Photochemical Reactions of *N*-(2-Halogenoalkanoyl) Derivatives of Anilines

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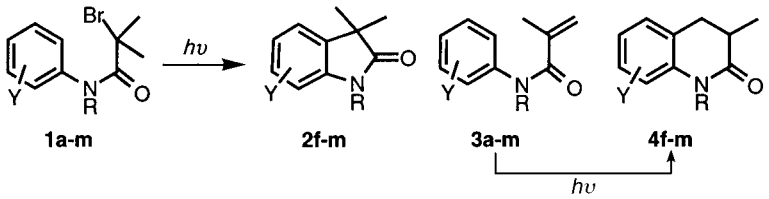
The photochemical reactions of 2-substituted *N*-(2-halogenoalkanoyl) derivatives **1** of anilines and **5** of cyclic amines are described. Under irradiation, 2-bromo-2-methylpropananilides **1a**–**e** undergo exclusively dehydrobromination to give *N*-aryl-2-methylprop-2-enamides (= methacrylanilides) **3a**–**e** (*Scheme 1* and *Table 1*). On irradiation of *N*-alkyl- and *N*-phenyl-substituted 2-bromo-2-methylpropananilides **1f**–**m**, cyclization products, *i.e.* 1,3-dihydro-2*H*-indol-2-ones (= oxindoles) **2f**–**m** and 3,4-dihydroquinolin-2(1*H*)-ones (= dihydrocarbostyrils) **4f**–**m**, are obtained, besides **3f**–**m**. On the other hand, irradiation of *N*-methyl-substituted 2-chloro-2-phenylacetanilides **1o**–**q** and 2-chloroacetanilide **1r** gives oxindoles **2o**–**r** as the sole product, but in low yields (*Scheme 3* and *Table 2*). The photocyclization of the corresponding *N*-phenyl derivatives **1s**–**v** to oxindoles **2s**–**v** proceeds smoothly. A plausible mechanism for the formation of the photoproducts is proposed (*Scheme 4*). Irradiation of *N*-(2-halogenoalkanoyl) derivatives of cyclic amines **5a**–**c** yields the cyclization products, *i.e.* five-membered lactams **6a**, **b**, and/or dehydrohalogenation products **7a**, **c** and their cyclization products **8a**, **c**, depending on the ring size of the amines (*Scheme 5* and *Table 3*).

1. Introduction. – Amide compounds in which the N-atom deactivates the carbonyl group are photochemically much less reactive than carbonyl compounds [1], although the photochemical cyclization of *N*-(halogenoacetyl) derivatives of aromatic amino acid and pharmacodynamic amines with a C_2- to C_5-alkane moiety between the aromatic group and the halogenoacetamide function for the syntheses of many medium-sized lactams has been reported by several groups [2][3]. There is only one report by *Yonemitsu* and co-workers on the photocyclization of 2-chloroacetanilides, where two functional groups (chloroacetamide and aromatic ring) are directly conjugated [3b]: the photocyclization yielding five-membered lactams, *i.e.* oxindoles, involved *N*-alkyl-*N*-(chloroacetyl)anisidines having electron-donating substituents at the benzene ring and *N*-(chloroacetyl)-*N*-methylaniline [3b]. However, the photochemical reactions of 2-substituted *N*-(2-halogenoalkanoyl) derivatives of various amines have received little attention. Herein we report the photochemical cyclization and dehydrohalogenation of *N*-(2-halogenoalkanoyl) derivatives **1** and **5** of various anilines and cyclic amines, respectively.

2. Results and Discussion. – 2.1. *Photochemical Reactions of* N-*(2-Halogenoalkanoyl) Derivatives* **1** *of Anilines.* Irradiation of *N*-(2-bromo-2-methylpropanoyl) derivatives **1a**–**e** of anilines having electron-withdrawing and -donating substituents Y such as chloro, ethoxycarbonyl, and methoxy at the benzene ring, in MeCN with a high-pressure mercury lamp through a *Pyrex* filter under Ar at room temperature, gave exclusively the *N*-aryl-2-methylprop-2-enamides (= methacrylanilides) **3a**–**e**

(*Scheme 1* and *Table 1*). The latter were formed in moderate-to-good yields by elimination of HBr at the side chain, and no evidence for any cyclized products was found. The structures of the photoproducts **3a–e** were established by spectroscopic data, particularly by ^{1}H-NMR spectra (δ 5.40–5.47 and 5.76–5.82 for CH_2=) and microanalyses.

Scheme 1[a])



[a]) For R and Y, see *Table 1*.

Table 1. *Yield of Photoproducts* **2–4**

Entry		**1**		Yield [%][a])		
		R	Y	**2**	**3**	**4**
1	**1a**	H	H	–	64	–
2[b])				–	29	–
3[c])				–	53	–
4	**1b**	H	4-Cl	–	54	–
5	**1c**	H	4-CO_2Et	–	40	–
6	**1d**	H	4-MeO	–	84	–
7	**1e**	H	2,4-(MeO)$_2$	–	76	–
8	**1f**	Me	H	21	10	13
9[d])				29	12	15
10[e])				33	14	19
11	**1g**	Me	4-Me	13	5	5
12	**1h**	Me	4-Cl	19	25	26
13	**1i**	Me	4-CO_2Et	[f])	25	56
14	**1j**	Me	4-MeO	12	16	21
15	**1k**	Et	H	17	31	34
16	**1l**	$PhCH_2$	H	18	36	34
17	**1m**	Ph	H	34	28	17

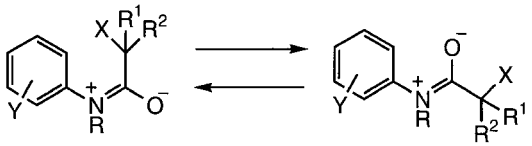
[a]) Yield of isolated product. [b]) In the presence of 2 mol-equiv. of 2,6-di(*tert*-butyl)phenol. [c]) In the presence of 2 mol-equiv. of triphenylmethane. [d]) In benzene. [e]) In MeOH. [f]) Traces.

