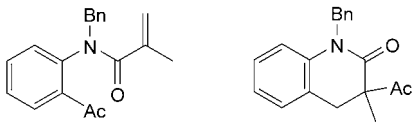
Photochemistry of *N*-(2-Acylphenyl)-2-methylprop-2-enamides: Competition between Photocyclization and Long-Range Hydrogen Abstraction

by **Takehiko Nishio***[a]), **Megumi Tabata**[b]), **Hiroyuki Koyama**[a]), and **Masami Sakamoto**[c])

[a]) Department of Chemistry, University of Tsukuba, Tsukuba-shi, Ibaraki, 305-8571, Japan
[b]) Graduate School of Environmental Sciences, University of Tsukuba, Tsukuba-shi, Ibaraki, 305-8571, Japan
[c]) Department of Materials Technology, Faculty of Engineering, Chiba University, Yayoi-cho, Inage-ku, Chiba, 263-8522, Japan

The photochemical reactions of various '*N*-methacryloyl acylanilides' (= *N*-(acylphenyl)-2-methylprop-2-enamides) have been investigated. Under irradiation, the acyl-substituted anilides **1a**–**1c** and **1o** afforded exclusively the corresponding quinoline-based cyclization products of type **2** (*Table 1*). In contrast, irradiation of the benzoyl (Bz)-substituted anilides **1e**–**1h** afforded a mixture of the open-chain amides **4e**–**4h** and the cyclization products **2e**–**2h**. Irradiation of the *para*-acyl-substituted anilides **6a**–**6e** and **6h** afforded the corresponding quinoline-based cyclization products of type **5** as the sole products (*Table 2*). The formation of the cyclization products **2a**–**2c** and **2o** can be rationalized in terms of 6π-electron cyclization, followed by thermal [1,5] acyl migration, and that of compounds **3p**, **5a**–**5e**, and **5h** can be explained by a 6π-electron cyclization only. The formation of the open-chain amides **4e**–**4h** probably follows a mechanism involving a 1,7-diradical, **C** and a spirolactam of type **D** (*Scheme*). Long-range ζ-H abstraction by the excited carbonyl O-atom of the benzoyl group on the aniline ring is expected to proceed *via* a nine-membered cyclic transition state, as proposed on the basis of X-ray crystallographic analyses (*Fig. 2*).

1. Introduction. – Owing to mesomerism, which confers to amides groups a partial double-bond character, aromatic enamides exhibit a photochemical behavior similar to that of conjugated hexatrienes. Indeed, the photo-induced electrocyclic ring closure of 6π-electron-conjugated enamides has been extensively exploited, and used in the preparation of a great variety of six-membered lactams [1]. *Ninomiya* and co-workers reported that irradiation of α,β-unsaturated acylanilides with *ortho*-substituents on the aniline ring leads to smooth photocyclization, followed by thermal [1,5] migration of a substituent to afford six-membered lactams [2]. For example, irradiation of *N*-(2-acetylphenyl)-*N*-benzyl-2-methylprop-2-enamide (**A**) afforded 3-acetyl-1-benzyl-3,4-dihydro-3-methylquinolin-2(1*H*)-one (**B**). However, benzophenones-*ortho*-amides undergo primarily photolytic deacetylation and dealkylation [3].



A **B**

In the course of our studies on the photochemistry of amides and thioamides [4], we have reported that irradiation of *N*-(2-halogenoalkanoyl)-substituted anilines (anilides) results in dehydrohalogenation products, which further undergo an electrocyclic ring closure to afford the corresponding 3,4-dihydroquinolin-2(1*H*)-ones [5]. We now report an investigation of the photochemical reactions of various substituted anilides of type **1** to illustrate the dramatic difference in the photochemical behavior of *ortho*-acetyl (Ac)- *vs. ortho*-benzoyl (Bz)-substituted anilides and related compounds.

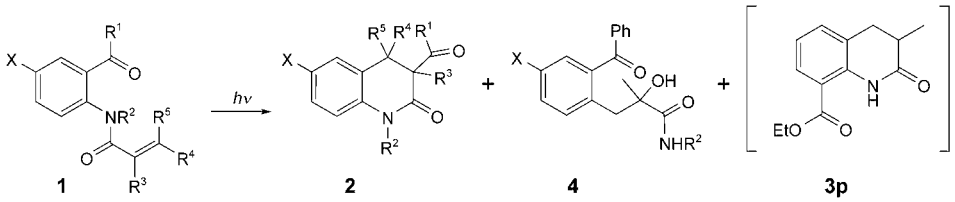
2. Results and Discussion. – Irradiation of the *N*-substituted prop-2-enoyl anilides **1a**–**1c** in MeCN and under Ar gas with a high-pressure Hg lamp (*Pyrex* filter, ambient temperature) led exclusively to the 3,4-dihydroquinolin-2(1*H*)-ones **2a**–**2c** in good yields (*Table 1*). The latter are products of the electrocylic ring closure of the parent 6π-electron-conjugated starting materials **1a**–**1c**, the intermediary products of which undergo a thermal [1,5] acyl migration (see below). Similar results were obtained when **1a** was irradiated in benzene (*Entry 2* in *Table 1*) instead of MeCN. The photocyclization of **1a**–**1c** proceeded in the same way as that of *N*-(α,β-unsaturated) acylanilides with an electron-withdrawing group in *ortho*-position of the aniline ring [2].

