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A NEW SYNTHESIS OF 4-ALKYL/ARYL-5,6-DIHYDRO-2*H*-PYRANO[3,2-*c*]QUINOLINE-2,5-DIONES AND MOLECULAR REARRANGEMENT OF THEIR 3-BROMO DERIVATIVES TO 2-ALKYL/ARYL-4-OXO-4,5-DIHYDROFURO[3,2-*c*]QUINOLINE-3-CARBOXYLIC ACIDS

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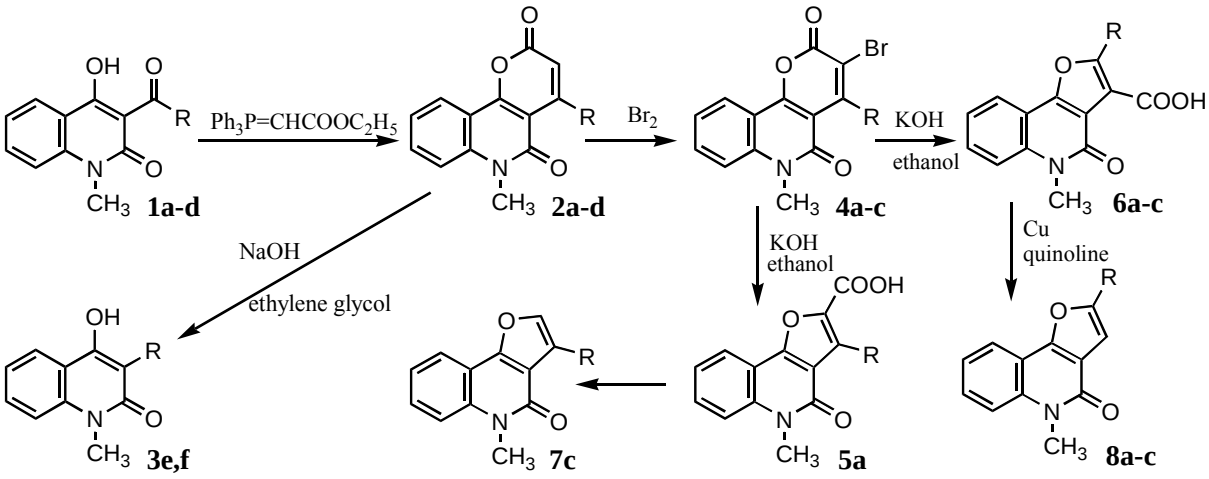
Abstract – The treatment of 3-acyl-4-hydroxy-1*H*-quinolin-2-ones (**1**) with ethyl (triphenylphosphoranylidene)acetate leads to 5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-diones (**2**), which were brominated to 3-bromo derivatives (**4**). Alkaline hydrolysis of **4** gives 2-alkyl/aryl-4-oxo-4,5-dihydrofuro[3,2-*c*]quinoline-3-carboxylic acids (**6**), which were decarboxylated to 2-alkyl/aryl-5*H*-furo[3,2-*c*]quinolin-4-ones (**8**). The reaction of 3-acetyl-4-hydroxy-1-methyl-1*H*-quinolin-2-one (**1a**) with ethyl (triphenylphosphoranylidene)chloroacetate proceeds not only at the acetyl but also at the amide group to give a mixture of ethyl 3,5-dimethyl-4-oxo-4,5-dihydrofuro[3,2-*c*]quinoline-2-carboxylate (**11a**) and ethyl 4,6-dimethyl-2-oxo-5,6-dihydro-2*H*-pyrano[3,2-c]quinolin-5-ylidene-(chloro)acetate (**12a**). The reaction mechanism of the molecular rearrangement of **4** to **6** is discussed.

Various substituted 5*H*-furo[3,2-*c*]quinolin-4-ones are abundant in the plant kingdom.[1] Compounds unsubstituted in the furan ring were prepared from 3-formyl-4-hydroxy-1*H*-quinolin-2-ones through 5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-diones as the key intermediates.[2] 2-Methyl derivatives of 5*H*-furo[3,2-*c*]quinolin-4-ones were prepared by condensation of diethyl 2-propynylmalonate with aniline,[4] by cyclization and following dehydrogenation of 4-allyloxy-1*H*-quinolin-2-ones or 3-allyl-4-hydroxy-1*H*-quinolin-2-ones, respectively,[5] and by cyclization of 4-(2-propynyl)oxy-1*H*-quinolin-2-ones.[6,7] 2,3-Disubstituted 5*H*-furo[3,2-*c*]quinolin-4-ones were prepared starting with substituted 2-

propynylbromides.[7] Some 3-aryl-5*H*-furo[3,2-*c*]quinolin-2-ones were prepared by cyclization of 4-aroylmethoxy-1*H*-quinolin-2-ones.[8] Recently, the preparation was described of 3,5-dimethyl-5*H*-furo[3,2]quinolin-4-one.[9]

4-Alkyl/Aryl-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-diones (**2**), arising from corresponding 4-hydroxy-1*H*-quinolin-2-ones by the modified Pechmann reaction with β-enamino esters or β-keto esters[10,11] were expected to be suitable starting compounds for the synthesis of 3-alkyl/aryl-5*H*-furo[3,2-*c*]quinolin-4-ones (**7**). However, the number of commercially available β-keto esters and, particularly, β-enamino esters is limited. Therefore, we decided to prepare compounds (**2**) by the Wittig reaction of ethyl (triphenylphosphoranylidene)acetate with 3-acyl-4-hydroxy-1*H*-quinolin-2-ones (**1**), which are accessible by partial hydrolysis of 4-hydroxy-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-diones[12] or by the Fries rearrangement of 4-aroyloxy-1*H*-quinolin-2-ones.[13]



a: R = CH_3; **b**: R = *n*-C_5H_{11}; **c**: R = Ph; **d**: R = CH_2Ph; **e**: R = H; **f**: R = (Ph)C=CH_2

Scheme 1

Wittig reaction of **1** with ethyl (triphenylphosphoranylidene)acetate (Scheme 1) proceeds with high stereoselectivity giving compounds (**2**) in good yields. Characteristic lactam (1644-1660 cm^{-1}) and lactone (1726-1737, 1747-1759 cm^{-1}) absorptions in their IR spectra as well as ^1H and ^{13}C NMR spectra (Tables I and II) were in agreement with the expected structures. These compounds are relatively stable to alkaline hydrolysis. However, their treatment with sodium hydroxide in boiling ethylene glycol produced complex mixture of products. With **2a**, 4-hydroxy-1-methyl-1*H*-quinolin-2-one (**3e**) was isolated and identified by comparison (IR, MS, ^1H and ^{13}C NMR – Table III) with the authentic compound. Its formation can be explained by addition of water to the opened intermediate and subsequent retroaldolization and decarboxylation. ^1H NMR spectrum of compound $C_{18}H_{15}NO_2$ obtained by hydrolysis of **2c** contained a phenolic OH, a *N*-methyl, four contiguous aromatic protons, signal of a phenyl group, and an isolated exomethylene. The structure (**3f**) was deduced using HMBC data (Figure 1, Table III).

