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# 3-ARYL- AND 2,3-DIARYL-4-OXO-4,5,6,7-TETRAHYDROINDAZOLES. 2*. REACTIONS OF ARYL- AND TOSYLHYDRAZONES OF DIMEDONE AND 1,3-CYCLOHEXANEDIONE WITH SOME AROMATIC AND HETEROAROMATIC ALDEHYDES

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*The reactions of the phenylhydrazone and 2-chlorophenyl-, 2,4-difluorophenyl-, 4-nitrophenyl-, and 2-pyridylhydrazones of dimedone with benzaldehyde, 4-bromo-, 4-fluoro-, 4-(dimethylamino)-, 4-nitrobenzaldehydes, 2-, 3-, and 4-pyridinecarbaldehydes and 2-thiophenecarbaldehyde have given 24 novel 2,3-diaryl-4-oxo-4,5,6,7-tetrahydroindazoles. Treatment of the tosylhydrazones of dimedone and 1,3-cyclohexanedione with pyridine- and thiophenecarbaldehydes yielded 7 novel 3-pyridyl- and 3-thienyl-4-oxo-4,5,6,7-tetrahydroindazoles.*

**Keywords:** arylhydrazones and tosylhydrazones of 1,3-cyclohexanedione, 3-aryl- and 2,3-diaryl-4-oxo-4,5,6,7-tetrahydroindazoles, substituted benzaldehydes, pyridine- and thiophenecarbaldehydes.

In extending studies [1] of the synthesis of 3-aryl- and 2,3-diaryl-4-oxo-4,5,6,7-tetrahydroindazoles we have concentrated attention in the present work on varying the aryl groups on $N_{(2)}$ in the 2,3-diarylindazoles and the introduction of heteroaromatic groups at $C_{(3)}$ in the 3-aryl- and 2,3-diarylindazoles.

As in [1, 2] we have used the reaction of the enehydrazines **1** with substituted benzaldehydes, 2-, 3-, and 4-pyridinecarbaldehydes and 2-thiophenecarbaldehyde to synthesize the 2,3-diaryl-4-oxo-4,5,6,7-tetrahydroindazoles.

The enehydrazines **1a,b** were prepared using the method in [2].

Synthesis of compounds **1c-e** was carried out by heating equimolar amounts of dimedone **2a** and 2-chloro-, 2,4-difluoro-, or 4-nitrophenylhydrazines in acetic acid and the enehydrazine **1f** by heating the pyridylhydrazine in ethanol. The proton signal at $C_{(2)}$ absorbs in the range 4.84-4.95 ppm for these compounds and the NH protons have a chemical shift of 7.77-9.07 ppm.

As in the studies [1, 3] the reactions of the enehydrazines **1a-f** with the aldehydes were carried out by heating in DMSO in the presence of piperidine acetate. Losses on crystallization markedly lowered the yields of the 2,3-diarylindazoles **3a-w** (see Table 1), particularly for the reactions involving the 4-nitrophenylhydrazone **1e**.

* For Communication 1 see [1].

