

## Photochemical Ring Opening of Pyrimidin-2(1*H*)-ones. Part 2.<sup>1</sup>

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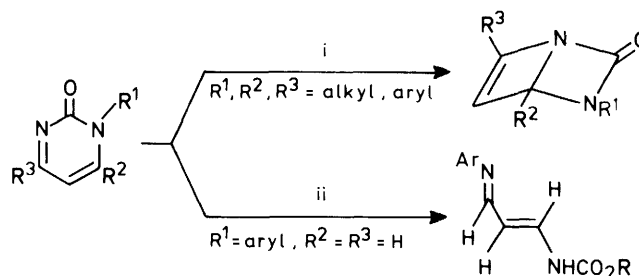
The photochemical reactions of 1-aryl-4,6-disubstituted pyrimidin-2(1*H*)-ones have been examined. Irradiation of 1-aryl-4,6-disubstituted pyrimidin-2(1*H*)-ones (1)—(6) in benzene in the presence of primary or secondary amines gave arylimine products (10)—(15) in high yields. The arylimines (10)—(15) were formed by trapping of the isocyanate intermediate, produced initially by the Norrish Type I cleavage of the ArN—CO bond of the pyrimidin-2(1*H*)-one, by amine.

Because of the biological importance of nucleoside bases, their photochemistry has been widely investigated.<sup>2</sup> We are interested in the photochemical behaviour of pyrimidin-2(1*H*)-ones and their derivatives in relation to that of cytosine, a nucleoside base;<sup>3</sup> however, these compounds have received little attention previously.<sup>4</sup> Recently, we reported the photochemical electrocyclicization of 1,4,6-trisubstituted pyrimidin-2(1*H*)-ones to 2-oxo-1,3-diazabicyclo[2.2.0]hex-5-enes<sup>5</sup> and the photochemical ring opening of *N*-arylpyrimidin-2(1*H*)-ones to aryliminopropenes;<sup>1</sup> these are produced *via* initial Type I cleavage of the ArN—CO bond of the pyrimidin-2(1*H*)-ones which are analogous to conjugated cyclohexadienones<sup>6</sup> and 2-pyrones<sup>7</sup> (Scheme 1). Thus, pyrimidin-2(1*H*)-ones typically undergo two different types of photochemical reaction depending upon the substituents at the 4- and 6-positions.† In this context, we report here the photochemical reactions of the 1-aryl-4,6-disubstituted pyrimidin-2(1*H*)-ones (1)—(6) in the presence of amines.

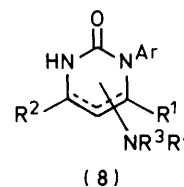
### Results and Discussion

When 1,4,6-triphenylpyrimidin-2(1*H*)-one (1) was irradiated in benzene in the presence of an excess of propylamine through a Pyrex filter with a high-pressure mercury lamp under argon for 15 h at room temperature, a yellow crystalline solid, m.p. 105—106.5 °C, was obtained. This compound had the molecular formula C<sub>25</sub>H<sub>25</sub>N<sub>3</sub>O (*m/z*, *M*<sup>+</sup> = 383), which was equivalent to the 1:1 adduct of the pyrimidin-2(1*H*)-one (1) and propylamine. There are two possible structures, (10a) and (8), for this photoproduct. It showed i.r. absorptions at 3 350, 1 685, and 1 620 cm<sup>-1</sup>, due to amino, ureido carbonyl, and imino groups, and its <sup>1</sup>H n.m.r. spectrum displayed two broad singlets at δ 1.72 (1 H, exchangeable with D<sub>2</sub>O) and 4.81 (1 H, exchangeable with D<sub>2</sub>O) and a singlet at δ 5.46 (1 H), which were assigned to amino and olefinic protons, respectively. The <sup>13</sup>C n.m.r. spectrum showed two olefinic carbons at δ 104.8 (d) and 157.5 (s), one ureido carbonyl carbon at δ 157.6 (s), and one imino carbon at δ 164.0 p.p.m. (s). Thus, the photoproduct was characterized as 1,3-diphenyl-3-phenylimino-1-(*N*'-propylureido)prop-2-ene (10a); the other possible structure (8) was ruled out by the absence of signals for tertiary carbons in the <sup>13</sup>C n.m.r. spectrum.

