# Cyclocondensation of α-Hydroxyimino-β-alkyl/arylimino-β-methylthioketones with Hydrazine Hydrate: Synthesis of 3(5)-Aryl-5(3)-alkyl/arylamino-4-nitroso (or amino) pyrazoles



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The title pyrazoles were synthesized through cyclocondensation of hydroxyiminoimine derivatives **1a-j** with hydrazine hydrate.

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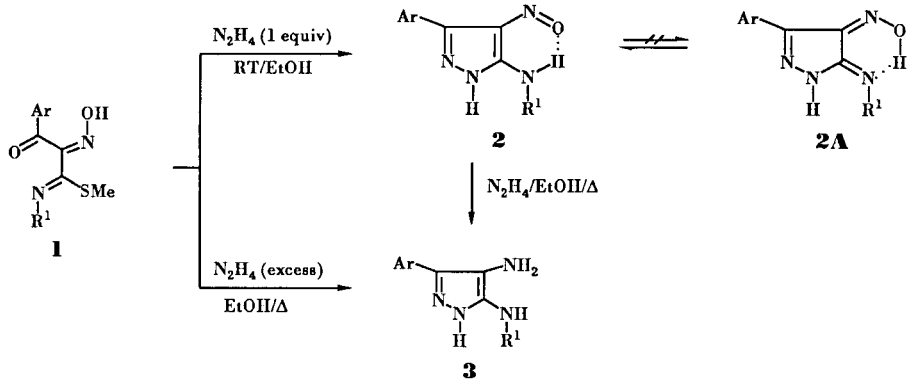
Earlier work from this laboratory has shown that α-oxoketene *N,S*-acetals [1,4] undergo facile electrophilic nitrosation to give the corresponding hydroxyiminoimines **1** which were shown to be versatile synthons for imidazoles, quinoxalines and thiazole derivatives [3,4,5]. Thus, thermal cyclodehydration of *N*-benzyl/alkylhydroxyiminoimines afforded 1*H*-imidazoles in high yields, while the corresponding *N*-aryl derivatives yielded substituted quinoxalines. During the course of these studies, it was considered of interest to utilize these hydroxyiminoimines as three carbon synthons for nitroso heterocycles by their reactions with bifunctional nucleophiles. It is pertinent to note that nitroso heterocycles like nitrosopyrazoles or pyrimidines are usually prepared by direct nitrosation of the respective heterocycles [6]. In the present paper we report the reaction of hydroxyiminoimines **1** with hydrazine hydrate which affords regiospecific 3(5)-alkyl/arylamino-4-nitrosopyrazoles **2a-j** or the corresponding 4-amino derivatives **3a-j** in good yields.

## Results and Discussion.

The desired hydroxyiminoimines **1a-j** for the present investigation were prepared according to the earlier reported procedure [3,4]. The structures of all the known hydroxyiminoimines were confirmed by comparison of their spectral and analytical data with those of authentic samples. In one of the typical experiments, when the hydroxyiminoimine **1a** was reacted with one equivalent of hydrazine hydrate in ethanol at room temperature, workup of the reaction mixture afforded an orange colored crystalline solid (95%), which was characterized as 5(3)-ethylamino-4-nitroso-3(5)-phenylpyrazole **2a** on the basis of its spectral and analytical data. The uv spectrum of **2a** displayed band at $\nu$ max 573 nm ($\epsilon$ 96) due to nitroso group which ruled out the tautomeric hydroxyiminopyrazole structure **2A**. Under similar reaction conditions, the other hydroxyiminoimines **1b-j** underwent smooth cyclocondensation with hydrazine hydrate to afford the corresponding 3(5)-aryl/alkylamino-4-nitrosopyrazoles **2b-j** 89-97% overall yields (Scheme 1). The analytical and spectral data (Tables 1 and 3) of these compounds were found to be in confirmity with the assigned structures. All the 4-nitrosopyrazoles **2a-j** exhibited in their mass spectra a conspicuous peak at $M^+$-17 due to loss of water as shown in Scheme 2. In an-

