Photolysis of 4,6,6-trimethyl-5,6-dihydro-2(1*H*)-pyridone. Intermediates and mechanism

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Irradiation of dihydropyridone 1a in water yields mainly the unsaturated amides 3 (73%), 4 (8%), and acetone. A 1.3% yield of photohydration product 5a is also obtained. Irradiation of 1a in anhydrous methanol yields carbinolamidoether 8 (57%), whereas in *t*-butyl alcohol enamide 7 is the reaction product. Irradiation of the *N*-methyl derivative of 1a (1b) yields 90% of starting material and 5% of a photo-hydrate 5b. The mechanistic path of the reaction is shown to involve the cleavage of compound 1a to the enolic form 9 of the acylimine 6 which reacts differently depending on the solvent used.

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Introduction

To date, the photochemical transformations of conjugated cyclohexenones in solution have led to a great number of investigations and have been observed to undergo mainly rearrangement, dimerization, and addition reactions (1). Work pioneered by Chapman, Jeger, and Zimmerman has led to our present understanding of these reactions.

On the other hand, it is also well known that saturated amides can react photochemically to give cleavage products of the Norrish type I and type II (2). Although no systematic work had been reported on the photochemistry of δ valerolactams in solution it nevertheless seemed interesting to undertake a study of the photochemical behavior of molecules combining both these types of functional groups i.e. α,β -unsaturated lactams. The first compound chosen for study was the readily available 4,6,6-trimethyl-5,6-dihydro-2(1*H*)-pyridone (1*a*) because of its relation to isophorone (2), the corresponding α,β -unsaturated ketone, which upon irradiation in polar solvents yields dimeric products only (3).



Preliminary results in this study have been reported in a short communication elsewhere (4).

In the present paper we wish to report the full experimental details of our findings and also to discuss recently accumulated evidence towards elucidation of the mechanism of the observed transformation (see Chart 1).

Photolysis of Dihydropyridone 1a in Water

As previously reported (4), dihydropyridone 1a (6.0 g) was irradiated for 7 h in water (600 ml) using 2537 Å light. A stream of nitrogen was bubbled through the solution during the irradiation. The reaction mixture thus obtained was separated to yield three products: amide 3, m.p. 117° , 3.12 g (73%); amide 4, m.p. 108–109°, 0.35 g (8%), and hydroxylactam 5a, m.p. 189–190°, 0.085 g (1.3%). No starting material was recovered from the reaction. In an alternate run where the bubbling of nitrogen was omitted, the distillation of part of the solvent permitted the isolation of acetone as its 2,4-dinitrophenylhydrazone derivative.

Structure of Photoproducts

The structure of compound **3** was established by the mass spectrum, the elemental analysis, the infrared (i.r.) spectrum, the nuclear magnetic resonance (n.m.r.) spectrum, and conversion to known isovaleramide by catalytic hydrogenation. The mass spectrum and the elemental analysis established a molecular weight of 99 and a molecular formula of C_5H_9NO . The i.r. spectrum showed characteristic bands at 3540 and 3420 (N—H), 1680 (C=O), 1650 (C=C), 1585 (N—H), and 900 cm⁻¹ (C—H, terminal methylene). The n.m.r. spectrum showed singlets at δ 1.82 (3H, methyl protons) and 2.95 (2H, methylene protons), a multiplet at 4.93 (2H, terminal methylene protons), and a broad band

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at 5.8 (amide protons on nitrogen, exchangeable with D_2O). Hydrogenation over palladium on charcoal (5%) gave an almost quantitative yield of isovaleramide identical in all respects with an authentic sample prepared from isovaleric acid.

