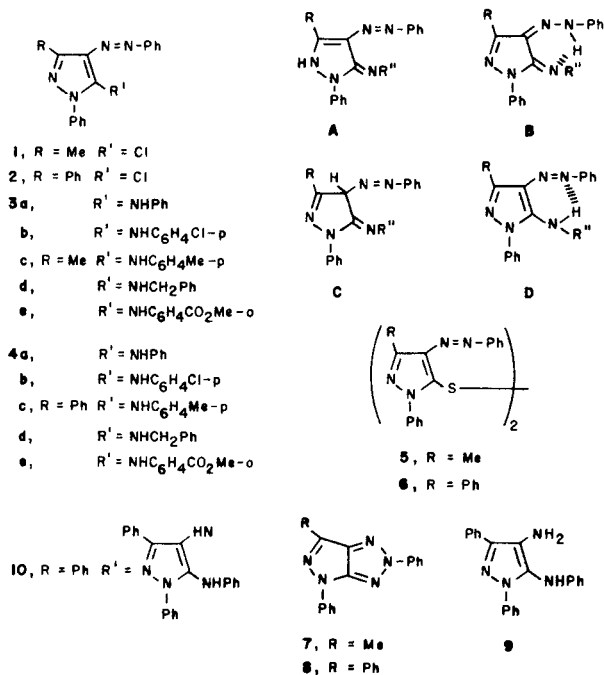
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3-Methyl or 3-phenyl-5-chloro-1-phenyl-4-phenylazopyrazole with primary amines, sodium polysulfide and sodium azide yielded amines, disulfides and 2,4-dihydropyrazolo[3,4-*d*]-1,2,3-triazoles respectively. 4-Amino-5-anilino-1,3-diphenylpyrazole was also prepared and characterized.

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Previous work [1] has shown that 5-chloropyrazoles with an electron withdrawing group (*e.g.* phenylazo) at C-4 have the chlorine activated towards nucleophilic aromatic substitution. This present work using 1-phenylpyrazoles confirms and extends this finding. Thus primary amines with the 3-methyl **1** and 3-phenyl **2** derivatives of 5-chloro-1-phenyl-4-phenylazopyrazole yield the corresponding crystalline 5-aminopyrazoles (**3a-e**; **4a-e**). These amines could exist in four possible tautomer forms [2]: **A**, the N-2 H form; **B**, the chelated hydrazone-used [3] but without evidence to represent the *N*-phenyl derivative **3a**; **C**, the C-4 H form and **D**, the amine. The 5-chloro compound **1** had a



strong Raman band (for the solid and for a carbon tetrachloride solution) at 1440 cm⁻¹, which can be assigned the conjugated *trans* N=N symmetric stretching vibration [4]. The 5-anilino compound **3a** showed a strong Raman band (for the solid and for a carbon tetrachloride solution) at 1385 cm⁻¹ - compare [5] 5-amino-3-methyl-1-phenyl-4-phenylazopyrazole at 1370 cm⁻¹ in dimethylformamide solution. The 1385 cm⁻¹ band is consistent [5] with the chelated amine form **D** or [4] with the hydrazone form **B**.

Reaction of sodium sulfide with the 5-chloride **1** yields [6] the 5-thiol which can be oxidized to the disulfide **5**. The same disulfide is obtained by reaction of the 5-chloride **1** with sodium polysulfide, but in our hands the product was deep red, not dark yellow and melted 20° lower. The 5-chloride **2** with sodium polysulfide similarly gave the disulfide **6**. The formation of the disulfides **5** and **6** parallels [7] the reaction of *o*-chloronitrobenzene with sodium polysulfide.

Treatment of the chlorides **1** and **2** with sodium azide yielded the corresponding 2,4-dihydropyrazolo[3,4-*d*]-1,2,3-triazoles **7** and **8**. Their formation can be explained by breakdown of the initially formed 5-azides. Indeed, thermal decomposition of aromatic azides which have an *o*-arylozo group is known [8] to yield 1,2,3-triazoles, but the method does not seem to have been applied before to the ring system of **7** and **8**.

