Reaction of 3-Hydroxyquinoline-2,4-diones with Isocyanates and Thermally Induced Transformation of the Reaction Products

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3-Hydroxyquinoline-2,4-diones **1** react with isocyanates to give novel 1,2,3,4-tetrahydro-2,4-dioxoquinolin-3-yl (alkyl/aryl)carbamates **2** and/or 1,9b-dihydro-9b-hydroxyoxazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-diones **3**. Both of these compounds are converted, by boiling in cyclohexylbenzene solution in the presence of Ph_3P or 4-(dimethylamino)pyridine, to give 3-(acyloxy)-1,3-dihydro-2*H*-indol-2-ones **8**. All compounds were characterized by IR, and ^{1}H- and ^{13}C-NMR spectroscopy, as well as by EI mass spectrometry.

1. Introduction. – In our laboratory, the reactivity of 3-hydroxyquinoline-2,4-diones **1**, natural metabolites of some *Pseudomonas* species, has been studied [1][2]. These compounds, which are easily accessible by the oxidation of 4-hydroxyquinolin-2-ones with peroxyacetic acid [3][4], react with ethyl (triphenylphosphoranylidene)acetate to give *(E)*-4-[(ethoxycarbonyl)methylidene]-3,4-dihydroquinolin-2-ones and, to a small extent, 3a-substituted furo[2,3-*c*]quinoline-2,4(3a*H*,5*H*)-diones [4]. On the other hand, 5,8-disubstituted 3-benzyl-3-hydroxyquinoline-2,4(1*H*,3*H*)-diones have been shown to react in a completely different manner, yielding primarily dihydroindole and benzoxazine products under the same reaction conditions [5].

The rearrangement of 3-hydroxyquinoline-2,4-diones **1** has been studied in refluxing xylene in the presence of 4-(dimethylamino)pyridine (DMAP) or Ph_3P as catalyst to afford 3-(acyloxy)-1,3-dihydro-2*H*-indol-2-ones and/or isomeric 4-acyl-1,4-dihydro-3,1-benzoxazin-2-ones [6]. In boiling cyclohexylbenzene, however, only 3-(acyloxy)-1,3-dihydro-2*H*-indol-2-ones were obtained in the presence of Ph_3P [7].

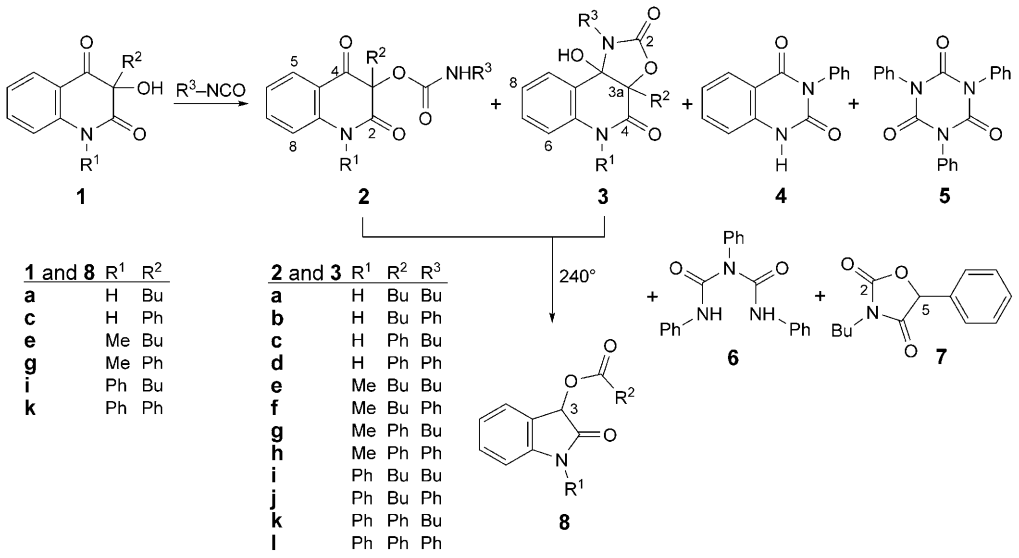
Recently, we have found that 3-aminoquinoline-2,4-diones react with isocyanates to give 3-(3′-alkyl/arylureido)quinoline-2,4(1*H*,3*H*)-diones and/or their cyclic isomers, 3,3a,5,9b-tetrahydro-9b-hydroxy-1*H*-imidazo[4,5-*c*]quinoline-2,4-diones [8]. Furthermore, through the reaction of 3-aminoquinoline-2,4-diones with isothiocyanates, 1,2,3,3a,5,9b-hexahydro-9b-hydroxy-2-thioxoimidazo[4,5-*c*]quinolin-4-ones were obtained [9][10]. Molecular rearrangement of these addition products in boiling AcOH or concentrated HCl solution yields products displaying quite exceptional structural diversity, including imidazoquinazolines, oxindoles, spiro[imidazo-oxindoles], indolylureas, imidazolones, 1,3-bis[2-(imidazolyl)phenyl]ureas, 2-thioxo-1′*H*-spiro[imidazoline-5,3′-indol]-2′-ones, 1*H*-imidazole-2(3*H*)-thiones, 1,3-bis[2-(2,3-dihydro-2-thioxo-1*H*-imidazol-5-yl)phenyl]ureas, and *N*-[2-(2,3-dihydro-2-thioxo-1*H*-imidazol-4-yl)phe-

nyl]acetamides [8–10]. These observations provided us with the incentive to perform an analogous reaction of 3-hydroxyquinolinediones **1** with isocyanates, and to examine how the products of this reaction behave in either an acidic environment or under thermal stress.

Here, we report on the reaction of compounds **1** with isocyanates to give 1,2,3,4-tetrahydro-2,4-dioxoquinolin-3-yl alkyl- and arylcarbamates **2**, and/or 1,9b-dihydro-9b-hydroxyoxazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-diones **3**. Both of these compounds are transformed in boiling cyclohexylbenzene in the presence of DMAP or Ph_3P to give 3-(acyloxy)-1,3-dihydro-2*H*-indol-2-ones **8**.

2. Results and Discussion. – Reactions of 3-hydroxyquinoline-2,4-diones **1** with isocyanates (*Scheme 1*) were performed by boiling the mixture in a MeCN solution. In this solvent, in constrast to $CHCl_3$ (used for similar addition reactions in the cases of 3-aminoquinolinediones) [8–10], starting compounds **1** were soluble. BuNCO and PhNCO were chosen as model isocyanates for this study. The substituent at N(1) was either a *H*-atom, or Me or Ph group, and a Bu or Ph group was selected as the substituent at C(3). Starting hydroxy ketones **1** were obtained by the oxidation of the corresponding 4-hydroxyquinolin-2-ones with AcOOH in accordance with the procedure described in [4].

Scheme 1



1 and 8	R^1	R^2
a	H	Bu
c	H	Ph
e	Me	Bu
g	Me	Ph
i	Ph	Bu
k	Ph	Ph

2 and 3	R^1	R^2	R^3
a	H	Bu	Bu
b	H	Bu	Ph
c	H	Ph	Bu
d	H	Ph	Ph
e	Me	Bu	Bu
f	Me	Bu	Ph
g	Me	Ph	Bu
h	Me	Ph	Ph
i	Ph	Bu	Bu
j	Ph	Bu	Ph
k	Ph	Ph	Bu
l	Ph	Ph	Ph

Preliminary experiments showed that the reactivity of the tertiary OH group in **1** towards isocyanates was very low, and that the reaction did proceed neither at room temperature nor after boiling a long time in MeCN. When a basic catalyst (DMAP) was added to the reaction mixture, however, the reaction occurred. In most of the cases, a mixture of the two products **2** and **3** was formed (*Table 1*, *Scheme 1*), which was then separated by fractional crystallization or by column chromatography.