The photoproduct (10a) was treated with hydrochloric acid in methanol at reflux temperature to convert it back into the starting pyrimidin-2(1*H*)-one (1), and was treated with potassium hydroxide to afford 4,6-diphenyl-1-propylpyrimidin-2(1*H*)-one (7) in almost quantitative yield (Scheme 2). Irradiation of the pyrimidin-2(1*H*)-one (1) in benzene in the presence of an excess of diethylamine also gave the arylimine



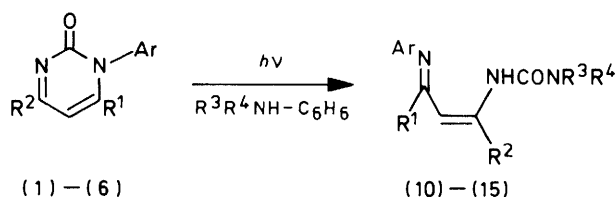
Scheme 1. Reagents: i, *hν* in C<sub>6</sub>H<sub>6</sub>; ii, *hν* in ROH



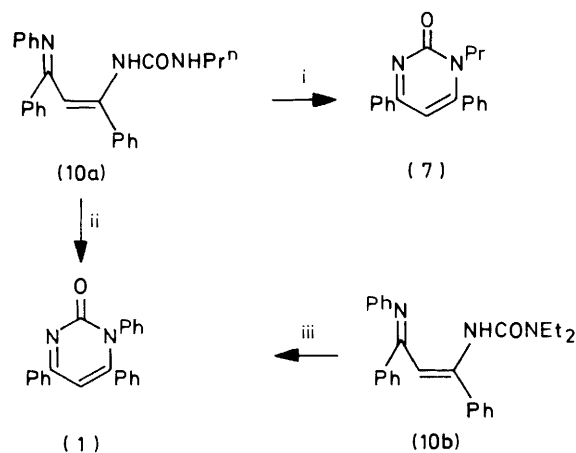
product (10c) ‡ in 85% yield, which was converted back into (1) by treatment with hydrochloric acid in dioxane; however, it did not give the arylimines (10a) and (10c) when refluxed with propylamine or diethylamine in benzene for 12 h. Similarly, irradiation of the 1-aryl-4,6-disubstituted pyrimidin-2(1*H*)-ones (1)—(6) in benzene in the presence of primary or secondary amines gave the corresponding arylimine products (10)—(15) in high yields. However, irradiation of the pyrimidinone (1) in benzene in the presence of aniline gave an intractable mixture. The structure of the arylimines (10)—(15) was elucidated on the basis of their spectroscopic properties and elemental analyses (see Experimental section). Compounds (13) and (15a) were converted back into the starting pyrimidin-2(1*H*)-ones (4) and (6) on being heated at higher temperature than their melting or boiling points. The photoreactions which ultimately yield the arylimine products (10)—(15) most probably occur by the Norrish Type I mechanism. The rearrangement of electronically excited pyrimidin-2(1*H*)-ones (1)—(6) *via* this mechanism would occur by initial homolytic cleavage of the ArN—CO bond giving a 1,6-diradical. Subsequent rearrangement would yield the isocyanate intermediate (16) which was trapped with amine to give the final products, the arylimines (10)—(15) (Scheme 3). The strained 2-oxo-1,3-diazabicyclo[2.2.0]hex-5-ene (9), formed by photochemical internal [2 + 2] electrocyclicization of 1,4,6-trisubstituted

† The hydrogen abstraction reaction of the nitrogen of the imino group was observed in the photochemistry of 1-alkyl-4,6-diarylpyrimidin-2(1*H*)-ones (ref. 8).

‡ In our previous paper, we assumed the structure of the photoproducts (15b—c) to be 4(or 6)-dialkylamino-4,6-dimethyl-1-phenyl-3,4(or 3,6)-dihydropyrimidin-2(1*H*)-one, *e.g.* (8) (ref. 1).



