

Reaction of Some 2-Quinolone Derivatives with Phosphoryl Chloride: Synthesis of Novel Phosphoric Acid Esters of 4-Hydroxy-2-quinolone

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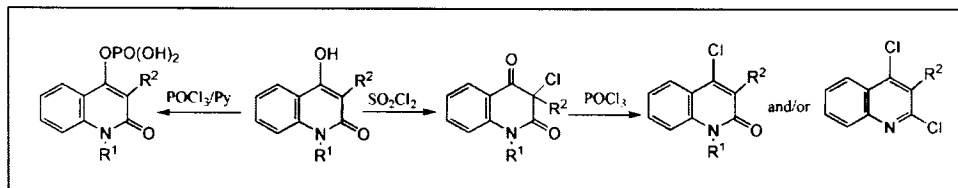
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3-Chloroquinoline-2,4-diones do not react with phosphoryl chloride, however, 2,4-dichloroquinolines and/or 4-chloroquinolin-2-ones are formed in the presence of *N,N*-dimethylaniline. Along with these compounds, small quantities of novel dihydrogen phosphates of 4-hydroxyquinolin-2-ones were isolated. We outline a simple procedure that allows for the preparation of these compounds in moderate to good yields. All compounds were characterized by ¹H and ¹³C NMR, IR, EI-MS, and ESI-MS spectroscopy, and in select cases by ³¹P NMR spectroscopy.

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INTRODUCTION

Phosphoryl chloride (phosphoryl trichloride, phosphorus oxychloride) is a popular reagent for the conversion of —CO—NH— groups to —C(Cl)=N— groups. Therefore, it is not surprising that more than 600 reactions that describe the conversion of quinoline-2-ones to 2-chloroquinolines have been reported in the literature. 1-Unsubstituted 4-hydroxyquinoline-2-ones react with phosphoryl chloride or a mixture of phosphoryl chloride and phosphorus pentachloride to give 2,4-dichloroquinolines [1–4]. To date, more than 230 2,4-dichloroquinolines are known, and some of them exhibit interesting biological activity. For example, the 7-dimethylamino-3-methyl derivative exhibits antiviral activity [5], the 3-butyl-6-(3,5-dimethylpyrazol-1-yl) derivative is mildly active against *Staphylococcus aureus* and *Saccharomyces cerevisiae* [6], the 3-(2-chloroethyl)-8-methyl derivative has the ability to inhibit (H⁺/K⁺)-ATPase affinity in lyophilized gastric vesicles [7], and the 3,7-dichloro and 3-chloro-6,7-difluoro derivatives exhibit affinity for pentacyclidine and glycine binding sites on NMDA receptors [8].

The dealkylation during the formation of 2-chloroquinolines occurs when 1-substituted quinoline-2-ones react with phosphoryl chloride. This happens most frequently in the presence of phosphorus pentachloride. This class

of reactions was studied extensively in the mid-twentieth century [9–14]. A series of studies since 1982 have found that reactions of 1-substituted 4-hydroxyquinoline-2-ones with phosphoryl chloride produce high yields of the corresponding 1-substituted 4-chloroquinoline-2-ones [15,16].

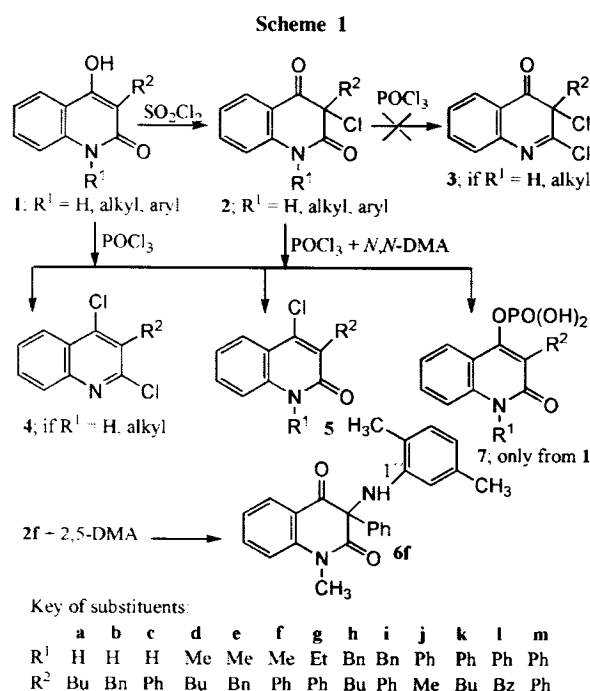
In 1991, Stadlbauer *et al.* [17] reported that the reaction of some 1-alkyl-3-aryl-7-methoxy-4-hydroxyquinoline-2-ones with phosphoryl chloride leads, without any catalyst, not only to the expected 1-alkyl-3-aryl-7-methoxy-4-chloroquinoline-2-ones but also to 3-aryl-2,4-dichloro-7-methoxyquinolines.

As a part of our institute's systematic research into 3,3-disubstituted 1*H*,3*H*-quinoline-2,4-diones we decided to study the previously undescribed reaction of 3-alkyl/aryl-3-chloroquinoline-2,4-diones **2** with phosphoryl chloride. We expected that 3-alkyl/aryl-2,3-dichloro-3*H*-quinolin-4-ones **3** would be formed, which subsequently could be reacted with amines to give two different types of the products suitable for biological testing.

RESULTS AND DISCUSSION

The initial 3-alkyl/aryl-3-chloroquinolin-2,4-diones **2** (Scheme 1) were prepared by reacting 3-alkyl/aryl-4-hydroxyquinolin-2-ones **1** with sulfonyl chloride [18,19].

SI



The preliminary experiments were carried out by boiling of starting compounds **2a,c–e,g,h** in phosphoryl chloride (Table 1, Method A). In most cases, only the starting material was isolated despite an extended reaction time (Table 1, entries 1, 6, 8, and 11). Compound **4c**

was isolated in addition to recovered starting material only with two starting compound (**2c** and **2i**), both of which bear a phenyl group in position 3.

Hence, we carried out further experiments in the presence of *N,N*-dimethylaniline (DMA), which is frequently used as a catalyst in the reaction of amides with phosphoryl chloride. Under these conditions (Table 1, Method B), the reactions take place. However, instead of the expected 3-alkyl/aryl-2,3-dichloro-3*H*-quinolin-4-ones **3**, only 2,4-dichloroquinolines **4a–c** were obtained from all starting compounds except those that have a phenyl group at position 1 (Table 1). These results show that the dealkylation of the N(1) atom proceeds in all compounds that have an alkyl group on the nitrogen atom in position 1, but conversion is low in the case of *N*-benzyl derivatives.

N-Phenyl substituted compounds **2j–m** react differently under of the same reaction conditions (Table 1, Method B). Mainly starting material was recovered; however, compounds **5k–m** were also isolated in small quantities (Table 1, entries 17–19).

The conversion of 3-chloro-1-phenylquinoline-2,4-diones **2k–m** to their corresponding 4-chloroquinolin-2-ones **5** is a net reduction. Therefore, we considered a cleavage of the C(3)–Cl bond as the first reaction step in the transformation of compounds **2k–m**. The transfer of a chlorine atom (or a bromine atom or a thiocyanato group) from position 3 of the corresponding quinoline-2,4-diones

Table 1

Reactions of 3-chloroquinoline-2,4-diones **2** with phosphoryl chloride (Method A: in the absence of a catalyst; Method B: in the presence of DMA).

Entry	2	Substituents		Method	Time (h)	Product(s) (yield, %) ^a
		R ¹	R ²			
1	a	H	Bu	A	120	2a (47) ^b
2	a			B	5	4a (83)
3	b	H	Bn	B	8	4b (75)
4	c	H	Ph	A	60	2c (32) ^b , 4c (40)
5	c			B	5	4c (84)
6	d	Me	Bu	A	10	2d (92) ^b
7	d			B	18	4a (65)
8	e	Me	Bn	A	23	2e (92) ^b
9	e			B	30	4b (46)
10	f	Me	Ph	B	10	4c (70)
11	g	Et	Ph	A	30	2g (92) ^b
12	g			B	30	4c (54)
13	h	Bn	Bu	B	8	2h (77) ^b , 4a (5)
14	i	Bn	Ph	A	18	2i (30) ^b , 4c (4)
15	i			B	16	4c (60)
16	j	Ph	Me	B	30	2j (73) ^b
17	k	Ph	Bu	B	20	2k (18) ^b , 5k (11)
18	l	Ph	Bn	B	20	2l (28) ^b , 5l (4)
19	m	Ph	Ph	B	30	2m (32) ^b , 5m (12)

^aRefers to isolated percent yield of pure product.

^bRecovered starting compound.

Table 2

Reaction of 4-hydroxyquinolin-2-ones **1** with phosphoryl chloride (*methods A and B*: see Table 1; *Method A1*: modified *Method A*)^a.