Table 1. *Preparation of 1,2,3,4-Tetrahydro-2,4-dioxoquinolin-3-yl Carbamates* **2**, *1,9b-Dihydro-9b-hydroxyoxazolo[5,4-c]quinoline-2,4(3aH,5H)-diones* **3**, *3-Phenylquinazoline-2,4(1H,3H)-dione* **4**, *and 1,3,5-Triphenyl-[1,3,5]triazinane-2,4,6-trione* **5** *from 3-Hydroxyquinoline-2,4(1H,3H)-diones* **1** (*Scheme 1*)

Entry	Starting compound	Substituents[a])			Reaction time [h]	Product(s) (yield [%])
		R^1	R^2	R^3		
1	**1a**	H	Bu	Bu	9	**2a** (25), **3a** (10)
2	**1a**	H	Bu	Ph	4	**2b** (14), **4** (34)
3	**1c**	H	Ph	Bu	12	**2c** (19), **3c** (31), **7** (18)
4	**1c**	H	Ph	Ph	11	**2d** (9), **4** (12)
5	**1e**	Me	Bu	Bu	14	**2e** (44), **3e** (14)
6	**1e**	Me	Bu	Ph	5	**2f** (62), DPU[b]) (10)
7	**1g**	Me	Ph	Bu	8	**3g** (78)
8	**1g**	Me	Ph	Ph	3	**2h** (62)
9	**1i**	Ph	Bu	Bu	14	**2i** (38), **3i** (35)
10	**1i**	Ph	Bu	Ph	4	**2j** (67), DPU[b]) (2)
11	**1k**	Ph	Ph	Bu	8	**2k** (11), **3k** (68)
12	**1k**	Ph	Ph	Ph	5	**2l** (73), **5** (9)

[a]) R^3 from isocyanate. [b]) DPU = 1,3-Diphenylurea, identical in all respects with the authentic compound.

The IR spectra of the first type of the products obtained exhibited two characteristic absorption bands of similar pattern at 1663–1688 cm^{-1} (lactam) and 1705–1731 cm^{-1} (ketone). The second type of the products obtained exhibited a characteristic absorption band at 1684–1702 cm^{-1} (lactam), but the position of the second characteristic absorption band was shifted to the region of 1745–1763 cm^{-1}, which is typical for cyclic carbamates [11]. Based on these observations, we preliminarily assigned the structure **2** for compounds of the first type and the cyclic structure **3** for compounds of the second type.

All the signals in the ^{1}H- and ^{13}C-NMR spectra of compounds **2** were assigned on the basis of COSY, HMBC, and HMQC experiments (*Table 2*), and their positions were found to be in accord with the proposed structure. The characteristic signals of C(3) appeared at 81.9–83.7 ppm. The only exception was the position of the signal of this atom in compound **2l** (66.4 ppm). Because typical resonances of **2l** were consistent with those of the analogous derivatives **2**, we considered the assignment of structure **2l** as correct. The assigned structure of **2l** was also confirmed by the thermally induced transformation of this compound to the expected product (see below). However, we have no clear explanation for the high-field position of the aforesaid signal of C(3) in compound **2l**. In compounds **2i**–**2l**, two signals of nonequivalent *o*- and *m*-H-atoms of the Ph–*N* group also appeared (*Table 2*), which was caused by the hindered rotation of the Ph–*N* group. In the EI mass spectra of compounds **2**, the molecular peaks, with relative abundance not exceeding 35%, were observed in all cases except for compound **2c**. The main fragmentation pathways began with the neutral loss of the corresponding isocyanate, while the next fragmentation was strongly dependent on the substituent at C(3). All 3-Ph compounds **2** lost a PhCO fragment, and its peak at *m*/*z* 105 was observed as the base peak. Fragment peaks resulting from the common loss of OH,

Table 2. *^{1}H- and ^{13}C-NMR Data* ((D_6)DMSO) *of Compounds* **2a**–**2l** (δ in ppm)

Position	**2a**		**2b**		**2c**		**2d**		**2e**		**2f**	
	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	–	170.1	–	169.7	–	169.0	–	169.6	–	169.5	–	169.2
3	–	81.9	–	82.7	–	82.8	–	83.4	–	82.2	–	82.9
4	–	192.5	–	192.1	–	190.8	–	190.5	–	191.7	–	191.4
4a	–	118.5	–	118.4	–	118.2	–	118.3	–	119.5	–	119.4
5	7.80	127.0	7.85	127.1	7.78	127.5	7.83	127.7	7.93	127.3	7.96	127.4
6	7.18	122.7	7.22	122.9	7.19	123.1	7.23	123.3	7.31	123.1	7.36	123.4
7	7.66	136.4	7.72	136.7	7.71	136.8	7.75	137.1	7.82	136.7	7.88	137.0
8	7.16	116.5	7.20	116.7	7.25	116.8	7.27	116.9	7.46	116.0	7.50	116.2
8a	–	141.6	–	141.6	–	141.5	–	141.4	–	142.6	–	142.6
O(*C*=O)	–	154.9	–	152.3	–	155.0	–	152.3	–	154.8	–	152.2
(C=O)N*H*R^2	7.70	–	10.25	–	7.94	–	10.49	–	7.73	–	10.27	–
1 (R^1)	10.98	–	11.15	–	11.29	–	11.48	–	3.45	29.7	3.46	29.8
2 (R^1)	–	–	–	–	–	–	–	–	–	–	–	–
3 (R^1)	–	–	–	–	–	–	–	–	–	–	–	–
4 (R^1)	–	–	–	–	–	–	–	–	–	–	–	–
1 (R^1)	1.88	35.5	1.97	35.5	–	133.3	–	132.7	1.87	35.7	1.95	35.7
	1.80		1.89						1.81		1.91	
2 (R^2)	1.24	24.3	1.37	24.4	7.44	125.9	7.48	126.1	1.25	24.4	1.34	24.5
3 (R^2)	1.26	22.1	1.28	22.0	7.44	129.1	7.54	129.2	1.25	22.0	1.26	22.0
4 (R^2)	0.82	13.7	0.85	13.8	7.44	129.5	7.48	129.8	0.82	13.7	0.84	13.7
1 (R^3)	2.93	40.1	–	138.4	3.01	40.2	–	138.3	2.94	40.1	–	138.4
2 (R^3)	1.37	31.5	7.43	118.2	1.43	31.5	7.48	118.3	1.37	31.4	7.43	118.2
3 (R^3)	1.29	19.4	7.30	128.9	1.31	19.4	7.35	129.0	1.28	19.4	7.30	128.9
4 (R^3)	0.89	13.7	7.05	123.0	0.91	13.7	7.08	123.2	0.89	13.7	7.05	123.0

Position	**2g**		**2h**		**2i**		**2j**		**2k**		**2l**	
	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	–	168.2	–	168.1	–	169.6	–	169.2	–	168.6	–	168.2
3	–	83.0	–	83.7	–	82.4	–	83.1	–	83.1	–	66.4
4	–	190.1	–	189.8	–	191.7	–	191.3	–	189.9	–	189.7
4a	–	119.4	–	119.4	–	119.2	–	119.1	–	119.0	–	119.1
5	7.88	127.8	7.92	127.9	7.97	127.5	8.00	127.6	7.93	128.0	7.97	128.2
6	7.30	123.5	7.33	123.8	7.30	123.4	7.30	123.6	7.28	123.8	7.30	124.1
7	7.83	137.0	7.87	137.3	7.58	136.3	7.60	136.9	7.69	136.7	7.66	136.8
8	7.52	116.3	7.57	116.5	6.44	116.7	6.48	116.9	6.53	117.1	6.57	117.3
8a	–	142.5	–	142.4	–	143.5	–	143.4	–	143.3	–	143.2
O(C=O)	–	154.9	–	152.3	–	154.9	–	152.3	–	155.0	–	152.4
(C=O)N*H*R^2	7.97	–	10.50	–	7.77	–	10.30	–	8.01	–	10.54	–
1 (R^1)	3.55	30.0	3.60	30.1	–	137.1	–	136.9	–	137.0	–	136.8
2 (R^1)	–	–	–	–	7.46	129.3	7.50	129.3	[a])	129.2	[b])	129.2
					7.18	128.9	7.23	128.9		128.8		128.8
3 (R^1)	–	–	–	–	7.66	130.5	7.65	130.5	[a])	130.7	[b])	130.8
						130.4		130.4		130.4		130.5
4 (R^1)	–	–	–	–	7.60	129.1	7.60	129.2	[a])	129.2	[b])	[c])
1 (R^2)	–	133.2	–	132.5	2.02	35.5	2.12	35.4	–	132.8	–	132.2
2 (R^2)	7.41	126.1	7.47	126.4	1.38	24.5	1.44	24.6	7.69	126.1	[b])	126.3
3 (R^2)	7.41	129.1	7.47	129.3	1.27	22.1	1.33	22.0	[a])	129.3	[b])	[c])
4 (R^2)	7.41	129.6	7.47	129.9	0.87	13.7	0.89	13.8	[a])	129.7	[b])	[c])

Table 2 (cont.)

Position	**2g**		**2h**		**2i**		**2j**		**2k**		**2l**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1 (R^3)	2.99	40.2	–	138.2	2.98	40.1	–	138.3	3.04	40.2	–	138.2
2 (R^3)	1.43	33.5	7.47	118.3	1.38	31.4	7.45	118.3	1.59	31.4	7.49	118.4
3 (R^3)	1.32	19.4	7.33	129.0	1.27	19.3	7.31	128.8	1.33	19.3	7.34	128.9
4 (R^3)	0.92	13.7	7.09	123.2	0.87	13.7	7.06	123.1	0.91	13.6	7.10	123.3

[a]) δ(H) = 7.28–7.71. [b]) δ(H) = 7.30–7.71. [c]) δ(C) = 130.1, 129.6, 129.5.

