Photoreactions of Diazines. Part 8.[1] A Di-π-methane Photorearrangement of 4-Substituted 1,4(or 3,4)-Dihydropyrimidines leading to 5-Substituted 1,2(or 2,3)-Dihydropyrimidines

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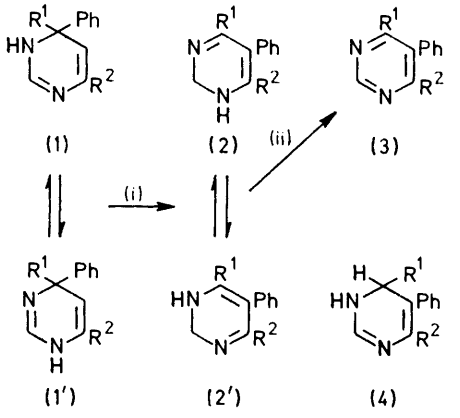
Photolysis of 4-R-1,4(or 3,4)-dihydropyrimidines (1) caused rearrangement to 5-R-1,2(or 2,3)-dihydropyrimidines (2) provided that the substituent R contained a π-bond in a position α to the heterocyclic ring (R = phenyl, isobutenyl, and phenylethynyl). 4-Methyl-1,4(or 3,4)-dihydropyrimidine did not show this rearrangement. Chemical evidence is presented that the rearrangement of (1) occurs *via* the di-π-methane mechanism leading to 6-R-2,4-diazabicyclo[3,1,0]hex-2(or 3)-ene. This latter intermediate undergoes a thermal homo[1,5]hydrogen shift into 5-R-2,5-dihydropyrimidine which on tautomerization gives (2). The reaction could be sensitized by acetone. 5-Substituted 4-phenyl-1,4(or 3,4)-dihydropyrimidines (9a—c) did not rearrange under photochemical conditions.

SIX-MEMBERED heterocyclic compounds have been shown to undergo many types of photochemical reactions.[2] Much research has been done on the photochemistry of the *N*-heteroaromatics, their *N*-oxides,[2,3] and *N*-benzoylimino-derivatives.[1a] In more recent years the photochemistry of several dihydro-pyridines, -pyridazines, and -pyrazines has attracted attention, in many cases giving rise to isomerization reactions.[2] Many of these isomerizations involve an initial ring-opening reaction



SCHEME 1 (*i*) *hν*; (*ii*) oxidation

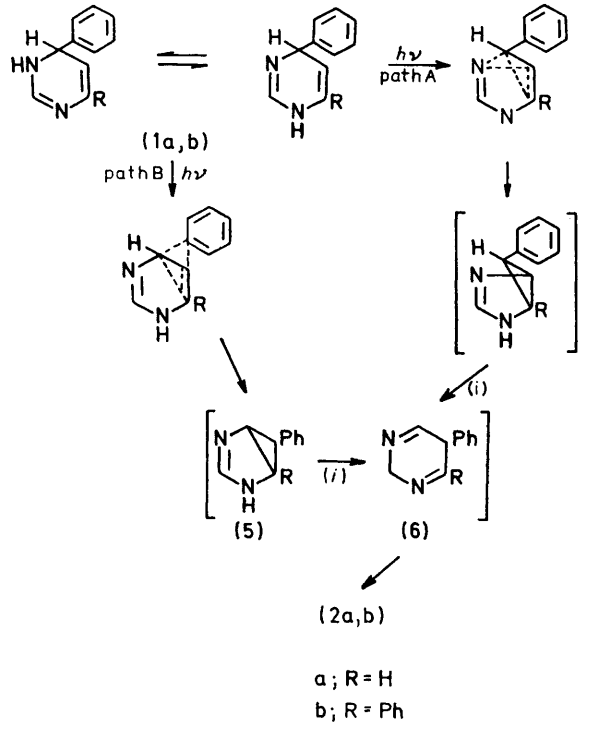
and a subsequent thermal or photochemical rearrangement. No data, however, are available on the behaviour of dihydropyrimidines on irradiation. In this paper we wish to report on a new photochemical rearrangement reaction of 4-substituted 1,4(or 3,4)-dihydropyrimidines.