Entry	1	Substituents		Method	Time (h)	Product(s) (yields, %) ^b
		R ¹	R ²			
1	a	H	Bu	<i>A1</i>	0.6	4a (79)
2	b	H	Bn	<i>A1</i>	0.6	4b (77)
3	c	H	Ph	<i>A1</i>	0.6	4c (74)
4	c			<i>B</i>	5	4c (97)
5	d	Me	Bu	<i>A</i>	1	5d (93)
6	e	Me	Bn	<i>A1</i>	0.5	5e (41), 7e (3)
7	f	Me	Ph	<i>A1</i>	0.5	4c (2), 5f (57), 7f (2)
8	f			<i>A1</i>	6	4c (15), 5f (60)
9	g	Et	Ph	<i>A1</i>	0.5	4c (1), 5g (60), 7g (3)
10	h	Bn	Bu	<i>A1</i>	0.5	4a (7), 5h (19), 7h (28)
11	h			<i>A1</i>	6	4a (19), 5h (25), 7h (24)
12	i	Bn	Ph	<i>A1</i>	0.5	4c (1), 5i (30), 7i (4)
13	i			<i>A1</i>	6	4c (31), 5i (39), 7i (15)
14	j	Ph	Me	<i>A1</i>	0.5	5j (59), 7j (5)
15	k	Ph	Bu	<i>A</i>	0.7	5k (39), 7k (22)
16	k	Ph	Bu	<i>A1</i>	0.7	5k (65)
17	l	Ph	Bn	<i>A</i>	1	5l (33), 7l (9)
18	l			<i>A1</i>	0.7	5l (36), 7l (32)
19	m	Ph	Ph	<i>A</i>	0.7	5m (33)
20	m			<i>A1</i>	0.7	5m (80)
21	m			<i>B</i>	2	5m (79)

^a See Experimental.^b Refers to isolated percent yield of pure product.

to a nucleophile has been observed previously [20–22]. Hydroxide ions [20], sulfide ions [21], amines [22], thioalcohols [22], or activated aromatic compounds [22] can act as nucleophile.

In the case of compounds **2k–m**, DMA can act as a nucleophile. We found that the reaction of **2c** and **2m** with DMA in chloroform, acetic acid, ethanol, or toluene solution affords compounds **1**. Unfortunately, we did not succeed in isolating the expected 4-chloro-*N,N*-dimethylaniline from the complex reaction mixture. Conversion of **2f** to **1f** also proceeds in the presence of *N,N*-dimethyl-*p*-toluidine. However, facile transport of a chlorine atom from **2m** was apparent in its reaction with 2-sulfanylbenzothiazole. In addition to **1m**, 2,2'-dithiobis(benzothiazole) was isolated. These results are similar to the transfer of thiocyanato groups from 3-thiocyanatoquinoline-2,4-diones to 2-sulfanylbenzothiazoles [22]. However, the reaction of **2f** with 2,5-dimethylaniline leads only to *N*-alkylation along with formation of compound **6f**.

To clarify the reaction mechanism, we also carried out the reaction of compounds **1** with phosphoryl chloride (Table 2). In the absence of a catalyst, compounds **4a–c** were obtained in high yields from **1a–c** (Methods A and A1). The reaction times were much shorter than those necessary for the conversion of **2a–c** to **4a–c**. However, compounds **1e–m** provide, in low yields, compounds **4**, but only if the starting compounds have a phenyl group at position 3 or a benzyl group at position

1 (1f–i). The yield of **4** can be increased by increasing the reaction time (cf. entries 7–8, 10–11, and 12–13 in Table 2). The main (or the only) products isolated from the reaction of **1d–m** with phosphoryl chloride were compounds **5**. As we expected, compounds **1** bearing the *N*-phenyl group afford mainly (or exclusively) compounds **5**. The NMR data of all products **4** and **5** are compiled in Table 3.

The proposed reaction mechanism of the conversion of **2** to **4** is depicted in Scheme 2. We anticipated that after transfer of the chlorine atom from **2** to a nucleophile, intermediate compound **1** would arise and react with phosphoryl chloride to give compound **5**, which is the final minor product of the reaction of compounds **2k–m**, as long as they bear a phenyl group at position 1. In the case of *N*-unsubstituted or *N*-alkyl substituted compounds **2a–i**, compound **1** is an intermediate, which is subsequently enolized to intermediate **A**. Then, the reaction of **A** with phosphoryl chloride produces intermediate **B** which dealkylates to compound **4**. The enolization of **1** in the formation of **A** is, as hypothesized by Bell *et al.* [23], facilitated by the catalytic effect of DMA. The resulting compound is converted to its hydrochloride, which protonates the carboxamide group and facilitates its enolization and subsequent dealkylation through intermediate **B**. If DMA is not present in the reaction mixture, the extent of enolization is lower, so mainly compounds **5** were obtained from **1** (Table 2).

Table 3
 ^1H and ^{13}C NMR data (δ , ppm) of compounds **2**, **4**, and **5** in $\text{DMSO}-d_6$.

Position	2h		4a		4b		4c		5d		5e		5f	
	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}
2	–	166.9	–	150.5	–	151.0	–	149.5	–	159.9	–	160.2	–	159.7
3	–	68.0	–	132.0	–	132.0	–	133.0	–	131.6	–	130.2	–	131.5
4	–	187.7	–	141.9	–	143.3	–	142.4	–	139.5	–	140.8	–	140.3
4a	–	119.2	–	125.2	–	125.2	–	125.0	–	118.2	–	118.2	–	118.3
5	8.00	128.3	8.20	124.1	8.27	124.4	8.29	124.6	7.98	125.2	8.02	125.5	8.09	126.0
6	7.30	123.9	7.80	128.8	7.86	129.0	7.88	129.0	7.40	122.7	7.42	122.9	7.46	122.9
7	7.71	137.0	7.90	131.2	7.95	131.6	8.00	131.9	7.70	131.1	7.73	131.6	7.80	132.0
8	7.28	116.6	8.01	128.4	8.07	128.5	8.13	128.5	7.60	115.0	7.64	115.2	7.70	115.2
8a	–	141.3	–	145.6	–	145.9	–	146.3	–	138.1	–	138.3	–	138.8
1'(N)	5.48	46.0	–	–	–	–	–	–	3.69	30.0	3.71	30.2	3.72	30.2
	5.23 ^a													
2'(N)	–	136.1	–	–	–	–	–	–	–	–	–	–	–	–
3'(N)	7.36	126.3	–	–	–	–	–	–	–	–	–	–	–	–
4'(N)	7.41	128.8	–	–	–	–	–	–	–	–	–	–	–	–
5'(N)	7.33	127.4	–	–	–	–	–	–	–	–	–	–	–	–
1'(C-3)	2.39	35.6	3.03	30.9	4.52	36.4	–	135.6	2.79	28.6	4.18	34.2	–	135.1
2'(C-3)	1.33	26.8	1.62	29.9	–	137.1	7.46	129.6	1.52	29.5	–	138.5	7.38	130.0
3'(C-3)	1.33	22.3	1.48	22.3	7.22	127.0	7.60	128.6	1.39	22.3	7.34	128.4	7.50	127.9
4'(C-3)	0.89	13.7	0.98	13.7	7.34	128.7	7.54	128.8	0.95	13.9	7.29	128.4	7.46	128.0
5'(C-3)	–	–	–	–	7.26	126.6	–	–	–	–	7.21	126.3	–	–
Position	5g		5h		5i		5j		5k		5l		5m	
	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}
2	–	159.3	–	160.3	–	160.1	–	160.3	–	160.0	–	160.2	–	159.7
3	–	131.5	–	131.7	–	131.5	–	128.1	–	132.1	–	130.7	–	131.9
4	–	140.5	–	140.2	–	140.9	–	140.4	–	140.3	–	141.7	–	141.1
4a	–	118.6	–	118.6	–	118.7	–	118.2	–	118.2	–	118.2	–	118.3
5	8.11	126.4	8.03	125.5	8.13	126.3	8.05	125.1	8.06	125.2	8.08	125.5	8.16	126.0
6	7.43	122.9	7.37	122.9	7.42	123.1	7.40	123.0	7.39	123.0	7.42	123.1	7.45	123.1
7	7.78	132.2	7.60	131.1	7.70	132.0	7.51	130.8	7.52	131.0	7.55	131.3	7.60	131.9
8	7.74	115.0	7.48	115.5	7.53	115.6	6.61	115.7	6.59	115.7	6.62	115.8	6.67	115.8
8a	–	137.8	–	137.3	–	138.1	–	139.0	–	139.1	–	139.3	–	139.8
1'(N)	4.37	37.8	5.61	45.6	5.63	45.7	–	137.7	–	137.6	–	138.4	–	137.6
2'(N)	1.30	12.7	–	136.6	–	136.5	7.39	129.0	7.39	129.0	7.42	128.5	7.45	129.0
3'(N)	–	–	7.23	126.5	7.31	126.7	7.69	130.2	7.69	130.2	7.68	130.2	7.69	130.2
4'(N)	–	–	7.35	128.8	7.36	128.8	7.62	129.0	7.61	129.0	7.61	129.1	7.63	129.0
5'(N)	–	–	7.26	127.2	7.30	127.3	–	–	–	–	–	–	–	–
1'(C-3)	–	135.10	2.88	28.7	–	135.0	2.53	14.9	2.83	28.4	4.21	33.9	–	134.6
2'(C-3)	7.38	130.1	1.60	29.6	7.47	130.1	–	–	1.59	29.6	–	137.6	7.45	130.2
3'(C-3)	7.50	128.0	1.43	22.4	7.52	128.0	–	–	1.43	22.4	7.38	128.4	7.52	128.0
4'(C-3)	7.45	128.1	0.97	13.9	7.47	128.1	–	–	0.96	13.9	7.32	128.5	7.43	128.2
5'(C-3)	–	–	–	–	–	–	–	–	–	–	7.24	126.3	–	–

^a Prochiral methylene group.

Unfortunately, when compounds **2** and phosphoryl chloride reacted in the presence of DMA, a significant quantity of an intensely blue compound was formed. This compound was isolated and its melting point, IR, and ^1H and ^{13}C NMR spectra were identical to those published [24] for 4,4',4''-tris(dimethylaminotriptylium) chloride (crystal violet, gentian violet, methyl violet 6B). An EI-MS spectrum of this compound (MW 408) exhibits a peak at m/z 373, which is almost identical to the mass of 4,4',4''-tris(dimethylamino)triphenyl-methane (leuco crystal violet, MW 373.5) [24]. In the litera-

ture, we found no information about this unintended side product of the reaction of secondary amides with phosphoryl chloride in the presence of DMA, although it must have been observed. When we refluxed a solution of DMA in phosphoryl chloride under aerobic conditions for 20 hours, crystal violet was obtained in 40% yield. This result shows that under these reaction conditions DMA oxidizes to *N*-methylformanilide and the subsequent Vilsmeier-Haack reaction between these two compounds generates *N,N*-dimethylbenzaldehyde [25]. This compound subsequently reacts with two molecules

of DMA and, under aerobic conditions, crystal violet is produced.

