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SYNTHESIS AND REACTIONS OF 1-(4-BROMO-, 4-FLUORO-, AND 4-TRIFLUOROMETHYLPHENYL)-6,6-DIMETHYL-4-OXO-4,5,6,7-TETRAHYDROINDAZOLES

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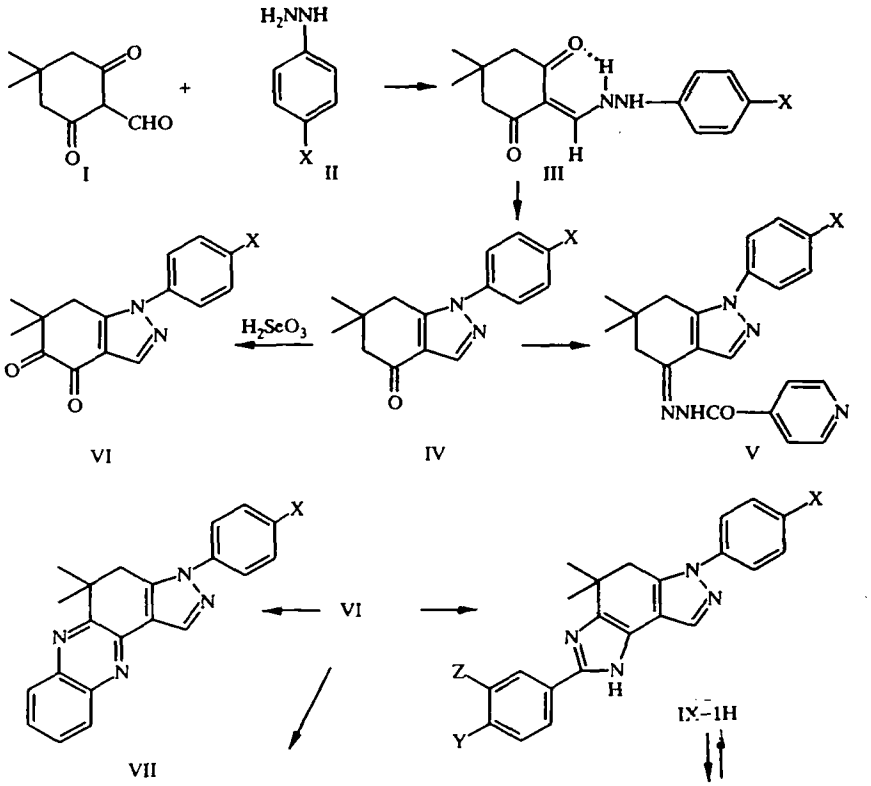
From 2-formyldimedone and 4-bromo-, 4-fluoro-, and 4-trifluoromethylphenylhydrazines we have obtained the corresponding 2-arylhydrazinomethylenedimedones, which in acid medium undergo ring closure to form 1-substituted 6,6-dimethyl-4-oxo-4,5,6,7-tetrahydroindazoles. Oxidation of the latter by selenous acid leads to the corresponding 4,5-dioxo-4,5,6,7-tetrahydroindazoles, which then were converted to derivatives of 4,5-dihydro-3H-pyrazolo[4,3-a]phenazine and 4,5-dihydro-1H(3H)-indazolo[4,5-d]imidazole.

Considering the unflagging interest in derivatives of hydrogenated indazoles and their related pyrazole-containing systems [1-7], in continuing the work in [8-12] we have synthesized 1-(4-substituted aryl)-4-oxo-4,5,6,7-tetrahydroindazoles and a number of their derivatives.

In reactions of 2-formyldimedone (I) with 4-bromo-, 4-fluoro-, and 4-trifluoromethylphenylhydrazines (II), we obtained (Scheme 1) the corresponding 2-arylhydrazinomethylenedimedones (III).