RESULTS AND DISCUSSION

Irradiation of 4-Phenyl-1,4(or 3,4)-dihydropyrimidines.—When a 6.3×10^{-3}M solution of 4-phenyl-1,4(or 3,4)-dihydropyrimidine (1a) [4] in acetone was photolysed until all starting material had disappeared (2 h), a reaction mixture was obtained which according to the spectral data contained as the main product 5-phenyl-1,2(or 2,3)-dihydropyrimidine (2a) (Scheme 1), along with 4-phenylpyrimidine. Because of its instability, isolation of (2a) by chromatography or crystallization failed. Evidence for the structure of (2a) was based on the following chemical and spectral data. Heating of the crude irradiation mixture in air, or oxidation of it with potassium permanganate, gave 5-phenylpyrimidine as proved by comparison with an authentic specimen.[5] The i.r. spectrum of the crude irradiation mixture of (1a) showed one NH stretching vibration at 3 465 cm^{-1} [starting material (1a) has two absorptions,[4] at 3 465 and 3 490 cm^{-1}]. The ^1H n.m.r. spectrum featured, in addition to the signals of the phenyl protons at δ 7.1—7.4 three broad absorptions at δ 5.8 (this signal shifted upon addition of D_2O, confirming the presence of an NH group), 4.5, and 7.4. This latter signal was partially masked by the phenyl proton signals. Using 4-(pentadeuteriophenyl)-1,4(or 3,4)-dihydropyrimidine (prepared from pyrimidine and pentadeuteriophenyl-lithium) the intensity ratio of the signals at δ 4.5 and 7.4 was found to be 1 : 1. The proton-coupled ^{13}C n.m.r. spectrum of the photolysis mixture of (1a) showed, in addition to the phenyl carbon atoms, a triplet at δ 58.7, a singlet at δ 111.5, and a doublet at δ 148.5, assigned to the C-2, C-5, and C-4,6 carbon atoms of the heterocyclic ring. Irradiation at the resonance frequencies of the δ 4.5 and 7.4 protons caused the triplet at δ 58.7 and the doublet at δ 148.5, respectively, to collapse into singlets.

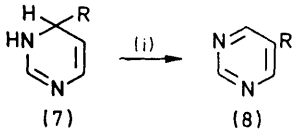
These spectral data favour the 1,2-dihydro-structure (2a) rather than the isomeric 3,4-dihydro-structure (4a); the 1,2-dihydropyrimidine (2a) is in rapid (on the n.m.r. time scale) equilibrium with its tautomer, 2,3-dihydropyrimidine (2'a), causing H-4 and H-6 (and C-4 and C-6) to appear as one signal in the n.m.r. spectra; the tautomerism also leads to one NH absorption in the i.r. spectrum. Supporting evidence for structure (2a) ⇌ (2'a) as the photolysis product of (1a) was found in the chemical and spectral data of the product formed from photolysis of 4,6-diphenyl-1,4(or 3,4)-dihydropyrimidine (1b). Oxidation of this irradiation product gave 4,5-diphenylpyrimidine. The ^1H n.m.r. spectrum of the irradiation mixture showed, in addition to the phenyl protons, two broad singlets at δ 7.8 and δ 4.6 (ratio 1 : 2)