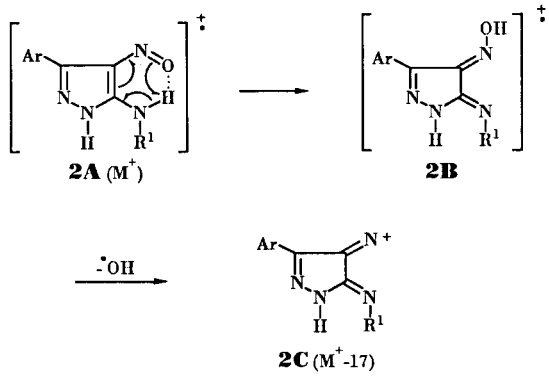
Scheme 1




**1-3a**, Ar = $C_6H_5$, $R^1$ = Et
**b**, Ar = 4-Me$C_6H_4$, $R^1$ = Et
**c**, Ar = $C_6H_5$, $R^1$ = Me
**d**, Ar = $C_6H_5$, $R^1$ = *n*-Pr
**e**, Ar = $C_6H_5$, $R^1$ = *n*-Bu
**f**, Ar = $C_6H_5$, $R^1$ = $C_6H_5CH_2$
**g**, Ar = $R^1$ = $C_6H_5$
**h**, Ar = 4-Me$OC_6H_4$, $R^1$ = $C_6H_5$
**i**, Ar = 4-$ClC_6H_4$, $R^1$ = $C_6H_5$
**j**, Ar = $C_6H_5$, $R^1$ = 4-$ClC_6H_4$

other experiment, when **1a** was reacted with excess of hydrazine hydrate in refluxing ethanol, the product analysis showed the formation of 4-amino-5(3)-ethylamino-3(5)-phenylpyrazole (**3a**) (92%) by further reduction of nitrosopyrazole **2a** [7,8]. This was confirmed by separately reacting **2a** with an excess of hydrazine hydrate in refluxing ethanol to give **3a** (superimposable ir, $^1$H nmr spectra).

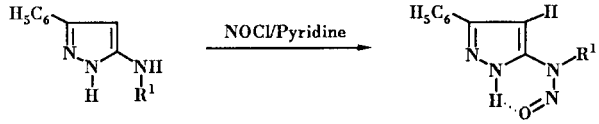
Scheme 2




The other substituted 4-amino-3(5)-aryl/alkylaminopyrazoles **3b-j** were similarly prepared from **1b-j** in 84-96% overall yields (Scheme 1, Tables 2 and 4).

Interestingly, when 3(5)-ethylamino-5(3)-phenylpyrazole (**4a**) was reacted with nitrosyl chloride (chloroform/pyridine), the product isolated (90%) was found to be 5(3)-(*N*-nitrosoethylamino)-3(5)-phenylpyrazole (**5a**) instead of the expected 4-nitroso derivative **2a** (Scheme 3). The structure of **5a** was supported by the presence of base peak at m/z 186 ($M^+$-NO, 100%) in its mass spectrum, besides its $^1$H

Scheme 3




**4,5a**, $R^1$ = Et
**b**, $R^1$ = $C_6H_5CH_2$
**4c**, $R^1$ = $C_6H_5$

Table 1

Physical and Analytical Data for the Products **2a-j**

| Compound | Yield (%) | Mp (°C) | Molecular Formula | Analysis (%) Calcd. C | H | N | Analysis (%) Found C | H | N |
|---|---|---|---|---|---|---|---|---|---|
| **2a** | 95 | 260-261 | $C_{11}H_{12}N_4O$ | 61.11 | 5.55 | 25.92 | 60.96 | 5.46 | 25.78 |
| **2b** | 95 | 200-201 | $C_{12}H_{14}N_4O$ | 62.59 | 6.13 | 24.33 | 62.48 | 5.90 | 24.23 |
| **2c** | 94 | 235-236 | $C_{10}H_{10}N_4O$ | 59.35 | 4.95 | 27.70 | 59.49 | 5.03 | 27.83 |
| **2d** | 91 | 230-231 | $C_{12}H_{14}N_4O$ | 62.59 | 6.13 | 24.32 | 62.63 | 6.24 | 24.17 |
| **2e** | 89 | 233-234 | $C_{13}H_{16}N_4O$ | 63.86 | 6.55 | 22.92 | 63.94 | 6.41 | 23.03 |
| **2f** | 94 | 240-241 | $C_{16}H_{14}N_4O$ | 68.99 | 5.03 | 20.12 | 69.13 | 5.27 | 19.98 |
| **2g** | 97 | 235-236 | $C_{15}H_{12}N_4O$ | 68.13 | 4.54 | 21.20 | 67.98 | 4.61 | 21.02 |
| **2h** | 95 | 241-242 | $C_{16}H_{14}N_4O_2$ | 65.24 | 4.76 | 19.03 | 65.38 | 4.66 | 18.97 |
| **2i** | 93 | 247-248 | $C_{15}H_{11}ClN_4O$ | 60.26 | 3.68 | 18.75 | 60.07 | 3.81 | 18.53 |
| **2j** | 93 | 238-329 | $C_{15}H_{11}ClN_4O$ | 60.26 | 3.68 | 18.75 | 60.34 | 3.71 | 18.86 |