The *N*-unsubstituted anilide **1d** ($R^2 = H$; *Table 1*) was unreactive upon irradiation in MeCN, in contrast to the *N*-methyl-substituted **1o** with an ester function on the benzene ring. The latter compound underwent smooth photocyclization followed by thermal [1,5] migration of the the COOEt group to afford the lactam **2o** in 83% yield. Irradiation of the corresponding *N*-unsubstituted analog of **1o**, *i.e.*, **1p**, gave ethyl 1,2,3,4-tetrahydro-3-methyl-2-oxoquinoline-8-carboxylate (**3p**) in almost quantitative yield. In contrast, irradiation of the *N*-substituted anilides **1e**–**1h**, with *ortho*-Bz substituents on the aromatic rings, afforded under the same conditions (in MeCN or MeOH) the quinolinones **2e**–**2h** (22–39%), together with the unexpected 2-hydroxypropanamides **4e**–**4h** (26–43%). Neither deacetylation nor dealkylation products were detected in the reaction mixtures of **1** [3], and no indole or indoline derivatives arising from δ-H abstraction at *N*-alkyl groups by the excited carbonyl O-atom were found [6].

Irradiation of the *N*-methylated anilides **1i** and **1j** with *ortho*-Bz groups on their aromatic rings yielded the cyclized compounds **2i** and **2j**, respectively, as the sole products, but in low yields. On the other hand, irradiation of the *ortho*-Bz anilides **1k** and **1l**, lacking α-substituents on the prop-3-enoyl moiety, afforded no products at all. Thus, α-alkyl substitution is necessary for 6π-electron cyclizations to occur. Moreover, the *N*-unsubstituted *ortho*-Bz anilides **1m** and **1n** were fully recovered after irradiation. This is probably due to NH···C=O H-bonding, which suppresses enolization (6π-electron-conjugated enamide).

Next, we investigated anilides with *para*- rather than *ortho*-acyl substituents on the aromatic ring (*Table 2*). The quinolinone cyclization products **5a**–**5e** and **5h** were produced in the photolysis of the anilides **6a**–**6e** and **6h**, respectively. In these reactions, the yields of **5a** and **5c** were especially low. Moreover, no reaction took place with **6f** and **6g**, lacking α-substituents (R^3) on their prop-2-enoyl moieties. These results are, thus, in accordance with those obtained in the photoreaction of the *ortho*-acyl anilides **1k**–**1n**.

Table 1. *Photochemical Reactions of the Anilides* **1**. Unless noted otherwise, all reactions were performed at ambient temperature. For details, see the *Exper. Part*.



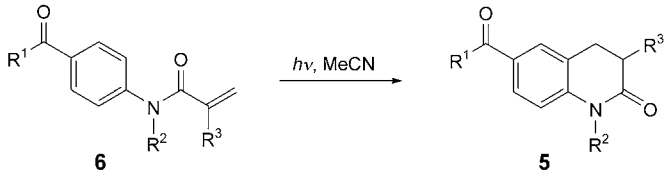
Entry	Compound	Substituents[a])					Solvent	Isolated Yield [%]		
		R^1	R^2	R^3	R^4	R^5		**2**	**4**	**3p**
1	**1a**	Me	Me	Me	H	H	MeCN	67	–	–
2	**1a**	Me	Me	Me	H	H	Benzene	72	–	–
3	**1b**	Me	Et	Me	H	H	MeCN	72	–	–
4	**1c**	Me	Bn	Me	H	H	MeCN	98	–	–
5	**1d**	Me	H	Me	H	H	MeCN	–	–	–
6	**1e**	Ph	Me	Me	H	H	MeCN	35	43	–
7	**1e**	Ph	Me	Me	H	H	MeCN/H_2O	35	33	–
8	**1e**	Ph	Me	Me	H	H	MeOH	22	32	–
9	**1e**	Ph	Me	Me	H	H	MeCN[b])	41	18	–
10	**1e**	Ph	Me	Me	H	H	Toluene	40	18	–
11	**1f**[a])	Ph	Me	Me	H	H	MeCN	38	30	–
12	**1g**	Ph	Et	Me	H	H	MeCN	39	26	–
13	**1h**	Ph	Bn	Me	H	H	MeCN	38	30	–
14	**1i**	Ph	Me	Me	H	Me	MeCN	29	–	–
15	**1j**	Ph	Me	H	H	H	MeCN	11	–	–
16	**1k**	Ph	Me	H	Me	H	MeCN	–	–	–
17	**1l**	Ph	Me	H	Me	Me	MeCN	–	–	–
18	**1m**	Ph	H	Me	H	H	MeCN	–	–	–
19	**1n**	Ph	H	H	Me	Me	MeCN	–	–	–
20	**1o**	EtO	Me	Me	H	H	MeCN	83	–	–
21	**1p**	EtO	H	Me	H	H	MeCN	–	–	99

[a]) X = H, except for **1f** (X = Cl; see formulae) and its products **2f** and **4f**, resp. [b]) Reaction performed at 60°.

The structures of the photoproducts described above were assigned on the basis of spectral and analytical evidence. In the case of the amide derivative **4e**, the assignment was further confirmed by an X-ray crystal-structure analysis (*Fig. 1*).

