Photochemical Ring Opening of 1-Arylpyrimidin-2(1*H*)-ones

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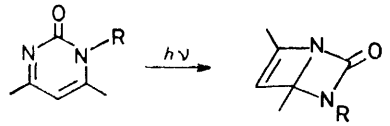
The photochemical reactions of 1-arylpyrimidin-2(1*H*)-ones have been examined. Irradiation of the 1-arylpyrimidin-2(1*H*)-ones (3a—f) in benzene–methanol gave 1-alkoxycarbonylamino-3-aryliminoprop-1-enes (4), (6), and (7), which were hydrolysed to give the corresponding 3-alkoxycarbonylaminoprop-2-enal (5), in 45—55% yield. The formation of the *N*-arylimine products (4), (6), and (7) was presumed to arise from an unstable isocyanate intermediate (8) formed initially by Type I cleavage of the 1-arylpyrimidin-2(1*H*)-one (3).

Because of the biological importance of nucleoside bases, the photochemistry of these compounds has been extensively studied,[1] especially the photochemical transformations of DNA and RNA. It was of interest therefore

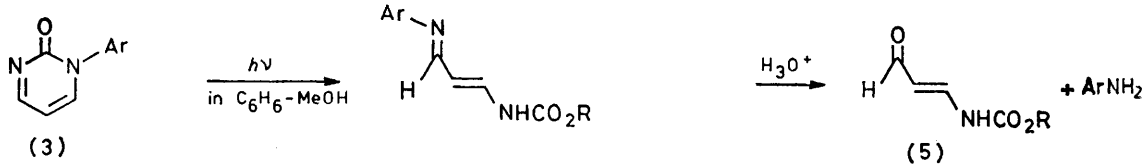


(1) (2)

to study the photochemical reactions of pyrimidin-2(1*H*)-ones related to those of cytosine, one of the nucleoside bases, and its derivatives. Furthermore, the pyrimidin-2(1*H*)-one system is particularly attractive to study since the analogous carboxylic system, the conjugated cyclohexadienone, has been studied in detail[2] and can be used for comparison. Little attention has however been paid to the photochemistry of pyrimidin-2(1*H*)-ones: Pfoertner[3] recently reported the photochemical addition of methanol to and dimerization of 4,6-dimethylpyrimidin-2-ol and Shetler *et al.*[4] reported the photochemical addition of propan-2-ol to 1-methyl-4-methylaminopyrimidin-2(1*H*)-one. Previously, we reported the photochemical electrocyclization of 1,4,6-trisubstituted pyrimidin-2(1*H*)-ones (1) to 3,4,6-trisubstituted 1,3-diazabicyclo[2.2.0]hex-5-en-2-ones (2).[5] We now report the photochemical reactions of the 1-arylpyrimidin-2(1*H*)-ones (3a—f) together with the formation of the *N*-arylimines (4), (6), and (7) initiated by Type I cleavage of (3)

Results and Discussion

When a solution of 1-phenylpyrimidin-2(1*H*)-one (3a) in benzene–methanol (45 : 1) was irradiated in a Pyrex vessel with a high-pressure mercury lamp under argon for 15 h at room temperature, 1-methoxycarbonylamino-3-phenyliminoprop-1-ene (4a) was obtained; † when chromatographed on silica gel this was hydrolysed to give 3-methoxycarbonylaminoprop-2-enal (5) and aniline in 51 and 54% yield, respectively. A similar result was obtained when (3a) was irradiated in methanol. The structure of (5) was determined on the basis of physical properties and elemental analysis. The n.m.r. spectrum of (5) in CD_3Cl–CD_3OD showed a singlet at