The structure of compound 4 was also established by spectroscopic and chemical means. The molecular weight as determined by mass spectrometry indicated that compounds 3 and 4 were isomers. The i.r. spectrum showed characteristic bands at 3550 and 3430 (N-H), 1675 (C=O), 1640 (C=C), and 1590 cm⁻¹ (N-H). The absence of an absorption band at 900 $\rm cm^{-1}$ suggested that compound 4 was the conjugated isomer of amide 3. This hypothesis was confirmed by the n.m.r. spectrum which showed singlets at δ 1.85 (3H, methyl protons, *trans* to $--CONH_2$) and 2.13 (3H, methyl protons cis to -CONH₂), a multiplet at 5.6 (1H, vinyl proton), and a broad singlet at 6.0 (2H, amide protons, exchangeable with D_2O). The proposed structure was then verified by comparison with an authentic sample prepared from 3,3-dimethylacrylic acid. That photoamides 3 and 4 were not photochemically interconvertible under the present conditions was shown by irradiating aqueous solutions of both photoamides for 7 h and recovering starting material exclusively in each case. It was also ascertained that photoamides 3 and 4 are not interconvertible under the conditions of chromatography.

Evidence for the structure of compound 5a was again obtained by spectroscopic and chemical means. The molecular ion in the mass spectrum was found at m/e 157, which corresponds to the addition of a water molecule (18 mass units (m.u.)) to the starting material. The i.r. spectrum showed characteristic bands at 3345, 3270, and 3190 (O—H and N—H), and at 1640 cm⁻¹ (C=O). The n.m.r. spectrum in dimethyl- d_6 sulfoxide showed singlets at δ 1.15 (6H, gem-dimethyl protons), 1.30 (3H, methyl protons), an AB system centered at 1.63 (2H, methylene protons), 2.10 (2H, methylene protons α to CO), 4.47 (1H, hydroxyl proton, exchangeable with D₂O), and 7.35 (1H, amide proton, exchangeable with D₂O). Further evidence in favor of the proposed structure was obtained by treating compound 5*a* with a 1:1 mixture of sulfuric acid and water at 80° for 1 h and showing by n.m.r. that the mixture of products obtained was composed of 56% of dihydropyridone 1*a* and 44% of its deconjugated isomer (5)².

Photolysis in Anhydrous t-Butyl Alcohol and Methanol

The results summarized in Chart 1 strongly suggest that an unstable intermediate formed in this reaction is hydrolyzed in a non-photochemical step to lead to products 3, 4, and acetone. A logical structure for this intermediate would be either the acylimines (6a and b) or the corresponding enamides (7a and b). However, it



is well known (6) that acylimines tautomerize rapidly to the corresponding enamide and that the reverse reaction generally does not take place under neutral conditions. In the isolated case (7*a*), where an enamide was found to tautomerize to the corresponding acylimine on treatment with acid, the transformation was ascribed (7*b*) to conformational factors.

The photolysis of dihydropyridone 1a in dry

²The pure deconjugated isomer of 1a has been prepared by J. Hébert of this laboratory and its n.m.r. spectrum shown to correspond exactly to the 44% component in the mixture.

t-butyl alcohol yielded a product mixture consisting for the greater part of starting material as shown by the i.r. spectrum. Nevertheless, separation of the mixture by chromatography gave a small amount of a new compound³ shown to be the unconjugated enamide 7b and having the following spectral characteristics. The mass spectrum established the molecular weight at 139 indicating that the compound isolated was an isomer of the starting material 1a. The i.r. spectrum showed characteristic bands at 3420 (N-H), 1680 (C=O), 1648 (C=C), 1505 (N-H), and 910 cm⁻¹ (C-H, terminal methylene). The n.m.r. spectrum showed singlets at δ 1.92 (3H, methyl protons on the enamide side). 3.02 (2H, methylene protons α to CO), an AX system with the high field component at 4.45 and the low field component at 5.43 (2H, terminal methylene protons of the enamide moiety (8), a doublet at 1.82 (3H, methyl protons on the olefin, J = 1 c.p.s.), and a multiplet at 4.91 (2H, terminal methylene protons of the olefin moiety). Finally, acid hydrolysis of chromatographic fractions containing either pure enamide 7a or a mixture of enamides 7a and b gave the corresponding photoamides 3 and 4 thus confirming the proposed structure. The isolation and characterization of enamide 7 is significant in that it confirms our hypothesis concerning the intervention of a water labile intermediate. One important problem however is to determine whether or not the acylimine intermediate 6 plays a role in this reaction. A priori, as will be shown later, one would expect initial formation of acylimine 6 followed by an irreversible tautomerization (6) to intermediate 7 ($6a \rightarrow 7a$ and $6b \rightarrow 7b$). Since it is known that enamides do not react

