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3-ARYL- AND 2,3-DIARYL-4-OXO-4,5,6,7-TETRAHYDRO-INDAZOLES. 1. REACTIONS OF PHENYL- AND TOSYL-HYDRAZONES OF DIMEDONE AND CYCLOHEXANE-1,3-DIONE WITH SUBSTITUTED BENZALDEHYDES

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Sixteen 3-aryl-4-oxo-2-phenyl-4,5,6,7-tetrahydroindazoles were obtained from the reaction of the phenylhydrazones of dimedone and cyclohexane-1,3-dione with 3-bromo-, 4-bromo-, 4-chloro-, 4-fluoro-, 2-hydroxy-, 4-hydroxy-, 4-methoxy-, 2-nitro-, 3-nitro-, 4-nitro-, and 4-dimethylamino-benzaldehydes. The interaction of the tosylhydrazones of dimedone and cyclohexane-1,3-dione with the substituted benzaldehydes gave thirteen 3-aryl-4-oxo-4,5,6,7-tetrahydroindazoles.

Keywords: 3-aryl- and 2,3-diaryl-4-oxo-4,5,6,7-tetrahydroindazoles, substituted benzaldehydes, phenyl- and tosylhydrazones of cyclohexane-1,3-diones.

In continuation of studies on the modification of hydrogenated indazoles and quinazolines, mainly in their carbocyclic structural fragment [1-5], we have turned to the synthesis of 3-aryl-4-oxo-4,5,6,7-tetrahydroindazoles. Two schemes are known for their synthesis. One is the interaction of enehydrazines, obtained from cyclohexane-1,3-diones and benzenesulfonic acid hydrazide, with aromatic aldehydes [6], and the other is the interaction of 2-benzoylcyclohexane-1,3-diones with hydrazines [7]. 2,3-Diaryl-4-oxo-4,5,6,7-tetrahydroindazoles are obtained by the interaction of phenylhydrazones of cyclohexane-1,3-diones with aromatic aldehydes [8] and by the reaction of 2,3-diphenyl-1,3,4-oxadiazolium perchlorate with dimedone [9].

We selected the reaction of 3-enehydrazino-2-cyclohexen-1-ones with aromatic aldehydes for the synthesis of 3-aryl- and 2,3-diaryl-4-oxo-4,5,6,7-tetrahydroindazoles [6, 8]. Such a selection was made, in spite of the extremely large number of known 2-aroylcyclohexane-1,3-diones [10-13] many of which are herbicides, because of the simplicity of the synthesis and the availability of a wide selection of aldehydes.

In the present work 16 new 2,3-diaryl-4-oxo-4,5,6,7-tetrahydroindazoles **6** were synthesized by the reaction of phenylhydrazones of dimedone **2,3A** and cyclohexane-1,3-dione **2,3B** with substituted benzaldehydes **4**.

It was shown previously [8] that on boiling the reactants in alcohol for 15 min pyrazolines of type **5** are formed predominantly with only a little of their dehydrogenation products **6**. However the procedure for separating these compounds is complex, and in addition pyrazolines **5** are unstable. We selected more rigid reaction conditions, heating a solution of equimolar quantities of reactants in DMSO at 100°C for 3-4 h, which leads to the formation of compounds **6** exclusively (Table 1).