The formation of the 3,4-dihydroquinolin-2(1*H*)-ones **2** can be rationalized by means of a mechanism involving a *conrotatory* electrocyclization, followed by thermal [1,5] acyl migration, as proposed previously (*Path A* in the *Scheme*) [2]. A reasonable mechanism for the formation of the unexpected amides **4** is depicted in the *Scheme* below (*Path B*). Allylic-H abstraction by the excited carbonyl O-atom would result in the 1,7-diradical **C**. Subsequent ring closure yields the spirolactam **D**, which may undergo two kinds of ring opening, either to the aziridinone **E** or to the enamide **F**. Addition of H_2O (present in trace amounts in the solvent or during workup) would then yield the observed products **4**. To remove potential traces of H_2O in the solvent, the photoreaction of **1e** was performed in the presence of molecular sieves. However, this had little effect, and similar results were obtained as before. Irradiation of **1e** in

Table 2. *Photocyclization of the* para-*Acyl-Substituted Anilides* **6**. All reactions were performed at ambient temperature (see *Exper. Part*).



6 **5**

Entry	Compound	Substituents			Yield[a]) [%] of **5**
		R^1	R^2	R^3	
1	**6a**	Me	H	Me	19
2	**6b**	Me	Me	Me	99
3	**6c**	Ph	H	Me	6
4	**6d**	Ph	Me	Me	90
5	**6e**	EtO	H	Me	68
6	**6f**	EtO	H	H	0
7	**6g**	EtO	Me	H	0
8	**6h**	EtO	Me	Me	90

[a]) Yield after chromatographic purification.

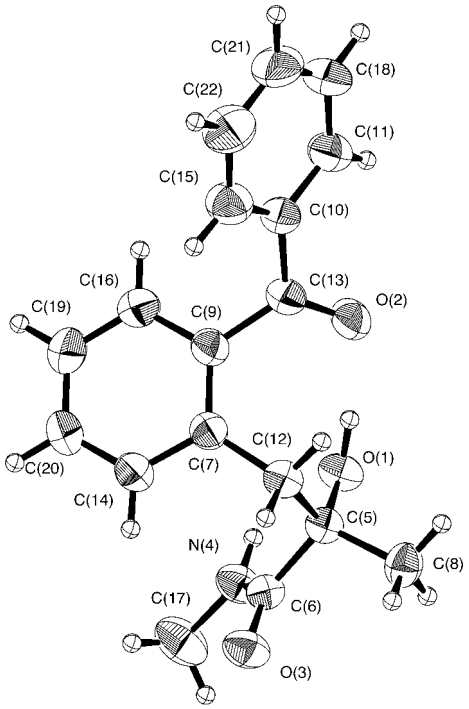
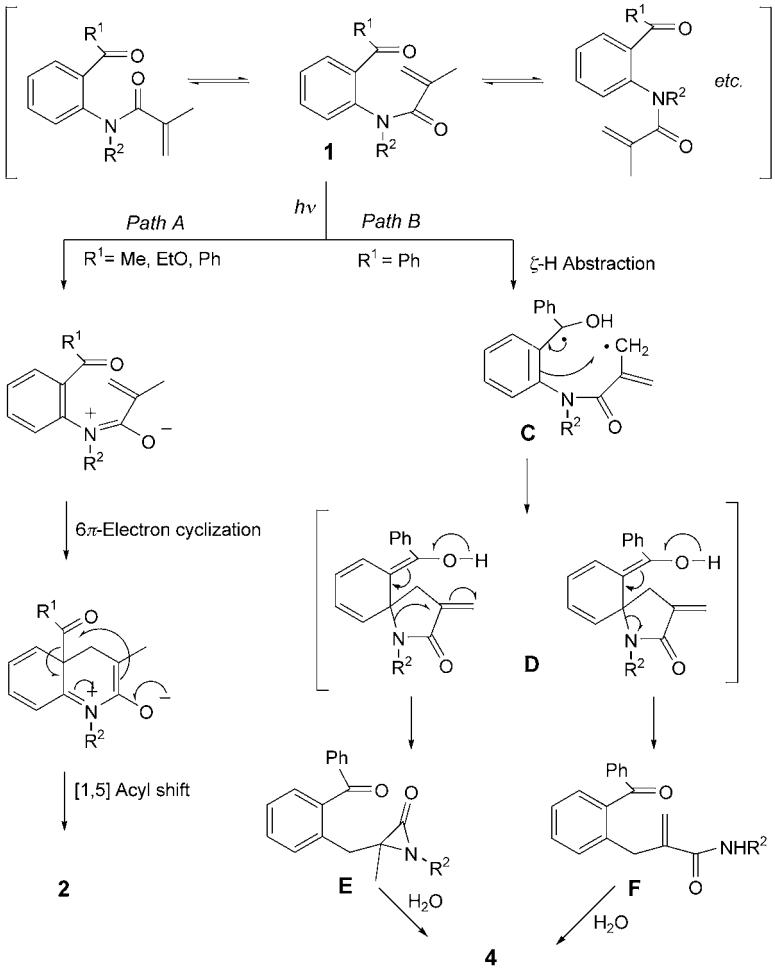


Fig. 1. *X-Ray crystal structure of compound* **4e** (ORTEP view)

MeCN saturated with H_2O also gave similar results (see *Entry 7* in *Table 1*). To shed more light on this transformation, the crude reaction mixture was examined by ^{1}H-NMR analysis immediately after evaporation of the solvent. However, no evidence for the formation of the anticipated intermediates **E** or **F** was found. Attempts to isolate the MeOH addition products of **E** or **F** were unsuccessful as well: irradiation of **1e** in MeOH gave **2e** and **4e** in 22 and 32% yield, respectively (*Entry 8* in *Table 1*).

