# A Novel Intramolecular Photocyclization of *N*-(2-Bromoalkanoyl) Derivatives of 2-Acylanilines *via* 1,8-Hydrogen Abstraction

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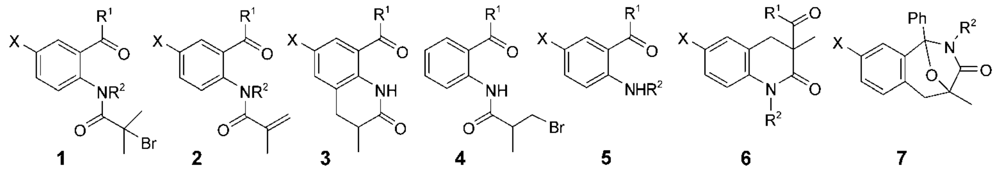
The photochemical reactions of different *N*-(2-acylphenyl)-2-bromo-2-methylpropanamides have been investigated. Irradiation of the *N*-unsubstituted anilides **1a** – **1c** gave the corresponding dehydrobromination, cyclization, and bromo-migration products **2**, **3**, and **4**, respectively (*Table 1*). Irradiation of the *N*-alkyl anilides **1e** – **1g** afforded the corresponding deacylation and cyclization products **5** and **6**, respectively, whereas irradiation of the *N*-alkyl anilides **1i** – **1k**, carrying 2-benzoyl groups on the aromatic rings, afforded the unexpected tricyclic lactams **7** (besides **2**, **5**, and **6**). The formation of the cyclization products **6** could be rationalized in terms of an electrocyclic ring closure of the 6π-electron-conjugated enamides **2** produced by dehydrobromination of **1**, followed by thermal 1,5-acyl migration (*Path B* in the *Scheme*). The formation of the bridged lactams **7** probably follows a mechanism involving the 1,7-diradical **8** generated by ζ-H-abstraction (1,8-H transfer) by an excited acyl O-atom (*Path A*).

**1. Introduction.** – Intramolecular H-abstraction reactions by an excited C=O group have been extensively investigated from synthetic and mechanistic points of view [1–3]. Generally, H-atoms in γ-position are abstracted most rapidly through a six-membered cyclic transition state (1,5-H transfer), as, *e.g.*, in *Norrish* type II reactions. This type of H-abstraction is greatly facilitated by favorable stereoelectronic and geometric conditions. However, carbonyl compounds that lack suitably aligned γ-H-atoms by reason of conformation or substitution can still undergo intramolecular reactions, *e.g.*, by abstraction of δ- or ε-H-atoms [2][3]. Abstraction from remote positions is a very attractive issue in the photochemistry of carbonyl groups [3–9], but these reactions are generally disfavored for medium- and large-sized cyclic transition states, both statistically and energetically. Elegant examples of remote H-abstractions induced by photoexcitation of aromatic carbonyl compounds have been reported by *Breslow* [10]. Long-distance *Norrish* type II abstractions *via* electron transfer have been observed in the photochemistry of imides [11], amino ketones [12], and sulfide-containing glyoxylates [13].

In this paper, we report a novel example of a photochemical ζ-H-abstraction (1,8-H transfer) effected by photocemical irradiation of different *N*-(2-acylphenyl)-2-bromo-2-methylpropanamides (anilides), and related compounds.

**2. Results and Discussion.** – Irradiation of *N*-(2-acetylphenyl)-2-bromo-2-methylpropanamide (**1a**) in MeCN with a high-pressure Hg lamp (with *Pyrex* filter) under Ar atmosphere at ambient temperature afforded the dehydrobromination product **2a**, the quinoline based cyclization product **3a**, and the bromo-migration product **4a** (*Table 1*).

Table 1. *Photoproducts of Compounds* **1a**–**1l**. Unless noted otherwise, irradiations were carried out for 1 h with a Hg lamp.



**1** **2** **3** **4** **5** **6** **7**

| Entry | | X | $R^1$ | $R^2$ | Solvent | Isolated yield [%] **2** | **3** | **4** | **5** | **6** | **7** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *1* | **1a** | H | Me | H | MeCN | 42 | 18 | 8 | – | – | – |
| *2*[a]) | **1a** | | | | MeCN | 33 | 39 | 15 | – | – | – |
| *3*[b]) | **1a** | | | | MeCN | 19 | 51 | 19 | – | – | – |
| *4* | **1b** | H | Ph | H | MeCN | 34 | trace | | – | – | – |
| *5*[b]) | **1b** | | | | MeCN | 71 | 7 | 6 | – | – | – |
| *6*[b]) | **1c** | Cl | Ph | H | MeCN | 48 | 24 | trace | – | – | – |
| *7*[b]) | **1d** | H | EtO | H | MeCN | 11 | 56 | – | trace | | |
| *8* | **1e** | H | Me | Me | MeCN | trace | – | – | 17 | 65 | – |
| *9* | **1e** | | | | Benzene | 8 | – | – | 17 | 38 | – |
| *10* | **1e** | | | | MeOH | trace | – | – | 6 | 24 | – |
| *11* | **1f** | H | Me | Et | MeCN | trace | – | – | 13 | 42 | – |
| *12* | **1g** | H | Me | Bn | MeCN | trace | – | – | 3 | 9 | – |
| *13* | **1h** | H | EtO | Me | MeCN | 6 | – | – | 13 | 41 | – |
| *14* | **1i** | H | Ph | Me | MeCN | 7 | – | – | 9 | 30 | 32 |
| *15*[c]) | **1i** | | | | MeCN | 34 | – | – | trace | 10 | 19 |
| *16* | **1i** | | | | Benzene | 16 | – | – | 14 | 28 | 28 |
| *17* | **1i** | | | | MeOH | 8 | – | – | 5 | 17 | 30 |
| *18* | **1j** | Cl | Ph | Me | MeCN | 15 | – | – | 19 | 30 | 35 |
| *19* | **1k** | H | Ph | Et | MeCN | 14 | – | – | 18 | 23 | 18 |
| *20* | **1l** | H | Ph | Bn | MeCN | 13 | – | – | 10 | – | – |

