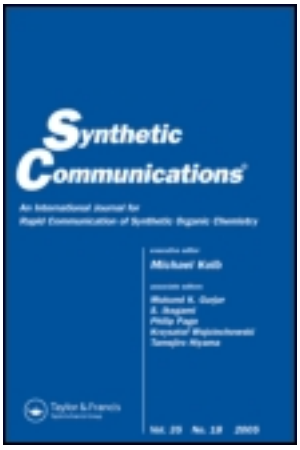

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Chemistry of Substituted Quinolinones. Part II Synthesis of Novel 4-Pyrazolylquinolinone Derivatives

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CHEMISTRY OF SUBSTITUTED QUINOLINONES. PART II

SYNTHESIS OF NOVEL 4-PYRAZOLYLQUINOLINONE DERIVATIVES

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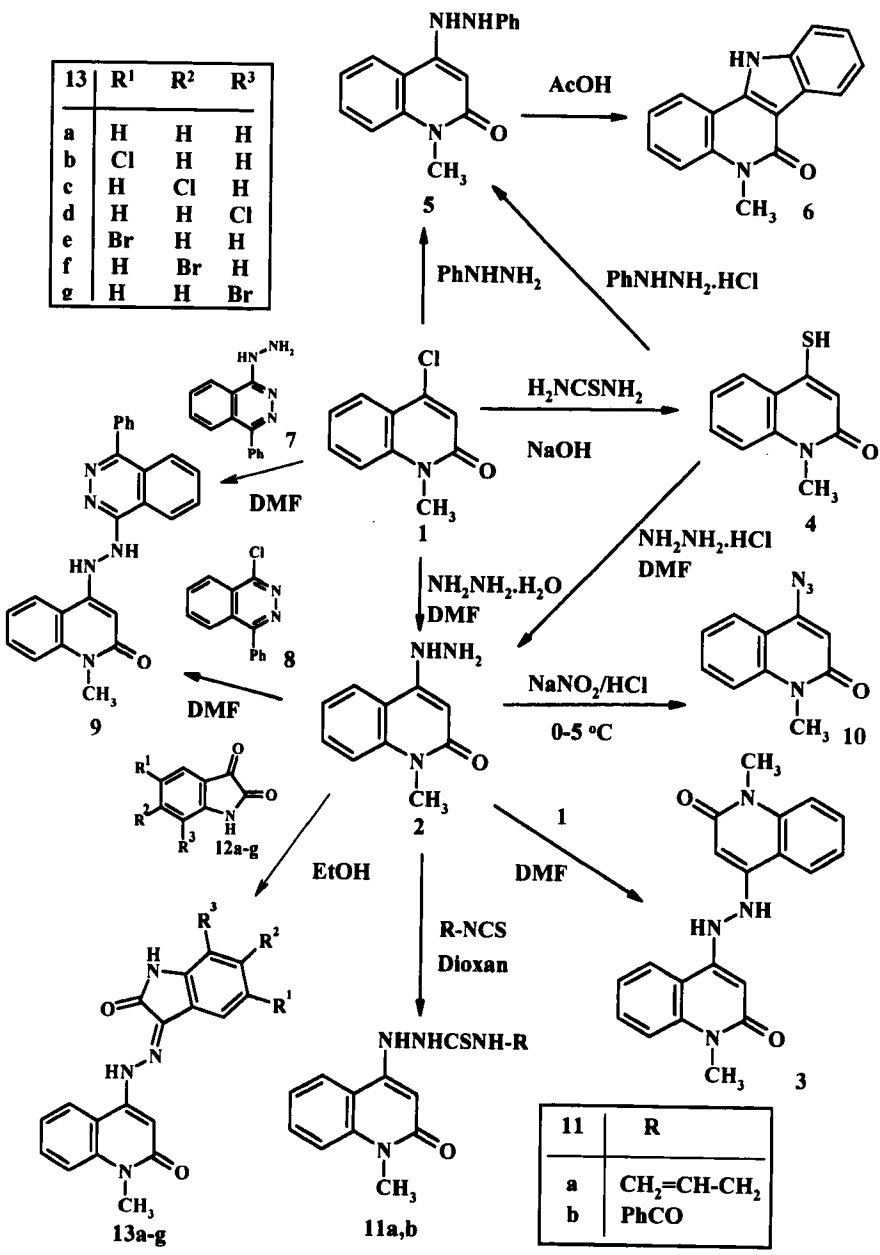
Abstract. 4-Hydrazino-1-methyl-2(1*H*)quinolinone (**2**) was treated with chlorophthalazine, nitrous acid, isothiocyanates and isatines, and also utilized as a precursor for some new 4-pyrazolylquinolinones. Reaction of **2** with certain 3-acylquinolinones afforded quinolinylpyrazoloquinolinones and/or quinolinylpyrazolylquinolinones.

The aim of this work dealt with the synthesis of new quinolinones substituted at position-4 with a pyrazolyl moiety. This arose from the recent notable biological applications of both quinolinones [1,2], and pyrazoles [3,4]. This encouraged us to prepare new heterocycles containing both moieties in one molecularframe, which may have promising biological activity. Thus, the present work is a continuation of our research devoted to synthesize novel heterocyclic quinolinone derivatives, which are of expected biological activity [5,6].

The reaction of 4-chloro-1-methyl-2(1*H*)quinolinone (**1**) [7] with excess hydrazine hydrate, in DMF, gave 4-hydrazino-1-methyl-2(1*H*)quinolinone (**2**). Treating compound **2** with an equimolar amount of the chloroquinolinone **1** furnished the quinolinylhydrazoquinolinone **3**, a product that was also obtained, as a by-product from the former reaction, when equimolar amounts of **1** reacted with hydrazine hydrate. On fusion of the chloroquinolinone **2** with thiourea, 4-mercapto-1-methyl-2(1*H*)quinolinone (**4**) was obtained. Trials to produce **2** from the mercaptoquinolinone **4** by action of hydrazine hydrate did not meet success unless a catalytic amount of hydrazinium chloride was added. When phenylhydrazine was allowed to react with compound **1**, in DMF, 1-methyl-4-phenylhydrazo-2(1*H*)quinolinone (**5**) was afforded. The latter product was achieved from reaction of the mercaptoquinolinone **4** with the same reagent but in the presence of a catalytic amount of phenylhydrazinium chloride. Surprisingly, during the trial of crystallization of compound **5**, using glacial acetic acid, a considerable change was observed. Characterization of the obtained material showed that an intramolecular cyclization took place, giving 5-methyl-11*H*-indolo[3,2-*c*]quinolin-6(5*H*)-one (**6**), which its analytical and spectral data are coincident with those cited in the literature [8]. The reaction of **1** with 1-hydrazino-4-phenylphthalazine (**7**), or **2** with 1-chloro-4-phenylphthalazine (**8**), gave the same product **9**. However, on using the latter precursors, **2** and **8**, the yield is nearly duplicated, comparing with using the former precursors, **1** and **7**. The hydrazinoquinolinone **2** showed a smooth conversion into 4-azido-1-methyl-2(1*H*)quinolinone (**10**), by action of nitrous acid. The structure of compound **10**

was confirmed by the presence of the characteristic azide vibrational band at *ν*: 2120 cm^{-1} in its IR spectrum, and also by preparation of an authentic sample from azidation reaction of compound **1** using sodium azide [9]. The thiosemicarbazides **11a** and **11b** were obtained in good yields when the hydrazinoquinolinone **2** was subjected to react with allyl isothiocyanate and/or benzoyl isothiocyanate, respectively. Also, the tendency of the hydrazinoquinolinone **2** towards addition-elimination reactions was investigated via its condensation with some haloisatine derivatives **12a-g** to give the colored isatine hydrazones **13a-g**. The broad bands centered at *ν*: 3122 and 3124 cm^{-1} due to stretching vibration of intramolecular hydrogen bonded N-H and the very broad downfield shift signals of the hydrazono proton at *δ*: 10.20 and 10.15 ppm suggest that compounds **13a,b** and similarly **13c-g** are present in the Z-form stereoisomer (*cf.* Scheme I).

