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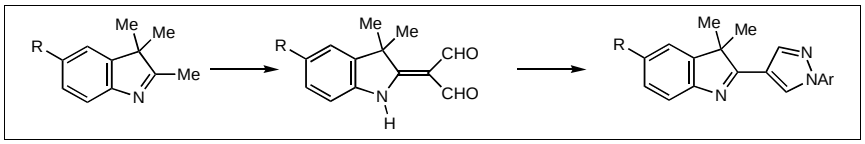
Received February 28, 2006

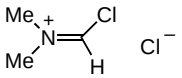


2,3,3-Trimethylindolenine and 5-chloro-2,3,3-trimethylindolenine were converted into β-diformyl compounds by the action of the Vilsmeier reagent at 50 °C. The dialdehydes reacted with various aryl-hydrazines and 2-pyridylhydrazine to produce mono-hydrazones as mixtures of *cis* and *trans* isomers. Heating the hydrazones in refluxing ethanol produced 3,3-dimethyl-2-(1-aryl-1*H*-pyrazol-4-yl)-3*H*-indoles in excellent yields. Reaction of the β-diformyl compounds with hydrazine itself led directly to 3,3-dimethyl-2-(pyrazol-4-yl)-3*H*-indoles.

J. Heterocyclic Chem., **43**, 1591 (2006).

Introduction.

The recognition of the power of the species produced by the combination of phosphoryl chloride with the amide of a secondary amine (*N*-methylformanilide and dimethyl formamide have been most often utilised) has its origins in a paper in 1896 [1]. Later work by Fischer, Muller and Vilsmeier, [2] and then by Vilsmeier and Haack [3] and later by the groups of Arnold [4] and Meth-Cohn [5] clarified the process and made it into a widely used regimen for the acylation, especially formylation, of reactive aromatic and hetero-aromatic compounds, and indeed, non-aromatic compounds [6]. The reactive electrophilic species is now recognized to be a chloroiminium ion – **1** in the particular case of the DMF/$POCl_3$ combination. The carbonyl group of the aldehyde (or ketone) products results from a second stage in the overall process in which aqueous alkali is used to hydrolyse the initial product of the reaction.

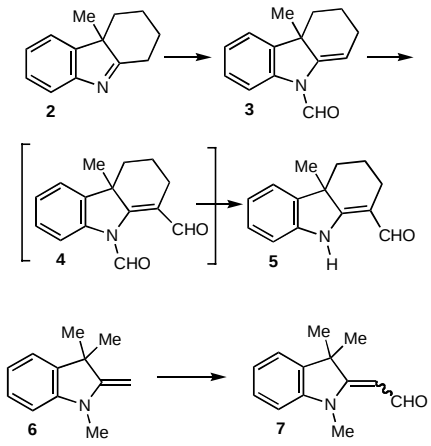


1

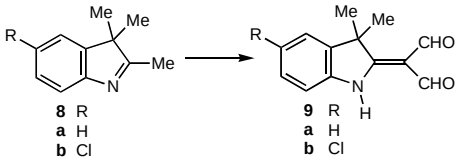
In 1959, Fritz [7] reported the *N*-formylation of the 3,3-disubstituted 3*H*-indole (indolenine) **2** giving **3** using the Vilsmeier reagent from DMF and $POCl_3$. Further reaction of **3** with the Vilsmeier reagent, and hydrolysis produced **5**. Formation of this product probably involves the intermediacy of **4**, from which the *N*-formyl group is hydrolytically removed. The enamine **6** was directly *C*-formylated, producing **7** [7]. No further studies of the formylation of these types of compound have been reported since.

Results and Discussion.

