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

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#### Abstract

The photochemical reactions of 1 -arylpyrimidin- $2(1 H)$-ones have been examined. Irradiation of the 1 -aryl-pyrimidin-2(1H)-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(1H)-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

to study the photochemical reactions of pyrimidin$2(1 \mathrm{H})$-ones related to those of cytosine, one of the nucleoside bases, and its derivatives. Furthermore, the pyri-midin-2(1H)-one system is particularly attractive to study since the analogous carboxylic system, the conjugated cyclohexadienone, has been studied in detail ${ }^{2}$
arylpyrimidin-2(1H)-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(1H)-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-methoxycarbonyl-amino-3-phenyliminoprop-l-ene (4a) was obtained; $\dagger$ 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 $\mathrm{CD}_{3} \mathrm{Cl}-\mathrm{CD}_{3} \mathrm{OD}$ showed a singlet at

(3)

$$
\begin{align*}
& \mathrm{a} ; \mathrm{Ar}=\mathrm{Ph} \\
& \mathrm{~b}: \mathrm{Ar}=p-\mathrm{MeC}_{6} \mathrm{H}_{4} \\
& \mathrm{c} ; \mathrm{Ar}=p-\mathrm{MeOC}_{6} \mathrm{H}_{4} \\
& \mathrm{~d}: \mathrm{Ar}=m-\mathrm{MeC}_{6} \mathrm{H}_{4} \\
& \mathrm{e}: \mathrm{Ar}=m-\mathrm{MeOC}_{6} \mathrm{H}_{4} \\
& \mathrm{f}: \mathrm{Ar}=0-\mathrm{MeC}_{6} \mathrm{H}_{4}
\end{align*}
$$

$$
\begin{array}{ll}
\text { (4a) }[\mathrm{Ar}=\mathrm{Ph}, \mathrm{R}=\mathrm{Me}] & \\
\text { (4b) } \mathrm{Ar}=p-\mathrm{MeC}_{6} \mathrm{H}_{4} \cdot \mathrm{R}=\mathrm{Me} & (45 \%) \\
\text { (4c) } \mathrm{Ar}=p-\mathrm{MeOC}_{6} \mathrm{H}_{4}, \mathrm{R}=\mathrm{Me} & (55 \%) \\
\text { (6) } \mathrm{Ar}=\mathrm{Ph}, \mathrm{R}=\mathrm{Et} & (45 \%) \\
\text { (7) } \mathrm{Ar}=\mathrm{Ph}, \mathrm{R}=\operatorname{Pr} \mathrm{Pr}^{\mathrm{i}} & (51 \%)
\end{array}
$$

and can be used for comparison. Little attention has however been paid to the photochemistry of pyrimidin-2(1H)-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 l-methyl-4-methylaminopyrimidin-2( $1 H$ )-one. Previously, we reported the photochemical electrocyclization of $1,4,6-$ trisubstituted pyrimidin-2(1H)-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 -

[^0]$\delta 3.75$ a double doublet at $\delta 5.62$, and two doublets at $\delta 7.71$ and 9.38 which were assigned to the methyl, $\alpha-$ olefinic, $\beta$-olefinic, and aldehydic protons, respectively. The product (5) was assigned the $E$ stereochemistry from the magnitude of the coupling constant $(14.6 \mathrm{~Hz})$ 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 l-p-methoxyphenyl-pyrimidin-2(1 $H$ )-one ( 3 c ) 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 ( 4 b and c), (6) and (7) were confirmed on the basis of the physical data and elemental analyses (see Experimental section). The stereochemistry was also
assigned as $E$, the n.m.r. coupling constants of the olefinic protons being in the range $13.6-14.6 \mathrm{~Hz}$. Meanwhile, when the 1 -arylpyrimidin- 2 - $(1 H)$-ones ( $3 \mathrm{~d}-\mathrm{f}$ ) 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 $\operatorname{ArN}-\mathrm{CO}$ bond of the pyrimidin-2( $\mathbf{1} H$ )-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 $\mathbf{1 , 4 , 6}$-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(lH)-one (la) ${ }^{5}$ was irradiated in methanol at $>3000 \AA$ or refluxed in methanol, arylimine products

were not obtained and (2a) was recovered quantitatively (Scheme 2). In contrast, irradiation of (2a) in benzene containing ethanethiol $\dagger$ afforded the bicyclic ketone (10a) in almost quantitative yield. The structure of