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with pure alcohols (9) and that acylimines add primary, secondary, and in certain cases tertiary alcohols (6, 9–11) an attempt was made to trap the acylimine intermediate by carrying out the irradiation of dihydropyridone 1a in anhydrous methanol. The latter should have a better chance to add to the acylimine than the bulky *t*-butyl alcohol. The reaction afforded a very good yield of an adduct which was shown after chromatographic purification to be the corresponding carbinolamidoether **8**.

The i.r. spectrum of this product showed characteristic bands at 3420 (N-H), 1672

(C=O), 1645 (C=C), 1503 (N-H), and 907 cm⁻¹ (C-H, terminal methylene). The n.m.r. spectrum showed singlets at δ 1.56 (6H, gemdimethyl protons), 1.80 (3H, methyl protons), 2.98 (2H, methylene protons), and 3.20 (3H, methyl protons), a multiplet at 4.86 (2H, terminal methylene protons), and a broad band at 7.52 (1H, amide proton). The mass spectrum did not show the molecular ion peak at m/e 171 as expected of structure **8**, but showed a strong



M-32 peak at m/e 139 corresponding to a loss of methanol. A molecular weight determination using a Mechrolab Vapor Pressure Osmometer gave a value of 167 $\pm 2\%$.

Finally, chromatographic fractions containing either pure carbinolamidoether 8a or a mixture of carbinolamidoether 8a and b were hydrolyzed in dilute acid to the corresponding photoamides 3 and 4 thus confirming the proposed structure.

Photolysis of N-Methyl Dihydropyridone 1b in Water

In an effort to gain further insight into the mechanism of this transformation, N-methyl dihydropyridone 1b was prepared and irradiated in water (300 mg/30 ml) for 7 h using 2537 Å light. The reaction mixture thus obtained was composed almost entirely of starting material, as evidenced by thin-layer chromatography (t.l.c.). A chromatographic separation yielded unreacted starting material (270 mg, 90%) and another product (15 mg, 5%) to which the hydroxylactam structure 5b was assigned. The mass spectrum of this product indicated a molecular weight of 171 which differs from that of the starting material by 18 m.u. indicating an addition of a molecule of water. The i.r. spectrum showed characteristic bands at 3620 and 3380 (O-H) and 1615 cm⁻¹ (C=O). The n.m.r. spectrum which is quite similar to that of 5a showed singlets at δ 1.30 (6H, gem-dimethyl protons), 1.46 (3H, methyl protons), an AB system centered at 1.85 (2H, methylene protons), 2.44 (2H, methylene protons α to CO), 2.89 (3H, methyl

³No attempt was made to isolate any pure conjugated isomer 7a present.

protons), and 3.14 (1H, hydroxyl proton, exchangeable with D_2O).

Multiplicity of the Cleavage Reaction

Evidence for the multiplicity of the excited intermediate in this reaction was obtained by one of us (12). It was shown (12) that acetophenone sensitization of the reaction led only to dimer formation and none of the cleavage products 3 and 4.

These results clearly demonstrated that the unsensitized irradiation of dihydropyridone 1a in water to yield photoamides **3** and **4** does not proceed via the lowest triplet state. It is also interesting to note that the reactivity of compound 1a seems to differ depending on the multiplicity of the excited intermediate produced in the reaction. Thus, while the direct photolysis of lactam 1a in water leads, via what is possibly a singlet state,⁴ to cleavage products **3** and **4**, the triplet sensitized reaction leads primarily to a photodimer of the starting material and none of the cleavage products **3** and **4** (12).