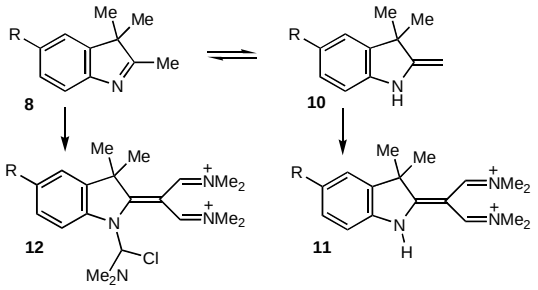
We expected 2,3,3-trimethylindolenines **8a** and **8b**, which were synthesized from the arylhydrazones of isopropyl methyl ketone, by the Fischer reaction, to react with the Vilsmeier reagent to form *N*-formylated products, in line with the result described for **2**. However, when both **8a** and its 5-chloro-analogue **8b** were subjected to the Vilsmeier conditions, at 50 °C, followed by the usual alkaline hydrolysis, *di*formyl products were obtained to which we assign the structures **9a**, **9b**. Thus, the ^{1}H NMR spectrum of **9a** showed the presence of two one-hydrogen singlets at δ 9.77 and δ 9.79 corresponding to CHO protons. In the case of **9b**, there was a two-hydrogen singlet at δ 9.77. Absorptions at 3153 cm^{-1} and 3190 cm^{-1} for **9a** and **9b** respectively were evidence for the presence of N-H bonds, further confirmed by ^{1}H NMR one-hydrogen signals



for the *N*-hydrogens appearing at δ 13.56 (**9a**) and 13.58 (**9b**) respectively. We concluded that both formyl groups are on carbon, and not the other possibility: one on nitrogen and one on carbon (as in the presumed intermediate **4**), and thus that **9a**,**b** represent the structures of these products. Final confirmation for these assignments came from a single crystal X-ray analysis of **9a** [8].

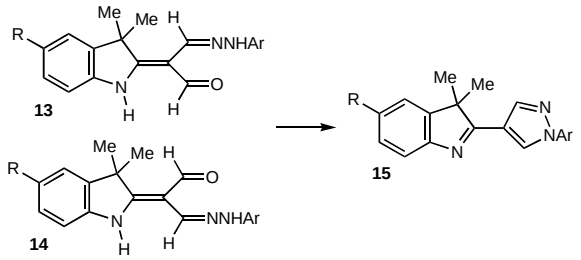


Using the standard interpretation of the Vilsmeier reaction sequence, there seem to be two possible alternative explanations for the formation of products **9**. One possibility is that formylation does *not* take place on nitrogen, but that a small equilibrium concentration of the enamine tautomer **10** is successively *C*-substituted twice and thus, that before hydrolysis, species **11** is present. Alternatively, if electrophilic attack at nitrogen *is* a first step, an intermediate of the form **12** would have to be present before hydrolysis. We favour the former explanation though we do not have direct evidence for the tautomeric equilibrium, **8** ⇔ **10**.



The reaction of diformyl compounds **9a**,**b** with phenylhydrazine, *p*-methoxyphenylhydrazine, *m*-methylphenylhydrazine, *p*-nitrophenylhydrazine and 2-pyridylhydrazine in ethanol at room temperature produced sharp-melting *mono*-hydrazones in excellent yields. It was not possible to ascertain which carbonyl group had reacted – **13** or **14** – but the purity suggested at least that mixtures of the two structural isomers were not obtained.

imine link. Thus there were two singlets at δ 12.07 and δ 12.18 in a ratio of 9:2, due to the NH protons, a pair of singlets at δ 9.98 and δ 10.05, again in a ratio of 9:2, assigned to the CHO protons, and finally two singlets at δ 6.80 and δ 6.74 for the imine hydrogens, as before, in a 9:2 ratio. We assume that the major isomer is the *trans* isomer.