[a]) Irradiation time: 3 h. [b]) Irradiation time: 5 h. [c]) Irradiation time: 0.5 h.

We noticed that, with increasing irradiation time, the yields of both the 3,4-dihydroquinolin-2(1*H*)-one **3a** and the migration product **4a** increased on the expense of the dehydrobromination product **2a** (*Entries 1–3* in *Table 1*). Similar results were obtained when compounds **1b** and **1c** were irradiated under the same conditions. Irradiation of the EtOCO-substituted anilide **1d** basically gave only the elimination product **2d** and the cyclization product **3d**.

The *N*-alkylated anilides **1e**–**1g**, when irradiated under similar conditions, yielded the deacylation products **5e**–**5g**[1]) and the 3-acetyl-3,4-dihydroquinolin-2(1*H*)-ones **6e**–**6g** (*Entries 8–12*). When benzene instead of MeCN was used as solvent, the dehydrobromination product **2e** was obtained in low yield, together with **5e** and **6e**. Irradiation of **1h**, which carries an ester function on the benzene ring, yielded the products **2h**, **5h**, and **6h**. In contrast, irradiation of the *N*-substituted anilides **1i**–**1k** carrying benzoyl substituents on the aniline ring afforded the unexpected tricyclic lactams **7i**–**7k** (besides **2i**–**2k**, **5i**–**5k**, and **6i**–**6k**; *Entries 14–19*). Irradiation of the *N*-

[1]) A similar photodeacylation was observed in the photolysis of 2-(*N*-acylamino)benzophenones [14].

benzyl (Bn) analog **1l** led to a complex product mixture, from which **2l** and **5l** were isolated by flash chromatography. The structures of the above photoproducts were assigned on the basis of spectral and analytical evidence. In the case of **7i**, the assignment was further confirmed by X-ray crystal-structure analysis (*Figure*).

