Photochemistry of Pyrimidin-2(1*H*)-ones: Intramolecular γ-Hydrogen Abstraction by the Nitrogen of the Imino Group

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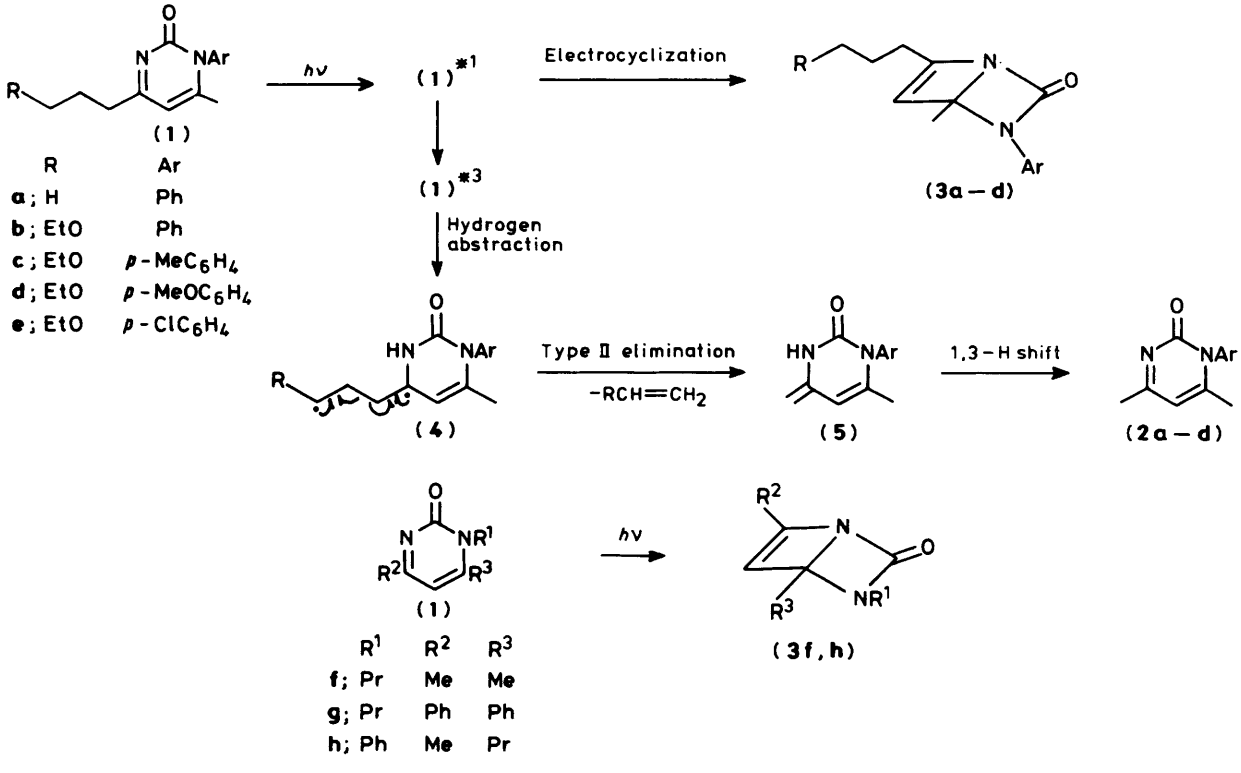
Irradiation of 1-aryl-4-propyl- (**1a**) and 1-aryl-4-(3-ethoxypropyl)-6-methylpyrimidin-2(1*H*)-ones (**1b—d**) gave the photoelimination products, 1-aryl-4,6-dimethylpyrimidin-2(1*H*)-ones (**2a—d**), *via* intramolecular γ-hydrogen atom abstraction of the excited imino nitrogen of the starting pyrimidin-2(1*H*)-one (**1**), in addition to the 1,3-diazabicyclo[2.2.0]hex-5-en-2-ones (**3a—d**). The pyrimidin-2(1*H*)-ones (**1f**) and (**1h**), which have no γ-hydrogens at the C-4 position, underwent photochemical electrocyclization to give the 1,3-diazabicyclo[2.2.0]hex-5-en-2-ones (**3f**) and (**3h**) as the sole products.