Table I. ^{1}H NMR Spectral Data (δ, ppm/Hz) of Compounds (**2a-d**) and (**4a-c**) (399.90 MHz, $CDCl_3$, 30°C)

Proton/$J_{i,j}$	**2a**[a]	**2b**	**2c**[b]	**2d**[a]	**4a**	**4b**	**4c**
H-3	6.166	6.195	6.231	5.891			
$J_{3,1'}$	*1.3*	*1.0*		*1.3*			
H-7	7.381	7.368	7.549	7.278	7.657	7.375	7.374
$J_{7,8}$	*8.6*	*8.6*	*8.5*	*7.6*	*8.6*	*8.6*	*8.7*
$J_{7,9}$	*1.0*	*1.0*		*1.0*	*1.0*	*1.6*	*1.0*
$J_{7,10}$	*0.6*	*0.5*		*n.d.*[c]	*n.d.*	*0.5*	*n.d.*
H-8	7.687	7.673	7.772	7.213	7.820	7.699	7.730
$J_{8,9}$	*7.2*	*7.2*	*7.1*	*7.7*	*7.1*	*7.2*	*7.2*
$J_{8,10}$	*1.6*	*1.6*	*1.5*	*1.6*	*1.5*	*1.6*	*1.5*
H-9	7.335	7.318	7.387	7.591	7.425	7.327	7.378
$J_{9,10}$	*8.0*	*8.1*	*8.1*	*8.1*	*8.2*	*8.1*	*8.4*
H-10	8.280	8.262	8.089	8.184	8.135	8.257	8.341
N-Me	3.717	3.712	3.504	3.619	3.670	3.732	3.596

[a]40°C; [b]DMSO-d_6; [c]n.d. not determined. Additional signals: **2a** – 2.728 (d, $J_{3,Me}$ = 1.3 Hz, 3H, 4-Me); **2b** – 3.127 (m, 2H, H-1′), 1.639 (m, 2H, H-2′), 1.443 (m, 2H, H-3′), 1.368 (m, 2H, H-4′), 0.917 (t, *J* = 7.1 Hz, 3H, H-5′); **2c** – 7.406 (m, 1H, H-4′), 7.401 (m, 2H, H-3′and H-5′), 7.336 (m, 2H, H-2′and H-6′); **2d** – 7.249 (m, 2H, H-4′and H-6′), 7.172 (m, 1H, H-5′), 7.166 (m, 2H, H-3′and H-7′), 4.494 (d, *J* = 13.0 Hz, 1H, H-1′d), 4.464 (d, *J* = 13.0 Hz, 1H, H-1′u); **4a** – 2.982 (s, 3H, 4-Me); **4b** – 3.437 (m, 2H, H-1′), 1.614 (m, 2H, H-2′), 1.522 (m, 2H, H-3′), 1.417 (m, 2H, H-4′), 0.942 (t, *J* = 7.2 Hz, 3H, H-5′); **4c** – 7.527 (m, 2H, H-3′and H-5′), 7.499 (m, 1H, H-4′), 7.143 (m, 2H, H-2′and H-6′).

Table II. ^{13}C Chemical Shifts (δ, ppm) of Compounds (**2a-d**) and (**4a-c**) (100.55 MHz, $CDCl_3$, 30°C)

Carbon	**2a**[a]	**2b**	**2c**[b]	**2d**[a]	**4a**	**4b**	**4c**
2	159.03	159.25	157.90	159.46	155.67	155.78	156.08
3	114.33	113.30	115.32	114.58	112.77	112.33	113.39
4	157.11	161.18	156.89	159.15	155.21	159.08	156.00
4a	107.99	107.45	106.34	107.40	108.00	107.45	107.72
5	160.15	159.59	158.23	158.85	159.48	158.85	158.03
6a	139.91	139.75	139.85	139.89	139.72	138.68	140.12
7	114.26	114.16	115.25	114.22	114.35	114.26	114.46
8	133.35	133.26	133.64	133.39	133.67	133.59	133.79

Table II – continued

9	122.81	122.70	122.70	122.80	123.07	122.94	123.01
10	124.63	124.53	123.47	124.61	124.52	124.42	124.45
10a	113.50	113.40	112.59	113.43	112.85	112.79	112.86
10b	158.99	159.22	158.61	159.13	156.95	157.36	157.37
N-Me	29.58	29.66	29.46	26.69	29.93	30.02	29.91
1′	23.92	35.20	138.06	40.56	23.21	35.00	138.68
2′		28.92	127.38[c]	137.33		27.82	126.19[c]
3′		31.62	127.43[c]	129.59[c]		32.18	128.29[c]
4′		22.48	128.20	128.77[c]		22.40	126.31
5′		13.95		128.86		13.99	

[a]40°C; [b]DMSO-d_6; [c]2C

Table III. ^{1}H and ^{13}C NMR Spectral Data of Compounds (**3e**, **3f**, **9b** and **10b**) (399.90 MHz and 100.55 MHz, DMSO-d_6, 30°C)

	^{1}H NMR (δ, ppm/Hz)				^{13}C NMR (δ, ppm)				
Proton/$J_{i,j}$	**3e**	**3f**	**9b**	**10b**	Carbon	**3e**	**3f**	**9b**	**10b**
H-3	5.883 s				2	162.56	161.56	162.66	154.26
H-5	7.889[a]	8.017	8.003		3	99.97	111.78	105.87	122.74
$J_{5,6}$	*8.0*	*8.0*	*8.0*		3a				113.97
$J_{5,7}$	*1.6*	*1.6*	*1.5*		4	161.07	156.71	157.22	158.19
H-6	7.231	7.289	7.269	7.564 m	4a	116.09	115.97	116.18	
$J_{6,7}$	*7.1*	*7.1*	*7.1*		5	123.13	123.72	123.17	
$J_{6,8}$	*1.0*	*1.0*	*1.1*		5a				137.287
H-7	7.616	7.648	7.613	7.543 m	6	121.19	121.53	121.34	115.36
$J_{7,8}$	*8.6*	*8.5*	*8.6*		7	131.31	131.19	130.63	128.87
H-8	7.459	7.505	7.489	7.300 m	8	114.50	114.52	114.36	121.97
H-9				7.887 m	8a	140.01	139.23	138.61	
N-Me	3.529	3.544	3.576	3.649	9				120.24
4-OH	11.318	10.134	10.350		9a				112.95
H-1′			3.707 s[c]	2.873 t[c]	9b				151.72
$J_{1',2'}$				*7.6*	*N*-CH_3	28.47	29.08	29.16	29.11
H-2′				1.676 m[c]	1′		140.03	38.47	26.50
H-3′		7.360 m	2.489 t[c]	1.327 m[c]	2′		139.59	207.44	27.55

Table III – continued

$J_{3',4'}$		*7.4*		3′	125.85	41.48	30.95
H-4′	7.291 m	1.497 tt[c]	1.318 m[c]	4′	128.27	23.00	21.87
$J_{4',5'}$		*7.3*	*7.0*	5′	127.46	30.82	13.90
H-5′	7.251 m	1.265 m[c]	0.871 t[d]	6′	128.27	21.95	
H-6′	7.291 m	1.240 m[c]		7′	125.8 5	13.82	
$J_{6',7'}$		*7.1*		=$\underline{C}H_2$	118.34		
H-7′	7.360 m	0.858 t[d]					
C=C$\underline{H}_2$[b]	6.075 d 5.261 d						