[^1](10a) was confirmed by the usual spectroscopic methods and by elemental analysis. The n.m.r. spectrum of (10a) showed two doublets at $\delta 1.45$ and 3.78 , and a multiplet at $\delta 4.44$ which assigned to the 6 -methyl, 5 -

methine, and 6-methine protons respectively. Furthermore, compounds ( 10 a and b ) were also obtained when (la) 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 (la) 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 (llb) was converted back into the pyrimidinone (la) on heating at a higher temperature ( $>150{ }^{\circ} \mathrm{C}$ at 2 mmHg ) in a sealed tube when dipropylamine was eliminated. Irradiation of (3a) in tetrahydrofuran $\ddagger$ 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

[^2]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 highpressure mercury lamp was used as an irradiation source.

Starting Materials.-The 1-arylpyrimidin-2(1H)-ones (3a and b) were prepared as described ${ }^{8}$ and ( $3 \mathrm{c}-\mathrm{f}$ ) were prepared by a modification of this method. 1-Phenylpyri-midin-2 $(1 H)$-one (3a) had m.p. $154-155{ }^{\circ} \mathrm{C}$ (lit., ${ }^{8} 155-$ $156{ }^{\circ} \mathrm{C}$ ); $\lambda_{\text {max. }}(\mathrm{EtOH}) 210(\varepsilon 10500)$ and $317 \mathrm{~nm}(5000)$; $v_{\text {max. }}(\mathrm{KBr}){ }^{1} 665 \mathrm{~cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}\right) 6.41(\mathrm{dd}, 1 \mathrm{H}, J 3.9$ and 6.8 Hz ), $7.38-7.48$ (m, 5 H ), 7.75 (dd, $1 \mathrm{H}, J 2.9$ and 6.8 Hz ), and 8.66 (dd, $1 \mathrm{H}, J 2.9$ and 3.9 Hz ). $1-p$-Tolylpyrimidin$2(1 H)$-one (3b) had m.p. $144-145{ }^{\circ} \mathrm{C}$ (lit., ${ }^{8} 142-143{ }^{\circ} \mathrm{C}$ ); $\lambda_{\max }(\mathrm{EtOH}) 215(\varepsilon 19600)$ and $320 \mathrm{~nm}(8900)$; $\nu_{\text {max }}$ $(\mathrm{KBr}) 1650 \mathrm{~cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}\right) 2.43(\mathrm{~s}, 3 \mathrm{H}), 6.37(\mathrm{dd}, 1 \mathrm{H}, J$ 3.9, 6.4 Hz ), $7.35(\mathrm{br} \mathrm{s}, 4 \mathrm{H}), 7.71(\mathrm{dd}, 1 \mathrm{H}, J 2.2$ and 6.4 Hz ), and 8.61 (dd, $1 \mathrm{H}, J 2.2$ and 3.9 Hz ). 1-p-Methoxy-phenylpyrimidin-2(1H)-one (3c) had m.p. $156-157^{\circ} \mathrm{C}$ (from chloroform-hexane); $\lambda_{\max }$ (EtOH) $220(\varepsilon 8700)$ and 323 $\mathrm{nm}(3400) ;{ }_{\text {max. }}(\mathrm{KBr}) 1655 \mathrm{~cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}\right) 3.85(\mathrm{~s}, 3 \mathrm{H})$, $6.40(\mathrm{dd}, 1 \mathrm{H}, J 4.0$ and 6.4 Hz$), 7.18(\mathrm{dd}, 4 \mathrm{H}, J 8.2$ and 21.8 Hz ), $7.74(\mathrm{dd}, 1 \mathrm{H}, J 2.6$ and 6.4 Hz$)$, and $8.70(\mathrm{dd}, 1 \mathrm{H}$, $J 2.6$ and 4.0 Hz ) (Found: C, 65.0; H, 4.95; N, 13.55. $\mathrm{C}_{11} \mathrm{H}_{10} \mathrm{~N}_{2} \mathrm{O}_{2}$ requires $\mathrm{C}, 65.3 ; \mathrm{H}, 5.0 ; \mathrm{N}, 13.85 \%$ ). $1-\mathrm{m}-$ Tolylpyrimidin-2(1H)-one (3d) had m.p. 73-74 ${ }^{\circ} \mathrm{C}$ (from chloroform-hexane); $\lambda_{\text {max. }}(\mathrm{EtOH}) 212(\varepsilon 13600)$ and 318 nm (6100); $\nu_{\text {max. }}(\mathrm{KBr}) 1660 \mathrm{~cm}^{-1}$; $\delta\left(\mathrm{CDCl}_{3}\right) 2.08(\mathrm{~s}$, 3 H ), 6.40 (dd, $1 \mathrm{H}, J 3.9$ and 6.4 Hz ), $7.13-7.47(\mathrm{~m}, 4 \mathrm{H})$, 7.73 (dd, $1 \mathrm{H}, J 2.9$ and 6.4 Hz ), and 8.66 (dd, $1 \mathrm{H}, J 2.9$ and 3.9 Hz ) (Found: C, 70.8; H, 5.35; N, 15.05. $\mathrm{C}_{11} \mathrm{H}_{10^{-}}$ $\mathrm{N}_{2} \mathrm{O}$ requires C, $70.95 ; \mathrm{H}, 5.4 ; \mathrm{N}, 15.05 \%$ ). 1-o-Tolyl-pyrimidin- $2\left(1 \mathrm{H}\right.$ )-one ( 3 e ) had m.p. $95-96{ }^{\circ} \mathrm{C}$ (from chloro-form-hexane); $\lambda_{\max }(\mathrm{EtOH}) 218(\varepsilon 7600)$ and 313 nm ( 5400 ) ; $\nu_{\text {max. }}(\mathrm{KBr}) 1660 \mathrm{~cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}\right) 2.18(\mathrm{~s}, 3 \mathrm{H})$, 6.41 (dd, 1 H, $J 3.9$ and 6.4 Hz ), $7.11-7.35(\mathrm{~m}, 4 \mathrm{H}), 7.62$ (dd, 1 H, J 2.9 and 6.4 Hz ), and 8.69 (dd, $1 \mathrm{H}, J 2.9$ and 3.9 Hz ) (Found: C, 70.65; H, 5.4; $\mathrm{N}, 15.05 . \mathrm{C}_{11} \mathrm{H}_{10} \mathrm{~N}_{2} \mathrm{O}$ requires $\mathrm{C}, 70.95 ; \mathrm{H}, 5.4 ; \mathrm{N}, 15.05 \%$ ). 1-m-Methoxy-phenylpyrimidin-2(1H)-one (3f) had m.p. $114-115{ }^{\circ} \mathrm{C}$ (from chloroform-hexane); $\lambda_{\text {max }}(\mathrm{EtOH}) 215(\varepsilon 14200)$ and $315 \mathrm{~nm}(4700)$; $\nu_{\text {max. }}(\mathrm{KBr}) 1665 \mathrm{~cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}\right) 3.84$ $(\mathrm{s}, 3 \mathrm{H}), 6.39(\mathrm{dd}, 1 \mathrm{H}, J 3.6$ and 6.4 Hz$), 6.5-7.2(\mathrm{~m}, 4 \mathrm{H})$, $7.31(\mathrm{~d}, 1 \mathrm{H}, J 6.4 \mathrm{~Hz})$, and $7.38(\mathrm{dd}, 1 \mathrm{H}, J 3.4$ and 6.4 Hz$)$ (Found: C, 65.0; H, 5.0; N, 13.55. $\mathrm{C}_{11} \mathrm{H}_{10} \mathrm{~N}_{2} \mathrm{O}_{2}$ requires $\mathrm{C}, 65.3 ; \mathrm{H}, 5.0 ; \mathrm{N}, 13.85 \%)$.

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.