Table 2

Physical and Analytical Data for the Products **3a-j**

| Compound | Yield (%) | Mp (°C) | Molecular Formula | Analysis (%) Calcd. C | H | N | Analysis (%) Found C | H | N |
|---|---|---|---|---|---|---|---|---|---|
| **3a** | 92 | 177-178 | $C_{11}H_{14}N_4$ | 65.35 | 6.93 | 27.72 | 65.05 | 7.11 | 27.83 |
| **3b** | 92 | 200-201 | $C_{12}H_{16}N_4$ | 66.66 | 7.40 | 25.93 | 66.50 | 7.51 | 26.06 |
| **3c** | 83 | 98-99 | $C_{10}H_{12}N_4$ | 63.76 | 6.38 | 29.76 | 63.51 | 6.47 | 29.88 |
| **3d** | 90 | 170-171 | $C_{12}H_{16}N_4$ | 66.66 | 7.40 | 25.93 | 66.58 | 7.31 | 26.04 |
| **3e** | 84 | 168-169 | $C_{13}H_{18}N_4$ | 67.83 | 7.83 | 24.36 | 67.94 | 7.71 | 24.41 |
| **3f** | 94 | 169-170 | $C_{16}H_{16}N_4$ | 72.72 | 6.06 | 21.21 | 72.61 | 5.92 | 21.16 |
| **3g** | 96 | 214-215 | $C_{15}H_{14}N_4$ | 72.00 | 5.60 | 22.40 | 71.92 | 5.81 | 22.35 |
| **3h** | 95 | 203-204 | $C_{16}H_{16}N_4O$ | 68.57 | 5.71 | 20.00 | 68.67 | 5.83 | 19.89 |
| **3i** | 95 | 194-195 | $C_{15}H_{13}ClN_4$ | 63.26 | 4.56 | 19.68 | 63.11 | 4.47 | 19.71 |
| **3j** | 92 | 174-175 | $C_{15}H_{13}ClN_4$ | 63.26 | 4.56 | 19.68 | 63.40 | 4.33 | 19.51 |

nmr spectrum displayed the signal due to H-4 proton at δ 6.91 (s, 1H). The corresponding 3(5)-benzylaminopyrazole **4b** also yielded the 5(3)-(*N*-nitrosobenzylamino)pyrazole **5b** (91%) under similar reaction conditions. However, the 3(5)-anilinopyrazole **4c** underwent ring nitrosation under these conditions to afford 4-nitrosopyrazole **2g** identical with that obtained by cyclization of **1g** with hydrazine hydrate.

After having developed a convenient method for the synthesis of diaminopyrazoles **3**, we have utilized them for the synthesis of condensed pyrazolo heterocycles. Thus, when diaminopyrazole **3a** was diazotized with sodium nitrite in the presence of acetic acid at 0°, workup of the reaction mixture afforded a yellow crystalline solid (63%) identified as 1-ethyl-4-phenylpyrazolo[3,4-*d*]-1,2,3-triazole (**6a**) (Scheme 4) [9]. Similarly, the pyrazolotriazoles **6b** and **6c** were obtained in 80% and 72% yields respectively. The spectral properties and analytical data of **6a-c** were in confirmity with the assigned structures. Condensation of aminopyrazole **3f** with ethyl acetoacetate similarly afforded the pyrazolo[3,4-*b*][1,4]diazepine derivative **7** in good yield (Scheme 4) [10]. However attempts to construct imidazolo[4,5-*c*]pyrazole ring by reacting diaminopyrazole **3d** with benzaldehyde in boiling ethanol gave only the open chain Schiff's base **8** in 72% yield (Scheme 4).