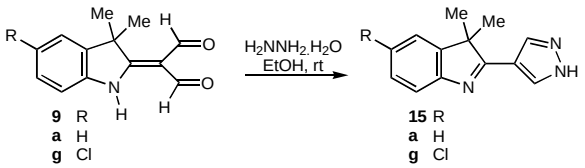


Simply heating the hydrazones in ethanol brought about a ring closure and the formation of a pyrazole ring, with a consequent migration of the C–C double bond to regenerate an indolenine unit. Either isomer – **13/14** – would produce the same ring closed pyrazole. The products, then, are 3,3-dimethyl-2-(1-aryl-1*H*-pyrazol-4-yl)-3*H*-indoles **15a-l**, and all were formed in very good yields (Table 1). Evidence for the ring closure came from a study of the ^{1}H NMR spectra of the products, in particular of the signals from the newly formed pyrazole ring. The ^{1}H NMR spectra of each of the pyrazoles carrying a substituent on a nitrogen (**15b-f** and **15h-l**) had two one-hydrogen singlets, in the range δ 8.28–8.46, for the pyrazole 5-hydrogen and δ 8.52–9.10 for the pyrazole 3-hydrogen.

The reaction of di-aldehydes **9** with hydrazine itself led directly to the (1*H*-pyrazol-4-yl)-3*H*-indoles **15a** and **15g** – an intermediate hydrazone was not isolated. These two products, with no substituent on a pyrazole nitrogen,

PYRAZOLE				HYDRAZONE			
Yield	**Ar**	**R**		**Yield**	**Ar**	**R**	
90%	*p*-$MeOC_6H_4$	H	**15b**	80%	*p*-$MeOC_6H_4$	H	**13/14b**
95%	*m*-MeC_6H_4	H	**15c**	80%	*m*-MeC_6H_4	H	**13/14c**
90%	*p*-$NO_2C_6H_4$	H	**15d**	74%	*p*-$NO_2C_6H_4$	H	**13/14d**
90%	2-Pyridyl	H	**15e**	73%	2-Pyridyl	H	**13/14e**
95%	Ph	H	**15f**	85%	Ph	H	**13/14f**
92%	*p*-ClC_6H_4	Cl	**15h**	80%	*p*-ClC_6H_4	Cl	**13/14h**
93%	*m*-MeC_6H_4	Cl	**15i**	80%	*m*-MeC_6H_4	Cl	**13/14i**
95%	*p*-$NO_2C_6H_4$	Cl	**15j**	75%	*p*-$NO_2C_6H_4$	Cl	**13/14j**
90%	2-Pyridyl	Cl	**15k**	85%	2-Pyridyl	Cl	**13/14k**
90%	Ph	Cl	**15l**	80%	Ph	Cl	**13/14l**

A study of the ^{1}H NMR spectrum of compound **13f/14f** confirmed the presence of *cis* and *trans* isomers about the displayed broad two-hydrogen singlets at δ 8.33 and 8.31 respectively for the pyrazole ring protons.



Although there are a few examples of 2-(pyrazol-4-yl)indoles [9], no examples of 2-(pyrazol-4-yl)-3*H*-indoles have been previously recorded.

EXPERIMENTAL

General.

Melting points were recorded on an Philipharris C4954718 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer, at 400 MHz and 100 MHz respectively. Chemical shifts δ are in parts per million (ppm) measured in $CDCl_3$ or DMSO-d_6 as solvent and relative to TMS as the internal standard. Infrared spectra were recorded on a Thermonicolet-Nexus 670 FT-IR instrument and elemental analyses were carried out on an Exeter analytical model CE440 C, H and N elemental analyser.

General procedure for the Synthesis of (**9a,b**).

To dimethylformamide (10 ml) cooled in an ice bath was added dropwise phosphorus oxychloride (6 ml, 66 mmol) with stirring over a period of 2 h at below 25 °C. After addition was completed, a solution of the trimethylindolenine (**8**) (12.6 mmol) in DMF (10 ml) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at 50 °C for 2 h. The resulting solution was added to ice-cooled water and the pH was adjusted to 8.0 by the addition of aq NaOH (35%) and the mixture was extracted with ethyl acetate (3x30 ml). The organic layer was washed with hot water and dried over Na_2SO_4. The solvent was evaporated and the resulting crude products were purified by chromatography on silica gel eluting with ethyl acetate:toluene (1:5) to give the pure diformyl compound (**9**) as yellow crystals.