Scheme 1



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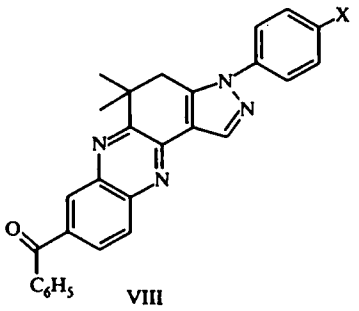
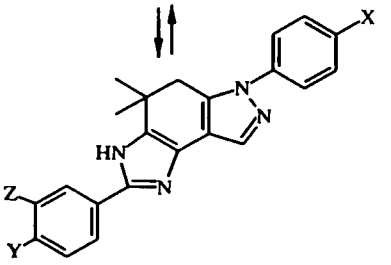


VIII



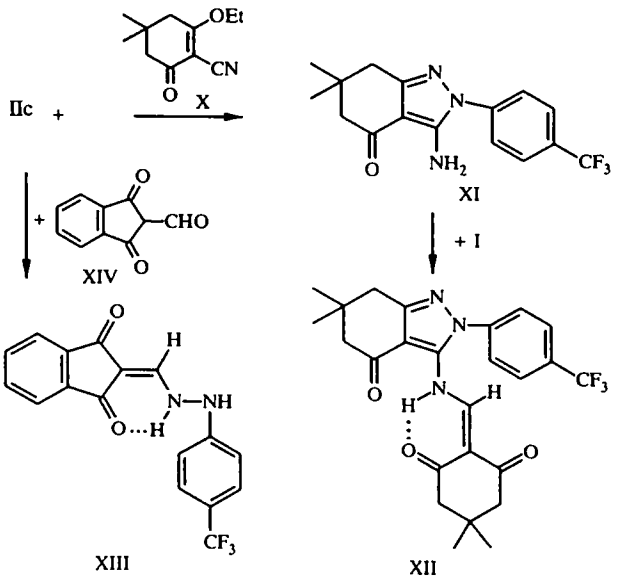
IX-3H

II-VII a X = Br, b X = F, c X = CF_3; VIII a X = H, b X = F; IX a X = Z = H, Y = Br, b X = F, Y = Br, Z = H, c X = Br, Y = OH, Z = H, d X = F, Y = OH, Z = H, e X = CF_3, Y = OH, Z = H, f X = Z = H, Y = $N(CH_3)_2$, g X = F, Y = $N(CH_3)_2$, Z = H, h X = H, YZ = OCH_2O

Boiling them in ethanol in the presence of hydrochloric acid leads to 4-oxo-4,5,6,7-tetrahydroindazoles IV. In reactions of these ketones with the hydrazide of isonicotinic acid, we obtained isonicotinoylhydrazones V. Oxidation of ketones IV with selenous acid according to the method used in [8,13] leads to the corresponding 4,5-dioxo-4,5,6,7-tetrahydroindazoles VI. On reaction of these α-diketones with *o*-phenylenediamine, we obtained 3-aryl-5,5-dimethyl-4,5-dihydro-3H-pyrazolo[4,3-*a*]phenazines (VII). We also reacted diketone VIb and 1-phenyl-6,6-dimethyl-4,5-dioxo-4,5,6,7-tetrahydroindazole [13] with 3,4-diaminobenzophenone. Since the most reactive electrophilic center of 4,5-dioxo-4,5,6,7-tetrahydroindazoles is the carbonyl carbon $C_{(5)}$ [8] while the amino functional group of 3,4-diaminobenzophenone in the 3 position is more nucleophilic [14], we assigned the structure of the 8-benzoyl derivative (VIII) to the sole phenazinopyrazole formed in each case. As a result of reactions of α-diketones VI with aromatic aldehydes and ammonium acetate, according to the method in [15,16] we obtained 2,6-diaryl-4,4-dimethyl-4,5-dihydro-1H(3H)-indazolo[4,5-*d*]imidazoles (IX), which are interesting in connection with the diverse possibilities for utilization of compounds including the 2-arylimidazole structural moiety [17-20]. 1-Phenyl-6,6-dimethyl-4,5-dioxo-4,5,6,7-tetrahydroindazole was implicated in these reactions back in [21].