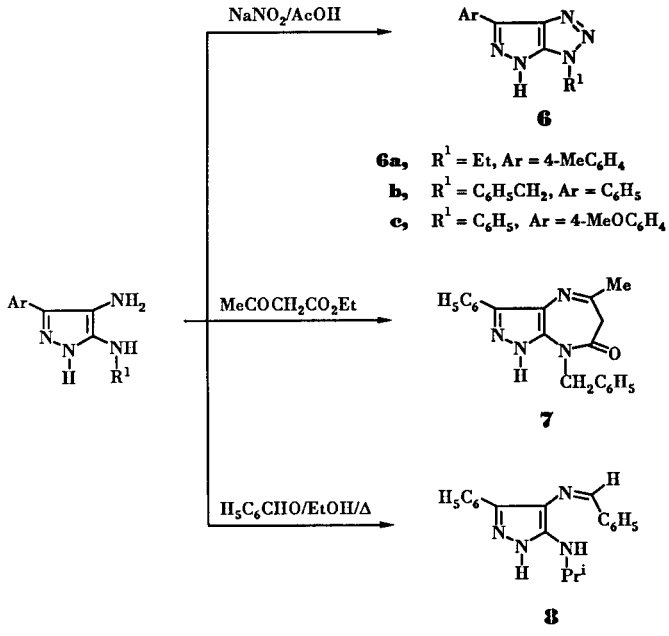
Table 3

Spectral Data for Compounds **2a-j**

| Compound | IR (potassium bromide) $cm^{-1}$<br>UV (methanol) λ max nm (ε) | $^1H$ NMR δ (ppm) | Ms m/z (%) |
|---|---|---|---|
| **2a** | 3040, 1655, 1510, 1300, 1280, 956 | 1.19 (t, J = 7 Hz, 3H, $CH_2CH_3$), 3.31 (quint, J = 7 Hz, 2H, $NHCH_2CH_3$), 7.29-7.58 (m, 3H, ArH), 8.10-8.36 (m, 2H, ArH), 9.41 (br s, 1H, $NHCH_2CH_3$), 12.70 (br s, 1H, NH) | 216 ($M^+$, 100), 200 (20), 199 (54) |
| **2b** | 3390, 1670, 1512, 1142, 960<br>573 (96), 378 (4635) | 1.15 (t, J = 7 Hz, 3H, $CH_2CH_3$), 2.37 (s, 3H, $CH_3$), 3.28 (quint, J = Hz, 2H, $NHCH_2CH_3$), 7.31 (d, J = 9 Hz, 2H, ArH), 8.21 (d, J = 9 Hz, 2H, ArH), 9.49 (br s, 1H, $NHCH_2CH_3$), 12.65 (br s, 1H, NH) | 230 ($M^+$, 100), 214 (17), 213 (62) |
| **2c** | 3250, 3170, 3055, 1660, 1550, 1300, 1160, 1222, 941 | 2.98 (d, J = 7 Hz, 3H, N-$CH_3$), 7.30-7.65 (m, 3H, ArH), 8.12-8.15 (m, 2H, ArH), 9.31 (br s, J = 6 Hz, 1H, $NHCH_3$), 12.40 (br s, 1H, NH) | 202 ($M^+$, 22), 185 (10) |
| **2d** [a] | 3220, 3050, 1640, 1495, 1242, 930 | 0.91 (t, J = 7 Hz, 3H, $CH_2CH_2CH_3$), 1.60 (sext, J = Hz, 2H, $CH_2CH_2CH_3$), 3.20 (q, J = 7 Hz, N-$CH_2CH_2CH_3$), 7.19-7.61 (m, 3H, ArH), 7.62-7.91 (m, 2H, ArH), 9.50 (br s, 1H, $NHCH_2$), 12.80 (br s, 1H, NH) | 230 ($M^+$, 22), 213 (75) |
| **2e** | 3210, 3050, 1642, 1496, 1152, 1133, 960<br>575 (95) 378 (5432) | 0.92 (t, J = 7 Hz, 4H, $CH_2CH_2CHCH_3$), 3.23 [q, J = 7 Hz, 2H, NH-$CH_2(CH_2)_3CH_3$], 7.30-7.65 (m, 3H, ArH), 8.20-8.50 (m, 2H, ArH), 9.50 (br t, 1H, $NHCH_2$), 12.80 (br s, 1H, NH) | 244 ($M^+$, 100), 228 (99), 227 (99) |
| **2f** | 3250, 3050, 1655, 1495, 1130, 928 | 4.49 (d, J = 6 Hz, 2H, $NCH_2C_6H_5$), 7.20-7.60 (m, 8H, ArH), 8.15-8.45 (m, 2H, ArH), 9.88 (br s, 1H, $NHCH_2$), 12.80 (br s, 1H, NH) | 278 ($M^+$, 28), 262 (20), 261 (38) |
| **2g** [b] | 3050 (br), 1639, 1598, 1560, 1520, 1490, 1280, 1135, 950<br>419 (577), 329 (8960), 610 (137) sh | 690-7.70 (m, 8H, ArH), 8.11-8.38 (m, 2H, ArH), 10.20 (br s, 1H, $NHCH_2$), 12.80 (br s, 1H, NH) | 264 ($M^+$, 65), 263 (24), 262 (88), 247 (100), 246 (22) |
| **2h** | 3160-3000 (br), 3160, 1592, 1568, 1547, 1495, 1285, 1251, 1160, 1131, 1025, 860<br>437 (751), 350 (10835), 610 (187) sh | 3.83 (s, 3H, $OCH_3$), 6.92-7.50 (m, 5H, ArH), 7.74 (d, J = 7 Hz, 2H, ArH), 8.29 (d, J = 7 Hz, 2H, ArH), 10.00 (br s, 1H, NHAr), 13.65 (br s, 1H, NH) | 294 ($M^+$, 80), 278 (28), 277 (100) |
| **2i** | 3160, 3000 (br), 3050, 1639, 1598, 1570, 1522, 1490, 1283, 1165, 1135, 1095, 862<br>404 (632), 328 (9240), 610 (277) sh | 7.00-7.70 (m, 7H, ArH), 8.26-8.45 (d, J = 9 Hz, 2H, ArH), 10.50 (br s, 1H, NHAr), 13.70 (br s, 1H, NH) | 300 (21), 298 ($M^+$, 70), 283 (40), 281 (100) |
| **2j** | 3180, 3050, 1641, 1600, 1577, 1538, 1492, 1405, 1290, 1170, 1140, 1098, 960, 838 | 6.97-8.02 (m, 7H, ArH), 8.34 (d, J = 9 Hz, 2H, ArH), 10.20 (br s, 1H, NHAr), 13.5 (br s, 1H, NH) | 300 (25), 298 ($M^+$, 76), 283 (34), 281 (100) |