(3) (5)

a; Ar = Ph (4a) [Ar = Ph, R = Me]

b; Ar = *p*-MeC_6H_4 (4b) Ar = *p*-MeC_6H_4, R = Me (45%)

c; Ar = *p*-$MeOC_6H_4$ (4c) Ar = *p*-$MeOC_6H_4$, R = Me (55%)

d; Ar = *m*-MeC_6H_4 (6) Ar = Ph, R = Et (45%)

e; Ar = *m*-$MeOC_6H_4$ (7) Ar = Ph, R = Pr^i (51%)

f; Ar = *o*-MeC_6H_4

R = Me

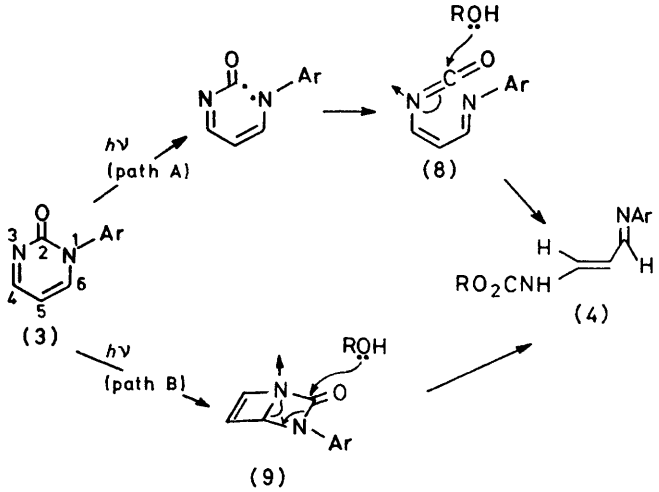
δ 3.75 a double doublet at δ 5.62, and two doublets at δ 7.71 and 9.38 which were assigned to the methyl, α-olefinic, β-olefinic, and aldehydic protons, respectively. The product (5) was assigned the *E* stereochemistry from the magnitude of the coupling constant (14.6 Hz) of the olefinic protons.

Irradiation of a solution of (3a) in benzene–ethanol (45 : 1) or benzene–propan-2-ol (45 : 1) under the same conditions gave the imines (6) (45%) or (7) (51%). Irradiation of 1-*p*-tolyl- (3b) and 1-*p*-methoxyphenylpyrimidin-2(1*H*)-one (3c) in benzene–methanol (45 : 1) under the same conditions also gave imines, (4b) in 45% and (4c) in 55% yield. The structures of the photoproducts (4b and c), (6) and (7) were confirmed on the basis of the physical data and elemental analyses (see Experimental section). The stereochemistry was also

† The photo-product (4a) could not be isolated in pure form by fractional recrystallization (from benzene–methanol); however, its formation was shown by i.r. and n.m.r. spectroscopy: $\nu_{max.}$ (KBr) 1 725, 1 660 and 1 630 cm^{-1}; δ ($CDCl_3$–CD_3OD) 3.75 (s, 3 H), 6.08 (dd, 1 H *J* 9.2 and 13.8 Hz), 7.0—7.7 (m, 6 H), and 8.23 (d, 1 H, *J* 9.2 Hz).