Scheme. *Proposed Mechanisms for the Photochemical Formation of the Quinolinones* **2** (*Path A*) vs. *the Open-Chain Amides* **4** (*Path B*) *from the* ortho-*Acyl-Substituted Anilides* **1**. For R^1 and R^2, see *Table 1*.



The observed photochemical behavior of the *N*-substituted anilides **1** reveals that the distribution of photoproducts strongly depends on the acyl group on the aromatic ring – probably due to conformational and steric effects between the neighboring acyl

and prop-2-enoyl groups. In the room-temperature ^{1}H-NMR spectrum of **1e**, the α-Me and NMe groups, and the olefinic resonances appeared, in $CDCl_3$, at δ(H) 1.68 (Me), 3.24 (Me), and at 4.96 and 5.03 (2×1 arom. H), respectively; in CD_3CN, the same resonances appeared as broad peaks at 1.57, 3.12, 4.84 and 5.00 ppm at room temperature, while, on increasing the temperature to *ca.* 60°, the peaks became more and more sharp. This strongly indicates that the conformation of **1e** is highly restricted at room temperature. However, there was no indication of such a conformational restriction in aromatic solvents such as (D_8)toluene, as observed by means of ^{1}H-NMR at ambient temperature.

To address these questions more precisely and to determine the contact geometry between the carbonyl chromophore and nearest H-atoms suitable for abstraction, an X-ray crystal-structure analysis of **1e** was performed (*Fig. 2*). In the solid state, **1e** adopts a conformation in which ζ-H abstraction is, indeed, likely to occur. The distance between the benzoyl (Bz) O-atom (C=O group) and one of the allylic ζ-H-atoms of the methacryloyl moiety, *i.e.*, O(1)···H(21), was found to be 2.82 Å, which falls within the typical range of 2.30–3.10 Å required for hydrogen abstraction [7]. In contrast, the distance O(2)···H(20), *i.e.*, that between the benzoyl C=O group and one of the δ-H-atoms of the NMe amido group, is 4.92 Å.

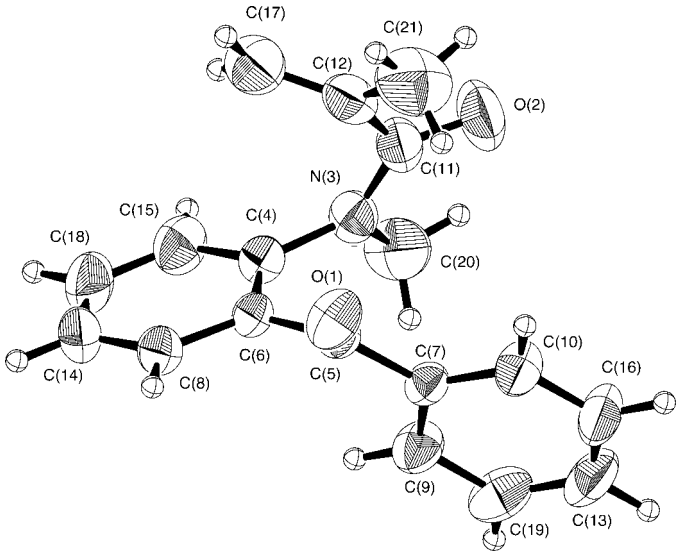


Fig. 2. *X-Ray crystal structure of compound* **1e** (ORTEP view)

Irradiation of **1e** in MeCN at 60°, or in toluene at r.t., resulted in a significant reduction in the yield of **4e** (*Entries 9* and *10* in *Table 1*), **2e** becoming the main product. Intramolecular hydrogen abstraction by excited C=O groups is very well-known, attack taking place preferentially at the γ-position, under formation of a six-membered cyclic transition state (*Norrish Type II* reaction) [7]. γ-H Abstraction is

facilitated by favorable stereoelectronic and geometric dispositions, long-range H-atom transfers, thus, being rare [8]. Many of the reactions involve amino ketone and amino imides or sulfide imides, and proceed *via* an electron-transfer process [9]. Our results, thus, underline that even long-range intramolecular hydrogen abstractions can proceed efficiently when a favorable conformation is adopted.

Experimental Part

General. Flash chromatography (FC): *Wakogel C-300* or *Merck 60* silica gel. M.p.: *Yanaco MP-J3* micro-melting-point apparatus; uncorrected. B.p.: *Shibata GTO-350-RD* glass-tube-oven distillation apparatus. IR Spectra: *Jasco FT/IR-300* spectrophotometer; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Jeol JNM-EX-270* (270 MHz) or *Varian Gemini-200* (200 MHz); in $CDCl_3$, with $MeSi_4$ as internal standard; δ in ppm, J in Hz.

General Procedure for Photochemical Reactions of Anilides of Type **1** *and* **6**. A soln. of the anilides **1** or **6** (1 mmol) in MeCN (70 ml), unless otherwise noted, was irradiated in a *Pyrex* tube with a high-pressure Hg lamp (*Halos EHP*, 500 W; *Eikosha*) under Ar gas for 3–10 h at r.t. After evaporation, the residue was subjected to FC (SiO_2; toluene/AcOEt 50:1:4:1) to afford a mixture of **2**–**4** (see *Table 1*).