[a] $^{13}C$ nmr (DMSO-$d_6$): $\delta_C$ 10.84 ($CH_3$), 21.7 ($CH_2$), 42.71 ($NHCH_2$), 127.76, 128.38, 129.08 (CH, arom), 131.1 (C-1' arom), 139.03 (C-4), 148.96 (C-3), 149. 90 (C-5). [b] $^{13}C$ nmr (DMSO-$d_6$): $\delta_C$ 119.67, 122.79, 127.56, 128.48, 128.84, 128.94 (CH, arom), 130.5, 137.92 (C-1, arom), 138.77 (C-4), 147.67 (C-3), 150.69 (C-5).

Scheme 4




## EXPERIMENTAL

Melting points were determined on Thomas Hoover apparatus and are uncorrected. The ir spectra were recorded on a Perkin Elmer 297 spectrophotometer, $^1$H nmr spectra were obtained on Varian EM-390, 90 MHz spectrometer using tetramethylsilane (TMS) as internal standard and chemical shifts are expressed in δ (ppm). The $^{13}$C nmr spectra were obtained on a Bruker WM-400 DS spectrometer while mass spectra were recorded on Jeol D 300 mass spectrometer. Elemental analysis were carried out on Hearaeus C,H,N elemental analyzer.

The starting hydroxyiminoimine **1a-j** were prepared according to the reported procedure [4].

General Procedure for 3(5)-Aryl-4-nitroso-5(3)-aryl/alkyl/benzyl-aminopyrazoles **2a-j**.

To a well stirred and ice-cooled solution of hydroxyiminoimine **1** (10 mmoles) in ethanol (15 ml), a solution of hydrazine hydrate (0.75 g, 15 mmoles) in ethanol (10 ml) was added slowly during 5 minutes and the reaction mixture was further stirred for 3 hours (monitored by tlc). The solvent was removed under reduced pressure and the residue was poured over ice-cooled water to give 4-nitroso-3(5)-alkylamino **2a-g** and 3(5)-arylaminopyrazoles **2h-j** as orange and maroon colored solids respectively. The crude