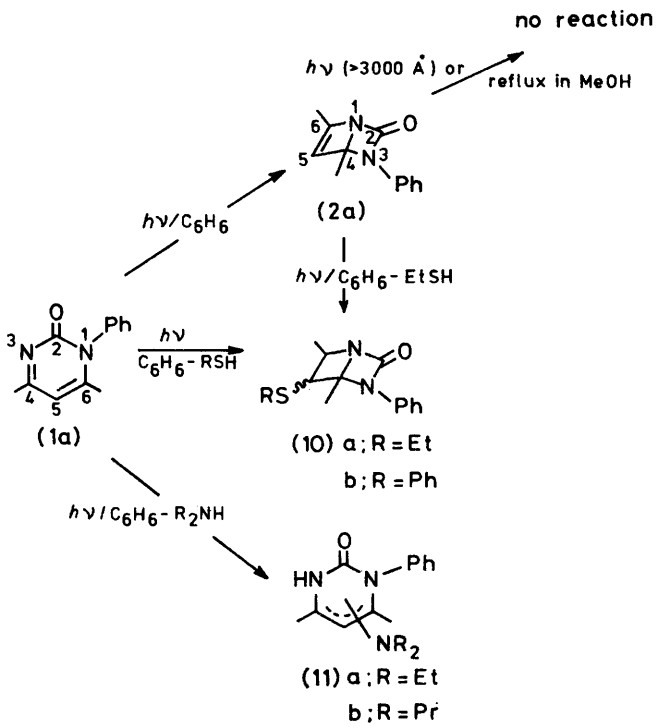
assigned as *E*, the n.m.r. coupling constants of the olefinic protons being in the range 13.6—14.6 Hz. Meanwhile, when the 1-arylpyrimidin-2-(1*H*)-ones (3d—f) were irradiated in benzene–methanol and the products were subjected to chromatography on silica gel (small amounts of by-products were observed by t.l.c.), 3-methoxycarbonylaminoprop-2-enal (5) was obtained in 57—63% yields, accompanied by the corresponding aniline derivative.

Reasonable mechanisms for the formation of the products (4), (6), and (7) are shown in Scheme 1. In path A, an unstable isocyanate intermediate (8), formed initially by Norrish Type I cleavage of the ArN–CO bond of the pyrimidin-2(1*H*)-one (3) upon irradiation (analogous to the conjugated cyclohexadienone system [2]), is trapped by the alcohol to give the *N*-arylimines (4), (6), and (7). In path B, the intermediate (9), formed by photochemical internal [2 + 2] electrocyclization of (3) by analogy with the photochemical electrocyclization of 1,4,6-trisubstituted pyrimidin-2(1*H*)-ones (1) to 1,3-diazabicyclo-[2.2.0]hex-5-en-2-ones (2),[5] is attacked by the alcohol to give the final products. Attempts to detect directly formation of the isocyanate (8) or of the bicyclic intermediate (9) by i.r. spectroscopy were unsuccessful.* The intermediacy of the isocyanate (8), however, was presumed from the following results. When the stable bicyclic ketone (2a), produced photochemically from the pyrimidin-2(1*H*)-one (1a) [5] was irradiated in methanol at >3 000 Å or refluxed in methanol, arylimine products



Scheme 1

were not obtained and (2a) was recovered quantitatively (Scheme 2). In contrast, irradiation of (2a) in benzene containing ethanethiol † afforded the bicyclic ketone (10a) in almost quantitative yield. The structure of (10a) was confirmed by the usual spectroscopic methods and by elemental analysis. The n.m.r. spectrum of (10a) showed two doublets at δ 1.45 and 3.78, and a multiplet at δ 4.44 which assigned to the 6-methyl, 5-



Scheme 2

methine, and 6-methine protons respectively. Furthermore, compounds (10a and b) were also obtained when (1a) was irradiated in benzene in the presence of the corresponding thiol. Compound (2a) did not give the product formed by cleavage at the 2,3- and 1,4-bonds on treatment with nucleophiles such as an alcohol and a thiol. On the other hand, irradiation of (1a) in benzene in the presence of a dialkylamine gave the 1 : 1-adduct (11) of (1a) and the dialkylamine. The structures of the 1 : 1-adducts (11) were confirmed on the basis of spectroscopic data and elemental analyses, except for the position of addition (4 or 6) of the amino-group which we were unable to determine. The 1 : 1-adduct (11b) was converted back into the pyrimidinone (1a) on heating at a higher temperature (>150 °C at 2 mmHg) in a sealed tube when dipropylamine was eliminated. Irradiation of (3a) in tetrahydrofuran ‡ in the presence of ethanethiol or dimethylamine as nucleophiles afforded an intractable mixture.§ These results seem to preclude the intermediacy of the bicyclic ketone (9) and suggest that an unstable isocyanate, the Type I cleavage product of the arylpyrimidinone (3), was the intermediate in the

* We measured the i.r. spectrum of the photolysate of (3a) in tetrahydrofuran owing to solubility problems in benzene or in a potassium bromide matrix at low temperature (*ca.* −10 °C) with time. An absorption due to isocyanate (*ca.* 2 250 cm^{-1}) or the fused ureide carbonyl group (*ca.* 1 770 cm^{-1})[8] was not observed in the i.r. spectrum.

