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SYNTHESIS AND REACTIONS OF 1-(4-CHLORO-, 3-CHLORO-, 2-CHLORO-, 2,4-DICHLORO-, AND 2,4-DIFLUOROPHENYL)-6,6-DIMETHYL-4-OXO-4,5,6,7-TETRAHYDROINDAZOLES

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Reaction of the potassium salt of 2-formyldimedone with hydrochlorides of 4-chloro-, 3-chloro-, 2-chloro-, 2,4-dichloro-, and 2,4-difluorophenylhydrazines gave the corresponding 2-arylhydrazinomethylene-dimedones which cyclized in acid media to 1-substituted 6,6-dimethyl-4-oxo-4,5,6,7-tetrahydroindazoles. Oxidation of the latter with selenious acid gave the corresponding 4,5-dioxo-4,5,6,7-tetrahydroindazoles which were further converted into 3-aryl-5,5-dimethyl-4,5-dihydro-3H-pyrazolo[4,3-a]phenazines and 2,6-diaryl-4,4-dimethyl-4,5-dihydro-1H(3H)-indazolo[4,5-g]imidazoles.

Keywords: 2,6-diaryl-4,4-dimethyl-4,5-dihydro-1H(3H)-indazolo[4,5-*g*]imidazoles, 4,5-dioxo- and 4-oxo-1-halophenyl-6,6-dimethyl-4,5,6,7-tetrahydroindazoles.

Bearing in mind the importance of modifying a number of indazoles with the objective of preparing biologically active compounds [1-10], in continuation of work [11] we synthesized a series of 1-halophenyl-4-oxo-4,5,6,7-tetrahydroindazoles and prepared some of their derivatives.

We obtained the corresponding 2-hydrazinomethylene derivatives of dimedone (**3**) from the reaction of the potassium salt of 2-formyldimedone (**1**) with the hydrochlorides of 4-chloro-, 3-chloro-, 2-chloro-, 2,4-dichloro-, and 2,4-difluorophenylhydrazines (**2**). These compounds were converted into 1-substituted 4-oxo-6,6-dimethyl-4,5,6,7-tetrahydroindazoles (**4**) on boiling in ethanol in the presence of hydrochloric acid. Oxidation of these ketones with selenious acid by a method [11, 12] gave the corresponding 4,5-dioxo-4,5,6,7-tetrahydroindazoles only with compounds **4a** and **4b**. Oxidation of the indazoles **4c-e** by this method gave resinous products from which it was not possible to isolate pure products. Therefore we boiled the compounds in dioxane with selenious acid to oxidize the indazoles **4c-e**. Resinous materials were formed again but the individual products, separated by thin-layer chromatography, were shown to be the hydrated forms of the 4,5-dioxo derivatives by IR spectroscopy (two carbonyl frequencies in the 1730-1670 cm^{-1} region, absorptions at 3400-3100 cm^{-1}). Heating these for a short time at 160-170°C gave the individual α-diketones **5c-e**. Reaction of the 4,5-dioxo compounds **5a,c,e** with equimolar amounts of hydroxylamine, isonicotinic and salicylic acid hydrazides gave the corresponding carbonyl derivatives at the more electrophilic $C_{(5)}$-carbonyl [11]. Reaction of the same α-diketones **5a,c,e** with *o*-phenylenediamine gave pyrazolo[4,3-*a*]phenazines **7a,c,d**. Reaction of the diketone **5a** with 2,3-diaminopyridine gave a single reaction product which we ascribe the structure 3-(4-chlorophenyl)-5,5-dimethyl-4,5-dihydro-3H-10-azapyrazolo[4,3-*a*]phenazine (**7b**), since the amino group at $C_{(3)}$ in 2,3-diaminopyridine is the better nucleophile.