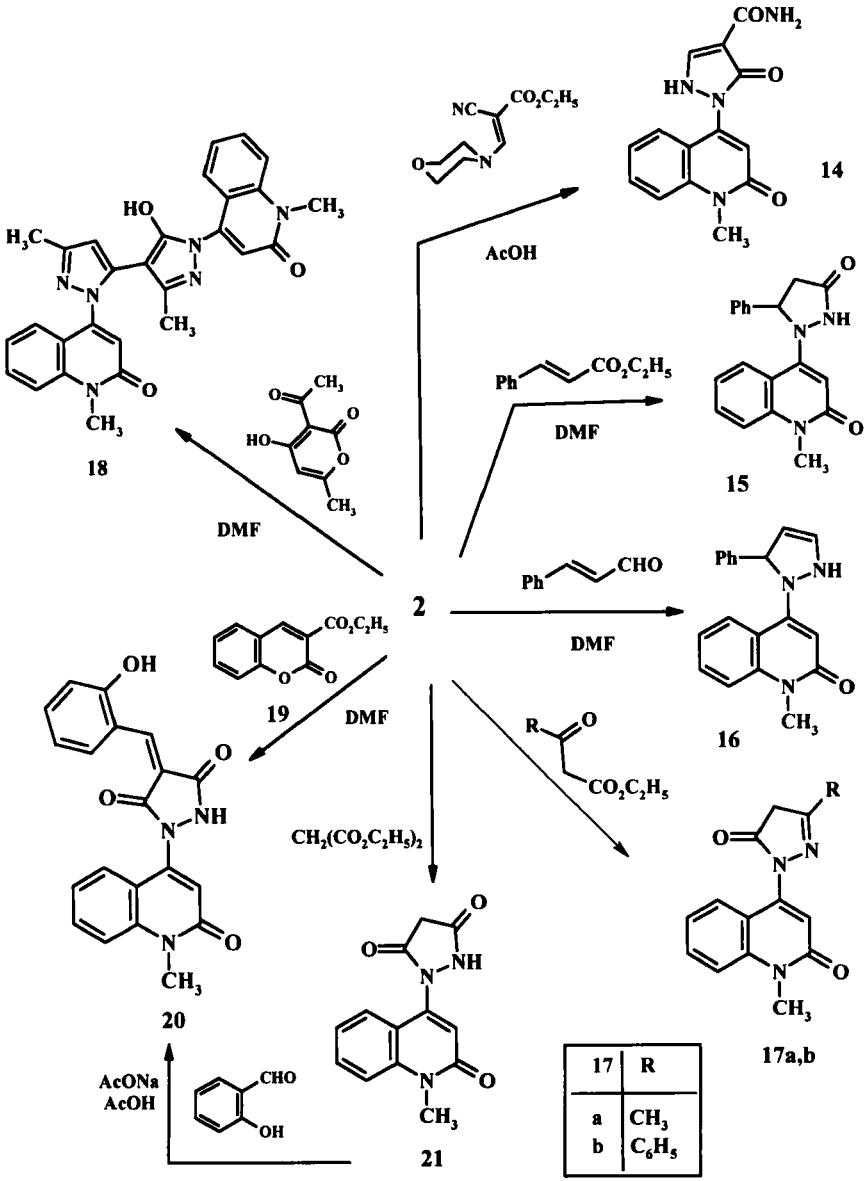
At the purpose of obtaining various pyrazolylquinolinones, compound **2** was treated with some selected reagents. Thus, **2** reacted with ethyl morpholinomethylenecyanoacetate, in glacial acetic acid, to give 4-(4-carbamyl-5-oxo-Δ^3-1-pyrazolinyl)-1-methyl-2(1*H*)quinolinone (**14**). The IR and ^{1}H NMR spectra of compound **14** showed the presence of a carboxamide group instead of the expected carbonitrile, which may be hydrolyzed during the course of the reaction. The condensation-addition cyclization reaction of **2** with ethyl cinnamate and/or cinnamaldehyde gave the corresponding 4-(3-oxo-1-pyrazolidenyl) quinolinone **15** and 4-(1-pyrazolinyl)quinolinone **16**, respectively. Heating **2** with *β*-ketoesters *viz.*; ethyl acetoacetate and ethyl benzoylacetate, afforded the 4-(5-oxopyrazolin-1-yl)quinolinones **17a,b**, respectively. When compound **2**



Scheme I

reacted with dehydroacetic acid, in DMF at the molar ratio 2:1, an interesting bipyrazolylquinolinone **18** was obtained. IR and ^{1}H NMR elucidated the structure **18**, revealing existence of two sets of protons belong to two 1-methyl-2(1*H*)quinolinone moieties. The result obtained from the latter reaction was supported by that reported for the reaction of hydrazinothiazoles with the same reagent [10]. Reaction of **2** with ethyl coumarin-3-carboxylate (**19**), in boiling DMF, gave 4-(4-(2-hydroxy-*z*-benzylidene)-3,5-dioxo-1-pyrazolidenyl)-1-methyl-2(1*H*)-quinolinone (**20**). The IR and ^{1}H NMR spectra were used to distinguish between which of the possible stereoisomers was obtained. Thus, a broad absorption band of O-H group appears at unusually short wavelength (ν: 2650 cm^{-1}) due to intramolecular hydrogen bonding, while aromatic proton at position-6 of benzylidene appears as a doublet signal ($J_{6,}J_5$ = 7 Hz) at a more downfield shift than others (δ: 8.15 ppm) due the deshielding effect of a pyrazoledione C=O group. These suggest that methylenic proton exists away from the space of position-6 proton and hence the obtained is only the Z-isomer. Beside the analytical and spectral evidences for the structure **20**, it was synthetically evidenced by the step-wise preparation. Thus, cyclization of the compound **2** with diethyl malonate furnished 4-(3,5-dioxo-1-pyrazolidenyl)-1-methyl-2(1*H*)-quinolinone (**21**), which in turn condensed with salicyladehyde, in the presence of sodium acetate, to give **20** (*cf.* Scheme II).

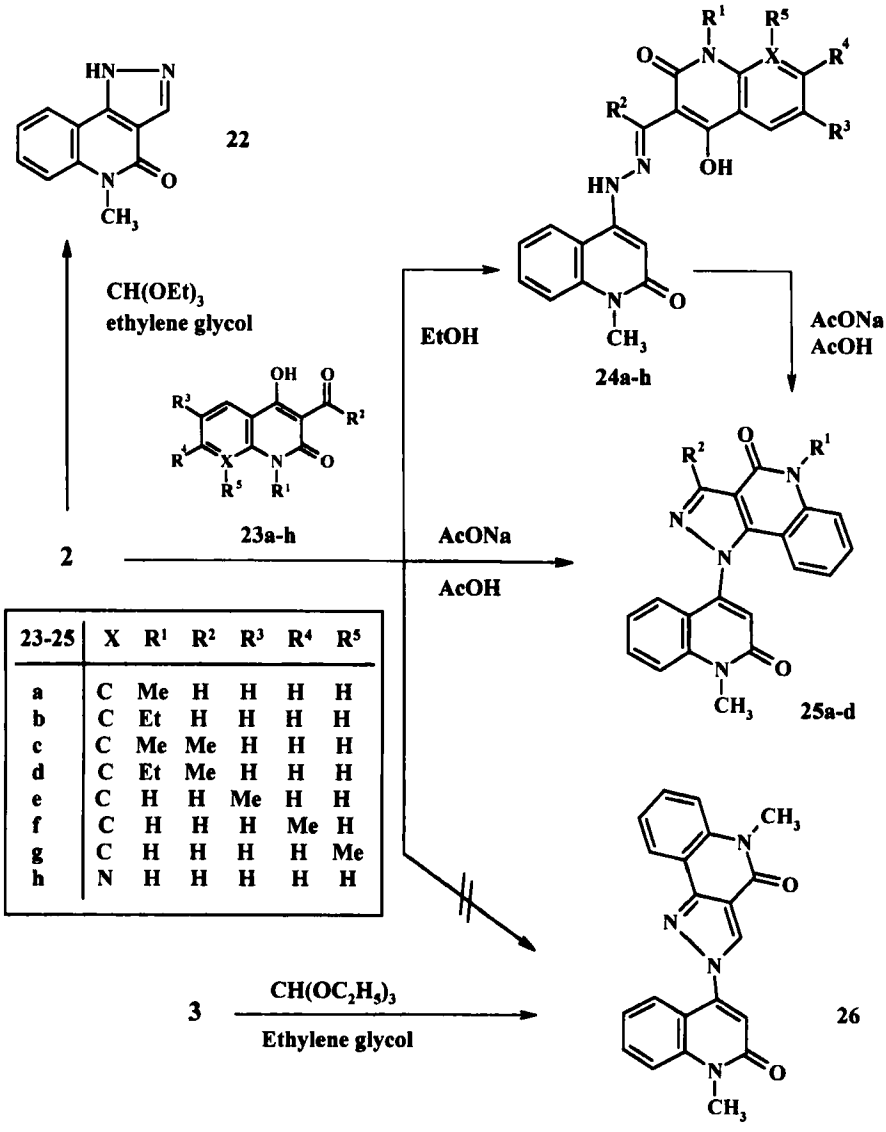
Treatment of **2** with triethyl orthoformate, in boiling ethylene glycol, afforded pyrazolo[4,5-*c*]quinolinone **22**, which was found similar in every respect with an authentic sample prepared by us in a previous work [11]. The hydrazones



Scheme II

24a-h were obtained when 3-formyl(or acetyl)-4-hydroxy-2(1*H*)quinolinones **23a-g** and/or 3-formyl-4-hydroxy-2(1*H*)-[1,8]naphthyridinone **23h** were treated with the hydrazino derivative **2**, in hot ethanol. Repeating the same reaction in glacial acetic acid, in the presence of sodium acetate, afforded 1-(4-quinolinyl)pyrazolo[4,5-*c*]quinolinones **25a-d**, which are also obtainable from boiling the hydrazones **24a-d** in glacial acetic acid, containing freshly fused sodium acetate. This absolutely excluded the possibility to obtain the isomeric derivative **26** from this reaction. However, the synthesis of 2-(4-quinolinyl)pyrazolo[4,3-*c*]quinolinone **26**, was achieved *via* thermal cyclization of the quinolinylhydrazoquinolinone **3** with triethyl orthoformate (*cf.* Scheme III).