Highly hydrophilic products besides **4** and **5** were obtained in small quantities from the reaction of **1e**–**1** with phosphoryl chloride (Table 2). The IR spectra of these compounds showed two broad bands of low intensity approximately in the ranges of 2320–2360 and 2560–2800 cm^{-1} . These bands correspond to the OH stretching vibrations of phosphoric acid esters, which usually appear in the regions of 2100–2300 and 2560–2700 cm^{-1} [26]. The IR and analytical data suggest the presence of phosphoric acid fragment in the structure of the isolated compounds. Therefore, we suggest structure **7** for those compounds. In the electron impact mass spectra of compounds **7**, a higher peak appears at a m/z that corresponds to 4-hydroxyderivatives **1**. The course of the fragmentation is also almost identical to that of compounds **1**. It stands to reason that esters **7** decompose during EI-MS acquisition and produces **1**. Hence, a softer ionization technique, namely electrospray, was used to obtain the proper MS data for compounds **7**. The ESI-IT-MS experiments were carried out in both positive and negative scanning mode. However, due to the acidic character of esters **7**, the negative ionization was more suitable for the MS analyses. In the first-order mass spectra, one dominant signal at m/z corresponding to the $[\text{M}-\text{H}]^-$ ion was accompanied by m/z signals about twice as high (exactly $[2\text{M}-\text{H}]^-$ and $[2\text{M}-2\text{H}+\text{Na}]^-$) for all examined structures. Moreover, the peak corresponding to the $[2\text{M}-\text{H}-\text{H}_3\text{PO}_4]^-$ ion was observed in the negative ESI mass spectra of compounds **7a**–**c**, **7e**, and **7j**–**m**.

To the best of our knowledge, compounds **7** have not been described in the literature. Only some phosphoric acid tri-esters, based on the 4-hydroxy-2-quinolone scaffold, have been reported. (3-Chloro-2-oxo-1,2-dihydroquinolin-4-yl) dimethyl and diethyl phosphates, prepared by the reaction of 3,3-dichloroquinoline-2,4-(1*H*,3*H*)-dione with their corresponding trialkyl phosphites, were noted for their anticholinesterase activity [27]. Several 1,3-disubstituted (2-oxo-1,2-dihydroquinolin-4-yl) diethyl

Table 4

Preparation of dihydrogen phosphates **7** from 4-hydroxy-2-quinolones **1** (Method C).

Entry	l	Substituents		Product (yield, %) ^a
		R ¹	R ²	
1	a	H	Bu	7a (54)
2	b	H	Bn	7b (49)
3	c	H	Ph	7c (51)
4	d	Me	Bu	7d (34)
5	e	Me	Bn	7e (39)
6	f	Me	Ph	7f (48)
7	g	Et	Ph	7g (34)
8	h	Bn	Bu	7h (37)
9	i	Bn	Ph	7i (32)
10	j	Ph	Me	7j (64)
11	k	Ph	Bu	7k (56)
12	l	Ph	Bn	7l (83)
13	m	Ph	Ph	7m (78)

^a Refers to isolated percent yield of pure compound.

phosphates, prepared by the Perkow reaction of fluorinated 3-acyloxyquinoline-2,4-diones with triethyl phosphate, exhibit significant cytostatic activity toward leukemic K-562 cells and breast carcinoma MCF-7 cells [28].

Therefore, we decided to prepare phosphoric esters **7** through a route that would provide higher yields. We found that the reaction of **1** with phosphoryl chloride at low temperature in the presence of pyridine leads to the formation of desired compounds **7**. According to the TLC analysis, the conversion of **1** to **7** is almost quantitative. Unfortunately, isolation and especially crystallization of the product are troublesome in some cases. One contributing cause is the low hydrolytic stability of compounds **7**, which convert to **1** in alkaline media and even in an acetic acid solution at elevated temperature. Nevertheless, most of the compounds **7** were obtained in moderate to good yields (Table 4).

The ¹H, ¹³C, and ³¹P NMR spectra of all prepared compounds **7a**–**m** are in agreement with the proposed structures. Proton spectra were assigned using gs-COSY. Protonated carbons were assigned by gs-HMQC and quaternary carbons by gs-HMBC. The ⁿJ(³¹P, ¹³C) coupling constants were used to assign the quaternary carbons situated near the phosphorus atom. ³¹P NMR chemical shifts in compounds **7** are very similar, being in the range –5.1 to –5.7 ppm. All NMR data are compiled in Table 5.

CONCLUSIONS

In conclusion, we would like to emphasize that our results reveal new information about the behavior of reactive quinoline-2,4-dione systems. We found that 3-chloroquinolinediones do not react with phosphoryl chloride.

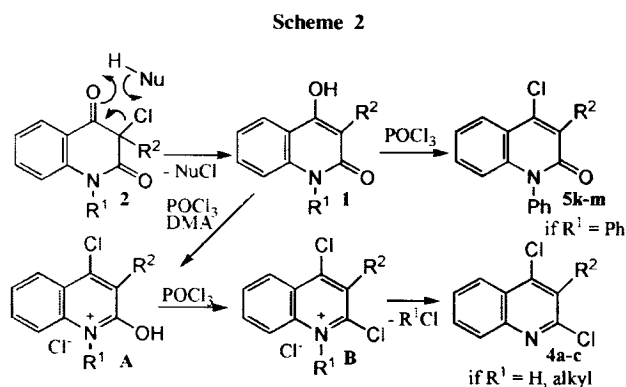


Table 5
¹H, ¹³C, and ³¹P NMR chemical shifts (δ, ppm) and ³J (J, ¹³C) coupling constants (Hz) of compounds **7** and **8f** in DMSO-d₆.

Position	7a		7b		7c		7d		7e		7f		7g	
	δ _H	δ _C	δ _H	δ _C	δ _H	δ _C	δ _H	δ _C	δ _H	δ _C	δ _H	δ _C	δ _H	δ _C
2	-	163.2 (1.3) ^a	-	163.1 (1.2) ^a	-	162.5 (1.3) ^a	-	162.5 (1.2) ^a	-	162.4 (1.4) ^a	-	162.0 (1.5) ^a	-	161.4 (1.4) ^a
3	-	123.2 (4.6) ^a	-	122.0 (4.4) ^a	-	122.8 (4.7) ^a	-	122.5 (4.4) ^a	-	121.3 (4.5) ^a	-	122.3 (4.7) ^a	-	122.2 (4.6) ^a
4	-	153.1 (7.7) ^a	-	153.8 (7.6) ^a	-	153.2 (7.5) ^a	-	152.1 (7.6) ^a	-	152.7 (7.7) ^a	-	152.4 (7.3) ^a	-	152.3 (7.4) ^a
4a	-	116.7 (1.6) ^a	-	116.6 (1.4) ^a	-	116.8 (1.4) ^a	-	117.3 (1.4) ^a	-	117.2 (1.4) ^a	-	117.5 (1.5) ^a	-	117.7 (1.6) ^a
5	7.92	123.9	7.98	124.2	8.08	124.8	8.02	124.3	8.07	124.6	8.18	125.2	8.19	125.4
6	7.23	121.5	7.23	121.6	7.28	121.7	7.34	121.8	7.36	121.9	7.37	122.0	7.35	121.8
7	7.51	130.0	7.53	130.3	7.59	130.8	7.65	130.5	7.67	130.9	7.73	131.3	7.74	131.4
8	7.33	114.8	7.34	114.9	7.39	114.9	7.57	114.4	7.58	114.5	7.64	114.6	7.69	114.3
8a	-	137.2	-	137.5	-	137.9	-	138.2	-	138.4	-	138.9	-	137.8
1'(N)	11.79	-	11.86	-	11.99	-	3.68	29.6	3.68	29.8	3.71	29.9	3.37	37.4
2'(N)	-	-	-	-	-	-	-	-	-	-	-	-	1.30	12.8
3'(N)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4'(N)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5'(N)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1'(C-3)	2.69	24.2	4.08	29.7	-	132.6 (1.4) ^a	2.74	25.0	4.13	30.6	-	133.0 (1.2) ^a	-	132.9 (1.4) ^a
2'(C-3)	1.53	29.9	-	140.3	7.39	127.3	1.53	29.8	-	140.1	7.40	127.4	7.37	127.3
3'(C-3)	1.34	22.5	7.33	128.1	7.44	130.9	1.36	22.5	7.34	128.2	7.40	130.9	7.42	130.9
4'(C-3)	0.93	14.0	7.25	128.6	7.35	127.2	0.94	14.0	7.26	128.6	7.40	127.2	7.34	127.2
5'(C-3)	-	-	7.17	125.8	-	-	-	-	7.17	125.9	-	-	-	-
δ (³¹ P)	-	-5.4	-	-5.1	-	-5.7	-	-5.3	-	-5.3	-	-5.4	-	-5.7
		7h		7i		7j		7k		7l		7m		8f
Position	δ _H	δ _C	δ _H	δ _C	δ _H	δ _C	δ _H	δ _C	δ _H	δ _C	δ _H	δ _C	δ _H	δ _C
2	-	162.8	-	162.3 (1.4) ^a	-	162.9 (1.4) ^a	-	162.6 (1.2) ^a	-	162.6 (1.3) ^a	-	162.0 (1.4) ^a	-	170.2
3	-	122.5 (4.7) ^a	-	122.2 (4.7) ^a	-	118.6 (4.4) ^a	-	122.9 (4.5) ^a	-	121.6 (4.6) ^a	-	122.4 (4.6) ^a	-	74.8
4	-	152.5 (7.7) ^a	-	152.7 (7.3) ^a	-	152.7 (7.6) ^a	-	152.8 (7.7) ^a	-	153.7 (7.7) ^a	-	153.1 (7.5) ^a	-	191.6
4a	-	117.7	-	117.9 (1.6) ^a	-	117.2 (1.6) ^a	-	117.3 (1.6) ^a	-	117.3 (1.4) ^a	-	117.5 (1.6) ^a	-	120.4
5	8.04	124.6	8.21	125.5	8.04	124.1	8.07	124.4	8.13	124.8	8.24	125.3	7.85	127.9
6	7.30	121.9	7.33	122.1	7.31	122.0	7.31	122.0	7.32	122.1	7.33	122.1	7.27	123.6
7	7.53	130.4	7.62	131.3	7.45	130.2	7.44	130.2	7.46	130.5	7.53	130.9	7.81	136.8
8	7.43	114.8	7.51	114.9	6.56	115.1	6.55	115.0	6.56	115.2	6.60	115.1	7.55	116.3
8a	-	137.4	-	139.3	-	139.0	-	139.2	-	139.4	-	139.8	-	142.0
1'(N)	5.59	45.2	5.61	45.5	-	137.9	-	137.9	-	137.9	-	137.9	-	30.3
2'(N)	-	137.1	-	137.0	7.36	129.2	7.35	129.2	7.33	129.2	7.39	129.2	-	-
3'(N)	7.24	128.7	7.30	126.7	7.69	130.1	7.67	130.1	7.66	130.2	7.68	130.2	-	-
4'(N)	7.36	126.6	7.36	128.8	7.60	128.8	7.60	128.8	7.58	128.9	7.61	128.8	-	-
5'(N)	7.27	127.1	7.36	128.8	-	-	-	-	-	-	-	-	-	-
1'(C-3)	2.81	25.0	-	132.9	2.20	11.5	2.76	24.8	4.15	30.4	-	132.6	-	134.7
2'(C-3)	1.58	29.9	-	131.0	-	-	1.56	29.9	-	140.2	7.49	131.0	-	127.0
3'(C-3)	1.39	22.5	7.42	127.3	-	-	1.38	22.5	7.39	128.2	7.38	127.2	-	129.3
4'(C-3)	0.96	14.0	7.28	127.2	-	-	0.94	14.0	7.27	128.7	7.34	127.3	-	129.4
5'(C-3)	-	-	-	-	-	-	-	-	7.18	125.9	-	-	-	-
δ (³¹ P)	-	-5.3	-	-5.7	-	-5.2	-	-5.2	-	-5.2	-	-5.3	-	-
NH ^b	-	-	-	-	-	-	-	-	-	-	-	-	-	5.15