CO_2, or CO were also observed. In the case of 3-Bu compounds **2**, the loss of butene, CO, and formally CHO was detected, but the stability and related relative abundance of fragments depended on the substituent at N(1). Thus, there was no mutual fragment with a base peak. The peak at 119 *m*/*z*, which appeared in the EI mass spectra of compounds **2b**, **2d**, **2f**, **2h**, **2j**, and **2l**, was related to a fragment based on phenyl isocyanate.

In the reaction of 3-aminoquinolinediones with BuNCO or PhNCO, cyclic isomers (3-aza analogs of **3**) formed predominantly in both cases [8][12]. However, in the analogous reaction of 3-hydroxyquinolinediones **1**, compounds **3** were obtained only in the reaction with BuNCO (*Tables 1* and *3*). This result suggested that the replacement of the N-atom by an O-atom in position 3 significantly restrains the formation of compounds **3**, possibly due to the lower nucleophilicity of the N-atom in carbamates as compared to that in carbamides. In carbamides, there are two N-atoms with nonbonded electron pairs for saturation of the electron-deficient C=O group. In contrast, the O-atom in carbamates was less prone to donate an electron pair, and the resonance effect proceeded preferably with the electron pair of the N-atom. In contrast to Ph, aliphatic *N*-alkyl chains in carbamates **2** significantly increased the electron density on the N-atom, and, therefore, compounds **3** formed only when BuNCO was used in the reaction. Their formation was positively affected by the presence of the Ph group in position 3 (*Table 1*, *Entries 3*, *7*, and *11*), an observation that could be explained by the stabilization of the transition state.

The fragmentation pattern of compounds **3** in the EI mass spectra was almost identical to that of compounds **2**. Hence, EI-MS was not a suitable tool for the differentiation of these isomers.

It can be seen from *Table 1* that several by-products also arose during the formation of compounds **2** and **3**, particularly in the reaction with PhNCO (*Table 1*, *Entries 2*, *4*, *6*, *10*, and *12*). 3-Phenylquinazoline-2,4(1*H*,3*H*)-dione (**4**) was formed besides **2b** and **2d** in the reaction of **1a** and **1c** with PhNCO (*Table 1*, *Entries 2* and *4*). At first, we presumed that this compound was formed by the dimerization of PhNCO in the presence of a basic catalyst (DMAP). However, after a long reflux period of PhNCO in MeCN in the presence of DMAP, only 1,3-diphenylurea, 1,3,5-triphenyl[1,3,5]triazinane-2,4,6-trione (**5**), and 1-(*N*-phenylcarbamoyl)-1,3-diphenylurea (**6**) were isolated as products of phenyl isocyanate. Therefore, compound **4** must have arisen from the reaction of PhNCO with a fragment based on the anthranilic acid structure, formed by deep degradation of **1a** and **1c**, or **2b** and **2d**. At present, we have no experimental data

Table 3. *^{1}H- and ^{13}C-NMR Data* ((D$_6$)DMSO) *of Compounds* **3a**, **3c**, **3e**, **3g**, **3i**, *and* **3k** (δ in ppm)

Position	**3a**		**3c**		**3e**		**3g**		**3i**		**3k**	
	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	–	156.1	–	155.8	–	156.1	–	155.8	–	156.2	–	155.9
3	–	–	–	–	–	–	–	–	–	–	–	–
3a	–	84.1	–	85.0	–	84.3	–	85.2	–	84.5	–	85.5
4	–	167.6	–	167.1	–	167.1	–	166.6	–	167.3	–	166.8
5a	–	136.4	–	135.3	–	136.9	–	137.1	–	137.3	–	138.0
6	6.99	115.4	7.12	115.7	7.27	115.1	7.43	115.6	6.27	116.1	6.42	115.5
7	7.41	130.8	7.50	131.2	7.55	131.1	7.64	131.4	7.35	130.8	7.44	131.2
8	7.18	123.9	7.22	123.3	7.29	123.5	7.34	123.9	7.25	123.7	7.29	124.1
9	7.75	127.2	7.74	127.9	7.87	127.1	7.83	127.8	7.92	127.6	7.88	128.3
9a	–	120.3	–	119.8	–	121.3	–	120.8	–	120.9	–	120.4
9b	–	87.1	–	88.3	–	86.2	–	87.3	–	86.5	–	87.7
OH	7.16	–	7.01	–	7.25	–	7.11	–	7.39	–	7.24	–
1′ (R^1)	10.81	–	11.10	–	–	29.8	3.46	30.1	–	137.8	–	137.1
2′ (R^1)	–	–	–	–	–	–	–	–	7.18	[a])	7.44	[a])
											7.22	
3′ (R^1)	–	–	–	–	–	–	–	–	7.66	130.5	7.66	130.5
4′ (R^1)	–	–	–	–	–	–	–	–	7.58	129.0	7.58	128.7
1′ (R^2)	1,96	30.4	–	133.0	1.97	30.4	-	132.7	2.06	30.3	–	132.5
	1.91				1.90				2.01			
2′ (R^2)	1.15	24.1	7.27	125.4	1.03	24.2	7.23	125.7	1.30	24.3	7.44	125.6
	1.05				0.97				1.20			
3′ (R^2)	1.27	22.3	7.39	128.4	1.18	22.3	7.38	128.4	1.30	22.4	7.44	128.7
4′ (R^2)	0.80	13.7	7.39	128.7	0.84	13.6	7.38	128.9	0.84	13.6	7.44	128.4
1′ (R^3)	3.07	38.8	3.18	39.2	3.08	38.8	3.18	39.2	3.21	38.8	3.30	39.3
	2.99		3.04		2.98		3.02		3.10		3.12	
2′ (R^3)	0.87	30.2	0.98	30.1	0.91	30.2	0.99	29.9	1.10	30.2	1.07	30.1
	0.82		0.85		0.80		0.84		0.99		0.99	
3′ (R^3)	1.32	18.8	1.01	18.8	0.95	18.7	0.95	18.7	1.11	18.9	1.09	18.9
	1.22		0.91		0.85		0.79		0.95		0.99	
4′ (R^3)	0.63	13.4	0.65	13.4	0.75	13.3	0.62	13.3	0.68	13.3	0.70	13.3

[a]) Signal not observed.

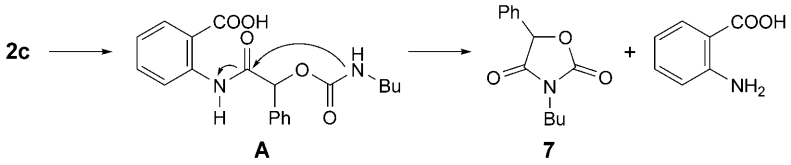
to discuss the reaction mechanism. In the literature, the preparation of **4** by the cyclization of 2-[(ethoxycarbonyl)amino]benzanilide was described [13].

In two cases (*Table 1*, *Entries 6* and *10*), the formation of 1,3-diphenylurea (probably from PhNCO and $PhNH_2$ arising from its partial hydrolysis with air humidity) was observed. 1,3,5-Triphenyl[1,3,5]triazinane-2,4,6-trione (**5**; *Entry 12*) was the product of the trimerization of PhNCO in the presence of DMAP.

The last by-product observed was 3-butyl-5-phenyloxazolidine-2,4-dione (**7**), which was produced in the reaction of **1c** with BuNCO (*Table 1*, *Entry 3*). Its structure was established on the basis of NMR and mass spectra. The formation of compound **7** as a by-product from the reaction of 2-chloro-2-phenylacetyl chloride with butylurea was already described in the literature [14]. The reaction mechanism of the formation of **7** was not clear, but the base-catalyzed cleavage of the C(3)–C(4) bond in the carbamate

2c under formation of a butyl carbamate of mandelamide **A** (*Scheme 2*) can be proposed as the first reaction step. The cyclization of this intermediate provide anthranilic acid and compound **7**.