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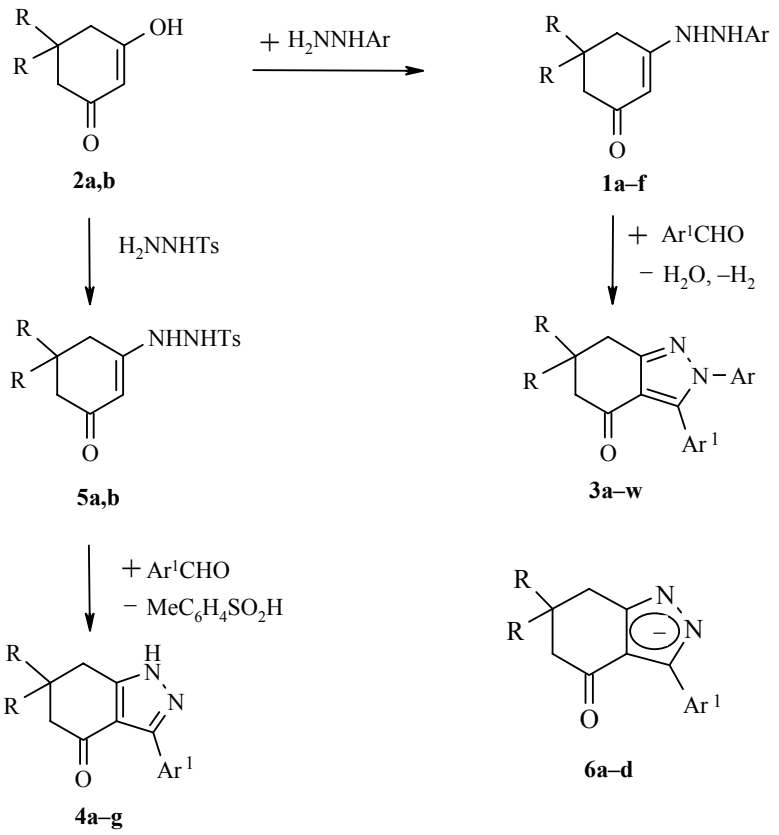


**1,2,5 a** R = Me, **b** R = H, **1c-f** R = Me, **a,b** Ar = Ph, **c** Ar = $C_6H_4Cl$-2, **d** Ar = $C_6H_3F_2$-2,4, **e** Ar = $C_6H_4NO_2$-4, **f** Ar = 2-$C_5H_4N$; **3a-d, i-w** R = Me, **e-h** R = H, **a-h** Ar = Ph, **i-m** Ar = $C_6H_4Cl$-2, **n-o** Ar = $C_6H_3F_2$-2,4, **p** Ar = $C_6H_4NO_2$-4, **q-w** Ar = 2-$C_5H_4N$, **a,e,t** $Ar^1$ = 2-$C_5H_4N$, **b,f,u** $Ar^1$ = 3-$C_5H_4N$, **c,g,m,v** $Ar^1$ = 4-$C_5H_4N$, **d,h,w** $Ar^1$ = 2-$C_4H_3S$, **i,n,p,q**, $Ar^1$ = Ph, **j** $Ar^1$ = $C_6H_4Br$-4, **k,o,s** $Ar^1$ = $C_6H_4NMe_2$-4, **l** $Ar^1$ = $C_6H_4NO_2$-4, **r** $Ar^1$ = $C_6H_4F$-4; **4,6a-d** R = Me, **e-g** R = H, **a** $Ar^1$ = 2-$C_5H_4N$, **b,e** $Ar^1$ = 3-$C_5H_4N$, **c,f** $Ar^1$ = 4-$C_5H_4N$, **d,g** $Ar^1$ = 2-$C_4H_3S$

The carbonyl group absorption bands for the 2,3-disubstituted 4-oxo-4,5,6,7-tetrahydroindazoles **3** appear in the region 1675-1655 $cm^{-1}$. The $^1H$ NMR spectra show proton signals for all of the structural fragments of the indazoles **3a-w** (Table 2).

In order to synthesize the 3-aryl-4-oxo-4,5,6,7-tetrahydroindazoles **4** which are unsubstituted on the nitrogen atom we have used the known enehydrazines **5** [1] which were prepared from the cyclohexanediones **2a,b** and tosylhydrazine. Reaction of these with pyridine- and thiophenecarbaldehydes using the method [1] gave the 3-pyridyl- and 3-thienyl-4-oxo-4,5,6,7-tetrahydroindazoles **4**.

The IR spectra of the 3-(3-pyridyl)indazoles **4b,e** and 3-(4-pyridyl)indazoles **4c,f** show typical strong $N^+H$ absorption in the range 2800-2500 $cm^{-1}$ which may point to a marked contribution from the betaine form **6**. By contrast with the 3-(2-thienyl)indazoles **4d,g** and 4-oxo-3-phenyl-4,5,6,7-tetrahydroindazoles [1], the absorption of these compounds in the 3300-3100 $cm^{-1}$ region is low. The $^1H$ NMR spectroscopic data for **4b,c,e,f** cannot confirm these proposals, however. The resonances observed for the 3- and 4-pyridyl substituent protons (Table 2) correspond more to a nonprotonated pyridine (δ 8.11-8.61 ppm) while the signals when they are protonated on the N atom would be at lower field (δ 8.50-9.23 ppm) [4].