and a very broad singlet at δ 5.2 which shifted upon the addition of D_2O (NH). The i.r. spectrum showed *two* NH absorptions at 3 440 and 3 475 cm^{-1}, as can be expected since the tautomeric 1,2-dihydro- (2b) and 2,3-dihydro-pyrimidine (2'b) are *not* identical. In the ^{13}C n.m.r. spectrum a triplet was observed at δ 60.2, supporting structure (2) and excluding 4,5-diphenyl-1,4(or 3,4)-dihydropyrimidine (4; R^1 = Ph, R^2 = H).* A possible alternative structure for the irradiation product of (1b), *i.e.* 5,6-diphenyl-1,4(or 3,4)-dihydropyrimidine (4b) was also ruled out; photolysis of 4-deuterio-4,6-diphenyl-1,4(or 3,4)-dihydropyrimidine (1c) gave a reaction mixture that did not show the δ 7.8 signal in the ^1H n.m.r. spectrum, and which upon oxidation gave 4,5-diphenylpyrimidine containing the *same* percentage of deuterium as the starting material. If (4c) had been an intermediate it would certainly have led to a considerable loss of deuterium upon oxidation. Irradiation of a solution of 4,4,6-triphenyl-1,4(or 3,4)-dihydropyrimidine (1d) in acetone or methanol and subsequent oxidation gave 4,5,6-triphenylpyrimidine (3d). This hitherto unknown compound was also synthesized independently from 4,5-diphenylpyrimidine



SCHEME 2 (*i*) homo[1,5]hydrogen shift

and phenyl-lithium. The quantum yield for the photochemical isomerization of (1a) to (2a) was found to be 0.06, when the irradiation was carried out in methanol with light of wavelength 254 nm and nitrogen was bubbled through the solution. The amount of (2a) was determined indirectly by oxidation of (2a) to 5-phenylpyrimidine, and g.l.c. analysis of the reaction product thus obtained. The photochemical reaction was sensitized by acetone. The quantum yield for the isomerization in acetone solution using light of wavelength 300



a; R = Me
b; R = CH=CMe$_2$
c; R = C≡CPh

SCHEME 3 (*i*) *hν*, then oxidation

nm was 0.02. These results indicate that the isomerization reaction can occur from the triplet excited state of (1a).

Mechanism of the Photochemical Rearrangement of 4-Phenyl-1,4(or 3,4)-dihydropyrimidines. Several mechanisms for the photochemical rearrangement of substituents in cycloalkenes and cycloalkadienes have appeared in the literature.[6] Photolysis of diaryl cyclohexadienes [7] and γ-pyrans [8] caused migration of an aryl group to an adjacent carbon atom accompanied by the synchronous formation of a three-membered ring thus leading to a bicyclo[3.1.0]hexene derivative *via* the di-π-methane rearrangement mechanism. Photolysis of cyclohexadienones and cyclohexenones, on the other hand, may lead to migration of a ring carbon *together* with the substituents, or, in the case of arylcyclohexenones, migration of the aryl group in a di-π-methane manner.[6] The photochemical rearrangement of 4-phenyl-1,4(or 3,4)-dihydropyrimidines into 5-phenyl-1,2(or 2,3)-dihydropyrimidines can be described similarly either *with* or *without* ring-carbon migration. (Scheme 2, paths A and B respectively.)

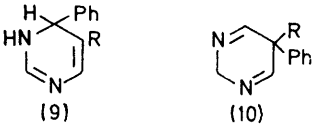
The mechanism *via* path A was proved to be unlikely, based on the facts that (*i*) in the product (3c), obtained by oxidation of the dihydro-intermediate (2c), the deuterium content is the same as in the starting material (1c); and (*ii*) on irradiation of (1d) 4,5,6-triphenylpyrimidine (3d) is obtained and not a compound containing two phenyl groups on one carbon atom. Both results exclude the occurrence of path A. Path B seems a more attractive way to describe the rearrangement. A necessary structural requirement is that the substituent at position 4 should contain a π-bond in the correct position. This means that 4-R-1,4(or 3,4)-dihydropyrimidines lacking the π-bond in the group R may not isomerize under these photochemical conditions. Thus 4-methyl-1,4(or 3,4)-dihydropyrimidine (7a) (synthesized from methyl-lithium and pyrimidine) when irradiated for several hours gave a reaction mixture which, after oxidation, did not show the presence of 5-methylpyrimidine (Scheme 3). On the other hand, 4-(2-methylprop-1-enyl)-1,4(or 3,4)-dihydropyrimidine (7b) and 4-(phenylethynyl)-1,4(or 3,4)-dihydropyrimidine

* 4,5-Diphenyl-1,4(or 3,4)-dihydropyrimidine was prepared from 5-phenylpyrimidine and phenyl-lithium (see Experimental section) and was found to have different spectral data.