Irradiation of *N*-alkyl- and *N*-phenyl-substituted *N*-(2-bromo-2-methylpropanoyl) derivatives of anilines **1f–m** under the same conditions as described for **1a–e** yielded as cyclization products the 1,3-dihydro-2*H*-indol-2-ones (=oxindoles) **2f–m** and the 3,4-dihydroquinolin-2(1*H*)-ones (=dihydrocarbostyrils) **4f–m**, and as dehydrobromination products the methacrylanilides **3f–m** (*Scheme 1* and *Table 1*). Similar results were obtained when **1f** was irradiated in benzene or MeOH (*Entries 9* and *10* in *Table 1*). ^{1}H-NMR Monitoring of the irradiation of **1m** showed that the yield of dihydrocarbostyril **4m** increased, while that of methacrylanilide **3m** decreased, with irradiation time. Upon irradiation of the isolated methacrylanilides **3f–g** and **3k–m** under similar conditions, the dihydrocarbostyrils **4f–g** and **4k–m** were obtained. The

formation of **4** can be explained in terms of an electrocyclic ring closure of the 6 π-electron conjugated enamides **3** [4] (see below).

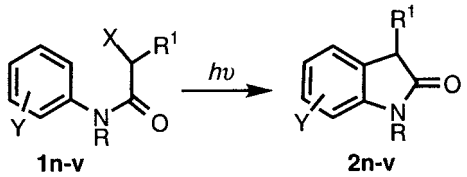
Owing to mesomerism, which confers to the amide group a partial double-bond character, *N*-(2-halogenoacyl)anilides **1a**–**e** (R = H) exist almost exclusively in the *trans* form with respect to the aromatic moiety and the halogenoalkyl group (see *Scheme 2*). On the other hand, in unsymmetrically *N*,*N*-disubstituted (2-halogenoacyl)anilides **1f**–**m** (R = alkyl, Ph), the prefered isomer has the halogenoalkyl group *cis* to the aromatic moiety [3b]. Therefore, on irradiation, **1a**–**e** (R = H) could not cyclize to oxindoles **2a**–**e** but underwent dehydrobromination to the methacrylanilides **3a**–**e**, while **1f**–**m** cyclized to oxindoles **2f**–**m**.

Scheme 2



Irradiation in MeCN of *N*-methyl-substituted 2-chloro-2-phenylacetanilide **1q**, which has no alkyl substituent at C(2), gave a cyclization product, the oxindole **2q**, as the sole product, though in only 9% yield (*Scheme 3* and *Table 2*). Similarly, the 2-chloro-2-phenylacetanilides **1n**–**p** having electron-donating or electron-withdrawing groups were cyclized in poor yields to oxindoles **2n**–**p**. Irradiation of the *N*-methyl-substituted 2-chloroacetyl derivative **1r** of *p*-anisidine (=4-methoxybenzenamine) in MeCN or in MeCN/H_2O gave the oxindole **2r** in low yield (*Entries 5–7* in *Table 2*) [3b]. On the other hand, photocyclization under similar conditions of *N*-phenyl-substituted 2-halogenoacetanilides **1s**–**v** possessing the bulky Ph substituent at the N-atom proceeded smoothly to yield oxindoles **2s**–**v** in 26–60% yields.

Scheme 3[a])



a) For R, R^1, X, and Y, see *Table 2*.

Irradiation of **1a** in the presence of a radical quencher such as 2,6-di(*tert* butyl)phenol or triphenylmethane resulted in a decrease of the dehydrohalogenation to methacrylanilide **3a** (*Entries 2* and *3* in *Table 1*). The yield of the cyclization product **2v** was slightly increased by the addition of magnesium perchlorate to the photoreaction of **1v** (*Entry 13* in *Table 2*) [5a]. The addition of silver trifluoromethanesulfate on irradiation of **1u** also affected the yield of the cyclization product **2u** (*Entry 11* in *Table 2*) [5b].

Table 2. *Yield of Oxindoles* **2n–v**

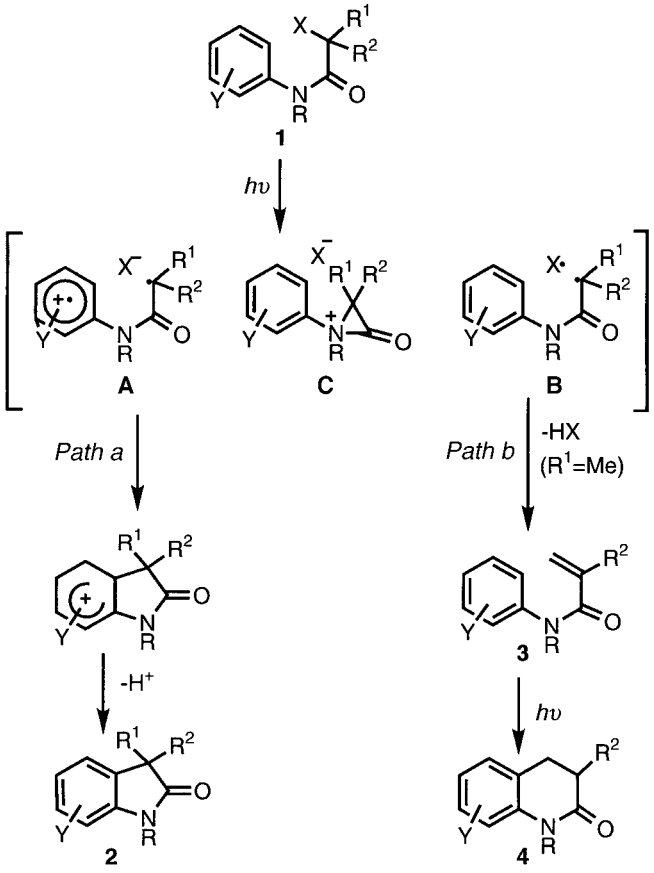
Entry		**1**				Yield [%] [a]
		R	R^1	X	Y	
1	**1n**	H	Ph	Cl	2,4-$(MeO)_2$	19
2	**1o**	Me	Ph	Cl	4-MeO	15
3	**1p**	Me	Ph	Cl	4-Cl	6
4	**1q**	Me	Ph	Cl	H	9
5	**1r**	Me	H	Cl	4-MeO	6
6 [b])						10
7 [c])						7
8	**1s**	Ph	H	Cl	H	39
9	**1t**	Ph	H	Br	H	26
10	**1u**	Ph	Ph	Cl	H	60
11 [d])						70
12	**1v**	Ph	Me	Cl	H	26
13 [e])						30

