

## Photochemical Reactions of *N*-Benzoylformyl $\alpha,\beta$ -Unsaturated Amides

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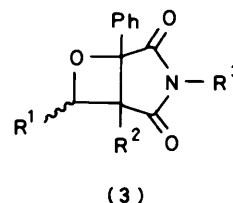
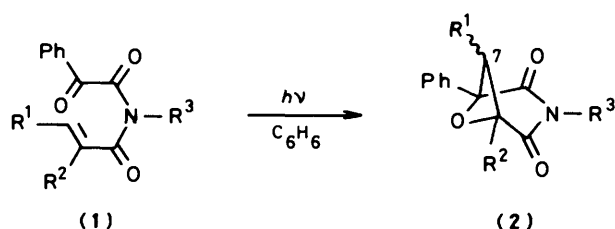
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*N*-Benzoylformyl  $\alpha,\beta$ -unsaturated amides (**1**) underwent photochemical intramolecular [2 + 2]cycloaddition to produce bicyclic imides, 1-phenyl-6-oxa-3-azabicyclo[3.1.1]pentane-2,4-diones (**2**), in good yield. Quantum yields for reaction of *N*-benzyl, *N*-(*p*-tolyl), and *N*-(2,6-xylyl)-*N*-benzoylformylmethacrylamide were 0.56, 0.04, and 0.10, respectively.

[2 + 2]Photocycloaddition of carbonyl compounds to olefins to give oxetanes is the well known Paterno-Büchi reaction, and is an important synthetic method for carbon-carbon bond formation. This process has been extensively studied from both theoretical and experimental points of view.<sup>1</sup> In relation to our studies of the photochemistry of  $\alpha$ -keto amides<sup>2</sup> and  $\alpha$ -keto imides,<sup>3</sup> now we report an oxetane-formation reaction involving intramolecular [2 + 2]photocycloaddition<sup>4</sup> of *N*-benzoylformyl  $\alpha,\beta$ -unsaturated amides.† The Paterno-Büchi reaction of  $\alpha$ -diketones with electron-rich olefins has been studied.<sup>5</sup> Furthermore, it is known that  $\alpha$ -diketones do not undergo intermolecular [2 + 2]cycloaddition with electron-deficient olefins.<sup>6</sup> The reaction reported herein thus provides the first example of  $\alpha$ -dicarbonyl compounds reacting with electron-deficient olefins.

two singlets, at  $\delta_c$  82.5 and 84.3 p.p.m., assigned to C-1 and C-5. The i.r. spectrum showed characteristic absorptions at 1 695s and 1 750m  $\text{cm}^{-1}$  due to C=O groups in six-membered cyclic imides. I.r. spectra of six-membered imides contain two typical carbonyl stretching bands at 1 695–1 710s and 1 750–1 755m  $\text{cm}^{-1}$ , whereas in the five-membered imides these bands are at 1 715–1 720s and 1 775–1 780m  $\text{cm}^{-1}$ , respectively.<sup>7</sup> Therefore, the other possible structure for the product, the oxetane-fused five-membered cyclic imide (**3a**), could be excluded. Photolysis of other *N*-benzoylformylmethacrylamides (**1b–f**) under the same conditions gave the corresponding bicyclic imides (**2b–f**) in excellent yields. Photolysis of crotonoyl and cinnamoyl derivatives (**1g**) and (**1i**) gave similar results and the corresponding bicyclic imides (**2g**) and (**2i**) were obtained as mixtures of two stereoisomers (*ca.* 2:1) (see Table, footnote). However, the imides (**1h**) and (**1j**) were inert to photolysis.

Table. Photolysis of glyoxylamides (**1**)



	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Yield (%)
a	H	Me	Me	94
b	H	Me	Et	89
c	H	Me	Pr <sup>i</sup>	96
d	H	Me	CH <sub>2</sub> Ph	>99
e	H	Me	<i>p</i> -tolyl	50
f	H	Me	2,6-xylyl	>99
g	Me	H	Pr <sup>i</sup>	48 <sup>a</sup>
h	Me	H	<i>p</i> -tolyl	( <b>1h</b> ) recovered
i	Ph	H	Pr <sup>i</sup>	44 <sup>a</sup>
j	Ph	H	<i>p</i> -tolyl	( <b>1j</b> ) recovered

<sup>a</sup> (**2g**) And (**2i**) are mixtures of stereoisomers (*syn* and *anti* at C-7).