Table 4

Spectral Data for Compounds **3a-j**

| Compound | IR (potassium bromide) cm$^{-1}$ UV (methanol) λ max nm (ε) | $^1$H NMR δ (ppm) | Ms m/z (%) |
|---|---|---|---|
| **3a** | 3340, 3160, 1600, 1540, 1240, 960, 920 | 1.20 (t, J = 8 Hz, 3H, $CH_2CH_3$), 3.18 (q, J = 7 Hz, 2H, $CH_2CH_3$), 4.72-6.23 (br s, 4H, 2NH + $NH_2$), 7.10-7.48 (m, 3H, ArH), 7.61-7.87 (m, 2H, ArH) | 202 ($M^+$, 100), 187 (67) |
| **3b** | 3345, 3180, 1605, 1540, 1250, 1020, 920 825 | 1.19 (t, J = 8 Hz, 3H, $CH_2CH_3$), 2.32 (s, 3H, $CH_3$), 3.15 (q, J = 8 Hz, 3H, $CH_2CH_3$), 3.46-5.51 (br s, 4H, 2NH + $NH_2$), 7.20 (d, J = 9 Hz, 2H, ArH), 7.61 (d, J = 9 Hz, 2H, ArH) | 216 ($M^+$, 100), 201 (41) |
| **3c** | 3347, 3157, 1600, 1540 | 2.75 (d, J = 6 Hz, 2H, N-$CH_3$), 4.70-6.21 (br s, 4H, 2NH + $NH_2$), 7.30-7.65 (m, 3H, ArH), 8.12-8.15 (m, 2H, ArH) | |
| **3d** | 3338, 3160, 1595, 1540, 1240, 950 | 0.98 (t, J = 8 Hz, 3H, $CH_2CH_2CH_3$), 1.60 (sext, J = 8 Hz, 2H, $CH_2CH_2CH_3$), 3.10 (t, J = 8 Hz, 2H, $CH_2CH_2CH_3$), 4.25-6.18 (br s, 4H, 2NH + $NH_2$), 7.10-7.52 (m, 3H, ArH), 7.60-7.88 (m, 2H, ArH) | 216 ($M^+$, 75), 187 (100) |
| **3e** [a] | 3320, 3173, 1597, 1540, 1228, 1223, 950 | 0.90 [t, J = 7 Hz, 3H, $(CH_2)_3CH_3$], 1.26-1.82 [m, 4H, $CH_2(CH_2)_2CH_3$], 3.15 [t, J = 7 Hz, 2H, $CH_2(CH_2)_2CH_3$], 4.09-6.01 (br s, 4H, 2NH + $NH_2$), 7.12-7.58 (m, 3H, ArH), 7.70-7.92 (m, 2H, ArH) | 230 ($M^+$, 92), 187 (100) |
| **3f** | 3340, 3180, 1603, 1539, 1280, 955 | 4.32 (s, 2H, $CH_2C_6H_5$), 4.89-5.45 (br s, 4H, 2NH + $NH_2$), 7.03-7.47 (m, 8H, ArH), 7.58-7.87 (m, 2H, ArH) | 264 ($M^+$, 100) |
| **3g** [b] | 3320, 3280, 3160, 1598, 1542, 1480, 740 | 3.01-4.89 (br s, 4H, 2NH + $NH_2$), 6.60-7.82 (m, 10H, ArH), | 250 ($M^+$, 100) |
| **3h** | 3175, 3000, 1595, 1525, 1280, 1248, 1160, 1130, 740 | 3.52 (br s, 4H, 2NH + $NH_2$), 3.78 (s, 3H, $OCH_3$), 6.48-7.32 (m, 7H, ArH), 7.50-7.70 (m, 2H, ArH) | 280 ($M^+$, 100) |
| **3i** | 3330, 3253, 3150, 1600, 1542, 1498, 1090, 960, 838 | 3.53-4.89 (br s, 4H, 2NH + $NH_2$), 6.60-7.98 (m, 9H, ArH) | 286 ($M^+$, 30), 284 ($M^+$, 96) |
| **3j** | 3270 (br), 1605, 1560, 1510, 1490, 1309, 1240, 1090, 820 | 3.37-4.39 (br s, 4H, 2NH + $NH_2$), 6.85-7.90 (m, 9H, ArH) | 286 ($M^+$, 32), 284 ($M^+$, 100) |

[a] $^{13}$C nmr (DMSO-$d_6$): $\delta_C$ 13.81 ($CH_3$), 19.91 ($CH_2$), 31.90 ($CH_2$), 43.66 ($NCH_2$), 112.45 (C-4),125.03, 126.09, 128.40 (CH, arom), 131.53 (C-3), 149.76 (C-5). [b] $^{13}$C nmr (DMSO-$d_6$): $\delta_C$ 114.3, 117.4, 124.85, 126.30, 128.51 (C-H, arom), 116 (C-4), 127.94, 130.60 (C-1', arom), 143.38 (C-3), 144.62 (C-5).

pyrazoles were filtered and crystallized from ethanol to give pure **2a-j** (Tables 1 and 3).