[a]) Yield of isolated product. [b]) In $MeCN/H_2O$ 6 : 1. [c]) In $MeCN/H_2O$ 3 : 4. [d]) In the presence of 1 mol-equiv. of CF_3SO_3Ag. [e]) In the presence of 1 mol-equiv. of $Mg(ClO_4)_2$.

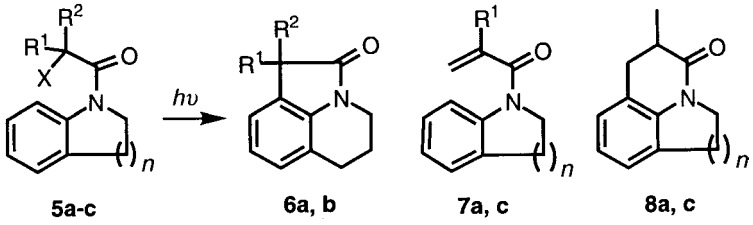
From these results, a plausible mechanism for the formation of photoproducts **2**–**4** can be deduced (*Scheme 4*). Excitation of the *N*-(2-halogenoalkanoyl) derivative **1** of aniline leads to the formation of the exciplex or the biradical ion intermediate **A** by an intramolecular electron transfer between the aromatic chromophore and the halogenoalkanoyl moiety, which readily cyclizes to the oxindole **2** with loss of a proton when R is an alkyl or phenyl substituent (*Path a*). The methacrylanilide **3** might be formed by a C-halogen bond homolysis (→ **B**), followed by dehydrohalogenation (*Path b*), and the formation of dihydrocarbostyril **4** can be best explained in terms of the conjugated 6-π-electron photocyclization of the enamide **3** [4b–c]. A possible alternative intermediate, the α-lactam **C**, is precluded since when **1r** was irradiated in $MeCN/H_2O$, no hydrolysis products of **C** could be detected [3b].

2.2. *Photochemical Reactions of* N*-(2-Halogenoalkanoyl) Derivatives* **5** *of Cyclic Amines.* Irradiation of *N*-(2-bromo-2-methylpropanoyl)tetrahydroquinoline **5a** in MeCN under the same conditions as described for **1a–e** gave the cyclization product **6a**, *N*-methacroyltetrahydroquinoline **7a**, and tricyclic lactam **8a** in 51, 13, and 8% yield, respectively, whereas the *N*-(2-chloro-2-phenylacetyl)tetrahydroquinoline **5b** furnished cyclization product **6b** in 37% yield (*Scheme 5* and *Table 3*). Under similar conditions, *N*-(2-bromo-2-methylpropanoyl)indoline **5c** did not cyclize, probably due to ring strain; only the dehydrohalogenation product **7c** (27%) and the tricyclic lactam **8c** (36%) were isolated. Longer irradiation of **5c** led to an increased yield (51%) of **8c**. The formation of the tricyclic lactams **8** can be understood in terms of a photochemical electrocyclic ring closure of enamides **7** [4], the latter being produced by photochemical elimination of hydrogen halide at the side chain of **5**.

Scheme 4



Scheme 5[a])



a) For R^1, R^2, and X, see *Table 3*.

Table 3. *Yield of Photoproducts* **6**–**8**

	5				Yield [%] [a])		
	n	R^1	R^2	X	**6**	**7**	**8**
5a	2	Me	Me	Br	51	13	8
5b	2	Ph	H	Cl	37	–	–
5c [b])	1	Me	Me	Br	–	27	36
5c [c])	1	Me	Me	Br	–	13	51

[a]) Yield of isolated product. [b]) Irradiation time 5 h. [c]) Irradiation time 10 h.

Experimental Part

General. Chromatography: silica gel *Wakogel C-300* and *Merck 60* for flash chromatography (FC). M.p. and b.p.: *Yanaco* micro melting-point apparatus (*MP-J3*) and *Shibata* glass tube oven distillation apparatus (*GTO-350RD*), resp.; uncorrected. 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 Me_4Si as an internal standard; δ in ppm, *J* in Hz.

Irradiation of N-*(2-Halogenoalkanoyl) Derivatives* **1** *and* **5**: *General Procedure.* A soln. of **1** or **5** (1–2 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 for 4–15 h at r.t. After evaporation, the residue was chromatographed (silica gel, toluene/AcOEt 50:1 → 4:1) to yield products **2**–**4** and **6**–**8**. The structures of **2f**,**k**–**m**,**q**,**s**–**v** were confirmed by direct comparison of their spectral data with those of previously described samples [5].

Irradiation of the methacrylanilide derivatives **3f**–**g**,**k**–**m** (1 mmol) in benzene or MeCN (70 ml) under the same conditions gave the dihydrocarbostyrils **4f**–**g**,**k**–**m** in 20–50% yield.