*3-Acetyl-3,4-dihydro-1,3-dimethylquinolin-2(1*H*)-one* (**2a**). B.p. 135°/3 Torr. IR (film): 1713, 1666, 1603. ^1H-NMR: 1.42 (*s*, 3 H); 2.13 (*s*, 3 H); 2.77 (*d*, J = 15.4, 1 H); 3.36 (*d*, J = 15.4, 1 H); 3.42 (*s*, 3 H); 6.95–7.07 (*m*, 2 H); 7.16–7.30 (*m*, 2 H). ^{13}C-NMR: 19.8; 25.5; 29.6; 34.7; 54.6; 114,1; 122.8; 123.7; 127.2; 127.6; 138.8; 170.2; 205.5. Anal. calc. for $C_{13}H_{15}NO_2$ (217.26): C 71.86, H 6.96, N 6.45; found: C 71.55, H 7.01, N 6.69.

*3-Acetyl-1-ethyl-3,4-dihydro-3-methylquinolin-2(1*H*)-one* (**2b**). B.p. 165°/3 Torr. IR (film): 1713, 1666, 1603. ^1H-NMR: 1.20 (*t*, J = 7.1, 3 H); 1.32 (*s*, 3 H); 2.02 (*s*, 3 H); 2.67 (*d*, J = 15.5, 1 H); 3.25 (*d*, J = 15.5, 1 H); 3.74–3.96 (*m*, 1 H); 3.99–4.11 (*m*, 1 H); 6.87–6.94 (*m*, 2 H); 7.06–7.22 (*m*, 2 H). ^{13}C-NMR: 11.8; 19.8; 25.4; 34.8; 37.7; 54.5; 114.0; 122.7; 124.1; 127.3; 128.1; 137.9; 169.7; 205.8. Anal. calc. for $C_{14}H_{17}NO_2$ (231.28): C 72.70, H 7.41, N 6.06; found: C 72.49, H 7.56, N 6.04.

*3-Acetyl-1-benzyl-3,4-dihydro-3-methylquinolin-2(1*H*)-one* (**2c**). M.p. 101–102° (lit. 102–103° [2b]). IR (KBr): 1713, 1680, 1650, 1603. ^1H-NMR: 1.48 (*s*, 3 H); 2.16 (*s*, 3 H); 2.85 (*d*, J = 5.8, 1 H); 3.38 (*d*, J = 5.8, 1 H); 5.02 (*d*, J = 16.5, 1 H); 5.31 (*d*, J = 16.5, 1 H); 6.84–7.30 (*m*, 9 H). ^{13}C-NMR (non-aromatic signals): 20.2; 25.6; 35.3; 46.9; 55.2; 170.4; 205.8.

*3-Benzoyl-3,4-dihydro-1,3-dimethylquinolin-2(1*H*)-one* (**2e**). B.p. 175°/3 Torr. IR (film): 1681, 1601. ^1H-NMR: 1.59 (*s*, 3 H); 2.78 (*d*, J = 15.4, 1 H); 3.35 (*s*, 3 H); 3.63 (*d*, J = 15.4, 1 H); 6.87–7.30 (*m*, 7 H); 7.74 (*d*, J = 8.7, 1 H). ^{13}C-NMR (non-aromatic signals): 20.7; 29.7; 36.6; 53.5; 170.9; 198.9. Anal. calc. for $C_{18}H_{17}NO_2$ (279.32): C 77.39, H 6.13, N 5.01; found: C 77.64, H 6.34, N 4.85.

*3-(2-Benzoylphenyl)-2-hydroxy-*N*,2-dimethylpropanamide* (**4e**). M.p. 120.5°. IR (KBr): 3345, 1645. ^1H-NMR: 1.53 (*s*, 3 H); 2.75 (*d*, J = 5.0, 3 H); 2.98 (*d*, J = 13.5, 1 H); 3.36 (*d*, J = 13.5, 1 H); 6.35 (br. *s*, 1 H); 6.99 (br. *s*, 1 H); 7.26–7.52 (*m*, 6 H); 7.61–7.68 (*m*, 1 H); 7.78–7.78 (*m*, 2 H). ^{13}C-NMR: 25.7; 27.7; 42.4; 76.4; 125.7; 128.5; 130.5; 131.3; 132.3; 133.9; 137.3; 137.6; 176.2; 200.5. Anal. calc. for $C_{18}H_{19}NO_3$ (297.34): C 72.70, H 6.44, N 4.71; found: C 72.44, H 6.34, N 4.96.

*3-Benzoyl-6-chloro-3,4-dihydro-1,3-dimethylquinolin-2(1*H*)-one* (**2f**). M.p. 148–150°. IR (KBr): 1660, 1596. ^1H-NMR: 1.61 (*s*, 3 H); 2.86 (*d*, J = 15.5, 1 H); 3.33 (*s*, 1 H); 3.59 (*d*, J = 15.5, 1 H); 6.81 (*d*, J = 8.6, 1 H); 7.15–7.21 (*m*, 2 H); 7.32–7.50 (*m*, 3 H); 7.73–7.78 (*m*, 2 H). ^{13}C-NMR: 21.4; 30.4; 36.9; 53.7; 115.8; 126.3; 127.4; 128.2; 128.5; 132.4; 135.7; 138.0; 170.9; 198.7. Anal. calc. for $C_{18}H_{16}ClNO_2$ (344.18): C 68.90, H 5.10, N 4.47; found: C 68.66, H 5.09, N 4.38.