General Procedure for 3(5)-Aryl-4-amino-5(3)-arylalkylbenzylaminopyrazoles **3a-j**.

A solution of appropriate hydroxyiminoimine (10 mmoles) or nitrosopyrazole **2a-j** (10 mmoles) and hydrazine hydrate (4 g, 80 mmoles) in 30 ml of ethanol was refluxed for 75 minutes (monitored by tlc). The solvent was removed on water bath and the residue was poured over ice-cold water to give crude 4-aminopyrazoles **3a-j** as white solids, which were further purified by recrystallization from ethanol (Tables 2 and 4).

General Procedure for Nitrosation of Pyrazoles **4a-c**.

To an ice-cooled and well stirred solution of 5(3)-arylalkylpyrazoles **4a-c** (0.01 mole) in dry pyridine (2 ml) and chloroform (25 ml), nitrosyl chloride solution (0.012 mole in 5 ml of dry ether) was added and the reaction mixture was further stirred for 10-15 minutes. It was then diluted with ice-cooled water (50 ml), extracted with chloroform (3 x 50 ml). The organic layer was washed with water (3 x 100 ml) to remove excess of pyridine, dried (sodium sulfate) and evaporated to give crude **5a-b** or **2g** which were purified by crystallization using boiling ethanol.

3(5)-(*N*-Nitrosoethylamino)-5(3)-phenylpyrazole (**5a**).

This compound was obtained as grey crystalline solid (ethanol) in 90% yield, mp 167-168°; ir (potassium bromide): ν max 3205, 1568, 1500, 1460, 1389, 1260, 1215, 1060, 770 $cm^{-1}$; $^1H$ nmr (deuteriochloroform/DMSO-$d_6$): δ 1.13 (t, J = 7 Hz, 3H, $CH_3CH_2$), 4.20 (q, J = 7 Hz, 2H, $CH_3CH_2$), 6.94 (s, 1H, H-4), 7.29-7.61 (m, 3H, Ar*H*), 7.70-7.98 (m, 2H, Ar*H*), 13.25 (br s, 1H, N*H*); ms: (m/z) 186 ($M^+$-NO).

*Anal.* Calcd. for $C_{11}H_{12}N_4O$: C, 61.11; H, 5.55; N, 25.92. Found: C, 68.99; H, 5.03; N, 19.98.

5(3)-(*N*-Nitrosobenzylamino)-3(5)-phenylpyrazole (**5b**).

This compound was obtained as grey solid (ethanol) in 91% yield, mp 177-178°; ir (potassium bromide): ν max 3205, 1498, 1420, 1390, 1225, 1160, 760 $cm^{-1}$; $^1H$ nmr (carbon tetrachloride/DMSO-$d_6$): 5.28 (s, 2H, $ArCH_2$), 6.91 (s, 1H, H-4), 7.21 (br s, 5H, Ar*H*), 7.20-7.51 (m, 3H, Ar*H*), 7.65-7.85 (m, 2H, Ar*H*), 13.5 (br s, 1H, N*H*); ms: (m/z) 248 ($M^+$-NO).

*Anal.* Calcd. for $C_{16}H_{14}N_4O$: C, 69.05; H, 5.07; N, 20.12. Found: C, 68.99; H, 5.03; N, 19.98.

General Procedure for 1-Alkyl/aryl-4-arylpyrazolo[3,4-*d*]-1,2,3-triazoles **6a-c**.

To an ice cooled and stirred solution of diaminopyrazole **3** (0.005 mole) in acetic acid (10 ml), a solution of sodium nitrite (0.04 g, 0.006 mole) in water (3 ml) was added dropwise and the reaction mixture was stirred for 3 hours at room temperature. It was then poured over water and the yellow solid separated was filtered and recrystallized from ethanol to afford pure pyrazolotriazoles **6a-c**.

1-Ethyl-4-(4-methylphenyl)pyrazolo[3,4-*d*]-1,2,3-triazole (**6a**).

This compound was obtained as yellow solid (ethanol) in 63% yield, mp 206-207°; ir (potassium bromide): ν max 3225 (NH), 1623, 1540 $cm^{-1}$; $^1H$ nmr (deuteriochloroform/DMSO-$d_6$): δ 1.19 (t, J = 7 Hz, 3H, N-$CH_2CH_3$), 2.40 (s, 3H, $CH_3$), 4.25 (q, J = 7 Hz, 2H, N-$CH_2CH_3$), 7.30 (d, J = 9 Hz, 2H, Ar*H*), 7.68 (d, J = 9 Hz, 2H, Ar*H*).