† The product (10a) could not be produced by stirring of (2a) in benzene–ethanethiol in the dark.

‡ Tetrahydrofuran was used as solvent since (3a) was insoluble in benzene.

§ In the case of dimethylamine, a small amount of *NN*-diethyl-*N'*-(2-formylvinyl)urea was detected by spectroscopy: $\nu_{max.}$ (KBr) 1 740, 1 690, and 1 630 cm^{-1}; δ ($CDCl_3$) 1.21 (t, 6 H), 3.42 (q, 4 H), 5.71 (m, 1 H), 7.71 (m, 1 H), and 9.31 (d 1 H).

formation of the *N*-arylimine (4) (*i.e.* path A).* Analogous ring-opening reactions have been observed in the photochemistry of 2-pyrones when a keten intermediate was proposed.[7]

EXPERIMENTAL

I.r. spectra were recorded on a Hitachi 260-30 spectrometer. U.v. spectra were determined with a JASCO UVIDEC-505 spectrometer. N.m.r. spectra were run on Hitachi R-24 and JEOL FX 100 spectrometers using tetramethylsilane as internal standard. A Ushio 450-W high-pressure mercury lamp was used as an irradiation source.

Starting Materials.—The 1-arylpyrimidin-2(1*H*)-ones (3a and b) were prepared as described [8] and (3c—f) were prepared by a modification of this method. 1-Phenylpyrimidin-2(1*H*)-one (3a) had m.p. 154—155 °C (lit.,[8] 155—156 °C); $\lambda_{max.}$ (EtOH) 210 (ε 10 500) and 317 nm (5 000); $\nu_{max.}$ (KBr) 1 665 cm^{-1}; δ($CDCl_3$) 6.41 (dd, 1 H, *J* 3.9 and 6.8 Hz), 7.38—7.48 (m, 5 H), 7.75 (dd, 1 H, *J* 2.9 and 6.8 Hz), and 8.66 (dd, 1 H, *J* 2.9 and 3.9 Hz). 1-*p*-Tolylpyrimidin-2(1*H*)-one (3b) had m.p. 144—145 °C (lit.,[8] 142—143 °C); $\lambda_{max.}$ (EtOH) 215 (ε 19 600) and 320 nm (8 900); $\nu_{max.}$ (KBr) 1 650 cm^{-1}; δ($CDCl_3$) 2.43 (s, 3 H), 6.37 (dd, 1 H, *J* 3.9, 6.4 Hz), 7.35 (br s, 4 H), 7.71 (dd, 1 H, *J* 2.2 and 6.4 Hz), and 8.61 (dd, 1 H, *J* 2.2 and 3.9 Hz). 1-p-*Methoxyphenylpyrimidin*-2(1H)-*one* (3c) had m.p. 156—157 °C (from chloroform–hexane); $\lambda_{max.}$ (EtOH) 220 (ε 8 700) and 323 nm (3 400); $\nu_{max.}$ (KBr) 1 655 cm^{-1}; δ($CDCl_3$) 3.85 (s, 3 H), 6.40 (dd, 1 H, *J* 4.0 and 6.4 Hz), 7.18 (dd, 4 H, *J* 8.2 and 21.8 Hz), 7.74 (dd, 1 H, *J* 2.6 and 6.4 Hz), and 8.70 (dd, 1 H, *J* 2.6 and 4.0 Hz) (Found: C, 65.0; H, 4.95; N, 13.55. $C_{11}H_{10}N_2O_2$ requires C, 65.3; H, 5.0; N, 13.85%). 1-m-*Tolylpyrimidin*-2(1H)-*one* (3d) had m.p. 73—74 °C (from chloroform–hexane); $\lambda_{max.}$ (EtOH) 212 (ε 13 600) and 318 nm (6100); $\nu_{max.}$ (KBr) 1 660 cm^{-1}; δ($CDCl_3$) 2.08 (s, 3 H), 6.40 (dd, 1 H, *J* 3.9 and 6.4 Hz), 7.13—7.47 (m, 4 H), 7.73 (dd, 1 H, *J* 2.9 and 6.4 Hz), and 8.66 (dd, 1 H, *J* 2.9 and 3.9 Hz) (Found: C, 70.8; H, 5.35; N, 15.05. $C_{11}H_{10}N_2O$ requires C, 70.95; H, 5.4; N, 15.05%). 1-o-*Tolylpyrimidin*-2(1H)-*one* (3e) had m.p. 95—96 °C (from chloroform–hexane); $\lambda_{max.}$ (EtOH) 218 (ε 7 600) and 313 nm (5 400); $\nu_{max.}$ (KBr) 1 660 cm^{-1}; δ($CDCl_3$) 2.18 (s, 3 H), 6.41 (dd, 1 H, *J* 3.9 and 6.4 Hz), 7.11—7.35 (m, 4 H), 7.62 (dd, 1 H, *J* 2.9 and 6.4 Hz), and 8.69 (dd, 1 H, *J* 2.9 and 3.9 Hz) (Found: C, 70.65; H, 5.4; N, 15.05. $C_{11}H_{10}N_2O$ requires C, 70.95; H, 5.4; N, 15.05%). 1-m-*Methoxyphenylpyrimidin*-2(1H)-*one* (3f) had m.p. 114—115 °C (from chloroform–hexane); $\lambda_{max.}$ (EtOH) 215 (ε 14 200) and 315 nm (4 700); $\nu_{max.}$ (KBr) 1 665 cm^{-1}; δ($CDCl_3$) 3.84 (s, 3 H), 6.39 (dd, 1 H, *J* 3.6 and 6.4 Hz), 6.5—7.2 (m, 4 H), 7.31 (d, 1 H, *J* 6.4 Hz), and 7.38 (dd, 1 H, *J* 3.4 and 6.4 Hz) (Found: C, 65.0; H, 5.0; N, 13.55. $C_{11}H_{10}N_2O_2$ requires C, 65.3; H, 5.0; N, 13.85%).