In continuing the work in [12, 22], from the enol ester of 2-cyanodimedone (X) and 4-trifluoromethylphenylhydrazine (IIc), we obtained 2-(4-trifluoromethylphenyl)-3-amino-6,6-dimethyl-4-oxo-4,5,6,7-tetrahydroindazole (XI), the reaction of which with 2-formyldimedone I leads to the 4,4-dimethyl-2,6-dioxocyclohexylidenemethylamino derivative XII (Scheme 2).

Scheme 2



XIII

XII

TABLE 1. PMR and IR Spectral Parameters for the Synthesized Compounds

Compound	IR spectrum, ν, cm^{-1}	PMR spectrum, δ, ppm (A — $CDCl_3$, B — DMSO-D_6)
1	2	3
IIIa	1650, 1600, 1540; 3250, 3190, 3120	A. 1,04 (6H, s, $2CH_3$); 2,40 (4H, s, $2CH_2$); 6,78 (2H, m, C_6H_4); 7,38 (2H, m, C_6H_4); 8,14 (1H, s, =CH-); 10,96 (1H, br.s, NH); 12,51 (1H, br.s, NH)
IIIb	1670, 1600, 1582, 1510; 3240...3220, 3180, 3140	A. 1,03 (6H, s, $2CH_3$); 2,31 (4H, s, $2CH_2$); 6,92 (4H, center m, C_6H_4); 8,30 (1H, s, =CH-); 9,70 (1H, br.s, NH); 12,33 (1H, br.s, NH)
IIIc	1670, 1625, 1600, 1588, 1578; 3240, 3160, 3130	B. 1,00 (6H, s, $2CH_3$); 2,31 (2H, s, CH_2); 2,40 (2H, s, CH_2); 6,87 (2H, m, C_6H_4); 7,53 (2H, m, C_6H_4); 8,07 (1H, e, J = 9 Hz, =CH-); 9,67 (1H, br.s, NH); 12,13 (1H, d, J = 9 Hz, NH)
IVa	1678, 1655, 1640, 1600, 1545, 1500; 3110	A. 1,11 (6H, s, $2CH_3$); 2,40 (2H, s, CH_2); 2,80 (2H, s, CH_2); 7,30 (2H, m, C_6H_4); 7,64 (2H, m, C_6H_4); 8,06 (1H, s, =CH-)
IVb	1677, 1650, 1640, 1540, 1515; 3080	A. 1,13 (6H, s, $2CH_3$); 2,42 (2H, s, CH_2); 2,78 (2H, s, CH_2); 7,18...7,50 (4H, m, C_6H_4); 8,08 (1H, s, =CH-)
IVc	1670, 1620, 1600, 1540, 1525; 3100	A. 1,11 (6H, s, $2CH_3$); 2,40 (2H, s, CH_2); 2,89 (2H, s, CH_2); 7,71 (4H, center m, C_6H_4); 8,09 (1H, s, =CH-)
Va	1660, 1620, 1570, 1540; 3280, 3050	B. 1,04 (6H, s, $2CH_3$); 2,50 (2H, s, CH_2); 2,87 (2H, s, CH_2); 7,58...8,82 (9H, m, C_6H_4, C_5H_4N, =CH-); 11,06 (1H, s, NH)
Vb	1640, 1600, 1590, 1515, 3350	B. 1,00 (6H, s, $2CH_3$); 2,53 (2H, s, CH_2); 2,83 (2H, s, CH_2); 7,29...8,82 (9H, m, C_6H_4, C_5H_4N, =CH-); 11,07 (1H, s, NH)
Vc	1640, 1620, 1590, 1545, 1520	B. 1,04 (6H, s, $2CH_3$); 2,60 (2H, s, CH_2); 2,96 (2H, s, CH_2); 7,76...8,84 (9H, m, C_6H_4, C_5H_4N, =CH-); 11,11 (1H, br.s, NH)