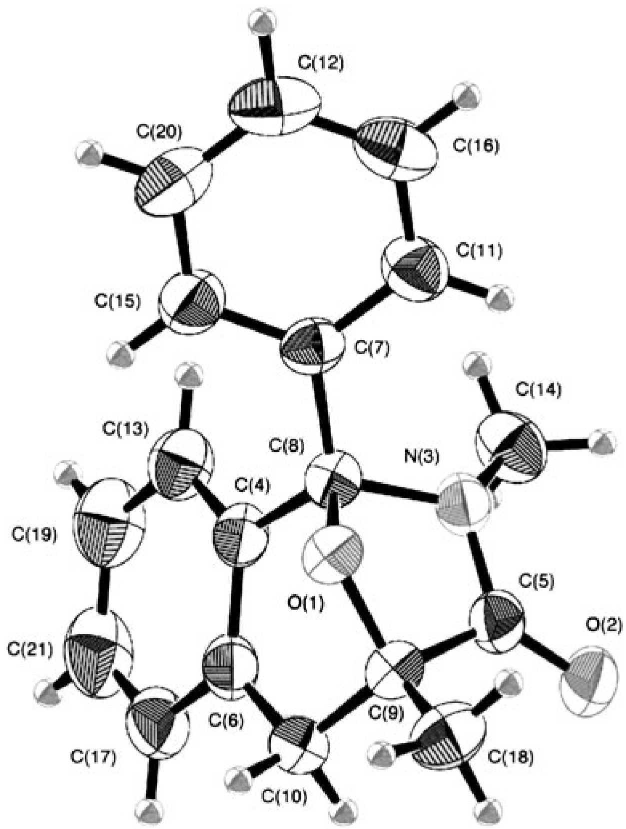
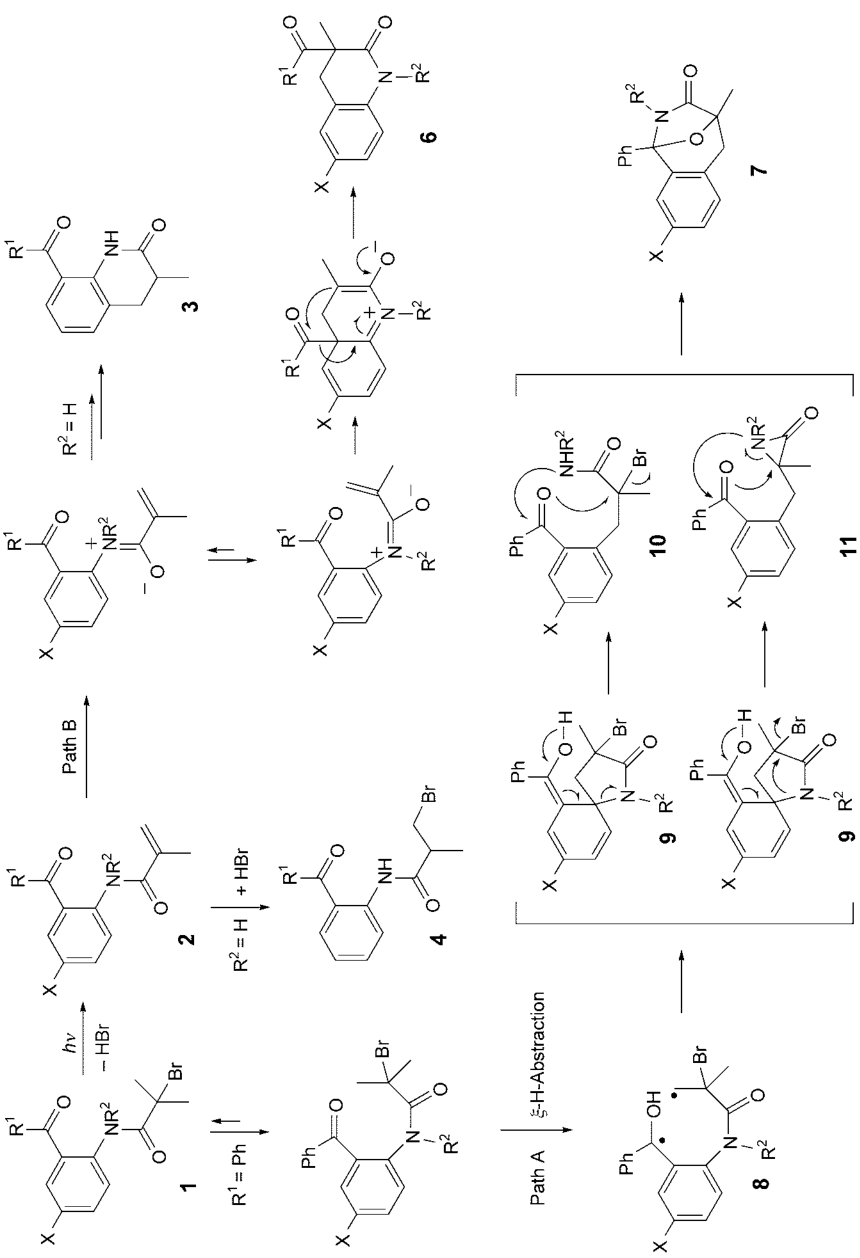



Figure. *X-Ray crystal structure of compound* **7i** (ORTEP view)

The formation of the cyclization products **3** can be rationalized in terms of an electrocyclic ring closure of **2** produced by C–Br bond homolysis, followed by dehydrobromination (*Path B* in the *Scheme*) [15e]. Thereby, for $R^2 = H$ (compounds **a**–**d**), cyclization occurred in *meta*-position to the acyl group due to strong H-bonding between the aniline NH and the acyl C=O groups. The formation of **6e**–**6k** can also be rationalized by ring closure of **2** (after change in enamide conformation), followed by a 1,5-acyl migration. Analogous electrocyclic reactions have been observed in the photochemistry of enamides [15][16]. The migration products **4** are probably formed by an elimination/addition sequence of HBr, compounds **2** acting as 'intermediates'.

The formation of the tricyclic lactams **7** can be rationalized by *Path A* in the *Scheme*. After amide bond isomerization, ζ-H-abstraction from the 2-methylpropanoyl group by the excited carbonyl O-atom of the acyl group on the aniline ring may take place *via*

*Scheme*


hν
– HBr
Path B
$R^1$ = Ph
$R^2$ = H
+ HBr
Path A
ξ-H-Abstraction
1
2
3
4
6
7
8
9
10
11

a nine-membered-ring transition state. This would result in formation of the hypothetical 1,7-biradical **8**. Subsequent ring closure would then yield the spirocyclic lactam **9**, which may undergo two kinds of ring opening, either to the amide **10** or to the aziridinone **11**. Finally, intramolecular ring closure affords **7**.

The photochemical behavior of the *N*-substituted anilides **1e** – **1g** and **1i** – **1k** reveals that the product distribution strongly depends on the acyl group on the aromatic ring, probably due to conformational and steric effects between the neighboring acyl and 2-bromo-2-methylpropanoyl groups. In the room-temperature $^1$H-NMR ($CDCl_3$) spectrum of **1i**, the signals for the two $\alpha$-Me groups and that of the NMe group at $\delta$(H) 1.75 (6 H) and 3.51 (3 H), respectively, were broadened. In $CD_3CN$, these signals were still broad, but became sharp on raising the temperature to *ca.* 60°. This strongly indicates that the conformation of **1i** is highly restricted at room temperature.