(7c) * did give rearrangement. Irradiation of (7b) in acetone for 2 h, and subsequent heating of the photolysis mixture in air gave 5-(2-methylprop-1-enyl)-pyrimidine (8b) in 14% yield. Irradiation of (7c) in acetone for 4 h and subsequent oxidation gave 5-(phenylethynyl)pyrimidine (8c) in 22% yield.

As noted above, the isomerization reaction can occur from the triplet excited state although most di-π-methane rearrangements were shown to be singlet reactions and could not be sensitized by triplet sensitizers.[9] The triplet state was considered to be deactivated by rotation about the excited π-bond (free rotor effect). That some compounds with the π-bond in a cyclic system, as in the dihydropyrimidines, under-went rearrangement from the triplet state was attributed to the absence of the free rotor effect in these rigid structures.

As indicated in Scheme 2 the postulated mechanism for the rearrangement of (1a) should give the intermediate 6-phenyl-2,4-diazabicyclo[3.1.0]hex-2(or 3)-ene (5a). However, since (2a) was obtained from photolysis of (1a), obviously a subsequent rearrangement of (5a) into (2a) had occurred. This rearrangement is best understood by a two-step reaction involving an opening of the three-membered ring with a concomitant hydrogen shift from nitrogen to carbon C-2 (a thermally allowed homo[1,5]sigmatropic hydrogen shift) [10] into 5-phenyl-2,5-dihydropyrimidine (6a) which then tautomerizes to the more conjugated 1,2(or 2,3)-dihydropyrimidine (2a). In order to establish more firmly whether the hydrogen on nitrogen in (5) migrates to the adjacent carbon atom C-2 in (6), the compound 4,6-diphenyl-1,4(or 3,4)-dihydropyrimidine (1b) was dissolved in acetone–D_2O (25 : 1) and irradiated. In this medium (1b) has been completely deuteriated on nitrogen. Oxidation of the photolysis mixture gave 4,5-diphenylpyrimidine containing 56.5% deuterium at C-2. It is nearly the amount expected for the homo[1,5]deuterium shift from nitrogen to C-2. (1b) and (2b) were shown not to incorporate deuterium on carbon significantly under thermal conditions, neither did (2b) under photochemical conditions.



(9) (10)

a; R = Ph
b; R = Me
c; R = Br

The 2,5-dihydropyrimidine (6) could neither be isolated, nor detected by spectroscopic means. Attempts to trap such an intermediate by irradiating 5-substituted-4-phenyl-1,4(or 3,4)-dihydropyrimidines (9) in order to obtain the stable (with respect to tautomerization) 5,5-disubstituted-2,5-dihydropyrimidines (10) failed. Surprisingly the 5-substituted-dihydropyrimidines (9a—c) were rather stable under photochemical conditions. 4,5-Diphenyl-1,4(or 3,4)-dihydropyrimidine (9a) and 5-methyl-4-phenyl-1,4(or 3,4)-dihydropyrimidine (9b) were only oxidized slowly to the corresponding heteroaromatics. 5-Bromo-4-phenyl-1,4(or 3,4)-dihydropyrimidine (9c) underwent, in addition to oxidation, some dehalogenation [11] leading to 4-phenylpyrimidine. In all these experiments no rearranged product could be detected after irradiation for several hours.

* One of the π-bonds in the di-π-methane rearrangement may be part of a triple bond (G. W. Griffin, D. M. Chihal, J. Perreten, and W. S. Bhacca, *J. Org. Chem.*, 1976, **41**, 3931.