Reduction of the azo group of the amine **4a** with sodium dithionite [9], gave the expected 4-amine **9**, which was characterized by its anils with benzaldehyde, anisaldehyde and cinnamaldehyde. Fusion of the amine **9** with the chloride **2** gave the 4-*N*-(pyrazol-5-yl)-4-aminopyrazole **10**. The structures of the amine **9** and its anils could each be represented by 4 tautomers similar to those for the 5-amines above.

Attempts to react the 5-chlorides **1** and **2** with thiourea did not proceed cleanly or produce a characterizable product.

EXPERIMENTAL

The electronic spectra were determined for ethanolic solutions with a 550S Perkin-Elmer spectrometer. The λ max are reported in nm and the molar absorptivity × 10⁻³ in l moles⁻¹cm⁻¹ are included in parentheses. Isobutane chemical ionization mass spectra were obtained with a VG Micromass 12F spectrometer. Raman spectra were recorded using a Coderg PHO spectrometer using an excitation wavelength of 647.1 nm. Melting points are uncorrected and measured with a Thomas Hoover capillary melting point apparatus. Light petroleum refers to the fraction with a bp of 60 - 80°.

5-Arylamino-1-phenyl-4-phenylazopyrazoles **3a-e**, **4a-e**.

An Equimolar mixture of amine and the 3-methyl [6] or 3-phenyl derivative [10] of 5-chloro-1-phenyl-4-phenylazopyrazole was fused in an oil bath at 140° for 2 hours. The resulting melt was cooled and light petroleum was added and the mixture was filtered.

The following 5-amino-3-methyl-1-phenyl-4-phenylazopyrazoles were obtained.

3-Methyl-5-*N*-phenylamino-1-phenyl-4-phenylazopyrazole (3a).

Compound **3a** was produced in 62% yield, mp 100-102° (lit 103° [3]); uv: 240 (10.332), 275 (6.888), 330 (8.179), 380 (7.749).

5-*N*-(*p*-Chlorophenylamino)-3-methyl-1-phenyl-4-phenylazopyrazole (3b).

Compound **3b** was produced in 65% yield, mp 155-156° from light petroleum; uv: 245 (14.531), 275 (10.656), 330 (11.624), 378 (10.171).

Anal. Calcd. for C₂₂H₁₈ClN₅: C, 68.12; H, 4.64; Cl, 9.16; N, 18.06. Found: C, 68.36; H, 4.80; Cl, 9.38; N, 18.21.

3-Methyl-5-*N*-(*p*-methylphenylamino)-1-phenyl-4-phenylazopyrazole (3c).

Compound **3c** was produced in 65% yield, mp 137-139° from light petroleum; uv: 240 (10.304), 275 (6.916), 328 (7.763), 385 (8.539).

Anal. Calcd. for C₂₃H₂₁N₅: C, 75.20; H, 5.72; N, 19.07. Found: C, 75.08; H, 5.75; N, 19.53.

5-*N*-Benzylamino-3-methyl-1-phenyl-4-phenylazopyrazole (3d).

Compound **3d** was synthesized in 50% yield, mp 232-234° from ethanol; uv: 260 (3.262), 280 (1.468), 378 (1.631).

Anal. Calcd. for C₂₃H₂₁N₅: C, 75.20; H, 5.72; N, 19.07. Found: C, 74.95; H, 5.81; N, 18.98.

5-*N*-[*o*-(Carboxymethyl)phenylamino]-3-methyl-1-phenyl-4-phenylazopyrazole (3e).

Compound **3e** was produced in 50% yield, mp 117-119° from ethanol-water; uv: 215 (21.182), 280 (8.220), 329 (15.807), 372 (9.326).