TABLE 1. Characteristics of the Compounds Synthesized

| Compound | Empirical formula | Found, % / Calculated, % | | | | mp, °C | Yield, % |
|---|---|---|---|---|---|---|---|
| | | C | H | N | Cl (S) | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| **1c** | $C_{14}H_{17}ClN_2O$ | 63.34 / 63.51 | 6.40 / 6.47 | 10.56 / 10.58 | 13.60 / 13.39 | 216-217 | 83 |
| **1d** | $C_{14}H_{16}F_2N_2O$ | 63.35 / 63.14 | 6.09 / 6.06 | 10.35 / 10.52 | | 175-177 | 93 |
| **1e** | $C_{14}H_{17}N_3O_3$ | 61.21 / 61.08 | 6.29 / 6.23 | 15.10 / 15.26 | | 232-233 | 48 |
| **1f** | $C_{13}H_{17}N_3O$ | 67.31 / 67.50 | 7.27 / 7.41 | 18.00 / 18.17 | | 200-202 | 67 |
| **3a** | $C_{20}H_{19}N_3O$ | 75.48 / 75.68 | 6.00 / 6.03 | 13.11 / 13.24 | | 173-175 | 50 |
| **3b** | $C_{20}H_{19}N_3O$ | 75.55 / 75.68 | 5.91 / 6.03 | 13.03 / 13.24 | | 166-167 | 50 |
| **3c** | $C_{20}H_{19}N_3O$ | 75.79 / 75.68 | 5.88 / 6.03 | 13.08 / 13.24 | | 166-167 | 43 |
| **3d** | $C_{19}H_{18}N_2OS$ | 70.57 / 70.78 | 5.55 / 5.63 | 8.51 / 8.69 | (9.70) / (9.94) | 150-151 | 58 |
| **3e** | $C_{18}H_{15}N_3O$ | 74.48 / 74.72 | 5.10 / 5.23 | 14.36 / 14.52 | | 126-127 | 20 |
| **3f** | $C_{18}H_{15}N_3O$ | 74.55 / 74.72 | 5.03 / 5.23 | 14.30 / 14.52 | | 150-151 | 43 |
| **3g** | $C_{18}H_{15}N_3O$ | 74.90 / 74.72 | 5.08 / 5.23 | 14.48 / 14.52 | | 168-169 | 46 |
| **3h** | $C_{17}H_{14}N_2OS$ | 69.15 / 69.36 | 4.70 / 4.79 | 9.33 / 9.52 | (10.60) / (10.89) | 114-115 | 34 |
| **3i** | $C_{21}H_{19}ClN_2O$ | 71.67 / 71.89 | 5.35 / 5.46 | 7.79 / 7.98 | 9.90 / 10.10 | 168-169 | 57 |
| **3j** | $C_{21}H_{18}BrClN_2O$ | 58.50 / 58.69 | 4.05 / 4.22 | 6.36 / 6.52 | | 178-180 | 47 |
| **3k** | $C_{23}H_{24}ClN_3O$ | 69.90 / 70.13 | 6.06 / 6.14 | 10.46 / 10.67 | 8.80 / 9.00 | 227-229 | 51 |
| **3l** | $C_{21}H_{18}ClN_3O_3$ | 63.53 / 63.72 | 4.40 / 4.58 | 10.70 / 10.62 | 8.70 / 8.96 | 180-182 | 46 |
| **3m** | $C_{20}H_{18}ClN_3O$ | 68.08 / 68.28 | 5.11 / 5.16 | 11.77 / 11.94 | 9.90 / 10.08 | 126-127 | 33 |
| **3n** | $C_{21}H_{18}F_2N_2O$ | 71.41 / 71.58 | 5.00 / 5.15 | 7.76 / 7.95 | | 125-126 | 56 |
| **3o** | $C_{23}H_{23}F_2N_3O$ | 69.70 / 69.86 | 5.75 / 5.86 | 10.45 / 10.63 | | 160-161 | 32 |
| **3p** | $C_{21}H_{19}N_3O_3$ | 69.62 / 69.79 | 5.17 / 5.30 | 11.50 / 11.63 | | 172-173 | 48 |
| **3q** | $C_{20}H_{19}N_3O$ | 75.46 / 75.68 | 6.01 / 6.03 | 13.10 / 13.24 | | 175-176 | 42 |
| **3r** | $C_{20}H_{18}FN_3O$ | 71.41 / 71.62 | 5.50 / 5.41 | 12.48 / 12.53 | | 163-165 | 30 |
| **3s** | $C_{22}H_{24}N_4O$ | 73.13 / 73.30 | 6.60 / 6.71 | 15.66 / 15.54 | | 210-211 | 52 |
| **3t** | $C_{19}H_{18}N_4O$ | 71.46 / 71.68 | 5.59 / 5.70 | 17.40 / 17.60 | | 168-170 | 22 |
| **3u** | $C_{19}H_{18}N_4O$ | 71.50 / 71.68 | 5.71 / 5.70 | 17.44 / 17.60 | | 162-163 | 25 |
| **3v** | $C_{19}H_{18}N_4O$ | 71.50 / 71.68 | 5.60 / 5.70 | 17.66 / 17.60 | | 158-159 | 25 |
| **3w** | $C_{18}H_{17}N_3OS$ | 66.96 / 66.85 | 5.21 / 5.30 | 12.87 / 12.99 | (9.70) / (9.91) | 124-126 | 20 |
| **4a** | $C_{14}H_{15}N_3O$ | 69.60 / 69.69 | 6.11 / 6.27 | 17.23 / 17.42 | | 160-162 | 30 |
| **4b** | $C_{14}H_{15}N_3O$ | 69.47 / 69.69 | 6.20 / 6.27 | 17.50 / 17.42 | | 165-167 | 38 |
| **4c** | $C_{14}H_{15}N_3O$ | 69.79 / 69.69 | 6.33 / 6.27 | 17.40 / 17.42 | | 235-237 | 78 |