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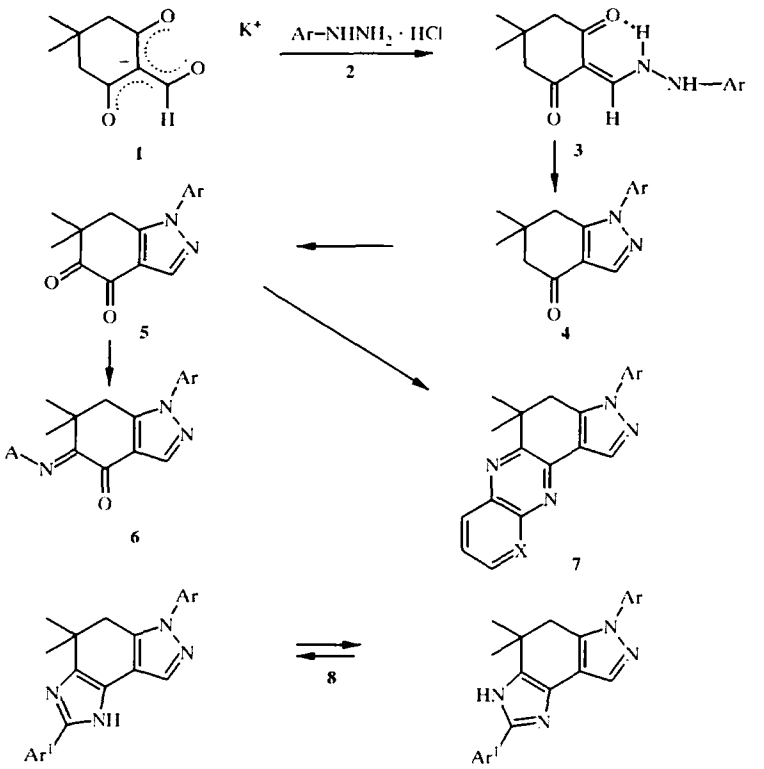
The reaction of the diketones **5a,b,e** with aromatic aldehydes and ammonium acetate according to a method [12, 13] gave 2,6-diaryl-4,4-dimethyl-4,5-dihydro-1H(3H)-indazolo[4,5-*d*]imidazoles (**8a-e**).



2-5a Ar = C_6H_4Cl-4; **b** C_6H_4Cl-3; **c** C_6H_4Cl-2; **d** $C_6H_3Cl_2$-2,4; **e** $C_6H_3F_2$-2,4.
6a Ar = C_6H_4Cl-4, A = OH; **b** Ar = C_6H_4Cl-4; A = $NHCOC_5H_4N$-4; **c** Ar = C_6H_4Cl-2, A = $NHCOC_6H_4OH$-2; **d** Ar = $C_6H_3F_2$-2,4, A = $NHCOC_5H_4N$-4. **7a** Ar = C_6H_4Cl-4, X = CH; **b** Ar = C_6H_4Cl-4, X = N; **c** Ar = C_6H_4Cl-2, X = CH; **d** Ar = $C_6H_3F_2$-2,4, X = CH.
8a Ar = C_6H_4Cl-4, Ar' = $C_6H_4N(CH_3)_2$-4; **b** Ar = C_6H_4Cl-4, Ar' = C_6H_4OH-4; **c** Ar = C_6H_4Cl-3, Ar' = $C_6H_4N(CH_3)_2$-4; **d** Ar = C_6H_4Cl-3, Ar' = C_6H_4OH-4; **e** Ar = $C_6H_3F_2$-2,4, Ar' = $C_6H_4N(CH_3)$-4; **f** Ar = C_5H_4N-2, Ar' = C_6H_4Br-4; **g** Ar = C_5H_4N-2, Ar' = $C_6H_4NO_2$-3; **h** Ar = C_5H_4N-2, A = $C_6H_4(OCH_3)_2$-3,4; **i** Ar = C_5H_4N-2, Ar' = $C_6H_3O_2CH_2$-3,4

1-(2-Pyridyl)-3,6,6-trimethyl-4,5-dioxo-4,5,6,7-tetrahydroindazole [11] also underwent this reaction to give indazolo[4,5-*d*]imidazoles **8f-i**.

The structures of the compounds synthesized were confirmed by ^{1}H NMR and IR spectroscopy. Comparison of the spectral characteristics of known compounds [12, 15] and the 2-hydrazinomethylene derivatives **3** and tetrahydroindazoles **4, 5** prepared in this work shows very similar patterns. For example, in the indazoles **4** the signals of the $C_{(7)}$-methylene groups appear at weaker field (2.50-2.82 ppm) than the signals of the $C_{(5)}$-methylene groups (2.36-2.41 ppm). Intense carbonyl frequencies are observed for the ketones **4** at 1676-1668 cm^{-1}, whereas the α-diketones are characterized by carbonyl frequencies at 1730-1723 cm^{-1} and 1691-1676 cm^{-1}.