*3-(2-Benzoyl-4-chlorophenyl)-2-hydroxy-*N*,2-dimethylpropanamide* (**4f**). M.p. 152–154°. IR (KBr): 3412, 3343, 1643, 1542. ^1H-NMR: 1.52 (*s*, 3 H); 2.76 (*d*, J = 4.8, 3 H); 2.88 (*d*, J = 14.0, 1 H); 3.33 (*d*, J = 14.0, 1 H); 7.01 (br. *s*, 1 H); 7.26–7.83 (*m*, 8 H). ^{13}C-NMR: 25.2; 27.3; 41.3; 128.3; 129.4; 130.7; 131.4; 133.1; 134.0; 135.6; 136.2; 138.9; 175.6; 198.8. Anal. calc. for $C_{18}H_{18}ClNO_3$ (331.78): C 65.16, H 5.47, N 4.22; found: C 64.96, H 5.49, N 4.04.

*3-Benzoyl-1-ethyl-3,4-dihydro-3-methylquinolin-2(1*H*)-one* (**2g**). B.p. 170°/3 Torr. IR (film): 1659, 1601. ^1H-NMR: 1.05 (*t*, J = 7.2, 3 H); 1.63 (*s*, 3 H); 2.79 (*d*, J = 15.6, 1 H); 3.60 (*d*, J = 15.6, 1 H); 3.68–3.87 (*m*, 1 H); 4.03–4.15 (*m*, 1 H); 6.99–7.61 (*m*, 7 H); 7.70 (*d*, J = 6.8, 2 H). ^{13}C-NMR (non-aromatic signals): 11.6; 21.0; 36.9; 37.9; 53.5; 170.4; 199.6. MS: 293 (M^+), 188, 105. HR-MS: 293.14090 (M^+, $C_{19}H_{19}NO_2^+$; calc. 293.3597).

*3-(2-Benzoylphenyl)-*N*-ethyl-2-hydroxy-2-methylpropanamide* (**4g**). B.p. 200°/3 Torr. IR (film): 3345, 1650. ^1H-NMR: 1.04 (*t*, J = 7.2, 3 H); 1.53 (*s*, 3 H); 2.98 (*d*, J = 13.9, 1 H); 3.17–3.30 (*m*, 2 H); 3.37 (*d*, J = 13.9, 2 H); 6.38 (br. *s*, 1 H); 7.20–7.67 (*m*, 7 H); 7.79 (*d*, J = 6.9, 2 H). ^{13}C-NMR: 14.9; 28.0; 34.1; 42.6; 77.7; 128.7; 130.7;

131.3; 131.5; 132.6; 134.1; 137.7; 137.9; 175.7; 200.7. Anal. calc. for $C_{19}H_{21}NO_3$ (311.37): C 73.29, H 6.80, N 4.50; found: C 73.67, H 6.60, N 4.65.

*3-Benzoyl-1-benzyl-3,4-dihydro-3-methylquinolin-2(1*H*)-one* (**2h**). B.p. 235°/3 Torr. IR (film): 1681, 1602. ^{1}H-NMR: 1.26 (*s*, 3 H); 2.99 (*d*, *J* = 13.5, 1 H); 3.41 (*d*, *J* = 13.5, 1 H); 6.39 (br. *s*, 1 H); 7.11 – 7.65 (*m*, 12 H); 7.78 (*d*, *J* = 7.6, 2 H). ^{13}C-NMR (non-aromatic signals): 21.9; 37.2; 47.4; 54.3; 171.2; 198.8. Anal. calc. for $C_{24}H_{21}NO_2$ (355.42): C 81.10, H 5.96, N 3.93; found: C 80.96, H 6.10, N 3.87.

3-(2-Benzoylphenyl)-N-*benzyl-2-hydroxy-2-methylpropanamide* (**4h**). M.p. 73.5 – 75.0°. IR (KBr): 3390, 1681, 1650. ^{1}H-NMR: 1.57 (*s*, 3 H); 2.99 (*d*, *J* = 13.5, 1 H); 3.42 (*d*, *J* = 13.5, 1 H); 4.29 – 4.40 (*m*, 2 H); 6.39 (br. *s*, 1 H); 7.11 – 7.65 (*m*, 12 H); 7.78 (*d*, *J* = 7.6, 2 H). ^{13}C-NMR (non-aromatic signals): 28.0; 42.3; 43.0; 76.3; 175.5; 200.4. Anal. calc. for $C_{24}H_{23}NO_3$ (355.42): C 77.19, H 6.21, N 3.75; found: C 76.97, H 6.14, N 3.61.

*3-Benzoyl-3,4-dihydro-1,3,4-trimethylquinolin-2(1*H*)-one* (**2i**). M.p. 86 – 87°. IR (KBr): 1667, 1601. ^{1}H-NMR: 1.55 (*d*, *J* = 7.2, 3 H); 1.73 (*s*, 3 H); 3.08 (*q*, *J* = 7.2, 1 H); 3.25 (*s*, 3 H); 7.05 – 7.59 (*m*, 9 H). ^{13}C-NMR (non-aromatic signals): 12.4; 19.9; 30.1; 39.7; 56.7; 171.2; 200.9. Anal. calc. for $C_{19}H_{19}NO_2$ (293.35): C 77.79, H 6.53, N 4.77; found: C 77.97, H 6.42, N 4.99.