EXPERIMENTAL

Infrared spectra of solutions in $CHCl_3$ were recorded on a Perkin-Elmer 237 spectrometer, u.v. spectra on a Beckman Acta CIII spectrometer in 96% ethanol, the ^1H n.m.r. spectra on JEOL-JNM C-60 or Perkin-Elmer R24-B spectrometers using $CDCl_3$ as solvent (unless otherwise stated) and $SiMe_4$ as the internal standard, and ^{13}C n.m.r. spectra with a Varian XL-100 spectrometer in the pulsed Fourier-transform mode using $CDCl_3$ as solvent and $SiMe_4$ as the internal standard. Mass spectra were recorded on an A.E.I.-MS 902 mass spectrometer. Deuterium contents were determined by a combined mass-spectroscopic and n.m.r. analysis. Reactions involving organometallic compounds were carried out in atmosphere of predried nitrogen. For these reactions the solvents diethyl ether and tetrahydrofuran (THF) were dried by addition of an ethereal solution of phenyl-lithium, and distilling the solvents directly into the reaction vessel. Benzene was dried over sodium wire. Pyrimidine,[12] 5-bromopyrimidine,[13] 5-methylpyrimidine,[14] 5-phenylpyrimidine,[5] 4,6-diphenylpyrimidine,[15] and 4-hydrazino-6-phenylpyrimidine [16] were prepared according to the literature. An ethereal solution of phenyl-lithium was prepared as described previously.[4] A solution of methyl-lithium in ether was purchased from Aldrich, a solution of butyl-lithium in hexane from Merck. A solution of isobutenyl-lithium in ether was prepared according to the literature.[17] Phenylethynyl-lithium was prepared by the addition of a solution of phenylacetylene (Merck) in THF to 1 equiv. of butyl-lithium in hexane.[18]

Preparation of the Dihydropyrimidines.—4-Phenyl-1,4-(or 3,4)-dihydropyrimidine (1a) and 4,6-diphenyl-1,4(or 3,4)-dihydropyrimidine (1b) were prepared according to the literature.[4] The other dihydropyrimidines were prepared by carefully adding a solution of the pyrimidine derivative in ether to a solution of the appropriate organolithium compound (1.4 equiv.) at room temperature, unless otherwise stated. Water was added, and after separation and subsequent extraction of the aqueous phase with chloroform (3 ×), the combined organic extracts were dried ($MgSO_4$), filtered, and the solvents evaporated off. In the case of the preparation of (1d), (7c), (9a), and (9c) the resulting mixture crystallized upon cooling and the crystalline product was washed with small portions of cold ether [(1d) and (9a)], acetone (7c), or butan-2-one (9c). When the dihydropyrimidine failed to crystallize [in the case of (7a), (7b), and (9b)] purification from neutral impurities was accomplished by a careful acid–base separation procedure. The dihydropyrimidines (7a—c) and (9b) could not be obtained in an analytically pure state (diffuse m.p.) due to oxidation and probably polymerization during purification procedures. Evidence for the structure, however, was based on spectral data and oxidation to the corresponding pyrimidines by potassium permanganate in acetone solution.[13]

4-*Deuterio*-4,6-*diphenyl*-1,4(*or* 3,4)-*dihydropyrimidine* (1c). To a suspension of 4-hydrazino-6-phenylpyrimidine (2.9 g) in D_2O (80 ml), silver acetate (14.0 g) was added portionwise, and the resulting mixture was then heated under reflux for 3 h. The precipitate was filtered off; the filtrate was extracted with chloroform, and the precipitate was subjected to continuous extraction with chloroform (5 h). The organic extracts were combined, dried ($MgSO_4$), filtered, and the solvent evaporated off. The residue was purified by column chromatography [silica gel, chloroform–ethyl acetate (4 : 1)] to give 4-phenylpyrimidine (1.2 g, 49%) with 94.8% deuterium incorporation at position 6. This compound was treated with phenyl-lithium as described [4] for the unlabelled compound to give (1c).