The ^{1}H NMR spectra of the indazoloimidazoles **8a-d** show that they exist in DMSO solutions as a 1:1 equilibrium mixture of the 1-H and 3-H forms, and the low field absorption of NH-proton appears as two signals of equal intensity, the total integrated intensity of which corresponds to one proton. A more rapid exchange process occurs for compounds **8e-i** as a result of which the NH resonance appears as a broad signal at 9.30-12.00 ppm.

TABLE 1. Characteristics of the Synthesized Compounds **3-8**

Compound	Empirical formula	Found, % / Calculated, %				mp, °C	Yield, %
		C	H	N	Cl		
3a	$C_{15}H_{17}ClN_2O_2$	61.31 / 61.54	5.80 / 5.85	9.44 / 9.57	12.00 / 12.11	192-194	95
3b	$C_{15}H_{17}ClN_2O_2$	61.50 / 61.54	5.86 / 5.85	9.39 / 9.57	12.10 / 12.11	192-193	94
3c	$C_{15}H_{17}ClN_2O_2$	61.28 / 61.54	5.76 / 5.85	9.41 / 9.57	11.90 / 12.11	152-153	90
3d	$C_{15}H_{16}Cl_2N_2O_2$	55.19 / 55.06	4.90 / 4.93	8.45 / 8.56	21.50 / 21.67	195-196	78
3e	$C_{15}H_{16}F_2N_2O_2$	61.02 / 61.22	5.40 / 5.48	9.37 / 9.52		169-170	95
4a	$C_{15}H_{15}ClN_2O$	65.42 / 65.57	5.50 / 5.50	10.08 / 10.20	12.80 / 12.90	134-135	88
4b	$C_{15}H_{15}ClN_2O$	65.50 / 65.57	5.54 / 5.50	10.15 / 10.20	12.90 / 12.90	137-138	62
4c	$C_{15}H_{15}ClN_2O$	65.36 / 65.57	5.42 / 5.50	10.06 / 10.20	12.70 / 12.90	91-92	84
4d	$C_{15}H_{14}Cl_2N_2O$	58.07 / 58.27	4.50 / 4.56	9.11 / 9.06	22.80 / 22.93	125-126	82
4e	$C_{15}H_{14}F_2N_2O$	61.05 / 61.22	5.46 / 5.48	9.40 / 9.52		105-106	92
5a	$C_{15}H_{13}ClN_2O_2$	62.20 / 62.39	4.49 / 4.54	9.57 / 9.70	12.20 / 12.28	136-138	63
5b	$C_{15}H_{13}ClN_2O_2$	62.26 / 62.39	4.41 / 4.54	9.61 / 9.70	12.20 / 12.28	195-196	65
5c	$C_{15}H_{13}ClN_2O_2$	62.16 / 62.39	4.41 / 4.54	9.52 / 9.70	12.10 / 12.28	125-126	37
5d	$C_{15}H_{12}Cl_2N_2O_2$	55.50 / 55.75	3.66 / 3.74	8.51 / 8.67	21.70 / 21.94	132-133	81
5e	$C_{15}H_{12}F_2N_2O_2$	62.12 / 62.07	4.10 / 4.17	9.60 / 9.65		151-152	85
6a	$C_{15}H_{14}ClN_3O_2$	59.12 / 59.31	4.48 / 4.65	13.66 / 13.83	11.50 / 11.67	139-140	43
6b	$C_{21}H_{18}ClN_3O_2$	61.62 / 61.84	4.36 / 4.45	17.01 / 17.17	8.47 / 8.69	222-223	44
6c	$C_{22}H_{19}ClN_4O_3$	62.30 / 62.49	4.42 / 4.53	13.08 / 13.25	8.30 / 8.38	197-200	52
6d	$C_{21}H_{17}F_2N_3O_2$	61.45 / 62.61	4.14 / 4.19	17.02 / 17.11		168-169	64
7a	$C_{21}H_{17}ClN_4$	69.73 / 69.90	4.70 / 4.75	15.46 / 15.53	9.70 / 9.82	149-150	72
7b	$C_{20}H_{16}ClN_5$	66.20 / 66.39	4.37 / 4.46	19.28 / 19.36	9.60 / 9.80	218-220	46
7c	$C_{21}H_{17}ClN_4$	69.70 / 69.90	4.71 / 4.75	15.42 / 15.53	9.70 / 9.82	153-154	46
7d	$C_{21}H_{16}F_2N_4$	69.36 / 69.60	4.31 / 4.45	15.50 / 15.46		200 (subl.)	73
8a	$C_{21}H_{24}ClN_5$	68.77 / 68.97	5.61 / 4.79	16.58 / 16.76	8.50 / 9.48	306-307	72
8b	$C_{22}H_{19}ClN_4O$	67.42 / 67.60	4.88 / 4.90	14.11 / 14.36	9.05 / 9.07	348-349	68
8c	$C_{24}H_{24}ClN_5$	68.75 / 68.97	5.60 / 5.79	16.61 / 16.76	8.30 / 8.48	308-310	66
8d	$C_{22}H_{19}ClN_4O$	67.37 / 67.60	4.80 / 4.90	14.14 / 14.36	8.90 / 9.07	336-337	58
8e	$C_{24}H_{23}F_2N_5$	68.60 / 68.72	5.38 / 5.53	16.72 / 16.70		291-292	54
8f	$C_{22}H_{20}BrN_5$	60.66 / 60.83	4.51 / 4.65	16.01 / 16.12	18.20 / 18.39	162-164	27
8g	$C_{22}H_{20}N_6O_2$	65.80 / 65.98	4.97 / 5.04	20.77 / 20.99		257-259	81
8h	$C_{24}H_{25}N_5O_2$	69.13 / 69.37	5.89 / 6.01	16.68 / 16.86		165-268	25
8i	$C_{23}H_{21}N_5O_2$	68.90 / 68.15	5.14 / 4.31	17.31 / 17.53		250-253	25