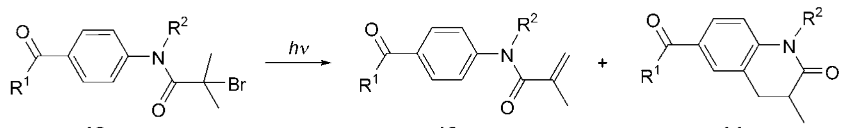
Irradiation of **1i** in $Me_3CN$ at 0° or at 60° led, in both cases, to the same products **2i**, **5i**, **6i**, and **7i**. However, their distribution depended on the temperature (*Table 2*). The yield of the H-abstraction product **7i** increased at lower temperature, the ratio (**2i** + **6i**)/**7i** changing from 1:2 to 1:0.37 upon raising the temperature from 0° to 60°.

Table 2. *Temperature-Dependent Distribution of Photoproducts in the Reaction of* **1i** *in MeCN Solution*

| Time | $T$ | Isolated yield [%] | | | | Ratio (**2** + **6**)/**7** |
|---|---|---|---|---|---|---|
| | | **2** | **5** | **6** | **7** | |
| 1 h | 25° | 7 | 9 | 30 | 32 | 1:0.86 |
| 1 h | 0° | 10 | 13 | 22 | 49 | 1:1.53 |
| 5 h | 0° | trace | 12 | 28 | 56 | 1:2.00 |
| 1 h | 60° | 31 | 22 | 18 | 18 | 1:0.37 |

Finally, we investigated analogous anilides with 4-acyl substituents on the benzene ring. However, irradiation of compounds **12a** – **12f** in MeCN gave only the corresponding dehydrobromination and cyclization products **13** and **14**, respectively (*Table 3*). Indolones were not detected [15e].

Table 3. *Yield of Photoproducts upon Irradiation of Substrates* **12a** – **12f**. Conditions: irradiation for 5 h in MeCN at 25°.




| | R¹ | R² | Isolated yield [%] | |
|---|---|---|---|---|
| | | | **13** | **14** |
| **12a** | Me | H | 19 | 33 |
| **12b** | Ph | H | 9 | 43 |
| **12c** | EtO | H | 40 | 5 |
| **12d** | Me | Me | 21 | 65 |
| **12e** | Ph | Me | 7 | 65 |
| **12f** | EtO | Me | 25 | 56 |

**Conclusions.** – Hydrogen-abstraction reactions by excited C=O O-atoms typically require favorable stereoelectronic and geometric conditions [2], long-range H-abstractions being rare [3]. Many of the known cases involve amino ketones, amino imides, or sulfide-containing imides, and proceed *via* electron-transfer reactions [11–13]. Our results concerning the photochemical reactions of 2-acyl-substituted anilides with an $\alpha$-Br substituent on the alkanoyl part demonstrate that long-range H-abstractions are feasible, given the molecules are present in favorable conformations.

## Experimental Part

*General*. Flash chromatography (FC): *Wakogel C-300* 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 $cm^{-1}$. $^1$H- and $^{13}$C-NMR Spectra: *Jeol JNM-EX 270* (270/67.5 MHz) or *Varian Gemini-200* (200/50 MHz) spectrometers; in $CDCl_3$, with $Me_4Si$ as internal standard; $\delta$ in ppm, *J* in Hz.

*General Procedure for the Photochemical Reactions of Anilides* **1** *or* **12**. A soln. of the anilide (1 mmol) in MeCN (70 ml), unless noted otherwise, was irradiated in a *Pyrex* tube with a high-pressure 500-W Hg lamp (*Halos EHP*; *Eikosha*) under Ar atmosphere for 0.5–5 h at r.t. After removal of the solvent, the residue was subjected to FC ($SiO_2$; toluene/AcOEt 19:1 → 4:1) to afford the photoproducts **2**–**7**, or **13** and **14** (*Tables 1* and *3*). The structures of the photoproducts **3a**, **3b**, **3d**, **5e**–**5l**, **6e**–**6k**, and **14a**–**14f** were confirmed by comparison of their spectral data with those given in the literature [16].

N-*(2-Acetylphenyl)-2-methylprop-2-enamide* (**2a**). B.p. 155°/3 Torr. IR (film): 3225, 1685, 1630. $^1$H-NMR: 2.12 (*s*, 3 H); 2.68 (*s*, 3 H); 5.54 (br. *s*, 1 H); 6.03 (*s*, 1 H); 7.09–7.16 (*m*, 1 H); 7.54–7.60 (*m*, 1 H); 7.89–7.94 (*m*, 1 H); 8.83–8.87 (*m*, 1 H); 12.21 (br. *s*, 1 H). $^{13}$C-NMR: 19.0; 29.0; 121.1; 122.3; 122.9; 133.2; 135.7; 141.0; 141.6; 167.6; 203.4. Anal. calc. for $C_{12}H_{13}NO_2$: C 70.91, H 6.45, N 6.89; found: C 70.95, H 6.24, N 6.60.