Scheme 2



Our aim in this study was to investigate the molecular rearrangement of the described compounds. In boiling AcOH, where adducts of the 3-aminoquinolinediones with isocyanates smoothly rearranged [8–10], compounds **2** and **3** did not react, and only starting material was recovered. However, the application of the reaction conditions previously used [7] for the rearrangement of compounds **1** (boiling cyclohexylbenzene, and DMAP or Ph_3P as catalyst) led to the formation of products **8**. These results indicated that compounds **2** and **3** decomposed under thermal stress to provide the corresponding isocyanate and compounds **1**, which are subject to α-ketol-type rearrangement to intermediate **B** (*Scheme 3*). This intermediate is too unstable to be isolated [6], and its further transformation to **8** proceeds by the acyl migration *via* an epoxide intermediate **C** and following tautomerization in accordance with literature data [6][7]. In the case of **2b**, both catalysts were tested, but only starting material was recovered. An interesting observation was the isomerization of **3g** to its acyclic isomer **2g**, which was obtained as a main product of the reaction besides the minor compound **8g**. In some cases, 3-hydroxyquinoline-2,4(1*H*,3*H*)-diones **1a** and **1c**, 3-butyl-4-hydroxy-1-methylquinolin-2(1*H*)-one, 1,3-diphenylurea, and benzanilide were obtained besides compounds **8** (*Table 4*).

Scheme 3

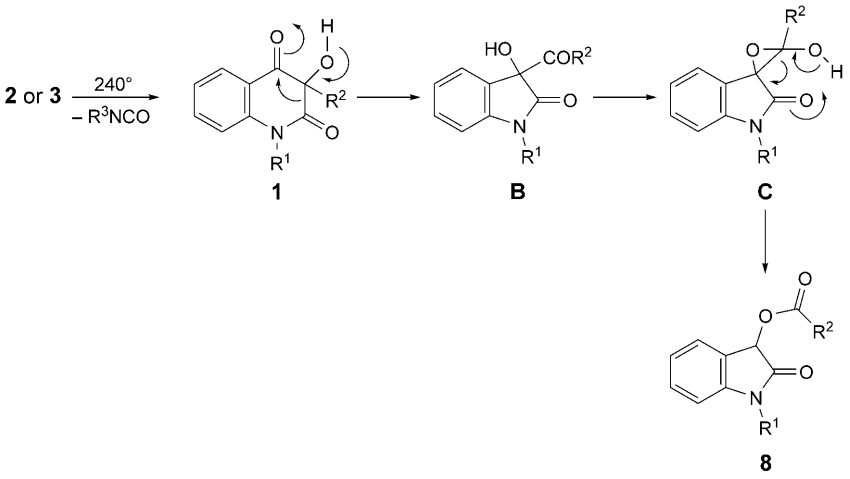


Table 4. *Transformation of Compounds* **2** *and* **3** *in Boiling Cyclohexylbenzene in the Presence of DMAP* (*Method A*) *or* Ph_3P (*Method B*)

Entry	Starting compound	*Method*	Reaction time [min]	Product(s) (yield [%])
1	**2a**	*B*	50	**8a**[a]) (4), **1a** (20)
2	**2b**	*A*	90	**2b**[b]) (82)
3	**2b**	*B*	90	**2b**[b]) (92)
4	**2c**	*B*	90	**8c**[a]) (14), **1c** (8)
5	**3c**	*B*	45	**8c**[a]) (20)
6	**2e**	*A*	90	**8e**[a]) (45)
7	**2e**	*B*	50	**8e**[a]) (46), **Xe**[c]) (9)
8	**2f**	*B*	45	**8e**[a]) (27), **2f**[b]) (6), DPU[d]) (5)
9	**3g**	*B*	35	**8g**[a]) (9), **2g** (35)
10	**2h**	*B*	45	**8g**[a]) (47), DPU[d]) (10)
11	**3i**	*B*	30	**8i**[a]) (23)
12	**2j**	*B*	45	**8i**[a]) (20), DPU[d]) (13)
13	**3k**	*B*	45	**8k**[a]) (47)
14	**2l**	*A*	15	**8k**[a]) (23), BA[e]) (3), DPU[d]) (5)
15	**2l**	*B*	40	**8k**[a]) (32), DPU[d]) (32)

[a]) Identical in all respects to the authentic compound [6][7]. [b]) Regenerated starting compound. [c]) **Xe** = 3-Butyl-4-hydroxy-1-methylquinoline-2(1*H*)-one, identical in all respects to the authentic sample [15]. [d]) DPU = 1,3-Diphenylurea. [e]) BA = Benzanilide, identical in all respects to the authentic sample.

The fragmentation pattern in the EI mass spectra of compounds **8** depended on the acyl group. Benzoates **8c**, **8g**, and **8k** lost a phenylcarbonyl cation to yield fragmention with a base peak at *m*/*z* 105. Additionally, although usually less frequent, peaks of $[R–O]^+$ ions were observed in all three cases with a relative abundance of 9, 57, and 50% of the base peak, respectively. On the other hand, pentanoates **8a**, **8e**, and **8i** lost neutral ketene (pent-1-en-1-one), and a corresponding fragment-ion peak at *m*/*z* 149, 163, and 225 appeared as a base peak, respectively. For all compounds **8**, the peaks of the molecular cations were observed with a relative abundance of 6–31% of the base peak.

3. Conclusions. – The described preparation of 1,2,3,4-tetrahydro-2,4-dioxoquinolin-3-yl alkyl- and arylcarbamates **2** and/or 1,9b-dihydro-9b-hydroxyoxazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-diones **3** represents an easy pathway to hitherto unknown heterocyclic compounds. Their thermally induced transformations offered an alternative pathway to dioxindole derivatives. Despite interesting biological activities, exemplified by the antihypoxic 3-acetoxy-5-bromo-2,3-dihydro-1*H*-indol-2-one [16], relatively few methods for the preparation of dioxindole esters have been described in the literature [7].

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Experimental Part

1. *General.* TLC: *Alugram®-SIL-G/UV$_{254}$* foils (*Macherey-Nagel*); elution with benzene/AcOEt 4:1, $CHCl_3$/EtOH 9:1 and/or 19:1, and $CHCl_3$/AcOEt 7:3. Column chromatography (CC): silica gel (SiO_2; *Merck*, grade *60*, 70–230 mesh); elution with $CHCl_3$, then $CHCl_3$/EtOH 99:1 → 8:2 or benzene, and then benzene/AcOEt 99:1 → 8:2. M.p.: *Kofler* block or *Gallencamp* apparatus. IR Spectra: *Nicolet Avatar-380* spectrophotometer; KBr pellets; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker Avance-500* spectrometer at 500.13 (^1H) and 125.76 MHz (^{13}C); (D_6)DMSO soln.; δ in ppm rel. to Me_4Si as internal standard; *J* in Hz; manufacturer's software for all 2D experiments (gradient-selected (gs)-COSY, gs-NOESY, gs-HMQC, and gs-HMBC); δ(C) assignments of protonated C-atoms by gs-HMQC and of quaternary C-atoms by gs-HMBC. EI-MS (pos.): *Shimadzu QP-2010* instrument within *m*/*z* 50–600 using direct inlet probe (DI); analysis of samples in CH_2Cl_2 (30 µg/ml), 10 µl of the soln. was evaporated in DI cuvette at 50°; ion-source temp. 200°, the energy of electrons 70 eV; only signals exceeding rel. abundance of 5% are listed. Elemental analysis (C, H, N): Flash *EA 1112* elemental analyzer (*Thermo Fisher Scientific*).

2. Starting *3-hydroxyquinoline-2,4(1*H*,3*H*)-diones* **1** were prepared by oxidation of corresponding 4-hydroxyquinolin-2-ones with AcOOH in accordance with the procedure described in [4].

3. *1,2,3,4-Tetrahydro-2,4-dioxoquinolin-3-yl Alkyl/Arylcarbamates* **2**, *5,9b-Dihydro-9b-hydroxy-[1,3]oxazolo[5,4-*c*]quinoline-2,4(1*H*,3a*H*)-diones* **3**, *3-Phenylquinazoline-2,4(1*H*,3*H*)-dione* (**4**), *1,3,5-Triphenyl[1,3,5]triazinane-2,4,6-trione* (**5**), *and 3-Butyl-5-phenyloxazolidine-2,4-dione* (**7**). *General Procedure.* 4-(Dimethylamino)pyridine (DMAP; 50 mg, 0.41 mmol) was added to the soln. of **1** (5 mmol) and BuNCO (6 mmol, 0.675 ml) or PhNCO (6 mmol, 0.652 ml) in MeCN (25 ml). After heating to reflux for the time given in *Table 1*, the mixture was evaporated to dryness, and the residue was crystallized from appropriate solvent. The mother liquors were separated by CC (SiO_2).