### Results and Discussion

When *N*-benzoylformyl-*N*-methylmethacrylamide (**1a**) was irradiated under argon with a high-pressure mercury lamp, 1,3-dimethyl-5-phenyl-6-oxa-3-azabicyclo[3.1.1]heptane-2,4-dione (**2a**) was obtained in 94% yield as the sole product. The structure of compound (**2a**) was determined on the basis of elemental analysis and spectral data. The <sup>13</sup>C n.m.r. spectrum exhibited

Quantum yields, sensitization and quenching experiments were carried out. *N*-Benzoylformyl-*N*-benzylmethacrylamide (**1d**) showed a u.v. spectrum with maxima at 214 ( $\epsilon$  15 200), 257 (12 200), and 360 nm (30). When the imide (**1d**) was irradiated at the  $\pi\pi^*$  band (>366 nm) selectively, the photoreaction proceeded efficiently. The photoreaction of (**1d**) to give compound (**2d**) was sensitized by benzophenone ( $E_T$  69 kcal mol<sup>-1</sup>). The addition of *trans*-stilbene or piperylene (penta-1,3-diene) did not lead to significant quenching of the rate of the production of compound (**2d**). The failure to quench the reaction makes it impossible for us to perform the usual kinetic studies, and it was difficult to determine the multiplicities of the reactive excited states in the direct photolysis because both singlet and rapid triplet reactions are possible from the available data. Quantum yield reactions of glyoxylamides (**1d–f**) to afford products (**2d–f**) were 0.56, 0.04, and 0.10, respectively. Although this interesting substituent effect for quantum yields cannot be explained completely at present, the difference in conformation of the imides may be one of the important factors in controlling the reactions of these imides. The conformations of ketones have been shown to be important in their Type-II processes, and conformational factors are expected to be more important in the photochemistry of imides. The conformations of imides have been studied<sup>8</sup> and can be conveniently described in

† *N*-Phenylglyoxyloxy  $\alpha,\beta$ -unsaturated amides.

terms of forms *Z,Z*; *E,Z*; and *E,E* (Figure).<sup>\*</sup> The conformer distribution is, to a large extent, defined by the steric demands of the substituents and dipole-dipole interactions.<sup>9</sup> When R<sup>3</sup> is less hindered (R<sup>3</sup> = *p*-tolyl; aryl group on the nitrogen atom is

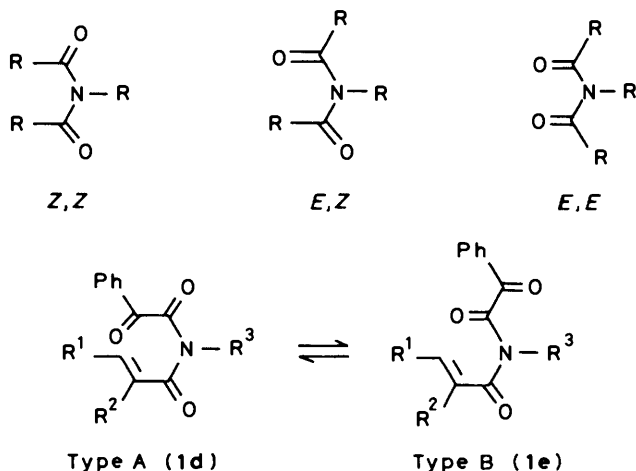


Figure.

perpendicular to the imide plane), the type-B conformer is more stable than the type A. In contrast to this, bulky substituents (R<sup>3</sup> = alkyl or 2,6-xylyl) on the nitrogen atom make the type-A conformer more stable. *N*-Benzyl derivative (**1d**) prefers to adopt a type A conformation, rather than type B. Photochemical cyclization of glyoxylamides of (**1**) from the type-A conformer is easier than from type B. This difference in conformation reflects upon the differences in both chemical yield and quantum yield. The inertness for photoreaction of substrates (**1h**) and (**1j**) may thus be explainable in terms of an unfavourable conformation.

In conclusion, *N*-benzoylformyl  $\alpha,\beta$ -unsaturated amides undergo photochemical intramolecular [2 + 2]cycloaddition to produce bicyclic oxetanes. There is no literature example of the Paterno-Büchi reaction of methacrylic acid derivatives with ketones to the best of our knowledge. It is interesting that, in our present reaction, methacrylamide, crotonamide, and cinnamide chromophores react efficiently with an  $\alpha$ -dicarbonyl moiety. Since it is known that  $\alpha$ -diketones do not give oxetanes with electron-deficient olefins,<sup>6</sup> this photochemical reaction provides the first example of a Paterno-Büchi reaction of some  $\alpha$ -dicarbonyl compounds with electron-poor olefins.