^aJ (J, ¹³C) (Hz, ± 0.2 Hz).
^b2,5-Dimethylphenyl at NH (position: δ_H/δ_C): 1'^o: -/143.2; 2'^o: -/121.1; 3'^o: 6.96/130.0; 4'^o: 6.44/118.4; 5'^o: -/136.2; 6'^o: 5.61/114.0; CH₃ (2'^o): 2.24/17.4; CH₃ (5'^o): 1.97/21.3.

However, in the presence of DMA, the chlorine atom is split-off from these compounds and 2,4-dichloroquinolines and/or 4-chloroquinoline-2-ones are formed. We have prepared several new compounds **4** and **5** in good yield.

A significant result of our experiments is the isolation of minor compounds **7**, whose formation during the reaction of **1** with phosphoryl chloride has not been previously described. We outlined a simple procedure for the preparation of compounds **7**, which are suitable for biological testing as well as further synthetic elaboration.

EXPERIMENTAL

General. Melting points were determined on a Kofler block or Gallencamp apparatus. IR (KBr) spectra were recorded on a Mattson 3000 spectrophotometer. NMR spectra were recorded on a Bruker Avance spectrometer (500.13 MHz for ^1H , 125.76 MHz for ^{13}C), and on a Bruker Avance II 400 spectrometer (161.97 MHz for ^{31}P) in DMSO- d_6 . ^1H and ^{13}C chemical shifts are given on the δ scale (ppm) and are referenced to internal TMS ($\delta = 0.0$). ^{31}P chemical shifts were referred to external neat 85% H_3PO_4 in a co-axial capillary ($\delta = 0.0$). All 2D experiments (gradient-selected (gs)-COSY, NOESY, gs-HMQC, gs-HMBC) were performed using manufacturer's software. The positive-ion EI mass spectra were measured on a Shimadzu QP-2010 instrument within the mass range $m/z = 50$ – 600 using direct inlet probe (DI). Samples were dissolved in dichloromethane (30 $\mu\text{g}/\text{mL}$), and 10 μL of the solution was evaporated in DI cuvette at 50°C . The ion source temperature was 200°C ; the energy of electrons was 70 eV. Only signals exceeding relative abundance of 5% are listed. The ESI-MS spectra were recorded on an amaZon X ion-trap mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with an electrospray ion source. Individual samples were infused into the ESI source as methanol solutions *via* a syringe pump at a constant flow rate of 4 $\mu\text{L min}^{-1}$. The other instrument conditions were as follows: electrospray voltage ± 4.2 kV, drying gas temperature 220°C , drying gas flow 6.0 $\text{dm}^3 \text{min}^{-1}$, nebulizer pressure 8.0 psi. Nitrogen was used as nebulizing as well as drying gas. Column chromatography was carried out on silica gel (Merck, grade 60, 70–230 mesh) using chloroform/ethanol (in ratios from 99:1 to 8:2) (S1), successive mixtures of benzene/ethyl acetate (in ratios from 99:1 to 8:2) (S2) and isopropylalcohol/acetic acid (9:1) (S3). Reactions as well as the course of separation and also the purity of substances were monitored by TLC (elution systems benzene/ethyl acetate (4:1) (S4), chloroform/ethanol (9:1 and 1:1) (S5 and S6), chloroform/ethyl acetate (7:3) (S7), and tetrahydrofuran/acetic acid (4:1) (S8) on Alugram® SIL G/UV $_{254}$ foils (Macherey-Nagel). Elemental analyses (C, H, N) were performed with a EA Flash EA 1112 Elemental Analyzer (Thermo Fisher Scientific).

Preparation of 3-alkyl/aryl-3-chloroquinolin-2,4(1H,3H)-diones (2). Starting compounds **2a**–**m** were prepared by the reaction of 3-alkyl/aryl-4-hydroxyquinolin-2-ones **1** with sulfur chloride according to the procedure described in literature [18,19]. One novel derivative (**2h**) was prepared.

1-Benzyl-3-butyl-3-chloroquinoline-2,4(1H,3H)-dione (2h). Compound was prepared from **1h** and sulfur chloride in 63% yield. Colorless crystals, mp 69 – 72°C (cyclohexane); IR (KBr) ν : 2953, 2930, 2969, 1706, 1678, 1599, 1488, 1467,

italic; no bold

1360, 1304, 1207, 1167, 950, 774, 755, 731, 698, 662, 626, 526 cm^{-1} ; For NMR spectra see Table 3; EI-MS (m/z , %) 341 (M^+ , 3), 307 (8), 306 (17), 285 (8), 265 (7), 174 (9), 92 (9), 91 (100), 65 (9). Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{ClNO}_2$: C, 70.27; H, 5.90; N, 4.10. Found: C, 70.31; H, 5.92; N, 4.10.

General procedure for the reaction of compounds 1, 2 and 6 with phosphoryl chloride. **Method A.** *N,N*-Dimethylaniline (DMA, 1.5 mL) was added to a solution of starting compound (3 mmol) in phosphoryl chloride (15 mL) and the reaction mixture was heated under reflux for the time given in Table 1. After cooling, the reaction mixture was poured onto crushed ice (100 g) and extracted with chloroform (3 \times 50 mL). The extract was filtered through a short column of silica gel to removing of crystal violet, the filtrate was evaporated to dryness and the residue was extracted with benzene or ethyl acetate. The extract was evaporated to dryness and the residue was crystallized from an appropriate solvent or separated by column chromatography.

Method A1. Appropriate starting compound (2 mmol) was dissolved in phosphoryl chloride (10 mL) and the mixture was heated under reflux for the time given in Table 2. After cooling, phosphoryl chloride was evaporated, the residue was mixed with crushed ice (100 g) and, after 10 min of stirring, the acidity was adjusted to pH 5 by successive addition of a solution of sodium hydroxide (10%). The precipitated product was filtered off with suction, washed with water, dried, and recrystallized from an appropriate solvent. In case when the product was of pasty consistence, the mixture was extracted with chloroform (three times, 30 mL each). After evaporation, the residue was crystallized from an appropriate solvent or column chromatographed. In all cases, the mother liquors were separated by column chromatography. Compounds **7** were isolated by the extraction of the chloroform solutions of crude reaction product or mother liquors with aqueous solution (6%) of sodium hydrogen carbonate. The aqueous extract was acidified with 5% hydrochloric acid and extracted with chloroform. The chloroform solution was dried, filtered, evaporated *in vacuo*, and crystallized to give product **7**.

Method B. The reaction was carried out analogously to Method A, but the addition of DMA was omitted.