TABLE 1 (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| **4d** | $C_{13}H_{14}N_2OS$ | 63.21<br>63.39 | 5.60<br>5.73 | 11.42<br>11.37 | (12.80)<br>(13.02) | 220-221 | 84 |
| **4e** | $C_{12}H_{11}N_3O$ | 67.66<br>67.59 | 5.22<br>5.20 | 19.50<br>19.71 | | 218-219 | 76 |
| **4f** | $C_{12}H_{11}N_3O$ | 67.40<br>67.59 | 5.07<br>5.20 | 19.55<br>19.71 | | 235 (subl.) | 83 |
| **4g** | $C_{11}H_{10}N_2OS$ | 60.45<br>60.53 | 4.64<br>4.62 | 12.68<br>12.83 | (14.50)<br>(14.69) | 235 (subl.) | 69 |

TABLE 2. IR and $^1$H NMR Spectra of the Compounds Synthesized

| Com-pound | IR spectrum, ν, $cm^{-1}$ | $^1$H NMR spectrum, δ, ppm (*J*, Hz)* |
|---|---|---|
| 1 | 2 | 3 |
| **1c** | 1610;<br>3250-3210 | 1.04 (6H, s, $2CH_3$); 2.01 (2H, s, $CH_2$); 2.24 (2H, s, $CH_2$);<br>4.95 (1H, s, =CH); 6.75 (2H, m, $C_6H_4$); 6.95-7.31 (2H, m, $C_6H_4$);<br>7.77 (1H, br. s, NH); 8.82 (1H, br. s, NH) |
| **1d** | 1608;<br>3250, 3210 | 1.01 (6H, s, $2CH_3$); 2.02 (2H, s, $CH_2$); 2.22 (2H, s, $CH_2$);<br>4.88 (1H, s, =CH); 7.04 (2H, m, $C_6H_3$); 7.51 (1H, m, $C_6H_3$);<br>8.33 (br. s, NH); 8.75 (br. s, NH) |
| **1e** | 1610;<br>3240-3210 | 1.03 (6H, s, $2CH_3$); 1.95 (2H, s, $CH_2$); 2.22 (2H, s, $CH_2$);<br>4.84 (1H, s, =CH); 6.71 (2H, m, $^3J$ = 8, $C_6H_4$);<br>8.04 (2H, m, $^3J$ = 8, $C_6H_4$); 8.91 (1H, br. s, NH); 9.07 (1H, br. s, NH) |
| **1f** | 1612;<br>3220, 3190,<br>3130 | 0.96 (6H, s, $2CH_3$); 1.93 (2H, s, $CH_2$); 2.20 (2H, s, $CH_2$);<br>4.93 (1H, s, =CH); 6.47 (1H, d, $^3J$ = 8, $C_5H_4N$); 6.67 (1H, dd, $^3J$ = 8,<br>$^3J$ = 5, $C_5H_4N$); 7.51 (1H, ddd, $^3J$ = 8, $^3J$ = 5, $^4J$ = 1, $C_5H_4N$);<br>8.02 (1H, d, $^3J$ = 5, $C_5H_4N$); 8.44 (1H, br. s, NH); 8.73 (1H, br. s, NH) |
| **3a** | 1665 | 1.09 (6H, s, $2CH_3$); 2.37 (2H, s, $CH_2$); 2.80 (2H, s, $CH_2$);<br>7.21 (6H, m, $C_6H_5$, $C_5H_4N$); 7.71 (2H, m, $C_5H_4N$);<br>8.40 (1H, dt, $^3J$ = 5, $^4J$ = 1.5, $C_5H_4N$) |