*3-Benzoyl-3,4-dihydro-1-methylquinolin-2(1*H*)-one* (**2j**). B.p. 180°/3 Torr. IR (film): 1681, 1603. ^{1}H-NMR: 3.06 (*dd*, *J* = 6.0, 10.0, 1 H); 3.39 (*s*, 3 H); 3.38 – 3.48 (*m*, 1 H); 4.59 (*dd*, *J* = 6.0, 16.0, 1 H); 7.00 – 7.60 (*m*, 7 H); 7.94 – 7.99 (*m*, 2 H). ^{13}C-NMR (non-aromatic signals): 28.1; 29.4; 48.2; 167.4; 185.9. Anal. calc. for $C_{17}H_{15}NO_2$ (265.30): C 76.96, H 5.70, N 5.23; found: C 76.62, H 5.73, N 5.18.

Ethyl 1,2,3,4-Tetrahydro-1,3-dimethyl-2-oxoquinolin-3-carboxylate (**2o**). B.p. 125°/3 Torr. IR (film): 1730, 1680, 1603. ^{1}H-NMR: 1.03 (*t*, *J* = 7.2, 3 H); 1.51 (*s*, 3 H); 2.85 (*d*, *J* = 15.4, 1 H); 3.35 (*d*, *J* = 15.4, 1 H); 3.40 (*s*, 3 H); 4.03 – 4.13 (*m*, 2 H); 6.95 – 7.05 (*m*, 2 H); 7.14 – 7.31 (*m*, 2 H). ^{13}C-NMR: 13.7; 20.4; 30.1; 30.7; 49.6; 61.2; 114.4; 122.9; 123.9; 127.7; 127.9; 139.8; 169.7; 172.1. Anal. calc. for $C_{14}H_{17}NO_3$ (247.28): C 67.99, H 6.93, N 5.66; found: C 67.68, H 6.90, N 5.89.

Ethyl 1,2,3,4-Tetrahydro-3-methyl-2-oxoquinoline-8-carboxylate (**3p**). M.p. 102.0 – 103.5°. IR (KBr): 3316, 1672, 1602. ^{1}H-NMR: 1.28 (*d*, *J* = 6.6, 3 H); 1.40 (*t*, *J* = 7.3, 1 H); 2.58 – 2.81 (*m*, 2 H); 3.02 (*dd*, *J* = 5.6, 15.2, 1 H); 3.67 (*q*, *J* = 7.3, 2 H); 6.94 – 7.00 (*m*, 1 H); 7.28 – 7.35 (*m*, 1 H); 7.88 (*dd*, *J* = 1.3, 8.3, 1 H). ^{13}C-NMR: 14.1; 15.1; 33.5; 34.2; 61.2; 113.1; 121.3; 124.5; 129.2; 132.7; 140.0; 167.0; 173.4. Anal. calc. for $C_{13}H_{15}NO_3$ (233.26): C 66.93, H 6.48, N 6.01; found: C 66.66, H 6.49, N 6.21.

*6-Acetyl-3,4-dihydro-3-methylquinolin-2(1*H*)-one* (**5a**). M.p. 169 – 170°. IR (KBr): 3200, 1666, 1605, 1590. ^{1}H-NMR: 1.32 (*d*, *J* = 6.6, 3 H); 2.58 (*s*, 3 H); 2.63 – 2.87 (*m*, 2 H); 3.04 – 3.14 (*m*, 1 H); 6.95 (*d*, *J* = 8.7, 1 H); 7.81 (br. *s*, 2 H); 9.51 (br. *s*, 1 H). ^{13}C-NMR: 14.7; 25.8; 32.5; 34.2; 114.4; 122.7; 127.9; 128.0; 131.5; 140.9; 174.5; 196.3. Anal. calc. for $C_{12}H_{13}NO_2$ (203.23): C 70.91, H 6.45, N 6.89; found: C 71.08, H 6.38, N 6.87.

*6-Acetyl-3,4-dihydro-1,3-dimethylquinolin-2(1*H*)-one* (**5b**). M.p. 88 – 89°. IR (KBr): 1685, 1667, 1600. ^{1}H-NMR: 1.27 (*d*, *J* = 6.9, 3 H); 2.58 (*s*, 3 H); 2.63 – 2.81 (*m*, 2 H); 2.97 – 3.14 (*m*, 1 H); 3.39 (*s*, 3 H); 7.02 (*d*, *J* = 8.3, 1 H); 7.79 (br. *s*, 1 H); 7.88 (*dd*, *J* = 2.0, 8.3, 1 H). ^{13}C-NMR: 15.6; 26.3; 29.9; 33.1; 35.3; 114.1; 125.9; 127.9; 128.3; 128.4; 131.6; 144.4; 173.2; 196.8. Anal. calc. for $C_{13}H_{15}NO_2$ (217.26): C 71.86, H 6.96, N 6.45; found: C 71.94, H 7.11, N 6.45.

*6-Benzoyl-3,4-dihydro-3-methylquinolin-2(1*H*)-one* (**5c**). M.p. 159.5 – 161°. IR (KBr): 3323, 1684, 1643, 1587. ^{1}H-NMR: 1.33 (*d*, *J* = 8.6, 3 H); 2,66 – 3.12 (*m*, 2 H); 3.01 – 3.12 (*m*, 1 H); 6.93 (*d*, *J* = 6.6, 1 H); 7.45 – 7.91 (*m*, 7 H); 9.22 (br. *s*, 1 H). ^{13}C-NMR: 14.7; 30.3; 32.5; 34.2; 114.2; 122.8; 127.7; 129.2; 129.7; 130.0; 131.6; 137.3; 140.6; 174.5; 195.0. Anal. calc. for $C_{17}H_{15}NO_2$ (265.30): C 76.96, H 5.70, N 5.28; found: C 77.18, H 5.70, N 5.45.