[a]$J_{5,8}$ = 0.5 Hz; [b]J_{gem} = 1.2 Hz; [c]2H; [d]3H

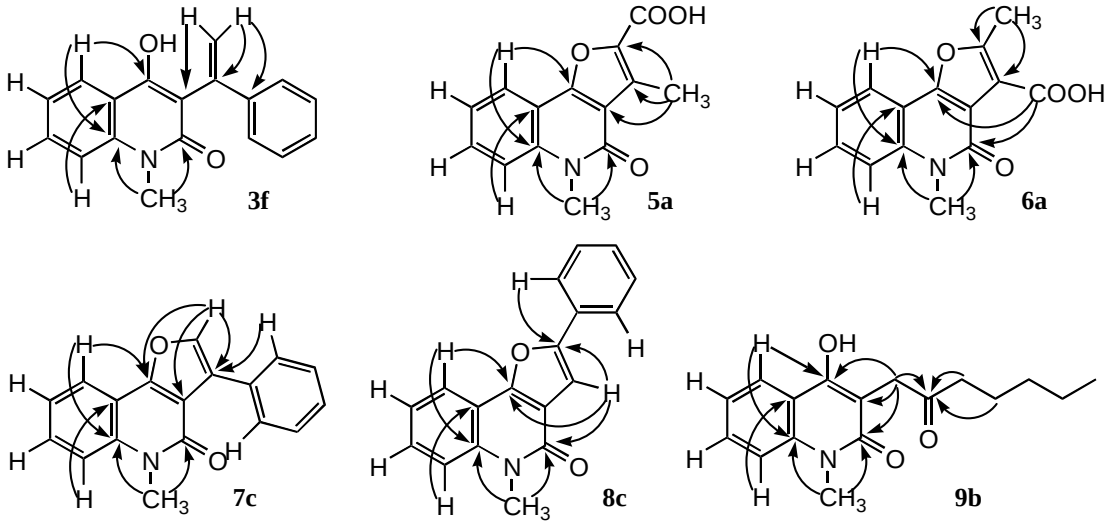


Figure 1. Results of HMBC correlation of compounds (**3f**, **5a**, **6a**, **7c**, **8c**, and **9b**)

Our strategy of preparing 3-alkyl/aryl-5*H*-furo[3,2-*c*]quinolin-4-ones (**7**) was based on the preassumption that 3-bromo derivatives (**4**) can be converted to **5** (Scheme 1) by treatment with alkali, in analogy with the described conversion of 3-bromo-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-diones unsubstituted in position 4.[2,3] This reaction is known as the Perkin rearrangement, common in the chemistry of coumarins; its reaction mechanism was presented recently.[14]

The bromination of compounds (**2**) afforded mixtures containing besides the required **4** additional compounds brominated at position 9. Because of poor solubility of these compounds, the separation was difficult or even unsuccessful (with **4d**). Their IR, ^{1}H and ^{13}C NMR spectra (Tables I and II) were very similar to those of parent compounds.

Our attempts to perform the Perkin rearrangement of bromo derivatives (**4**) in ethanolic potassium hydroxide produced complex mixtures. We believed that pure acids, isolated in moderate yields, had structures (**5a-c**) (assuming the regular course of the Perkin rearrangement). However, the melting points

of their decarboxylation (quinoline/Cu dust) products, 117-119°C (**a**-series) and 213-215°C (**c**-series) did not agree with those reported for 3-substituted furoquinolones (**7a**) (155-156°C, ref.[9]) and (**7c**) (105-106°C, prepared to according ref.[8]). Furthermore, the mp of the former matched that given for 2-substituted furoquinolone (**8a**) (118-119°C, ref.[6]; 118°C, ref.[7]). Also the comparison of NMR spectra of the **c**-series decarboxylation product and **7c** showed that both compounds were different (Tables IV and V). Large values of ^1J=180.8 Hz (**8a**) of the furan =CH and heteronuclear coupling of H-9 to a =C-O- type quaternary carbon (**8a-c**) confirm the formation of a furan ring. However, chemical shifts of corresponding carbons (Table V) are too low for furan α-carbons. HMBC results (Figure 1) showed that the side chains are in all cases attached to a =C-O- carbon (i.e., indeed α-). Another evidence is the weak coupling of the furan proton to C-4 (in turn unambiguously assigned using its coupling to the *N*-methyl), which is observable in 2-substituted derivatives only. Thus, the decarboxylation products under discussion have structures (**8a**, **8b**, and **8c**); the corresponding acids are **6a**, **6b**, and **6c**.

Table IV. ^{1}H NMR Spectral Data (δ, ppm/Hz) of Compounds (**5a**), (**6a-c**), (**7c**), and (**8a-c**) (399.90 MHz, $CDCl_3$, 30°C)

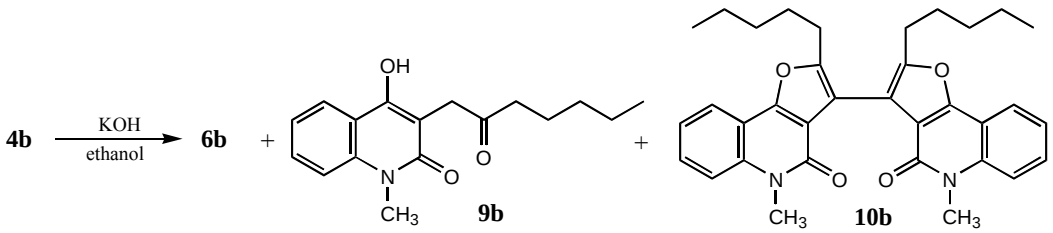
Proton/$J_{i,j}$	**5a**[b]	**6a**[a,b]	**6b**[a,b]	**6c**[b]	**7c**	**8a**	**8b**	**8c**
2					7.716			
3						6.644	6.661	7.275
6	7.553	7.874	7.870	7.838	7.438	7.415	7.423	7.443
$J_{6,7}$	*8.5*	*8.5*	*8.6*	*8.6*	*8.6*	*8.5*	*8.6*	*8.6*
$J_{6,8}$	*1.0*	*1.0*	*1.0*	*1.0*	*1.0*	*1.1*	*1.1*	*1.0*
$J_{6,9}$	*≠0*	*≠0*	*0.6*	*≠0*	*0.6*	*0.5*	*0.4*	*0.5*
7	7.639	7.769	7.774	7.771	7.567	7.505	7.508	7.551
$J_{7,8}$	*7.2*	*7.2*	*7.1*	*7.1*	*7.2*	*7.2*	*7.1*	*7.2*
$J_{7,9}$	*1.5*	*1.6*	*1.5*	*1.5*	*1.6*	*1.6*	*1.6*	*1.6*
8	7.329	7.533	7.536	7.516	7.323	7.282	7.287	7.333
$J_{8,9}$	*7.8*	*7.8*	*7.9*	*7.9*	*7.9*	*7.8*	*7.9*	*7.8*
9	7.871	8.067	8.100	8.180	8.041	7.943	7.963	8.080
N-Me	3.577	3.808	3.819	3.814	3.772	3.767	3.776	3.794