| **3b** | 1672 | 1.09 (6H, s, $2CH_3$); 2.35 (2H, s, $CH_2$); 2.80 (2H, s, $CH_2$);<br>7.16-7.31 (6H, m, $C_6H_5$, $C_5H_4N$); 7.80 (1H, dt, $^3J$ = 8, $^4J$ = 2, $C_5H_4N$);<br>8.40 (1H, dd, $^4J$ = 2, $^4J$ = 1.5, $C_5H_4N$);<br>8.53 (1H, dd, $^3J$ = 4.5, $^4J$ = 1.5, $C_5H_4N$) |
| **3c** | 1672 | 1.13 (6H, s, $2CH_3$); 2.40 (2H, s, $CH_2$); 2.78 (2H, s, $CH_2$);<br>7.24 (7H, m, $C_6H_5$, $C_5H_4N$); 8.51 (2H, m, $^3J$ = 6, $C_5H_4N$) |
| **3d** | 1665 | 1.05 (6H, s, $2CH_3$); 2.36 (2H, s, $CH_2$); 2.75 (2H, s, $CH_2$);<br>6.93 (1H, dd, $^3J$ = 5, $^3J$ = 3.5, $C_4H_3S$); 7.27 (6H, m, $C_6H_5$, $C_4H_3S$);<br>7.51 (1H, dd, $^3J$ = 3.5, $^4J$ = 1.5, $C_4H_3S$) |
| **3e** | 1670 | 2.09-3.05 (6H, m, $3CH_2$); 7.18-7.27 (6H, m, $C_6H_5$, $C_5H_4N$);<br>7.46 (2H, m, $C_5H_4N$); 8.40 (1H, m, $C_5H_4N$) |
| **3f** | 1674 | 2.02-3.05 (6H, m, $3CH_2$); 7.27 (6H, m, $C_6H_5$, $C_5H_4N$);<br>7.71 (1H, dt, $^3J$ = 8, $^4J$ = 1.5, $C_5H_4N$); 8.38 (1H, d, $^4J$ = 1.5, $C_5H_4N$);<br>8.53 (1H, dd, $^3J$ = 5, $^4J$ = 1.5, $C_5H_4N$) |
| **3g** | 1674 | 2.09-3.05 (6H, m, $3CH_2$); 7.24 (7H, m, $C_6H_5$, $C_5H_4N$);<br>7.67 (2H, m, $^3J$ = 5, $C_5H_4N$) |
| **3h** | 1664 | 2.09-2.96 (6H, m, $3CH_2$); 6.91-7.49 (8H, m, $C_6H_5$, $C_4H_3S$) |
| **3i** | 1675 | 1.09 (6H, s, $2CH_3$); 2.36 (2H, s, $CH_2$); 2.75 (2H, s, $CH_2$);<br>7.20 (9H, m, $C_6H_5$, $C_6H_4$) |
| **3j** | 1678 | 1.06 (6H, s, $2CH_3$); 2.37 (2H, s, $CH_2$); 2.78 (2H, s, $CH_2$);<br>7.11-7.42 (8H, m, $2C_6H_4$) |
| **3k** | 1673 | 1.06 (6H, s, $2CH_3$); 2.33 (2H, s, $CH_2$); 2.73 (2H, s, $CH_2$);<br>2.82 (6H, s, $N(CH_3)_2$); 6.46 (2H, m, $^3J$ = 8, $C_6H_4$); 7.16 (2H, m, $^3J$ = 8,<br>$C_6H_4$); 7.33 (4H, m, $C_6H_4$) |
| **3l** | 1670 | 1.11 (6H, s, $2CH_3$); 2.37 (2H, s, $CH_2$); 2.81 (2H, s, $CH_2$);<br>7.37 (4H, m, $C_6H_4$); 7.49 (2H, m, $^3J$ = 8, $C_6H_4$);<br>8.07 (2H, m, $^3J$ = 8, $C_6H_4$) |