Anal. Calcd. for C₂₄H₂₁N₅O₂: C, 70.07; H, 5.10; N, 17.03. Found: C, 69.89; H, 4.93; N, 17.31.

The following 5-amino-1,3-diphenyl-4-phenylazopyrazoles were obtained:

1,3-Diphenyl-5-*N*-(phenylamino)-4-phenylazopyrazole (4a).

Compound **4a** was produced in 72% yield, mp 180-182° from light petroleum; uv: 248 (9.219), 335 (5.377).

Anal. Calcd. for C₂₇H₂₁N₅: C, 78.07; H, 5.06; N, 16.86. Found: C, 78.06; H, 5.08; N, 16.94.

5-*N*-(*p*-Chlorophenylamino)-1,3-diphenyl-4-phenylazopyrazole (4b).

Compound **4b** was produced in 60% yield, mp 199-201° from light petroleum; uv: 248 (20.094), 335 (11.898).

Anal. Calcd. for C₂₇H₂₀ClN₅: C, 72.08; H, 4.44; Cl, 7.89; N, 15.57. Found: C, 71.96; H, 4.36; Cl, 8.00; N, 15.53.

5-*N*-(*p*-Methylphenylamino)-1,3-diphenyl-4-phenylazopyrazole (4c).

Compound **4c** was produced in 55% yield, mp 163-165° from light petroleum; uv: 245 (24.476), 385 (15.266).

Anal. Calcd. for C₂₈H₂₃N₅: C, 78.32; H, 5.36; N, 16.31. Found: C, 78.20; H, 5.60; N, 16.16.

5-*N*-Benzylamino-1,3-diphenyl-4-phenylazopyrazole (4d).

Compound **4d** was produced in 55% yield, mp 245-247° from ethanol; uv: 265 (2.002), 280 (3.003), 372 (26.871).

Anal. Calcd. for C₂₈H₂₃N₅: C, 78.32; H, 5.36; N, 16.31. Found: C, 78.51; H, 5.42; N, 15.95.

5-*N*-[*o*-(Carboxymethyl)phenylamino]-1,3-diphenyl-4-phenylazopyrazole (4e).

Compound **4e** was produced in 60% yield, mp 77-79° from ethanol-water; uv: 215 (8.277), 245 (5.617), 275 (5.026), 330 (2.956).

Anal. Calcd. for C₂₉H₂₃N₅O₂: C, 73.57; H, 4.86; N, 14.79. Found: C, 73.41; H, 4.75; N, 14.95.

1-Phenyl-4-phenylazo-5-pyrazolyl disulfides 5 and 6.

A solution of 5-chloride **1** or **2** (2 mmole) in ethanol was refluxed with sodium polysulfide solution (1 ml) for a few minutes. The solid obtained

after evaporating the solvent, was crystallized from aqueous ethanol to give the deep red disulfide.

Bis(3-methyl-1-phenyl-4-phenylazo-5-pyrazolyl) Disulfide (5).

Compound **5** was produced in 49% yield, mp 95° dec (lit [6] mp 115°); ms: *m/z* 587 [M + 1]⁺, 293.

Anal. Calcd. for C₃₂H₂₆N₈S₂: C, 65.52; H, 4.43; N, 19.11; S, 10.92. Found: C, 65.41; H, 4.51; N, 19.31; S, 10.87.

Bis(1,3-diphenyl-4-phenylazo-5-pyrazolyl) Disulfide (6).

Compound **6** was produced in 50% yield, mp 150° dec; ms: *m/z* 711 [M + 1]⁺, 355.

Anal. Calcd. for C₄₂H₃₀N₈S₂: C, 70.98; H, 4.22; N, 15.77; S, 9.01. Found: C, 70.61; H, 4.27; N, 15.81; S, 8.99.

2,4-Dihydropyrazolo[3,4-*d*]-1,2,3-triazoles 7 and 8.