2-Methyl-N-*phenylprop-2-enamide* (= *Methacrylanilide*; **3a**). M.p. 84.5–86.5° ([4a]): 86°). IR (KBr): 3292, 1656, 1619, 1595, 1491, 1439, 759, 696. ^1H-NMR: 2.04 (*d*, *J* = 0.7, 3 H); 5.44 (br. *s*, 1 H); 5.78 (*d*, *J* = 0.7, 1 H); 7.08–7.14 (*m*, 1 H); 7.25–7.36 (*m*, 1 H); 7.54–7.60 (*m*, 2 H); 7.65 (br. *s*, 1 H). ^{13}C-NMR: 18.8; 119.8; 120.1; 124.4; 129.0; 137.8; 140.9; 166.7.

N-*(4-Chlorophenyl)-2-methylprop-2-enamide* (**3b**). B.p. 180°/3 Torr. IR (film): 3440, 1682, 1630, 1592, 1511, 1493, 790, 735. ^1H-NMR: 2.04 (br. *s*, 3 H); 5.46 (br. *s*, 1 H); 5.78 (*s*, 1 H); 7.28 (*d*, *J* = 8.6, 2 H); 7.51 (*d*, *J* = 8.6, 2 H); 7.63 (br. *s*, 1 H). ^{13}C-NMR: 18.7; 120.2; 121.3; 129.0; 136.4; 140.6; 166.6. Anal. calc. for $C_{10}H_{10}ClNO$ (195.65): C 61.38, H 5.12, N 7.16; found: C 61.42, H 5.03, N 6.89.

4-[(2-Methyl-1-oxoprop-2-enyl)amino]benzoic Acid Ethyl Ester (**3c**). M.p. 98–99°. IR (KBr): 3386, 1685, 1615, 1596, 1525, 1281, 852, 770. ^1H-NMR: 1.37 (*t*, *J* = 7.3, 3 H); 2.04 (*s*, 3 H); 4.34 (*q*, *J* = 7.3, 2 H); 5.47 (*d*, *J* = 1.3, 1 H); 5.82 (*s*, 1 H); 7.69 (*d*, *J* = 8.6, 2 H); 7.96–8.01 (*m*, 2 H); 8.19 (br. *s*, 1 H). ^{13}C-NMR: 14.2; 18.6; 60.8; 119.1; 120.4; 125.8; 130.5; 140.5; 142.0; 166.1; 166.9. Anal. calc. for $C_{13}H_{15}NO_3$ (233.26): C 66.93, H 6.48, N 6.01; found: C 66.91, H 6.53, N 5.81.

N-*(4-Methoxyphenyl)-2-methylprop-2-enamide* (**3d**). M.p. 86–87°. IR (KBr): 3313, 1654, 1625, 1514, 1251, 826. ^1H-NMR: 2.02 (*s*, 3 H); 3.77 (*s*, 3 H); 5.40 (*s*, 1 H); 5.76 (*s*, 1 H); 6.83 (*d*, *J* = 8.9, 2 H); 7.45 (*d*, *J* = 8.9, 2 H); 7.72 (br. *s*, 1 H). ^{13}C-NMR: 18.7; 55.3; 114.0; 119.6; 122.0; 130.9; 140.7; 156.4; 166.6. Anal. calc. for $C_{11}H_{13}NO_2$ (191.22): C 69.09, H 6.85, N 7.33; found: C 68.89, H 6.91, N 7.21.

N-*(2,4-Dimethoxyphenyl)-2-methylprop-2-enamide* (**3e**). M.p. 49.5–51°. IR (KBr): 3338, 1657, 1617, 1534, 1500, 1214, 830. ^1H-NMR: 2.06 (*d*, *J* = 1.0, 3 H); 3.79 (*s*, 3 H); 3.86 (*s*, 3 H); 5.42 (br. *s*, 1 H); 5.81 (*d*, *J* = 1.0, 1 H); 6.47–6.50 (*m*, 2 H); 8.02 (br. *s*, 1 H); 8.30 (*dd*, *J* = 1.0, 9.2, 1 H). ^{13}C-NMR: 18.6; 55.5; 55.7; 98.5; 103.7; 119.6; 120.5; 121.2; 140.8; 149.3; 156.3; 165.8. Anal. calc. for $C_{12}H_{15}NO_3$ (221.25): C 65.14, H 6.84, N 6.33; found: C 65.13, H 6.83, N 6.11.

N,*2-Dimethyl*-N-*phenylprop-2-enamide* (**3f**). M.p. 54–55°. IR (KBr): 1655, 1627, 1594, 1496, 1242, 783, 708. ^1H-NMR: 1.76 (br. *s*, 3 H); 3.35 (*s*, 3 H); 5.00 (*d*, *J* = 1.0, 1 H); 5.03 (br. *s*, *J* = 1.0); 7.12–7.16 (*m*, 2 H); 7.24–7.40 (*m*, 3 H). ^{13}C-NMR: 20.1; 37.5; 119.4; 126.5; 126.9; 129.2; 140.7; 144.6; 172.0. Anal. calc. for $C_{11}H_{13}NO$ (175.22): C 75.40, H 7.48, N 7.99; found: C 75.18, H 7.58, N 8.08.

*3,4-Dihydro-1,3-dimethylquinolin-2(1*H*)-one* (**4f**). B.p. 175°/3 Torr. IR (film): 1673, 1603, 1498, 1472, 1375, 1267, 755, 735, 688. ^1H-NMR: 1.25 (*d*, *J* = 6.6, 3 H); 2.60–2.73 (*m*, 2 H); 2.88–2.96 (*m*, 1 H); 3.35 (*s*, 3 H);

6.94 – 7.03 (*m*, 2 H); 7.21 – 7.28 (*m*, 1 H); 7.13 – 7.17 (*m*, 1 H). ^{13}C-NMR: 15.7; 29.8; 33.3; 35.3; 114.4; 122.6; 125.7; 127.3; 127.8; 140.4; 173.2. Anal. calc. for $C_{11}H_{13}NO$ (175.22): C 75.40, H 7.48, N 7.99; found: C 75.11, H 7.24, N 8.05.