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

Compound	IR spectra, ν, cm^{-1}	^{1}H NMR spectra, δ, ppm (A – $CDCl_3$, B – DMSO-d_6)
3a	1645, 1605-1585, 1540; 3260, 3180, 3130, 3060	A. 1.07 (6H, s, $2CH_3$); 2.32 (2H, s, CH_2); 2.41 (2H, s, CH_2); 6.74 (2H, m, ^3J = 9 Hz, C_6H_4); 7.14 (4H, m, ^3J = 9 Hz, C_6H_4); 8.21 (1H, d, ^3J = 13 Hz, =CH–); 8.45 (1H, br. s, NH); 12.12 (1H, d, ^3J = 13 Hz, NH)
3b	1667, 1605-1580, 1535, 1500; 3250, 3170, 3120	A. 1.05 (6H, s, $2CH_3$); 2.34 (2H, s, CH_2); 2.43 (2H, s, CH_2); 6.62-7.22 (4H, m, C_6H_4); 8.25 (1H, d, ^3J = 10 Hz, =CH–); 8.50 (1H, br. s, NH); 11.94 (1H, d, ^3J = 10 Hz, NH)
3c	1655, 1605-1585, 1555; 3230, 3130, 3080	B. 0.93 (6H, s, $2CH_3$); 2.24 (2H, s, CH_2); 2.29 (2H, s, CH_2); 6.76-7.24 (4H, m, C_6H_4); 8.00 (1H, d, ^3J = 11 Hz, =CH–); 8.71 (1H, br. s, NH); 11.91 (1H, d, ^3J = 11 Hz, NH)
3d	1648, 1590-1575, 1520; 3210, 3150, 3070	B. 0.98 (6H, s, $2CH_3$); 2.27 (2H, s, CH_2); 2.36 (2H, s, CH_2); 6.78 (1H, ^3J = 9 Hz, C_6H_3); 7.29 (1H, dd, ^3J = 9, ^4J = 2 Hz, C_6H_3); 7.49 (1H, d, ^3J = 2 Hz, C_6H_3); 8.05 (1H, d, J = 10 Hz, =CH–); 8.93 (1H, br. s, NH); 11.92 (1H, d, J = 10 Hz, NH)
3e	1661, 1593,1519; 3270, 3160	1.02 (6H, s, $2CH_3$); 2.25 (2H, s, CH_2); 2.37 (2H, s, CH_2); 6.85-7.42 (3H, m, C_6H_3); 8.15 (1H, d, ^3J = 12 Hz, =CH–); 8.57 (1H, br. s, NH); 11.98 (1H, d, ^3J = 12 Hz, NH)
4a	1668, 1605, 1550	A. 1.10 (6H, s, $2CH_3$); 2.40 (2H, s, CH_2); 2.61 (2H, s, CH_2); 7.44 (4H, m, C_6H_4); 8.05 (1H, s, =CH–)
4b	1672, 1594, 1546	A. 1.12 (6H, s, $2CH_3$); 2.41 (2H, s, CH_2); 2.82 (2H, s, CH_2); 7.45 (4H, m, C_6H_4); 8.10 (1H, s, =CH–)
4c	1672, 1596, 1546, 1506	A. 1.06 (6H, s, $2CH_3$); 2.36 (2H, s, CH_2); 2.53 (2H, s, CH_2); 7.47 (4H, m, C_6H_4); 8.08 (1H, s, =CH–)
4d	1676, 1590,1546, 1555, 1508	A. 1.08 (6H, s, $2CH_3$); 2.36 (2H, s, CH_2); 2.50 (2H, s, CH_2); 7.30-7.49 (3H, m, C_6H_3); 8.01 (1H, s, =CH–)