Discussion

From the above results it appears reasonable to suggest that the irradiation of dihydropyridone 1a leads to an excited singlet which could react according to two competing pathways (a and b)prior to crossing over to the corresponding triplet state. (a) The excited molecule (or a strained ground-state derived from it) may add the elements of water to form the 4-hydroxypiperidone 5a. Similar photoinduced additions of protic solvents have been reported for various α,β -unsaturated carbonyl compounds such as uracil (13), 4a-methyl-4,4a,9,10-2(3H)-phenanthrone (14), Pummerer's ketone (15), 1-acetylcyclohexene (16), and 2-cycloheptenone (17). It is interesting to note that Lamola and Mittal (13) have stated that "the photohydration of uracil probably does not involve the triplet state". Our results would also seem to eliminate the lowest triplet state as the excited intermediate leading to hydroxypiperidone 5a; however, the small amount of the compound isolated from the reaction mixture renders this conclusion very tenuous. (b) In an alternate reaction pathway, the excited molecule may undergo cleavage of the 5-6 bond concerted with the migration of the

proton from nitrogen to oxygen.⁵ Evidence in favor of this hypothesis rests on the fact that the presence of hydrogen on nitrogen is necessary for the reaction to take place. Thus, when *N*-methyl dihydropyridone 1*b* was irradiated in water, no appreciable reaction had taken place after 7 h as shown by t.l.c. Chromatographic analysis indicated that 90% of the starting material had remained unchanged and that 5% was converted to hydroxylactam 5*b*. Such a cleavage of the 5-6 bond in 1*a*, accompanied by proton migration, would then lead to intermediate 9, which is the enolic form of the proposed acylimine **6** (vide supra).



This labile intermediate might then be expected to undergo two competing transformations (see Chart 2) namely: recyclization to the starting dihydropyridone (1*a*) or tautomerization to the corresponding acylimines **6***a* and *b* or, in the case of *t*-butyl alcohol, to the corresponding enamides 7*a* and *b*. The predominance of the unconjugated isomer **6***a* or **7***a* would seem to indicate that protonation of **9** is a kinetically controlled process favoring protonation at the α -carbon in accordance with the Hughes-Ingold rule (18).

In an effort to test the possible recyclization of 9, dihydropyridone 1a was irradiated in *t*-butyl alcohol containing 1% of water. Thus, after 15 h of irradiation, under conditions otherwise identical to those used in the experiment with anhydrous *t*-butyl alcohol where low conversion to enamide 7 was observed, an i.r. spectrum of the crude material showed that all of the starting dihydropyridone 1a had disappeared and that only the photoamides 3 and 4 were present. It can be concluded therefore that intermediate 9, which does not seem to react appreciably with *t*-butyl alcohol, can recyclize to the starting lactam 1a and that this reaction can be prevented

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⁴The possibility of reaction from an upper triplet state cannot be ruled out at this point.

⁵The all importance of the double bond in this reaction was illustrated by irradiating an aqueous solution of the corresponding piperidone and showing that no reaction takes place.

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if a small amount of water is present in the mixture to trap the intermediate.

On the other hand, as previously stated, (vide supra) the tautomeric equilibrium between acylimines and enamides has been shown to lie completely on the enamide side in acyclic systems (6). In the present photochemical reaction, direct evidence for the possible formation of enamide 7 was obtained from the irradiation of dihydropyridone 1a in anhydrous *t*-butyl alcohol which permitted the isolation and characterization of pure enamide 7a and a mixture of 7a and b. (Chart 2).

The intervention of enamide 7 as a reaction intermediate could raise the question as to which of the intermediates, 6, 7, or 9 is responsible for the observed hydrolysis and methanol addition reactions. It seems quite evident from the preceding discussion that acylimine 6 (or perhaps the corresponding enolic form 9) undergoes nucleophilic attack by solvent rather than enamide 7.

Finally, in an attempt to gain evidence for the intervention of a diradical-like intermediate (10) in this reaction, the photolysis of dihydropyridone 1a was investigated in isopropyl alcohol which is known to be a good photoreducing agent. Unfortunately, as in the case of methanol, the reaction led to the addition of solvent to give 11 as the sole product.