VIa	1732, 1690...1680, 1590, 1550, 1500; 3120	A. 1,31 (6H, s, $2CH_3$); 3,20 (2H, s, CH_2); 7,40 (2H, m, C_6H_4); 7,69 (2H, m, C_6H_4); 8,16 (1H, s, =CH-)
VIb	1728, 1690, 1550, 1515; 3070	A. 1,31 (6H, s, $2CH_3$); 3,16 (2H, s, CH_2); 7,40 (4H, center m, C_6H_4); 8,18 (1H, s, =CH-)
VIc	1725, 1675, 1610, 1540. 1515	A. 1,36 (6H, s, $2CH_3$); 3,27 (2H, s, CH_2); 7,73 (4H, center m, C_6H_4); 8,22 (1H, c, =CH-)
VIIa	1620, 1595, 1580, 1510; 3060	A. 1,47 (6H, s, $2CH_3$); 3,13 (2H, s, CH_2); 7,44...7,96 (8H, m, $2C_6H_4$); 8,36 (1H, s, =CH-)
VIIb	1620, 1585, 1520; 3080	A. 1,49 (6H, s, $2CH_3$); 3,09 (2H, s, CH_2); 7,20...7,98 (8H, m, $2C_6H_4$); 8,38 (1H, s, =CH-)
VIIc	1620, 1580, 1530; 3060	A. 1,49 (6H, s, $2CH_3$); 3,20 (2H, s, CH_2); 7,60...7,97 (8H, m, $2C_6H_4$); 8,40 (1H, s, =CH-)
VIIIa	1650, 1635, 1618, 1575, 1550, 1510, 3090	B. 1,51 (6H, s, $2CH_3$); 3,18 (2H, s, CH_2); 7,48...8,42 (14H, m, $2C_6H_5$, C_6H_3, =CH-)
VIIIb	1674, 1638, 1620, 1580, 1555, 1515; 3080	A. 1,48 (6H, s, $2CH_3$); 3,33 (2H, s, CH_2); 7,10...8,88 (12H, m, C_6H_4, C_6H_5, C_6H_3); 9,50 (1H, s, =CH-)
IXa	1605, 1525, 1510; 3080, 2800...2600	B. 1,31 (6H, s, $2CH_3$); 3,00 (2H, s, CH_2); 7,72 (10H, center m, C_6H_5, C_6H_4, =CH-); 12,31 (0,5H, br.s, NH); 12,72 (0,5H, br. s, NH)
IXb	1625, 1595, 1520; 3090, 2800...2600	B. 1,28 (6H, s, $2CH_3$); 2,97 (2H, s, CH_2); 7,67 (9H, center m, $2C_6H_4$, =CH-); 12,27 (1H, br.s, NH)
IXc	1620, 1540, 1505; 3080, 2800...2600	B. 1,24 (6H, s, $2CH_3$); 3,00 (2H, s, CH_2); 6,80...7,69 (9H, m, $2C_6H_4$, =CH-); 9,62 (1H, br.s, OH); 11,86 (0,5H, br.s, NH); 12,24 (0,5H, br.s, NH)
IXd	1615, 1540, 1520, 3120...3080	B. 1,24 (6H, s, $2CH_3$); 2,96 (2H, s, CH_2); 6,84...7,64 (9H, $2C_6H_4$, =CH-); 9,64 (1H, br.s, OH); 12,08 (1H, br.s, NH)
IXe	1618, 1535, 1520	B. 1,22 (6H, s, $2CH_3$); 3,04 (2H, s, CH_2); 6,82...7,78 (9H, center m, $2C_6H_4$, =CH-); 9,50 (1H, s, OH); 11,84 (0,5H, br.s, NH); 12,31 (0,5H, br.s, NH)
IXf	1650, 1610, 1595, 1540, 1500; 3060	B. 1,29 (6H, s, $2CH_3$); 2,96 (2H, s, CH_2); 2,99 (6H, s, $N(CH_3)_2$); 6,73 (2H, m, C_6H_4); 7,51 (5H, center m, C_6H_5); 7,78 (1H, s, =CH-); 7,82 (2H, m, C_6H_4); 11,82 (1H, br.s, NH)