Pyrimidin-2(1H)-one	Ar	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	Photoproduct (yield %)
(1)	Ph	Ph	Ph	Pr <sup>n</sup>	H	(10a) (81)
(1)	Ph	Ph	Ph	Bu <sup>t</sup>	H	(10b) (95)
(1)	Ph	Ph	Ph	Et	Et	(10c) (85)
(1)	Ph	Ph	Ph	Pr <sup>n</sup>	Pr <sup>n</sup>	(10d) (79)
(1)	Ph	Ph	Ph	Ph	H	Intractable mixture
(2)	Ph	Ph	Me	Et	H	(11) (28)
(3)	Ph	Me	Ph	Et	Et	(12) (70)
(4)	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Ph	Ph	Et	Et	(13) (95)
(5)	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	Ph	Ph	Et	Et	(14) (95)
(6)	Ph	Me	Me	Pr <sup>n</sup>	H	(15a) (39)
(6)	Ph	Me	Me	Et	Et	(15b) (62)
(6)	Ph	Me	Me	Pr <sup>n</sup>	Pr <sup>n</sup>	(15c) (50)



Scheme 2. Reagents: i, heat, KOH-MeOH; ii, heat, HCl-MeOH; iii, heat, HCl-dioxane

pyrimidin-2(1H)-ones,<sup>5</sup> was also considered as a possible, alternative precursor for the formation of the arylimines (10)–(15). Irradiation of 4,6-dimethyl-2-oxo-3-phenyl-1,3-diazabicyclo[2.2.0]hex-5-ene (9; Ar = Ph, R<sup>2</sup> = R<sup>3</sup> = Me), prepared independently<sup>5</sup> in benzene in the presence of diethylamine under the same conditions as described above, did not give the arylimine (15b), and the starting compound was recovered quantitatively. Furthermore, the arylimine product (15b) was not obtained by thermal reaction of the bicyclic ketone (9) with diethylamine. These results seem to preclude the intermediacy of the bicyclic ketone (9) and suggest that the formation of the arylimines (10)–(15) involves the isocyanate (16) as an intermediate. Analogous ring opening reactions have been observed in the photochemistry of 2-pyrones.<sup>7</sup>

### Experimental

M.p.s and b.p.s are uncorrected. M.p.s were measured with a Yanaco micro-melting point apparatus (MP-J3) and b.p.s were measured with Büchi Kugel Rohr (KR-3) apparatus. U.v. spectra were determined with a JASCO UVIDEK-505 spectrometer. I.r. spectra were recorded on a Hitachi 260-30

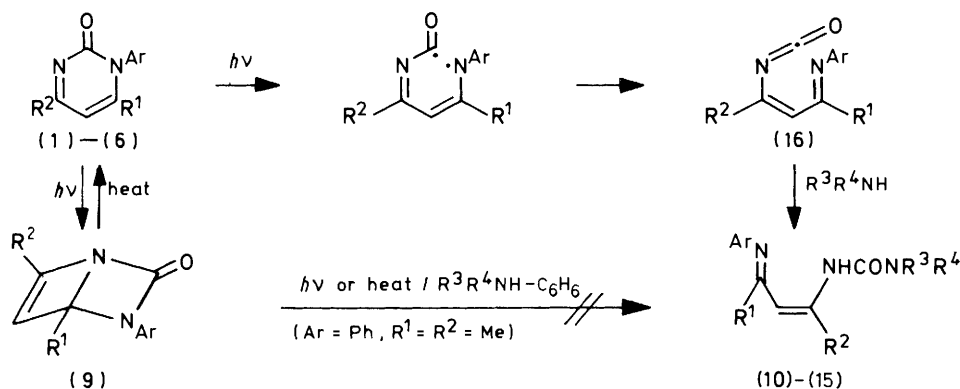
spectrometer. <sup>1</sup>H and <sup>13</sup>C N.m.r. spectra were obtained with a JEOL FX-100 spectrometer. Mass spectra were obtained with a Hitachi M-80 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 240 analyzer. A HALōs (Eikosha EHP-300 W) high-pressure mercury lamp was used as the irradiation source.