*1,3-Dihydro-1,3,3,5-tetramethyl-2*H-*indol-2-one* (**2g**). M.p. 57 – 58°. IR (KBr): 1709, 1618, 1507, 1381, 1349, 800. ^{1}H-NMR: 1.35 (*s*, 6 H); 2.34 (*s*, 3 H); 3.19 (*s*, 3 H); 6.73 (*d*, *J* = 7.5, 1 H); 7.04 (*d*, *J* = 7.5, 2 H). ^{13}C-NMR: 21.1; 24.4; 26.2; 44.2; 107.7; 123.1; 127.8; 131.9; 135.9; 140.2; 181.3. Anal. calc. for $C_{12}H_{15}NO$ (189.25): C 76.15, H 7.99, N 7.40; found: C 75.89, H 8.08, N 7.21.

N,*2-Dimethyl*-N-*(4-methylphenyl)prop-2-enamide* (**3g**). B.p. 195°/2 Torr. IR (film): 1713, 1651, 1615, 1505, 1366, 1279, 809. ^{1}H-NMR: 1.76 (*s*, 3 H); 2.35 (*s*, 3 H); 3.32 (*s*, 3 H); 4.99 (br. *s*, 1 H); 5.02 (br. *s*, 1 H); 7.02 (*d*, *J* = 7.9, 1 H); 7.14 (*d*, *J* = 7.9, 2 H). ^{13}C-NMR: 20.3; 20.9; 37.6; 119.1; 126.2; 129.7; 136.7; 140.7; 141.9; 172.0. Anal. calc. for $C_{12}H_{15}NO$ (189.25): C 76.15, H 7.99, N 7.40; found: C 76.48, H 7.99, N 7.41.

*3,4-Dihydro-1,3,6-trimethylquinolin-2(1*H*)-one* (**4g**). M.p. 38 – 39°. IR (KBr) 1673, 1615, 1508, 1473, 1366, 1278, 812. ^{1}H-NMR: 1.24 (*d*, *J* = 6.6, 3 H); 2.30 (*s*, 3 H); 2.59 – 2.70 (*m*, 2 H); 2.83 – 2.91 (*m*, 1 H); 3.33 (*s*, 3 H); 6.85 (*d*, *J* = 8.3, 1 H); 6.97 – 7.15 (*m*, 3 H). ^{13}C-NMR: 15.7; 20.6; 29.8; 33.3; 35.6; 114.4; 127.7; 128.6; 129.5; 132.2; 136.9; 173.1. Anal. calc. for $C_{12}H_{15}NO$ (189.25): C 76.15, H 7.99, N 7.40; found: C 76.39, H 8.01, N 7.27.

*5-Chloro-1,3-dihydro-1,3,3-trimethyl-2*H-*indol-2-one* (**2h**). M.p. 88 – 89°. IR (KBr): 1708, 1610, 1491, 1344, 813. ^{1}H-NMR: 1.37 (*s*, 6 H); 3.21 (*s*, 3 H); 6.76 (*d*, *J* = 8.2, 1 H); 7.17 – 7.27 (*m*, 2 H). ^{13}C-NMR: 24.3; 26.3; 44.5; 108.9; 122.9; 127.6; 127.9; 137.5; 141.2; 180.8. Anal. calc. for $C_{11}H_{12}ClNO$ (209.67): C 63.01, H 5.77, N 6.68; found: C 62.95, H 5.84, N 6.59.

N-*(4-Chlorophenyl)*-N,*2-dimethylprop-2-enamide* (**3h**). M.p. *ca.* 37°. IR (KBr): 1739, 1651, 1590, 1494, 1455, 1380, 1229, 839. ^{1}H-NMR: 1.78 (*d*, *J* = 1.0, 3 H); 3.34 (*s*, 3 H); 4.99 (br. *s*, 1 H); 5.08 (br. *s*, 1 H); 7.09 (*d*, *J* = 8.6, 2 H); 7.33 (*d*, *J* = 8.6, 2 H). ^{13}C-NMR: 20.2; 37.6; 119.7; 127.7; 129.3; 132.5; 140.3; 143.1; 171.8. Anal. calc. for $C_{11}H_{12}ClNO$ (209.67): C 63.01, H 5.77, N 6.68; found: C 63.38, H 5.90, N 6.39.

*6-Chloro-3,4-dihydro-1,3-dimethylquinolin-2(1*H*)-one* (**4h**). M.p. 53 – 54°. IR (KBr): 1682, 1598, 1495, 1471, 1422, 1361, 1268, 812. ^{1}H-NMR: 1.25 (*d*, *J* = 6.6, 3 H); 2.57 – 2.72 (*m*, 2 H); 2.85 – 2.93 (*m*, 1 H); 3.33 (*s*, 3 H); 6.88 (*d*, *J* = 8.6, 1 H); 7.13 – 7.28 (*m*, 2 H). Anal. calc. for $C_{11}H_{12}ClNO$ (209.67): C 63.01, H 5.77, N 6.68; found: C 63.04, H 5.94, N 6.58.

4-[Methyl(2-methyl-1-oxoprop-2-enyl)amino]benzoic Acid Ethyl Ester (**3i**). B.p. 175°/3 Torr. IR (film): 1714, 1568, 1631, 1603, 1509, 1366, 1276, 1105, 775, 707. ^{1}H-NMR: 1.40 (*t*, *J* = 6.3, 3 H); 1.81 (*d*, *J* = 1.7, 3 H); 3.38 (*s*, 3 H); 4.34 – 4.44 (*m*, 2 H); 4.99 (br. *s*, 1 H); 5.00 (br. *s*, 1 H); 7.21 (*d*, *J* = 8.6, 2 H); 8.03 (*d*, *J* = 8.6, 2 H). ^{13}C-NMR: 14.1; 20.0; 37.2; 61.0; 119.9; 125.7; 128.4; 130.5; 140.2; 148.5; 165.6; 171.6. Anal. calc. for $C_{14}H_{17}NO_3$ (247.28): C 67.99, H 6.93, N 5.66; found: C 67.72, H 6.93, N 5.63.