3-Butyl-1,2,3,4-tetrahydro-2,4-dioxoquinolin-3-yl Butylcarbamate (**2a**). Prepared from **1a** and BuNCO (besides **3a**). Colorless crystals. M.p. 142–144° (benzene/hexane). IR: 3316, 3066, 2961, 2933, 2863, 1718, 1688, 1657, 1611, 1524, 1486, 1467, 1455, 1438, 1377, 1301, 1280, 1258, 1166, 1129, 1110, 1092, 1061, 1016, 989, 944, 910, 778, 742, 687, 665, 566. ^1H- and ^{13}C-NMR: *Table 2*. EI-MS: 332 (M^+, 3), 234 (5), 233 (24), 215 (8), 190 (33), 188 (5), 186 (8), 178 (7), 177 (60), 174 (8), 162 (10), 149 (21), 148 (26), 146 (6), 130 (5), 128 (7), 126 (11), 120 (14), 119 (7), 114 (14), 112 (8), 104 (7), 100 (5), 98 (8), 97 (10), 96 (6), 95 (9), 93 (8), 92 (16), 90 (5), 86 (8), 83 (11), 82 (5), 81 (8), 77 (6), 74 (37), 73 (6), 72 (49), 69 (20), 68 (5), 67 (13), 65 (9), 60 (19), 59 (100), 57 (41), 56 (15), 55 (63), 54 (9). Anal. calc. for $C_{18}H_{24}N_2O_4$ (332.39): C 65.04, H 7.28, N 8.43; found: C 65.23, H 7.29, N 8.39.

3-Butyl-1,2,3,4-tetrahydro-2,4-dioxoquinolin-3-yl Phenylcarbamate (**2b**). Prepared from **1a** and PhNCO (besides **4**). Colorless crystals. M.p. 190–202° (AcOEt). IR: 3303, 3201, 3143, 3087, 3002, 2929, 2874, 1706, 1671, 1612, 1549, 1503, 1486, 1446, 1380, 1316, 1231, 1158, 1096, 1029, 1011, 996, 944, 900, 875, 852, 752, 691, 667, 599, 550, 508. ^1H- and ^{13}C-NMR: *Table 2*. EI-MS: 353 (5), 352 (M^+, 23), 234 (7), 233 (49), 191 (7), 190 (71), 188 (10), 186 (6), 177 (28), 175 (6), 174 (15), 162 (20), 150 (6), 149 (78), 148 (57), 146 (7), 144 (7), 132 (6), 139 (9), 120 (60), 119 (100), 103 (6), 102 (5), 93 (67), 92 (51), 91 (58), 90 (13), 89 (5), 77 (35), 76 (7), 66 (11), 65 (51), 64 (46), 63 (23), 57 (5), 52 (10), 51 (20), 50 (14). Anal. calc. for $C_{20}H_{20}N_2O_4$ (352.38): C 68.17, H 5.72, N 7.95; found: C 68.14, H 5.95, N 7.73.

1,2,3,4-Tetrahydro-2,4-dioxo-3-phenylquinolin-3-yl Butylcarbamate (**2c**). Prepared from **1c** and BuNCO (besides **3c** and **7**). Colorless crystals. M.p. 200–206° (hexane/AcOEt). IR: 3410, 3240, 3063, 2958, 2925, 2860, 1726, 1686, 1614, 1525, 1485, 1451, 1360, 1322, 1264, 1249, 1226, 1184, 1157, 1129, 1106, 1049, 1004, 934, 913, 774, 749, 704, 664, 581, 517. ^1H- and ^{13}C-NMR: *Table 2*. EI-MS: 352 (M^+, 1), 254 (5), 253 (34), 236 (5), 148 (12), 120 (7), 106 (7), 105 (100), 92 (8), 77 (24), 57 (12), 56 (6), 55 (5), 51 (5). Anal. calc. for $C_{20}H_{20}N_2O_4$ (352.38): C 68.17, H 5.72, N 7.95; found: C 67.98, H 5.69, N 8.08.

1,2,3,4-Tetrahydro-2,4-dioxo-3-phenylquinolin-3-yl Phenylcarbamate (**2d**). Prepared from **1c** and PhNCO (besides **4**). Colorless crystals. M.p. 210–222° (AcOEt). IR: 3294, 3198, 3129, 3067, 2933, 1727, 1699, 1673, 1662, 1608, 1545, 1485, 1447, 1402, 1383, 1355, 1314, 1290, 1247, 1230, 1189, 1144, 1100, 1079, 1048, 1017, 928, 915, 897, 874, 851, 821, 763, 746, 707, 688, 666, 625, 578, 550. ^1H- and ^{13}C-NMR: *Table 2*. EI-MS: 372 (M^+, 1), 253 (18), 236 (6), 180 (5), 148 (14), 120 (12), 119 (46), 106 (8), 105 (100), 93 (5), 92 (16), 91 (26), 90 (5), 77 (44), 76 (5), 74 (10), 72 (7), 69 (5), 65 (15), 64 (25), 63 (12), 59 (12), 57 (8), 55

(9), 52 (5), 51 (17), 50 (8) Anal. calc. for $C_{22}H_{16}N_2O_4$ (372.37): C 70.96, H 4.33, N 7.52; found: C 70.76, H 4.34, N 7.74.

3-Butyl-1,2,3,4-tetrahydro-1-methyl-2,4-dioxoquinolin-3-yl Butylcarbamate (**2e**). Prepared from **1e** and BuNCO (besides **3e**). Colorless crystals. M.p. 76–80° (hexane). IR: 3375, 2959, 2934, 2873, 1705, 1673, 1600, 1532, 1471, 1407, 1359, 1299, 1252, 1178, 1109, 1094, 1039, 944, 926, 769, 731, 666, 651, 558. ^{1}H- and ^{13}C-NMR: *Table 2*. EI-MS: 346 (M^+, 2), 191 (30), 163 (14), 162 (14), 149 (6), 147 (5), 134 (5), 126 (11), 114 (34), 112 (11), 106 (5), 104 (17), 99 (6), 98 (7), 97 (7), 95 (8), 86 (9), 83 (9), 81 (8), 74 (100), 73 (5), 72 (47), 70 (6), 69 (22), 67 (12), 62 (8), 60 (18), 59 (88), 57 (17), 56 (14), 55 (51), 54(8). Anal. calc. for $C_{19}H_{26}N_2O_4$ (346.42): C 65.87, H 7.56, N 8.09; found C 65.61, H 7.45, N 7.94.

3-Butyl-1,2,3,4-tetrahydro-1-methyl-2,4-dioxoquinolin-3-yl Phenylcarbamate (**2f**). Prepared from **1e** and PhNCO (besides DPU). Colorless crystals. M.p. 169–175° (benzene). IR: 3313, 3145, 3086, 2950, 2872, 1731, 1706, 1663, 1602, 1552, 1500, 1473, 1446, 1365, 1314, 1227, 1183, 1153, 1099, 1039, 1023, 991, 915, 899, 866, 847, 788, 767, 757, 736, 687, 665, 583, 528. ^{1}H- and ^{13}C-NMR: *Table 2*. EI-MS: 367 (5), 366 (M^+, 19), 248 (6), 247 (36), 204 (6), 200 (7), 192 (5), 191 (34), 188 (10), 176 (23), 164 (9), 163 (100), 162 (79), 160 (6), 146 (9), 134 (38), 132 (6), 130 (6), 120 (7), 119 (48), 118 (5), 117 (6), 116 (7), 106 (12), 105 (11), 104 (13), 93 (15), 92 (16), 91 (33), 90 (6), 79 (6), 78 (11), 77 (37), 66 (6), 65 (18), 64 (22), 63 (12), 52 (5), 51 (14), 50 (6). Anal. calc. for $C_{21}H_{22}N_2O_4$ (366.41): C 68.84, H 6.05, N 7.65; found: C 68.95, H 5.98, N 7.58.

1,2,3,4-Tetrahydro-1-methyl-2,4-dioxo-3-phenylquinolin-3-yl Phenylcarbamate (**2h**). Prepared from **1g** and PhNCO. Colorless crystals. M.p. 186–193° (benzene). IR: 3329, 3306, 3143, 3089, 3067, 3036, 1705, 1668, 1602, 1553, 1493, 1473, 1448, 1361, 1318, 1300, 1239, 1183, 1129, 1104, 1072, 1043, 1028, 1000, 928, 849, 760, 719, 696, 680, 663, 576, 509. ^{1}H- and ^{13}C-NMR: *Table 2*. EI-MS: 386 (M^+, 11), 267 (28), 251 (11), 250 (40), 222 (11), 162 (44), 134 (7), 119 (34), 106 (10), 105 (100), 91 (21), 78 (7), 77 (41), 65 (7), 64 (14), 63 (8), 52 (5), 51 (9). Anal. calc. for $C_{23}H_{18}N_2O_4$ (386.40): C 71.49, H 4.70, N 7.25; found C 71.65, H 4.89, N 6.97.