TABLE 1 (continued)

Compound	IR spectrum, ν, cm^{-1}	PMR spectrum, δ, ppm (A — $CDCl_3$, B — DMSO-D_6)
1	2	3
IXg	1655, 1610, 1545, 1515; 3060	B. 1,27 (6H, s, $2CH_3$); 2,75 (2H, s, CH_2); 3,00 (6H, s, $N(CH_3)_2$); 6,73 (2H, m, C_6H_4; 7,60 (4H, m, C_6H_4); 7,80 (2H, m, C_6H_4); 7,81 (1H, s, =CH-); 11,91 (0,5H, br.s, NH); 12,35 (0,5H, br.s, NH)
IXh	1620, 1598, 1535, 1505; 3060	B. 1,24 (6H, s, $2CH_3$); 3,00 (2H, s, CH_2); 6,07 (2H, s, O—CH_2—O); 7,00...7,67 (9H, m, C_6H_5, C_6H_3, =CH-); 11,96 (0,5H, br.s, NH); 12,40 (0,5H, br.s, NH)
XI	1640, 1630, 1612, 1550, 1540, 1520; 3410, 3310, 3210	A. 1,11 (6H, s, $2CH_3$); 2,30 (2H, s, CH_2); 2,60 (2H, s, CH_2); 5,53 (2H, br.s, NH_2); 7,76 (4H, center m, C_6H_4)
XII	1690, 1675, 1650, 1605...1595, 1545, 1530, 1505; 3320	A. 1,06 (6H, s, $2CH_3$); 1,67 (6H, s, $2CH_3$); 2,40 (4H, s, $2CH_2$); 2,49 (2H, s, CH_2); 2,75 (2H, s, CH_2); 7,82 (4H, center m, C_6H_4); 9,64 (1H, d, J = 11,3 Hz, =CH-); 13,50 (1H, d, J = 11,3 Hz, NH)
XIII	1710, 1670...1650, 1620, 1590, 1525, 1500; 3300, 3260	A. 6,90...7,67 (8H, m, $2C_6H_4$); 9,37 (1H, s, =CH-); 10,89 (1H, br.s, NH)

2-(4-Trifluoromethylphenylaminomethylene)-1,3-indanedione (XIII), obtained from 2-formyl-1,3-indanedione (XIV) and hydrazine IIc, could not be converted to the corresponding indenopyrazole under the conditions used for cyclization of the hydrazino derivatives III.

The structure of the synthesized compounds was confirmed by PMR and IR spectra. Comparison of the spectral characteristics of known samples [8,11] and the 2-hydrazinomethylene derivatives (III) and also the tetrahydroindazoles (IV, VI) obtained in this work showed a very similar pattern. Thus the signals from the methylene groups in the 4 and 6 positions of the hydrazinomethylene derivatives IIIa,b appear as a single singlet at δ 2.31-2.40 ppm, while in indazoles IV the signals from the methylene group in the 7 position are observed downfield (δ 2.78-2.89 ppm) relative to the methylene group at the 5 position (δ 2.40-2.42 ppm). The very intense carbonyl band of ketones IV is observed at 1670-1678 cm^{-1}, while the α-diketones VI are characterized by carbonyl frequencies at 1732-1725 and 1690-1675 cm^{-1}. Absorption of the primary amino group of the indazole XI is observed in the PMR spectrum at δ 5.53 ppm, while it is observed in the IR spectrum at frequencies 3410, 3310 cm^{-1}. In the PMR spectrum of compound XII, we clearly detect a *trans*-aminomethylene structural moiety.