In our exploration of the photochemical reactivity of cyclic conjugated nitrogen–carbonyl systems such as pyrimidinones[1] and pyrazinones,[2] we have reported the photochemical electrocyclization of 1,4,6-trisubstituted pyrimidin-2(1*H*)-ones to 2-oxo-1,3-diazabicyclo[2.2.0]hex-5-enes,[1a] photochemical ring opening of *N*-arylpyrimidin-2(1*H*)-ones to arylimine compounds,[1b] and intermolecular hydrogen abstraction reactions of 1-alkyl-4,6-diarylpyrimidin-2(1*H*)-ones.[1c]

Results and Discussion

When 6-methyl-1-phenyl-4-propylpyrimidin-2(1*H*)-one (**1a**) was irradiated in benzene through a Pyrex filter with a high-pressure mercury lamp under argon for 20 h at room tempera-



Scheme.

It is generally accepted that the excited states of imines have little tendency to undergo hydrogen abstraction.[3,4] The main reason for this low reactivity is probably the rapid radiationless decay which results from twisting around the carbon–nitrogen double bond.[3,5] We report here a photoelimination reaction of the pyrimidin-2(1*H*)-ones (**1a—d**) which resembles the Type II photoelimination reaction of ketones and might involve γ-hydrogen abstraction by the nitrogen of a carbon–nitrogen double bond.

ture, the photoelimination products, 4,6-dimethyl-1-phenylpyrimidin-2(1*H*)-one (**2a**) and 4-methyl-3-phenyl-6-propyl-1,3-diazabicyclo[2.2.0]hex-5-en-2-one (**3a**), were obtained in trace and 42% yields, respectively. The yield of the photoelimination product (**2a**) increased to 20% yield when 4-(3-ethoxypropyl)-6-methyl-1-phenylpyrimidin-2(1*H*)-one (**1b**), in which the γ-hydrogen on the side chain at C-4 was activated by an ethoxy

Table. Yield of photoproducts (**2**) and (**3**)

Compd.	Solvent	Additive	Conversion (%)	Yield (%) (**2**)	Yield (%) (**3**)
(**1a**)	Benzene		60	Trace	42
(**1b**)	Benzene		50	20	50
(**1b**)	Acetone		65	20	54
(**1b**)	Benzene	*m*-Methoxyacetophenone	43	42	10
(**1b**)	Benzene	2,5-Dimethylhexa-2,4-diene	*ca.* 100		66
(**1b**)	Benzene	Cyclohexa-1,3-diene	67		69
(**1c**)	Benzene		38	21	53
(**1d**)	Benzene		20	Trace	15
(**1e**)	Benzene		12		
(**1f**)	Benzene		45		83
(**1g**)	Benzene		~0		
(**1h**)	Benzene		50		76