[^3]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. $148-150{ }^{\circ} \mathrm{C}$; $\nu_{\text {max. }}(\mathrm{KBr}) 3190,1725$, and 1640 $\mathrm{cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}-\mathrm{CD}_{3} \mathrm{OD}\right) 2.34(\mathrm{~s}, 3 \mathrm{H}), 3.82(\mathrm{~s}, 3 \mathrm{H}), 5.97$ (dd, $1 \mathrm{H}, J 9.4$ and 13.6 Hz ), 7.10 (br s, 4 H ), 7.40 (d, 1 H , $J 13.6 \mathrm{~Hz}$ ), and $8.10(\mathrm{~d}, 1 \mathrm{H}, J 9.4 \mathrm{~Hz})$ (Found: C, $66.0 ; \mathrm{H}$, $6.35 ; \mathrm{N}, 12.85$. $\mathrm{C}_{12} \mathrm{H}_{14} \mathrm{~N}_{2} \mathrm{O}_{2}$ requires $\mathrm{C}, 66.05 ; \mathrm{H}, 6.45$; N , $\quad 12.85 \%$ ). 1-Methoxycarbonylamino-3-p-methoxy-phenyliminoprop-1-ene (4c) had m.p. $172-173{ }^{\circ} \mathrm{C}$; $\nu_{\max }$ ( KBr ) 3190,1720 , and $1630 \mathrm{~cm}^{-1}$; $\delta\left(\mathrm{CDCl}_{3}-\mathrm{CD}_{3} \mathrm{OD}\right) 3.81$ ( $\mathrm{s}, 6 \mathrm{H}$ ), $6.04(\mathrm{dd}, 1 \mathrm{H}, J 9.4$ and 13.6 Hz ), 7.05 (dd, 4 H ), $7.45(\mathrm{~d}, 1 \mathrm{H}, J 13.6 \mathrm{~Hz}$ ), and $8.15(\mathrm{~d}, 1 \mathrm{H}, J 9.4 \mathrm{~Hz})$ (Found:
C, 61.2; H, 6.0; N, 11.7. $\quad \mathrm{C}_{12} \mathrm{H}_{14} \mathrm{~N}_{2} \mathrm{O}_{3}$ requires $\mathrm{C}, 61.5 ; \mathrm{H}$, 6.0 ; $\mathrm{N}, 11.95 \%$ ). 3-Methoxycarbonylaminoprop-2-enal (5) had m.p. $158-160^{\circ} \mathrm{C}$; $\nu_{\text {max. }}(\mathrm{KBr}) 3200,1735$, and 1635 $\mathrm{cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}-\mathrm{CD}_{3} \mathrm{OD}\right) 3.75(\mathrm{~s}, 3 \mathrm{H}), 5.62(\mathrm{dd}, 1 \mathrm{H}, J 8.4$ and 14.6 Hz ), $7.71(\mathrm{~d}, 1 \mathrm{H}, J 14.6 \mathrm{~Hz}$ ), and $9.38(\mathrm{~d}, 1 \mathrm{H}, J$ 8.4 Hz ) (Found: C, 46.65 ; H, 5.35; N, 10.8. $\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{NO}_{3}$ requires $\mathrm{C}, 46.5 ; \mathrm{H}, 5.55 ; \mathrm{N}, 10.85 \%$ ). 1-Ethoxycarbonyl-amino-3-phenyliminoprop-1-ene (6) had m.p. $158-160^{\circ} \mathrm{C}$; $v_{\text {max }}(\mathrm{KBr}) 3180,1720$, and $1630 \mathrm{~cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}-\mathrm{CD}_{3} \mathrm{OD}\right)$ $1.24(\mathrm{t}, 3 \mathrm{H}), 4.17(\mathrm{q}, 2 \mathrm{H}), 6.01(\mathrm{dd}, 1 \mathrm{H}, J 9.2$ and 13.6 Hz$)$, $6.9-7.6(\mathrm{~m}, 6 \mathrm{H})$, and $8.13(\mathrm{~d}, 1 \mathrm{H}, J 9.2 \mathrm{~Hz})$ (Found: C, $66.1 ; \mathrm{H}, 6.45 ; \mathrm{N}, 12.75 . \quad \mathrm{C}_{12} \mathrm{H}_{14} \mathrm{~N}_{2} \mathrm{O}_{2}$ requires C , 66.05 ; H, 6.45; $\mathrm{N}, 12.85 \%$ ). 