4,4,6-*Triphenyl*-1,4(*or* 3,4)-*dihydropyrimidine* (1d). The solution of phenyl-lithium was added to a 0.2M solution of 4,6-diphenylpyrimidine in benzene,* to yield (1d) (24%), m.p. 236—238 °C (from ethanol); $\nu_{max.}$ 3 470 (shoulder), 3 450, 1 680, 1 636, 1 603, and 1 580 cm^{-1}; $\lambda_{max.}$ 237 and 293 nm (log ε 4.35 and 3.26); δ 7.66 (2 H, m), 7.24 (15 H, m), and 5.59 (1 H, s, broad) (Found: C, 85.1; H, 5.9. $C_{22}H_{18}N_2$ requires C, 85.13; H, 5.85%).

4-*Methyl*-1,4(*or* 3,4)-*dihydropyrimidine* (7a). The reaction was carried out at −70 °C.* $\nu_{max.}$ 3 475 (shoulder), 3 455, 1 675, 1 638, and 1 585 cm^{-1}; $\lambda_{max.}$ 286 nm (log ε 3.94); δ 6.98 (1 H, s, broad), 6.87 (NH), 6.05 (1 H, d, *J* 7.5 Hz), 4.62 (1 H, m), 4.15 (1 H, m), and 1.26 (3 H, d, *J* 6.7 Hz). Oxidation of (7a) gave 4-methylpyrimidine.[13]

4-(2-*Methylprop*-1-*enyl*)-1,4(*or*3,4)-*dihydropyrimidine* (7b). $\nu_{max.}$ 3 430, 1 685, 1 638, and 1 588 cm^{-1}; $\lambda_{max.}$ 235 and 278 nm (log ε 3.65 and 3.24); δ 6.98 (1 H, s, broad), 6.58 (NH), 6.04 (1 H, d, *J* 7.0 Hz), 5.32 (1 H, m), 4.66 (2 H, m), 1.72 (3 H, d, *J* 1.2 Hz), and 1.66 (3 H, d, *J* 1.2 Hz). Oxidation of (7b) gave 4-(2-methylprop-1-enyl)pyrimidine (8b), as an oil which was purified by column chromatography [SiO_2, chloroform–ethyl acetate (4 : 1)]; δ 9.01 (1 H, s, broad), 8.64 (1 H, d, *J* 7.5 Hz), 7.07 (1 H, dd, *J* 7.5 and 1.0 Hz), 6.20 (1 H, m), 2.19 (3 H, d, *J* 1.2 Hz), and 1.98 (3 H, d, *J* 1.2 Hz). Picrate, melting range 140—149 °C (Found: C, 46.2; H, 3.8. $C_{14}H_{13}N_5O_7$ requires C, 46.28; H, 3.61%).

4-(*Phenylethynyl*)-1,4(*or* 3,4)-*dihydropyrimidine* (7c). Pyrimidine in THF solution was added to the organolithium solution at 0 °C * and the mixture was set aside overnight at room temperature to yield (7c) (54%), crystals, $\nu_{max.}$ 3 470, 1 675, 1 625, 1 598, and 1 570 cm^{-1}; $\lambda_{max.}$ 242 and 285 nm (shoulder) (log ε 4.03 and 3.48); δ 7.50—7.20 (5 H, m), 7.06 (1 H, s, broad), 6.09 (1 H, d, *J* 7.5 Hz), 5.14 (1 H, d, *J* 3.0 Hz), 4.99 (NH), and 4.69 (1 H, dd). Oxidation of (7c) gave 4-(phenylethynyl)pyrimidine (8c) which was purified by column chromatography [SiO_2, chloroform–ethyl acetate (4 : 1)], m.p. 73—74 °C [from light petroleum (b.p. 40—60 °C)] (Found: C, 80.0; H, 4.7. $C_{12}H_8N_2$ requires C, 79.98; H, 4.48%).