3-Butyl-2,4-dichloroquinoline (4a). Compound was prepared from **1a**, **1h** (Method A1, Table 2), **2a** and **2d** (Method B, Table 1). Colorless crystals, mp 47 – 49°C (hexane); IR (KBr) ν : 2961, 2924, 2858, 1571, 1557, 1482, 1466, 1454, 1384, 1367, 1328, 1303, 1277, 1219, 1149, 1141, 1087, 1048, 961, 916, 802, 764, 724, 707, 699, 598 cm^{-1} ; For NMR see Table 3; EI-MS (m/z , %): 255 (23), 254 (M^+ , 5), 253 (36), 218 (8), 214 (13), 213 (18), 212 (65), 211 (28), 210 (100), 197 (7), 176 (22), 175 (9), 174 (31), 153 (8), 152 (11), 151 (5), 141 (7), 140 (46), 139 (10), 127 (10), 126 (11), 125 (8), 114 (16), 113 (18), 101 (6), 99 (8), 89 (6), 88 (8), 87 (9), 77 (7), 76 (7), 75 (12), 74 (6), 73 (6), 63 (18), 62 (7), 51 (9), 43 (21), 41 (25). Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{Cl}_2\text{N}$: C, 61.43; H, 5.16; N, 5.51. Found: C, 61.28; H, 5.15; N, 5.55.

3-Benzyl-2,4-dichloroquinoline (4b). Compound was prepared from **1b** (Method A1, Table 2), **2b**, and **2e** (Method B, Table 1). Colorless crystals, mp 71 – 72°C (hexane); For **4b**, mp 72 – 73°C (ethanol) was referred [1]; For NMR see Table 3; EI-MS (m/z , %): 289 (14), 288 (5), 287 (22), 254 (6), 253 (6), 252 (19), 251 (9), 250 (7), 217 (25), 216 (100), 215 (9), 214 (13), 189 (8), 126 (13), 125 (6), 113 (6), 108 (27), 95

(15), 94 (6), 89 (6), 63 (11), 51 (11). Anal. Calcd. for $C_{16}H_{11}Cl_2N$: C, 66.69; H, 3.85; N, 4.86. Found: C, 66.75; H, 3.83; N, 4.89.

2,4-Dichloro-3-phenylquinoline (4c). Compound was prepared from **1c,f,g,i** (Method A1, Table 2), **2c,f,g**, and **2i** (Method B, Table 1). Colorless crystals, mp 85–87°C (hexane); For **4c**, mp 90°C was referred [29]; For NMR see Table 3; EI-MS (m/z , %): 276 (11), 275 (69), 274 (18), 273 (100), 240 (15), 239 (9), 238 (45), 204 (10), 203 (60), 202 (26), 201 (19), 177 (9), 176 (27), 175 (17), 174 (7), 151 (11), 150 (13), 149 (7), 136 (10), 126 (6), 123 (5), 120 (9), 119 (24), 105 (5), 101 (23), 99 (11), 98 (8), 88 (45), 87 (20), 86 (7), 77 (9), 76 (9), 75 (26), 74 (15), 63 (11), 62 (9), 51 (19), 50 (11). Anal. Calcd. for $C_{15}H_9Cl_2N$: C, 65.72; H, 3.31; N, 5.11. Found: C, 65.91; H, 3.32; N, 5.14.

3-Butyl-4-chloro-1-methylquinolin-2-one (5d). Compound was prepared from **1d** (Method A, Table 2) in 93% yield. Colorless crystals, mp 67–70°C (hexane); IR (KBr) ν : 3079, 3029, 2956, 2929, 2859, 1633, 1592, 1573, 1497, 1461, 1412, 1351, 1316, 1299, 1280, 1253, 1216, 1167, 1107, 1087, 1047, 1019, 943, 904, 812, 777, 753, 733, 662, 609, 593, 504 cm^{-1} ; For NMR see Table 3; EI-MS (m/z , %): 249 (M^+ , 11), 234 (8), 222 (10), 221 (5), 220 (31), 215 (8), 214 (48), 209 (33), 208 (17), 207 (100), 206 (20), 179 (7), 178 (11), 172 (7), 144 (8), 143 (9), 142 (8), 140 (6), 128 (13), 116 (6), 115 (20), 102 (6), 101 (8), 89 (5), 77 (5). Anal. Calcd. for $C_{14}H_{16}ClNO$: C, 67.33; H, 6.46; N, 5.61. Found: C, 67.44; H, 6.46; N, 5.65.

3-Benzyl-4-chloro-1-methylquinolin-2-one (5e). Compound was prepared from **1e** in 41% yield besides **7e** (Method A1, Table 2). Colorless crystals, mp 133–138°C (benzene-ethyl acetate). For **5e**, mp 122°C (ligroin) was reported [16]; IR (KBr) ν : 3059, 3026, 1638, 1613, 1591, 1567, 1492, 1453, 1349, 1333, 1314, 1290, 1211, 1091, 1047, 1027, 950, 937, 880, 849, 757, 736, 695, 645, 620, 592 cm^{-1} ; For NMR see Table 3; EI-MS (m/z , %): 285 (34), 284 (23), 283 (M^+ , 100), 282 (12), 267 (10), 266 (25), 249 (14), 248 (77), 247 (19), 233 (12), 232 (16), 231 (10), 220 (7), 218 (10), 217 (7), 216 (6), 205 (7), 204 (16), 203 (8), 189 (5), 178 (7), 177 (5), 142 (10), 128 (5), 124 (34), 116 (6), 115 (13), 108 (9), 102 (13), 101 (9), 95 (6), 91 (11), 88 (7), 77 (7), 75 (6), 65 (8), 63 (7), 51 (6). Anal. Calcd. for $C_{17}H_{14}ClNO$: C, 71.96; H, 4.97; N, 4.94. Found: C, 72.03; H, 4.93; N, 4.81.

4-Chloro-1-methyl-3-phenylquinolin-2-one (5f). Compound was prepared from **1f** in 57% yield besides **4c** and **7f** (Method A1, Table 2). Colorless crystals, mp 121–122°C (benzene-cyclohexane); For **5f**, mp 106°C (aqueous ethanol) was reported [15]; IR (KBr) ν : 1630, 1608, 1560, 1586, 1567, 1496, 1458, 1444, 1330, 1313, 1239, 1062, 965, 844, 754, 745, 697, 668, 609, 524 cm^{-1} ; For NMR see Table 3; EI-MS (m/z , %): 271 (21), 270 (42), 269 (64), 268 (M^+ , 100), 253 (6), 205 (6), 204 (12), 190 (8), 176 (6), 117 (25), 102 (13), 89 (6), 88 (9), 76 (5). Anal. Calcd. for $C_{16}H_{12}ClNO$: C, 71.25; H, 4.48; N, 5.19. Found: C, 71.38; H, 4.51; N, 5.13.

4-Chloro-1-ethyl-3-phenylquinolin-2-one (5g). Compound was prepared from **1g** in 60% yield besides **4c** and **7g** (Method A1, Table 2). Colorless crystals, mp 124–125°C (benzene-cyclohexane); IR (KBr) ν : 3050, 2984, 1635, 1609, 1601, 1587, 1564, 1488, 1452, 1374, 1337, 1309, 1294, 1216, 958, 921, 844, 818, 782, 752, 695, 662, 612 cm^{-1} ; For NMR see Table 3; EI-MS (m/z , %): 285 (20), 284 (31), 283 (M^+ , 60), 282 (66), 257 (13), 256 (36), 255 (38), 254 (100), 238 (10),

220 (7), 219 (14), 205 (5), 204 (16), 203 (7), 191 (6), 190 (15), 176 (9), 165 (9), 164 (6), 163 (6), 110 (10), 102 (13), 96 (5), 89 (9), 88 (11), 75 (5), 63 (5). Anal. Calcd. for $C_{17}H_{14}ClNO$: C, 71.96; H, 4.97; N, 4.94. Found: C, 71.95; H, 4.98; N, 4.81.

1-Benzyl-3-butyl-4-chloroquinolin-2-one (5h). Compound was prepared from **1h** in 25% yield besides **4a** and **7h** (Method A1, Table 2). Colorless crystals, mp 77–79°C (hexane-cyclohexane); IR (KBr) ν : 2955, 2925, 2859, 1634, 1614, 1593, 1567, 1492, 1462, 1425, 1320, 1129, 1076, 934, 754, 703, 649, 458 cm^{-1} ; For NMR see Table 3; EI-MS (m/z , %): 325 (M^+ , 9), 290 (13), 285 (5), 283 (16), 194 (10), 192 (30), 92 (8), 91 (100), 65 (12). Anal. Calcd. for $C_{20}H_{20}ClNO$: C, 73.72; H, 6.19; N, 4.30. Found: C, 73.85; H, 6.20; N, 4.42.

1-Benzyl-4-chloro-3-phenylquinolin-2-one (5i). Compound was prepared from **1i** in 39% yield besides **4c** and **7i** (Method A1, Table 2). Colorless crystals, mp 197–199°C (benzene-cyclohexane); IR (KBr) ν : 2956, 1635, 1608, 1600, 1588, 1565, 1489, 1453, 1444, 1312, 1064, 1028, 948, 906, 781, 757, 708, 694, 671, 662, 639, 535 cm^{-1} ; For NMR see Table 3; EI-MS (m/z , %): 347 (15), 346 (19), 345 (M^+ , 44), 344 (32), 310 (12), 204 (16), 190 (5), 92 (8), 91 (100), 65 (16), 57 (5). Anal. Calcd. for $C_{22}H_{16}ClNO$: C, 76.41; H, 4.66; N, 4.05. Found: C, 76.54; H, 4.69; N, 3.94.

4-Chloro-3-methyl-1-phenylquinolin-2-one (5j). Compound was prepared from **1j** besides **7j** in 59% yield (Method A1, Table 2). Colorless crystals, mp 223–224°C (ethyl acetate); IR: 3069, 3056, 2923, 1645, 1613, 1593, 1567, 1491, 1452, 1351, 1322, 1296, 1216, 1121, 1020, 911, 767, 753, 696, 666, 513 cm^{-1} ; For NMR see Table 3; EI-MS (m/z , %): 271 (26), 270 (44), 269 (M^+ , 79), 268 (100), 234 (7), 233 (5), 206 (6), 205 (8), 204 (23), 140 (12), 135 (6), 128 (9), 117 (9), 103 (8), 102 (36), 101 (12), 89 (7), 88 (7), 77 (20), 76 (6), 75 (6), 63 (7), 51 (16). Anal. Calcd. for $C_{16}H_{12}ClNO$: C, 71.25; H, 4.48; N, 5.19. Found: C, 71.48; H, 4.48; N, 4.97.