group, was irradiated in benzene under the same conditions as described above. Similarly, irradiation of 1-*p*-tolyl-(**1c**) and 4-(3-ethoxypropyl)-1-*p*-methoxyphenyl-6-methylpyrimidin-2(1*H*)-one (**1d**) in benzene under the same conditions gave the photoelimination products, 1-*p*-tolyl- (**2c**) and 1-*p*-methoxyphenyl-4,6-dimethylpyrimidin-2(1*H*)-one (**2d**) in addition to the corresponding 1,3-diazabicyclo[2.2.0]hex-5-en-2-ones (**3c**) and (**3d**). However, the photoelimination product (**2e**) could not be detected. There was a >88% recovery of 1-*p*-chlorophenyl-4-(3-ethoxypropyl)-6-methylpyrimidin-2(1*H*)-one (**1e**) after it had been irradiated. The structure of the photoproducts (**2a**), (**2c**), and (**2d**) was confirmed by direct comparison of i.r. and n.m.r. spectra with those of authentic materials.[1a] The structure of the 1,3-diazabicyclo[2.2.0]hex-5-en-2-ones (**3a**—**d**) was elucidated on the basis of their physical properties and elemental analyses (see Experimental section). A mechanism for the formation of the photoelimination products, 1-aryl-4,6-dimethylpyrimidin-2(1*H*)-ones (**2**), of which the analogy in ketone photochemistry is the Norrish type II process, is shown in the Scheme. By this mechanism the nitrogen of the excited starting pyrimidin-2(1*H*)-one (**1**) would abstract a γ-hydrogen from the side chain at C-4 yielding a 1,4-diradical (**4**). Subsequent elimination of propene or ethyl vinyl ether followed by 1,3-hydrogen shift would generate 1-aryl-4,6-dimethylpyrimidin-2(1*H*)-one (**2**). The formation of the 1,3-diazabicyclo[2.2.0]hex-5-en-2-ones (**3**) can be readily explained in terms of the photochemical electrocyclization reaction. The formation of 4,6-dimethyl-1-phenylpyrimidin-2(1*H*)-ones (**2a**) was completely quenched by the addition of triplet quenchers such as 2,5-dimethylhexa-2,4-diene (E_T = 58.7 kcal/mol) and cyclohexa-1,3-diene (E_T = 52.4 kcal/mol) and sensitized by the addition of a triplet sensitizer, *m*-methoxyacetophenone (E_T = 72.4 kcal/mol). On the other hand, the formation of the 1,3-diazabicyclo-[2.2.0]hex-5-en-2-one (**3a**) was not influenced by the presence of triplet quenchers. These facts suggested that the γ-hydrogen abstraction by the imino nitrogen proceeded *via* the n–π* triplet state and the photochemical electrocyclization of (**1**) to (**3**) proceeded *via* the singlet state. In order to probe the possibility of a hydrogen abstraction reaction of the ureide carbonyl oxygen or the carbon of the C=C double bond of the pyrimidin-2(1*H*)-ones (**1**), we studied the photochemistry of the pyrimidin-(2*H*)-ones (**1f**—**g**) which contain a long alkyl side chain at the N-1 or C-6 position. Irradiation of the pyrimidin-2(1*H*)-ones (**1f**) and (**1h**) in benzene under the same conditions as described above yielded the 1,3-diazabicyclo[2.2.0]hex-5-en-2-ones (**3f**) and (**3h**) as the sole products, and no Type II photoelimination products could be detected. Irradiation of 4,6-diphenyl-1-propylpyrimidin-2(1*H*)-one (**1g**) in benzene resulted in recovery of the starting material (**1g**).

Experimental

M.p.s and b.p.s are uncorrected and were measured with a Yanaco micro-melting point apparatus (MP-J3) and a Büchi Kugelrohr (KR-3) apparatus, respectively. U.v. spectra were determined with a Shimadzu UV-365 spectrophotometer, i.r. spectra were recorded on a JASCO IR-1 spectrophotometer, n.m.r. spectra were run on a JEOL FX-100 spectrometer (100 MHz), and mass spectra were recorded on a Hitachi M-80 mass spectrometer. An Ushio 450-W high-pressure mercury lamp was used as an irradiation source. Silica gel (Merck, Kieselgel 60 for flash chromatography) was used for column chromatography.

Starting Materials.—The pyrimidin-2(1*H*)-ones (**1a**—**h**) were prepared by a modification of the method described in literature.[6–8] The properties of compounds (**1a**—**h**) are listed below.

6-*Methyl*-1-*phenyl*-4-*propylpyrimidin*-2(1H)-*one* (**1a**) had m.p. 163—164 °C (from benzene–hexane) (Found: C, 73.6; H, 7.05; N, 12.25. $C_{14}H_{16}N_2O$ requires C, 73.65; H, 7.05; N, 12.25%); $\nu_{max.}$(KBr) 1 650, 1 600, 1 540, 1 365, 760, and 700 cm^{-1}; δ_H ($CDCl_3$) 1.00 (3 H, t, CH_2CH_2Me), 1.59—1.95 (2 H, m, CH_2-CH_2Me), 2.00 (3 H, d, *J* 0.7 Hz, Me), 2.60 (2 H, t, CH_2CH_2Me), 6.22 (1 H, d, *J* 0.7 Hz, =CH–), and 6.97—7.58 (5 H, m, Ph).