4,5-*Diphenyl*-1,4(*or* 3,4)-*dihydropyrimidine* (9a). The solution of phenyl-lithium was added to a 0.20M solution of 5-phenylpyrimidine in benzene,* to yield crystals of (9a) (69%). Purification by column chromatography (SiO_2, acetone) and subsequent recrystallization from acetone without heating afforded an analytical sample, melting range 96—112 °C (despite a broad melting range due to oxidation and polymerization during melting, the sample had a correct microanalysis); $\nu_{max.}$ 3 470, 3 450, 1 678, 1 630, 1 585, and 1 565 cm^{-1}; $\lambda_{max.}$ 223 and 320 nm (log ε 4.11 and 3.26); δ 7.31—7.13 (10 H, m), 6.91 (1 H, s, broad), 6.77 (1 H, s), 6.64 (NH), and 5.48 (1 H, s) (Found: C, 82.1; H, 5.9. $C_{16}H_{14}N_2$ requires C, 82.02; H, 6.02%). Oxidation of (9a) gave 4,5-diphenylpyrimidine.[19]

5-*Methyl*-4-*phenyl*-1,4(*or* 3,4)-*dihydropyrimidine* (9b). $\nu_{max.}$ 3 470, 3 440, 1 697, 1 648, 1 630, and 1 596 cm^{-1}; $\lambda_{max.}$ 269 and 284 nm (shoulder) (log ε 3.06 and 2.98); δ 7.77 (NH), 7.29 (5 H, s), 6.74 (1 H, s), 5.95 (1 H, s, broad), 4.87 (1 H, s), and 1.37 (3 H, s). Oxidation of (9b) gave 5-methyl-4-phenylpyrimidine.[20]

5-*Bromo*-4-*phenyl*-1,4(*or* 3,4)-*dihydropyrimidine* (9c). Crystals (54%), $\nu_{max.}$ 3 470, 3 445, 1 677, 1 632 (shoulder), 1 623, and 1 580 cm^{-1}; $\lambda_{max.}$ 293 nm (log ε 3.63); δ 7.41 (NH), 7.27 (5 H, s), 6.74 (1 H, s, broad), 6.38 (1 H, s), and 5.15 (1 H, s). Oxidation of (9c) gave 5-bromo-4-phenylpyrimidine.[21]

Irradiations.—Preparative irradiations were performed in a Rayonet RPR-208 preparative photoreactor equipped with eight RUL 300 lamps at room temperature. Nitrogen was bubbled through solutions of the dihydropyrimidine (0.50 g) in acetone (500 ml) in quartz vessels for 1.5 h before and during irradiation. The solutions of the dihydropyrimidines were irradiated for variable periods of time until all starting material had disappeared. After irradiation the solvent was evaporated off *in vacuo* and the residue worked-up as specified below. Oxidations were performed with $KMnO_4$ in acetone.

4-*Phenyl*-1,4(*or* 3,4)-*dihydropyrimidine* (1a). The solution of (1a) was irradiated for 2 h. The reaction product obtained after oxidation was analysed by g.l.c. using a stainless steel column (length 200 cm, o.d. 0.125 in, filled with 8.9% Carbowax high polymer on Chromosorb W-HP 100—120, operating at 190 °C). The g.l.c. yield of 5-phenylpyrimidine (3a) (35%) was determined with biphenyl as the internal standard. Compound (3a) was isolated by column chromatography [silica gel, chloroform–ethyl acetate (4 : 1)] in 24% yield.

4,6-*Diphenyl*-1,4(*or* 3,4)-*dihydropyrimidine* (1b) *and* 4-*deuterio*-4,6-*diphenyl*-1,4(*or* 3,4)*dihydropyrimidine* (1c). The solution of (1b) was irradiated for 1.5 h and after oxidation the reaction product was analysed by g.l.c. using a glass column (length 200 cm, o.d. 0.125 in, filled with 9.2% OV-275 on Chromosorb WHP 100—200 mesh, operating at 190—230 °C). The g.l.c. yield of 4,5-diphenylpyrimidine (3b) (38%) was determined with benzophenone as the internal standard. Compound (3b) was isolated by column chromatography (silica gel, chloroform) in 32% yield. (1c) was treated as the unlabelled compound (1b).