2-(Diformylmethylidene)-2,3-dihydro-3,3-dimethylindole (**9a**).

56% Yield; mp 118-120°; ir: NH 3153, CO 1663, 1630, 1509, 1467, 1273, 1198, 752, 865, 548; ^{1}H nmr (deuteriochloroform): δ 1.75 (s, 6H), 7.19 (bd, 1H, J = 7.6 Hz,), 7.26 (td, 1H, J = 7.6, 1.1 Hz), 7.31 (dd, 1H, J = 7.6, 1.1 Hz), 7.33-7.35 (m, 1H), 9.77 (s, 2H), 13.56 (bs, NH); ^{13}C nmr (DMSO-d_6): δ 23.4, 26.9, 50.60, 190,113.6, 122, 125, 125.4, 128.1,139.5, 140.3, 177.8, 189.7.

Anal. Calcd. for $C_{13}H_{13}NO_2$ C, 72.54; H, 6.09; N, 6.51. Found C, 72.71; H, 6.10; N, 6.60.

5-Chloro-2-(diformylmethylidene)-2,3-dihydro-3,3-dimethylindole (**9b**).

61% Yield; mp 163-167°; ir: NH 3190, CO 1657, 1610, 1479, 1400, 1223, 1886, 817, 733; ^{1}H nmr (deuteriochloroform): δ 1.74 (s, 6H), 7.15 (d, 1H, J = 8.16 Hz), 7.3 (m, 2H), 9.7 (s, 2H), 13.58(s, 1H); ^{13}C nmr (deuteriochloroform): δ 22.19, 178, 141.36, 136.9, 108.42, 50.44, 112.51, 121.8, 127.3, 130.22, 191.39, 186.57.

Anal. Calcd. for $C_{13}H_{12}ClNO_2$ C, 62.53; H, 4.84; Cl, 14.20; N, 5.61; Found C, 62.50; H, 4.80; Cl, 14.31; N, 5.62.

General Procedure for the Synthesis of (**13/14b-f**) and (**13/14h-l**).

A mixture of the malondialdehyde (**9**) (1.1 mmol) and the arylhydrazine (1.11 mmol) in absolute ethanol (10 ml) was stirred at room temperature for 2 h. The resulting yellow crystals were collected by filtration and recrystallised from EtOH to produce the desired hydrazone in excellent yields.

2-(Diformylmethylidene)-2,3-dihydro-3,3-dimethylindole Mono-4-methoxyphenylhydrazone (**13/14b**).

80% Yield; mp 140-142°; ir: NH 3266, CO 1619, 1593, 1575, 1552, 1481, 1377, 1299, 748.

2-(Diformylmethylidene)-2,3-dihydro-3,3-dimethylindole Mono-3-methylphenylhydrazone (**13/14c**).

80% Yield; mp 130-132°; ir: NH 3276, CO 1627, 1558, 1479, 1364, 1208.

2-(Diformylmethylidene)-2,3-dihydro-3,3-dimethylindole Mono-4-nitrophenylhydrazone (**13/14d**).

74% Yield; mp 189-192°; ir: NH 3271, CO 1629, 1576, 1556, 1299, 1318, 1275, 1111.

2-(Diformylmethylidene)-2,3-dihydro-3,3-dimethylindole Mono-pyridin-2-ylhydrazone (**13/14e**).

73% Yield; mp 134-136°; ir: NH 3266, CO 1618, 1592, 1552, 1524, 1481, 1376, 1442, 1252, 1199, 748.

2-(Diformylmethylidene)-2,3-dihydro-3,3-dimethylindole Mono-phenylhydrazone (**13/14f**).