To obtain the targeted quinolinylpyrazolylquinolinones, compound **2** was subjected to react with appropriately substituted quinolinones. Hence, the reaction of **2** with 4-hydroxy-6-methylpyrano[3,2-*c*]quinoline-2,5(6*H*)-dione (**27**)[12] was carried out, in boiling DMF, to give 3-(2-(4-quinolinyl)pyrazolin-3-yl) quinolinone **28**. The probability of obtaining the isomeric 3-(1-(4-quinolinyl)-pyrazolin-3-yl)quinolinone **30**, was excluded by the independent synthesis of the latter derivative from cyclization of **2** with 3-ethoxycarbonyl-acetyl-4-hydroxy-1-methyl-2(1*H*)quinolinone (**29**) [13]. Moreover, the IR and ^{1}H NMR spectra of **28** revealed the presence of a pyrazolinone N-H characterized by a vibrational absorption at ν: 3277 cm^{-1} and a chemical shift at δ: 10 ppm, while spectra of **30** showed a very characteristic pyrazolinyl CH_2 signal at δ: 2.9 ppm. The reaction of the 1,3-diketones **31a-c** [13,14] with compound **2** afforded the intended 3-(1-(1,2-dihydro-1-methyl-2-oxo-4-quinolinyl)-3-pyrazolyl)-4-hydroxy-1-methyl-2(1*H*)-



23-25	X	R¹	R²	R³	R⁴	R⁵
a	C	Me	H	H	H	H
b	C	Et	H	H	H	H
c	C	Me	Me	H	H	H
d	C	Et	Me	H	H	H
e	C	H	H	Me	H	H
f	C	H	H	H	Me	H
g	C	H	H	H	H	Me
h	N	H	H	H	H	H

Scheme III

quinolinones **32a-c**. On the other hand, the hydrazinoquinolinone **2** underwent condensation-addition cyclization reaction with 3-cinnamoyl (or 5-phenyl-2,4-pentadienoyl)-4-hydroxy-2(1*H*)quinolinones **33a-e** [13], to give the corresponding 3-(1-(1,2-dihydro-1-methyl-2-oxo-4-quinolinyl)-Δ^2-3-pyrazolinyl)-4-hydroxy-1-methyl-2(1*H*)quinolinones **34a-e** (*cf.* Scheme IV). The structures of all the newly obtained compounds were verified on the basis of their elemental microanalyses, and IR and ^{1}H NMR spectral data (*cf.* Tables I and II).

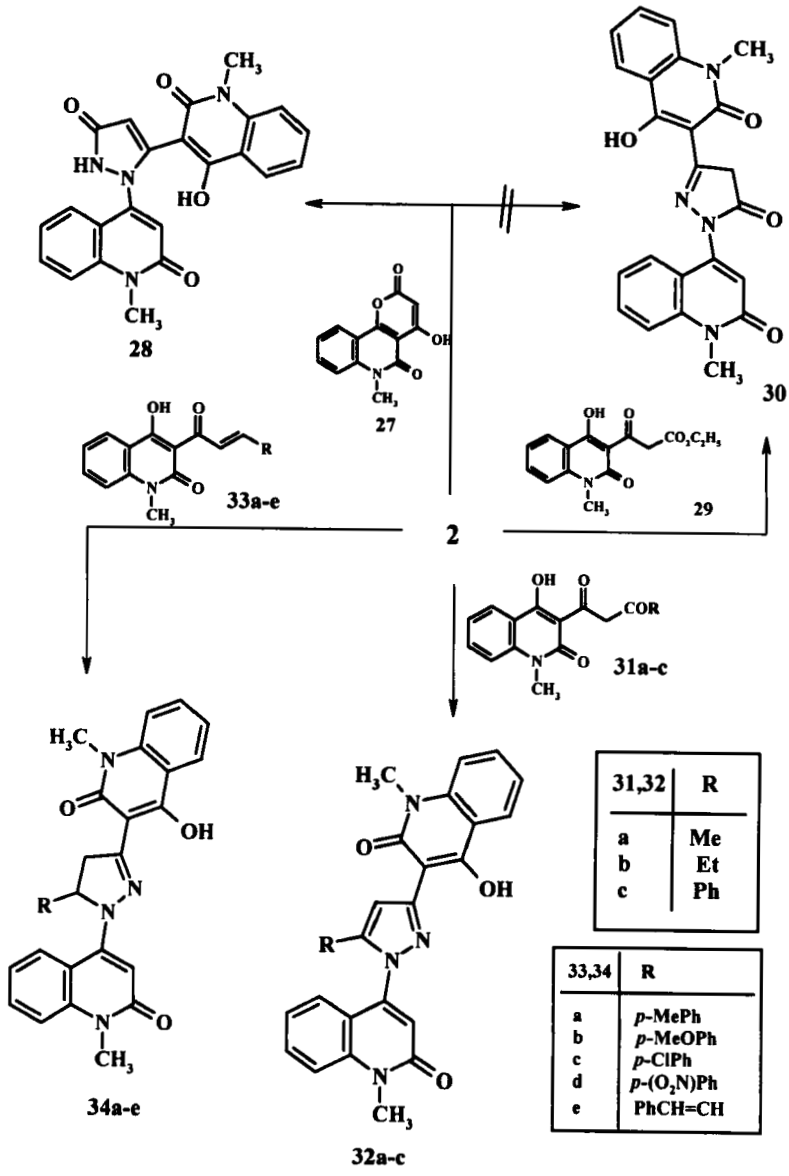
EXPERIMENTAL

Melting points are uncorrected and were determined in open capillary tubes on a digital Gallen Kamp MFB-595 apparatus. IR spectra were taken on Perkin-Elmer 598 and FT-IR 1650 spectrophotometers, using samples in KBr disks. ^{1}H NMR spectra were recorded on Jeol FX-90 (90 MHz) and EX-270 NMR spectrometers (270 MHz), using DMSO-d_6 as solvent and TMS as internal standard. Elemental microanalyses were performed at Ain Shams University Microanalytical Central Lab. Compound **1** was prepared according to the literature method [7]. Analytical and spectral data are cited in tables I and II.

4-Hydrazino-1-methyl-2(1*H*)quinolinone (2) and

1-Methyl-4-phenylhydrazo-2(1*H*)quinolinone (5).

A. To a solution of chloroquinolinone **1** (19.35 g, 0.1 mol), in DMF (200 mL), hydrazine hydrate (10.01 g, 0.2 mol) and/or phenylhydrazine (21.63 g, 0.2 mol) was added. The reaction mixture was heated under reflux for 3h. The crystalline



31,32	R
a	Me
b	Et
c	Ph

33,34	R
a	*p*-MePh
b	*p*-MeOPh
c	*p*-ClPh
d	*p*-(O_2N)Ph
e	PhCH=CH

Scheme IV

deposits so obtained were then filtered off and recrystallized to give **2** (13.05 g) and **5** (13.53 g), respectively.

B. A mixture of mercaptoquinolinone **4** (5.75 g, 0.03 mol), hydrazine hydrate (3 g, 0.06 mol) or phenylhydrazine (6.5 g, 0.06 mol), and hydrazinium chloride (1.05 g, 0.015 mol) or phenylhydrazinium chloride (2.2 g, 0.015 mol), in DMF (75 mL), was refluxed for 6h and then left to cool at room temperature. The solid so separated was filtered off and recrystallized to give **2** (1.81 g) and **5** (1.11 g), respectively.