The ^1H NMR data suggest that indazoloimidazoles IX exist in DMSO solutions as an equilibrium mixture of 1-H and 3-H forms in 1:1 ratio. In this case, in compounds IXa, c, e, g, h, where the rate of NH-proton migrations is fairly low, the low-field absorption of the NH-proton is represented by two signals of equal intensity (δ 11.84-12.31 and 12.24-12.72 ppm), the total integral of which corresponds to a single proton. For compounds IXb,d,f, more rapid exchange processes are characteristic, leading to averaging of the spectral parameters; as a result, absorption of the NH proton is represented by a single broad signal recorded at 12.08-12.27 ppm.

EXPERIMENTAL

The IR spectra were taken on a Specord IR-75 spectrometer in Nujol (1800-1500 cm^{-1}) and hexachlorobutadiene (3600-2000 cm^{-1}) mulls. The frequencies of the stretching vibrations of the C—H bonds in the 3050-2800 cm^{-1} region are not given. The PMR spectra were taken in $CDCl_3$ and DMSO-D_6 on a Bruker WH-90/DS spectrometer (90 MHz), internal standard TMS. We present the general procedures for synthesis of similar compounds (III-IX). For the IR and PMR data for all the synthesized compounds, see Table 1; for mp, yield, and elemental analysis data, see Table 2.

2-(4-Bromophenylhydrazinomethylene)-(IIIa) and 2-(4-Fluorophenylhydrazinomethylene)-5,5-dimethyl-1,3-cyclohexanedione (IIIb). A solution of 5 mmoles 4-bromo- (IIa) or 4-fluorophenylhydrazine (IIb) hydrochloride in 40 ml water, heated up to 80-90°C, was added to a solution of 5 mmoles of the potassium salt of 2-formyldimedone in 40 ml distilled water, also heated up to the same temperature. The precipitate of IIIa and IIIb was recrystallized from ethanol.

2-(4-Trifluoromethylphenylhydrazinomethylene)-5,5-dimethyl-1,3-cyclohexanedione (IIIc). To a solution of 0.84 g (5 mmoles) formyldimedone in 15 ml ethanol, brought to the boiling point, a solution of 0.88 g (5 mmoles) 4-trifluoromethyl-