85% Yield; mp 154-158°; ir: NH 3278, CO 1617, 1511, 1358, 871, 598.

5-Chloro-2-(diformylmethylidene)-2,3-dihydro-3,3-dimethylindole Mono-4-chlorophenylhydrazone (**13/14h**).

80% Yield; mp 168-170°; ir: NH 3285, 2972, CO 1624, 1596, 1553, 1487, 1429, 1364, 1257, 1208, 817, 682.

5-Chloro-2-(diformylmethylidene)-2,3-dihydro-3,3-dimethylindole Mono-3-methylphenylhydrazone (**13/14i**).

80% Yield; mp 128-130°; ir: NH 3270, CO 1635, 1558, 1475, 1179.

5-Chloro-2-(diformylmethylidene)-2,3-dihydro-3,3-dimethylindole mono-4-nitrophenylhydrazone (**13/14j**).

75% Yield; mp 124-126°; ir: NH 3259, CO 1629, 1595, 1530, 1479, 1364, 1322, 1264, 1207, 816, 764.

5-Chloro-2-(diformylmethylidene)-2,3-dihydro-3,3-dimethylindole Mono-pyridin-2-ylhydrazone (**13/14k**).

85% Yield; mp 127-129°; ir: NH 3192, CO 1637, 1592, 1561, 1479, 1368, 1315, 1284, 1230, 1211, 1129, 813, 766, 661.

5-Chloro-2-(diformylmethylidene)-2,3-dihydro-3,3-dimethylindole Mono-phenylhydrazone (**13/14l**).

80% Yield; mp 168-170°; ir: NH 3285, CO 1624, 1596, 1553, 1487, 1429, 1364, 1257, 1208, 817, 682.

General Procedure for the Synthesis of (**15b-f** and **15 h-l**).

The hydrazone (**13/14b-f**, **h-l**) (0.597 mmol) was heated at reflux in ethanol (10 ml) for 2 h. The resulting solid product was collected by filtration and recrystallized from ethanol to give the pyrazolo-indolenine (**15b-f, 15h-j**) in very good yields.

3,3-Dimethyl-2-[1-(4-methoxyphenyl)-1*H*-pyrazol-4-yl]-3*H*-indole (**15b**).

90% yield; mp 125-127°; ir: 2961, 1558, 1515, 1558, 1443, 1301, 1248, 1178, 1034, 841, 758; ^{1}H nmr (deuteriochloroform): δ 1.6 (s, 6H), 3.85 (s, 3H), 7.01 (dd, 1H, J = 2.2, 6.85 Hz), 7.63 (dd, 1H, J = 1.2, 6.8 Hz), 7.24 (td, 1H, J = 1.05, 7.7 Hz), 7.35 (m, 2H), 7.67 (dd, 1H, J = 2.1, 6.84 Hz), 8.28 (s, 1H), 8.52 (s, 1H); ^{13}C nmr (deuteriochloroform) δ 23.72, 54.42, 52.17, 157.78, 177.52, 112.93, 132.16, 152.6, 145.1, 124.2, 126.1, 126.8, 132.1, 119.92, 120.05, 139.2, 119.9.

Anal. Calcd. for $C_{20}H_{19}N_3O$ C, 75.69; H, 6.03; N, 13.24; Found C, 75.88; H, 6.04; N, 13.31.

3,3-Dimethyl-2-(1-(3-methylphenyl)-1*H*-pyrazol-4-yl)-3*H*-indole (**15c**).

95% Yield; mp 95-98°; ir: 2963, 1594, 1561, 1482, 1439, 775; ^{1}H nmr (deuteriochloroform): δ 1.54 (s, 6H), 2.43 (s, 3H), 7.16 (d, 1H, J = 7.46 Hz), 7.24 (t, 1H, J = 7.39 Hz), 7.36 (m, 3H), 7.55 (d, 1H, J = 8.05 Hz), 7.63 (m, 2H), 8.31 (s, 1H), 8.59 (s, 1H); ^{13}C nmr (deuteriochloroform) δ 23.67, 20.41, 139.47, 119.9, 119.16, 119.09, 126.8, 126, 127, 128.3, 138.7, 145.15, 152.7, 52.17, 138.43, 177.13, 115.42, 116.9.