*6-Benzoyl-3,4-dihydro-1,3-dimethylquinolin-2(1*H*)-one* (**5d**). M.p. 117 – 118°. IR (KBr): 1665, 1645, 1600. ^{1}H-NMR: 1.28 (*d*, *J* = 6.6, 3 H); 2.63 – 2.81 (*m*, 2 H); 3.01 (*dd*, *J* = 4.3, 14.2, 1 H); 3.41 (*s*, 3 H); 7.03 (*d*, *J* = 8.3, 1 H); 7.45 – 7.62 (*m*, 4 H); 7.70 – 7.79 (*m*, 3 H). ^{13}C-NMR: 15.5; 29.9; 32.9; 35.2; 113.8; 125.4; 128.2; 128.7; 130.3; 131.6; 132.1; 137.8; 144.0; 173.1; 195.4. Anal. calc. for $C_{18}H_{17}NO_2$ (279.32): C 77.39, H 6.13, N 5.01; found: C 77.56, H 6.09, N 5.27.

Ethyl 1,2,3,4-Tetrahydro-3-methyl-2-oxoquinoline-6-carboxylate (**5e**). M.p. 211 – 213°. IR (KBr): 3205, 1713, 1672, 1614. ^{1}H-NMR: 1.31 (*d*, *J* = 6.6, 3 H); 1.39 (*t*, *J* = 7.3, 3 H); 2.69 – 2.83 (*m*, 2 H); 3.03 – 3.11 (*m*, 1 H); 4.36 (*q*, *J* = 7.3, 2 H); 6.90 (*d*, *J* = 7.9, 1 H); 7.87 (*s*, 1 H); 7.88 (*d*, *J* = 7.9, 1 H); 9.56 (br. *s*, 1 H). ^{13}C-NMR: 15.4; 16.3; 34.1; 35.8; 61.9; 115.9; 124.1; 126.0; 130.5; 130.6; 142.2; 167.2; 176.0. Anal. calc. for $C_{13}H_{15}NO_3$ (233.26): C 66.93, H 6.48, N 6.01; found: C 66.86, H 6.53, N 6.24.

Ethyl 1,2,3,4-Tetrahydro-1,3-dimethyl-2-oxoquinoline-6-carboxylate (**5h**). M.p. 78 – 79°. IR (KBr): 1710, 1639, 1607. ^{1}H-NMR: 1.27 (*d*, *J* = 6.6, 3 H); 1.40 (*t*, *J* = 7.3, 3 H); 2.60 – 2.79 (*m*, 2 H); 2.96 – 3.04 (*m*, 1 H); 3.39 (*s*, 3 H); 4.37 (*q*, *J* = 7.3, 2 H); 6.99 (*d*, *J* = 8.6, 1 H); 7.85 (br. *s*, 1 H); 7.95 (*dd*, *J* = 8.6, 2.0, 1 H). ^{13}C-NMR: 14.3; 15.6; 29.9; 33.0; 35.3; 60.8; 114.0; 124.6; 125.3; 129.1; 129.3; 133.2; 166.1; 173.2. Anal. calc. for $C_{14}H_{17}NO_3$ (247.28): C 67.99, H 6.93, N 5.65; found: C 67.89, H 6.90, N 5.66.

X-Ray Crystal-Structure Determinations[1]). Crystals of **4e** and **1e** were grown from $CHCl_3$/hexane. The intensity data were collected on a *Mac Science MXC-18* diffractometer, with graphite-monochromated CuK_α radiation ($\lambda = 1.54178$ Å), in the ω-2θ scan-mode ($2\theta < 69.99°$). Out of 3176 total reflections, 2630 reflections with intensities greater than $3\sigma(I)$ were used in the case of **4e**, and 2494 out of 2987 reflections were used in the case of **1e**. No absorption corrections were made. The structures were solved by direct methods with the maXus program. Least-squares refinements were performed, including anisotropic thermal parameters for non-H-atoms and isotropic refinement of H-atoms located in difference *Fourier* synthesis.

Crystal Data of **4e**: $C_{18}H_{19}NO_3$; M_r 297.354; $Z = 4$, $D_x = 1.224$ Mg cm^{-3}; monoclinic, space group $P\,2_1/c$; $a = 16.222(3)$, $b = 5.2468(13)$, $c = 22.887(6)$ Å; $\alpha = 90.00°$, $\beta = 124.05(3)°$, $\gamma = 90.00°$; $V = 1614.0(7)$ Å^3; $R = 0.052$, $Rw = 0.046$.

Crystal data of **1e**: $C_{18}H_{17}NO_2$, $M_r = 279.339$; $Z = 2$; $D_x = 1.209$ Mg cm^{-3}; triclinic, space group $P\,1$; $a = 8.1796(14)$, $b = 8.431(3)$, $c = 12.386(4)$ Å; $\alpha = 93.94(3)°$, $\beta = 94.87(2)°$, $\gamma = 114.84(2)°$; $V = 767.1(4)$ Å^3; $R = 0.075$, $Rw2 = 0.069$.

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[1]) The crystallographic data (excluding structure factors) for **4e** and **1e** have been deposited with the *Cambridge Crystallographic Data Centre* (*CCDC*) as supplementary publication numbers CCDC-239873 and CCDC-239874, resp. Copies of the data can be obtained, free of charge, by application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk), or *via* the internet (http://www.ccdc.cam.ac.uk/products/csd/request).