*Starting Materials.*—The pyrimidin-2(1H)-ones (1)–(6) were prepared as described in ref. 9.

*General Procedure for the Photochemical Reactions of the Pyrimidin-2(1H)-ones (1)–(6) in the Presence of Amine.*—A solution of the pyrimidin-2(1H)-one (200 mg) in benzene (50 ml) in the presence of an excess of amine (*ca.* 1 ml) was irradiated under argon with a high-pressure mercury lamp through a Pyrex filter for 12–15 h at room temperature. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene-ethyl acetate (4:9–9:1) as eluant to give the corresponding arylimine. The following products were obtained.

*1,3-Diphenyl-3-phenylimino-1-(N'-propylureido)prop-1-ene* (10a), m.p. 105–106.5 °C (from chloroform-hexane) (Found: C, 78.0; H, 6.55; N, 10.95. C<sub>25</sub>H<sub>25</sub>N<sub>3</sub>O requires C, 78.3; H, 6.55; N, 10.95%); λ<sub>max</sub> (EtOH) 206 (ε 30 700), 221sh (19 000), 250sh (15 600), 331 (13 000), and 358sh nm (12 400); ν<sub>max</sub> (KBr) 3 350 (NH), 1 685 (C=O), and 1 620 cm<sup>-1</sup> (C=N); δ<sub>H</sub> (100 MHz; CDCl<sub>3</sub>) 0.79 (3 H, t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.26–1.62 (2 H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.72 (1 H, br s, NH, exchangeable with D<sub>2</sub>O), 3.12 (2 H, q, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.81 (1 H, br s, NH, exchangeable with D<sub>2</sub>O), 5.46 (1 H, s, =CH-), 6.65–6.72 (2 H, m, arom.), and 6.94–7.57 (13 H, m, arom.); δ<sub>C</sub> (CDCl<sub>3</sub>) 11.2 (q, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 23.0 (t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 42.3 (t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 104.8 (d, =CH-), 157.5 (s, =C<), 1 577.6 (s, -CO-), and 164.0 p.p.m. (s, -C=N) in addition to aromatic carbons; *m/z* 383 (M<sup>+</sup>), 297 (M<sup>+</sup> - 86), and 93 (M<sup>+</sup> - 290, 100%).

*1-(N'-Butylureido)-1,3-diphenyl-3-phenyliminoprop-1-ene* (10b), m.p. 154–155 °C (from chloroform-hexane) (Found: C, 78.55; H, 6.85; N, 10.7. C<sub>26</sub>H<sub>27</sub>N<sub>3</sub>O requires C, 78.55; H, 6.85; N, 10.55%); λ<sub>max</sub> (EtOH) 206 (ε 34 500), 223sh (21 400), 250sh (18 600), and 350 nm (14 900); ν<sub>max</sub> (KBr) 3 380, 3 340, 3 300 (NH), 1 690 (C=O), 1 655, and 1 615 cm<sup>-1</sup> (C=N); δ<sub>H</sub> (100 MHz; CDCl<sub>3</sub>) 1.22 (9 H, C(CH<sub>3</sub>)<sub>3</sub>), 4.69 (1 H, br s, NH), 5.40 (1 H, s, =CH-), 6.68–6.78 (2 H, m, arom.), 6.99–7.53



Scheme 3.

(13 H, m, arom.), and 12.17 (1 H, br s, NH);  $\delta_c$  (CDCl<sub>3</sub>) 28.8 [s, C(CH<sub>3</sub>)<sub>3</sub>], 50.7 [s, C(CH<sub>3</sub>)<sub>3</sub>], 104.0 (d, =CH-), 157.0 (s, =C<), 158.5 (s, -CO-), and 163.0 p.p.m. (s, -C=N) in addition to aromatic carbons;  $m/z$  397 ( $M^+$ ) and 297 ( $M^+ - 100$ , 100%).