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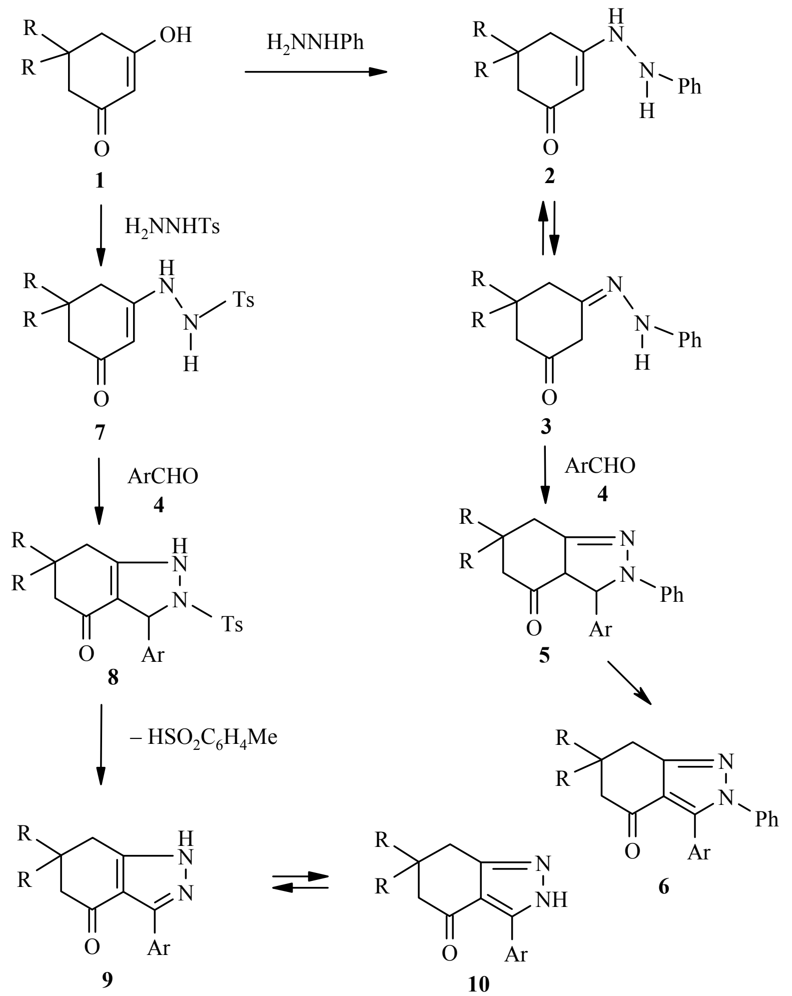

1-10 A R = Me, **B** R =H; **4-6, 8, 9 a** Ar = 3-BrC$_6$H$_4$, **b** Ar = 4-BrC$_6$H$_4$, **c** Ar = 4-C$_6$H$_4$Cl,
d Ar = 4-C$_6$H$_4$F, **e** Ar = 2-C$_6$H$_4$OH, **f** Ar = 4-C$_6$H$_4$OH, **g** Ar = 4-C$_6$H$_4$OMe,
h Ar = 2-C$_6$H$_4$NO$_2$, **i** Ar = 3-C$_6$H$_4$NO$_2$, **j** Ar = 4-C$_6$H$_4$NO$_2$, **k** Ar = 4-C$_6$H$_4$NMe$_2$

The structures of diarylindazoles **6** were confirmed by data of ^{1}H NMR and IR spectra. The absorption band of the carbonyl group of 4-oxo-4,5,6,7-tetrahydroindazoles **6** appeared at 1656-1671 cm^{-1}. In the ^{1}H NMR spectra signals were detected for the protons of all the structural fragments of indazoles **6** (Table 2).

We also used the known reaction [6] of arylhydrazones with aldehydes for the synthesis of 3-aryl-4-oxo-4,5,6,7-tetrahydroindazoles **9** unsubstituted at the nitrogen atom. We used enehydrazines **7**, obtained from cyclohexanediones **1** and the readily available tosylhydrazine. On heating enehydrazines **7** with aromatic aldehydes in DMSO in the presence of piperidine acetate and an excess of piperidine, fission of toluenesulfonic acid also occurs under the action of the latter and indazoles **9** are formed. We obtained 13 new 3-arylindazoles by this procedure, for which a structure of both $N_{(1)}$–$H_{(9)}$ and $N_{(2)}$–$H_{(10)}$ derivatives is possible. In [6] a preference was given for the 2H structure without material proof.

The spectroscopic data on indazoles **9** and **10** (ν_{CO} 1621-1632, ν_{NH} 3050-3150 cm^{-1}, δ_{NH} 9.25-13.40 ppm) do not permit rejection of either of the tautomeric forms **9** and **10**. However the results of the alkylation and acylation of this indazole [14-16], leading to a mixture of the $N_{(1)}$- and $N_{(2)}$-substituted derivatives, indicate only the real existence of a tautomeric equilibrium.

TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %				mp, °C	Yield, %
		C	H	N	Hal, S		
6Aa	$C_{21}H_{19}BrN_2O$	63.60/63.81	4.70/4.84	6.91/7.09	20.00/22.22	118-119	46
6Ab	$C_{21}H_{19}BrN_2O$	63.66/63.81	4.77/4.84	6.96/7.09	20.10/22.22	182-183	52
6Ac	$C_{21}H_{19}ClN_2O$	71.66/71.89	5.25/5.46	7.90/7.98	10.00/10.10	173	61
6Ad	$C_{21}H_{19}FN_2O$	75.20/75.43	5.63/5.73	8.18/8.38		165	57
6Af	$C_{21}H_{20}N_2O_2$	75.95/75.88	6.00/6.07	8.20/8.43		252-253	54
6Ag	$C_{22}H_{22}N_2O_2$	76.05/76.27	6.39/6.40	7.88/8.09		140-141	65
6Ah	$C_{21}H_{19}N_3O_3$	69.90/69.79	5.22/5.30	11.50/11.63		175-176	28
6Ai	$C_{21}H_{19}N_3O_3$	69.71/69.79	5.21/5.30	11.61/11.63		167-168	45
6Aj	$C_{21}H_{19}N_3O_3$	69.58/69.79	5.26/5.30	11.53/11.63		184-186	51
6Ak	$C_{23}H_{25}N_3O$	77.11/77.28	6.33/6.49	11.64/11.76		201-203	47
6Bb	$C_{19}H_{15}BrN_2O$	62.01/62.14	4.10/4.12	7.50/7.63	21.50/21.76	190-192	55
6Bc	$C_{19}H_{15}ClN_2O$	70.52/70.70	4.55/4.68	8.56/8.68	10.80/10.98	191-192	54
6Bd	$C_{19}H_{15}FN_2O$	74.40/74.49	4.98/4.94	9.00/9.14		133-134	49
6Be	$C_{19}H_{16}N_2O_2$	74.77/74.98	5.18/5.30	9.01/9.20		108-110	41
6Bg	$C_{20}H_{18}N_2O_2$	75.22/75.45	5.66/5.70	8.70/8.80		148-149	47
6Bk	$C_{21}H_{21}N_3O$	76.17/76.10	6.30/6.39	12.51/12.68		173-174	45
7A	$C_{15}H_{20}N_2O_3S$	58.18/58.42	6.60/6.54	8.87/9.08	10.20/10.40	215-216	88
7B	$C_{13}H_{16}N_2O_3S$	55.46/55.70	5.60/5.75	10.11/9.99	11.20/11.44	213-214	84
9Ab	$C_{15}H_{15}BrN_2O$	56.20/56.44	4.66/4.74	8.59/8.78	24.80/25.04	244-245	78
9Ad	$C_{15}H_{15}FN_2O$	69.61/69.75	5.80/5.85	10.66/10.84		198-199	76
9Ae	$C_{15}H_{16}N_2O_2$	70.10/70.29	6.13/6.29	10.88/10.93		246-247	78
9Af	$C_{15}H_{16}N_2O_2$	70.33/70.29	6.20/6.29	10.85/10.93		254-256	61
9Ag	$C_{16}H_{18}N_2O_2$	71.20/71.09	6.70/6.71	10.19/10.36		198-200	75
9Aj	$C_{15}H_{15}N_3O_3$	62.96/63.15	5.11/5.30	14.55/14.73		280-282	75
9Ak	$C_{17}H_{21}N_3O$	71.81/72.05	7.37/7.47	14.70/14.83		216-218	81
9Bb	$C_{13}H_{11}BrN_2O$	53.50/53.63	3.73/3.81	9.49/9.62	27.20/27.45	260-262	77
9Bc	$C_{13}H_{11}ClN_2O$	63.10/63.29	4.42/4.50	11.11/11.35	14.10/14.37	252-254	72
9Bd	$C_{13}H_{11}FN_2O$	67.61/67.81	4.70/4.82	11.98/12.17		210-212	70
9Bf	$C_{13}H_{12}N_2O_2$	68.21/68.41	5.17/5.30	12.09/12.27		264-265	78
9Bg	$C_{14}H_{14}N_2O_2$	69.17/69.40	5.72/5.82	11.35/11.56		216-217	63
9Bk	$C_{15}H_{17}N_3O$	70.50/70.56	6.59/6.71	16.23/16.46		253-255	70