General Procedure for Photochemical Reactions of (3a—f).—A solution of the pyrimidin-2(1*H*)-one (3) (200 mg) in benzene (45 ml) and methyl alcohol (1 ml) was irradiated in a Pyrex vessel under argon for 15 h at room temperature. After removal of the solvent, the residue was purified by fractional recrystallization from benzene–methanol or chromatography on silica gel (eluant: benzene–ethyl acetate, 2 : 1) to give the photo-product (4)—(7). 1-*Methoxycarbonylamino*-3-p-*tolyliminoprop*-1-*ene* (4b) had m.p. 148—150 °C; $\nu_{max.}$ (KBr) 3 190, 1 725, and 1 640 cm^{-1}; δ($CDCl_3$–CD_3OD) 2.34 (s, 3 H), 3.82 (s, 3 H), 5.97 (dd, 1 H, *J* 9.4 and 13.6 Hz), 7.10 (br s, 4 H), 7.40 (d, 1 H, *J* 13.6 Hz), and 8.10 (d, 1 H, *J* 9.4 Hz) (Found: C, 66.0; H, 6.35; N, 12.85. $C_{12}H_{14}N_2O_2$ requires C, 66.05; H, 6.45; N, 12.85%). 1-*Methoxycarbonylamino*-3-p-*methoxyphenyliminoprop*-1-*ene* (4c) had m.p. 172—173 °C; $\nu_{max.}$ (KBr) 3 190, 1 720, and 1 630 cm^{-1}; δ($CDCl_3$–CD_3OD) 3.81 (s, 6 H), 6.04 (dd, 1 H, *J* 9.4 and 13.6 Hz), 7.05 (dd, 4 H), 7.45 (d, 1 H, *J* 13.6 Hz), and 8.15 (d, 1 H, *J* 9.4 Hz) (Found: C, 61.2; H, 6.0; N, 11.7. $C_{12}H_{14}N_2O_3$ requires C, 61.5; H, 6.0; N, 11.95%). 3-*Methoxycarbonylaminoprop*-2-*enal* (5) had m.p. 158—160 °C; $\nu_{max.}$ (KBr) 3 200, 1 735, and 1 635 cm^{-1}; δ($CDCl_3$–CD_3OD) 3.75 (s, 3 H), 5.62 (dd, 1 H, *J* 8.4 and 14.6 Hz), 7.71 (d, 1 H, *J* 14.6 Hz), and 9.38 (d, 1 H, *J* 8.4 Hz) (Found: C, 46.65; H, 5.35; N, 10.8. $C_5H_7NO_3$ requires C, 46.5; H, 5.55; N, 10.85%). 1-*Ethoxycarbonylamino*-3-*phenyliminoprop*-1-*ene* (6) had m.p. 158—160 °C; $\nu_{max.