## Experimental

M.p.s were measured on a Yanagimoto Micro melting point apparatus and are uncorrected. Yields are isolated yields. I.r. spectra were recorded for CHCl<sub>3</sub> solutions on a JASCO IRA-1 spectrometer. <sup>1</sup>H and <sup>13</sup>C N.m.r. spectra were measured for CDCl<sub>3</sub> solutions on a Hitachi R-24 or a JEOL-100 spectrometer. U.v. visible spectra were obtained for cyclohexane solutions on a Shimadzu UV-356 spectrophotometer.

**Materials.**—The following *N*-benzoylformyl  $\alpha,\beta$ -unsaturated amides were obtained by condensation of the corresponding  $\alpha,\beta$ -unsaturated amides with benzoylformyl chloride in the presence of triethylamine. Crystalline products were recrystallized from chloroform-hexane.

\* Strictly speaking, *s-cis*, *s-cis*; *s-trans*, *s-cis*; and *s-trans*, *s-trans* conformations of a carbonyl group with respect to the alkyl/aryl substituent on N.

*N*-Benzoylformyl-*N*-methylmethacrylamide (**1a**), liquid,  $\lambda_{\text{max}}$  218 ( $\epsilon$  10 400 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), 256 (10 000), and 350 nm (90);  $\nu_{\text{max}}$  1 625 (C=O) and 1 655 cm<sup>-1</sup> (C=O);  $\delta_{\text{H}}$  1.85 (3 H, d, *J* 1 Hz, Me), 3.33 (3 H, s, NMe), 5.23 (1 H, m, C=CHH), 5.40 (1 H, br s, C=CHH), 7.3–7.7 (3 H, m, ArH), and 7.9–8.1 (2 H, m, ArH). This material underwent decarbonylation to produce *N*-benzoyl-*N*-methylmethacrylamide quantitatively on distillation.

*N*-Benzoylformyl-*N*-ethylmethacrylamide (**1b**),  $\lambda_{\text{max}}$  216 ( $\epsilon$  8 400), 258 (7 500) and 355 nm (60);  $\nu_{\text{max}}$  1 620 (C=O) and 1 660 cm<sup>-1</sup> (C=O);  $\delta_{\text{H}}$  1.28 (3 H, t, *J* 7 Hz, NCH<sub>2</sub>Me), 1.83 (3 H, d, *J* 1 Hz, Me), 3.93 (2 H, q, *J* 7 Hz, NCH<sub>2</sub>Me), 5.13 (1 H, m, C=CHH), 5.33 (1 H, br s, C=CHH), 7.3–7.7 (3 H, m, ArH), and 7.9–8.1 (2 H, m, ArH). This material was unstable toward distillation as was (**1a**).

*N*-Benzoylformyl-*N*-isopropylmethacrylamide (**1c**), m.p. 62–63 °C;  $\lambda_{\text{max}}$  219 ( $\epsilon$  13 200), 258 (14 900), and 360 nm (140);  $\nu_{\text{max}}$  1 625 (C=O) and 1 660 cm<sup>-1</sup> (C=O);  $\delta_{\text{H}}$  1.43 (6 H, d, *J* 7 Hz, Me<sub>2</sub>), 1.7 (3 H, d, *J* 1 Hz, Me), 3.83 (1 H, sept, *J* 7 Hz, CHMe<sub>2</sub>), 5.1 (1 H, m, C=CHH), 5.35 (1 H, s, C=CHH), 7.1–7.5 (3 H, m, ArH), and 7.7–8.0 (2 H, m, ArH) (Found: C, 69.4; H, 6.6; N, 5.4. C<sub>15</sub>H<sub>17</sub>NO<sub>3</sub> requires C, 69.47; H, 6.60; N, 5.40%).