4-(3-*Ethoxypropyl*)-6-*methyl*-1-*phenylpyrimidin*-2(1H)-*one* (**1b**) had m.p. 102—103 °C (from chloroform–hexane) (Found: C, 70.6; H, 7.4; N, 10.1. $C_{16}H_{20}N_2O_2$ requires C, 70.55; H, 7.4; N, 10.25%); $\lambda_{max.}$(EtOH) (ε) 205 (1.53 × 10^4), 237 sh (6.8 × 10^3), and 307 nm (5.1 × 10^3); $\nu_{max.}$(KBr) 1 640, 1 600, 1 520, 1 355, 1 120, 1 100, 760, and 695 cm^{-1}; δ_H($CDCl_3$) 1.20 (3 H, t, *J* 7.9 Hz, OCH_2Me), 1.85—2.15 (2 H, m, $OCH_2CH_2CH_2$), 1.99 (3 H, d, *J* 0.7 Hz, Me), 2.71 (2 H, t, *J* 7.2 Hz, $OCH_2CH_2CH_2$), 3.47 (2 H, t, *J* 7.1 Hz, $OCH_2CH_2CH_2$), 3.48 (2 H, q, *J* 7.9 Hz, OCH_2Me), 6.26 (1 H, q, *J* 0.7 Hz, =CH–), and 6.89—7.85 (5 H, m, Ph); δ_C($CDCl_3$) 15.2 (q, OCH_2Me), 21.1 (q, Me), 27.7 (t, $OCH_2CH_2CH_2$), 35.5 (t, $OCH_2CH_2CH_2$), 66.0 (t, OCH_2-CH_2CH_2), 69.6 (t, OCH_2Me), 104.9 (d, =CH–), 127.3 (d), 129.0 (d), 129.9 (d), 137.7 (s) (ArC), 156.9 (s, =C–Me), 157.1 (s, C=N), and 178.9 (s, C=O).

4-(3-*Ethoxypropyl*)-6-*methyl*-1-p-*tolylpyrimidin*-2(1H)-*one* (**1c**) had m.p. 109.5—110.5 °C (from chloroform–hexane) (Found: C, 71.2; H, 7.8; N, 9.5. $C_{17}H_{22}N_2O_2$ requires C, 71.3; H, 7.75; N, 9.75%); $\lambda_{max.}$(EtOH) (ε) 307 nm (7.3 × 10^3); $\nu_{max.}$(KBr) 1 650, 1 610, 1 525, 1 350, 1 105, and 820 cm^{-1}; δ_H($CDCl_3$) 1.20 (3 H, t, *J* 6.8 Hz, OCH_2Me), 1.98 (3 H, s, Me), 1.9—2.2 (2 H, m, $OCH_2CH_2CH_2$), 2.40 (3 H, s, Me), 2.71 (2 H, t, *J* 6.8 Hz, $OCH_2CH_2CH_2$), 3.48 (2 H, q, *J* 6.8 Hz, OCH_2Me), 3.51 (2 H, t, *J* 6.4 Hz, $OCH_2CH_2CH_2$), 6.22 (1 H, s, =C–), 7.07 (2 H, d, *J* 8.8 Hz, Ph), and 7.31 (2 H, *J* 8.8 Hz, Ph); δ_C($CDCl_3$) 15.2 (q, OCH_2Me), 21.2 (2 × q, 2 × Me), 27.7 (t, $OCH_2CH_2CH_2$), 35.4 (t, $OCH_2CH_2CH_2$), 66.0 (t, $OCH_2CH_2CH_2$), 69.6 (t, OCH_2-Me), 104.9 (d, =CH–), 126.9 (d), 130.5 (d), 135.1 (s), 139.0 (s) (ArC), 157.1 (s, =C–Me), 157.3 (s, C=N), and 178.8 (s, C=O).