3-Butyl-1,2,3,4-tetrahydro-2,4-dioxo-1-phenylquinolin-3-yl Butylcarbamate (**2i**). Prepared from **1i** and BuNCO (besides **3i**). Colorless crystals. M.p. 136–140° (benzene/hexane). IR: 3370, 2959, 2933, 2873, 1718, 1706, 1674, 1601, 1534, 1493, 1463, 1349, 1327, 1299, 1260, 1143, 1111, 1073, 1026, 1003, 967, 943, 903, 834, 772, 707, 695, 661, 577, 516. ^{1}H- and ^{13}C-NMR: *Table 2*. EI-MS: 408 (M^+, 10), 309 (9), 292 (5), 291 (5), 262 (11), 254 (16), 253 (100), 252 (6), 238 (6), 226 (8), 225 (51), 224 (31), 197 (6), 196 (38), 195 (10), 168 (7), 167 (11), 166 (6), 92 (7), 77 (14), 51 (7). Anal. calc. for $C_{24}H_{28}N_2O_4$ (408.49): C 70.57, H 6.91, N 6.86; found: C 70.68, H 6.88, N 6.92.

3-Butyl-1,2,3,4-tetrahydro-2,4-dioxo-1-phenylquinolin-3-yl Phenylcarbamate (**2j**). Prepared from **1i** and PhNCO (besides DPU). Yellowish crystals. M.p. 210–214° (benzene/hexane). IR: 3319, 3140, 3087, 2960, 2931, 2859, 1727, 1708, 1677, 1601, 1551, 1492, 1464, 1444, 1351, 1318, 1298, 1231, 1163, 1135, 1095, 1085, 1047, 1028, 967, 946, 908, 856, 756, 707, 695, 678, 663, 607, 512. ^{1}H- and ^{13}C-NMR: *Table 2*. EI-MS: 429 (9), 428 (M^+, 31), 310 (6), 309 (27), 292 (6), 266 (5), 262 (9), 254 (10), 253 (50), 252 (6), 251 (5), 250 (8), 238 (17), 226 (15), 225 (100), 224 (48), 222 (73), 197 (11), 196 (71), 195 (13), 180 (6), 168 (10), 167 (18), 166 (8), 139 (6), 120 (7), 119 (49), 97 (9), 93 (11), 92 (15), 91 (24), 77 (27), 65 (11), 64 (17), 63 (8), 57 (10), 55 (7), 51 (11), 44 (6), 41 (8). Anal. calc. for $C_{26}H_{24}N_2O_4$ (428.48): C 72.88, H 5.65, N 6.54; found: C 73.01, H 5.78, N 5.95.

1,2,3,4-Tetrahydro-2,4-dioxo-1,3-diphenylquinolin-3-yl Butylcarbamate (**2k**). Prepared from **1k** and BuNCO. Colorless crystals. M.p. 206–210° (benzene/hexane). IR: 3394, 3063, 2960, 2933, 2873, 1711, 1680, 1600, 1518, 1492, 1460, 1342, 1302, 1249, 1188, 1143, 1112, 1069, 1043, 1007, 925, 905, 840, 778, 754, 709, 693, 663, 585, 516. ^{1}H- and ^{13}C-NMR: *Table 2*. EI-MS: 428 (M^+, 5), 330 (5), 329 (23), 225 (5), 224 (32), 196 (16), 167 (6), 106 (9), 105 (100), 77 (27), 57 (5), 51 (7). Anal. calc. for $C_{26}H_{24}N_2O_4$ (428.48): C 72.88, H 5.65, N 6.54; found C 73.06, H 5.62, N 6.38.

1,2,3,4-Tetrahydro-2,4-dioxo-1,3-diphenylquinolin-3-yl Phenylcarbamate (**2l**). Prepared from **1k** and PhNCO (besides **5**). Colorless crystals. M.p. 244–256° (dioxane). IR: 3320, 3199, 3142, 3073, 1712, 1677, 1519, 1551, 1492, 1462, 1446, 1342, 1302, 1251, 1236, 1180, 1144, 1111, 1071, 1052, 1021, 973, 929, 906, 859, 784, 763, 743, 707, 696, 662, 608, 582, 511. ^{1}H- and ^{13}C-NMR: *Table 2*. EI-MS: 448 (M^+, 5), 330 (7), 329 (28), 313 (8), 312 (18), 284 (7), 225 (5), 224 (31), 196 (25), 195 (5), 167 (9), 119 (35), 106 (8), 105 (100),

91 (16), 77 (40), 64 (13), 63 (6), 51 (11). Anal. calc. for $C_{28}H_{20}N_2O_4$ (448.47): C 74.99, H 4.50, N 6.25; found: C 74.78, H 4.71, N 6.08.

*1,3a-Dibutyl-5,9b-dihydro-9b-hydroxy[1,3]oxazolo[5,4-*c*]quinoline-2,4(1*H*,3a*H*)-dione* (**3a**). Prepared from **1a** and BuNCO (besides **2a**). Colorless crystals. M.p. 174–190° (hexane/AcOEt). IR: 3322, 3208, 3083, 2963, 2930, 2874, 1745, 1687, 1601, 1496, 1468, 1447, 1407, 1380, 1319, 1251, 1221, 1195, 1158, 1131, 1085, 1063, 1044, 1025, 1003, 936, 849, 763, 734, 677, 629, 581, 546. ^{1}H- and ^{13}C-NMR: *Table 3*. EI-MS: 332 (M^+, 10), 234 (8), 233 (27), 216 (11), 215 (9), 190 (36), 188 (7), 186 (10), 178 (12), 177 (100), 175 (10), 174 (12), 163 (8), 162 (24), 150 (5), 149 (54), 148 (33), 146 (16), 144 (5), 132 (8), 130 (6), 128 (7), 126 (5), 120 (31), 119 (10), 112 (5), 104 (6), 103 (5), 100 (5), 98 (6), 97 (8), 95 (5), 93 (11), 92 (23), 91 (6), 90 (7), 86 (5), 85 (15), 83 (10), 81 (5), 77 (10), 74 (17), 72 (28), 71 (10), 70 (7), 69 (18), 67 (8), 65 (16), 64 (5), 60 (8), 59 (49), 57 (65), 56 (18), 55 (52), 54 (5). Anal. calc. for $C_{18}H_{24}N_2O_4$ (332.39): C 65.04, H 7.28, N 8.43; found: C 65.08, H 7.31, N 8.44.

*1-Butyl-5,9b-dihydro-9b-hydroxy-3a-phenyl[1,3]oxazolo[5,4-*c*]quinoline-2,4(1*H*,3a*H*)-dione* (**3c**). Prepared from **1c** and BuNCO (besides **2c** and **7**). Colorless crystals. M.p. 215–220° (EtOH). IR: 3397, 3197, 3064, 2958, 2933, 2876, 1763, 1685, 1620, 1600, 1495, 1449, 1411, 1393, 1377, 1312, 1253, 1224, 1175, 1159, 1141, 1102, 1068, 1051, 1032, 990, 942, 900, 863, 753, 707, 680, 657, 604, 563, 535. ^{1}H- and ^{13}C-NMR: *Table 3*. EI-MS: 352 (M^+, 2), 253 (44), 236 (5), 148 (14), 120 (6), 106 (8), 105 (100), 92 (7), 77 (24), 56 (8), 43 (10), 41 (14). Anal. calc. for $C_{20}H_{20}N_2O_4$ (352.38): C 68.17, H 5.72, N 7.95; found C 68.27, H 5.78, N 8.06.

*1,3a-Dibutyl-5,9b-dihydro-9b-hydroxy-5-methyl[1,3]oxazolo[5,4-*c*]quinoline-2,4(1*H*,3a*H*)-dione* (**3e**). Prepared from **1e** and BuNCO (besides **2e**). Colorless crystals. M.p. 137–140° (benzene/hexane). IR: 3297, 2950, 2928, 2870, 1745, 1685, 1605, 1473, 1393, 1366, 1346, 1299, 1271, 1217, 1196, 1173, 1123, 1096, 1069, 1052, 1032, 986, 946, 900, 817, 794, 770, 674, 652, 584, 541. ^{1}H- and ^{13}C-NMR: *Table 3*. EI-MS: 346 (M^+, 8), 230 (6), 192 (7), 191 (57), 177 (5), 176 (9), 163 (19), 162 (18), 160 (5), 149 (22), 146 (6), 134 (16), 128 (6), 126 (12), 125 (5), 114 (11), 113 (5), 112 (11), 111 (9), 109 (7), 106 (8), 105 (6), 104 (13), 100 (6), 99 (9), 98 (11), 97 (18), 96 (8), 95 (12), 91 (5), 86 (9), 85 (20), 84 (8), 83 (21), 85 (7), 81 (12), 79 (6), 77 (9), 74 (51), 73 (6), 72 (57), 71 (28), 70 (13), 69 (38), 68 (7), 67 (17), 60 (18), 59 (100), 58 (5), 57 (6), 56 (22), 55 (73), 54 (8). Anal. calc. for $C_{19}H_{26}N_2O_4$ (346.42): C 65.87, H 7.56, N 8.09; found: C 66.15, H 7.62, N 8.14.