*N*-Benzoylformyl-*N*-benzylmethacrylamide (**1d**), m.p. 115–116 °C;  $\lambda_{\text{max}}$  214 ( $\epsilon$  15 200), 257 (12 200), and 360 nm (30);  $\nu_{\text{max}}$  1 620 (C=O) and 1 660 cm<sup>-1</sup> (C=O);  $\delta_{\text{H}}$  1.75 (3 H, d, *J* 1 Hz, Me), 5.07 (3 H, br s, CH<sub>2</sub>Ph + C=CHH), 5.26 (1 H, br s, C=CHH), 7.0–7.6 (8 H, m, ArH), and 7.8–8.1 (2 H, m, ArH) (Found: C, 73.95; H, 5.6; N, 4.5. C<sub>19</sub>H<sub>17</sub>NO<sub>3</sub> requires C, 74.25; H, 5.57; N, 4.55%).

*N*-Benzoylformyl-*N*-(*p*-tolyl)methacrylamide (**1e**), m.p. 109–110 °C;  $\lambda_{\text{max}}$  213 ( $\epsilon$  17 300) and 253 nm (16 500);  $\nu_{\text{max}}$  1 625 (C=O) and 1 675 cm<sup>-1</sup> (C=O);  $\delta_{\text{H}}$  1.78 (3 H, d, *J* 1 Hz, Me), 2.40 (3 H, s, Me), 5.43 (1 H, m, C=CHH), 5.62 (1 H, br s, C=CHH), 7.1–7.7 (7 H, m, ArH), and 7.9–8.2 (2 H, m, ArH) (Found: C, 73.9; H, 5.6; N, 4.5. C<sub>19</sub>H<sub>17</sub>NO<sub>3</sub> requires C, 74.25; H, 5.57; N, 4.55%).

*N*-Benzoylformyl-*N*-(2,6-xylyl)methacrylamide (**1f**), m.p. 109–109.5 °C;  $\lambda_{\text{max}}$  225 ( $\epsilon$  14 000) and 253 nm (16 600);  $\nu_{\text{max}}$  1 625 (C=O) and 1 670 cm<sup>-1</sup> (C=O);  $\delta_{\text{H}}$  1.72 (3 H, d, *J* 1 Hz, Me), 2.25 (6 H, s, Me<sub>2</sub>), 5.18 (1 H, m, C=CHH), 5.33 (1 H, br s, C=CHH), 7.0–7.6 (6 H, m, ArH), and 7.8–8.0 (2 H, m, ArH) (Found: C, 74.65; H, 6.0; N, 4.4. C<sub>20</sub>H<sub>19</sub>NO<sub>3</sub> requires C, 74.74; H, 5.95; N, 4.35%).

*N*-Benzoylformyl-*N*-isopropylcrotonamide (**1g**), liquid,  $\lambda_{\text{max}}$  229 ( $\epsilon$  14 300) and 253 nm (14 400);  $\nu_{\text{max}}$  1 630 (C=O) and 1 670 cm<sup>-1</sup> (C=O);  $\delta_{\text{H}}$  1.57 (6 H, d, *J* 7 Hz, Me<sub>2</sub>), 1.88 (3 H, dd, *J* 1.5 and 7 Hz, Me), 4.54 (1 H, sept, *J* 7 Hz, CHMe<sub>2</sub>), 6.29 (1 H, dq, *J* 15 and 1.5 Hz, C=CHC=O), 6.67 (1 H, dq, *J* 15 and 7 Hz, MeCH=C), 7.3–7.7 (3 H, m, ArH), and 7.9–8.1 (2 H, m, ArH).

This material underwent decarbonylation to give *N*-benzoyl-*N*-isopropylcrotonamide on distillation.

*N*-Benzoylformyl-*N*-(*p*-tolyl)crotonamide (**1h**), m.p. 118–119 °C;  $\lambda_{\text{max}}$  240 nm ( $\epsilon$  24 900);  $\nu_{\text{max}}$  1 630 (C=O) and 1 680 cm<sup>-1</sup> (C=O);  $\delta_{\text{H}}$  1.73 (3 H, dd, *J* 1.5 and 6 Hz, Me), 2.42 (3 H, s, Me), 5.77 (1 H, dq, *J* 15 and 1.5 Hz, C=CHC=O), 6.8–7.7 (8 H, m, MeCH=C + ArH), and 7.9–8.2 (2 H, m, ArH) (Found: C, 74.2; H, 5.6; N, 4.55. C<sub>19</sub>H<sub>17</sub>NO<sub>3</sub> requires C, 74.25; H, 5.57; N, 4.55%).