1,2,3,4-Tetrahydro-1,3-dimethyl-2-oxoquinoline-6-carboxylic Acid Ethyl Ester (**4i**). M.p. 78 – 79°. IR (KBr): 1710, 1639, 1607, 1497, 1366, 1284, 1187, 1120, 1027, 769. ^{1}H-NMR: 1.27 (*d*, *J* = 6.6, 3 H); 1.40 (*t*, *J* = 7.3, 3 H); 2.60 – 2.76 (*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* = 2.0, 8.6, 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; 144.2; 166.1; 173.2. Anal. calc. for $C_{14}H_{17}NO_3$ (247.28); C 67.99, H 6.93, N 5.66; found: C 67.89, H 6.90, N 5.65.

*1,3-Dihydro-5-methoxy-1,3,3-trimethyl-2*H-*indol-2-one* (**2j**). Oil. IR (film): 1713, 1602, 1503, 1470, 1434, 1289, 1218, 1066, 805, 695. ^{1}H-NMR: 1.37 (*s*, 6 H); 3.20 (*s*, 3 H); 3.80 (*s*, 3 H); 6.73 – 6.84 (*m*, 3 H). ^{13}C-NMR: 24.3; 26.2; 44.6; 55.7; 108.2; 110.0; 111.5; 115.8; 137.2; 156.0; 181.0. Anal. calc. for $C_{12}H_{15}NO_2$ (205.25): C 70.22, H 7.37, N 6.82; found: C 70.14, H 7.54, N 6.58.

N-*(4-Methoxyphenyl)*-N,*2-dimethylprop-2-enamide* (**3j**). B.p. 190°/3 Torr. IR (film): 1651, 1632, 1513, 1454, 1366, 1290, 1248, 838. ^{1}H-NMR: 1.74 (*s*, 3 H); 3.30 (*s*, 3 H); 3.80 (*s*, 3 H); 4.99 (br. *s*, 1 H); 5.03 (be. *s*, 1 H); 6.85 (*d*, *J* = 6.9, 2 H); 7.05 (*d*, *J* = 6.9, 2 H). ^{13}C-NMR: 20.4; 37.8; 55.4; 114.4; 118.9; 127.8; 137.4; 140.9; 158.3; 172.1. Anal. calc. for $C_{12}H_{15}NO_2$ (205.25): C 70.22, H 7.37, N 6.82; found: C 70.57, H 7.54, N 6.73.

*3,4-Dihydro-6-methoxy-1,3-dimethylquinolin-2(1*H*)-one* (**4j**). Oil. IR (film): 1667, 1591, 1506, 1473, 1433, 1374, 1297, 1244, 1034, 807. ^{1}H-NMR: 1.24 (*d*, *J* = 6.3, 3 H); 2.58 – 2.71 (*m*, 2 H); 2.82 – 2.91 (*m*, 1 H); 3.33 (*s*, 3 H); 3.71 (*s*, 3 H); 6.72 – 6.90 (*m*, 3 H). Anal. calc. for $C_{12}H_{15}NO_2$ (205.25): C 70.22, H 7.37, N 6.82; found: C 70.47, H 7.54, N 6.73.

N-*Ethyl-2-methyl*-N-*phenylprop-2-enamide* (**3k**). B.p. 175°/3 Torr. IR (film): 1650, 1625, 1595, 1495, 1455, 1394, 1227, 766, 699. ^{1}H-NMR: 1.15 (*t*, *J* = 7.2, 3 H); 1.75 (br. *s*, 3 H); 3.38 (*q*, *J* = 7.3, 2 H); 4.89 – 5.0 (*m*, 2 H); 7.02 – 7.13 (*m*, 2 H); 7.19 – 7.39 (*m*, 3 H). ^{13}C-NMR: 12.9; 20,4; 44.6; 119.0; 127.1; 127.6; 129.2; 141.1; 142.9; 171.6. Anal. calc. for $C_{12}H_{15}NO$ (189.25): C 76.15, H 7.99, N 7.40; found: C 76.39, H 7.94, N 7.43.

*1-Ethyl-3,4-dihydro-3-methylquinolin-2(1*H*)-one* (**4k**). B.p. 190°/2 Torr. IR (film): 1665, 1601, 1493, 1460, 1384, 1243, 819, 756. ^{1}H-NMR: 1.25 (*t*, *J* = 6.9, 3 H); 1.25 (*d*, *J* = 6.6, 3 H); 2.57 – 2.68 (*m*, 2 H); 2.87 – 2.94 (*m*,

1 H); 3.88–4.06 (*m*, 2 H); 6.95–7.02 (*m*, 2 H); 7.14–7.27 (*m*, 2 H). Anal. calc. for $C_{12}H_{15}NO$ (189.25): C 76.15, H 7.99, N 7.40; found: C 76.15, H 7.84, N 7.37.

N-*Benzyl-2-methyl*-N-*phenylprop-2-enamide* (**3l**). M.p. 49–50°. IR (KBr): 1647, 1619, 1595, 1491, 1455, 1389, 756, 697. ^{1}H-NMR: 1.78 (*s*, 3 H); 4.97 (*s*, 2 H); 5.00–5.05 (*m*, 2 H); 6.97 (*dd*, *J* = 1.3, 7.6, 2 H); 7.19–7.30 (*m*, 7 H). ^{13}C-NMR: 20.4; 53.2; 119.4; 127.3; 127.4; 128.4; 129.0; 137.8; 140.7; 143.2; 171.8. Anal. calc. for $C_{17}H_{17}NO$ (251.31): C 81.24, H 6.84, N 5.57; found: C 81.13, H 6.84, N 5.53.