}$ (KBr) 3 180, 1 720, and 1 630 cm^{-1}; δ($CDCl_3$–CD_3OD) 1.24 (t, 3 H), 4.17 (q, 2 H), 6.01 (dd, 1 H, *J* 9.2 and 13.6 Hz), 6.9—7.6 (m, 6 H), and 8.13 (d, 1 H, *J* 9.2 Hz) (Found: C, 66.1; H, 6.45; N, 12.75. $C_{12}H_{14}N_2O_2$ requires C, 66.05; H, 6.45; N, 12.85%). 1-*Isopropoxycarbonylamino*-3-*phenyliminoprop*-1-*ene* (7) had m.p. 160—161 °C; $\nu_{max.}$ (KBr) 3 450, 3 180, 1 715, and 1 635 cm^{-1}; δ($CDCl_3$–CD_3OD) 1.30 (d, 6 H), 5.0 (m, 1 H), 6.01 (dd, 1 H, *J* 9.4, 13.8 Hz), 7.05—7.7 (m, 6 H), and 8.15 (d, 1 H, *J* 9.4 Hz) (Found: C, 67.4; H, 6.7; N, 12.3. $C_{13}H_{16}N_2O_2$ requires C, 67.2; H, 6.95; N, 12.05%).

Irradiation of 4,6-*Dimethyl*-1-*phenylpyrimidin*-2(1H)-*one* (1a) *in the Presence of the Thiol.*—A solution of (1a) (200 mg) and the thiol (1 ml) in benzene (45 ml) was irradiated under the conditions described above for 15 h. After removal of the solvent, the residual oil was chromatographed on a silica gel column with benzene–ethyl acetate (4 : 1) as eluant to yield 5-*ethylthio*-4,6-*dimethyl*-3-*phenyl*-1,3-*diazabicyclo*[2.2.0]-*hexan*-2-*one* (10a) (67%), b.p. 158 °C at 2 mmHg (Kugelrohr); $\nu_{max.}$ (neat) 1 780 cm^{-1}; δ($CDCl_3$) 1.19 (t, 3 H), 1.45 (d, 3 H, *J* 6.8 Hz), 1.75 (s, 3 H), 2.50 (q, 2 H), 3.78 (d, 1 H, *J* 8.4 Hz), 4.44 (m, 1 H), and 7.0—7.45 (m, 5 H) (Found: C, 63.8; H, 6.85; N, 10.65. $C_{14}H_{18}N_2OS$ requires C, 64.1; H, 6.9; N, 10.65%); and 4,6-*dimethyl*-3-*phenyl*-5-*phenylthio*-1,3-*diazabicyclo*[2.2.0]*hexan*-2-*one* (10b) (51%), m.p. 154 °C (from hexane); $\nu_{max.}$ (KBr) 1 780 cm^{-1}; δ($CDCl_3$) 1.51 (d, 3 H, *J* 7.0 Hz), 1.82 (s, 3 H), 4.31 (d, 1 H, *J* 8.4 Hz), 4.88 (m, 1 H), and 7.1—7.45 (m, 10 H) (Found: C, 69.7; H, 5.75; N, 8.95. $C_{18}H_{18}N_2OS$ requires C, 69.65; H, 5.85; N, 9.0%).