N-*(2-Acetylphenyl)-3-bromo-2-methylpropanamide* (**4a**). M.p. 56.5–58.0°. IR (KBr): 3204, 1696, 1651. $^1$H-NMR: 1.42 (*d*, *J* = 6.9, 3 H); 2.68 (*s*, 3 H); 2.87–2.96 (*m*, 1 H); 2.91 (*dd*, *J* = 7.3, 13.2, 1 H); 3.71 (*dd*, *J* = 7.3, 9.9, 1 H); 7.51 (*dt*, *J* = 1.0, 8.6, 1 H); 7.57 (*dt*, *J* = 1.3, 7.3, 1 H); 7.92 (*dd*, *J* = 1.7, 7.9, 1 H); 8.78 (*dd*, *J* = 1.0, 8.6, 1 H); 11.92 (br. *s*, 1 H). Anal. calc. for $C_{12}H_{14}BrNO_2$: C 50.72, H 4.97, N 4.93; found: C 50.96, H 4.99, N 4.87.

N-*(2-Benzoylphenyl)-2-methylprop-2-enamide* (**2b**). Compounds **2b** and **4b** could not be completely separated by FC. Thus, for spectral analysis, **2b** was prepared independently by reaction of 2-amino-benzophenone and methacryloyl chloride in the presence of $Et_3N$. B.p. 225°/3 Torr. IR (film): 3301, 1681, 1632. $^1$H-NMR: 2.13 (*s*, 3 H); 5.54 (*d*, *J* = 0.7, 1 H); 6.04 (*s*, 1 H); 7.06–7.13 (*m*, 1 H); 7.45–7.71 (*m*, 7 H); 8.74–8.79 (*m*, 1 H); 11.47 (br. *s*, 1 H). $^{13}$C-NMR: 18.5; 121.3; 121.3; 122.0; 123.0; 128.2; 129.8; 132.3; 133.8; 134.3; 138.7; 140.3; 140.8; 166.8; 199.9. Anal. calc. for $C_{17}H_{15}NO_2$: C 76.96, H 5.70, N 5.28; found: C 76.61, H 5.85, N 5.12.

N-*(2-Benzoylphenyl)-3-bromo-2-methylpropanamide* (**4b**). $^1$H-NMR: 1.42 (*d*, *J* = 6.9, 3 H); 2.84–2.95 (*m*, 1 H); 3.51 (*dd*, *J* = 5.6, 9.9, 1 H); 3.71 (*dd*, *J* = 7.6, 9.9, 1 H); 7.06–7.14 (*m*, 1 H); 7.45–7.72 (*m*, 7 H); 8.75 (*d*, *J* = 1.3, 1 H); 11.09 (br. *s*, 1 H). $^{13}$C-NMR (non-aromatic signals only): 17.0; 34.4; 45.4; 176.2; 199.2.

N-*(2-Benzoyl-4-chlorophenyl)-2-methylprop-2-enamide* (**2c**). The products **2c** and **3c** could not be completely separated by FC. Thus, **2c** was prepared independently by reaction of 2-amino-4-chlorobenzophenone and methacryloyl chloride in the presence of $Et_3N$. M.p. 92–93°. IR (KBr): 3277, 1693, 1629. $^1$H-NMR: 2.11 (*s*, 3 H); 5.55 (*s*, 1 H); 6.02 (*s*, 1 H); 7.15–7.28 (*m*, 2 H); 7.39–7.72 (*m*, 5 H); 8.74 (*d*, *J* = 8.9, 1 H); 11.29 (br. *s*, 1 H). $^{13}$C-NMR (non-aromatic and non-olefinic signals only): 18.8; 167.0; 199.0. Anal. calc. for $C_{17}H_{14}ClNO_2$: C 68.11, H 4.67, N 4.67; found: 68.00, H 4.43, N 4.35.

*8-Benzoyl-6-chloro-3,4-dihydro-3-methylquinolin-2(1*H*)-one* (**3c**). $^1$H-NMR: 1.40 (*d*, *J* = 6.9, 3 H); 2.89 (*dd*, *J* = 7.3, 12.9, 1 H); 3.46–3.53 (*m*, 1 H); 3.65–3.72 (*m*, 1 H); 7.15–7.28 (*m*, 2 H); 7.49–7.72 (*m*, 4 H); 8.65 (*d*, *J* = 9.5, 1 H); 10.88 (br. *s*, 1 H). $^{13}$C-NMR (non-aromatic signals only): 17.4; 34.6; 45.7; 172.6; 198.8. Anal. calc. for $C_{17}H_{14}ClNO_2$ (mixture of **2c** and **3c**): C 68.11, H 4.67, N 4.67; found: 68.32, H 4.62, N 4.92.