1-(N',N'-Diethylureido)-1,3-diphenyl-3-phenyliminoprop-1-ene (10c), m.p. 138–139 °C (from chloroform-hexane) (Found: C, 78.35; H, 6.8; N, 10.55. C<sub>26</sub>H<sub>27</sub>N<sub>3</sub>O requires C, 78.55; H, 6.85; N, 10.55%);  $\lambda_{max}$  (EtOH) 206 ( $\epsilon$  33 200), 225sh (17 700), 250 (16 100), 340sh (13 800), and 370 nm (17 300);  $\nu_{max}$  (KBr) 3 440 (NH), 1 680 (C=O), and 1 620 cm<sup>-1</sup> (C=N);  $\delta_H$  (100 MHz; CDCl<sub>3</sub>) 1.11 [6 H, t, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 3.38 [4 H, q, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 5.49 (1 H, s, =CH-), 6.65–6.75 (2 H, m, arom.), 6.92–7.53 (13 H, m, arom.), and 12.61 (1 H, br s, NH);  $\delta_c$  (CDCl<sub>3</sub>) 13.8 [q, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 41.5 [t, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 105.0 (d, =CH-), 157.2 (s, =C<), 158.5 (s, -CO-), and 164.0 p.p.m. (s, -C=N) in addition to aromatic carbons;  $m/z$  397 ( $M^+$ ) and 323 ( $M^+ - 74$ , 100%).

1-(N',N'-Dipropylureido)-1,3-diphenyl-3-phenyliminoprop-1-ene (10d), m.p. 116–116.5 °C (from chloroform-hexane) (Found: C, 78.9; H, 7.35; N, 9.9. C<sub>28</sub>H<sub>31</sub>N<sub>3</sub>O requires C, 79.0; H, 7.35; N, 9.85%);  $\lambda_{max}$  (EtOH) 206 ( $\epsilon$  33 700), 250 (15 500), 340sh (13 600), and 373 nm (16 700);  $\nu_{max}$  (KBr) 3 450 (NH), 1 670 (C=O), and 1 620 cm<sup>-1</sup> (C=N);  $\delta_H$  (100 MHz; CDCl<sub>3</sub>) 0.77 [6 H, t, -(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 1.38–1.69 [4 H, m, -(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 3.26 [4 H, t, -(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 5.50 (1 H, s, =CH-), 6.65–6.74 (2 H, m, arom.), 6.83–7.53 (13 H, m, arom.), and 12.51 (1 H, br s, NH);  $\delta_c$  (CDCl<sub>3</sub>) 11.2 [q, -(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 21.5 [t, -(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 49.1 [t, -(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 105.0 (d, =CH-), 157.2 (s, >C=), 158.5 (s, -CO-), and 164.0 p.p.m. (s, -C=N) in addition to aromatic carbons;  $m/z$  425 ( $M^+$ ) and 323 ( $M^+ - 102$ , 100%).

3-(N',N'-Diethylureido)-1-phenyl-1-phenyliminobut-2-ene (11), m.p. 82–83 °C (from chloroform-hexane) (Found: C, 74.85; H, 7.4; N, 12.4. C<sub>21</sub>H<sub>25</sub>N<sub>3</sub>O requires C, 75.2; H, 7.5; 12.5%);  $\nu_{max}$  (KBr) 3 450 (NH), 1 680 (C=O), and 1 625 (C=N);  $\delta_H$  (100 MHz; CDCl<sub>3</sub>) 1.12 [6 H, t, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 2.40 (3 H, s, =CCH<sub>3</sub>), 3.37 [2 H, q, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 5.17 (1 H, s, =CH-), 6.58–6.69 (2 H, m, arom.), 6.80–7.26 (8 H, m, arom.), and 12.76 (1 H, br s, NH);  $\delta_c$  (CDCl<sub>3</sub>) 13.7 [q, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 22.6 (q, =CCH<sub>3</sub>), 41.6 [t, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 102.9 (d, =CH-), 157.3 (s, >C=), 158.1 (s, -CO-), and 164.0 p.p.m. (s, -C=N) in addition to aromatic carbons;  $m/z$  335 ( $M^+$ ) and 263 ( $M^+ - 72$ , 100%).