4e	1681, 1609, 1523	A. 1.07 (6H, s, $2CH_3$); 2.36 (2H, s, CH_2); 2.56 (2H, s, CH_2); 6.90-7.40 (3H, m, C_6H_3); 7.96 (1H, s, =CH–)
5a	1730, 1686, 1538, 1500	A. 1.31 (6H, s, $2CH_3$); 3.16 (2H, s, CH_2); 7.45 (4H, centr m, C_6H_4); 8.14 (1H, s, =CH–)
8a	1615, 1580, 1545	B. 1.28 (6H, s, $2CH_3$); 2.93 (8H, s, CH_2, $N(CH_3)_2$); 6.80 (2H, m, ^3J = 9 Hz, C_6H_4); 7.54-7.82 (7H, m, $2C_6H_4$, =CH–); 11.81 (0.5H, br. s, NH); 12.30 (0.5H, br. s, NH)
8b	1618, 1578, 1542; 3100, 2800-2600	B. 1.27 (6H, s, $2CH_3$); 2.98 (2H, s, CH_2); 6.87 (2H, m, ^3J = 9 Hz, C_6H_4); 7.56-7.76 (7H, m, $2C_6H_4$, =CH–); 9.53 (1H, s, OH); 11.87 (0.5H, br. s, NH); 12.29 (0.5 H, br. s, NH)
8c	1605, 1595, 1525; 3070	B. 1.30 (6H, s, $2CH_3$); 2.93 (6H, s, $N(CH_3)_2$); 3.02 (2H, s, CH_2); 6.82 (2H, m, ^3J = 9 Hz, C_6H_4); 7.47-7.83 (7H, m, $2C_6H_4$, =CH–); 11.70 (0.5H, br. s, NH); 1.25 (0.5 H, br. s, NH)
8d	1605, 1595, 1525; 3100	B. 1.26 (6H, s, $2CH_3$); 3.00 (2H, s, CH_2); 6.85 (2H, m, ^3J = 9 Hz, C_6H_4); 7.42-7.89 (7H, m, $2C_6H_4$, =CH–); 9.49 (1H, s, OH); 1.90 (0.5 H, br. s, NH); 12.30 (0.5 H, br. s, NH)
8e	1617, 1560, 1545, 1525; 3100	B. 1.25 (6H, s, $2CH_3$); 2.65 (2H, s, CH_2); 2.92 (6H, s, $N(CH_3)_2$); 8.76 (2H, m, ^3J = 9 Hz, C_6H_4); 7.14-7.83 (6H, m, C_6H_4, C_6H_3, =CH–); 7.50 (1H, s, =CH–); 11.76 (1H, br. s, NH)
8f	1605, 1595, 1586, 1530; 3160	A. 1.24 (6H, s, $2CH_3$); 2.51 (3H, s, CH_3); 3.35 (2H, s, CH_2); 7.02-8.30 (8H, m, C_6H_4, C_5H_4N); 11.14 (1H, br. s, NH)
8g	1605, 1594, 1510; 3300	A. 1.22 (6H, s, $2CH_3$); 2.45 (3H, s, CH_3); 3.28 (2H, s, CH_2); 7.06-8.80 (8H, m, C_6H_4, C_5H_4N); 12.00 (1H, br. s, NH)
8h	1590, 1570, 1550, 1505; 3240	A. 1.26 (6H, s, $2CH_3$); 2.55 (3H, s, CH_3); 3.44 (2H, s, CH_2); 3.90 (6H, s, $2OCH_3$); 6.90-8.44 (7H, m, C_6H_3, C_5H_4N); 8.85 (1H, br. s, NH)
8i	1594, 1588, 1568, 1510; 3200	A. 1.26 (6H, s, $2CH_3$); 2.55 (3H, s, CH_3); 3.44 (2H, s, CH_2); 5.96 (2H, s, OCH_2O); 7.02-8.33 (7H, m, C_6H_3, C_5H_4N); 8.95 (1H, br. s, NH)