Irradiation of 4,6-*Dimethyl*-1-*phenylpyrimidin*-2(1H)-*one* (1a) *in the Presence of the Dialkylamine.*—A solution of (1a) (200 mg) and the dialkylamine (1 ml) in benzene (45 ml) was irradiated under the conditions described above for 15 h. After removal of the solvent, the residual oil was chromatographed on silica gel with benzene–ethyl acetate (4 : 1) as eluant to give the 1 : 1 adducts (11) of (1a) and dialkylamine: 4 (or 6)-diethylamino-4,6-dimethyl-1-phenyl-3,4 (or 3,6)-dihydropyrimidin-2(1*H*)-one (11a) (62%) had b.p. 130 °C at 2 mmHg (Kugelrohr); $\lambda_{max.}$ (EtOH) 225 (ε 14 100) and 308 nm (14 100); $\nu_{max.}$ (neat) 1 660 and 1 640 cm^{-1}; δ($CDCl_3$) 1.06 (t, 6 H), 1.87 (s, 3 H), 2.41 (d, 3 H, *J* 1.0 Hz), 3.30 (q, 4 H), 4.97 (d, 1 H, *J* 1.0 Hz), 6.47—6.97 (m, 2 H),

* The difference in the photochemical reactivity between the pyrimidin-2(1*H*)-ones (1) and (3), *e.g.*, the fact that (1) affords 1,3-diazabicyclo[2.2.0]hex-5-en-2-one (2) but (3) affords a cleavage product (4), may be explained in terms of the differences of the bond order [(1a) : 0.4319; (3a) : 0.4309] at the 1,2-bond (–PhN–CO–) calculated by the INDO method [6] and those of the excited states (n–π^* or π–π^*) as described for the conjugated cyclohexadienone system.[2]

7.04—7.39 (m, 3 H), and 12.91 (br s, 1 H) (Found: C, 69.85; H, 8.5; N, 15.35. $C_{16}H_{23}N_3O$ requires C, 70.05; H, 8.8; N, 15.3%); 4 (or 6)-dipropylamino-4,6-dimethyl-1-phenyl-3,4-(or 3,6)-dihydropyrimidin-2(1*H*)-one (11b) (50%) had b.p. 145 °C at 2 mmHg (Kugelrohr); $\lambda_{max.}$ (EtOH) 225 (ε 14 000) and 308 nm (14 100); $\nu_{max.}$ (neat) 1 670 and 1 640 cm^{-1}; δ($CDCl_3$) 0.68 (t, 6 H), 1.33—1.7 (m, 4 H), 1.86 (s, 3 H), 2.42 (d, 3 H, *J* 1.0 Hz), 3.18 (t, 4 H), 4.97 (d, 1 H, *J* 1.0 Hz), 6.7—6.81 (m, 2 H), 7.04—7.37 (m, 3 H), and 12.97 (br s, 1 H) (Found: C, 71.45; H, 8.95; N, 14.0. $C_{18}H_{27}N_3O$ requires C, 71.7; H, 9.0; 13.95%).

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