4-(3-*Ethoxypropyl*)-1-p-*methoxyphenyl*-6-*methylpyrimidin*-2(1H)-*one* (**1d**) had m.p. 82—83.5 °C (from chloroform–hexane) (Found: C, 67.25; H,7.3; N, 9.2. $C_{17}H_{22}N_2O_3$ requires C, 67.5; H, 7.35; N, 9.25%); $\lambda_{max.}$(EtOH) (ε) 233 (1.45 × 10^4) and 307 nm (8.3 × 10^3); $\nu_{max.}$(KBr) 1 645, 1 605, 1 525, 1 240, 1 105,

1 030, and 790 cm^{-1}; $\delta_H(CDCl_3)$ 1.20 (3 H, t, *J* 6.8 Hz, OCH_2Me), 1.9—2.2 (2 H, m, $OCH_2CH_2CH_2$), 1.99 (3 H, s, Me), 2.71 (2 H, t, *J* 7.8 Hz, $OCH_2CH_2CH_2$), 3.48 (2 H, q, *J* 6.8 Hz, OCH_2Me), 3.50 (2 H, t, *J* 6.4 Hz, $OCH_2CH_2CH_2$), 3.83 (3 H, s, OMe), 6.21 (1 H, s, =CH–), 6.98 (2 H, d, *J* 9.3 Hz, Ph), and 7.13 (2 H, d, *J* 9.3 Hz, Ph); $\delta_C(CDCl_3)$ 15.2 (q, OCH_2Me), 21.2 (q, Me), 27.8 (t, $OCH_2CH_2CH_2$), 35.5 (t, $OCH_2CH_2CH_2$), 55.5 (q, OMe), 66.0 (t, $OCH_2CH_2CH_2$), 69.6 (t, OCH_2Me), 104.9 (d, =CH–), 115.1 (d), 128.3 (d), 130.3 (s), 157.6 (s), (ArC), 157.4 (s, =C–Me), 159.7 (s, C=N), and 178.8 (s, C=O).

1-p-*Chlorophenyl*-4-(3-*ethoxypropyl*)-6-*methylpyrimidin*-2(1H)-*one* (**1e**) had m.p. 147—148 °C (from chloroform–hexane) (Found: C, 62.45; H, 6.2; N, 9.05. $C_{16}H_{19}ClN_2O_2$ requires C, 62.25; H, 6.25; N, 9.15%); $\lambda_{max.}$(EtOH) (ε) 216 (1.49×10^4) and 307 nm (7.5×10^3); $\nu_{max.}$(KBr) 1 640, 1 610, 1 525, 1 345, 1 125, 1 105, 835, and 790 cm^{-1}; $\delta_H(CDCl_3)$ 1.19 (3 H, t, *J* 6.8 Hz, OCH_2Me), 1.99 (3 H, s, Me), 1.9—2.2 (2 H, m, $OCH_2CH_2CH_2$), 2.71 (2 H, t, *J* 6.8 Hz, $OCH_2CH_2CH_2$), 3.49 (2 H, q, *J* 6.8 Hz, OCH_2Me), 3.50 (2 H, t, *J* 6.2 Hz, $OCH_2CH_2CH_2$), 6.25 (1 H, s, =CH–), 7.16 (2 H, d, *J* 8.8 Hz, Ph), and 7.48 (2 H, d, *J* 8.8 Hz, Ph); $\delta_C(CDCl_3)$ 14.9 (q, OCH_2Me), 20.8 (q, Me), 27.4 (t, $OCH_2CH_2CH_2$), 35.2 (t, $OCH_2CH_2CH_2$), 65.6 (t, $OCH_2CH_2CH_2$), 69.2 (t, OCH_2Me), 104.8 (d, =CH–), 128.6 (d), 129.8 (d), 134.6 (s), 135.9 (s) (ArC), 156.3 (s, =C–Me), 156.6 (s, C=N), and 179.0 (s, C=O).

4,6-*Dimethyl*-1-*propylpyrimidin*-2(1H)-*one* (**1f**) had m.p. 92—94 °C (from benzene–hexane) (Found: C, 64.85; H, 8.5; N, 16.55. $C_9H_{14}N_2O$ requires C, 65.05; H, 8.5; N, 16.85%); $\nu_{max.}$(KBr) 1 650, 1 605, 1 540, and 1 365 cm^{-1}; $\delta_H(CDCl_3)$ 0.99 (3 H, t, CH_2CH_2Me), 1.57—1.87 (2 H, m, $-CH_2CH_2Me$), 2.31 (3 H, s, Me), 2.37 (3 H, s, Me), 3.92 (2 H, t, CH_2CH_2Me), and 6.07 (1 H, =CH–).