*Ethyl 2-[(2-Methyl-1-oxoprop-2-enyl)amino]benzoate* (**2d**). M.p. 43.0–44.5°. IR (KBr): 3254, 1684. $^1$H-NMR: 1.42 (*t*, *J* = 7.1, 3 H); 2.17 (*s*, 3 H); 4,39 (*q*, *J* = 7.1, 2 H); 5.53 (*s*, 1 H); 6.00 (*s*, 1 H); 7.05–7.12 (*m*, 1 H); 7.52–7.59 (*m*, 1 H); 8.04–8.09 (*m*, 1 H); 8.79–8.87 (*m*, 1 H); 11.62 (br. *s*, 1 H). $^{13}$C-NMR: 14.1; 18.5; 61.3; 115.3; 120.3; 121.0; 122.4; 130.8; 134.5; 130.7; 141.6; 144.7; 166.7; 168.4. Anal. calc. for $C_{13}H_{15}NO_3$: C 66.93, H 6.48, N 5.84; found: C 66.62, H 6.53, N 5.84.

N-*(2-Acetylphenyl)*-N-*methyl-2-methylprop-2-enamide* (**2e**). B.p. 165°/3 Torr. IR (film): 1691, 1649. $^1$H-NMR: 1.69 (br. *s*, 3 H); 2.53 (*s*, 3 H); 3.31 (br. *s*, 3 H); 4.90 (br. *s*, 1 H); 4.99 (br. *s*, 1 H); 7.22–7.30 (*m*, 1 H); 7.35 – 7.41 (*m*, 1 H); 7.49 – 7.52 (*m*, 1 H); 7.55 – 7.69 (*m*, 1 H). $^{13}$C-NMR: 19.3; 28.4; 37.2; 115.3; 119.3; 127,1; 128.8; 129.5; 132.2; 135.1; 139.7; 170.7; 198.3. Anal. calc. for $C_{13}H_{15}NO_2$: C 71.86, H 6.96, N 6.45; found: C 71.61, H 6.81, N 6.15.

*Ethyl 2-[Methyl(2-methyl-1-oxoprop-2-enyl)amino]benzoate* (**2h**). M.p. 86 – 87°. IR (KBr): 1715, 1620. $^1$H-NMR: 1.38 (*t*, *J* = 6.9, 3 H); 1.70 (br. *s*, 3 H); 3.30 (br. *s*, 3 H); 4.30 – 4.39 (*m*, 2 H); 4.90 (br. *s*, 1 H); 4.96 (br. *s*, 1 H); 7.21 – 7.27 (*m*, 1 H); 7.34 – 7.41 (*m*, 1 H); 7.50 – 7.57 (*m*, 1 H); 7.93 – 7.97 (*m*, 1 H). $^{13}$C-NMR: 14.1; 20.0; 37.6; 61.5; 119.3; 127.6; 128.6; 129.5; 131.8; 133.0; 140.3; 144.5; 165.5; 171.5. Anal. calc. for $C_{14}H_{17}NO_3$: C 67.99, H 6.93, N 5.66; found: C 67.92, H 7.01, N 5.60.

N-*(2-Benzoylphenyl)*-N-*methyl-2-methylprop-2-enamide* (**2i**). M.p. 74 – 75°. IR (KBr): 1664, 1621. $^1$H-NMR: 1.61 (br. *s*, 3 H); 3.23 (br. *s*, 3 H); 4.96 (br. *s*, 1 H); 5.03 (br. *s*, 1 H); 7.27 – 7.62 (*m*, 7 H); 7.77 – 7.80 (*m*, 2 H). Anal. calc. for $C_{18}H_{17}NO_2$: C 77.32, H 6.39, N 5.01; found: C 77.59, H 6.31, N 4.91.

*1,2,4,5-Tetrahydro-2,4-dimethyl-1-phenyl-1,4-epoxy-2-benzazepin-3(3*H*)-one* (**7i**). M.p. 122.5 – 124.0°. IR (KBr): 1713. $^1$H-NMR: 1.63 (*s*, 3 H); 2.65 (*s*, 3 H); 2.92 (*d*, *J* = 17.2, 1 H); 3.12 (*d*, *J* = 17.2, 1 H); 7.01 (*dd*, *J* = 1.0, 7.6, 1 H); 7.12 – 7.19 (*m*, 2 H); 7.25 – 7.33 (*m*, 1 H); 7.46 – 7.57 (*m*, 5 H). $^{13}$C-NMR. 21.1; 28.0; 35.8; 80.2; 95.8; 125.1; 126.1; 128.6; 128.7; 129.6; 130.3; 133.6; 134.5; 176.8. Anal. calc. for $C_{18}H_{17}NO_2$: C 77.39, H 6.13, N 5.01; found: C 77.40, H 6.27, N 4.95.

N-*(2-Benzoyl-4-chlorophenyl)*-N-*methyl-2-methylprop-2-enamide* (**2j**). B.p. 210°/3 Torr. IR (film): 1667, 1650, 1630. $^1$H-NMR: 1.70 (br. *s*, 3 H); 3.23 (br. *s*, 3 H); 4.92 (br. *s*, 1 H); 5.07 (*s*, 1 H); 7.25 – 7.59 (*m*, 6 H); 7.77 – 7.81 (*m*, 2 H). Anal. calc. for $C_{18}H_{16}ClNO_2$: C 68.90, H 5.10, N 4.47; found: C 69.00, H 5.34, N 4.35.