[a]40°C; [b]DMSO-d_6. Additional signals: **5a** – 2.579 (m, 3H, 3-Me); **6a** – 2.794 (s, 3H, 3-Me); **6b** – 3.239 (t, *J* = 7.8 Hz, H-1′), 1.761 (m, 2H, H-2′), 1.349 (m, 2H, H-3′), 1.340 (m, 2H, H-4′), 0.877 (t, *J* = 7.1 Hz, 3H, H-5′); **6c** – 8.018 (m, 2H, H-2′and H-6′), 7.562 (m, 1H, H-4′), 7.554 (m, 2H, H-3′and H-5′); **7c** – 7.817 (m, 2H, H-2′and H-6′), 7.457 (m, 2H, H-3′and H-5′), 7.375 (m, 1H, H-4′); **8a** – 2.494 (d, $J_{3,Me}$ = 1.1 Hz, 2-Me); **8b** – 2.798 (dt, *J* = 1.0 and 7.5 Hz, 2H, H-1′), 1.763 (m, 2H, H-2′), 1.391 (m, 2H, H-3′), 1.373 (m, 2H, H-4′), 0.918 (t, *J* = 7.0 Hz, 3H, H-5′); **8c** – 7.836 (m, 2H, H-2′and H-6′), 7.464 (m, 2H, H-3′and H-5′), 7.362 (m, 1H, H-4′).

Table V. ^{13}C NMR Chemical Shifts (δ, ppm) of Compounds (**5a**), (**6a-c**), (**7c**), and (**8a-c**) (100.55 MHz, $CDCl_3$, 30°C)

Carbon	**5a**[b]	**6a**[a,b]	**6b**[a,b]	**6c**[b]	**7c**	**8a**	**8b**	**8c**
2	141.16	163.71	166.87	157.62	140.75	154.58	159.07	155.88
3	128.80	110.90	110.99	112.37	126.77	104.04	103.26	102.88
3a	114.64	111.10	110.75	113.23	112.99	116.47	116.31	117.21
4	158.49	160.37	160.36	159.71	159.33	159.35	159.49	159.33
5a	138.92	137.05	136.94	137.54	138.28	137.72	137.74	138.18
6	115.80	116.88	116.80	116.65	114.83	114.92	114.92	115.07
7	131.08	130.99	130.89	131.17	129.67	128.84	128.82	129.39
8	122.54	124.25	124.13	123.86	121.27	122.12	120.83	122.34
9	121.17	120.95	120.88	121.34	122.16	120.77	122.10	121.12
9a	112.34	111.81	111.75	111.66	112.83	113.20	113.29	113.09
9b	154.64	153.38	153.34	153.79	156.28	154.13	154.02	154.47
N-Me	28.77	30.22	30.16	30.11	29.29	29.36	29.37	29.45
1′	10.03	13.66	26.69	130.31	130.24	13.80	28.11	129.72
2′			26.73	128.67[c]	129.17[c]		27.42	124.49[c]
3′			30.64	128.44[c]	128.17[c]		31.22	128.88[c]
4′			21.61	130.38	127.77		22.32	128.58
5′			13.66				13.91	
COOH	160.67	161.87	161.64	162.24				

[a]40°C; [b]DMSO-d_6; [c]two carbons.

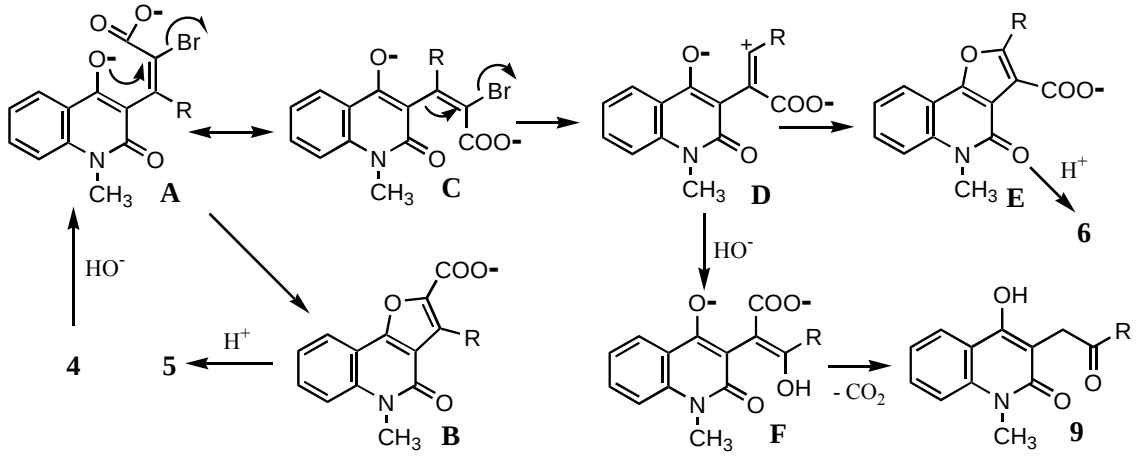


Scheme 2

Three compounds (**6b**, **9b**, and **10b**) were isolated from the alkaline hydrolysis of **4b** (Scheme 2). The structure of carboxylic acid (**6b**) is based on the examination of its decarboxylation product (**8b**) (see above). IR spectrum of acidic compound $C_{17}H_{21}NO_3$ excluded the presence of a carboxyl. According to the ^{13}C NMR spectrum (Table III) the molecule contained two =C-O- and one aliphatic C=O. The ^{1}H NMR spectrum (Table III) displayed singlets of a phenolic hydroxyl, *N*-methyl, and isolated methylene, in addition to an ABCD spin system of four vicinal aromatic protons and a $–(CH_2)_4CH_3$ moiety. HMBC

experiment (Figure 1) leads to structure (**9b**). This structure was confirmed by intramolecular condensation of **9b** to **8b** in conc. sulfuric acid. The intense ion with the highest mass in the MS spectrum of the third component from the hydrolysis of **4b** had *m*/*z* 269 and elemental composition $C_{17}H_{19}NO_2$. However, the observed ^{1}H NMR spectrum (Table III) accounted for 18 protons only; an ABCD spin system of four aromatic protons, a *N*-methyl, and *n*-pentyl. No evidence for an OH group was found neither in IR nor in ^{1}H NMR spectra. Seventeen signals observed in the ^{13}C NMR spectrum (Table III) represent two methyls, four aliphatic methylenes, four =CH, and seven sp^2 hybridized carbons. Three of these quaternary carbons are attached to oxygen. One (coupled to the *N*-methyl) is C-4; the second (coupled to H-9) belongs to C-9b; the remaining one (coupled to the terminal CH_2 of the side chain) is therefore C-2. Thus a structure (**10b**) of symmetric 3-3´dimer analogous to **8b** is proposed for this compound. A weak molecular ion was indeed found at *m*/*z* 536. The ion *m*/*z* 269 might arise by breakdown of the bond connecting both parts followed by hydrogen transfer.

It is evident from the foregoing that acids obtained by alkaline hydrolysis of bromo derivatives (**4**) have not the expected structure (**5**), but isomeric structure (**6**). However, a detailed spectroscopic investigation of crude mixture of acids obtained upon alkaline hydrolysis of **4a** showed two components: a minor one, **5a** and a major one **6a**. These were differentiated using the HMBC coupling pattern of the CH_3-C= group: three crosspeaks (C-2, C-3, C-3b) for **5a** and two (C-2, C-3) for **6a**.