Anal. Calcd. for $C_{20}H_{19}N_3$ C, 79.70; H, 6.35; N, 13.94; Found: C, 79.70; H, 6.45; N, 14.11.

3,3-Dimethyl-2-(1-(4-nitrophenyl)-1*H*-pyrazol-4-yl)-3*H*-indole (**15d**).

90% Yield; mp 176-178°; ir: 1598, 1527, 2966, 1518, 1338, 950, 853; ^{1}H nmr (deuteriochloroform): δ 1.56 (s, 6H), 7.27 (t, 1H, J = 7.5 Hz), 7.37 (t, 2H, J = 7.3 Hz), 7.64 (d, 1H, J = 7.4 Hz), 8.03 (dd, 2H, J = 2.8, 7.2 Hz), 8.38 (t, 2H, J = 7.2 Hz), 8.77 (s, 1H), 8.4 (s, 1H); ^{13}C nmr (deuteriochloroform) δ 23.26, 119.08, 125.9, 176.17, 152.2, 144.64, 118.26, 52.034, 142.53, 140.86, 126.7, 124.49, 119.8, 117.83, 124.18, 144.96.

Anal. Calcd. for $C_{19}H_{16}N_4O_2$ C, 68.66; H, 4.85; N, 16.86; Found C, 68.95; H, 4.75; N, 16.97.

3,3-Dimethyl-2-(1-(pyridin-2-yl)-1*H*-pyrazol-4-yl)-3*H*-indole (**15e**).

90% Yield; mp 138-140°; ir: 2966, 1594, 1570, 3103, 1470, 1404, 1254, 1190, 954, 774; ^{1}H nmr (deuteriochloroform): δ 1.54 (s, 6H), 7.25 (m, 3H), 8.05 (d, 1H, J = 4 Hz), 7.85 (td, 1H, J = 1.8, 7.7 Hz), 7.36 (m, 2H), 7.66 (d, 1H, J = 6.7 Hz), 8.46 (s, 1H), 9.1 (s, 1H); ^{13}C nmr (deuteriochloroform) δ 177.02, 152.73, 149.94, 145.34, 116.8, 52.23, 23.73, 121, 124.36, 119.9, 125.35, 147.14, 119.28, 111.6, 141.18, 137.85, 126.8.

Anal. Calcd. for $C_{18}H_{16}N_4$ C, 74.98; H, 5.59; N, 19.43; Found C, 74.82; H, 5.58; N, 19.51.

3,3-Dimethyl-2-(1-phenyl-1*H*-pyrazol-4-yl)-3*H*-indole (**15f**).

95% Yield; mp 164-166°; ir: 3060, 2963, 1622, 1569, 1376, 1253, 1074, 868, 775, 690; ^{1}H nmr (deuteriochloroform): δ 1.55 (s, 6H), 7.26-7.30 (m, 1H), 7.33-7.39 (m, 3H), 7.47-7.51 (m, 2H), 7.70-7.72 (m, 1H), 7.78-7.81 (m, 2H), 8.36 (s, 1H), 9.05 (s, 1H); ^{13}C nmr (deuteriochloroform) δ 187.8, 152.8, 151.8, 141.9, 129.4, 128.9, 127.5, 127.3, 127.0, 126.3, 122.0, 120.2, 107.0, 37.1, 25.0.

Anal. Calcd. for $C_{19}H_{17}N_3$ C, 79.44, H, 5.92; N, 14.63; Found C, 79.63; H, 5.96; N, 14.91.