*1-Butyl-5,9b-dihydro-9b-hydroxy-5-methyl-3a-phenyl[1,3]oxazolo[5,4-*c*]quinoline-2,4(*1 H*,3a*H*)-dione* (**3g**). Prepared from **1g** and BuNCO. Colorless crystals. M.p. 188–193° (benzene). IR: 3381, 2962, 2932, 2870, 1757, 1684, 1605, 1474, 1387, 1364, 1326, 1269, 1227, 1178, 1137, 1070, 1056, 1046, 1017, 975, 944, 861, 834, 765, 755, 724, 699, 654, 593, 530. ^{1}H- and ^{13}C-NMR: *Table 3*. EI-MS: 366 (M^+, 15), 267 (12), 251 (8), 250 (21), 237 (6), 234 (6), 233 (39), 223 (8), 222 (8), 177 (19), 162 (25), 149 (5), 134 (13), 116 (6), 106 (12), 105 (100), 104 (10), 91 (7), 79 (5), 78 (8), 77 (48), 71 (5), 57 (16), 56 (8), 55 (7), 51 (8). Anal. calc. for $C_{21}H_{22}N_2O_4$ (366.41): C 68.84, H 6.05, N 7.65; found: C 68.75, H 6.05, N 7.62.

*1,3a-Dibutyl-5,9b-dihydro-9b-hydroxy-5-phenyl[1,3]oxazolo[5,4-*c*]quinoline-2,4(1*H*,3a*H*)-dione* (**3i**). Prepared from **1i** and BuNCO (besides **2i**). Colorless crystals. M.p. 171–174° (benzene/hexane). IR: 3357, 3065, 2962, 2934, 2864, 1751, 1687, 1606, 1593, 1499, 1465, 1395, 1350, 1339, 1300, 1268, 1229, 1206, 1186, 1170, 1148, 1131, 1090, 1055, 1031, 961, 945, 911, 825, 767, 735, 705, 655, 627, 611, 589, 517. ^{1}H- and ^{13}C-NMR: *Table 3*. EI-MS: 409 (5), 408 (M^+, 15), 309 (10), 292 (5), 262 (7), 254 (17), 253 (100), 252 (7), 251 (6), 250 (7), 239 (7), 238 (7), 226 (10), 225 (68), 224 (25), 222 (5), 197 (8), 196 (53), 195 (12), 180 (6), 169 (5), 168 (11), 167 (21), 166 (7), 139 (5), 119 (8), 105 (5), 92 (8), 77 (22), 57 (26), 56 (19), 55 (8), 51 (13). Anal. calc. for $C_{24}H_{28}N_2O_4$ (408.49): C 70.57, H 6.91, N 6.86; found: C 70.68, H 6.92, N 6.79.

*1-Butyl-5,9b-dihydro-9b-hydroxy-3a,5-diphenyl[1,3]oxazolo[5,4-*c*]quinoline-2,4(1*H*,3a*H*)-dione* (**3k**). Prepared from **1k** and BuNCO (besides **2k**). Colorless crystals. M.p. 229–236° (AcOEt). IR: 3371, 3075, 2960, 2932, 2857, 1755, 1702, 1604, 1591, 1497, 1489, 1464, 1389, 1348, 1299, 1263, 1224, 1140, 1104, 1067, 1048, 1008, 942, 926, 890, 833, 757, 705, 653, 607, 522. ^{1}H- and ^{13}C-NMR: *Table 3*. EI-MS: 429 (5), 428 (M^+, 17), 330 (8), 329 (36), 313 (6), 312 (11), 295 (8), 285 (5), 284 (5), 239 (5), 225 (6), 224 (38), 196 (24), 195 (7), 167 (9), 106 (9), 105 (100), 77 (28), 51 (5), 43 (5), 41 (9). Anal. calc. for $C_{26}H_{24}N_2O_4$ (428.48): C 72.88, H 5.65, N 6.54; found: C 72.68, H 5.71, N 6.48.

*3-Phenylquinazoline-2,4(1*H*,3*H*)-dione* (**4**). Prepared from **1a** and PhNCO (besides **2b**). Colorless crystals. M.p. 282–284° (AcOEt; 280–281° [13]). IR: identical to that published in [17]. ^{1}H-NMR

((D$_6$)DMSO): 7.26 (*m*, H–C(6)); 7.28 (*m*, H–C(8)); 7.36 (*m*, 2 *o*-H, Ph); 7.46 (*tt*, *J* = 7.2, 1.4, 1 *p*-H, Ph); 7.53 (*m*, 2 *m*-H, Ph); 7.75 (*ddd*, *J* = 8.6, 7.8, 1.5, H–C(7)); 7.98 (*dd*, *J* = 8.6, 1.6, H–C(5)); 11.61 (NH). ^{13}C-NMR ((D$_6$)DMSO): 114.4 (C(4a)); 115.3 (C(8)); 122.6 (C(6)); 127.7 (C(5)); 128.2 (C(4) of Ph); 128.9 (C(2) of Ph); 129.2 (C(3) of Ph); 135.3 (C(7)); 135.9 (C(1) of Ph); 139.9 (C(8a)); 150.3 (C(2)); 162.3 (C(4)). EI-MS: 239 (10), 238 (M^+, 61), 237 (22), 146 (45), 120 (8), 119 (100), 92 (41), 91 (14), 90 (16), 77 (5), 65 (7), 64 (20), 63 (12), 51 (6). Anal. calc. for $C_{14}H_{10}N_2O_2$ (238.24): C 70.58, H 4.23, N 11.76; found: C 70.63, H 4.27, N 11.62.

1,3,5-Triphenyl[1,3,5]triazinane-2,4,6-trione (**5**). Prepared from **1k** and PhNCO (besides **2l**). Colorless crystals. M.p. 281–282° ([18]: 280–281° (benzene)). ^{1}H-NMR ((D$_6$)DMSO): 7.50 (*m*, 6 *o*-H, Ph); 7.56 (*m*, 6 *m*-H, Ph); 7.48 (*m*, 3 *p*-H, Ph). ^{13}C-NMR ((D$_6$)DMSO): 128.8 (3 C(4) of Ph); 129.0 (6 C(3) of Ph); 129.1 (6 C(2) of Ph); 134.9 (3 C(1) of Ph); 149.0 (3 C=O). EI-MS: 358 (5), 357 (M^+, 19), 120 (8), 119 (100), 91 (24), 64 (9). Anal. calc. for $C_{21}H_{15}N_3O_3$ (357.36): C 70.58, H 4.23, N 11.76; found C 70.78, H 4.21, N 11.55.

3-Butyl-5-phenyl-1,3-oxazolidine-2,4-dione (**7**). Prepared from **1c** and BuNCO (besides **2c** and **3c**). Colorless crystals. M.p. 70–73° ([14]: 75–76° (benzene/hexane)). IR: 3049, 2958, 2937, 2874, 1732, 1527, 1500, 1458, 1435, 1384, 1353, 1338, 1292, 1279, 1255, 1195, 1126, 1117, 1041, 1026, 1007, 930, 854, 830, 797, 763, 736, 699, 682, 648, 628, 548. ^{1}H-NMR ((D$_6$)DMSO): 0.94 (*t*, *J* = 7.3, Me(4) of Bu); 1.33 (*m*, CH$_2$(3) of Bu); 1.60 (*m*, CH$_2$(2) of Bu); 3.52, 3.56 (2*m*, CH$_2$(1) of Bu); 6.16 (*s*, ^1J(C,H) = 158.4, H–C(5)); 7.44 (*m*, 2 *o*-H, Ph); 7.52 (*m*, 2 *m*-H, 1 *p*-H, Ph). ^{13}C-NMR ((D$_6$)DMSO): 13.5 (C(4) of Bu); 19.3 (C(3) of Bu); 29.0 (C(2) of Bu); 39.5 (C(1) of Bu); 80.1 (C(5)); 127.0 (2 *o*-C, Ph); 129.1 (2 *m*-C, Ph); 129.7 (1 *p*-C, Ph); 132.6 (1 *ipso*-C, Ph); 155.4 (C(2)); 171.7 (C(4)). EI-MS: 233 (M^+, 14), 178 (45), 161 (5), 160 (50), 149 (8), 147 (8), 146 (5), 134 (18), 132 (24), 127 (7), 119 (8), 118 (79), 107 (21), 106 (24), 105 (80), 104 (5), 100 (70), 99 (25), 98 (5), 91 (33), 90 (100), 89 (45), 79 (12), 78 (10), 77 (41), 70 (18), 65 (6), 64 (7), 63 (14), 57 (13), 56 (35), 55 (14), 52 (6), 51 (23), 50 (7). Anal. calc. for $C_{13}H_{15}NO_3$ (233.26): C 66.94, H 6.48, N 6.00; found: C 66.94, H 6.48, N 6.04.