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

Com-pound	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm (*J*, Hz)*
1	2	3
6Aa	1670	1.11 (6H, s, 2CH$_3$); 2.40 (2H, s, CH$_2$); 2.85 (2H, s, CH$_2$); 7.18-7.56 (9H, m, C$_6$H$_5$, C$_6$H$_4$)
6Ab	1668	1.09 (6H, s, 2CH$_3$); 2.41 (2H, s, CH$_2$); 2.81 (2H, s, CH$_2$); 7.01-7.16 (9H, m, C$_6$H$_5$, C$_6$H$_4$)
6Ac	1665	1.12 (6H, s, 2CH$_3$); 2.41 (2H, s, CH$_2$); 2.81 (2H, s, CH$_2$); 7.30-7.32 (9H, m, C$_6$H$_5$, C$_6$H$_4$)
6Ad	1671	1.07 (6H, s, 2CH$_3$); 2.42 (2H, s, CH$_2$); 2.78 (2H, s, CH$_2$); 6.99-7.41 (9H, m, C$_6$H$_5$, C$_6$H$_4$)
6Af	1665; 3400-3250	1.16 (6H, s, 2CH$_3$); 2.36 (2H, s, CH$_2$); 2.81 (2H, s, CH$_2$); 6.78 (2H, m, ^3J = 8, C$_6$H$_4$); 7.24-7.26 (5H, m, C$_6$H$_5$); 7.25 (2H, m, ^3J = 8, C$_6$H$_4$); 8.09 (1H, br. s, OH)
6Ag	1666	1.09 (6H, s, 2CH$_3$); 2.41 (2H, s, CH$_2$); 2.81 (2H, s, CH$_2$); 3.78 (3H, s, OCH$_3$); 6.82 (2H, m, ^3J = 8, C$_6$H$_4$); 7.28-7.30 (7H, m, C$_6$H$_4$, C$_6$H$_5$)
6Ah	1661	1.07 (6H, s, 2CH$_3$); 2.31 (2H, s, CH$_2$); 2.82 (2H, s, CH$_2$); 7.25-8.15 (9H, m, C$_6$H$_4$, C$_6$H$_5$)
6Ai	1656	1.16 (6H, s, 2CH$_3$); 2.42 (2H, s, CH$_2$); 2.86 (2H, s, CH$_2$); 7.15-8.16 (9H, m, C$_6$H$_4$, C$_6$H$_5$)
6Aj	1667	1.11 (6H, s, 2CH$_3$); 2.41 (2H, s, CH$_2$); 2.81 (2H, s, CH$_2$); 7.28-7.30 (5H, m, C$_6$H$_5$); 7.53 (2H, m, ^3J = 8, C$_6$H$_4$); 8.14 (2H, m, ^3J = 8, C$_6$H$_4$)
6Ak	1662	1.16 (6H, s, 2CH$_3$); 2.44 (2H, s, CH$_2$); 2.82 (2H, s, CH$_2$); 2.89 (6H, s, N(CH$_3$)$_2$); 6.62 (2H, m, ^3J = 8, C$_6$H$_4$); 7.28-7.30 (7H, m, C$_6$H$_5$, C$_6$H$_4$)
6Bb	1660	2.16 (2H, m, CH$_2$); 2.52 (2H, t, ^3J = 7, CH$_2$); 2.91 (2H, t, ^3J = 7, CH$_2$); 7.29-7.33 (9H, m, C$_6$H$_5$, C$_6$H$_4$)
6Bc	1664	2.15 (2H, m, CH$_2$); 2.51 (2H, t, ^3J = 7, CH$_2$); 2.92 (2H, t, ^3J = 7, CH$_2$); 7.34-7.36 (9H, m, C$_6$H$_5$, C$_6$H$_4$)