*Anal.* Calcd. for $C_{12}H_{13}N_5$: C, 63.38; H, 5.72; N, 30.80. Found: C, 63.21; H, 5.91; N, 30.73.

1-Benzyl-4-phenylpyrazolo[3,4-*d*]-1,2,3-triazole (**6b**).

This compound was obtained as yellow solid (ethanol) in 80% yield, mp 138-139°; ir (potassium bromide): ν max 3271 (NH), 1625, 1543 $cm^{-1}$; $^1H$ nmr (deuteriochloroform/TFA): δ 5.28 (s, 2H, N-$CH_2C_6H_5$), 7.34 (s, 5H, Ar*H*), 7.72 (s, 5H, Ar*H*); ms: (m/z) 275 ($M^+$, 13), 274 (11), 246 (19).

*Anal.* Calcd. for $C_{16}H_{13}N_5$: C, 69.74; H, 4.72; N, 25.42. Found: C, 69.83; H, 4.59; N, 25.61.

4-(4-Methoxyphenyl)-1-phenylpyrazolo[3,4-*d*]-1,2,3-triazole (**6c**).

This compound was obtained as yellow solid (ethanol) in 72% yield, mp 233-234°; ir (potassium bromide): ν max 3225 (NH), 1623, 1540, 1258, 812 $cm^{-1}$; $^1H$ nmr (deuteriochloroform/DMSO-$d_6$): δ 3.88 (s, 3H, $OCH_3$), 7.10 (d, J = 9 Hz, 2H, Ar*H*), 7.37-7.73 (m, 4H, Ar*H*), 8.02-8.21 (m, 3H, Ar*H*) ms: (m/z) 291 ($M^+$, 100), 265 (40).

*Anal.* Calcd. for $C_{16}H_{13}N_5O$: C, 65.93; H, 4.46; N, 24.03. Found: C, 66.07; H, 4.37; N, 23.96.

8-Benzyl-5-methyl-3-phenyl-1,6-dihydropyrazolo[3,4-*b*][1,4]-diazepin-7(8*H*)-one (**7**).

A solution of aminopyrazole **3f** (0.53 g, 0.002 mole) and methyl acetoacetate (0.25 g, 0.002 mole) in 10 ml of glacial acetic acid was refluxed for 10 hours (monitored by tlc). The reaction mixture after cooling was poured over crushed ice, the solid separated was collected by filtration and recrystallized from boiling ethanol, mp 102°, yield 73%; ir (potassium bromide): ν max 1690, 1610 $cm^{-1}$; $^1H$ nmr (deuteriochloroform): δ 2.31 (s, 3H, $CH_3$), 3.32 (s, 2H, $CH_2$), 5.25 (s, 2H, $C_6H_5CH_2$-N), 7.00-7.51 (m, 8H, Ar*H*), 7.52-7.90 (m, 2H, Ar*H*), 12.50 (br s, 1H, N*H*); ms: (m/z) 330 ($M^+$, 8%).

Condensation of Pyrazole **3d** with Benzaldehyde.

A solution of **3d** (0.43 g, 2 mmoles) and benzaldehyde (0.3 g, 2.5 mmoles) was refluxed in ethanol (20 ml) for 30 hours. The reaction mixture was concentrated and the residue was passed through a small column of silica gel (ethyl acetate-hexane as eluent) to afford **8** as a yellow solid in 72% yield, mp 155-156°; ir (potassium bromide): ν max 3180, 1610, 1528 $cm^{-1}$; $^1H$ nmr (deuteriochloroform/DMSO-$d_6$): δ 1.00 (t, J = 7 Hz, 3H, $CH_3CH_2$ $CH_2N$), 1.73 (sext, J = 7 Hz, 2H, N-$CH_2CH_2CH_3$), 3.23 (t, J = 7 Hz, 2H, $NCH_2CH_2CH_3$), 7.18-7.60 (m, 6H, Ar*H*), 7.71-8.18 (m, 4H, Ar*H*), 8.78 (s, 1H, N=C*H*Ar).

*Anal.* Calcd. for $C_{19}H_{20}N_4$: C, 74.92; H, 6.57; N, 18.40. Found: C, 75.03; H, 6.71; N, 18.29.

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