4. *Transformation of PhNCO in the Presence of DMAP.* The soln. of PhNCO (0.91 ml, 8.4 mmol) and DMAP (77 mg, 0.63 mmol) in MeCN (10 ml) was heated under reflux for 16 h. After evaporation of solvent, the residue was crystallized, and mother liquors were separated by CC (SiO_2). Three compounds were isolated:

a) *1,3-Diphenylurea* (9%). M.p. 246–249°, identical in all respects to the authentic compound.

b) *1,3,5-Triphenyl[1,3,5]triazinane-2,4,6-trione* (**5**; 7%). M.p. 280–281°, identical in all respects to compound isolated from the reaction of **1k** with phenyl isocyanate (*Table 1, Entry 12*).

c) *1-(*N*-Phenylcarbamoyl)-1,3-diphenylurea* (**6**; 3%). M.p. 151–154° (benzene/hexane). For compound **6**, prepared from 1,3-diphenylurea and PhNCO. M.p. 148° was reported [19]. IR: 3313, 3179, 3144, 3054, 1708, 1676, 1599, 1590, 1531, 1498, 1484, 1440, 1329, 1319, 1263, 1241, 1224, 1185, 1156, 1110, 1097, 1071, 1033, 902, 865, 830, 753, 694, 687, 631, 565, 507. ^{1}H-NMR ((D$_6$)DMSO): 7.13 (*tt*, *J* = 7.3, 1.2, 2 *p*-H, (CONH*Ph*)$_2$); 7.36 (*m*, 4 *m*-H (CONH*Ph*)$_2$); 7.44 (*d*, *J* = 7.6, 2 *o*-H, NPh); 7.49 (*t*, *J* = 7.0, 1 *p*-H, NPh); 7.55 (*m*, 2 *m*-H, NPh); 7.50 (*d*, *J* = 8.4, 4 *o*-H, (CONH*Ph*)$_2$); 9.78 (br. *s*, 2 NH). ^{13}C-NMR ((D$_6$)DMSO): 121.0 (C(2) of (CONH*Ph*)$_2$); 123.8 (C(4) of (CONH*Ph*)$_2$); 128.2 (C(4) of NPh); 128.7 (C(3) of (CONH*Ph*)$_2$); 129.3 (C(2) of NPh); 129.4 (C(3) of NPh); 137.7 (C(1) of NPh); 138.3 (C(1) of (CONH*Ph*)$_2$); 153.7 ((*C*ONHPh)$_2$). EI-MS: 331 (M^+, 5), 212 (22), 119 (21), 93 (100), 77 (12), 66 (14), 51 (5). Anal. calc. for $C_{20}H_{17}N_3O_2$ (331.37): C 72.49, H 5.17, N 12.68; found: C 72.31, H 5.15, N 12.58.

5. *Reaction of Anthranilic Acid with Phenyl Urea.* A mixture of anthranilic acid (1.4 g, 10.2 mmol) and phenylurea (1.4 g, 10.3 mmol) was heated to 200° for 1 h. The product was pulverized and extracted three times with 15% aq. NH_3 (20 ml). The insoluble portion was washed with H_2O, dried, and crystallized from AcOEt. Compound **4** (m.p. 282–284°), identical in all respects to the compound obtained from the reaction of **1a** or **1c** with PhNCO (*Table 1*, *Entries 2* and *4*), was obtained in 23% yield.

6. *Thermally Induced Transformation of* **2** *and* **3**. *Preparation of 1,2,3,4-Tetrahydro-1-methyl-2,4-dioxo-3-phenylquinolin-3-yl Butylcarbamates* (**2g**) *and 2,3-Dihydro-2-oxo-1*H*-indol-3-yl Pentanoates and Benzoates* **8**. *General Procedure.* A mixture of **2** or **3** (1 mmol) and DMAP (0.2 mmol; *Method A*) or Ph_3P (0.2 mmol; *Method B*) in cyclohexylbenzene (3 ml) was heated under reflux for the time given in *Table 4*. After cooling, the residue was separated by CC (SiO_2). For yields of isolated compounds, see *Table 4*.

1,2,3,4-Tetrahydro-1-methyl-2,4-dioxo-3-phenylquinolin-3-yl Butylcarbamate (**2g**). Prepared from **3g** (besides **8g**) by *Method B*. Colorless crystals. M.p. 126–131° (benzene/cyclohexane). IR: 3063, 2955, 2932, 2871, 1723, 1703, 1659, 1599, 1536, 1494, 1473, 1449, 1361, 1297, 1268, 1253, 1182, 1135, 1112, 1065, 1041, 1020, 999, 923, 908, 787, 773, 752, 718, 701, 661, 631, 574, 532. ^{1}H- and ^{13}C-NMR: *Table 3*. EI-MS: 366 (M^+, 5), 268 (6), 267 (35), 163 (6), 162 (56), 106 (9), 105 (100), 77 (20), 41 (5). Anal. calc. for $C_{21}H_{22}N_2O_4$ (366.41): C 68.84, H 6.05, N 7.65; found: C 69.03, H 6.09, N 7.78.

*2,3-Dihydro-2-oxo-1*H-*indol-3-yl Pentanoate* (**8a**). Prepared from **2a** by *Method B* (besides **1a**). Colorless crystals. M.p. 68–74° (hexane); identical in all respects to authentic compound with m.p. 72–74° [6]. EI-MS: 233 (M^+, 6), 149 (100), 132 (12), 104 (6), 93 (7), 85 (6), 77 (10), 57 (21), 41 (10).

*2,3-Dihydro-2-oxo-1*H-*indol-3-yl Benzoate* (**8c**). Prepared from **2c** and **3c** by *Method B* (besides **1c**). Colorless crystals. M.p. 136–138° (benzene/hexane); identical in all respects to authentic compound **8c** with m.p. 136–138° [7]. EI-MS: 253 (M^+, 11), 148 (9), 132 (7), 106 (8), 105 (100), 77 (28), 51 (8).

*2,3-Dihydro-1-methyl-2-oxo-1*H-*indol-3-yl Pentanoate* (**8e**). Prepared from **2e** by *Method A* and *Method B*, and from **2f** by *Method B* (besides **2f** and DPU). Yellowish oil; identical in all respects to authentic compound [6]. EI-MS: 247 (M^+, 8), 164 (10), 163 (100), 162 (15), 146 (12), 117 (5), 91 (6), 77 (5), 57 (11).

*2,3-Dihydro-1-methyl-2-oxo-1*H-*indol-3-yl Benzoate* (**8g**). Prepared from **3g** and **2h** by *Method B* (besides **2g** and DPU). Colorless crystals. M.p. 117–119° (benzene/cyclohexane); identical in all respects to authentic compound with m.p. 116–118° [7]. EI-MS: 267 (M^+, 17), 163 (6), 162 (57), 146 (12), 117 (11), 106 (9), 105 (100), 91 (13), 77 (41), 51 (15).

*2,3-Dihydro-2-oxo-1-phenyl-1*H-*indol-3-yl Pentanoate* (**8i**). Prepared from **3i** and **2j** by *Method B* (besides DPU). Colorless crystals. M.p. 78–81° (hexane); identical in all respects to authentic compound with m.p. 81–82° [7]. EI-MS: 309 (M^+, 8), 226 (15), 225 (100), 208 (5), 196 (9), 180 (8), 168 (8), 167 (5), 119 (5), 77 (9), 57 (11), 51 (5), 41 (9).

*2,3-Dihydro-2-oxo-1-phenyl-1*H-*indol-3-yl Benzoate* (**8k**). Compound was prepared from **3k** by *Method B* and from **2l** by *Methods A* and *B* (besides BA and DPU). Colorless crystals. M.p. 134–137°; identical in all respects to authentic compound with m.p. 133–136° [7]. EI-MS: 329 (M^+, 28), 225 (7), 224 (47), 196 (21), 180 (11), 167 (5), 152 (6), 106 (8), 105 (100), 77 (43), 51 (14).

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