EXPERIMENTAL

IR spectra in nujol (1800-1500 cm^{-1}) or hexachlorobutadiene mulls (3600-2000 cm^{-1}; C–H stretching vibrations in the 3050-2800 cm^{-1} region are not reported) were recorded on a Specord IR-75 spectrometer. ^1H NMR spectra in $CDCl_3$ or DMSO-d_6 solutions with TMS as internal standard were recorded on a Bruker WH-90/DS spectrometer (90 MHz).

Halogen-substituted phenylhydrazine hydrochlorides were obtained from the Acros company. General synthetic procedures were used. Characteristics of the compounds synthesized are given in Table 1 and IR and ^1H NMR spectra are given in Table 2.

2-(4-Chlorophenylhydrazinomethylene)- (3a), 2-(3-Chlorophenylhydrazinomethylene)- (3b), 2-(2-Chlorophenylhydrazinomethylene)- (3c), 2-(2,4-Dichlorophenylhydrazinomethylene)- (3d), and 2-(2,4-Difluorophenylhydrazinomethylene)- (3e) 5,5-Dimethyl-1,3-cyclohexandiones. A solution of the corresponding halogenophenylhydrazine hydrochloride (5 mmol) in distilled water (40 ml), heated to 80-90°C, was added to a solution of the potassium salt of 2-formyldimedone (5 mmol) in distilled water (40 ml) heated to the same temperature. The precipitate of compound **3** was filtered after cooling and recrystallized from ethanol.

1-(4-Chloro- (4a), 3-Chloro- (4b), 2-Chloro- (4c), 2,4-Dichloro- (4d), and 2,4-Difluoro- (4e) Phenyl)-6,6-Dimethyl-4-oxo-4,5,6,7-tetrahydroindazoles. The corresponding hydrzinomethylene derivatives **3a-e** (5 mmol) in ethanol (40 ml) in the presence of conc. hydrochloric acid (1 ml) were boiled for 3 h, two volumes of water were added, and the mixture was kept in a refrigerator for 24 h. In the case of compound **4e** two thirds of the ethanol was removed on a rotary evaporator after boiling and water was then added to give a volume of 50 ml. The precipitated indazole was filtered off and recrystallized from 1:1 ethanol–water.

1-(4-Chlorophenyl)- (5a) and 1-(3-Chlorophenyl)- (5b) 6,6-Dimethyl-4,5-dioxo-4,5,6,7-tetrahydroindazoles. A mixture of indazole **4a,b** (5 mmol), finely powdered selenious acid (5 mmol), glacial acetic acid (15 ml), and conc. H_2SO_4 (0.5 ml) was kept at 20°C for 10 days with occasional shaking, then heated for 5 min on a boiling water bath, and the hot mixture was filtered from the black selenium precipitate.

In the case of compound **5a** an equal volume of water and 15% aqueous ammonia (30 ml) were added to the filtrate. The precipitate was filtered off and recrystallized from glacial acetic acid.

Compound **5b** separated well from the filtrate on cooling. It was filtered off and recrystallized from glacial acetic acid.

1-(2-Chlorophenyl)- (5c), 1-(2,4-Dichlorophenyl)- (5d), and 1-(2,4-Difluorophenyl)- (5e) 6,6-Dimethyl-4,5-dioxo-4,5,6,7-tetrahydroindazoles. A mixture of compound **4c-e** (10 mmol), finely powdered selenious acid (10 mmol), and conc. H_2SO_4 (0.6 ml) in dioxane (40 ml) was boiled for 8 h, filtered, two thirds of the solvent was distilled off, and water (20 ml) was added, followed by 15% aqueous ammonia to basify the solution. The water–dioxane solution was removed from the oily product, which was then kept in the same flask for 10 min at 160-170°C (bath temperature). The products which solidified on cooling were recrystallized from a 1:3 ethyl acetate–hexane mixture.