4,6-*Diphenyl*-1-*propylpyrimidin*-2(1H)-*one* (**1g**) had m.p. 169—171 °C (from chloroform–hexane) (Found: C, 78.45; H, 6.25; N, 9.65. $C_{19}H_{18}N_2O$ requires C, 78.6; H, 6.25; N, 9.65%); $\nu_{max.}$(KBr) 1 660, 1 645, 1 610, 1 575, 1 365, 780, and 700 cm^{-1}; $\delta_H(CDCl_3)$ 0.75 (3 H, t, CH_2CH_2Me), 1.59—1.81 (2 H, m, CH_2CH_2Me), 3.88 (2 H, t, CH_2CH_2Me), 6.67 (1 H, s, =CH–), 7.34—7.58 (8 H, m, Ph), and 8.04—8.16 (2 H, m, Ph).

4-*Methyl*-1-*phenyl*-6-*propylpyrimidin*-2(1H)-*one* (**1h**) had m.p. 125—126 °C (from benzene–hexane) (Found: C, 73.45; H, 7.00; N, 12.25. $C_{14}H_{16}N_2O$ requires C, 73.65; H, 7.05; N, 12.25%); $\nu_{max.}$(KBr) 1 640, 1 610, 1 545, 1 355, 750, and 700 cm^{-1}; $\delta_H(CDCl_3)$ 0.82 (3 H, t, CH_2CH_2Me), 1.2—1.7 (2 H, m, CH_2CH_2Me), 2.11 (2 H, t, CH_2CH_2Me), 2.41 (3 H, s, Me), 6.35 (1 H, s, =CH–), and 7.1—7.65 (5 H, m, Ph).

General Procedure for the Photochemical Reactions of the Pyrimidin-2(1H)-*ones* (**1a**—**h**).—A solution of the pyrimidin-2(1*H*)-one (**1**) (200 mg) in benzene (50 ml) was irradiated in a Pyrex vessel with a high-pressure mercury lamp (450 W) under argon for 20 h at room temperature. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–ethyl acetate (4:1) followed by dichloromethane–methanol (9:1) as eluant to give the 1-aryl-4,6-dimethylpyrimidin-2-(1*H*)-one (**2**), the 1,3-diazabicyclo[2.2.0]hex-5-en-2-one (**3**), and recovered (**1**). The structures of the 1-aryl-4,6-dimethylpyrimidin-2(1*H*)-ones (**2a**—**d**) were determined by direct comparison of i.r. and n.m.r. spectra with those of authentic samples.[1a]

4-*Methyl*-3-*phenyl*-6-*propyl*-1,3-*diazabicyclo*[2.2.0]*hex*-5-*en*-2-*one* (**3a**), b.p. 115 °C at 2 mmHg (Found: C, 73.7; H, 6.95; N, 12.5. $C_{14}H_{16}N_2O$ requires C, 73.65; H, 7.05; N, 12.25%); $\nu_{max.}$(CHCl$_3$) 1 760, 1 630, 1 595, 1 500, 1 380, 1 275, and 1 180 cm^{-1}; $\delta_H(CDCl_3)$ 0.96 (3 H, *J* 7.3 Hz, CH_2CH_2Me), 1.44—1.73 (2 H, m, CH_2CH_2Me), 1.85 (3 H, s, Me), 2.37 (2 H, dt, *J* 1.7, 7.6 Hz, CH_2CH_2Me), 6.12 (1 H, t, *J* 1.7 Hz, =CH–), and 7.02—7.45 (5 H, m, Ph).