Following the above discussion, the reaction could be represented as a polar cleavage of 1a (see Chart 3). This mechanism is similar to that

already proposed (4) by us and is somewhat analogous to that operative in the photochemistry of 4,4-dialkyl substituted cyclohexene-2 ones (14, 19). In addition however, a proton migration must take place from nitrogen to oxygen in a manner concomitant with ring opening.

On the other hand, this very migration of hydrogen to oxygen and the formation of an intermediate of structure 9 suggests a much more reasonable fragmentation path of the electrocyclic type as was envisaged in our previous communication (4). Indeed, the reaction could proceed through the lactim 12 which is liable to undergo electrocyclic ring opening (20) to intermediate 9 as shown in Chart 4.



This hypothesis, however, could not be substantiated experimentally. It had been anticipated that the photolysis of dihydroazepinone 13 could yield information on the cleavage path



operative in this reaction. Indeed, a cleavage such as that described in Chart 4 could not have taken place in this seven-membered ring model. There remained two possibilities, namely, dimerization or cyclization to a bicyclic β -lactam (21).

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Unfortunately, upon photolysis at room temperature, dihydroazepinone 13 yielded only a mixture of two dimers (12).

Finally, in a second attempt to substantiate the fragmentation path described in Chart 4, the corresponding lactim ether⁶ (14) of dihydropyridone 1a was irradiated in *t*-butyl alcohol and to date we have been unable to obtain conclusive evidence for an electrocyclic cleavage of this molecule. Further investigation of the mechanism and scope of this reaction is in progress.

Experimental

Irradiations were carried out in quartz vessels, using a Rayonet Photochemical Reactor (16 low pressure Hg lamps, 2537 Å). A stream of oxygen-free nitrogen was bubbled through the solutions before and during irradiations. The alumina used for column chromatography was obtained from Woelm and the activity described is in accordance with the prescriptions of the Company. The t.l.c. was done on Eastman Chromagram sheets coated with alumina containing a fluorescent indicator. Melting points were taken on a Büchi apparatus and are uncorrected. The i.r. spectra were recorded in chloroform (unless otherwise stated) on a Beckman IR-8 spectrophotometer and n.m.r. spectra were obtained partly on a Varian A-60 instrument and partly on a Jeolco JNM-C-60H instrument using deuteriochloroform as solvent and tetramethylsilane as internal standard. Ultraviolet (u.v.) spectra were recorded on a Bausch & Lomb Spectronic 505 and mass spectra were measured on a Hitachi-Perkin-Elmer RMU 6-D spectrometer. A molecular weight determination was made on a Mechrolab Vapor Pressure Osmometer. Elemental analyses were carried out by Dr. C. Daesslé, Montreal.

4,6,6-Trimethyl-5,6-dihydro-2(1H)-pyridone (1a)

The procedure of Hall (22) was followed with a slight modification. Mesityl oxide (50 g, 0.51 mole) was stirred overnight with an equal volume of 28% aqueous ammonium hydroxide, at room temperature. The excess ammonia was removed by evaporation *in vacuo* or by bubbling nitrogen for 2 h. The solution was then chilled in ice and ethyl cyanoacetate (50 g, 0.442 mole) added with stirring. The reaction product which precipitated over a period of 2 h was filtered, washed with ether, and dried *in vacuo* to give 3-cyano-4,6,6-trimethyl-5,6-dihydro-2(1*H*)-pyridone (52 g, 62%), m.p. 196–197° (lit. (22) m.p. 194–196°).

The dihydrocyanopyridone thus obtained (20 g, 0.122 mole) was heated to reflux for 48 h in 18 N sulfuric acid (75 ml). The solution was then neutralized at 0° to pH 6 using a potassium hydroxide solution. After extraction of the mixture with chloroform, drying over sodium sulfate, and removing the solvent, a good yield (12.5 g, 74%) of crude dihydropyridone 1a was obtained. Recrystallization from dichloromethane-hexane gave the

pure product (10.4 g), m.p. 116–118°. Further purification by sublimation (0.05 mm, 110°) brought the m.p. to 118° (lit. (22) 116.5–118°). The u.v. spectrum (95% EtOH) showed λ_{max} 213 nm (ε 15 600).