4-(1,2-Dihydro-1-methyl-2-oxo-4-quinolinyl)hydrazo-1-methyl-2(1*H*)quinolinone (3).

Using the above method A, compound **3** (1.73g) was obtained from equimolar amounts (0.01 mol) of compounds **1** (1.94 g) and **2** (1.89 g).

4-Mercapto-1-methyl-2(1*H*)quinolinone (4).

Equimolar amounts (0.1 mol) of chloroquinolinone **1** (19.35 g) and thiourea (7.7 g) were mixed and heated gently without solvent at 120-125 °C for 20 min. Afterwards, pre-heated DMF (200 mL) was added and the mixture was refluxed for 2h, then poured onto crushed ice and made alkaline using sodium hydroxide (150 mL, 2*N*). The solution so obtained was filtered from insoluble materials and the alkaline filtrate was acidified with hydrochloric acid till complete precipitation. The precipitate so separated was filtered off and crystallized to give **4** (8.42 g).

5-Methyl-11*H*-indolo[3,2-*c*]quinolin-6(5*H*)-one (6).

The phenylhydrazoquinolinone **5** (2.65 g, 0.01 mol) was dissolved in

Table I. Analytical Data of the New Compounds.

Compd. No.	M.P.(°C) Crystn.Solvent	Yield (%)	Mol. Formula (Mol. Weight)	Microanalysis Calcd.(%)/Found(%)		
				C	H	N
2	214-216	69[a]	$C_{10}H_{11}N_3O$	63.48	5.86	22.21
	Dioxan	32[b]	(189.22)	63.50	5.60	21.90
3	262-264	50	$C_{20}H_{18}N_4O_2$	69.35	5.24	16.17
	DMF		(346.39)	69.10	5.20	16.00
4	242-243	44	$C_{10}H_9NOS$	62.81	4.74	7.32
	DMF		(191.25)	62.50	4.60	7.10
5	324-325	51[a]	$C_{16}H_{15}N_3O$	72.43	5.70	15.84
	DMF	14[b]	(265.32)	72.20	5.50	15.80
6	294-296[c]	62	$C_{16}H_{12}N_2O$	77.40	4.87	11.28
	AcOH		(248.29)	77.30	4.50	11.10
9	218-220	43[a]	$C_{24}H_{19}N_3O$	73.27	4.87	17.80
	DMF	75[b]	(393.45)	73.40	4.60	17.50
10	131-133[d]	76	$C_{10}H_8N_4O$	60.00	4.03	27.99
	EtOH		(200.20)	60.10	4.00	27.80
11a	200-202	81	$C_{14}H_{16}N_4OS$	58.31	5.56	19.43
	Dioxan		(288.38)	58.20	5.40	19.10
11b	207-208	85	$C_{18}H_{16}N_4O_2S$	61.35	4.58	15.90
	Dioxan		(352.41)	61.30	4.60	15.80
13a	320-322	79	$C_{18}H_{14}N_4O_2$	67.92	4.43	17.60
	AcOH		(318.34)	68.10	4.20	17.50
13b	308-309	83	$C_{18}H_{13}N_4O_2Cl$	61.28	3.71	15.88
	DMF		(352.78)	61.20	3.70	15.60
13c	312-313	77	$C_{18}H_{13}N_4O_2Cl$	61.28	3.71	15.88
	DMF		(352.78)	61.40	3.50	15.50
13d	302-305	64	$C_{18}H_{13}N_4O_2Cl$	61.28	3.71	15.88
	DMF		(352.78)	61.00	3.40	15.80
13e	325-326	84	$C_{18}H_{13}N_4O_2Br$	54.43	3.30	14.10
	AcOH		(397.23)	54.10	3.20	13.90
13f	280-282	78	$C_{18}H_{13}N_4O_2Br$	54.43	3.30	14.10
	AcOH		(397.23)	54.30	3.10	14.30
13g	309-311	65	$C_{18}H_{13}N_4O_2Br$	54.43	3.30	14.10
	AcOH		(397.23)	54.50	3.20	14.00
14	184-185	62	$C_{14}H_{12}N_4O_3$	59.15	4.25	19.71
	DMF		(284.28)	59.40	4.20	19.90
15	286-287	83	$C_{19}H_{17}N_3O_2$	71.46	5.37	13.16
	DMF		(319.37)	71.60	5.30	13.10
16	278-280	89	$C_{19}H_{17}N_3O$	75.23	5.65	13.85
	EtOH		(303.37)	75.10	5.50	13.50
17a	198-200	58	$C_{14}H_{13}N_3O_2$	65.87	5.13	16.46
	AcOH		(255.28)	65.70	5.00	16.20
17b	152-154	60	$C_{19}H_{15}N_3O_2$	71.91	4.76	13.24
	AcOH		(317.35)	71.80	4.80	13.10
18	230-232	74	$C_{28}H_{24}N_6O_3$	68.28	4.90	17.06
	DMF		(492.54)	68.20	4.70	16.90
20	298-299	77[a]	$C_{20}H_{15}N_3O_4$	66.48	4.18	11.63
	AcOH	80[b]	(361.36)	66.30	4.20	11.50
21	216-218	65	$C_{13}H_{11}N_3O_3$	60.70	4.31	16.33
	Dioxan		(257.25)	60.50	4.20	16.60

Table I. *continued*

Compd. No.	M.P.(°C) Crystn.Solvent	Yield (%)	Mol. Formula (Mol. Weight)	Microanalysis Calcd.(%)/Found(%)		
				C	H	N
22	309-311[c]	61	$C_{11}H_9N_3O$	66.32	4.55	21.09
	DMF		(199.21)	66.40	4.30	21.20
24a	298-300	82	$C_{21}H_{18}N_4O_3$	67.37	4.85	14.96
	Dioxan		(374.40)	67.10	4.80	14.80
24b	281-282	83	$C_{22}H_{20}N_4O_3$	68.03	5.19	14.42
	Dioxan		(388.43)	67.80	5.10	14.30
24c	256-257	90	$C_{22}H_{20}N_4O_3$	68.03	5.19	14.42
	EtOH		(388.43)	68.20	5.20	14.10
24d	258-260	87	$C_{23}H_{22}N_4O_3$	68.64	5.51	13.92
	MeOH		(402.46)	68.40	5.20	13.60
24e	325-326	74	$C_{21}H_{18}N_4O_3$	67.37	4.85	14.96
	Dioxan		(374.40)	67.00	4.50	14.90
24f	329-330	69	$C_{21}H_{18}N_4O_3$	67.37	4.85	14.96
	Dioxan		(374.40)	67.20	4.60	15.20
24g	312-314	85	$C_{21}H_{18}N_4O_3$	67.37	4.85	14.96
	Dioxan		(374.40)	67.30	4.70	14.80
24h	292-294	62	$C_{19}H_{15}N_5O_3$	63.15	4.18	19.38
	DMSO		(361.36)	63.10	4.00	19.20
25a	271-272	74	$C_{21}H_{16}N_4O_2$	70.78	4.53	15.72
	AcOH		(356.39)	70.60	4.50	15.40
25b	251-252	78	$C_{22}H_{18}N_4O_2$	71.34	4.90	15.13
	1-PrOH		(370.41)	71.10	4.70	14.90
25c	182-183	55	$C_{22}H_{18}N_4O_2$	71.34	4.90	15.13
	EtOH		(370.41)	71.30	4.80	15.00
25d	118-119	57	$C_{23}H_{20}N_4O_2$	71.86	5.24	14.57
	EtOH		(384.44)	71.60	5.10	14.60
26	258-260	63	$C_{21}H_{16}N_4O_2$	70.78	4.53	15.72
	AcOH		(356.39)	70.70	4.30	15.50
28	306-308	87	$C_{23}H_{18}N_4O_4$	66.66	4.38	13.52
	DMF		(414.42)	66.30	4.20	13.50
30	235-236	74	$C_{23}H_{18}N_4O_4$	66.66	4.38	13.52
	AcOH		(414.42)	66.50	4.10	13.30
32a	245-246	60	$C_{24}H_{20}N_4O_3$	69.89	4.89	13.58
	DMF		(412.45)	69.70	4.60	13.60
32b	228-230	58	$C_{25}H_{22}N_4O_3$	70.41	5.20	13.14
	EtOH		(426.48)	70.20	5.00	12.90
32c	210-212	68	$C_{29}H_{22}N_4O_3$	73.40	4.67	11.81
	n-BuOH		(474.52)	73.20	4.40	11.50
34a	195-197	53	$C_{30}H_{26}N_4O_3$	73.45	5.34	11.42
	Acetone		(490.57)	73.60	5.20	11.30
34b	153-155	59	$C_{30}H_{26}N_4O_4$	71.13	5.17	11.06
	MeOH		(505.57)	71.30	4.90	10.80
34c	150-152	58	$C_{29}H_{23}N_4O_3Cl$	68.17	4.54	10.96
	Chloroform		(510.98)	68.10	4.40	10.70
34d	205-207	50	$C_{29}H_{23}N_5O_5$	66.79	4.45	13.43
	Dioxan		(521.54)	66.50	4.40	13.20
34e	115-116	66	$C_{31}H_{26}N_4O_3$	74.09	5.21	11.15
	EtOH		(502.58)	73.80	5.10	11.10

[a], [b] The yields (%) using methods A and B, respectively.
[c] Lit.8 M.P.: 295 °C, [d] Lit.9 M.P.: 130 °C, [e] Lit.11 M.P.: >300 °C.