6-(3-*Ethoxypropyl*)-4-*methyl*-3-*phenyl*-1,3-*diazabicyclo*[2.2.0]-*hex*-5-*en*-2-*one* (**3b**), b.p. 113 °C at 2 mmHg (Found: C, 70.45; H, 7.3; N, 10.5. $C_{16}H_{20}N_2O_2$ requires C. 70.55; H, 7.4; N, 10.3%); $\nu_{max.}$(CHCl$_3$) 1 770, 1 640, 1 600, 1 495, 1 380, 1 185, and 1 105 cm^{-1}; $\delta_H(CDCl_3)$ 1.17 (3 H, t, *J* 7.0 Hz, OCH_2Me), 1.86 (3 H, s, Me), 1.75—2.0 (2 H, m, $OCH_2CH_2CH_2$), 2.50 (2 H, dt, *J* 1.7, 7.9 Hz, $OCH_2CH_2CH_2$), 3.45 (2 H, q, *J* 7.0 Hz, OCH_2Me), 3.45 (2 H, t, *J* 6.8 Hz, $OCH_2CH_2CH_2$), 6.14 (1 H, t, *J* 1.7 Hz, =CH–), and 7.02—7.45 (5 H, m, Ph); $\delta_C(CDCl_3)$ 15.1 (q, OCH_2Me), 17.3 (q, Me), 26.0 (t, $OCH_2CH_2CH_2$), 26.8 (t, $OCH_2CH_2CH_2$), 66.0 (t, $OCH_2CH_2CH_2$), 69.2 (t, OCH_2Me), 76.3 (s, C-4), 115.7 (d, =CH–), 119.5 (d), 123.8 (d), 129.3 (d), 137.1 (s) (ArC), 156.2 (s, =C–), and 163.6 (s, C=O); *m*/*z* (c.i.) 273 ($M^+ + 1$).

6-(3-*Ethoxypropyl*)-4-*methyl*-3-p-*tolyl*-1,3-*diazabicyclo*-[2.2.0]*hex*-5-*en*-2-*one* (**3c**), b.p. 125 °C at 2.5 mmHg (Found: C, 71.3; H, 7.95; N, 9.5. $C_{17}H_{22}N_2O_2$ requires C, 71.3; H, 7.75; N, 9.8%); $\nu_{max.}$(CHCl$_3$) 1 770, 1 630, 1 610, 1 515, 1 390, 1 280, 1 185, 1 105, 1 000, and 810 cm^{-1}; $\delta_H(CDCl_3)$ 1.17 (3 H, t, *J* 6.8 Hz, OCH_2Me), 1.84 (3 H, s, Me), 1.8—2.0 (2 H, m, $CH_2CH_2CH_2$), 2.32 (3 H, s, Me), 2.50 (2 H, dt, *J* 1.5, 7.8 Hz, $OCH_2CH_2CH_2$), 3.45 (2 H, q, *J* 6.8 Hz, OCH_2Me), 3.45 (2 H, t, *J* 7.8 Hz, $OCH_2CH_2CH_2$), 6.13 (1 H, t, *J* 1.5 Hz, =CH–), and 7.15 (4 H, s, Ph); $\delta_C(CDCl_3)$ 15.1 (q, OCH_2Me), 17.3 (q, Me), 20.8 (q, Me), 26.1 (t, $OCH_2CH_2CH_2$), 26.8 (t, $OCH_2CH_2CH_2$), 66.1 (t, $OCH_2CH_2CH_2$), 69.3 (t, OCH_2Me), 76.4 (s, C-4), 115.8 (d, =CH–), 119.5 (d), 129.8 (d), 133.6 (s), 134.6 (s) (ArC), 156.2 (s, =C–), and 163.6 (s, C=O); *m*/*z* (c.i.) 287 ($M^+ + 1$).

6-(3-*Ethoxypropyl*)-3-p-*methoxyphenyl*-4-*methyl*-1,3-*diaza-bicyclo*[2.2.0]*hex*-5-*en*-2-*one* (**3d**), b.p. 162 °C at 2 mmHg (Found: C, 67.35; H, 7.15; N, 9.15. $C_{17}H_{22}N_2O_3$ requires C, 67.5; H, 7.35; N, 9.25%); $\nu_{max.}$(CHCl$_3$) 1 760, 1 630, 1 505, 1 375, 1 295, 1 240, 1 180, 1 100, and 825 cm^{-1}; $\delta_H(CDCl_3)$ 1.18 (3 H, t, *J* 7.8 Hz, OCH_2Me), 1.7—2.0 (2 H, m, $OCH_2CH_2CH_2$), 1.83 (3 H, s, Me), 2.50 (2 H, dt, *J* 1.5, 6.8 Hz, $OCH_2CH_2CH_2$), 3.46 (2 H, t, *J* 6.8 Hz, $OCH_2CH_2CH_2$), 3.46 (2 H, q, *J* 7.8 Hz, OCH_2Me), 3.71 (3 H, s, OMe), 6.12 (1 H, t, *J* 1.5 Hz, =CH–), 6.89 (2 H, d, *J* 9.3 Hz, Ph), and 7.18 (2 H, d, *J* 9.3 Hz, Ph); $\delta_C(CDCl_3)$ 15.2 (q, OCH_2Me), 17.3 (q, Me), 26.1 (t, $OCH_2CH_2CH_2$), 26.9 (t, $OCH_2CH_2CH_2$), 55.5 (q, OMe), 66.1 (t, $OCH_2CH_2CH_2$), 69.3 (t, OCH_2Me), 76.5 (s, C-4), 114.7 (d, =CH–), 117.4 (d), 119.5 (d), 130.5 (s), 156.3 (s) (ArC), 156.4 (s, =C–), and 163.7 (s, C=O); *m*/*z* (c.i.) 303 ($M^+ + 1$).