3-Butyl-4-chloro-1-phenylquinolin-2-one (5k). Compound was prepared from **1k** in 65% yield (Method A1, Table 2). Colorless crystals, mp 98–99°C (hexane); IR (KBr) ν : 2952, 2927, 2863, 1640, 1612, 1595, 1564, 1492, 1455, 1350, 1328, 1302, 1277, 1250, 1219, 1128, 1105, 1078, 1025, 977, 925, 908, 856, 813, 778, 753, 697, 671, 658, 631, 559, 518 cm^{-1} ; For NMR see Table 3; EI-MS (m/z , %): 311 (M^+ , 8), 296 (11), 284 (10), 283 (7), 282 (29), 277 (16), 276 (78), 271 (33), 270 (37), 269 (100), 268 (65), 240 (9), 217 (7), 205 (10), 204 (34), 203 (6), 128 (5), 102 (9), 77 (17), 51 (10). Anal. Calcd. for $C_{19}H_{18}ClNO$: C, 73.19; H, 5.82; N, 4.49. Found: C, 73.37; H, 5.86; N, 4.71.

3-Benzyl-4-chloro-1-phenylquinolin-2-one (5l). Compound was prepared from **1l** in 36% yield besides **7l** (Method A1, Table 2). Colorless crystals, mp 170–173 °C (benzene-hexane). For **5l**, mp 146–148°C was reported [16]; IR (KBr) ν : 3080, 3026, 3001, 2934, 1645, 1609, 1596, 1563, 1492, 1452, 1428, 1349, 1328, 1291, 1247, 1215, 1186, 1162, 1108, 1073, 1029, 977, 942, 923, 901, 880, 827, 773, 755, 745, 735, 696, 651, 623, 511, 584, 519 cm^{-1} ; For NMR see Table 3; EI-MS (m/z , %): 348 (8), 347 (36), 346 (M^+ , 29), 345 (100), 344 (15), 328 (12), 311 (18), 310 (76), 309 (15), 308 (12), 280 (12), 266 (11), 232 (13), 218 (6), 217 (5), 216 (14), 205 (5), 204 (23), 203 (8), 173 (6), 155 (6), 139 (8), 134 (9), 91 (9), 77 (20), 51 (13). Anal. Calcd. for $C_{22}H_{16}ClNO$: C, 76.41; H, 4.66; N, 4.05. Found: C, 76.58; H, 4.71; N, 4.08.

1,3-Diphenyl-4-chloroquinolin-2-one (5m). Compound was prepared from **1m** in respective yields 80% (Method A1) or 79% (Method B, Table 2); Colorless crystals, mp 186–188°C (benzene-hexane); For **5m**, mp 164–166°C was reported [15]; IR (KBr) ν : 1652, 1605, 1589, 1560, 1489, 1451, 1349, 1310, 1292, 1261, 1224, 1177, 1151, 1056, 1017, 970, 914, 898, 837, 806, 780, 763, 745, 734, 698, 671, 634, 606, 567, 521 cm^{-1} ; For NMR see Table 3; EI-MS (m/z , %): 333 (25), 332 (M^+ , 47), 331 (73), 330 (100), 268 (5), 267 (17), 266 (14), 265 (8), 195 (5), 165 (12), 164 (5), 148 (8), 134 (20), 133 (15), 121 (8), 77 (11), 51 (9). Anal. Calcd. for $\text{C}_{21}\text{H}_{14}\text{ClNO}$: C, 76.02; H, 4.25; N, 4.22. Found: C, 76.08; H, 4.21; N, 4.28.

General procedure for the preparation of dihydrogen phosphates 7 from 4-hydroxy-2-quinolones 1 (Method C). A stirred suspension of compound **1** (2 mmol) in pyridine (0.485 mL, 6 mmol) and acetonitrile (5 mL) was cooled to 0°C and phosphoryl chloride (0.92 g, 0.559 mL, 6 mmol) was added in one portion. The mixture was stirred at 0°C for 1 h and then warmed slowly to the room temperature. In most cases, the suspension changed into a turbid solution. After overnight stirring, water (1 mL) was added under cooling and the mixture was evaporated to dryness *in vacuo*. The residue was crushed with water (10 mL), the precipitate was filtered off, dried, and recrystallized from an appropriated solvent. In several cases (**7b**, **7g**), the precipitate was purified by trituration with the solution of sodium hydrogen carbonate (6%); the solution was filtered, the filtrate was acidified with concentrated hydrochloric acid, the precipitate was filtered off and recrystallized from appropriate solvent. If the precipitate was of gummy or pasty character (**7d**), it was decanted three times with water, dried, and recrystallized from an appropriate solvent or column chromatographed using solvent system S1 or S3. The mother liquors were extracted with ethyl acetate, the extract was dried, evaporated to dryness and column chromatographed using solvent system S3. The results are given in Table 4.

3-Butyl-1,2-dihydro-2-oxoquinolin-4-yl dihydrogen phosphate (7a). Compound was prepared from **1a** in 54% yield (Method C, Table 4); Colorless crystals, mp 226–230°C (benzene-DMF); IR (KBr) ν : 2960, 2934, 2863, 2356br, 1649, 1606, 1526, 1467, 1449, 1331, 1274, 1220, 1187, 1127, 1071, 940, 886, 794, 755, 650, 625, 557, 459 cm^{-1} ; For NMR see Table 5; EI-MS (m/z , %): 217 (19), 202 (8), 200 (10), 188 (26), 176 (11), 175 (100), 174 (38), 161 (14), 120 (21), 119 (9), 115 (5), 92 (18), 77 (14), 65 (11), 55 (23), 44 (10). ESI-MS (m/z , %): 615.1 [2M–2H+Na]⁺ (5), 593.1 [2M–H][–] (83), 495.2 [2M–H–H₃PO₄][–] (24), 476 (24), 296.1 [M–H][–] (100). Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{NO}_5\text{P}$: C, 52.53; H, 5.43; N, 4.71. Found: C, 52.57; H, 5.52; N, 4.88.

3-Benzyl-1,2-dihydro-2-oxoquinolin-4-yl dihydrogen phosphate (7b). Compound was prepared from **1b** in 49% yield (Method C, Table 4). Colorless crystals, mp 246–250°C (DMF-benzene); IR (KBr) ν : 3427, 3067, 3030, 2948, 2799, 2362br, 1650, 1604, 1529, 1494, 1455, 1379, 1334, 1299, 1275, 1220, 1185, 1133, 1100, 944, 895, 788, 774, 759, 735, 702, 677, 650, 625, 556, 526 cm^{-1} ; For NMR see Table 5; EI-MS (m/z , %): 252 (18), 251 (100), 250 (26), 235 (6), 234 (32), 222 (7), 204 (8), 174 (8), 173 (6), 172 (7), 146 (18), 131 (23), 125 (10), 124 (5), 120 (16), 103 (13), 93 (6), 92 (18), 91 (25), 90 (8), 89 (7), 77 (22), 76 (7), 65 (16), 63 (7), 51 (11); ESI-MS (m/z , %): 683.1 [2M–2H+Na]⁺ (5), 661.1 [2M–H][–] (8), 563.2

[2M–H–H₃PO₄][–] (88), 348.0 [2M–H+H₂O][–] (56), 330.1 [M–H][–] (100). Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{NO}_5\text{P}$: C, 58.01; H, 4.26; N, 4.23. Found: C, 57.85; H, 4.40; N, 4.37.

1,2-Dihydro-2-oxo-3-phenylquinolin-4-yl dihydrogen phosphate (7c). Compound was prepared from **1c** in 51% yield (Method C, Table 4); Colorless crystals, mp 245–255°C (DMF-benzene); IR (KBr) ν : 2790, 2351br, 1674, 1607, 1537, 1502, 1447, 1366, 1334, 1287, 1127, 1110, 1074, 989, 938, 886, 863, 801, 760, 680, 651, 560, 500, 458 cm^{-1} ; For NMR see Table 5; EI-MS (m/z , %): 238 (16), 237 (99), 236 (100), 180 (8), 121 (7), 120 (92), 119 (9), 118 (6), 92 (44), 91 (7), 90 (10), 89 (9), 77 (16), 76 (10), 65 (23), 64 (7), 63 (11), 51 (7), 44 (21); ESI-MS (m/z , %): 655.1 [2M–2H+Na]⁺ (28), 633.1 [2M–H][–] (49), 535.1 [2M–H–H₃PO₄][–] (7), 316.1 [M–H][–] (100). Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{NO}_5\text{P}$: C, 56.79; H, 3.81; N, 4.42. Found: C, 56.72; H, 3.85; N, 4.47.