TABLE 2. Characteristics of Compounds III-IX, XI-XIII

Compound	Empirical formula	Found, % / Calculated, %				mp, °C	Yield, %
		C	H	N	Br		
IIIa	$C_{15}H_{17}BrN_2O_2$	53,25 / 53,43	5,05 / 5,08	8,20 / 8,30	23,50 / 23,70	210...211	86
IIIb	$C_{15}H_{17}FN_2O_2$	65,15 / 65,20	6,27 / 6,20	10,23 / 10,14		188...190	77
IIIc	$C_{16}H_{17}F_3N_2O_2$	58,71 / 58,88	5,24 / 5,25	8,39 / 8,58		214...215	95
IVa	$C_{15}H_{15}BrN_2O$	56,27 / 56,44	5,70 / 4,74	8,59 / 8,78	25,20 / 25,03	116...117	92
IVb	$C_{15}H_{15}FN_2O$	69,60 / 69,75	5,70 / 5,85	10,71 / 10,84		108...110	81
IVc	$C_{16}H_{15}F_3N_2O$	62,15 / 62,33	4,78 / 4,90	9,00 / 9,09		127...129	96
Va	$C_{21}H_{20}BrN_5O$	57,35 / 57,54	4,47 / 4,60	16,12 / 15,98	18,30 / 18,23	228...230	96
Vb	$C_{21}H_{20}FN_5O$	66,67 / 66,83	5,31 / 5,34	18,40 / 18,56		215...216	88
Vc	$C_{22}H_{20}F_3N_5O$	61,92 / 61,82	4,70 / 4,72	16,52 / 16,39		228...230	54
VIa	$C_{15}H_{13}BrN_2O_2$	54,25 / 54,07	4,01 / 3,93	8,30 / 8,41	23,72 / 23,98	200...202	83
VIb	$C_{15}H_{13}FN_2O_2$	66,32 / 66,17	4,80 / 4,81	10,15 / 10,29		162...163	90
VIc	$C_{16}H_{13}F_3N_2O_2$	59,46 / 59,63	4,13 / 4,05	8,60 / 8,69		127...129	74
VIIa	$C_{21}H_{17}BrN_4$	62,20 / 62,23	4,37 / 4,23	14,01 / 13,83	19,80 / 19,71	114...116	79
VIIb	$C_{21}H_{17}FN_4$	73,30 / 73,24	5,05 / 4,98	16,39 / 16,27		150...151	46
VIIc	$C_{22}H_{17}F_3N_4$	67,17 / 67,00	4,30 / 4,35	14,08 / 14,21		136...138	55
VIIIa	$C_{28}H_{22}N_4O$	78,01 / 78,12	5,20 / 5,15	13,01 / 13,02		216...217	42
VIIIb	$C_{28}H_{21}FN_4O$	75,78 / 74,98	4,80 / 4,72	12,52 / 12,49		194...196	90
IXa	$C_{22}H_{18}BrN_4$	63,00 / 63,17	4,42 / 4,34	13,30 / 13,40	19,30 / 19,10	286...287	70
IXb	$C_{22}H_{17}BrFN_4$	60,41 / 60,56	4,05 / 3,93	12,88 / 12,84	18,45 / 18,31	224...226	71
IXc	$C_{22}H_{19}BrN_4O$	60,60 / 60,70	4,24 / 4,40	12,95 / 12,87	18,48 / 18,36	348...350	63
IXd	$C_{22}H_{19}FN_4O$	70,72 / 70,57	5,06 / 5,11	15,13 / 14,97		304...305	67
IXe	$C_{23}H_{19}F_3N_4O$	65,32 / 65,09	4,40 / 4,51	13,34 / 13,20		344...345	60
IXf	$C_{24}H_{25}N_5$	75,00 / 75,16	6,66 / 6,57	18,20 / 18,26		311...312	51
IXg	$C_{24}H_{24}FN_5$	71,90 / 71,80	5,88 / 6,03	17,40 / 17,45		285...286	55
IXh	$C_{23}H_{19}N_4O_2$	71,90 / 72,05	5,05 / 4,99	14,71 / 14,61		290...291	58
XI	$C_{16}H_{16}F_3N_3O$	59,26 / 59,44	5,07 / 4,99	13,12 / 13,00		145...148	53
XII	$C_{25}H_{26}F_3N_3O_3$	63,60 / 63,41	5,51 / 5,54	8,99 / 8,87		190...192	71
XIII	$C_{17}H_{11}F_3N_2O_2$	61,62 / 61,45	3,50 / 3,34	8,53 / 8,43		210...211	90

phenylhydrazine in 40 ml ethanol at the same temperature was added. After 24 h, the IIIc precipitated was filtered off and recrystallized from ethanol.

1-(4-Bromo-, 4-Fluoro-, and 4-Trifluoromethylphenyl)-6,6-dimethyl-4-oxo-4,5,6,7-tetrahydroindazoles (IVa-c). 5 millimoles of the hydrazinomethylene derivative IIIa-c was boiled for 3 h in 40 ml ethanol in the presence of 1 ml conc. hydrochloric acid. This was placed in a refrigerator for 24 hours and the indazole precipitate was recrystallized from ethanol.

1-(4-Bromo-,4-Fluoro-,and4-Trifluoromethylphenyl)-5,5-dimethyl-4-isonicotinoylhydrazono-4,5,6,7-tetrahydro-indazoles (Va-c). Indazole IIIa-c (2 mmoles) and an equimolar amount of the hydrazide of isonicotinic acid in 5 ml pyridine

were boiled for 3 h. This was cooled and the precipitate of Va-c was filtered off. The filtrate was poured over ice and an additional amount of Va-c was obtained. Both precipitates were combined and recrystallized from ethanol.