4,4,6-*Triphenyl*-1,4(*or* 3,4)-*dihydropyrimidine* (1d). The solution of (1d) was irradiated for 80 min and after oxidation the reaction mixture was analysed by g.l.c. using the column as described in the previous section. The g.l.c. yield of 4,5,6-triphenylpyrimidine (3d) (45%) was determined with 4,6-diphenylpyrimidine as the internal standard. Compound (3d) was isolated by column chromatography (silica gel, chloroform) in 40% yield. An analytical sample was prepared by recrystallization from ethanol, m.p. 239—239.5 °C; δ 9.32 (1 H, s, broad) and 7.24—7.00 (15 H, m) (Found: C, 85.6; H, 5.4. $C_{22}H_{16}N_2$ requires C, 85.68; H, 5.23%).

4-*Methyl*-1,4(*or* 3,4)-*dihydropyrimidine* (7a). Compound (7a) was irradiated in acetone or methanol for 5 h. After evaporation of the solvent, ^1H n.m.r. analysis revealed only starting material and some 4-methylpyrimidine. Oxidation of the reaction mixture and analysis by g.l.c. (stainless steel column, length 200 cm, o.d. 0.125 in, filled with 8% DC-430

* Modification of the general procedure.

on Chromosorb W-HP 100—120) showed the absence of 5-methylpyrimidine.[14]

4-(2-*Methylprop*-1-*enyl*)-1,4(*or* 3,4)-*dihydropyrimidine* (7b). The solution of (7b) was irradiated for 1.5 h. The reaction product, after heating in air for 1 h at 100 °C, was subjected to column chromatography [silica gel, chloroform–ethyl acetate (4 : 1)] to give 5-(2-methylprop-1-enyl)pyrimidine (8b) as an oil (14%). An analytical sample was prepared by preparative g.l.c. using a stainless-steel column (length 200 cm, o.d. 0.375 in, filled with 27.5% OV-17 on 30.8 kieselguhr 40—60 at 200 °C); δ 9.00 (1 H, s), 8.57 (2 H, s), 6.15 (1 H, m), 1.98 (3 H, d, *J* 1.2 Hz), and 1.88 (3 H, d, *J* 1.2 Hz) (Found: C, 71.7; H, 7.5. $C_8H_{10}N_2$ requires C, 71.61; H, 7.51%).

4-(*Phenylethynyl*)-1,4(*or* 3,4)-*dihydropyrimidine* (7c). The solution of (7c) was irradiated for 4 h. After oxidation the reaction product was subjected to column chromatography [silica gel, chloroform–ethyl acetate (4 : 1)] to give 5-(phenylethynyl)pyrimidine (8c) (22%). An analytical sample was prepared by preparative g.l.c. using the column as described for compound (7a) at 190 °C; the colourless oil obtained crystallized after standing for several days, m.p. 43—45 °C; δ 9.11 (1 H, s), 8.81 (2 H, s), and 7.30 (5 H, m) (Found: C, 80.0; H, 4.5. $C_{12}H_8N_2$ requires C, 79.98; H, 4.47%).

4,5-*Diphenyl*- (9a), 5-*methyl*-4-*phenyl*- (9b), *and* 5-*bromo*-4-*phenyl*-1,4(*or* 3,4)-*dihydropyrimidine* (9c). Compounds (9a), (9b), or (9c) were irradiated in acetone or methanol for 5 h. After evaporation of the solvent ^{1}H n.m.r. analysis revealed only starting material and some oxidized product. In the case of (9c) some 4-phenylpyrimidine had also been formed.

Quantum Yields.—The quantum yields were determined by ferrioxalate actinometry [22] with use of the merry-go-round in RPR-100 chamber reactor equipped with four RPR-300-nm lamps and solutions in Pyrex vessels for the acetone-sensitized reaction. For the unsensitized reaction in methanol the reactor was equipped with four RPR-254-nm lamps and quartz vessels were used. Before and during irradiations nitrogen was bubbled through the solutions.

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