1-Isopropoxycarbonylamino-3-phenyliminoprop-1-ene (7) had m.p. $160-161{ }^{\circ} \mathrm{C}$; $\nu_{\text {max. }}$ $(\mathrm{KBr}) 3450,3180,1715$, and $1635 \mathrm{~cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}-\right.$ $\left.\mathrm{CD}_{3} \mathrm{OD}\right) 1.30(\mathrm{~d}, 6 \mathrm{H}), 5.0(\mathrm{~m}, 1 \mathrm{H}), 6.01$ (dd, $1 \mathrm{H}, J 9.4$, $13.8 \mathrm{~Hz}), 7.05-7.7(\mathrm{~m}, 6 \mathrm{H})$, and $8.15(\mathrm{~d}, 1 \mathrm{H}, J 9.4 \mathrm{~Hz})$ (Found: $\mathrm{C}, 67.4 ; \mathrm{H}, 6.7 ; \mathrm{N}, 12.3 . \mathrm{C}_{13} \mathrm{H}_{16} \mathrm{~N}_{2} \mathrm{O}_{2}$ 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-etliyl acetate ( $4: 1$ ) as eluant to yield 5-ethylthio-4,6-dimethyl-3-phenyl-1,3-diazabicyclo[2.2.0]-hexan-2-one (10a) $\left(67 \%\right.$ ), b.p. $158{ }^{\circ} \mathrm{C}$ at 2 mmHg (Kugelrohr); $v_{\text {max. }}$ (neat) $1780 \mathrm{~cm}^{-1}$; $\delta\left(\mathrm{CDCl}_{3}\right) 1.19(\mathrm{t}, 3 \mathrm{H}), 1.45(\mathrm{~d}, 3 \mathrm{H}$, $J 6.8 \mathrm{~Hz}), 1.75(\mathrm{~s}, 3 \mathrm{H}), 2.50(\mathrm{q}, 2 \mathrm{H}), 3.78(\mathrm{~d}, 1 \mathrm{H}, J 8.4$ Hz ), $4.44(\mathrm{~m}, 1 \mathrm{H})$, and $7.0-7.45(\mathrm{~m}, 5 \mathrm{H})$ (Found: C, $63.8 ; \mathrm{H}, 6.85 ; \mathrm{N}, 10.65 . \mathrm{C}_{14} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{OS}$ requires $\mathrm{C}, 64.1$; $\mathrm{H}, 6.9 ; \mathrm{N}, 10.65 \%$ ) ; and 4,6-dimethyl-3-phenyl-5-phenylthio-1,3-diazabicyclo 2.2 .0$]$ hexan-2-one (10b) ( $51 \%$ ), m.p. $154{ }^{\circ} \mathrm{C}$ (from hexane); $v_{\text {max }}(\mathrm{KBr}) 1780 \mathrm{~cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}\right) 1.51(\mathrm{~d}$, $3 \mathrm{H}, J 7.0 \mathrm{~Hz}$ ), $1.82(\mathrm{~s}, 3 \mathrm{H}), 4.31(\mathrm{~d}, 1 \mathrm{H}, J 8.4 \mathrm{~Hz}), 4.88(\mathrm{~m}$, 1 H ), and $7.1-7.45(\mathrm{~m}, 10 \mathrm{H})$ (Found: C, 69.7 ; H, 5.75; $\mathrm{N}, 8.95 . \quad \mathrm{C}_{18} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{OS}$ requires $\mathrm{C}, 69.65 ; \mathrm{H}, 5.85 ; \mathrm{N}, 9.0 \%$ ).