*8-Chloro-1,2,4,5-tetrahydro-2,4-dimethyl-1-phenyl-1,4-epoxy-2-benzazepin-3(3*H*)-one* (**7j**). M.p. 153 – 154°. IR: 1720. $^1$H-NMR: 1.62 (*s*, 3 H); 2.68 (*s*, 3 H); 2.88 (*d*, *J* = 17.2, 1 H); 3.06 (*d*, *J* = 17.2, 1 H); 7.01 (*d*, *J* = 2.0, 1 H); 7.18 – 7.23 (*m*, 1 H); 7.25 – 7.31 (*m*, 1 H); 7.51 (*s*, 5 H). $^{13}$C-NMR: 21.3; 29.4; 35.6; 80.3; 126.4; 128.8; 129.1; 129.3; 130.2; 132.0; 132.4; 134.2; 174.0. Anal. calc. for $C_{18}H_{16}ClNO_2$: C 68.90, H 5.10, N 4.47; found: C 68.76, H 5.20, N 4.39.

N-*(2-Benzoylphenyl)*-N-*ethyl-2-methylprop-2-enamide* (**2k**). M.p. 106 – 107°. IR: 1660, 1622. $^1$H-NMR: 1.42 (*t*, *J* = 7.3, 3 H); 1.72 (br. *s*, 3 H); 3.24 (br. *s*, 1 H); 4 20 (br. *s*, 1 H); 7.14 – 7.57 (*m*, 7 H); 7.78 (br. *d*, *J* = 7.3, 2 H). Anal. calc. for $C_{19}H_{19}NO_2$: C 77.79, H 6.53, N 4.77; found: C 77.65, H 6.60, N 4.60.

*1,2,4,5-Tetrahydro-2-ethyl-4-methyl-1-phenyl-1,4-epoxy-2-benzazepin-3(3*H*)-one* (**7k**). M.p. 126.5 – 127.0°. IR (KBr): 1712. $^1$H-NMR: 0.98 (*t*, *J* = 7.3, 3 H); 1.61 (*s*, 3 H); 2.92 (*d*, *J* = 17.1, 1 H); 3.10 (*d*, *J* = 17.2, 1 H); 3.18 (*q*, *J* = 7.3, 2 H); 7.01 – 7.35 (*m*, 4 H); 7.46 – 7.61 (*m*, 5 H). $^{13}$C-NMR: 12.0; 21.0; 35.7; 38.3; 79.8; 95.9; 125.3; 125.6; 128.6; 129.6; 130.1; 133.6; 134.9; 136.4; 177.0. Anal. calc. for $C_{19}H_{19}NO_2$: C 77.79, H 6.53, N 4.77; found: C, 77.61, H 6.52 N 4.97.

N-*(2-Benzoylphenyl)-2-methyl*-N-*phenylprop-2-enamide* (**2l**). M.p. 135 – 136°. IR (KBr): 1667. $^1$H-NMR: 1.73 (*s*, 3 H); 4.13 (br. *s*, 1 H); 5.03 (br. *s*, 2 H); 5.56 (br. *s*, 1 H); 6.95 (*d*, *J* = 7.6, 1 H); 7.21 – 7.60 (*m*, 12 H); 7.77 (*d*, *J* = 7.6, 1 H). Anal. calc. for $C_{24}H_{21}NO_2$: C 81.10. H 5.96, N 3.13; found: C 80.87, H 5.87, N 4.10.

*N-(4-Acetylphenyl)-2-methylprop-2-enamide* (**13a**). M.p. 124 – 126°. IR (KBr): 3326, 1672, 1627. $^1$H-NMR: 2.07 (*s*, 3 H); 2.58 (*s*, 3 H); 5.51 (*s*, 1 H); 5.85 (*s*, 1 H); 6.73 (*d*, *J* = 8.6, 2 H); 7.94 (*d*, *J* = 8.6, 1 H); 8.08 (br. *s*, 1 H). $^{13}$C-NMR: 18.1; 36.1; 118.7; 120.1; 129.1; 132.3; 149.0; 141.6; 166.3; 196.3. Anal. calc. for $C_{12}H_{13}NO_2$: C 70.91, H 6.45, N 6.89; found: C 70.71, H 6.55, N 7.12.

N-*(4-Benzoylphenyl)-2-methylprop-2-enamide* (**13b**). M.p. 111.5 – 113°. IR (KBr): 3323, 1684, 1643. $^1$H-NMR: 2.06 (*s*, 3 H); 5,49 (*s*, 1 H); 5.83 (*s*, 1 H); 7.11 – 7.29 (*m*, 2 H); 7.39 – 7.62 (*m*, 3 H); 7.66 – 7.84 (*m*, 4 H); 8.09 (br. *s*, 1 H). $^{13}$C-NMR: 18.1; 113.0; 118.5; 120.0; 127.7; 129.3; 131.7; 132.4; 137.2; 140.2; 141.3; 166.3; 195.2 Anal. calc. for $C_{17}H_{15}NO_2$: C 76.96, H 5.70, N 5.28; found: C 76.74, H 5.85, N 5.21.