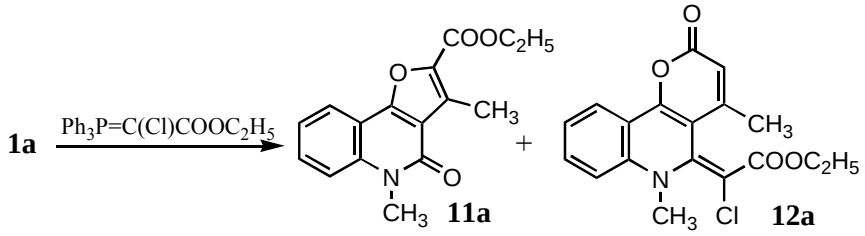


Scheme 3

Our findings show that the hydrolysis of bromo derivatives (**4**) proceeds in analogy with the Perkin rearrangement of 3-bromocoumarins to benzofuran-2-carboxylic acids in only a small extent to give **5a**. The formation of major product (**6a**) must proceed by some other molecular rearrangement. A proposed reaction mechanism of the molecular rearrangement of **4** to acids (**6**) is given in Scheme 3. By the opening of the pyrane ring of **4** in an alkaline medium, dianion (**A**) arises, the conversion of which can proceeds in two independent ways. The first is represented by the regular Perkin rearrangement in which anion (**B**) is formed and which, after acidification, yields the expected acid (**5**). The second and main way

passes through a conformer (**C**), the occurrence of which is more probable than **A** due to the longer distance of two negatively charged functional groups. The following elimination of halogen atom at the sp^2 hybridized carbon atom is accompanied by a migration of the substituent in *trans*-position to the departing halogen atom. This migratory group exhibits a partial carbanionic character due to its possible tautomerism. This rearrangement, which is formally of the Wagner-Meerwein type, leads to the formation of intermediate (**D**), which produces compound (**E**) and, consequently, product (**6**) after acidification. It is probable that the conversion of **C** to **E** is concerted. This proposal also well explains the formation of side product (**9b**) in the reaction of **4b**. The addition of hydroxyl ion to intermediate (**D**) leads to the formation of intermediate (**F**), which, according to its β-oxoacid character, smoothly decarboxylates with formation of the anion of the isolated compound (**9b**). The origin of side product (**10b**) remains unanswered; it probably arises through a dehydrogenative coupling of some reaction intermediate. However, **8b** and **9b** cannot be precursors of **10b** as their work-up in alkaline medium in the presence of air oxygen produced no changes.

The observation of the new molecular rearrangement of **4** to **6** described above brings a doubt about the correct structure of acid (**5e**), the preparation of which was described[2] as the Perkin rearrangement of bromo derivative (**4e**). The same is true of the structure of acid prepared[3] from the *N*-unsubstituted analogue of **4e**. Unfortunately, the NMR spectra of both latter acids were not reported so that problem remains unsolved.



Scheme 4

Owing to the unexpected molecular rearrangement of 3-bromo derivatives (**4**), our idea to prepare **7** starting from **2** failed. Therefore, we were looked for a new reaction path leading to compounds (**5**). We have been studying the reaction of 3-acetyl-4-hydroxy-1*H*-quinolin-2-one (**1a**) with ethyl (triphenylphosphoranylidene)chloroacetate[15] (Scheme 4). In boiling xylene, the reaction gives a complex mixture of compounds from which compound $C_{16}H_{15}NO_4$ was isolated by repeated column chromatography and identified as ethyl ester (**11a**) of **5a**. The yield of the reaction is low, however, according to our best knowledge, this is the first case of the successful reaction of a very stable chlorinated ylide with ketones. The second reaction product $C_{18}H_{16}NO_4Cl$ contained an unsaturated lactone moiety similar to **2a**, an ethyl group and one additional sp^2-type quaternary carbon. The configuration of the new tetrasubstituted double bond in structure (**12a**) was not determined because of

lack of protons in its vicinity. Its formation can be explained by the reaction of **1a** with dechlorinated Wittig reagent and the following reaction of so formed intermediate with chlorinated ylide at the lactam group. The origin of dechlorinated Wittig reagent (ethyl (triphenylphosphoranylidene)acetate) in the reaction mixture is so far not clear.

EXPERIMENTAL

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 Varian INOVA-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) in the respective solvents and temperatures stated. Chemical shifts are given on the δ scale (ppm) and are referenced to internal TMS. All 2D experiments (gCOSY, HMQC, HMBC) were performed using manufacturer´s software. The sequence for 1D-TOCSY experiments[16] was obtained through Varian User Library; sequence for gradient-selected HMBC[17,18] was provided by Varian Application Laboratory (Darmstadt, Germany). Proton spectra were assigned using gCOSY. The NOE difference experiment (irradiation of *N*-methyl) was performed to find the *peri*-disposed aromatic proton. The chemical shifts and coupling constants of some ABCD system proton buried in the envelope were extracted from 1D-TOCSY spectra. Benzene ring protons were assigned according to their characteristic multiplet pattern. Protonated carbons were assigned by HMQC; where the direct observation of ^{13}C NMR spectrum was not possible, HMQC readouts were used instead. Quaternary carbons were assigned by HMBC or gHMQC, respectively. Positive ion electron impact mass spectra were measured on a Finnigan MAT 95 spectrometer (70 eV, ion source temperature 250°C); perfluorokerosene was used as a standard for the high-resolution measurement. Column chromatography was carried out on silica gel (Merck, grade 60, 70-230 mesh) using a mixture of chloroform – ethanol (19:1, S_1) and benzene – ethyl acetate (9:1, S_2) respectively, as eluent. The course of separation and also the purity of isolated substances were monitored by TLC (elution systems benzene-ethyl acetate, 4:1, and chloroform-ethanol, 9:1 and/or 19:1) on Silufol UV 254 foils (Kavalier, Votice). Elemental analyses (C, H, N) were performed with an EA 1108 Elemental Analyzer (Fisons Instrument).

3-Acyl-4-hydroxy-1*H*-quinolin-2-ones (**1**) were prepared according to ref.[19] (**1a**), ref.[12] (**1b** and **1d**), and ref.[13] (**1c**).

General Procedure for the Preparation of 4-Alkyl/Aryl-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-diones (2a-d). A mixture of **1** (5 mmol) and ethyl (triphenylphosphoranylidene)acetate (1.92 g, 5.5 mmol) in xylene (20 mL) was refluxed for 4 h. After cooling, the precipitate was filtered off with suction and recrystallized. From mother liquors, a further portion of **2** was obtained after concentration *in vacuo*.

4,6-Dimethyl-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-dione (2a): Colorless crystals, yield 70%, mp 279-282°C (DMF) (lit.,[10] mp 283-284°C), IR (cm^{-1}): 3087, 2986, 2926, 1760, 1737, 1717, 1655, 1630, 1595, 1580, 1543, 1500, 1453, 1425, 1417, 1394, 1384, 1304, 1169, 1103, 1075, 1040, 917, 846, 768, 674, 644. EIMS, *m/z* (%): 241 (M^+, 73), 213 (100), 198 (7), 184 (54), 170 (6), 156 (7), 132 (6), 115 (5), 104 (5), 77 (7), 63 (2), 51 (3). Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81. Found: C, 69.54; H, 4.76; N, 5.64.