Irradiation of 4,6-Dimethyl-1-phenylpyrimidin-2(1H)-one (1a) in the Presence of the Dialkylamine.-A solution of (la) ( 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(1H)-one (11a) ( $62 \%$ ) had b.p. $130^{\circ} \mathrm{C}$ at 2 mmHg (Kugelrohr); $\lambda_{\text {max. }}(\mathrm{EtOH}) 225(\varepsilon 14100)$ and $308 \mathrm{~nm}(14100)$; $\nu_{\max }$ (neat) 1660 and $1640 \mathrm{~cm}^{-1}$; $\delta\left(\mathrm{CDCl}_{3}\right) 1.06(\mathrm{t}, 6 \mathrm{H}), 1.87(\mathrm{~s}, 3 \mathrm{H}), 2.41(\mathrm{~d}, 3 \mathrm{H}, J 1.0 \mathrm{~Hz})$, $3.30(\mathrm{q}, 4 \mathrm{H}), 4.97(\mathrm{~d}, 1 \mathrm{H}, J 1.0 \mathrm{~Hz}), 6.47-6.97(\mathrm{~m}, 2 \mathrm{H})$,
$7.04-7.39$ (m, 3 H ), and 12.91 (br s, 1 H ) (Found: C, 69.85 ; $\mathrm{H}, 8.5$; $\mathrm{N}, 15.35$. $\mathrm{C}_{16} \mathrm{H}_{23} \mathrm{~N}_{3} \mathrm{O}$ requires $\mathrm{C}, 70.05$; $\mathrm{H}, 8.8$; $\mathrm{N}, 15.3 \%$ ); 4 (or 6)-dipropylamino-4,6-dimethyl-1-phenyl-3,4-(or 3,6)-dihydropyrimidin-2(1H)-one (11b) $(50 \%$ ) had b.p. $145{ }^{\circ} \mathrm{C}$ at 2 mmHg (Kugelrohr); $\lambda_{\max .}$ (EtOH) 225 ( $\varepsilon 14000$ ) and $308 \mathrm{~nm}(14100)$; $v_{\text {max. }}($ neat $) 1670$ and 1640 $\mathrm{cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}\right) 0.68(\mathrm{t}, 6 \mathrm{H}), 1.33-1.7(\mathrm{~m}, 4 \mathrm{H}), 1.86(\mathrm{~s}$, $3 \mathrm{H}), 2.42(\mathrm{~d}, 3 \mathrm{H}, J 1.0 \mathrm{~Hz}), 3.18(\mathrm{t}, 4 \mathrm{H}), 4.97(\mathrm{~d}, 1 \mathrm{H}, J 1.0$ $\mathrm{Hz}), 6.7-6.81(\mathrm{~m}, 2 \mathrm{H}), 7.04-7.37(\mathrm{~m}, 3 \mathrm{H})$, and 12.97 (brs, l H) (Found: C, 71.45; H, 8.95; N, 14.0. $\mathrm{C}_{18} \mathrm{H}_{27} \mathrm{~N}_{3} \mathrm{O}$ requires $\mathrm{C}, 71.7 ; \mathrm{H}, 9.0 ; 13.95 \%$ ).
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[^0]:    $\dagger$ 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: $\cdot \nu_{\text {max. }}$, $(\mathrm{KBr}) 1725,1660$ and $1630 \mathrm{~cm}^{-1} ; \delta\left(\mathrm{CDCl}_{3}-\mathrm{CD}_{3} \mathrm{OD}\right) 3.75(\mathrm{~s}, 3 \mathrm{H})$, 6.08 (dd, $1 \mathrm{H} J 9.2$ and 13.8 Hz ), $7.0-7.7(\mathrm{~m}, 6 \mathrm{H})$, and 8.23 (d, $1 \mathrm{H}, J 9.2 \mathrm{~Hz}$ ).