6Bd	1667	2.15 (2H, m, CH$_2$); 2.50 (2H, t, ^3J = 6.5, CH$_2$); 2.95 (2H, t, ^3J = 6.5, CH$_2$); 7.15-7.35 (9H, m, C$_6$H$_5$, C$_6$H$_4$)
6Be	1660; 3400-3250	2.17 (2H, m, CH$_2$); 2.54 (2H, t, ^3J = 6.5, CH$_2$); 2.92 (2H, t, ^3J = 6.5, CH$_2$); 6.59-7.29 (9H, m, C$_6$H$_5$, C$_6$H$_4$); 8.45 (1H, br. s, OH)
6Bg	1664	2.17 (2H, m, CH$_2$); 2.52 (2H, t, ^3J = 6.5, CH$_2$); 2.92 (2H, t, ^3J = 6.5, CH$_2$); 3.73 (3H, s, OCH$_3$); 6.89 (2H, m, ^3J = 9, C$_6$H$_4$); 7.24-7.26 (7H, m, C$_6$H$_5$, C$_6$H$_4$)
6Bk	1668	2.15 (2H, m, CH$_2$); 2.53 (2H, t, ^3J = 6.5, CH$_2$); 2.89 (2H, t, ^3J = 6.5, CH$_2$); 2.90 (6H, s, N(CH$_3$)$_2$); 6.59 (2H, m, ^3J = 9, C$_6$H$_4$); 7.19 (2H, m, ^3J = 9, C$_6$H$_4$); 7.28-7.30 (5H, m, C$_6$H$_5$)
7A	1600; 3250-3150	0.92 (6H, s, 2CH$_3$); 1.90 (2H, s, CH$_2$); 2.05 (2H, s, CH$_2$); 2.37 (3H, s, CH$_3$); 5.05 (1H, s, =CH-); 7.40 (2H, m, ^3J = 6, C$_6$H$_4$); 7.71 (2H, m, ^3J = 6, C$_6$H$_4$); 8.62 (1H, br. s, NH); 9.74 (1H, br. s, NH)
7B	1595; 3250-3150	1.61-2.27 (6H, m, 3CH$_2$); 2.41 (3H, s, CH$_3$); 5.07 (1H, s, =CH-); 7.40 (2H, m, ^3J = 6, C$_6$H$_4$); 7.69 (2H, m, ^3J = 6, C$_6$H$_4$); 8.59 (1H, br. s, NH); 9.70 (1H, br. s, NH)
9Ab	1626; 3100	1.01 (6H, s, 2CH$_3$); 2.37 (2H, s, CH$_2$); 2.81 (2H, s, CH$_2$); 7.54 (2H, m, ^3J = 8.5, C$_6$H$_4$); 7.87 (2H, m, ^3J = 8.5, C$_6$H$_4$); 9.25 (1H, br. s, NH)
9Ad	1621; 3140-3080	1.03 (6H, s, 2CH$_3$); 2.36 (2H, s, CH$_2$); 2.49 (2H, s, CH$_2$); 6.96-7.17 (2H, m, C$_6$H$_4$); 7.86-8.06 (2H, m, C$_6$H$_4$); 11.16 (1H, br. s, NH)
9Ae	1623; 3400, 3120	1.11 (6H, s, 2CH$_3$); 2.45 (2H, s, CH$_2$); 2.76 (2H, s, CH$_2$); 6.83-7.34 (3H, m, C$_6$H$_4$); 8.76-8.78 (1H, m, C$_6$H$_4$); 10.98 (2H, br. s, NH, OH)
9Af	1620; 3450, 3100	1.00 (6H, s, 2CH$_3$); 2.34 (2H, s, CH$_2$); 2.68 (2H, s, CH$_2$); 6.78 (2H, m, ^3J = 9, C$_6$H$_4$); 7.93 (2H, m, ^3J = 9, C$_6$H$_4$); 9.80 (1H, br. s, NH); 12.37 (1H, br. s, OH)