3-Butyl-1,2-dihydro-1-methyl-2-oxoquinolin-4-yl dihydrogen phosphate (7d). Compound was prepared from **1d** in 34% yield (Method C, Table 4). Colorless crystals, mp 162–170°C (water); IR (KBr) ν : 3396br, 2965, 2930, 2878, 2716br, 2359br, 2329, 2208br, 1631, 1610, 1557, 1503, 1457, 1420, 1376, 1332, 1292, 1226, 1154, 118, 1100, 1085, 1057, 958, 880, 811, 785, 755, 743, 684, 614, 547, 521 cm^{-1} ; For NMR see Table 5; EI-MS (m/z , %): 231 (26), 216 (7), 214 (5), 203 (12), 202 (13), 190 (22), 189 (100), 188 (28), 186 (9), 160 (17), 146 (26), 145 (6), 136 (14), 135 (12), 134 (42), 133 (15), 132 (6), 131 (7), 128 (5), 127 (11), 126 (7), 125 (5), 119 (6), 118 (6), 117 (7), 114 (26), 112 (6), 106 (6), 104 (6), 99 (7), 97 (10), 96 (7), 91 (7), 84 (11), 83 (13), 82 (5), 79 (12), 77 (32), 72 (21), 71 (6), 70 (9), 69 (27), 68 (10), 67 (14), 63 (9), 60 (13), 59 (33), 57 (18), 55 (19), 53 (9), 45 (9), 43 (19), 41 (25), 40 (7); ESI-MS (m/z , %): 643.2 [2M–2H+Na]⁺ (27), 621.2 [2M–H][–] (37), 310.1 [M–H][–] (100). Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{NO}_5\text{P}$: C, 54.02; H, 5.83; N, 4.50. Found: C, 54.22; H, 5.89; N, 4.56.

3-Benzyl-1,2-dihydro-1-methyl-2-oxoquinolin-4-yl dihydrogen phosphate hydrate (7e). Compound was prepared from **1e** in respective yields 3% (Method A1, Table 2) or 39% (Method C, Table 4). Colorless crystals, mp 170–185°C (water); IR (KBr) ν : 3030, 2946, 2931, 2853, 2320br, 1631, 1611, 1577, 1495, 1461, 1418, 1373, 1330, 1222, 1181, 1101, 1030, 959, 898, 867, 787, 751, 704, 627, 583, 532 cm^{-1} ; For NMR see Table 5; EI-MS (m/z , %): 266 (14), 265 (73), 264 (18), 248 (20), 236 (6), 160 (12), 149 (35), 134 (11), 131 (14), 128 (9), 127 (12), 126 (18), 125 (10), 124 (7), 123 (9), 115 (7), 114 (15), 113 (9), 112 (17), 111 (17), 110 (9), 109 (13), 104 (16), 103 (10), 100 (7), 99 (11), 98 (16), 97 (28), 96 (14), 95 (18), 91 (17), 86 (12), 85 (17), 84 (13), 83 (32), 82 (13), 81 (20), 77 (16), 74 (57), 73 (15), 72 (80), 71 (35), 70 (18), 69 (53), 68 (11), 67 (22), 60 (24), 59 (100), 58 (6), 57 (58), 56 (18), 55 (64), 54 (9), 45 (8), 44 (15), 43 (78), 42 (13), 41 (58); ESI-MS (m/z , %): 711.1 [2M–2H+Na]⁺ (13), 689.2 [2M–H][–] (29), 591.2 [2M–H–H₃PO₄][–] (5), 344.1 [M–H][–] (100). Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{NO}_5\text{P}$: C, 56.20; H, 4.99; N, 3.86. Found: C, 56.39; H, 4.89; N, 3.72.

1,2-Dihydro-1-methyl-2-oxo-3-phenylquinolin-4-yl dihydrogen phosphate hydrate (7f). Compound was prepared from **1f** in respective yields 2% (Method A1, Table 2), or 48% (Method C, Table 4). Colorless crystals, mp 212–217°C (water); IR (KBr) ν : 3642, 3313, 3198, 3083, 3057, 3034, 2948, 2660br, 2178br, 1629, 1590, 1574, 1450, 1460, 1418, 1367, 1285,

1237, 1142, 1103, 960, 882, 850, 805, 774, 754, 699, 683, 629, 563, 554, 493 cm^{-1} ; For NMR see Table 5: EI-MS (m/z , %): 251 (34), 250 (36), 162 (7), 155 (6), 139 (9), 134 (18), 127 (12), 125 (20), 111 (28), 105 (20), 97 (40), 96 (16), 95 (23), 85 (43), 71 (62), 57 (80), 43 (100); ESI-MS (m/z , %): 683.1 $[2\text{M}-2\text{H}+\text{Na}]^-$ (24), 661.1 $[2\text{M}-\text{H}]^-$ (41), 330.1 $[\text{M}-\text{H}]^-$ (100). Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{NO}_6\text{P}$: C, 55.02; H, 4.62; N, 4.01. Found: C, 54.86; H, 4.66; N, 4.11.

1,2-Dihydro-1-ethyl-2-oxo-3-phenylquinolin-4-yl dihydrogen phosphate hydrate (7g). Compound was prepared from **1g** in respective yields 3% (Method A1, Table 2) or 34% (Method C, Table 4). Colorless crystals, mp 150–160°C (water); IR (KBr) ν : 3584, 3324, 3051, 2978, 2936, 2875, 2560, 2260br, 1640, 1620, 1606, 1593, 1499, 1456, 1368, 1305, 1222, 1144, 1113, 1085, 1040, 979, 884, 847, 819, 780, 753, 702, 681, 633, 533, 505 cm^{-1} ; For NMR see Table 5; EI-MS (m/z , %): 266 (16), 265 (88), 264 (82), 238 (6), 237 (55), 236 (100), 180 (7), 146 (10), 132 (10), 130 (16), 120 (39), 118 (10), 92 (11), 91 (15), 90 (8), 89 (6), 77 (30), 76 (8), 65 (8), 63 (6), 44 (24); ESI-MS (m/z , %): 711.1 $[2\text{M}-2\text{H}+\text{Na}]^-$ (12), 689.1 $[2\text{M}-\text{H}]^-$ (67), 641.2 $[2\text{M}-\text{H}-4\text{H}]^-$ (17), 344.1 $[\text{M}-\text{H}]^-$ (100), 296.1 $[\text{M}-\text{H}-4\text{H}]^-$ (11). Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{NO}_6\text{P}$: C, 56.20; H, 4.99; N, 3.86. Found: C, 56.10; H, 4.99; N, 3.85.

1-Benzyl-3-butyl-1,2-dihydro-2-oxoquinolin-4-yl dihydrogen phosphate (7h). Compound was prepared from **1h** in 28% yield besides **4a** and **5h** (Method A1, Table 2) or 37% (Method C, Table 4). Colorless crystals, mp 220–225°C (ethyl acetate); IR (KBr) ν : 3450, 3064, 3030, 2964, 2928, 2861, 2679, 2321, 2190, 1625, 1607, 1526, 1499, 1455, 1444, 1383, 1334, 1259, 1229, 1207, 1181, 1145, 1114, 1044, 1019, 959, 877, 799, 763, 734, 699, 648, 577, 552, 526 cm^{-1} ; For NMR see Table 5; EI-MS (m/z , %): 307 (20), 278 (5), 265 (26), 264 (9), 174 (37), 132 (5), 92 (9), 91 (100), 65 (10); ESI-MS (m/z , %): 795.2 $[2\text{M}-2\text{H}+\text{Na}]^-$ (10), 773.2 $[2\text{M}-\text{H}]^-$ (12), 386.1 $[\text{M}-\text{H}]^-$ (100). Anal. Calcd. for $\text{C}_{20}\text{H}_{22}\text{NO}_5\text{P}$: C, 62.01; H, 5.72; N, 3.62. Found: C, 61.88; H, 5.67; N, 3.40.

1-Benzyl-1,2-dihydro-2-oxo-3-phenylquinolin-4-yl dihydrogen phosphate (7i). Compound was prepared from **1i** in 40% yield besides **4c** and **5i** (Method A1, Table 2) or 32% (Method C, Table 4). Colorless crystals, mp 235–247 °C (water); IR (KBr) ν : 3057, 3032, 2971, 2944, 2360br, 2340br, 1642, 1597, 1573, 1496, 1453, 1437, 1357, 1314, 1299, 1247, 1161, 1125, 1078, 1034, 971, 951, 880, 855, 823, 805, 766, 741, 731, 703, 644, 605, 557, 535, 516, 501 cm^{-1} ; For NMR see Table 5; EI-MS (m/z , %): 327 (63), 326 (52), 236 (8), 220 (18), 152 (5), 91 (100), 77 (10), 65 (14), 46 (15), 45 (14), 44 (26); ESI-MS (m/z , %): 835.1 $[2\text{M}-2\text{H}+\text{Na}]^-$ (8), 813.2 $[2\text{M}-\text{H}]^-$ (24), 406.1 $[\text{M}-\text{H}]^-$ (100). Anal. Calcd. for $\text{C}_{22}\text{H}_{18}\text{NO}_5\text{P}$: C, 64.87; H, 4.45; N, 3.44; Found: C, 64.81; H, 4.51; N, 3.58.

1,2-Dihydro-3-methyl-2-oxo-1-phenylquinolin-4-yl dihydrogen phosphate (7j). Compound was prepared from **1j** besides **5j** in 5% yield (Method A1, Table 2) or 64% (Method C, Table 4). Colorless crystals, mp 242–247°C (ethyl acetate); IR (KBr) ν : 2956, 2927, 2361, 2332br, 1633, 1596, 1552, 1492, 1459, 1387, 1366, 1343, 1313, 1249, 1223, 1168, 1157, 1141, 1108, 1043, 957, 844, 783, 756, 695, 683, 642, 569, 520 cm^{-1} ; For NMR see Table 5; EI-MS (m/z , %): 252 (17), 251 (100), 250 (90), 222 (9), 196 (11), 195 (34), 194 (9), 167 (27), 166 (12), 146 (11), 140 (6), 139 (7), 92 (9), 91 (7), 83 (9), 77 (23), 51 (14); ESI-MS (m/z , %): 683.1 $[2\text{M}-2\text{H}+\text{Na}]^-$ (12), 661.1 $[2\text{M}-\text{H}]^-$ (7), 563.2 $[2\text{M}-\text{H}-\text{H}_3\text{PO}_4]^-$

(13), 510.1 (23), 330.1 $[\text{M}-\text{H}]^-$ (100). Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{NO}_5\text{P}$: C, 58.01; H, 4.26; N, 4.23. Found: C, 58.21; H, 4.33; N, 4.17.