*Ethyl 4-[(2-Methyl-1-oxoprop-2-enyl)amino]benzoate* (**13c**). M.p. 116 – 118°. IR (KBr): 1719, 1671. $^1$H-NMR: 1.38 (*t*, *J* = 7.3, 3 H); 2.05 (*s*, 3 H); 4.29 – 4.39 (*m*, 2 H); 5.48 (*s*, 1 H); 5.81 (*s*, 1 H); 7.67 (*d*, *J* = 7.9, 2 H); 8.01 (*d*, *J* = 7.79, 2 H). $^{13}$C-NMR: 13.9; 18.2; 60.4; 113.3; 118.7; 120.0; 127.9; 130.3; 131.1; 140.2; 141.6; 165.7; 166.3. Anal. calc. for $C_{13}H_{15}NO_3$: C 66.93, H 6.48, N 6.01; found: C 67.01, H 6.62, N 5.93.

N-*(4-Acetylphenyl)*-N-*methyl-2-methylprop-2-enamide* (**13d**). B.p. 165°/3 Torr. IR (film): 1681, 1657, 1630. $^1$H-NMR: 1.82 (*s*, 3 H); 2.61 (*s*, 3 H); 3.39 (*s*, 3 H); 5.01 (*s*, 1 H); 5.10 (*s*, 1 H); 7.24 (*d*, *J* = 6.8, 3 H); 7.51 (*d*, *J* = 6.8, 2 H). $^{13}$C-NMR: 19.5; 26.0; 36.8; 119.6; 125.4; 128.8; 134.4; 139.7; 148.3; 171.2; 196.3. Anal. calc. for $C_{13}H_{15}NO_2$: C 71.86, H 6.96, N 6.45; found: C 72.00, H 7.17, N 6.41.

N-*(4-Benzoylphenyl)*-N-*methyl-2-methylprop-2-enamide* (**13e**). M.p. 85 – 86°. IR (KBr): 1653. $^1$H-NMR: 1.84 (*s*, 3 H); 3.42 (*s*, 3 H); 5.04 (*s*, 1 H); 5.13 (*s*, 1 H); 7.26 (*d*, *J* = 8.4, 2 H); 7.45 – 7.66 (*m*, 3 H); 7.77 – 7.85 (*m*, 4 H). $^{13}$C-NMR: 19.6; 36.9; 119.7; 125.2; 127.8; 129.3; 130.6; 132.9; 134.9; 136.7; 139.7; 147.8; 171.3; 195.0. Anal. calc. for $C_{18}H_{17}NO_2$: C 77.39, H 6.13, N 5.01; found: C 77.50, H 6.24, N 4.90.

*Ethyl 4-[Methyl(2-methyl-1-oxoprop-2-enyl)amino]benzoate* (**13f**). B.p 175°/3 Torr. IR (film): 1714, 1658, 1631. $^1$H-NMR: 1.40 (*t*, *J* = 7.3, 3 H); 1.81 (*d*, *J* = 1.0, 3 H); 3.38 (*s*, 3 H); 4.28 (*q*, *J* = 7.3, 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: 14.2; 20.0; 37.3; 61.0; 120.0; 125.7; 128.5; 130.5; 140.2; 148.6; 165.6; 171.7. Anal. calc. for $C_{14}H_{17}NO_3$: C 67.99, H 6.93, N 5.66; found: C 68.22, H 6.93, N 5.63.

*X-Ray Crystal-Structure Analysis.* A crystal of **7i** was grown from $CH_2Cl_2$/hexane. The intensity data were collected on a *Mac Science MXC-18* diffractometer, with graphite-monochromated Cu$K_\alpha$ radiation ($\lambda$ = 1.54178 Å), in the $\omega - 2\theta$ scan mode ($2\theta < 69.99°$). Out of 3041 total reflections, 2005 reflections with intensities greater than $3\sigma(I)$ were used. No absorption corrections were made. The structure was 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 for **7i**: formula, $C_{18}H_{17}O_2N$; $M_r$ 279.339; $V = 2960(2)$ Å; $Z = 8$; $D_x = 1.254$ g cm$^{-3}$; orthorhombic system, space group *Pbca*; $a = 15.962(4)$, $b = 21.813(8)$, $c = 8.501(2)$ Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 90.00°$; $V = 2960(2)$ Å$^3$; $R = 0.092$, $Rw_2 = 0.089$.

The crystallographic data (excluding structure factors) for **7i** have been deposited with the *Cambridge Crystallographic Data Centre* (*CCDC*) as supplementary publication number CCDC-264914. Copies of the data can be obtained, free charge, by application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: data_request@ccdc.cam.ac.uk), or *via* the internet (http://www.ccdc.cam.ac.uk/products/csd/request).

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