TABLE 2 (continued)

1	2	3
9Ag	1630; 3150-3050	1.07 (6H, s, $2CH_3$); 2.34 (2H, s, CH_2); 2.74 (2H, s, CH_2); 3.82 (3H, s, OCH_3); 6.92 (2H, m, ^3J = 8.5, C_6H_4); 8.04 (2H, m, ^3J = 8.5, C_6H_4); 10.80 (1H, br. s, NH)
9Aj	1625; 3130-3050	1.05 (6H, s, $2CH_3$); 2.38 (2H, s, CH_2); 2.75 (2H, s, CH_2); 8.31-8.33 (4H, m, C_6H_4); 11.7 (1H, br. s, NH)
9Ak	1626; 3150-3050	1.03 (6H, s, $2CH_3$); 2.28 (2H, s, CH_2); 2.65 (2H, s, CH_2); 2.97 (6H, s, $2CH_3$); 6.77 (2H, m, ^3J = 8, C_6H_4); 7.99 (2H, m, ^3J = 8, C_6H_4); 13.1 (1H, br. s, NH)
9Bb	1630; 3100	2.08 (2H, m, CH_2); 2.47 (2H, t, ^3J = 6.5, CH_2); 2.89 (2H, t, ^3J = 6.5, CH_2); 7.49 (2H, m, ^3J = 8, C_6H_4); 8.09 (2H, m, ^3J = 8, C_6H_4); 13.27 (1H, br. s, NH)
9Bc	1632; 3120-3070	1.93-2.97 (6H, m, $3CH_2$); 7.47 (2H, m, ^3J = 8, C_6H_4); 8.11 (2H, m, ^3J = 8, C_6H_4); 13.4 (1H, br. s, NH)
9Bd	1626; 3100-3050	2.16 (2H, m, CH_2); 2.50 (2H, t, ^3J = 6.5, CH_2); 2.87 (2H, t, ^3J = 6.5, CH_2); 7.02-7.21 (2H, m, C_6H_4); 8.01-8.17 (2H, m, C_6H_4); 12.51 (1H, br. s, NH)
9Bf	1634; 3400-3100	1.99-2.32 (6H, m, $3CH_2$); 6.80 (2H, m, ^3J = 8.5, C_6H_4); 7.91 (2H, m, ^3J = 8.5, C_6H_4); 9.66 (1H, br. s, OH); 13.16 (1H, br. s, NH)
9Bg	1630; 3100	2.11 (2H, m, CH_2); 2.52 (2H, t, ^3J = 6.5, CH_2); 2.89 (2H, t, ^3J = 6.5, CH_2); 3.75 (3H, s, OCH_3); 6.94 (2H, m, ^3J = 9, C_6H_4); 8.02 (2H, m, ^3J = 9, C_6H_4); 12.7 (1H, br. s, NH)
9Bk	1630; 3120-3070	2.11 (2H, m, CH_2); 2.51 (2H, t, ^3J = 6.5, CH_2); 2.92 (2H, t, ^3J = 6.5, CH_2); 2.98 (6H, s, $N(CH_3)_2$); 6.77 (2H, m, ^3J = 9, C_6H_4); 7.97 (2H, m, ^3J = 9, C_6H_4); 12.51 (1H, br. s, NH)

* Spectra were taken in $CDCl_3$ (compounds **6Aa-Ak, Bb-Be, Bg, Bk, 9Ab, Ad, Ae, Ag, Bd**), DMSO-d_6 (compounds **7A,B, 9Af, Aj, Ak, Bb, Bc, Bf**), and $CDCl_3$ + DMSO-d_6 (compounds **9Bg, Bk**).

EXPERIMENTAL

The IR spectra were taken on a Specord 75-IR instrument for suspensions of substances in nujol (1500-1800 cm^{-1}) and in hexachlorobutadiene (2000-3600 cm^{-1}). Only the absorption bands of the carbonyl group are given in the 1500-1800 cm^{-1} region. The absorption bands of the stretching vibrations of C–H bonds in the 2800-3050 cm^{-1} region are not given. The ^1H NMR spectra were recorded on a Bruker WH/90DS (90 MHz) instrument in $CDCl_3$ and DMSO-d_6, internal standard was TMS.

3-(3-Bromophenyl)- (6Aa), 3-(4-Bromophenyl)- (6Ab), 3-(4-Chlorophenyl)- (6Ac), 3-(4-Fluorophenyl)- (6Ad), 3-(4-Hydroxyphenyl)- (6Af), 3-(4-Methoxyphenyl)- (6Ag), 3-(2-Nitrophenyl)- (6Ah), 3-(3-Nitrophenyl)- (6Ai), 3-(4-Nitrophenyl)- (6Aj), and 3-(4-Dimethylaminophenyl)-6,6-dimethyl-4-oxo-2-phenyl-4,5,6,7-tetrahydroindazoles (6Ak) (General Procedure). A mixture of phenylhydrazone **3A** (4 mmol) and the appropriate aldehyde **4** (4 mmol) in DMSO (5 ml) with added glacial AcOH (0.2 ml) and piperidine (0.8 ml) was heated on a boiling water bath for 3 h. After cooling, the reaction mixture was diluted with water (30-40 ml) with stirring, the precipitated solid was triturated, filtered off, and recrystallized from ethanol.