Photolysis of 4,6,6-Trimethyl-5,6-dihydro-2(1H)-

pyridone (1a) in Water

A 1% solution (6 g/600 ml) of dihydropyridone 1a in distilled water was irradiated for 7 h after which time no more starting material could be observed by t.l.c. Distillation of part (\sim 50 ml) of the solvent permitted the isolation of acetone as its 2,4-dinitrophenylhydrazone derivative. The remaining solution was saturated with ammonium sulfate, extracted with chloroform, and the organic layer dried over sodium sulfate. After evaporation of the solvent, the residue was taken up in ether and hydroxylactam 5a (85 mg, 1.3%), m.p. 189-190°, remained insoluble. The m.p. remained unchanged after recrystallization from chloroform-ether. The i.r. spectrum (nujol) showed absorption in the 3620 to 3200 region and at 1640 cm⁻¹ while the n.m.r. spectrum (dimethyl- d_6 sulfoxide) had δ 1.15 (6H, singlet), 1.30 (3H, singlet), 1.61 (2H, quadruplet), 2.10 (2H, singlet), 4.47 (1H, singlet, exchanged with D_2O), and 7.35 (1H, broad singlet, exchanged with D₂O). The mass spectrum revealed a weak molecular ion at m/e 157.

Anal. Calcd. for $C_8H_{15}NO_2$: C, 61.11; H, 9.61; N, 8.91. Found: C, 61.50; H, 9.72; N, 8.92.

Further evidence for the structure of 5a was obtained by treating the above compound (50 mg) with a 1:1 mixture of sulfuric acid – water at 80° for 1 h. Extraction with chloroform in the usual manner yielded a mixture of two products (t.l.c.), the n.m.r. spectrum of which indicated 56% of dihydropyridone 1a and 44% of its deconjugated isomer.

Evaporation of the remaining ethereal solution containing the photolysis mixture gave a solid residue which upon recrystallization from acetone-hexane yielded a first crop of the unconjugated amide 3. Evaporation of the mother liquors and chromatography on neutral alumina, activity IV yielded after elution with chloroform the conjugated amide 4 (351 mg, 8%). Further elution with chloroform gave more of the unconjugated isomer 3 for a total yield of 3.12 g (73%).

Amide 3 had m.p. 117° after recrystallization from acetone-hexane. The i.r. spectrum showed characteristic absorptions at 3540, 3420, 1680, 1650, 1585, and 900 cm⁻¹. The n.m.r. spectrum had δ 1.82 (3H, singlet), 2.95 (2H, singlet), 4.93 (2H, multiplet), and 5.8 (1H, flat band) while the u.v. spectrum (95% EtOH) indicated an end-absorption only. The mass spectrum showed a molecular ion peak at *m/e* 99.

Anal. Calcd. for C₅H₉NO: C, 60.57; H, 9.04; N, 14.14. Found: C, 60.72; H, 9.23; N, 14.38.

The proposed structure 3 was confirmed by carrying out a catalytic hydrogenation over palladium on charcoal (5%) in methanol. The isovaleramide obtained, m.p. 138–139° (acetone-hexane), was identical in all respects (mixed m.p. and i.r. spectra) with an authentic sample prepared from isovaleric acid by the standard procedure.

Conjugated amide 4 had m.p. 108–109° after recrystallization from acetone–hexane. The i.r. spectrum showed characteristic absorptions at 3550, 3430, 1675, 1640, and 1590 cm⁻¹. The n.m.r. spectrum had δ 1.85

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⁶This compound was prepared by J. Hébert of this laboratory.