Table II. Spectral Data of the New Compounds.

Compd. No.	IR, ν (cm^{-1})	^1H NMR, δ (ppm)
2	3305, 3244 (NH_2, NH), 3072 (CH_{arom}), 2961 (CH_{aliph}), 1661 ($C=O_{quinolone}$), 1611, 1581, 1540, 1484, 1447.	8.20 (s, 1H, NH disappears with D_2O), 7.90-7.12 (m, 4H, H_{arom}), 5.85 (s, 1H, 3-$H_{quinolone}$), 4.20 (s, 2H, NH_2 disappears with D_2O), 3.50 (s, 3H, NCH_3).
3	3268-3160 (NH), 3077(CH_{arom}), 2929 (CH_{aliph}), 1671 ($C=O_{quinolone}$), 1630, 1611, 1590, 1547, 1481, 1452.	8.15 (s, 2H, 2 X NH disappears with D_2O), 7.85-7.10 (m, 8H, H_{arom}), 5.80 (s, 2H, 2 X 3-$H_{quinolone}$), 3.45 (s, 6H, 2 X NCH_3).
4	3073 (CH_{arom}), 2981 (CH_{aliph}), 2585 (SH), 1660 ($C=O_{quinolone}$), 1616, 1603, 1574, 1548, 1497, 1454.	7.95-7.20 (m, 4H, H_{arom}), 5.85 (s, 1H, 3-$H_{quinolone}$), 3.50 (s, 3H, NCH_3), 2.55(s, 1H, SH disappears with D_2O).
5	3241-3124 (NH), 3047(CH_{arom}), 2931 (CH_{aliph}), 1642 ($C=O_{quinolone}$), 1605, 1573, 1540, 1500, 1452, 1408.	8.20, 8.05 (two s, 2H, 2 X NH disappear with D_2O), 7.85-7.10 (m, 9H, H_{arom}), 5.86 (s, 1H, 3-$H_{quinolone}$), 3.52 (s, 3H, NCH_3).
9	3205-3160 (NH), 3056(CH_{arom}), 2946 (CH_{aliph}), 1675 ($C=O_{quinolone}$), 1618 (C=N), 1606, 1599, 1548, 1482, 1445.	8.33, 8.15 (two s, 2H, 2 X NH disappear with D_2O), 7.95-6.90 (m, 13H, H_{arom}), 6.20 (s, 1H, 3-$H_{quinolone}$), 3.50 (s, 3H, NCH_3).
11a	3261, 3197-3159 (NHs), 3073(CH_{arom}), 2981 (CH_{aliph}), 1653 ($C=O_{quinolone}$), 1637 (C=C), 1613, 1580, 1537, 1484, 1452, 1252 (C=S).	9.55, 9.05, 8.45 (three s, 3H, 3 X NH disappear with D_2O), 8.00-7.20 (m, 4H, H_{arom}), 5.85 (m, 1H, CH_2-C*H*=CH_2), 5.80 (s, 1H, 3-$H_{quinolone}$), 5.05 (d, 2H, CH_2-CH=C*H*$_2$), 4.10 (d, 2H, C*H*$_2$-CH=CH_2), 3.50 (s, 3H, NCH_3).
11b	3246, 3230-3190 (NHs), 3079 (CH_{arom}), 2960 (CH_{aliph}), 1675 ($C=O_{benamide}$), 1640 ($C=O_{quinolone}$), 1615, 1600, 1590, 1580, 1515, 1485, 1452, 1265 (C=S).	9.75, 9.10, 8.40 (three s, 3H, 3 X NH disappear with D_2O), 8.05-7.00 (m, 9H, H_{arom}), 5.65 (s, 1H, 3-$H_{quinolone}$), 3.55 (s, 3H, NCH_3).
13a	3159, 3122 (NHs), 3094, 3061 (CH_{arom}), 2990 (CH_{aliph}), 1725 ($C=O_{indolone}$), 1680 ($C=O_{quinolone}$), 1637 (C=N), 1609, 1578, 1534, 1485, 1453.	11.35 (s, 1H, $NH_{indolone}$ disappears with D_2O), 10.20 (s, 1H, $NH_{hydrazino}$ disappears with D_2O), 8.05-7.15 (m, 8H, H_{arom}), 6.15 (s, 1H, 3-$H_{quinolone}$), 3.62 (s, 3H, NCH_3).
13b	3154, 3124 (NHs), 3083, 3055 (CH_{arom}), 2962(CH_{aliph}), 1723 ($C=O_{indolone}$), 1672 ($C=O_{quinolone}$), 1630 (C=N), 1605, 1584, 1540 1485, 1452.	11.38 (s, 1H, $NH_{indolone}$ disappears with D_2O), 10.15 (s, 1H, $NH_{hydrazino}$ disappears with D_2O), 8.00-7.15 (m, 7H, H_{arom}), 6.15 (s, 1H, 3-$H_{quinolone}$), 3.55 (s, 3H, NCH_3).
13c	3162, 3120 (NHs), 3077, 3060 (CH_{arom}), 2985(CH_{aliph}), 1726 ($C=O_{indolone}$), 1678 ($C=O_{quinolone}$), 1626 (C=N), 1608, 1595, 1583, 1546 1486, 1450.	
13d	3172, 3126 (NHs), 3070, 3052 (CH_{arom}), 2980(CH_{aliph}), 1717 ($C=O_{indolone}$), 1678 ($C=O_{quinolone}$), 1635 (C=N), 1606, 1587, 1543, 1488, 1453.	
13e	3180, 3135 (NHs), 3082, 3031 (CH_{arom}), 2978(CH_{aliph}), 1725 ($C=O_{indolone}$), 1680 ($C=O_{quinolone}$), 1626 (C=N), 1605, 1590, 1547, 1503, 1485, 1456.	11.85 (s, 1H, $NH_{indolone}$ disappears with D_2O), 9.95 (s, 1H, $NH_{hydrazino}$ disappears with D_2O), 8.05-7.18 (m, 7H, H_{arom}), 5.80 (s, 1H, 3-$H_{quinolone}$), 3.65 (s, 3H, NCH_3).