[^1]:    - 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. - $10{ }^{\circ} \mathrm{C}$ ) with time. An absorption due to isocyanate (ca. $2250 \mathrm{~cm}^{-1}$ ) or the fused ureide carbonyl group ( $c a .1770 \mathrm{~cm}^{-1}$ ) ${ }^{5}$ was not observed in the i.r. spectrum.
    $\dagger$ The product (10a) could not be produced by stirring of (2a) in benzene-ethanethiol in the dark.

[^2]:    $\ddagger$ Tetrahydrofuran was used as solvent since (3a) was insoluble in benzene.
    § In the case of dimethylamine, a small amount of $N N$-diethyl-$N^{\prime}$-(2-formylvinyl)urea was detected by spectroscopy: $\nu_{\text {max. }}$ ( KBr ) 1740,1690 , and $1630 \mathrm{~cm}^{-1}$; $\delta\left(\mathrm{CDCl}_{3}\right) 1.21$ (t, 6 H ), 3.42 (q, $4 \mathrm{H}), 5.71(\mathrm{~m}, 1 \mathrm{H}), 7.71(\mathrm{~m}, 1 \mathrm{H})$, and $9.31(\mathrm{~d} 1 \mathrm{H})$.

[^3]:    * The difference in the photochemical reactivity between the pyrimidin-2(1H)-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 [(la):0.4319; (3a):0.4309] at the 1,2-bond ( $-\mathrm{PhN}-\mathrm{CO}-$ ) calculated by the INDO method ${ }^{6}$ and those of the excited states ( $n-\pi^{*}$ or $\pi-\pi^{*}$ ) as described for the conjugated cyclohexadienone system. ${ }^{2}$