(3H, singlet), 2.13 (3H, singlet), 5.6 (1H, multiplet), and 6.0 (2H, broad band). The u.v. spectrum (95% EtOH) indicated λ_{max} 217 nm (ϵ 12 600) and the mass spectrum showed a molecular ion peak at m/e 99. The assignment of structure 4 was verified by comparison (mixed m.p., n.m.r. spectra, and i.r. spectra) with an authentic sample prepared from 3,3-dimethyl acrylic acid.

Photolysis of 4,6,6-Trimethyl-5,6-dihydro-2(1H)pyridone (1a) in t-Butyl Alcohol

A 1% solution (6 g/600 ml) of dihydropyridone 1*a* in dry *t*-butyl alcohol (distilled over sodium *t*-butoxide and kept on Molecular Sieves, Linde type 4A) was photolyzed for 12 h. A stream of dry and oxygen-free nitrogen was bubbled through the solution for 20 min prior to and during the entire irradiation. An i.r. spectrum of the crude product obtained after evaporation of the solvent showed a great amount of unreacted starting material; however, a new characteristic band appeared at 1505 cm⁻¹ and a new spot, of lower R_f than the starting material, was revealed by t.l.c. analysis.

The crude material was therefore washed with 30 ml of hexane, which dissolved the new product, plus a small amount of the starting material 1a. A simple filtration through alumina activity II, using hexane-dichloromethane (2:1) as eluent, yielded the pure enamide 7b as a pale yellow oil in the first fraction. The second and third fractions contained a mixture of 7b and its conjugated isomer 7a, as shown by dilute acid hydrolysis to a mixture of the known amides 3 and 4. Further fractions eluted with methylene chloride – ether (1:1) contained dihydropyridone 1a and the primary amides 3 and 4, which were separated in a subsequent chromatography on alumina activity IV. No yields are reported in this experiment as the enamides sought are partially hydrolyzed on the column.

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The i.r. spectrum of the pure enamide 7b showed characteristic absorptions at 3420, 1680, 1648, 1505, and 910 cm⁻¹. The n.m.r. spectrum had δ 1.82 (3H, doublet, J = 1 c.p.s.), 1.92 (3H, singlet), 3.02 (2H, singlet), 4.91 (2H, multiplet, J = 1 c.p.s.), 4.45 and 5.43 (2H, AX system). The mass spectrum revealed a molecular ion peak at m/e 139.

Photolysis of 4,6,6-Trimethyl-5,6-dihydro-2(1H)pyridone (1a) in t-Butyl Alcohol Containing 1% of Water

A 1% solution (6 g/600 ml) of dihydropyridone 1a in *t*-butyl alcohol, containing 1% of distilled water (6 g/600 ml), was photolyzed for 15 h under the same conditions as stated above. An i.r. spectrum of the crude product clearly showed the primary amides. No starting material 1a and no enamide 7 were observed.

Irradiation of Photoamides 3 and 4 in Water

When a 1% solution (300 mg/30 ml) of either photoamide 3 or photoamide 4 in water was irradiated for 18.5 h, no photochemical interconversion could be observed as shown by melting points, thin-layer chromatograms, and u.v. and i.r. spectra. Also, it is of importance to note that no interconversion was observed when the pure amides were chromatographed on alumina.

Photolysis of 4,6,6-Trimethyl-2-piperidone

The above piperidone (22), m.p. $119-121^{\circ}$, was prepared by catalytic hydrogenation of dihydropyridone 1ain acetic acid, using palladium (5%) on powdered charcoal as catalyst.

No photoreaction could be observed when an aqueous solution of the piperidone (300 mg/30 ml) was photolyzed during 7 h.