Table II. *continued*

Compd. No.	IR, ν (cm^{-1})	^1H NMR, δ (ppm)
13f	3182, 3125 (NHs), 3078, 3035 (CH_{arom}), 2970(CH_{aliph}), 1720 ($C=O_{indolone}$), 1675 ($C=O_{quinolone}$), 1628 (C=N), 1606, 1588, 1545, 1500, 1483, 1452.	11.80 (s, 1H, $NH_{indolone}$ disappears with D_2O), 10.05 (s, 1H, $NH_{hydrazino}$ disappears with D_2O), 8.05-7.15 (m, 7H, H_{arom}), 5.80 (s, 1H, 3-$H_{quinolone}$), 3.55 (s, 3H, NCH_3).
13g	3180, 3134 (NHs), 3070, 3041 (CH_{arom}), 2981CH_{aliph}), 1718($C=O_{indolone}$), 1672 ($C=O_{quinolone}$), 1630 (C=N), 1600, 1590, 1547, 1508, 1485, 1456.	
14	3369, 3260, 3205-3156 (NH_2, NH), 3080 (CH_{arom}), 2991 (CH_{aliph}), 1697 ($C=O_{amide}$), 1676 ($C=O_{pyrazolone}$), 1655 ($C=O_{quinolone}$), 1620 (C=C), 1600, 1585, 1556, 1505, 1464,	12.25 (s, 1H, $NH_{pyrazolone}$ disappears with D_2O), 8.55 (s, 2H, $NH_{2\ amide}$ disappears with D_2O), 8.05-7.10 (m, 5H, H_{arom} + 3-$H_{pyrazolone}$), 6.25 (s, 1H, 3-$H_{quinolone}$), 3.45 (s, 3H, NCH_3).
15	3230 (NH), 3058 (CH_{arom}), 2970 (CH_{aliph}), 1680 ($C=O_{pyrazolone}$), 1645 ($C=O_{quinolone}$), 1610, 1580, 1550, 1505, 1484, 1454.	10.90 (s, 1H, $NH_{pyrazolone}$ disappears with D_2O), 8.00-7.15 (m, 9H, H_{arom}), 6.15 (s, 1H, 3-$H_{quinolone}$), 4.10 (t, 1H, 5-$H_{pyrazolone}$), 3.55 (s, 3H, NCH_3), 2.85 (d, 2H, $COCH_2$).
16	3080 (CH_{arom}), 2990 (CH_{aliph}), 1645 ($C=O_{quinolone}$), 1633 ($C=N_{pyrazoline}$), 1612, 1590, 1576, 1505, 1495, 1455.	8.10-7.15 (m, 10H, H_{arom} + C3-$H_{pyrazoline}$), 5.85 (s, 1H, 3-$H_{quinolone}$), 3.55 (s, 3H, NCH_3), 3.22 (t, 1H, 5-$H_{pyrazoline}$), 2.60 (m, 2H, CH_2).
17a	3082 (CH_{arom}), 2972 (CH_{aliph}), 1676 ($C=O_{pyrazolone}$), 1646 ($C=O_{quinolone}$), 1625 ($C=N_{pyrazoline}$), 1580, 1530, 1484, 1455.	8.05-7.20 (m, 4H, H_{arom}), 5.85 (s, 1H, 3-$H_{quinolone}$), 3.55 (s, 3H, NCH_3), 2.85 (s, 2H, CH_2), 2.40 (s, 3H, CH_3).
17b	3080 (CH_{arom}), 2976 (CH_{aliph}), 1664 ($C=O_{pyrazolone}$), 1656 ($C=O_{quinolone}$), 1633 ($C=N_{pyrazoline}$), 1572, 1552, 1500, 1455.	8.05-7.00 (m, 9H, H_{arom}), 5.80 (s, 1H, 3-$H_{quinolone}$), 3.60 (s, 3H, NCH_3), 2.90 (s, 2H, CH_2).
18	3120-2650 (br H-*bonded* OH), 1665, 1659 ($C=O_{quinolone}$), 1632, 1618($C=N_{pyrazole}$), 1590, 1580, 1543, 1505, 1460, 1444.	11.10 (s, 1H, OH disappears with D_2O), 7.95-7.20 (m, 8H, H_{arom}), 6.30 (s, 1H, 4-$H_{pyrazole}$), 6.00, 5.85 (two s, 2H, 2 X 3-$H_{quinolone}$), 3.65, 3.55 (two s, 6H, 2 X NCH_3), 2.40 (s, 3H, CH_3), 2.35 (s, 3H, CH_3).
20	3240-2620 (NH + H-*bonded* OH), 1718, 1682 ($C=O_{pyrazoledione}$), 1645($C=O_{quinolone}$), 1620, 1610, 1578, 1551, 1489, 1456.	10.80 (s, 1H, OH disappears with D_2O), 10.30 (s, 1H, NH disappears with D_2O), 8.68 (s, 1H, $H_{methine}$) 8.15-6.90 (m, 8H, H_{arom}), 6.20 (s, 1H, 3-$H_{quinolone}$), 3.52 (s, 3H, NCH_3).
21	3185, 3122 (NH), 3086 (CH_{arom}), 2980 (CH_{aliph}), 1715, 1690 ($C=O_{pyrazoledione}$), 1650 ($C=O_{quinolone}$), 1625, 1603, 1575, 1545, 1485, 1452.	10.22 (s, 1H, NH disappears with D_2O), 8.05-7.10 (m, 4H, H_{arom}), 6.15 (s, 1H, 3-$H_{quinolone}$), 3.50 (s, 3H, NCH_3), 2.95 (s, 2H, CH_2).
24a	3230, 3125-2650 (NH + H-*bonded* OH), 1670, 1648 ($C=O_{quinolone}$), 1628 (C=N), 1610, 1587, 1555, 1487, 1450.	13.30 (s, 1H, OH disappears with D_2O), 11.02 (s, 1H, NH disappears with D_2O), 8.90 (s, 1H, $CH_{azomethine}$), 8.05-7.10 (m, 8H, H_{arom}), 5.85 (s, 1H, 3-$H_{quinolone}$), 3.50 (two s, 6H, 2 X NCH_3).
24b	3230, 3126-2620 (NH + H-*bonded* OH), 1668, 1645 ($C=O_{quinolone}$), 1626 (C=N), 1610, 1585, 1552, 1485, 1454.	13.35 (s, 1H, OH disappears with D_2O), 11.00 (s, 1H, NH disappears with D_2O), 8.95 (s, 1H, $H_{azomethine}$), 8.10-7.25 (m, 8H, H_{arom}), 5.85 (s, 1H, 3-$H_{quinolone}$), 4.22 (q, 2H, $NC\underline{H_2}CH_3$), 3.50 (s, 3H, NCH_3), 1.20 (t, 3H, $NCH_2C\underline{H_3}$).

(*continued*)

Table II. *continued*

Compd. No.	IR, ν (cm^{-1})	^1H NMR, δ (ppm)
24c	3201, 3153-2637 (NH + H-*bonded* OH), 1660, 1645 ($C=O_{quinolone}$), 1621 (C=N), 1609, 1586, 1543, 1487, 1451.	13.30 (s, 1H, OH disappears with D_2O), 9.95 (s, 1H, NH disappears with D_2O), 8.05-7.15 (m, 8H, H_{arom}), 5.85 (s, 1H, 3-$H_{quinolone}$), 3.65, 3.50 (two s, 6H, 2 X NCH_3), 2.82 (s, 3H, CH_3).
24d	3215, 3140-2620 (NH + H-*bonded* OH), 1664, 1648 ($C=O_{quinolone}$), 1626 (C=N), 1604, 1585, 1547, 1489, 1456.	13.20 (s, 1H, OH disappears with D_2O), 9.87 (s, 1H, NH disappears with D_2O), 8.20-7.22 (m, 8H, H_{arom}), 5.85 (s, 1H, 3-$H_{quinolone}$), 4.25 (q, 2H, NCH_2CH_3), 3.60 (s, 3H, NCH_3), 2.80 (s, 3H, CH_3), 1.22 (t, 3H, NCH_2CH_3).
24e	3240, 3172-2640 (NHs + H-*bonded* OH), 1665, 1642 ($C=O_{quinolone}$), 1624 (C=N), 1610, 1588, 1549, 1472, 1453.	11.68 (s, 1H, OH disappears with D_2O), 10.85 (s, 1H, $NH_{quinolone}$ disappears with D_2O), 9.75 (s, 1H, $NH_{hydrazone}$ disappears with D_2O), 8.85 (s, 1H, $H_{azomethine}$), 8.05-7.10 (m, 7H, H_{arom}), 5.95 (s, 1H, 3-$H_{quinolone}$), 3.55 (s, 3H, NCH_3), 2.35 (s, 3H, 6-CH_3).
24f	3242, 3155-2648 (NHs + H-*bonded* OH), 1668, 1652 ($C=O_{quinolone}$), 1625 (C=N), 1610, 1601, 1557, 1511, 1482, 1452.	11.85 (s, 1H, OH disappears with D_2O), 10.83 (s, 1H, $NH_{quinolone}$ disappears with D_2O), 9.65 (s, 1H, $NH_{hydrazone}$ disappears with D_2O), 8.80 (s, 1H, $H_{azomethine}$), 8.10-7.10 (m, 7H, H_{arom}), 5.95 (s, 1H, 3-$H_{quinolone}$), 3.50 (s, 3H, NCH_3), 2.26 (s, 3H, 7-CH_3).
24g	3240, 3160-2620 (NHs + H-*bonded* OH), 1660, 1645 ($C=O_{quinolone}$), 1620 (C=N), 1608, 1588, 1550, 1515, 1487, 1448.	11.65 (s, 1H, OH disappears with D_2O), 10.72 (s, 1H, $NH_{quinolone}$ disappears with D_2O), 9.80 (s, 1H, $NH_{hydrazone}$ disappears with D_2O), 8.85 (s, 1H, $CH_{azomethine}$), 8.08-7.15 (m, 7H, H_{arom}), 6.10 (s, 1H, C3-$H_{quinolone}$), 3.65 (s, 3H, NCH_3), 2.30 (s, 3H, 8-CH_3).
24h	3252, 3172-2658 (NHs + H-*bonded* OH), 1684 ($C=O_{naphthyridone}$), 1641 ($C=O_{quinolone}$), 1625-1618 (C=N), 1600, 1582, 1545, 1495, 1472, 1460.	12.20 (s, 1H, OH disappears with D_2O), 10.45 (s, 1H, $NH_{naphthyridone}$ disappears with D_2O), 9.43 (s, 1H, $NH_{hydrazone}$ disappears with D_2O), 8.85 (s, 1H, $H_{azomethine}$), 8.15-7.20 (m, 7H, H_{arom}), 5.95 (s, 1H, 3-$H_{quinolone}$), 3.50 (s, 3H, NCH_3).
25a	3082, 3038 (CH_{arom}), 2990, 2930 (CH_{aliph}), 1660, 1645 ($C=O_{quinolone}$), 1625 (C=N), 1608, 1595, 1567, 1540, 1522, 1487, 1448.	8.22 (s, 1H, 3-$H_{pyrazole}$), 8.05-7.10 (m, 8H, H_{arom}), 6.25 (s, 1H, 3-$H_{quinolone}$), 3.55, 3.50 (two s, 6H, 2 X NCH_3).
25b	3088, 3040 (CH_{arom}), 2987, 2935 (CH_{aliph}), 1661, 1644 ($C=O_{quinolone}$), 1620(C=N), 1610, 1586, 1567, 1488, 1452.	8.25 (s, 1H, 3-$H_{pyrazole}$), 8.05-7.10 (m, 8H, H_{arom}), 6.10 (s, 1H, 3-$H_{quinolone}$), 4.25 (q, 2H, NCH_2CH_3), 3.50 (s, 3H, NCH_3), 1.24 (t, 3H, NCH_2CH_3).
25c	3085, 3038 (CH_{arom}), 2985, 2932 (CH_{aliph}), 1655, 1652 ($C=O_{quinolone}$), 1625 (C=N), 1608, 1592, 1577, 1534, 1516, 1472, 1454.	8.05-7.15 (m, 8H, H_{arom}), 5.85 (s, 1H, 3-$H_{quinolone}$), 3.50 (two s, 6H, 2 X NCH_3), 2.70 (s, 3H, CH_3).
25d	3080, 3040 (CH_{arom}), 2975, 2940 (CH_{aliph}), 1660, 1648 ($C=O_{quinolone}$), 1625 (C=N), 1611, 1586, 1565, 1544, 1503, 1470, 1445.	8.05-7.10 (m, 8H, H_{arom}), 6.10 (s, 1H, 3-$H_{quinolone}$), 4.20 (q, 2H, NCH_2CH_3), 3.50 (s, 3H, NCH_3), 2.72 (s, 3H, CH_3), 1.20 (t, 3H, NCH_2CH_3).