TABLE 2 (continued)

| 1 | 2 | 3 |
|---|---|---|
| **3m** | 1670 | 1.11 (6H, s, $2CH_3$); 2.42 (2H, s, $CH_2$); 2.80 (2H, s, $CH_2$); 7.20 (2H, m, $^3J = 6$, $C_5H_4N$); 7.33 (4H, m, $C_6H_4$); 8.49 (2H, m, $^3J = 6$, $C_5H_4N$) |
| **3n** | 1672 | 1.04 (6H, s, $2CH_3$); 2.36 (2H, s, $CH_2$); 2.73 (2H, s, $CH_2$); 6.82-7.26 (8H, m, $C_6H_5$, $C_6H_3$) |
| **3o** | 1672 | 1.09 (6H, s, $2CH_3$); 2.36 (2H, s, $CH_2$); 2.73 (2H, s, $CH_2$); 2.84 (6H, s, $N(CH_3)_2$); 6.51-7.47 (7H, m, $C_6H_4$, $C_6H_3$) |
| **3p** | 1670 | 1.06 (6H, s, $2CH_3$); 2.37 (2H, s, $CH_2$); 2.83 (2H, s, $CH_2$); 7.27 (5H, m, $C_6H_5$); 7.29 (2H, m, $^3J = 8$, $C_6H_4$); 8.11 (2H, m, $^3J = 8$, $C_6H_4$) |
| **3q** | 1670 | 1.13 (6H, s, $2CH_3$); 2.36 (2H, s, $CH_2$); 2.82 (2H, s, $CH_2$); 7.11-7.73 (8H, m, $C_6H_5$, $C_5H_4N$); 8.37 (1H, m, $C_5H_4N$) |
| **3r** | 1668 | 1.07 (6H, s, $2CH_3$); 2.37 (2H, s, $CH_2$); 2.78 (2H, s, $CH_2$); 6.89-7.76 (7H, m, $C_6H_4$, $C_5H_4N$); 8.36 (1H, dd, $^3J = 5$, $^4J = 1.5$, $C_5H_4N$) |
| **3s** | 1668 | 1.07 (6H, s, $2CH_3$); 2.36 (2H, s, $CH_2$); 2 .81 (2H, s, $CH_2$); 2.93 (6H, s, $N(CH_3)_2$); 6.56 (2H, m, $^3J = 8$, $C_6H_4$); 7.10-7.25 (4H, m, $C_6H_4$, $C_5H_4N$); 7.58 (1H, dt, $^3J = 8$, $^4J = 2$, $C_5H_4N$); 8.54 (1H, dt, $^3J = 5$, $^4J = 2$, $C_5H_4N$) |
| **3t** | 1674 | 1.03 (6H, s, $2CH_3$); 2.36 (2H, s, $CH_2$); 2.81 (2H, s, $CH_2$); 7.16-8.31 (8H, m, $2C_5H_4N$) |
| **3u** | 1672 | 1.09 (6H, s, $2CH_3$); 2.38 (2H, s, $CH_2$); 2.81 (2H, s, $CH_2$); 7.13-8.53 (8H, m, $2C_5H_4N$) |
| **3v** | 1669 | 1.04 (6H, s, $2CH_3$); 2.38 (2H, s, $CH_2$); 2.81 (2H, s, $CH_2$); 7.24-7.82 (5H, m, $2C_5H_4N$); 8.28 (1H, m, $C_5H_4N$); 8.53 (2H, m, $C_5H_4N$) |