1-(4-Chlorophenyl)-5-hydroximino-6,6-dimethyl-4-oxo-4,5,6,7-tetrahydroindazole (6a). Diketone **5a** (5 mmol), and equimolar amounts of hydroxylamine hydrochloride and potassium carbonate were boiled for 3 h in ethanol (50 ml). The mixture was cooled, water (100 ml) was added, the precipitate was filtered off and recrystallized from 50% ethanol.

1-(4-Chlorophenyl)-5-isonicotinoylhydrazono- (6b), 1-(2-Chlorophenyl)-5-(2-hydroxybenzoyl-hydrazono)- (6c), and 1-(2,4-Difluorophenyl)-5-isonicotinoylhydrazono- (6d) 6,6-Dimethyl-5-oxo-4,5,6,7-tetrahydroindazoles. Diketone **5a,c,e** (5 mmol) and isonicotinc or salicylic acid hydrazide (5 mmol) were boiled in ethanol (50 ml) for 3h. Water (50 ml) was added and the mixture was kept in a refrigerator for one day. The precipitate of **6b** was recrystallized from ethanol, while compounds **6c** and **6d** were recrystallized from 50% ethanol.

3-(4-Chlorophenyl)- (7a), 3-(2-Chlorophenyl)- (7c), and 3-(2,4-Difluorophenyl)- (7d) 5,5-Dimethyl-4,5-dihydro-3H-pyrazolo[4,3-*a*]phenazines. Diketones **5a,c,e** (3 mmol), *o*-phenylenediamine (3 mmol), and KOH (0.05 g) in absolute ethanol (30 ml) were boiled for 5 h. The reaction mixture was diluted with an equal volume of water, the precipitate of compound **7** was filtered off and recrystallized from ethanol.

3-(4-Chlorophenyl)-5,5-dimethyl-4,5-dihydro-3H-10-azapyrazolo[4,3-*a*]phenazine (7b) which was obtained analogously to **7a,c,d** from diketone **5a** and 2,3-diaminopyridine. The product was recrystallized from 50% ethanol.

2-(4-Dimethylaminophenyl)-6-(4-chlorophenyl)- (8a), 2-(4-Hydroxyphenyl)-6-(4-chlorophenyl)- (8b), 2-(4-Diaminophenyl)-6-(3-chlorophenyl)- (8c), 2-(4-Hydroxyphenyl)-6-(3-chlorophenyl)- (8d), and 2-(4-Dimethylaminophenyl)-6-(2,4-difluorophenyl)- (8e) 4,4-Dimethyl-4,5-dihydro-1H(3H)-indazolo[4,5-*d*]-imidazoles. A mixture of diketone **5a-c** (2 mmol), the relevant aromatic aldehyde (2 mmol), ammonium acetate (10 g), and glacial acetic acid (10 ml) was boiled for 5 h. In the case of **8c,d**, the precipitate from the cooled mixture was filtered off and recrystallized from DMF, in the remaining cases water (2-3 ml) was added and the reaction mixture was kept for one day. The precipitates of compounds **8a,b,e** were filtered off and recrystallized: **8a** – from DMF, **8b** – from 5:1 DMF–water, and **8e** – from 5:1 DMF–ethanol.

2-(4-Bromophenyl)- (8f), 2-(3-Nitrophenyl)- (8g), 2-(3,4-Dimethoxyphenyl)- (8h), and 2-(3,4-Methylenedioxyphenyl)- (8i) 4,4,8-Trimethyl-6-(2-pyridyl)-4,5-dihydro-1H(3H)-indazolo[4,5-*d*]-imidazoles. A mixture of 3,6,6-trimethyl-4,5-dioxo-1-(2-pyridyl)-4,5,6,7-tetrahydroindazole [12] (2 mmol), the relevant aromatic aldehyde (2 mmol), ammonium acetate (10 g), and glacial acetic acid (20 ml) was boiled for 3.5 h and cooled with a mixture of powdered ice and aqueous ammonia. The precipitates of compounds **8f-i** were filtered off and recrystallized from toluene.

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