Photolysis of 4,6,6-Trimethyl-5,6-dihydro-2(1H)pyridone (1a) in Methanol

A 1% solution (4 g/400 ml) of dihydropyridone 1*a* in dry methanol (distilled over sodium methoxide) was irradiated during 7 h. The solution was then evaporated to dryness and the i.r. spectrum of the crude product revealed a new characteristic band at 1505 cm⁻¹. Purification by filtration through a short column of alumina activity I, using dichloromethane-hexane, (1:1) as eluent gave the following results. The first few fractions gave the carbinolamidoethers, 8*a* and *b* (2.8 g, 57%, containing mostly the unconjugated isomer in a ratio of about 6:1). Elution with dichloromethane and dichloromethaneether gave some unreacted starting material (1.3 g, 32%) and mixtures of the photoamides 3 and 4 which probably arose via partial hydrolysis of the labile amidoethers 8*a* and *b* on the column.

One fraction containing almost pure unconjugated amidoether 8b was further purified by distillation at 50° and 0.5 mm. The solid obtained melted at room temperature and was shown to contain a very small percentage of the conjugated amidoether 8a by n.m.r. and t.l.c. The i.r. spectrum showed characteristic absorptions at 3420, 1672, 1645, 1503, and 907 cm⁻¹. The n.m.r. spectrum had δ 1.56 (6H, singlet), 1.80 (3H, singlet), 2.98 (2H, singlet), 3.20 (3H, singlet), 4.86 (2H, multiplet), 7.52 (1H. broad band).

The mass spectrum did not reveal a molecular ion but showed an intense peak at m/e 139 corresponding to a loss of methanol. A molecular weight determination was however obtained by means of a "Mechrolab" Vapor Pressure Osmometer. Calcd.: 171. Found: 167.

Anal. Calcd. for $C_9H_{17}NO_2$: C, 63.20; H, 9.94; N, 8.19. Found: C, 63.16; H, 9.93; N, 8.23.

N-Methyl-3-cyano-4,6,6-trimethyl-5,6-dihydro-2-pyridone

The general procedure of Hall (22) (vide supra) was followed with the exception that aqueous methylamine was used instead of aqueous ammonia. The compound obtained in a low yield (16%) had m.p. 139–140° (methanol-water). The i.r. spectrum showed characteristic absorptions at 2240, 1655, 1620, and 1575 cm⁻¹. The n.m.r. spectrum had δ 1.32 (6H, singlet), 2.27 (3H, singlet), 2.52 (2H, singlet), and 2.97 (3H, singlet). The mass spectrum revealed a molecular ion peak at *m/e* 178.

N-Methyl-4,6,6-trimethyl-5,6-dihydro-2-pyridone (1b)

Hydrolysis and decarboxylation of the above cyanopyridone was carried out according to the procedure of Hall (22) (vide supra). The N-methyl lactam 1b obtained in a good yield (67%) had m.p. 43-44° (pentane-ether). The i.r. spectrum showed characteristic absorptions at 1675 and 1615 cm⁻¹. The n.m.r. had δ 1.25 (6H, singlet), 1.87 (3H, singlet), 2.23 (2H, singlet), 2.90 (3H, singlet), and 5.75 (1H, singlet). The mass spectrum revealed a molecular ion peak at m/e 153.

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Photolysis of N-Methyl-4,6,6-trimethyl-5,6-dihydro-2pyridone (1b)

A 1% solution (300 mg/30 ml) of N-methyl dihydropyridone 1b in distilled water was irradiated during 7 h. The solution was then saturated with ammonium sulfate and extracted with chloroform. After drying and evaporating the solvent, a t.l.c. of the crude product revealed the presence of a large amount of starting material along with a new compound of lower $R_{\rm f}$.

Chromatography of the mixture on silica gel using acetone-ether 1:4 as eluent gave unreacted starting material (270 mg, 90%) in the first fractions. Further elution using the same solvent system afforded a solid, m.p. 125° (15 mg, 5%). The i.r. spectrum of the compound showed characteristic bands at 3620, 3380, and 1615 cm⁻¹. The n.m.r. spectrum had δ 1.30 (6H, singlet), 1.45 (3H, singlet), 1.85 (2H, AB system with low field component showing additional splitting), 2.45 (2H, broad singlet), 2.89 (3H, singlet), and 3.14 (1H, singlet, exchangeable with D₂O). The mass spectrum revealed a molecular ion peak at m/e 171.

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