5-Chloro-2-(1-(4-chlorophenyl)-1*H*-pyrazol-4-yl)-3,3-dimethyl-3*H*-indole (**15h**).

92% Yield; mp 130-132°; ir: 2970, 2930, 1590, 1523, 1530, 1500, 1449, 1396, 1247, 1096, 954, 867, 829; ^{1}H nmr (deuteriochloroform): δ 1.53 (s, 6H), 7.31 (dd, 2H, J = 2, 6.8 Hz), 7.54 (dd, 2H, J = 2.1, 6.8 Hz), 7.53 (dd, 1H, J = 2.1, 6.7 Hz), 7.7 (dd, 2H, J = 2.1, 6.8 Hz), 8.28 (s, 1H), 8.54 (s, 1H); ^{13}C nmr (deuteriochloroform) δ 23.45, 120.58, 139.7, 52.55, 117.12, 130, 131.8, 136.89, 146.8, 151.19, 177.12, 119.47, 128.6, 119.9, 125.8, 127.

Anal. Calcd. for $C_{19}H_{15}Cl_2N_3$ C, 64.06; H, 4.24; Cl, 19.90; N, 11.80; Found C, 64.21; H, 4.24; Cl, 20.12; N, 11.80.

5-Chloro-3,3-dimethyl-2-(1-(3-methylphenyl)-1*H*-pyrazol-4-yl)-3*H*-indole (**15i**).

93% Yield; mp 103-105°; ir: 2966, 1593, 1558, 1608, 1401, 1449, 1402, 1253, 1197; ^{1}H nmr (deuteriochloroform): δ 1.54 (s, 6H), 2.43 (s, 3H), 7.16 (d, 1H, J = 7.28), 7.31 (dd, 2H, J = 2.0, 6.7 Hz), 7.36 (t, 1H, J = 7.7 Hz), 7.5 (m, 2H), 7.6 (s, 1H), 8.29 (s, 1H), 8.55 (s, 1H); ^{13}C nmr (deuteriochloroform) δ 20.40, 23.54, 52.56, 116.67, 126.01, 129.87, 177.44, 151.34, 146.8, 138.34, 120.56, 139.42, 119.9, 127.1, 128.34, 115.43, 119.16, 126, 128.34.

5-Chloro-3,3-dimethyl-2-(1-(3-nitrophenyl)-1*H*-pyrazol-4-yl)-3*H*-indole (**15j**).

95% Yield; mp 150-153°; ir: 1564, 1480, 2964, 1450, 1400, 1254, 1195, 1033, 869, 764; ^{1}H nmr (deuteriochloroform): δ 1.54 (s, 6H), 7.32 (m, 3H), 7.42 (t, 1H, J = 8 Hz), 7.5 (dd, 1H, J = 2.2, 6.5 Hz), 7.64 (m, 1H), 7.8 (st, 1H, J = 1.9 Hz), 8.3 (s, 1H), 8.56 (s, 1H); ^{13}C nmr (deuteriochloroform) δ 23.47, 177, 151.17, 146.83, 139.27, 116.17, 130, 117.21, 52.57, 125.8, 139.8, 120, 127, 126.2, 118.69, 120.6, 129.6, 134.4.

Anal. Calcd. for $C_{19}H_{15}ClN_4O_2$ C, 62.21; H, 4.12; Cl, 9.67; N, 15.27; Found C, 62.10; H, 4.13; Cl, 9.81; N, 15.27.

5-Chloro-3,3-dimethyl-2-(1-(pyridin-2-yl)-1*H*-pyrazol-4-yl)-3*H*-indole (**15k**).