Table II. *continued*

Compd. No.	IR, ν (cm^{-1})	^1H NMR, δ (ppm)
26	3086, 3038 (CH_{arom}), 2980, 2932 (CH_{aliph}), 1668, 1655 ($C{=}O_{quinolone}$), 1635 (C=N), 1600, 1586, 1546, 1522, 1486, 1458.	8.05-7.15 (m, 9H, H_{arom} + $H_{pyrazole}$), 5.85 (s, 1H, 3-$H_{quinolone}$), 3.60, 3.50 (two s, 6H, 2 X NCH_3).
28	3277, 3235-2629 (NH + H-*bonded* OH), 1688 ($C{=}O_{pyrazolone}$), 1661, 1645 ($C{=}O_{quinolone}$), 1612, 1582, 1547, 1499, 1455.	13.40 (s, 1H, OH disappears with D_2O), 10.00 (s, 1H, NH disappears with D_2O), 8.10-7.15 (m, 8H, H_{arom}), 6.75 (s, 1H, 4-$H_{pyrazoline}$), 5.80 (s, 1H, 3-$H_{quinolone}$), 3.65, 3.50 (two s, 6H, 2 X NCH_3).
30	3077-2620 (H-*bonded* OH), 1686 ($C{=}O_{pyrazolone}$), 1658, 1650 ($C{=}O_{quinolone}$), 1630 (C=N), 1600, 1578, 1552, 1476, 1453.	13.15 (s, 1H, OH disappears with D_2O), 8.10-7.15 (m, 8H, H_{arom}), 5.90 (s, 1H, 3-$H_{quinolone}$), 3.60, 3.50 (two s, 6H, 2 X NCH_3), 2.90 (s, 2H, CH_2).
32a	3081-2565 (H-*bonded* OH), 1661, 1645 ($C{=}O_{quinolone}$), 1630 (C=N), 1600, 1585, 1554, 1502, 1468, 1444.	13.40 (s, 1H, OH disappears with D_2O), 8.10-7.00 (m, 9H, H_{arom} + $H_{pyrazole}$), 5.95 (s, 1H, 3-$H_{quinolone}$), 3.65, 3.50 (two s, 6H, 2 X NCH_3), 2.80 (s, 3H, CH_3).
32b	3084-2660 (H-*bonded* OH), 1665, 1648 ($C{=}O_{quinolone}$), 1630 (C=N), 1603, 1587, 1564, 1505, 1472, 1452.	13.28 (s, 1H, OH disappears with D_2O), 8.10-7.05 (m, 9H, H_{arom} + $H_{pyrazole}$), 5.90 (s, 1H, 3-$H_{quinolone}$), 3.60, 3.50 (two s, 6H, 2 X NCH_3), 2.40 (q, 2H, $C\underline{H_2}CH_3$), 1.05 (t, 3H, $CH_2C\underline{H_3}$).
32c	3085-2640 (H-*bonded* OH), 1660, 1652 ($C{=}O_{quinolone}$), 1630 (C=N), 1610, 1589, 1560, 1530, 1495, 1474, 1456.	13.30 (s, 1H, OH disappears with D_2O), 8.15-7.05 (m, 14H, H_{arom} + $H_{pyrazole}$), 5.85 (s, 1H, 3-$H_{quinolone}$), 3.65, 3.50 (two s, 6H, 2 X NCH_3).
34a	3087-2584 (H-*bonded* OH), 1664, 1646 ($C{=}O_{quinolone}$), 1628 (C=N), 1600, 1573, 1537, 1510, 1500, 1478, 1455.	12.00 (s, 1H, OH disappears with D_2O), 8.15-7.00 (m, 12H, H_{arom}), 6.35 (s, 1H, 3-$H_{quinolone}$), 4.60 (t, 1H, 5-$H_{pyrazoline}$), 3.60, 3.50 (two s, 6H, 2 X NCH_3), 2.70 (d, 2H, CH_2), 1.75 (s, 3H, CH_3).
34b	3088-2586 (H-*bonded* OH), 1665, 1645 ($C{=}O_{quinolone}$), 1628 (C=N), 1602, 1578, 1540, 1490, 1476, 1454, 1050 (C-O-C).	12.45 (s, 1H, OH disappears with D_2O), 8.10-7.05 (m, 12H, H_{arom}), 6.40 (s, 1H, 3-$H_{quinolone}$), 4.50 (t, 1H, 5-$H_{pyrazoline}$), 4.20 (s, 3H, OCH_3), 3.65, 3.55 (two s, 6H, 2 X NCH_3), 2.72 (d, 2H, CH_2).
34c	3077-2620 (H-*bonded* OH), 1668, 1652 ($C{=}O_{quinolone}$), 1626 (C=N), 1610, 1588, 1542, 1500, 1488, 1455, 782 (C-Cl).	12.35 (s, 1H, OH disappears with D_2O), 8.05-7.00 (m, 12H, H_{arom}), 6.20 (s, 1H, 3-$H_{quinolone}$), 4.45 (t, 1H, 5-$H_{pyrazoline}$), 3.65, 3.55 (two s, 6H, 2 X NCH_3), 2.68 (d, 2H, CH_2).
34d	3089-2574 (H-*bonded* OH), 1660, 1652 ($C{=}O_{quinolone}$), 1620 (C=N), 1600, 1585, 1530 (NO_2), 1510, 1500, 1478, 1455, 1352.	12.42 (s, 1H, OH disappears with D_2O), 8.20-7.15 (m, 12H, H_{arom}), 6.42 (s, 1H, 3-$H_{quinolone}$), 4.45 (t, 1H, 5-$H_{pyrazoline}$), 3.65, 3.50 (two s, 6H, 2 X NCH_3), 2.75 (d, 2H, CH_2).
34e	3085-2578 (H-*bonded* OH), 1670, 1642 ($C{=}O_{quinolone}$), 1625 (C=N), 1608 (C=C), 1598, 1572, 1495, 1488, 1456.	13.15 (s, 1H, OH disappears with D_2O), 8.20-7.00 (m, 13H, H_{arom}), 6.85 (dd, J,J = 7+2 Hz, 1H, $CHC\underline{H}$=CHPh), 6.45 (s, 1H, 3-$H_{quinolone}$) 6.05 (d, 1H, CH=$C\underline{H}$Ph), 4.60 (m, 1H, 5-$H_{pyrazoline}$), 3.60, 3.50 (two s, 6H, 2 X NCH_3), 2.80 (d, 2H, CH_2).

glacial acetic acid (50 mL) and heated under reflux for 1 h. The solid so obtained during the course of the reaction was filtered off, washed with ethanol and recrystallized giving 1.54 g of compound **6**.