3-Butyl-1,2-dihydro-2-oxo-1-phenylquinolin-4-yl dihydrogen phosphate hydrate (7k). Compound was prepared from **1k** in 22% yield besides **5k** (Method A, Table 2) or 56% (Method C, Table 4). Colorless crystals, mp 232–237°C (ethyl acetate); IR (KBr) ν : 3426br, 3083, 3065, 2958, 2937, 2920, 2876, 2830, 2668br, 2333br, 1621, 1499, 1457, 1437, 1378, 1349, 1334, 1316, 1288, 1266, 1251, 1228, 1202, 1161, 1110, 1075, 1052, 971, 952, 852, 804, 788, 772, 762, 748, 738, 697, 685, 676, 643, 568, 558, 525 cm^{-1} ; For NMR see Table 5; EI-MS (m/z , %): 293 (16), 278 (10), 276 (11), 265 (7), 264 (32), 252 (17), 251 (100), 250 (60), 237 (9), 196 (16), 195 (11), 168 (7), 167 (9), 166 (6), 77 (16), 51 (6), 44 (7); ESI-MS (m/z , %): 767.2 $[2\text{M}-2\text{H}+\text{Na}]^-$ (13), 745.2 $[2\text{M}-\text{H}]^-$ (10), 647.3 $[2\text{M}-\text{H}-\text{H}_3\text{PO}_4]^-$ (33), 372.1 $[\text{M}-\text{H}]^-$ (100). Anal. Calcd. for $\text{C}_{19}\text{H}_{22}\text{NO}_6\text{P}$: C, 58.31; H, 5.67; N, 3.58. Found: C, 58.11; H, 5.45; N, 3.40.

3-Benzyl-1,2-dihydro-2-oxo-1-phenylquinolin-4-yl dihydrogen phosphate hydrate (7l). Compound was prepared from **1l** in 32% yield besides **5l** (Method A1, Table 2) or 83% (Method C, Table 4). Colorless crystals, mp 178–182°C (DMF-benzene); IR (KBr) ν : 3430br, 3083, 3026, 2975, 2934, 2802br, 2359br, 1643, 1599, 1570, 1494, 1457, 1372, 1326, 1305, 1263, 1226, 1158, 1090, 1048, 1021, 969, 956, 931, 820, 769, 756, 743, 705, 686, 643, 598, 570, 562, 545, 521 cm^{-1} ; For NMR spectra see Table 5; EI-MS (m/z , %): 328 (24), 327 (100), 326 (26), 310 (17), 250 (5), 248 (12), 222 (17), 196 (17), 195 (11), 167 (14), 166 (7), 131 (9), 103 (8), 92 (5), 91 (13), 77 (20), 51 (8), 44 (7); ESI-MS (m/z , %): 835.2 $[2\text{M}-2\text{H}+\text{Na}]^-$ (11), 813.2 $[2\text{M}-\text{H}]^-$ (8), 715.3 $[2\text{M}-\text{H}-\text{H}_3\text{PO}_4]^-$ (13), 406.2 $[\text{M}-\text{H}]^-$ (100). Anal. Calcd. for $\text{C}_{22}\text{H}_{20}\text{NO}_6\text{P}$: C, 62.12; H, 4.74; N, 3.29. Found: C, 62.11; H, 4.86; N, 3.47.

1,2-Dihydro-1,3-diphenyl-2-oxo-quinolin-4-yl dihydrogen phosphate (7m). Compound was prepared from **1m** in 78% yield (Method C, Table 4). Colorless crystals, mp 177–181°C (DMF-benzene); IR (KBr) ν : 3410br, 3132, 3096, 3065, 2840br, 1636, 1596, 1568, 1526, 1494, 1454, 1363, 1316, 1268, 1230, 1194, 1166, 1143, 1099, 1073, 1023, 963, 869, 824, 802, 787, 758, 700, 682, 641, 608, 576, 554, 522 cm^{-1} ; For NMR spectra see Table 5; EI-MS (m/z , %): 314 (19), 313 (91), 312 (100), 256 (5), 196 (35), 195 (23), 167 (27), 166 (7), 157 (6), 152 (5), 139 (6), 127 (8), 105 (9), 89 (6), 77 (18), 51 (10), 46 (11), 45 (14), 44 (15); ESI-MS (m/z , %): 807.2 $[2\text{M}-2\text{H}+\text{Na}]^-$ (22), 785.2 $[2\text{M}-\text{H}]^-$ (11), 687.3 $[2\text{M}-\text{H}-\text{H}_3\text{PO}_4]^-$ (74), 392.2 $[\text{M}-\text{H}]^-$ (100). Anal. Calcd. for $\text{C}_{21}\text{H}_{16}\text{NO}_5\text{P}$: C, 64.13; H, 4.10; N, 3.56. Found: C, 63.91; H, 4.25; N, 3.53.

Isolation of crystal violet.

- Chloroform extracts obtained using the Method A were filtered through a short column of silica gel. The adsorbed blue compound was obtained by washing of the column with ethanol, evaporating the filtrate to dryness and crystallization of the residue from ethanol. In all cases, crystal violet, identical to the authentic sample, was obtained in yields of 10–20%.
- The mixture of DMA (5 mL, 39.4 mmol) and phosphoryl chloride (50 mL) was heated to reflux for 20 h. The reaction mixture was cooled, poured onto ice (100 g) and the

mixture was extracted with chloroform. After drying and evaporation of the extract, the residue was crystallized from ethanol. Blue crystals of mp 202–204°C (dec.), whose IR and ¹H NMR spectra were identical to those of crystal violet (C₂₅H₃₀N₃Cl, MW 407.98) [24] were obtained in 64% yield. For commercial crystal violet (Aldrich), mp 205°C (dec.) is presented; EI-MS (*m/z*, %): 374 (13), 373 (47), 372 (16), 254 (21), 253 (100), 252 (68), 238 (7), 237 (26), 208 (8), 186 (10), 126 (18), 118 (6), 18 (8).

Reactions of compounds 2 with some nucleophiles.

- A. A solution of 2-sulfanylbenzothiazol (334.5 mg, 2 mmol) and **2f** (571.5 mg, 2 mmol) in chloroform (50 mL) was stirred at room temperature for 2 h and subsequently heated to reflux for 3 h. After cooling, the mixture was evaporated to dryness and the residue was column chromatographed. 4-Hydroxy-1-methyl-3-phenyl-2-quinolone (**1f**), (382 mg, 76%) of mp 223–225°C (ethanol) and 2,2'-dithiobis(benzothiazole) (256 mg, 77%) of mp 177–178°C (benzene) were obtained. Both compounds were identical in all respects to the authentic specimens [22].
- B. A solution of 2,5-dimethylaniline (121 mg, 1 mmol) and **2f** (285.7 mg, 1 mmol) in chloroform (25 mL) was stirred at room temperature for 1 h and subsequently heated to reflux for 6 h. After cooling, deposited 2,5-dimethylaniline hydrochloride (31%) was filtered with suction. The filtrate was evaporated to dryness and column chromatographed on silica gel. Besides starting compound **2f** (42%), 3-(2,5-dimethylphenylamino)-1-methyl-3-phenylquinoline-2,4(1*H*,3*H*)-dione (**6f**) was obtained in 31% yield. Colorless crystals, mp 202–210°C (benzene-hexane); IR (KBr) ν : 3409, 3055, 3021, 2937, 2916, 2859, 1704, 1664, 1599, 1585, 1519, 1493, 1471, 1447, 1420, 1354, 1305, 1296, 1189, 1169, 1133, 1105, 1056, 1037, 1001, 914, 792, 765, 745, 735, 717, 699, 651, 588, 545, 529 cm⁻¹; For NMR see Table 5; EI-MS (*m/z*, %): 371 (7), 370 (M⁺, 24), 337 (5), 222 (13), 209 (13), 208 (73), 194 (5), 193 (7), 126 (13), 120 (14), 114 (17), 112 (11), 105 (13), 104 (11), 103 (7), 98 (11), 97 (13), 96 (7), 95 (10), 91 (6), 86 (9), 84 (5), 83 (16), 82 (6), 81 (11), 79 (12), 77 (16), 74 (29), 73 (7), 72 (64), 71 (7), 70 (7), 69 (29), 67 (14), 60 (20), 59 (100), 57 (18), 56 (10), 55 (47), 54 (8), 44 (14), 43 (35), 41 (34). Anal. Calcd. for C₂₄H₂₂N₂O₂: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.52; H, 6.04; N, 7.48.
- C. A solution of DMA (121 mg, 1 mmol) and compound **2** (1 mmol) in corresponding solvent (25 mL) was stirred at room temperature for 1 h and subsequently heated to reflux for 4.5 h. After cooling, the solution was evaporated to dryness and column chromatographed on silica gel. In all cases, besides the starting compound, only compounds **1** were isolated from the complex reaction mixture in the following yields: (a) in chloroform: **1f** (37%); (b) in acetic acid: **1c** (81%); (c) in ethanol: **1c** (12%); (d) in toluene: **1f** (6%).

Conversion of compounds 7 to 1.

- A. A solution of **7m** (50 mg) in 3% solution of potassium carbonate (5 mL) was stirred at 100°C for 4.5 h. After cooling and acidification with concentrated hydrochloric acid, the

precipitate was filtered off with suction, washed with water and dried. 1,3-Diphenyl-4-hydroxyquinolin-2-one (**1m**), mp 231–234°C, identical in all respect to the authentic sample, was isolated in 41% yield.

- B. A solution of **7m** (101 mg) in acetic acid (10 mL) was heated to reflux for 2.5 h. The reaction mixture was evaporated to dryness and the residue was crystallized from ethanol. Colorless crystals, mp 232–234°C (ethanol), identical in all respects to **1m**, were isolated in 30% yield.

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