1-(4-Bromo-, 4-Fluoro-, and 4-Trifluoromethylphenyl)-5,5-dimethyl-4,5-dioxo-4,5,6,7-tetrahydroindazoles (VIa-c). A mixture of 5 mmoles indazole IIIa-c, 5 mmoles of finely triturated selenous acid, 15 ml glacial acetic acid, and 0.5 ml conc. H_2SO_4 were allowed to stand for 72 h at 20°C, shaking occasionally. Then this was boiled for half an hour, and the hot mixture was filtered to remove the black selenium precipitate. The filtrate was poured over a mixture of crushed ice and an aqueous solution of ammonium hydroxide. The precipitate of diketone VI was filtered off and recrystallized from a small amount of CH_3OOH.

3-(4-Bromo-, 4-Fluoro-, and 4-Trifluoromethylphenyl)-5,5-dimethyl-4,5-dihydro-3H-pyrazolo[4,3-*a*]phenazines (VIIa-c). Diketone VI (5 mmoles) and an equimolar amount of *o*-phenylenediamine in 30 ml ethanol were boiled for 3 h. The hot reaction mixture was filtered, and one-third of the solvent volume was removed on a rotary evaporator. After 24 h, the pyrazolophenazines VII were filtered off and recrystallized from ethanol.

3-Phenyl- (VIIIa) and 3-(4-Fluorophenyl)-5,5-dimethyl-8-benzoyl-4,5-dihydro-3H-pyrazolo[4,3-*a*]phenazine (VIIIb). Concentrated hydrochloric acid (1 ml) was added to 2 mmoles 3,4-diaminobenzophenone and 2 mmoles 1-phenyl-6,6-di-methyl-4,5-dioxo-4,5,6,7-tetrahydroindazole [13] or diketone VIa and 30 ml ethanol. The mixture was boiled for half an hour and then cooled. The precipitate of VIII was filtered off and recrystallized from ethanol.

2,6-Diaryl-4,4-dimethyl-4,5-dihydro-1H(or 3H)-indazolo[4,5-*d*]imidazoles (IXa-h). A mixture of 2 mmoles diketone V, 2 mmoles aromatic aldehyde, 10 g ammonium acetate, and 15 ml glacial acetic acid was boiled for 3 h, cooled, and poured over a mixture of crushed ice and an aqueous solution of ammonium hydroxide. The precipitate IX was filtered off and recrystallized from acetic acid (in the case of IXa,b) or from DMF (in the case of IXc-h).

2-(4-Trifluoromethylphenyl)-3-amino-6,6-dimethyl-4-oxo-4,5,6,7-tetrahydroindazole (XI). 0.48 g (2.5 mmoles) of the enol ester X and 0.44 g of the 4-trifluoromethylphenylhydrazine IIc in 25 ml ethanol were boiled for 3 h. Two-thirds of the solvent volume was driven off on a rotary evaporator and it was allowed to stand in a refrigerator for 24 hours. XI was filtered off and recrystallized from 70% ethanol.

2-(4-Trifluoromethylphenyl)-3-(4,4-dimethyl-2,6-dioxocyclohexylidenemethylamino)-6,6-dimethyl-4-oxo-4,5,6,7-tetrahydroindazole (XII) was obtained by boiling for two hours 0.32 g (1 mmole) amine and 0.17 g (1 mmole) 2-formyldimedone in 25 ml ethanol. 15 ml of ethanol was removed on a rotary evaporator, then it was cooled and the precipitate XII was filtered off and recrystallized from ethanol.

2-(4-Trifluoromethylphenylhydrazinomethylene)-1,3-indanedione (XIII). To a solution of 0.86 g (5 mmoles 2-formyl-1,3-indanedione in 30 ml ethanol, brought to the boiling point, a solution of 0.88 g (5 mmoles) 4-trifluoromethlyphenylhydrazine in 40 ml ethanol at the same temperature was added. After 24 h, the precipitate was filtered off and recrystallized from ethanol.

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