6-Methyl-4-pentyl-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-dione (2b): Colorless crystals, yield 65%, mp 162-164°C (benzene), IR (cm^{-1}): 3077, 2953, 2930, 2857, 1760, 1729, 1654, 1620, 1594, 1538, 1453, 1397, 1321, 1302, 1162, 1139, 1113, 1074, 1040, 990, 925, 882, 841, 758, 674, 633. EIMS, *m/z* (%): 297 (M^+, 46), 269 (49), 254 (58), 240 (42), 226 (92), 213 (100), 198 (9), 184 (24), 170 (6), 154 (11), 132 (7), 115 (7), 104 (9), 77 (13), 63 (2), 51 (3). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.53; H, 6.57; N, 4.56.

6-Methyl-4-phenyl-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-dione (2c): Colorless crystals, yield 71%, mp 218-224°C (benzene-methanol), IR (cm^{-1}): 3086, 3032, 2938, 2886, 1742, 1660, 1616, 1594, 1571, 1530, 1497, 1453, 1397, 1386, 1317, 1302, 1181, 1143, 1117, 1085, 1041, 984, 925, 896, 857, 849, 762, 699, 689, 597. EIMS, *m/z* (%): 303 (M^+, 73), 302 (100), 275 (58), 274 (31), 246 (15), 232 (10), 218 (15), 204 (7), 104 (5), 77 (8), 63 (2), 51 (2). Anal. Calcd for $C_{19}H_{13}NO_3$: C, 75.24; H, 4.32; N, 4.62. Found: C, 74.96; H, 4.12; N, 4.43.

4-Benzyl-6-methyl-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-dione (2d): Colorless crystals, yield 64%, mp 199-202°C (benzene-ethanol), IR (cm^{-1}): 3085, 3063, 3030, 2945, 2921, 2891, 1751, 1726, 1660, 1624, 1603, 1596, 1579, 1545, 1498, 1456, 1404, 1392, 1156, 1098, 1068, 986, 929, 910, 891, 843, 834, 763, 701, 680, 623, 550. EIMS, m/z (%): 317 (M^+, 76), 289 (100), 274 (9), 260 (18), 134 (6), 115 (3), 104 (3), 77 (6), 65 (2), 51 (1). Anal. Calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.92; H, 5.00; N, 4.64.

Alkaline Hydrolysis of 5,6-Dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-diones (2a and 2c).

A mixture of **2** (0.7 mmol) and sodium hydroxide (0.14 g, 3.5 mmol) in water (0.21 mL) was diluted with ethylene glycol (1.4 mL) and refluxed for 1 h. After cooling, water (6 mL) was added and the solution was acidified with conc. hydrochloric acid. The separated precipitate was filtered off with suction and crystallized. From **2a**, compound (**3e**), identical in all respect with authentic specimen,[10] was obtained in 59% yield (72 mg). From **2c**, compound (**3f**) was obtained in 55% yield (107 mg).

4-Hydroxy-3-(1-phenylethenyl)-1*H*-quinolin-2-one (3f): Colorless crystals, yield 55%, mp 246-252°C (ethanol), IR (cm^{-1}): 3096, 3077, 3041, 2949, 2896, 2817, 1728, 1610, 1574, 1508, 1492, 1418, 1402, 1339, 1329, 1196, 1187, 1161, 1101, 1071, 1043, 1027, 918, 866, 780, 758, 746, 714, 696, 632, 542. EIMS, *m/z* (%): 277 (M^+, 94), 276 (100), 262 (13), 248 (6), 234 (4), 200 (6), 115 (4), 104 (5), 77 (12), 63 (2), 51 (2). Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.68; H, 5.22; N, 5.02.

General Procedure for the Preparation of 3-Bromo-6-methyl-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-diones (4a-d). To the solution of appropriate pyranoquinolinedione (**2**) (10 mmol) in chloroform (330 mL) bromine (2.4 g, 15 mmol) was added and the mixture was allowed to stand for 160 h (**2a**), 4h (**2b**), 18 h (**2c**), or 70 h (**2d**), respectively. The separated precipitate was filtered off with suction and washed with chloroform. After concentration of mother liquor, the additional portion of product was obtained. Crude products (**4a**) and (**4c**) exhibit only one spot on TLC in several solvent systems. However, according to NMR spectrum, the crude **4b** contain about 10% of 9-bromo derivative and was purified by repeated crystallization. The crude product (**4d**) consists, according to NMR spectrum, of the mixture of three compounds. All attempts on its purification by crystallization failed and it was no used for further reaction.

3-Bromo-4,6-dimethyl-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-dione (4a): Yellow crystals, yield 82%, mp 323-327°C (chloroform), IR (cm^{-1}): 3077, 2947, 1746, 1725, 1657, 1619, 1590, 1572, 1540, 1), 212 (10), 188 (9), 154 (9), 104 (3), 525, 1500, 1450, 1418, 1376, 1345, 1308, 1301, 1254, 1189, 1111, 1078, 1035, 955, 898, 873, 765, 694, 638, 526. EIMS, *m/z* (%): 319 (M^+, 100), 291 (36), 262 (51), 240 (95), 212 (68), 184 (51), 169 (17), 154 (22), 140 (16), 128 (16), 115 (10), 104 (9), 77 (20), 63 (7), 51 (10). Anal. Calcd for $C_{14}H_{10}NO_3Br$: C, 52.52; H, 3.15; N, 4.38. Found: C, 52.79; H, 3.17; N, 4.17.

3-Bromo-6-methyl-4-pentyl-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-dione (4b): Yellow crystals, yield 79%, mp 167-169°C (ethyl acetate), IR (cm^{-1}): 2949, 2930, 2867, 1750, 1740, 1643, 1616, 1590, 1572, 1515, 1497, 1374, 1346, 1314, 1297, 1171, 1161, 1112, 1095, 1072, 1038, 950, 877, 789, 760, 696, 650, 525. EIMS, *m/z* (%): 375 (M^+, 15), 332 (11), 319 (26), 296 (100), 268 (22), 252 (11), 240 (18), 226 (9), 212 (10), 188 (9), 154 (9), 104 (3), 77 (6), 63 (1), 51 (2). Anal. Calcd for $C_{18}H_{18}NO_3Br$: C, 57.46; H, 4.82; N, 3.72. Found: C, 57.27; H, 4.67; N, 3.64.

3-Bromo-6-methyl-4-phenyl-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-dione (4c): Yellow crystals, yield 77%, mp 281-284°C (benzene-methanol), IR (cm^{-1}): 3078, 3058, 3024, 2948, 1745, 1699, 1656, 1618, 1591, 1572, 1515, 1450, 1418, 1376, 1352, 1315, 1296, 1254, 1189, 1122, 1078, 1035, 955, 936,

921, 879, 788, 775, 758, 689, 654, 602, 537. EIMS, *m/z* (%): 381 (M^+, 100), 353 (36), 324 (10), 302 (39), 274 (13), 246 (87), 231 (6), 217 (31), 203 (14), 189 (14), 132 (6), 113 (9), 104 (8), 77 (14), 63 (6), 51 (4). Anal. Calcd for $C_{19}H_{12}NO_3Br$: C, 59.71; H, 3.16; N, 3.66. Found: C, 59.43; H, 3.01; N, 3.53.