*N*-Benzoylformyl-*N*-isopropylcinnamamide (**1i**), m.p. 92.5–94 °C;  $\lambda_{\text{max}}$  211 ( $\epsilon$  11 700), 222 (12 100), 228 (12 400), 258 (14 200), and 291 nm (18 500);  $\nu_{\text{max}}$  1 690 cm<sup>-1</sup> (C=O);  $\delta_{\text{H}}$  1.60 (6 H, d, *J* 7 Hz, Me<sub>2</sub>), 4.58 (1 H, sept, *J* 7 Hz, CHMe<sub>2</sub>), 6.73 (1 H, d, *J* 16 Hz, C=CHC=O), 7.2–7.6 (m, 9 H, PhCH=C + ArH), and 7.8–8.0 (m, 2 H, ArH) (Found: C, 74.7; H, 6.0; N, 4.3. C<sub>20</sub>H<sub>19</sub>NO<sub>3</sub> requires C, 74.74; H, 5.95; N, 4.35%).

*N*-Benzoylformyl-*N*-(*p*-tolyl)cinnamamide (**1j**), m.p. 113–114 °C;  $\lambda_{\text{max}}$  230 ( $\epsilon$  22 700), 250 (19 700), and 305 nm (28 100);  $\nu_{\text{max}}$  1 690 cm<sup>-1</sup> (C=O);  $\delta_{\text{H}}$  2.42 (3 H, s, Me), 6.20 (1 H, d, *J* 16

Hz, C=CHC=O), 7.0–7.7 (13 H, m, PhCH=C + ArH), and 7.8–8.1 (2 H, m, ArH) (Found: C, 77.9; H, 5.2; N, 3.75.  $C_{24}H_{19}NO_3$  requires C, 78.03; H, 5.18; N, 3.79%).

**General Procedure for the Photochemical Reactions of Glyoxylamides (1).**—A solution of the amide (1) (200 mg) in benzene (40 ml) under argon was irradiated in a Pyrex vessel with a 450-W high-pressure mercury lamp (Ushio). After the starting material had disappeared, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (flash chromatography). The following compounds were thus prepared and recrystallized from chloroform–hexane.

**1,3-Dimethyl-5-phenyl-6-oxa-3-azabicyclo[3.1.1]heptane-2,4-dione (2a)**, m.p. 89–90 °C;  $\lambda_{max}$  225 ( $\epsilon$  5 600), 251 (490), 257 (500), and 264 nm (400);  $\nu_{max}$  1 695s (C=O) and 1 750m  $cm^{-1}$  (C=O);  $\delta_H$  1.66 (3 H, s, 1-Me), 3.10 and 3.29 (2 H, ABq,  $J$  10 Hz, 7-H<sub>2</sub>), 3.21 (3 H, s, NMe), and 7.2–7.5 (5 H, m, Ph);  $\delta_C$  19.9 (q, 1-Me), 25.3 (q, 3-Me), 48.4 (t, C-7), 82.5 (s, C-1), 84.3 (s, C-5), 125.1 (d, Ph), 128.3 (d, Ph), 128.8 (d, Ph), 135.7 (s, Ph), 172.4 (s, C=O), and 173.2 (s, C=O) (Found: C, 67.5; H, 5.7; N, 6.05.  $C_{13}H_{13}NO_3$  requires C, 67.52; H, 5.66; N, 6.05%).

**3-Ethyl-1-methyl-5-phenyl-6-oxa-3-azabicyclo[3.1.1]heptane-2,4-dione (2b)**, m.p. 74–75 °C;  $\lambda_{max}$  218 ( $\epsilon$  8 300), 252 (360, 258 (390), and 264 nm (320);  $\nu_{max}$  1 690s (C=O) and 1 750m  $cm^{-1}$  (C=O);  $\delta_H$  1.17 (3 H, t,  $J$  7 Hz,  $NCH_2Me$ ), 1.58 (3 H, s, 1-Me), 3.01 and 3.19 (2 H, ABq,  $J$  9 Hz, 7-H<sub>2</sub>), 3.79 (2 H, q,  $J$  7 Hz,  $NCH_2Me$ ), and 7.1–7.6 (m, 5 H, Ph) (Found: C, 68.5; H, 6.2; N, 5.7.  $C_{14}H_{15}NO_3$  requires C, 68.55; H, 6.16; N, 5.71%).