*1-Benzyl-3,4-dihydro-3-methylquinolin-2(1*H*)-one* (**4l**). B.p. 205°/2 Torr. IR (film): 1679, 1599, 1495, 1454, 1389, 1263, 1225, 756, 695. ^{1}H-NMR: 1.33 (*d*, *J* = 6.6, 3 H); 2.72–2.82 (*m*, 2 H); 2.94–3.01 (*m*, 1 H); 5.15 (*AB* ('*q*'), *J* = 6.2, 14.4, 2 H); 6.85 (*d*, *J* = 8.3, 1 H); 6.92–6.98 (*m*, 1 H); 7.01–7.36 (*m*, 8 H). ^{13}C-NMR: 15.7, 33.4; 35.6; 46.5; 115.4; 122.8; 125.7; 126.3; 127.0; 127.4; 128.0; 128.7; 137.2; 139.7; 173.3. Anal. calc. for $C_{17}H_{17}NO$ (251.31): C 81.24, H 6.84, N 5.57; found: C 81.59, H 6.63, N 5.60.

2-Methyl-N,N-*diphenylprop-2-enamide* (**3m**). The products **3m** and **4m** could not be completely separated by FC. Amide **3m** was prepared independently by the reaction of diphenylamine and methacryloyl chloride in the presence of Et_3N. M.p. 101–102°. IR (KBr): 1658, 1625, 1590, 1490, 1340, 1229, 759, 693. ^{1}H-NMR: 1.84 (br. *s*, 3 H); 5.17 (br. *s*, 1 H); 5.23 (*d*, *J* = 1.0, 1 H); 7.13–7.36 (*m*, 10 H). ^{13}C-NMR: 19.8; 120.9; 126.5; 127.1; 127.4; 129.0; 129.5; 141.1; 143.4; 171.9. Anal. calc. for $C_{16}H_{15}NO$ (237.29): C 80.98, H 6.37, N 5.90; found: C 81.09, H 6.23, N 5.84.

*3,4-Dihydro-3-methyl-1-phenylquinolin-2(1*H*)-one* (**4m**). M.p. (**3m**/**4m** 1:1) 77–80°. IR (KBr): 1686, 1662, 1620, 1590, 1491, 1458, 1328, 1268, 758, 696. ^{1}H-NMR: 1.33 (*d*, *J* = 6.6, 3 H); 2.76–2.91 (*m*, 2 H); 2.97–3.09 (*m*, 1 H); 6.33 (*dd*, *J* = 1.0, 7.6, 1 H); 6.92–7.05 (*m*, 2 H); 7.13–7.51 (*m*, 6 H). ^{13}C-NMR: 15.5; 33.5; 35.9; 172.9; signals for arom. and olef. C-atoms. Anal. (**3m**/**4m**) calc. for $C_{16}H_{15}NO$ (237.29): C 80.78, H 6.35, N 5.92; found: C 81.09, H 6.23, N 5.84.

*1,3-Dihydro-5,7-dimethoxy-3-phenyl-2*H-*indol-2-one* (**2n**). B.p. 175°/3 Torr. IR (film): 3640, 1700, 1507. ^{1}H-NMR: 3.75 (*s*, 3 H); 3.77 (*s*, 3 H); 5.11 (*s*, 1 H); 6.35–6.53 (*m*, 2 H); 7.24–7.59 (*m*, 5 H); 8.61 (br. *s*, 1 H). ^{13}C-NMR: 55.4; 55.7; 74.6; 98.6; 103.6; 120.4; 126.7; 128.5; 128.7; 139.4; 149.6; 156.6; 168.7.

*1,3-Dihydro-5-methoxy-1-methyl-3-phenyl-2*H-*indol-2-one* (**2o**). M.p. 118–119°. IR (KBr): 1730, 1601, 1495, 1455, 696. ^{1}H-NMR: 3.22 (*s*, 3 H); 3.75 (*s*, 3 H); 4.64 (*s*, 1 H); 6.77–6.88 (*m*, 3 H); 7.13–7.53 (*m*, 5 H). ^{13}C-NMR: 26.7; 52.6; 58.9; 172.5; signals for arom. C-atoms. Anal. calc. for $C_{16}H_{15}NO_2$ (253.29): C 75.88, H 5.97, N 5.53; found: C 75.50, H 5.89, N 5.40.

*5-Chloro-1,3-dihydro-1-methyl-3-phenyl-2*H-*indol-2-one* (**2p**). M.p. 131–132°. IR (KBr): 1701, 1601, 1490, 1350, 1341, 1099, 815, 728, 699. ^{1}H-NMR: 3.23 (*s*, 3 H); 4.59 (*s*, 1 H); 6.81 (*d*, *J* = 8.6, 1 H); 7.13–7.21 (*m*, 3 H); 7.25–7.38 (*m*, 4 H). ^{13}C-NMR: 26.7; 52.0; 109.0; 125.4; 127.8; 128.0; 128.3; 128.6; 129.0; 130.4; 135.8; 143.0; 175.4. Anal. calc. for $C_{15}H_{13}ClNO$ (258.73): C 69.90, H 4.46, N 5.44; found: C 69.61, H 4.72, N 5.44.

*1,3-Dihydro-5-methoxy-1-methyl-2*H-*indol-2-one* (**2r**). M.p. 45°. IR (KBr): 1701, 1560, 1457, 752, 705. ^{1}H-NMR: 3.17 (*s*, 3 H); 3.49 (*s*, 2 H); 3.78 (*s*, 3 H); 6.69–7.11 (*m*, 3 H). ^{13}C-NMR: 26.1; 36.0; 55.4; 108.1; 111.8; 112.0; 122.8; 138.1; 138.7; 155.7; 174.6.