1-(N',N'-Diethylureido)-1-phenyl-3-phenyliminobut-1-ene (12), m.p. 101.5–102.5 °C (from chloroform-hexane) (Found: C, 75.3; H, 7.45; N, 12.5. C<sub>21</sub>H<sub>25</sub>N<sub>3</sub>O requires C, 75.2; H, 7.5; N, 12.5%);  $\lambda_{max}$  (EtOH) 206 ( $\epsilon$  23 400), 226 (17 400), and 322 nm (16 500);  $\nu_{max}$  (KBr) 1 665 (C=O) and 1 635 cm<sup>-1</sup>

(C=N);  $\delta_H$  (100 MHz; CDCl<sub>3</sub>) 1.07 [6 H, t, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 1.95 (3 H, s, CH<sub>3</sub>C=N), 3.29 [4 H, q, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 5.29 (1 H, s, =CH-), 6.78–6.87 (2 H, m, arom.), 6.99–7.49 (8 H, m, arom.), and 12.56 (1 H, br s, NH);  $\delta_c$  (CDCl<sub>3</sub>) 13.6 [q, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 21.6 (q, CH<sub>3</sub>C=N), 41.4 [t, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 106.1 (d, =CH-), 152.4 (s, >C=), 154.6 (s, -CO-), and 166.6 p.p.m. (s, -C=N) in addition to aromatic carbons;  $m/z$  335 ( $M^+$ ) and 261 ( $M^+ - 74$ , 100%).

1-(N',N'-Diethylureido)-1,3-diphenyl-3-(p-tolylimino)prop-1-ene (13), m.p. 169.5–170.5 °C (from chloroform-hexane) (Found: C, 79.0; H, 7.1; N, 10.05. C<sub>27</sub>H<sub>29</sub>N<sub>3</sub>O requires C, 78.8; H, 7.1; N, 10.2%);  $\lambda_{max}$  (EtOH) 205 ( $\epsilon$  17 100), 225sh (8 900), 250 (8 200), 335sh (6 300), and 376 nm (8 600);  $\nu_{max}$  (KBr) 1 675 (C=O) and 1 615 cm<sup>-1</sup> (C=N);  $\delta_H$  (100 MHz; CDCl<sub>3</sub>) 1.10 [6 H, t, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 2.21 (3 H, s, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 3.37 [4 H, q, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 5.46 (1 H, s, =CH-), 6.60 (2 H, d, *J* 8.3 Hz, arom.), 6.91 (2 H, d, *J* 8.3 Hz, arom.), 7.21–7.53 (10 H, m, arom.), and 12.64 (1 H, br s, NH);  $\delta_c$  (CDCl<sub>3</sub>) 13.7 [q, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 20.8 (q, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 41.4 [t, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 104.7 (d, =CH-), 157.4 (s, >C=), 158.7 (s, -CO-), and 163.6 p.p.m. (s, -C=N) in addition to aromatic carbons;  $m/z$  441 ( $M^+$ ) and 337 ( $M^+ - 78$ , 100%).

1-(N',N'-Diethylureido)-1,3-diphenyl-3-(p-methoxyphenyl)iminoprop-1-ene (14), m.p. 160–161 °C (from chloroform-hexane) (Found: C, 78.85; H, 6.75; N, 9.6. C<sub>27</sub>H<sub>29</sub>N<sub>3</sub>O requires C, 78.85; H, 6.85; N, 9.8%);  $\nu_{max}$  (KBr) 1 665 (C=O) and 1 618 cm<sup>-1</sup> (C=N);  $\lambda_{max}$  (EtOH) 206 ( $\epsilon$  33 400), 230 (17 800), 255sh (15 100), 332 (11 500), and 381 nm (15 700);  $\delta_H$  (100 MHz; CDCl<sub>3</sub>) 1.11 [6 H, t, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 3.38 [4 H, q, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 3.69 (3 H, s, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>), 5.46 (1 H, s, =CH-), 6.66 (4 H, s, arom.), 7.22–7.50 (10 H, m, arom.), and 12.67 (1 H, br s, NH);  $\delta_c$  (CDCl<sub>3</sub>) 13.8 [q, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 41.4 [t, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 55.2 (q, CH<sub>3</sub>O), 104.7 (d, =CH-), 157.3 (s, >C=), 158.2 (s, -CO-), and 163.9 p.p.m. (s, -C=N) in addition to aromatic carbons;  $m/z$  427 ( $M^+$ ) and 353 ( $M^+ - 74$ , 100%).