1-Methyl-4-(4-phenyl-1-phthalazinyl)hydrazo-2(1*H*)quinolinone (9).

A. Compound **9** (1.69 g) was obtained from **1** (1.94 g, 0.01 mol) and 1-hydrazino-4-phenylphthalazine (**7**) (2.36 g, 0.01 mol), using a method similar to method (A) that used to prepare compounds **2** and **5**.

B. From **2** (1.89 g, 0.01 mol) and 1-chloro-4-phenylphthalazine (**8**) (2.4 g, 0.01 mol), using the same above method, the same product **9** (2.95 g) was obtained.

4-Azido-1-methyl-2(1*H*)quinolinone (10).

4-Hydrazinoquinolinone **2** (0.95 g, 0.005 mol) was dissolved in hydrochloric acid (10 mL, 1*N*), and the solution was cooled in a crushed ice-bath at 0-5 °C. An aqueous solution of sodium nitrite (5 mL, 1*N*) was added drop-wise over 20 min. The solid deposits were filtered off and crystallized to give the azidoquinolinone **10** (0.76 g).

4-(4-Substituted thiosemicarbazido)-1-methyl-2(1*H*)quinolinones 11a,b.

To a suspension of **2** (1.89 g, 0.01 mol), in dioxan (25 mL), allyl isothiocyanate (1.25 g, 0.012 mol) and/or benzoyl isothiocyanate (2 g, 0.012 mol) was added and the mixture was refluxed on a boiling water-bath for 2h. The mixture was then left to cool and the precipitate so formed was filtered off and recrystallized to give **11a** (2.34 g) and **11b** (2.98 g), respectively.

1-Methyl-4-(2-oxo-3-Z-indolylidene)hydrazo-2(1*H*)quinolinones 13a-g.

A mixture of equimolar amounts (0.005 mol) of hydrazinoquinolinone **2** (0.95 g) and isatine **12a** (0.74 g) or chloroisatines **12b-d** (0.9 g) or bromoisatines

12e-g (1.13 g), in ethanol (50 mL), was refluxed for 1h. Then the reaction mixture was left to cool at room temperature and the solid so separated was filtered off, washed with hot ethanol, dried and crystallized to give **13a-g**, respectively.

Synthesis of 4-Pyrazolinyl (or pyrazolidenyl)-1-methyl-2(1*H*)quinolinones 14, 15, 16, 17a,b and 21.

A mixture of hydrazinoquinolinone **2** (0.95 g, 0.005 mol) and ethyl morpholinomethylenecyanoacetate (1.26 g, 0.006 mol), in acetic acid (30 mL), or 0.006 mol of ethyl cinnamate (1.05 g), or cinnamaldehyde (0.79 g), or ethyl acetoacetate (0.77 g), or ethyl benzoylacetate (1.09 g), or diethyl malonate (0.95 g), in DMF (30 mL), was refluxed for 2-4h. The reaction mixture was poured onto crushed ice and the solid so obtained was filtered off and crystallized to yield compounds **14** (0.88 g), **15** (1.33 g), **16** (1.35 g), **17a** (0.74 g), **17b** (0.95 g) and **21** (0.84 g), respectively.

4-[4-(1-(1,2-Dihydro-2-oxo-1-methyl-4-quinolinyl)-3-methyl-5-pyrazolyl)-5-hydroxy-3-methyl-1-pyrazolyl]-1-methyl-2(1*H*)quinolinone (18).

A mixture of **2** (1.89 g, 0.01 mol) and dehydroacetic acid (0.86 g, 0.005 mol), in DMF (50 mL), was heated under reflux for 4h. The solid so obtained during the course of the reaction was collected by filtration and recrystallized to give **18** (1.82 g).

4-[3,5-Dioxo-4-(2-hydroxy-Z-benzylidene)-1-pyrazolidenyl)-1-methyl-2(1*H*)quinolinone (20).

A. A mixture of **2** (1.89 g, 0.01 mol) and ethyl coumarin-3-carboxylate (**19**) (2.18 g, 0.01 mol), in DMF (50 mL), was heated under reflux for 4h. The

reaction mixture was then left to cool and the crystals so separated were collected by filtration and recrystallized to yield **20** (2.78 g).

B. Equimolar amounts (0.005 mol) of the pyrazolidenylquinolinone **21** (1.3 g), salicylaldehyde (0.62 g) and freshly fused sodium acetate (0.4 g), in glacial acetic acid (30 mL), were heated under reflux for 2h. The crystalline deposit so separated during the course of the reaction was filtered off and recrystallized to give 1.45 g of compound **21**.

5-Methyl-1*H*-pyrazolo[4,5-*c*]quinolin-4(5*H*)-one (22).

A suspension of **2** (0.95 g, 0.005 mol), in ethylene glycol (30 mL), was treated with triethyl orthoformate (1.06 g, 0.007 mol) and the mixture was refluxed using a short air condenser for 1h. After cooling, the obtained pasty material was triturated with diethyl ether (50 mL), and the solid so formed was filtered off and crystallized to produce 0.61 g of **22**. An authentic sample was obtained from formylquinolinone **23a** (1.02 g, 0.005 mol) and hydrazine hydrate (0.28 mL, 0.0055) according to the literature method [11].

3-Formyl (or acetyl)-4-hydroxy-2(1*H*)quinolinone(or [1,8]naphthyridinone) 1,2-Dihydro-1-methyl-2-oxo-4-quinolinylhydrazones 24a-h.

General method

A mixture of appropriate 3-formyl(or acetyl)quinolinone derivatives **23a-g** (0.01 mol) and/or 3-formylnaphthyridinone **23h** (1.9 g, 0.01 mol) and compound **2** (1.89 g, 0.01 mol), in ethanol (50 mL), was heated under reflux on a water-bath for 2h. The yellowish colored deposits those separated during the course of the reaction were collected by filtration, while hot, and recrystallized to give hydrazones **24a-h**.

3,5-Disubstituted 1-(1,2-dihydro-1-methyl-2-oxo-4-quinolinyl)pyrazolo[4,5-*c*]-quinolin-4(5*H*)-ones 25a-d.

General method

To a mixture of **23a-d** (0.005 mol) and **2** (0.95 g, 0.005 mol), in glacial acetic acid (30 mL), freshly fused sodium acetate (0. 2 g) was added and the mixture was refluxed for 4h. Then the reaction mixture was left to cool at room temperature and the solid so precipitated was filtered off and recrystallized to give **25a-d**. Treatment of the appropriate **24a-d** derivative (0.005 mol) with glacial acetic acid (30 mL) and freshly fused sodium acetate (0.2 g), as described herebefore, furnished the same product **25a-d**.

2-(1,2-Dihydro-1-methyl-2-oxo-4-quinolinyl)-5-methylpyrazolo-[4,3-*c*]quinolin-4(5*H*)-one (26).

Equimolar amounts (0.0025 mol) of the quinolinylhydrazoquinolinone **3** (0.87 g) and triethyl orthoformate (0.38 g), in ethylene glycol (30 mL) were treated, using a method similar to that described for the compound **22**, and worked up to yield 0.56 g of compound **26**.

Synthesis of Quinolinyloxopyrazolinylquinolinones 28 and 30 and Quinolinylpyrazolyl(or pyrazolinyl)quinolinones 32a-c and 34a-e.

General method

Equimolar amounts (0.005 mol) of **2** (0.95 g) and the pyrone **27** (1.22 g), or the β-ketoester **29** (1.95 g), or the 1,3-diketones **31a** (1.3 g), **31b** (1.37 g), **31c** (1.6 g), or the α,β-unsaturated ketones **33a** (1.6 g), **33b** (1.67 g), **33c** (1.7 g), **33d** (1.75 g), **33e** (1.65 g), were heated under reflux, in boiling DMF (25 mL), for 2-

4h. The reaction mixture was then left to cool to the room temperature, or poured onto crushed ice. The solid so obtained was filtered off and crystallized to give compounds **28** (1.8 g), **30** (1.5 g), **32a** (1.23 g), **32b** (1.24 g), **32c** (1.61 g) and **34a** (1.3 g), **34b** (1.49 g), **34c** (1.48 g), **34d** (1.3 g), **34e** (1.66 g), respectively.

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