| **3w** | 1665 | 1.09 (6H, s, $2CH_3$); 2.38 (2H, s, $CH_2$); 2.76 (2H, s, $CH_2$); 6.97-7.80 (6H, m, $C_5H_4N$, $C_4H_3S$); 8.40 (1H, m, $C_5H_4N$) |
| **4a** | 1626; 3150-3050 | 1.03 (6H, s, $2CH_3$); 2.42 (2H, s, $CH_2$); 2.81 (2H, s, $CH_2$); 7.27-9.08 (4H, m, $C_5H_4N$); 12.28 (1H, br. s, NH) |
| **4b** | 1630; 3140-3050 | 1.03 (6H, s, $2CH_3$); 2.36 (2H, s, $CH_2$); 2.67 (2H, s, $CH_2$); 7.31 (1H, dd, $^3J = 5$, $^3J = 8$, $C_5H_4N$); 8.57 (2H, m, $C_5H_4N$); 9.27 (1H, d, $^4J = 2$, $C_5H_4N$); 12.56 (1H, br. s, NH) |
| **4c** | 1630; 3150-3050 | 0.97 (6H, s, $2CH_3$); 2.33 (2H, s, $CH_2$); 2.72 (2H, s, $CH_2$); 8.11 (2H, m, $^3J = 5$, $C_5H_4N$); 8.67 (2H, m, $^3J = 5$, $C_5H_4N$); 10.82 (1H, br. s, NH) |
| **4d** | 1635; 3110-3050 | 0.97 (6H, s, $2CH_3$); 2.31 (2H, s, $CH_2$); 2.67 (2H, s, $CH_2$); 7.11 (1H, dd, $^3J = 3.8$, $^3J = 5$, $C_4H_3S$); 7.44 (1H, dd, $^3J = 5$, $^4J = 1$, $C_4H_3S$); 8.31 (1H, dd, $^3J = 3.8$, $^4J = 1$, $C_4H_3S$); 13.25 (1H, br. s, NH) |
| **4e** | 1628; 3140-3050 | 2.01-2.92 (6H, m, $3CH_2$); 7.31 (1H, dt, $^3J = 8$, $^4J = 1.5$, $C_5H_4N$); 7.42 (1H, dd, $^3J = 5$, $^3J = 8$, $C_5H_4N$); 8.56 (1H, dd, $^3J = 5$, $^4J = 1.5$, $C_5H_4N$); 9.14 (1H, d, $^4J = 1.5$, $C_5H_4N$); 13.50 (1H, br. s, NH) |
| **4f** | 1630; 3150-3050 | 2.11-2.89 (6H, m, $3CH_2$); 8.11 (2H, m, $^3J = 5$, $C_5H_4N$); 8.61 (2H, m, $^3J = 5$, $C_5H_4N$); 13.20 (1H, br. s, NH) |
| **4g** | 1630; 3150-3050 | 1.97-2.89 (6H, m, $3CH_2$); 7.08 (1H, dd, $^3J = 4$, $^3J = 5$, $C_4H_3S$); 7.50 (1H, dd, $^3J = 5$, $^4J = 1.5$, $C_4H_3S$); 8.31 (1H, dd, $^3J = 4$, $^4J = 1.5$, $C_4H_3S$); 13.25 (1H, br. s, NH) |

* Spectra recorded in $CDCl_3$ (compounds **3a-w, 4a,b,f**) or in DMSO-$d_6$ (compounds **1c-f, 4c-e,g**).