Alkaline Hydrolysis of 4-Alkyl/Aryl-3-bromo-6-methyl-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-diones (4a-c). Bromo derivative (**4**) (2.8 mmol) was added to the solution prepared by dissolving of potassium hydroxide (0.79 g, 14 mmol) in water (1 mL) and dilution with ethanol (20 mL) and the mixture was refluxed for 2 h. After evaporation to dryness, water (5 mL) and conc. hydrochloric acid (1 mL) were added. The deposited precipitate was filtered off with suction, washed with water and recrystallized. In the case of **4a**, 47 mg of an impure compound of mp 285-9°C was isolated from mother liquors after separation of **6a**. According to NMR spectrum, it is a mixture of compounds (**5a**) and (**6a**). Attempts on the separation of pure compound (**5a**) by crystallization and column chromatography were unsuccessful. From compound (**4b**), compound (**6b**) was obtained by crystallization with ethanol. Two further compounds, (**9b**) and (**10b**), were isolated by column chromatography of mother liquors on silica gel (solvent system S_1).

2,5-Dimethyl-4-oxo-4,5-dihydrofuro[3,2-*c*]quinoline-3-carboxylic acid (**6a**)**:** Colorless crystals, yield 28%, mp 268-269°C (ethanol), IR (cm^{-1}): 3096, 2989, 2954, 2518, 1731, 1639, 1604, 1589, 1561, 1508, 1459, 1435, 1381, 1373, 1348, 1250, 1112, 1080, 1040, 963, 924, 869, 762, 698, 677, 670, 644. 515. EIMS, *m/z* (%): 257 (M^+, 93), 239 (100), 213 (78), 212 (60), 198 (15), 184 (26), 170 (16), 154 (11), 140 (7), 132 (17), 115 (11), 104 (11), 77 (14), 63 (4), 51 (5). Anal. Calcd for $C_{14}H_{11}NO_4$: C, 65.37; H, 4.31; N, 5.44. Found: C, 65.55; H, 4.08; N, 5.24.

5-Methyl-2-pentyl-4-oxo-4,5-dihydrofuro[3,2-*c*]quinoline-3-carboxylic acid (**6b**)**:** Colorless crystals, yield 26%, mp 187-188°C (benzene), IR (cm^{-1}): 3439, 3194, 2950, 2929, 2859, 1731, 1640, 1607, 1587, 1554, 1503, 1467, 1434, 1410, 1357, 1248, 1112, 1056, 1043, 1017, 994, 964, 922, 791, 759, 658, 633, 554. EIMS *m/z* (%): 313 (M^+, 45), 295 (67), 284 (19), 270 (27), 266 (34), 252 (100), 239 (17), 226 (11), 212 (48), 198 (6), 184 (7), 154 (6), 132 (13), 115 (5), 104 (5), 77 (7), 51 (1). HR EIMS Calcd for $C_{18}H_{19}NO_4$: 313.1314, Found: 313.1302.

5-Methyl-2-phenyl-4-oxo-4,5-dihydrofuro[3,2-*c*]quinoline-3-carboxylic acid (**6c**)**:** Colorless crystals, yield 34%, mp 271-280°C (benzene-ethanol), IR (cm^{-1}): 3061, 3026, 2957, 2353, 1725, 1636, 1602, 1549, 1504, 1486, 1467, 1430, 1410, 1351, 1284, 1251, 1218, 1116, 1056, 1042, 990, 942, 891, 779, 760, 690, 657, 567. EIMS *m/z* (%): 319 (M^+, 43), 275 (100), 246 (6), 232 (6), 132 (6), 105 (8), 77 (11), 63 (1), 51 (2). HR EIMS Calcd for $C_{19}H_{13}NO_4$: 319.0845, Found: 319.0834.

1-Methyl-3(2-oxoheptyl)-4-hydroxy-1*H*-quinolin-2-one (9b): Colorless crystals, yield 15%, mp 124-127°C (benzene), IR ($cm^{-}1$): 3166, 2953, 2922, 2860, 1711, 1630, 1601, 1584, 1505, 1460, 1342, 1330, 1192, 1181, 1148, 1120, 1096, 1042, 754, 677. EIMS *m/z* (%): 287 (M^+, 15), 244 (3), 230 (4), 216 (2), 202 (5), 189 (100), 188 (33), 175 (6), 160 (4), 146 (6), 134 (10), 104 (5), 77 (6), 55 (2), 51 (1). HR EIMS Calcd for $C_{17}H_{21}NO_3$: 287.1521, Found: 287.1513.

5,5´-Dimethyl-2,2´-dipentyl-4´,5´-dihydro-5*H*-[3,3´]bi[furo[3,2-*c*]quinolinyl]-4,4´-dione (10b). Colorless crystals, yield 20%, mp 270-274°C (benzene-ethanol), IR (cm^{-1}): 3399, 3106, 2965, 2950, 2930, 2870, 1659, 1601, 1579, 1557, 1503, 1468, 1450, 1393, 1347, 1229, 1108, 990, 816, 777, 746, 707, 658. EIMS *m/z* (%): 536 (M^+, 0.1), 269 (48), 252 (7), 238 (2), 212 (100), 188 (3), 154 (3), 140 (2), 132 (5), 115 (3), 104 (2), 77 (4), 63 (1), 55 (2). HR EIMS Calcd for $C_{17}H_{19}NO_2$: 269.1416, Found: 269.1405.

Methyl-3-phenyl-5*H*-furo[3,2-*c*]quinolin-4-one (7c), yield 39%, mp 108-109°C (cyclohexane) was prepared according to lit.,[8] (mp 105-106°C). EIMS *m/z* (%): 275 (M^+, 100), 274 (21), 246 (6), 232 (5), 217 (11), 189 (6), 77 (3), 63 (1), 51 (1).

General Procedure for the Preparation of 5-Methyl-5*H*-furo[3,2-*c*]-quinolin-4-ones (8). To the solution of appropriate acid (**6**) (0.6 mmol) in quinoline (3 mL) copper dust (0.1 g) was added and the mixture was heated under stirring for 30 min at 170-80°C and then 20 min at 180-200°C. After cooling, copper was filtered off and the filtrate was diluted with benzene (70 mL). The solution was washed three times with 5% hydrochloric acid (40 mL). Benzene layer was washed with water to the neutral reaction, dried with sodium sulfate and evaporated to dryness. The dark residue was dissolved in ethanol, the solution was filtered with charcoal, the filtrate was evaporated to dryness and the residue was crystallized.

2,5-Dimethyl-5*H*-furo[3,2-*c*]quinolin-4-one (8a): Colorless crystals, yield 47%, mp 117-119°C (benzene-cyclohexane), (lit.,[6] mp 118-119°C, lit.,[7] mp 118°C), IR (cm^{-1}): 2986, 2947, 2919, 2848, 1660, 1597, 1582, 1509, 1452, 1436, 1416, 1356, 1312, 1302, 1251, 1107, 1042, 971, 928, 828, 815, 756, 746, 643. EIMS, *m/z* (%): 213 (M^+, 100), 212 (29), 198 (7), 184 (10), 170 (7), 156 (2), 142 (6), 115 (5), 104 (2), 77 (5), 63 (1), 51 (2). Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.12; H, 5.34; N, 6.41.