3-(4-Bromophenyl)- (6Bb), 3-(4-Chlorophenyl)- (6Bc), 3-(4-Fluorophenyl)- (6Bd), 3-(2-Hydroxyphenyl)- (6Be), 3-(4-Methoxyphenyl)- (6Bg), 3-(4-Dimethylaminophenyl)-4-oxo-2-phenyl-4,5,6,7-tetrahydroindazoles (6Bk) (General Procedure). A mixture of phenylhydrazone **3B** (4 mmol) and the appropriate aldehyde **4** (4 mmol) in DMSO (5 ml) with added glacial AcOH (0.2 ml) and piperidine (0.8 ml) was heated on a boiling water bath for 2 h. Water (30-40 ml) was then added with stirring to the reaction mixture, the solid was triturated, and filtered off. Indazoles **6Bb,e** were recrystallized from ethanol, and indazoles **6Bc,d,g,k** from an ethanol–water, 2:1 mixture.

5,5-Dimethyl-3-tosylhydrazinocyclohex-2-en-1-one (7A). Solutions of dimedone (2.80 g, 20 mmol) in glacial AcOH (20 ml) and tosylhydrazine (3.72 g, 20 mmol) in glacial AcOH (20 ml) were prepared separately, then mixed, and the mixture heated for 10 min on a boiling water bath. Water (20 ml) was added to the hot mixture. The mixture was cooled, the solid enehydrazine **7A** was filtered off, and recrystallized from ethanol.

3-Tosylhydrazinocyclohex-2-en-1-one (7B). Solutions of cyclohexane-1,3-dione (2.24 g, 20 mmol) in water (20 ml) and tosylhydrazine (3.72 g, 20 mmol) in 80% AcOH (20 ml) were prepared separately, then mixed, and the mixture heated for 3-5 min on a boiling water bath. Further water (25 ml) was added to the hot reaction mixture, which was then cooled. The solid enehydrazine **7B** was filtered off, and recrystallized from ethanol.

3-(4-Bromophenyl)- (9Ab), 3-(4-Fluorophenyl)- (9Ad), 3-(2-Hydroxyphenyl)- (9Ae), 3-(4-Hydroxyphenyl)- (9Af), 3-(4-Methoxyphenyl)- (9Ag), 3-(4-Nitrophenyl)- (9Aj), 3-(4-Dimethylaminophenyl)-6,6-dimethyl-4-oxo-4,5,6,7-tetrahydroindazoles (9Ak) (General Procedure). Enehydrazine **7A** (4 mmol) was dissolved with heating in DMSO (5 ml), glacial AcOH (0.2-0.3 ml) was added, then the appropriate aldehyde (4 mmol) (the solid substance was previously dissolved in the minimum quantity of DMSO), and finally piperidine (0.8 ml) was added. The reaction mixture was heated for 2 h on a boiling water bath, on cooling water (50-60 ml) was added with stirring, the precipitated solid was triturated, then filtered off, and recrystallized from 80% ethanol.

3-(4-Bromophenyl)- (9Bb), 3-(4-Chlorophenyl)- (9Bc), 3-(4-Fluorophenyl)- (9Bd), 3-(4-Hydroxyphenyl)- (9Bf), 3-(4-Methoxyphenyl)- (9Bg), and 3-(4-Dimethylaminophenyl)-4-oxo-4,5,6,7-tetrahydroindazole (9Bk) (General Procedure). Enehydrazine **7B** (4 mmol) was dissolved with heating in DMSO (5 ml), glacial AcOH (0.2 ml) was added, then the appropriate aldehyde (4 mmol) or a solution of it in DMSO was added dropwise, and finally piperidine (0.8 ml) was added. The reaction mixture was heated on a boiling water bath for 1.5-2 h, after cooling, water (50-60 ml) was added with stirring, the precipitated solid was triturated, filtered off, and recrystallized from ethanol.

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