2-Phenylimino-4-(N'-propylureido)pent-3-ene (15a), m.p. 103–105 °C (from chloroform-hexane) (Found: C, 69.55; H, 8.2; N, 16.0. C<sub>15</sub>H<sub>21</sub>N<sub>3</sub>O requires C, 69.45; H, 8.15; N, 16.2%);  $\nu_{max}$  (KBr) 3 240 (NH), 1 690 (C=O), and 1 635 cm<sup>-1</sup> (C=N);  $\delta_H$  (100 MHz; CDCl<sub>3</sub>) 0.83 (3 H, t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.30–1.58 (2 H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.86 (3 H, s, CH<sub>3</sub>C=N), 2.36 (3 H, d, *J* 1.0 Hz, CH<sub>3</sub>C=), 3.10 (2 H, q, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.73 (1 H, br s, NH), 4.94 (1 H, d, *J* 1.0 Hz, =CH-), 6.75–6.85 (2 H, m, arom.), 7.00–7.40 (3 H, m, arom.), and 12.72 (1 H, br s, NH);  $\delta_c$  (CDCl<sub>3</sub>) 11.1 (q, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 21.4 (q, CH<sub>3</sub>C=), 21.7 (q, CH<sub>3</sub>C=N), 23.2 (t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 42.3 (t,

CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 102.5 (d, =CH-), 121.0 (d), 123.3 (d), 128.8 (d), 149.4 (s) (arom.), 151.4 (s, >C=), 155.4 (s, -CO-), and 166.8 p.p.m. (s, -C=N).

4-(N',N'-Diethylureido)-2-phenyliminopent-3-ene (15b), b.p. 130 °C at 2 mmHg (Found: C, 69.85; H, 8.5; N, 15.35). C<sub>16</sub>H<sub>23</sub>N<sub>3</sub>O requires C, 70.05; H, 8.8; N, 15.3%; λ<sub>max</sub> (EtOH) 225 (ε 14 100), and 308 nm (14 100); ν<sub>max</sub> (film) 1 660 (C=O) and 1 640 cm<sup>-1</sup> (C=N); δ<sub>H</sub> (100 MHz; CDCl<sub>3</sub>) 1.06 [6 H, t, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 1.87 (3 H, s, CH<sub>3</sub>C=N), 2.42 (3 H, d, J 1.0 Hz, =CCH<sub>3</sub>), 3.30 [4 H, q, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 4.97 (1 H, d, J 1.0 Hz, =CH-), 6.73–6.97 (2 H, m, arom.), 7.05–7.39 (3 H, m, arom.), and 12.91 (1 H, br s, NH); δ<sub>C</sub> (CDCl<sub>3</sub>) 13.3 [q, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 21.0 (q, CH<sub>3</sub>C=), 21.8 (q, CH<sub>3</sub>C=N), 41.2 [t, -(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 102.5 (d, =CH-), 120.5 (d), 122.9 (d), 128.5 (d), 149.2 (s) (aromatic carbons), 151.4 (s, >C=), 154.5 (s, -CO-), and 166.4 p.p.m. (s, -C=N); m/z 273 (M<sup>+</sup>) and 201 (M<sup>+</sup> - 72, 100%).