A solution of sodium azide (0.5 g) in water (0.5 ml) was added to a solution of 5-chloride **1** or **2** (1 g) in dimethylformamide (15 ml) and the mixture was refluxed for 3 hours. The solid formed after cooling and addition of water. The solid was then filtered off and recrystallized from benzene to give the colorless triazole.

2,4-Dihydro-2,4-diphenyl-6-methylpyrazolo[3,4-*d*]-1,2,3-triazole (7).

Compound **7** was produced in 42% yield, mp 133-135°.

Anal. Calcd. for C₁₆H₁₃N₅: C, 69.81; H, 4.72; N, 25.45. Found: C, 69.61; H, 4.53; N, 25.10.

2,4-Dihydro-2,4,6-triphenylpyrazolo[3,4-*d*]-1,2,3-triazole (8).

Compound **8** was produced in 55% yield, mp 236-238°.

Anal. Calcd. for C₂₁H₁₅N₅: C, 74.78; H, 4.45; N, 20.77. Found: C, 74.87; H, 4.33; N, 20.87.

4-Amino-5-anilino-1,3-diphenylpyrazole (9).

The phenylazopyrazole (**4a**) (0.1 g) was slurried in boiling aqueous 80% ethanol (*ca.* 100 ml) and small portions of powdered sodium dithionite were added until the orange solid had dissolved and a light yellow solution resulted. The solution was then diluted to *ca.* 200 ml with hot water, and aniline and ethanol were distilled from the mixture. The solid obtained after cooling was crystallized from light petroleum to give the colorless amine, 95% yield, mp 121-123°; uv: 242 (1.418), 293 (0.945).

Anal. Calcd. for C₂₁H₁₈N₄: C, 77.30; H, 5.52; N, 17.17. Found: C, 77.01; H, 5.62; N, 17.17.

Anils of 4-Amino-5-anilino-1,3-diphenylpyrazole (9).

Equimolar amounts of **9** and aldehyde were heated on a boiling water bath and stirred gently with a glass rod. After a few minutes the mixture was cooled, whereupon the product solidified in quantitative yield. It was recrystallized from light petroleum.

Benzaldehyde Anil of 4-Amino-5-anilino-1,3-diphenylpyrazole (9).

This anil had the following physical and spectral properties, mp 152-154°; uv: 242 (3.726), 293 (3.933).

Anal. Calcd. for C₂₈H₂₂N₄: C, 81.16; H, 5.31; N, 13.52. Found: C, 81.09; H, 5.01; N, 13.53.

***p*-Methoxybenzaldehyde Anil of 4-Amino-5-anilino-1,3-diphenylpyrazole (9).**

This anil had the following physical and spectral properties, mp 182-184°; uv: 240 (2.220), 282 (2.933).

Anal. Calcd. for C₂₉H₂₄N₄O: C, 78.38; H, 5.40; N, 12.61. Found: C, 78.34; H, 5.47; N, 12.62.

Cinnamaldehyde Anil of 4-Amino-5-anilino-1,3-diphenylpyrazole (9).

This anil had the following physical and spectral properties, mp 175-177°; uv: 238 (2.910), 287 (2.987).

Anal. Calcd. for C₃₀H₂₄N₄: C, 81.81; H, 5.45; N, 12.72. Found: C, 81.52; H, 5.43; N, 12.52.

4-*N*-(1,3-Diphenyl-4-phenylazopyrazol-5-yl)-4-amino-5-anilino-1,3-diphenylpyrazole (**10**).

Equimolar portions of the amine **9** and the 5-chloride **2** were fused at 140° for 1 hour. The resulting melt was washed with light petroleum, and crystallized from benzene-light petroleum, yielding brown crystals, 65%, mp 215° dec; uv: 246 (1.295).

Anal. Calcd. for C₄₂H₃₂N₈: C, 77.78; H, 4.94; N, 17.28. Found: C, 77.99; H, 5.17; N, 17.07.

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