## EXPERIMENTAL

IR spectra were recorded on a Specord 75-IR instrument for suspensions in vaseline oil (1800-1500 $cm^{-1}$ region) or in hexachlorobutadiene (3600-2000 $cm^{-1}$ region). Only the carbonyl frequency is reported in the range 1800-1500 $cm^{-1}$. The frequencies for the C–H stretching vibrations in the range 3050-2800 $cm^{-1}$ are not given. $^1H$ NMR spectra were recorded on a Bruker WH/90DS (90 MHz) instrument with TMS as internal standard.

The hydrazines and aldehydes used in this work came from the "Acros" company.

**3-(2-Chlorophenylhydrazino)-5,5-dimethylcyclohex-2-en-1-one (1c) and 3-(2,4-Difluorophenylhydrazino)-5,5-dimethylcyclohex-2-en-1-one (1d).** A mixture prepared from the corresponding arylhydrazine hydrochloride (20 mmol), water (10 ml), KOH (1.12 g, 20 mmol), and acetic acid (10 ml) was added with stirring to dimedone (2.80 g, 20 mmol) in acetic acid (20 ml). The reaction mixture was heated on a refluxing water bath for 30 min. After 1 day the precipitated enehydrazine was filtered off and recrystallized from 60% ethanol.

**5,5-Dimethyl-3-(4-nitrophenylhydrazino)cyclohex-2-en-1-one (1e).** A solution of 4-nitrophenylhydrazine (1.53 g, 10 mmol) in acetic acid (5 ml) was added to a solution of dimedone (1.40 g, 10 mmol) in acetic acid (5 ml). The precipitated nitrophenylhydrazone was filtered off and recrystallized from ethanol.

**5,5-Dimethyl-3-(2-pyridylhydrazino)cyclohex-2-en-1-one (1f).** A solution of 2-pyridylhydrazine (3.27 g, 30 mmol) in ethanol (20 ml) was added dropwise to a solution of dimedone (4.20 g, 30 mmol) in ethanol (20 ml). The mixture was heated for 15 min at 60-70°C with stirring. Water (15 ml) was added to the hot mixture. After 1 day the precipitated product **1f** was filtered off, washed on the filter with 30% aqueous ethanol, and recrystallized from a mixture of methanol and water (2:1).

**2,3-Diaryl-6,6-dimethyl-4-oxo- and 2,3-Diaryl-4-oxo-4,5,6,7-tetrahydroindazoles 3a-w.** Glacial acetic AcOH (0.2 ml), piperidine (0.4 ml), and the corresponding aldehyde (or its solution in DMSO) (4 mmol) were added to a solution of the enehydrazine **1** (4 mmol) in DMSO (5 ml). The mixture was heated for 2 h on a refluxing water bath, cooled, and poured into water (50 ml). The precipitated indazole **3** was filtered off, thoroughly washed on the filter with water, and recrystallized from ethanol (**3a-d,h,n-p**), 50-60% ethanol (**3e-g,i-m,q-s**), or a 1:5 mixture of benzene and hexane (**3t-w**).

**3-Aryl-4-oxo-4,5,6,7-tetrahydroindazoles 4a-g.** Glacial acetic acid (0.2 ml), piperidine (0.4 ml), and the corresponding aldehyde (or its solution in DMSO) (4 mmol) were added to a solution of the tosylhydrazone (4 mmol) in DMSO (5 ml). The mixture was heated for 2 h on a refluxing water bath, cooled, and poured into water (50 ml). The precipitated indazole **4** was filtered off and recrystallized from a 1:5 mixture of benzene and hexane (**4a,b**) or from ethanol (**4c-g**).

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