*5,6-Dihydro-1,1-dimethyl-4*H-*pyrrolo[3,2,1-*ij*]quinolin-2(1*H*)-one* (**6a**). B.p. 185°/2 Torr. IR (film): 1712, 1627, 1603, 1485, 1387, 1352, 1240, 1169, 752. ^{1}H-NMR: 1.37 (*s*, 6 H); 2.03 (*quint.*, *J* = 5.9, 2 H); 2.78 (*t*, *J* = 5.9, 2 H); 3.71 (*t*, *J* = 5.9, 2 H); 6.90–7.05 (*m*, 3 H). ^{13}C-NMR: 21.1; 24.0; 24.5; 38.7; 45.4; 119.9; 120.0; 121.8; 126.3; 134.2; 138.2; 180.2. Anal. calc. for $C_{13}H_{15}NO$ (201.26): C 77.58, H 7.51, N 6.96; found: C 77.27, H 7.50, N 6.67.

1,2,3,4-Tetrahydro-1-(2-methyl-1-oxoprop-2-enyl)quinoline (**7a**). B.p. 167°/2 Torr. IR (film): 1650, 1493, 1452, 1381, 1294, 1224, 765. ^{1}H-NMR: 1.87 (br. *s*, 3 H); 1.98 (*quint.*, *J* = 6.6, 2 H); 2.76 (*t*, *J* = 6.6, 2 H); 3.80 (*t*, *J* = 6.6, 2 H); 5.14 (br. *s*, 1 H); 5.18 (br. *s*, 1 H); 7.02–7.28 (*m*, 4 H). ^{13}C-NMR: 19.8; 23.9; 26.7; 43.9; 119.0; 124.1; 124.7; 125.8; 128.3; 131.3; 138.9; 141.2; 171.4. Anal. calc. for $C_{13}H_{15}NO$ (201.26): C 77.58, H 7.51, N 6.96; found: C 77.45, H 7.48, N 6.75.

*1,2-Dihydro-2-methyl-3*H,*5*H-*pyrido[3,2,1-*ij*]quinolin-3-one* (**8a**). M.p. 49–50°. IR (KBr): 1667, 1596, 1474, 1380, 1256, 761. ^{1}H-NMR: 1.26 (*d*, *J* = 6.3, 3 H); 1.90–2.00 (*m*, 2 H); 2.65–2.75 (*m*, 2 H); 2.78–2.96 (*m*, 1 H); 3.66–3.81 (*m*, 2 H); 3.98–4.08 (*m*, 2 H); 6.88–7.08 (*m*, 3 H). ^{13}C-NMR: 15.7; 21.5; 27.2; 33.2; 35.2; 41.1; 122.2; 124.9; 125.0; 125.8; 127.6; 135.9; 172.4. Anal. calc. for $C_{13}H_{15}NO$ (201.26): C 77.58, H 7.51, N 6.96; found: C 77.86, H 7.26, N 7.05.

*5,6-Dihydro-1-phenyl-4*H-*pyrrolo[3,2,1-*ij*]quinolin-2(1*H*)-one* (**6b**). M.p. 124–125°. IR (KBr): 1706, 1625, 1600, 1480, 1345, 1240, 767. ^{1}H-NMR: 2.04 (*dd*, *J* = 0.9, 7.8, 2 H); 2.81 (*t*, *J* = 5.3, 2 H); 3.66–3.86 (*m*, 2 H); 4.61 (*s*, 1 H); 6.91–7.39 (*m*, 8 H). ^{13}C-NMR: 21.2; 24.6; 39.1; 52.9; 120.2; 122.1; 122.7; 127.3; 127.4; 128.4; 128.8; 136.5; 140.33; 174.9. Anal. calc. for $C_{17}H_{15}NO$ (249.30): C 81.90, H 6.06, N 5.62; found: C 81.76, H 6.16, N 5.39.

*2,3-Dihydro-1-(2-methyl-1-oxoprop-2-enyl)-1*H-*indole* (**7c**). M.p. 66.5–67°. IR (KBr): 1655, 1631, 1594, 1482, 1449, 1415, 1392, 1254, 772. ^{1}H-NMR: 2.04 (br. *s*, 3 H); 3.10 (*t*, *J* = 8.3, 2 H); 4.09 (*t*, *J* = 8.3, 2 H); 5.25 (br.

s, 1 H); 5.33 (*d*, *J* = 1.3, 1 H); 6.98–7.05 (*m*, 1 H); 7.15–7.27 (*m*, 3 H). ^{13}C-NMR: 19.8; 27.9; 49.7; 116.7; 123.9; 124.9; 127.3; 132.4; 141.8; 142.3; 169.9. Anal. calc. for $C_{12}H_{13}NO$ (187.23): C 76.97, H 7.00, N 7.48; found: C 76.75, H 7.05, N 7.34.

*1,2,5,6-Tetrahydro-5-methyl-4*H-*pyrrolo[3,2,1*-ij*]quinolin-4-one* (**8c**). B.p. 170°/2 Torr. IR (film): 1667, 1595, 1485, 1393, 764. ^{1}H-NMR: 1.29 (*d*, *J* = 6.6, 3 H); 2.63–2.77 (*m*, 2 H); 2.97–3.09 (*m*, 1 H); 3.14–3.22 (*m*, 2 H); 3.97–4.17 (*m*, 2 H); 6.88–7.08 (*m*, 3 H). ^{13}C-NMR: 16.2; 27.7; 32.5; 36.3; 45.2; 119.8; 123.0; 123.1; 125.3; 128.6; 141.0; 170.6. MS: 187 (100, M^+), 172 (14), 159 (23), 144 (35), 130 (21), 117 (12). Anal. calc. for $C_{12}H_{13}NO$ (187.23): C 76.97, H 7.00, N 7.48; found: C 76.82, H 7.16, N 7.25.

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