5-Methyl-2-pentyl-5*H*-furo[3,2-*c*]quinolin-4-one (8b): Colorless crystals, yield 58%, mp 50-53°C (benzene-hexane), IR (cm^{-1}): 2966, 2924, 2853, 1665, 1588, 1576, 1516, 1505, 1418, 1459, 1435, 1365, 1311, 1296, 1234, 1110, 1100, 1038, 941, 862, 774, 746, 738, 726. EIMS, *m/z* (%): 269 (M^+, 51), 212

(100), 184 (4), 175 (9), 154 (2), 132 (7), 115 (2), 104 (2), 77 (14), 63 (1), 51 (1). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.58; H, 7.32; N, 5.17.

5-Methyl-2-phenyl-5*H*-furo[3,2-*c*]quinolin-4-one (8c): Colorless crystals, yield 43%, mp 213-215°C (ethanol), IR (cm^{-1}): 2984, 2942, 2884, 1650,1640sh, 1584, 1509, 1487, 1464, 1432, 1409, 1363, 1329, 1314, 1246, 1156, 1107, 1037, 1017, 967, 915, 868, 758, 688, 673, 658. EIMS, *m/z* (%): 275 (M^+, 100), 246 (6), 232 (6), 217 (3), 170 (2), 115 (2), 105 (4), 77 (7), 63 (1), 51 (1). Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.65; H, 4.93; N, 5.13.

Conversion of 1-Methyl-3(2-oxoheptyl)-4-hydroxy-1*H*-quinolin-2-one (9b) to 5-Methyl-2-pentyl-5*H*-furo[3,2-*c*]quinolin-4-one (8b). Compound (**9b**) (29 mg, 0.1 mmol) was dissolved in conc. sulfuric acid (0.5 mL) at rt. After 10 min, the reaction mixture was diluted with water (5 mL) and extracted three times with chloroform (5 mL). Chloroform extract was dried with potassium carbonate and evaporated to dryness. Compound (**8b**) (21 mg, 78%), identical in all respects with that isolated from decarboxylation of **6b**, was obtained by crystallization with benzene-hexane.

Reaction of 1a with Ethyl (Triphenylphosphoranylidene)chloroacetate. A mixture of **1a** (1.09 g, 5 mmol) and ethyl (triphenylphosphoranylidene)chloroacetate[15] (2.2 g, 5.75 mmol) in xylene (30 mL) was refluxed for 2.5 h. After cooling, the solution was evaporated to dryness *in vacuo* and the dark residue of resinous character was repeatedly extracted with boiling cyclohexane. The extract was concentrated *in vacuo* and two pure compounds were isolated by column chromatography on silica gel using solvent system S_2.

Ethyl 3,5-Dimethyl-4-oxo-4,5-dihydrofuro[3,2-*c*]quinoline-2-carboxylate (11a): Pale yellow crystals, yield 133 mg (19%), mp 182-189°C (benzene-cyclohexane). IR (cm^{-1}): 3088, 2983, 2931, 2852, 1712, 1658, 1635, 1596, 1576, 1563, 1440, 1367, 1328, 1295, 1259, 1200, 1140, 1111, 1094, 1042, 984, 966, 861, 784, 769, 753, 673, 620, 543. ^{1}H NMR ($CDCl_3$, 30°C): 1.453 (t, *J*=7.1 Hz, 3H, CH_3), 2.787 (s, 3H, 2-Me), 3.750 (s, 3H, N-Me), 4.453 (q, *J*=7.1 Hz, 2H, OCH_2), 7.325 (ddd, *J*=7.9, 7.2, and 1.0 Hz, 1H, H-8), 7.435 (ddd, *J*=8.7, 1.0, and 0.5 Hz, 1H, H-6), 7.607 (ddd, *J*=8.7, 7.2, and 1.6 Hz, 1H, H-7), 8.145 (ddd, *J*=7.9, 1.6, and 0.5 Hz, 1H, H-9). ^{13}C NMR ($CDCl_3$, 30°C): 10.38 (2-Me), 14.38 (CH_3), 29.05 (N-Me), 61.09 (OCH_2), 112.51 (C-9a), 115.04 (C-6), 115.52 (C-3a), 122.37 (C-9), 122.46 (C-8), 130.60 (C-3), 130.88 (C-7), 139.43 (C-5a), 141.05 (C-2), 155.84 (C-9b), 159.62 (C=O), 159.81 (C-4). EIMS, *m/z* (%): 285 (M^+, 100), 257 (21), 240 (11), 213 (41), 184 (29), 154 (7), 140 (3), 115 (2), 77 (2), 63 (1), 51 (1). HR EIMS Calcd for $C_{16}H_{15}NO_4$: 285.1001, Found: 285.0992.

Ethyl 4,6-Dimethyl-2-oxo-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinolin-5-ylidene(chloro)acetate (12a): Orange crystals, yield 62 mg (7%), mp 202-211°C (benzene-cyclohexane), IR (cm^{-1}): 3084, 3040, 2977, 2920, 2869, 1688, 1649, 1629, 1600, 1587, 1561, 1545, 1504, 1455, 1424, 1391, 1382, 1365, 1318, 1295, 1218, 1184, 1170, 1123, 1060, 985, 866, 829, 784, 754, 677, 521. ^{1}H NMR: ($CDCl_3$), 30°C): 1.391 (t, *J*=7.1 Hz, 3H, CH_3), 2.590 (d, *J*=1.4 Hz, 3H, 4-Me), 3.663 (s, 3H, N-Me), 4.314 (q, *J*=7.1 Hz, 2H, OCH_2), 7.306 (ddd, *J*=8.4, 7.2, and 0.9 Hz, 1H, H-9), 7.316 (dd, *J*=8.6 and 0.9 Hz, 1H, H-7), 7.631 (ddd, *J*=8.6, 7.2, and 1.6 Hz, 1H, H-8), 7.707 (q, *J*=1.4 Hz, 1H, H-3), 8.170 (dd, *J*=8.4 and 1.6 Hz, 1H, H-10). ^{13}C NMR ($CDCl_3$, 30°C): 14.36 (CH_3), 23.00 (4-Me), 29.46 (N-Me), 61.26 (OCH_2), 108.49 (C-4a), 113.47 (C-10a), 114.02 (C-7), 117.55 (C-3), 122.70 (C-9), 124.11 (C-10), 124.97 (=C-Cl), 132.75 (C-8), 139.64 (C-6a), 142.26 (C-4), 155.96 (C-10b), 156.63 (C-2), 159.88 (C-5), 163.92 (C=O). EIMS, *m/z* (%): 345 (M^+, 100), 317 (12), 300 (11), 285 (8), 273 (68), 266 (85), 238 (23), 208 (7), 184 (7), 154 (2), 140 (2), 132 (4), 115 (2), 104 (3), 77 (6), 63 (1), 51 (2). HR EIMS Calcd for $C_{18}H_{16}NO_4Cl$: 345.0768, Found: 345.0760.

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