4,6-*Dimethyl*-3-*propyl*-1,3-*diazabicyclo*[2.2.0]*hex*-5-*en*-2-*one* (**3f**), b.p. 85 °C at 2 mmHg (Found: C, 64.8; H, 8.5; N, 16.75. $C_9H_{14}N_2O$ requires C, 65.05; H, 8.5; N, 16.85%); $\nu_{max.}$(film) 1 775, 1 645, and 1 380 cm^{-1}; $\delta_H(CDCl_3)$ 0.94 (3 H, t, CH_2CH_2Me), 1.4—1.75 (2 H, m, CH_2CH_2Me), 1.64 (3 H, s, Me), 2.07 (3 H, d, *J* 1.7 Hz, Me), 2.9—3.5 (2 H, m, CH_2CH_2Me), and 5.94 (1 H, q, *J* 1.7 Hz, =CH–).

6-*Methyl*-3-*phenyl*-4-*propyl*-1,3-*diazabicyclo*[2.2.0]*hex*-5-*en*-2-*one* (**3h**), b.p. 115 °C at 2 mmHg (Found: C, 73.95; H, 7.25; N, 11.95. $C_{14}H_{16}N_2O$ requires C, 73.65; H, 7.05; N, 12.25%); $\nu_{max.}$(film) 1 770, 1 640, 1 600, 1 500, 1 380, 750, and 695 cm^{-1}; $\delta_H(CDCl_3)$ 0.93 (3 H, t, CH_2CH_2Me), 1.26—1.87 (4 H, m, CH_2CH_2Me), 2.10 (3 H, d, *J* 1.7 Hz, Me), 6.11 (1 H, q, *J* 1.7 Hz, =CH–), and 7.02—7.43 (5 H, m, Ph).

Sensitization and Quenching of 4-(3-*Ethoxypropyl*)-6-*methyl*-1-*phenylpyrimidin*-2(1H)-*one* (**1b**).—(*a*) *Sensitization.* A solution of the pyrimidin-2(1*H*)-one (**1b**) (200 mg) and *m*-methoxyacetophenone (E_T = 72.4 kcal/mol) as a sensitizer (in such a ratio that the sensitizer absorbs more than 95% of the incident light) in benzene (50 ml) was irradiated under the same con-

ditions as described above. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–ethyl acetate (4:1) followed by dichloromethane–methanol (9:1) to yield 1-phenyl-4,6-dimethylpyrimidin-2(1*H*)-one (**2a**), the 1,3-diazabicyclo[2.2.0]hex-5-en-2-one (**3b**), and recovered (**1**).

(*b*) *Quenching*. A solution of the pyrimidin-2(1*H*)-one (**1b**) (200 mg) in benzene (50 ml) in the presence of 2,5-dimethylhexa-2,4-diene (E_T = 58.7 kcal/mol) (10 equiv.) or cyclohexa-1,3-diene (E_T = 52.4 kcal/mol) (10 equiv.) as triplet quencher was irradiated under the same conditions. Work-up gave the 1,3-diazabicyclo[2.2.0]hex-5-en-2-one (**3a**) as the sole product, and 1-phenyl-4,6-dimethylpyrimidin-2(1*H*)-one (**3a**) could not be detected.

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