90% Yield; mp 156-158°; ir: 1597,1569, 1472, 1452, 1406, 1118, 956, 772; ^{1}H NMR (deuteriochloroform) δ 1.54 (s, 6H), 7.24 (m, 1H), 7.31 (m, 2H), 7.84 (m, 1H), 7.54 (d, 1H, J = 8.9 Hz), 8.03 (d, 1H, J = 8.23 Hz), 8.44 (m, 1H), 8.41 (s, 1H), 9.09 (s, 1H); ^{13}C nmr (deuteriochloroform) δ 23.57, 177.31, 151.36, 111.62, 147.1, 147.06, 129.9, 52.58, 137.83, 126.93, 116.5, 121.06, 125.37, 141.06, 149.8, 120.1, 120.5.

Anal. Calcd. for $C_{18}H_{15}ClN_4$ C, 66.98; H, 4.68; Cl, 10.98; N, 17.36; Found C, 67.26; H, 4.70; Cl, 10.87; N, 17.39.

5-Chloro-3,3-dimethyl-2-(1-phenyl-1*H*-pyrazol-4-yl)-3*H*-indole (**15l**).

90% Yield; mp148-150°; ir: 2970, 1561,1527, 1527, 1443, 1462, 1247, 865, 759; ^{1}H nmr (deuteriochloroform): δ 1.54 (s, 6H), 7.3 (m, 3H), 7.5 (m, 3H), 7.76 (d, 2H, J = 7.7 Hz), 8.3 (s, 1H), 8.58 (s, 1H); ^{13}C nmr (deuteriochloroform) δ 23.4, 52.51,

177.3, 151.2, 146.8, 138.34, 129.87, 116.74, 128.51, 126.95, 126.28, 125.95, 119.8, 118.34, 139.5, 120.54.

Anal. Calcd. for $C_{19}H_{16}ClN_3$ C, 70.91; H, 5.01; Cl, 11.02; N, 13.06; Found C, 70.91; H, 5.02; Cl, 11.12; N, 13.11.

General Procedure for the Synthesis of (**15a**) and (**15g**).

A solution of dialdehyde (**9a** or **9b**) (0.24 g, 0.962 mmol) and hydrazine hydrate (0.12 g, 2.4 mol) in absolute ethanol (5 ml) was stirred at room temperature for 2 h. The solvent was evaporated with rotary evaporator and the resulting crude product was recrystallized from absolute ethanol to give desired pyrazolo indolenine (**15a** and **15g**) as yellow crystals.

3,3-Dimethyl-2-(1*H*-pyrazol-4-yl)-3*H*-indole (**15a**).

90% Yield; mp 188-190°; ir: 940, 630; ^{1}H nmr (deuteriochloroform): δ 1.44 (s, 6H), 3.40 (bs, 1H, N-H), 7.14-7.50 (m, 4H), 8.33 (bs, 2H); ^{13}C nmr (deuteriochloroform) δ 24.2, 52.7, 114.6, 119.2, 121.3, 125, 127.6, 134, 146.2, 153, 179.

Anal. Calcd. for $C_{13}H_{13}N_3$ C, 73.91; H, 6.20; N, 19.89; Found C, 74.02; H, 6.21; N, 19.89.

5-Chloro-3,3-dimethyl-2-(1*H*-pyrazol-4-yl)-3*H*-indole (**15g**).

95% Yield; mp 250-254°; ir: NH 3166, 1608, 1555, 1450, 1394, 1419, 1339, 1232, 1182, 1107, 939, 818, 625; ^{1}H nmr (deuteriochloroform): δ 1.25 (s, 6H), 7.3 (m, 2H), 7.5 (dd, 1H, J = 1.2, 7.55 Hz), 8.31 (s, 2H); ^{13}C nmr (deuteriochloroform) δ 23.59, 52.65, 114.70, 119.70, 120.60, 127.00, 129.90, 146.82, 151.09, 178.01.

Anal. Calcd. for $C_{13}H_{12}ClN_3$ C, 63.55; H, 4.92; Cl, 14.43; N, 17.10; Found C, 63.56; H, 4.92; Cl, 14.63; N, 17.21.

Acknowledgement.

The authors are grateful to the University of Urmia for financial support of this work.

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