**3-Isopropyl-1-methyl-5-phenyl-6-oxa-3-azabicyclo[3.1.1]heptane-2,4-dione (2c)**, m.p. 68.5–70.0 °C;  $\lambda_{max}$  218 ( $\epsilon$  10 400), 252 (410), 257 (450), and 264 nm (400);  $\nu_{max}$  1 685s (C=O) and 1 745m  $cm^{-1}$  (C=O);  $\delta_H$  1.42 (6 H, d,  $J$  7 Hz,  $Me_2$ ), 1.57 (3 H, s, 1-Me), 2.94 and 3.11 (2 H, ABq,  $J$  10 Hz, 7-H<sub>2</sub>), 4.73 (1 H, sept,  $J$  7 Hz,  $CHMe_2$ ), and 7.0–7.4 (5 H, m, Ph) (Found: C, 69.5; H, 6.6; N, 5.4.  $C_{15}H_{17}NO_3$  requires C, 69.47; H, 6.60; N, 5.40%).

**3-Benzyl-1-methyl-5-phenyl-6-oxa-3-azabicyclo[3.1.1]heptane-2,4-dione (2d)**, b.p. 160 °C/10<sup>-3</sup> mmHg;  $\lambda_{max}$  215 ( $\epsilon$  15 400), 252 (710), 258 (760), and 264 nm (640);  $\nu_{max}$  1 690s (C=O) and 1 745m  $cm^{-1}$  (C=O);  $\delta_H$  1.62 (3 H, s, 1-Me), 2.98 and 3.20 (2 H, ABq,  $J$  10 Hz, 7-H<sub>2</sub>), 4.87 (2 H, s,  $NCH_2$ ), and 7.1–7.5 (10 H, m, Ph) (Found: C, 74.15; H, 5.6; N, 4.55.  $C_{19}H_{17}NO_3$  requires C, 74.25; H, 5.57; N, 4.55%).

**1-Methyl-5-phenyl-3-(p-tolyl)-6-oxa-3-azabicyclo[3.1.1]heptane-2,4-dione (2e)**, m.p. 136.5–138.0 °C;  $\lambda_{max}$  222 ( $\epsilon$  9 700), 257 (1 100), and 264 nm (820);  $\nu_{max}$  1 700s, (C=O) and 1 760m  $cm^{-1}$  (C=O);  $\delta_H$  1.67 (3 H, s, 1-Me), 2.33 (3 H, s,  $ArMe$ ), 3.25 (2 H, br, 7-H<sub>2</sub>), and 7.1–7.5 (9 H, m, ArH) (Found: C, 73.95; H, 5.6; N, 5.5.  $C_{19}H_{17}NO_3$  requires C, 74.25; H, 5.57; N, 5.55%).

**1-Methyl-5-phenyl-3-(2,6-xylyl)-6-oxa-3-azabicyclo[3.1.1]heptane-2,4-dione (2f)**, m.p. 168–170 °C;  $\lambda_{max}$  217 ( $\epsilon$  15 600), 258 (810), 259 (850), and 272 nm (610);  $\nu_{max}$  1 700s (C=O) and 1 755m  $cm^{-1}$  (C=O);  $\delta_H$  1.72 (3 H, s, 1-Me), 2.15 (6 H, s,  $ArMe_2$ ), 3.33 (2 H, br, 7-H<sub>2</sub>), and 7.0–7.4 (8 H, m, ArH) (Found: C, 74.4; H, 5.9; N, 4.3.  $C_{20}H_{19}NO_3$  requires C, 74.74; H, 5.95; N, 4.35%).

**3-Isopropyl-7-methyl-1-phenyl-6-oxa-3-azabicyclo[3.1.1]heptane-2,4-dione (2g)**, m.p. 131–134 °C;  $\lambda_{max}$  218 ( $\epsilon$  18 500), 252 (890), 258 (970), and 263 nm (860);  $\nu_{max}$  1 690s (C=O) and 1 745m  $cm^{-1}$  (C=O);  $\delta_H$  (major isomer) 1.48 (6 H, d,  $J$  7 Hz,  $Me_2$ ), 1.50 (3 H, d,  $J$  7 Hz, 7-Me), 3.83 (1 H, quint,  $J$  7 Hz, 7-H), 4.80 (1 H, m,  $CHMe_2$ ), 4.82 (1 H, d,  $J$  7 Hz, 5-H), and 7.2–7.5 (5 H, m, Ph);  $\delta_C$  (major isomer) 10.5 (q, 7-Me), 19.5 (q,  $Me_2$ ), 44.2 (d, NCH), 51.0 (d, C-7), 82.3 (d, C-5), 92.1 (s, C-1), 171.4 (s, C=O), and 172.1 (s, C=O);  $\delta_H$  (minor isomer) 1.23 (6 H, d,  $J$  7 Hz,  $Me_2$ ), 1.45 (3 H, d,  $J$  7 Hz, 7-Me), 3.21 (1 H, qd,  $J$  7 and 1 Hz, 7-H), 4.48 (1 H, d,  $J$  1 Hz, 5-H), 4.80 (1 H, m,  $CHMe_2$ ), and