4-(N',N'-Dipropylureido)-2-phenyliminopent-3-ene (15c), b.p. 145 °C at 2 mmHg (Found: C, 71.45; H, 8.95; N, 14.0). C<sub>18</sub>H<sub>27</sub>N<sub>3</sub>O requires C, 71.7; H, 9.0; N, 13.95%; λ<sub>max</sub> (EtOH) 225 (ε 14 000) and 308 nm (14 100); ν<sub>max</sub> (film) 1 670 (C=O) and 1 640 cm<sup>-1</sup> (C=N); δ<sub>H</sub> (100 MHz; CDCl<sub>3</sub>) 0.68 [6 H, -(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 1.33–1.7 [4 H, m, -(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 1.86 (3 H, s, CH<sub>3</sub>C=N), 2.42 (3 H, d, J 1.0 Hz, =CCH<sub>3</sub>), 3.18 [4 H, t, -(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 4.97 (1 H, d, J 1.0 Hz, =CH-), 6.7–6.81 (2 H, m, arom.), 7.04–7.32 (3 H, m, arom.), and 12.97 (1 H, br s, NH); δ<sub>C</sub> (CDCl<sub>3</sub>) 10.8 [q, -(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 21.3 (q, CH<sub>3</sub>C=N), 21.3 [t, -(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 22.1 (q, CH<sub>3</sub>-C=), 49.1 [t, -(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 102.7 (d, =CH-), 120.6 (d), 123.0 (d), 128.6 (d), 149.5 (d) (arom. carbons), 151.5 (s, -CO-), and 166.6 p.p.m. (s, -C=N); m/z 301 (M<sup>+</sup>) and 201 (M<sup>+</sup> - 100, 100%).

*Thermal Reactions of 1,4,6-Triphenylpyrimidin-2(1H)-one (1) in The Presence of Amine.*—A solution of the pyrimidin-2(1H)-one (1) (100 mg) in benzene (30 ml) in the presence of propylamine (1 ml) was refluxed for 12 h. Similar experiments were performed with compound (1) and diethylamine. T.l.c. and i.r. analyses indicated no product formation.

*Thermal Reactions of the Photoproducts (10a) and (10c).*—(i) A solution of the photoproduct (10a) (50 mg) in MeOH (5 ml) in the presence of 5 drops of hydrochloric acid was refluxed for 1 h. The reaction mixture was poured into water and extracted with methylene dichloride. The extract was washed with sodium hydrogen carbonate solution and water and dried (MgSO<sub>4</sub>). After removal of the solvent, the residue was recrystallized from chloroform–hexane to afford the

pyrimidin-2(1H)-one (1) in 83% yield. The photoproduct (10c) (40 mg) was refluxed with hydrochloric acid (5 drops) in dioxane (5 ml) for 1 h and then treated in a similar manner to give the pyrimidin-2(1H)-one (1) in quantitative yield.

(ii) A solution of the photoproduct (10a) (50 mg) and potassium hydroxide (20 mg) in MeOH (5 ml) was refluxed for 1 h. Usual work-up gave 1-propyl-4,6-diphenylpyrimidin-2(1H)-one (7) (75%), m.p. 169–170 °C (from chloroform–hexane) (Found: C, 78.45; H, 6.25; N, 9.65). C<sub>19</sub>H<sub>18</sub>N<sub>3</sub>O requires C, 78.6; H, 6.25; N, 9.65%; ν<sub>max</sub> (KBr) 1 660 and 1 645 cm<sup>-1</sup> (C=O); δ<sub>H</sub> (100 MHz; CDCl<sub>3</sub>) 0.75 (3 H, t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.59–1.81 (2 H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.88 (2 H, t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 6.67 (1 H, s, =CH-), 7.34–7.58 (8 H, m, arom.), and 8.04–8.14 (2 H, m, arom.).

*Thermal and Photochemical Reactions of 4,6-Dimethyl-3-phenyl-1,3-diazabicyclo[2.2.0]hex-5-ene (9) in the Presence of Diethylamine.*—A solution of bicyclic ketone (9) (100 mg) and diethylamine (1 ml) in benzene (30 ml) was refluxed for 12 h or irradiated for 6 h under argon. T.l.c. and i.r. analyses indicated no product formation and the bicyclic ketone (9) was recovered quantitatively.

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