7.2–7.5 (5 H, m, Ph);  $\delta_C$  (minor isomer) 13.3 (q, 7-Me), 19.3 (q,  $Me_2$ ), 44.0 (d, NCH), 50.1 (d, C-7), 82.4 (d, C-5), 90.6 (s, C-1), 170.1 (s, C=O), and 171.8 (s, C=O) (Found: C, 69.5; H, 6.6; N, 5.4.  $C_{15}H_{17}NO_3$  requires C, 69.47; H, 6.60; N, 5.40%).

**3-Isopropyl-1,7-diphenyl-6-oxa-3-azabicyclo[3.1.1]heptane-2,4-dione (2i)**, m.p. 92.5–94.0 °C;  $\lambda_{max}$  218 ( $\epsilon$  19 900), 253 (1 400), 259 (1 570), and 263 nm (1 460);  $\nu_{max}$  1 690s (C=O) and 1 745m  $cm^{-1}$  (C=O);  $\delta_H$  (major isomer) 1.02 (6 H, d,  $J$  7 Hz,  $Me_2$ ), 4.55 (1 H, sept,  $J$  7 Hz,  $CHMe_2$ ), 5.16 (1 H, d,  $J$  7 Hz, 5- or 7-H), 5.26 (1 H, d,  $J$  7 Hz, 7- or 5-H), and 7.0–7.6 (10 H, m, Ph);  $\delta_C$  (major isomer) 18.7 (q,  $Me_2$ ), 43.7 (d, NCH), 57.0 (d, C-7), 81.6 (d, C-5), 91.8 (s, C-1), 170.8 (s, C=O), and 171.4 (s, C=O);  $\delta_H$  (minor isomer) 1.50 (3 H, d,  $J$  7 Hz,  $Me$ ), 1.52 (3 H, d,  $J$  7 Hz,  $Me$ ), 4.19 (1 H, br s, 5- or 7-H), 4.86 (1 H, sept,  $J$  7 Hz, NCH), 5.01 (1 H, br s, 7- or 5-H), and 7.0–7.6 (10 H, m, Ph);  $\delta_C$  (minor isomer) 19.3 (q,  $Me_2$ ), 44.2 (d, NCH), 59.8 (d, C-7), 82.3 (d, C-5), 92.3 (s, C-1), 171.1 (s, C=O), and 171.5 (s, C=O) (Found: C, 74.5; H, 5.9; N, 4.3.  $C_{20}H_{19}NO_3$  requires C, 74.74; H, 5.95; N, 4.35%).

**Sensitization and Quenching of Glyoxylamide (1d) in the Photochemical Formation of Compound (2d).**—Irradiations were performed in a merry-go-round apparatus. Radiation of wavelength 366 nm was isolated with a filter solution (0.04M-naphthalene in methanol). The concentration of the sensitizer was adjusted so that  $\geq 95\%$  of the incident light was absorbed by the sensitizer. In the case of compound (1d), the sensitized reaction was as efficient as the direct photolysis ( $\Phi_{sens}/\Phi \approx 1$ ). Quenching of the photoreaction of compound (1d) was carried out in the presence of stilbene (0.1M) or piperylene (1.0M in benzene). The efficiency of the sensitized/quenched photoreaction was not very different from that of the direct photolysis.

**Quantum Yield Determination for Photoreaction of Glyoxylamides (1).**—Benzophenone–benzhydrol (Ph<sub>2</sub>CHOH) actinometry was used for the quantum yield determination. Radiation with 366 nm was isolated. Samples (0.05M benzene solution) in Pyrex tubes were degassed to ca. 10<sup>-3</sup> mmHg in three freeze-pump-thaw cycles and sealed. These samples were irradiated in a merry-go-round apparatus. Photolyses were carried out to 30–40% conversion. The extent of reaction was determined by n.m.r. spectroscopy. It was confirmed that the photoproducts (2) did not absorb at 366 nm.

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