Photochemistry of 5-Methylpyrimidin-4-ones in Acetic Acid Solution: Thermal Rearrangements of Dewar Pyrimidinones and 4-Acetoxyazetidin-2-ones

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Irradiation of 3,6-dialkyl-5-methylpyrimidin-4-ones (1a-f) in acetic acid-acetonitrile (1:2, v/v) solution at 0 °C gave 4-acetoxy-3-(1-imino-2,2-dimethylpropyl)-1,3,4-trimethylazetidin-2-one (3a), 6-acetoxy-7-(1-imino-2,2-dimethylpropyl)-7-methyl-1-azabicyclo[4.2.0]octan-8-one (3b), 4-acetoxy-3-acetyl-1,3,4-trialkylazetidin-2-ones (4c-e), 4-acetoxy-3-acetyl-1,3-dimethylazetidin-2-one (4f), 3-acetyl-4-alkylidene-1,3-dimethylazetidin-2-ones (5d) and (5e) as the major products. Reaction of 1,4,6-trimethyl-3-t-butyl-2,6-diazabicyclo[2.2.0]hex-2-en-5-one (2a) (Dewar pyrimidinone) in acetic acid-acetonitrile (1:14, v/v) solution at 0 °C and thermolysis of (2a) without solvent at 80 °C gave the imine azetidin-2-one (3a) and 2,3,5-trimethyl-6-t-butylpyrimidin-4(3H)-one (1a) respectively as the major products. Reactions of the imino azetidin-2-ones (3a) and (3b) and the 4-acetoxyazetidin-2-ones (4c-e) in the presence of acetic acid at 21-40 °C and without solvent at 100-110 °C were carried out to elucidate the rearrangements. The major products from (3a) and (3b) in acidic solutions at 40 °C were N-acetyl-3-acetamido-2,4,4,N-tetramethylpent-2-enamide (6a), N-methylacetamide (9a), 2,5-dimethyl-4-t-butyl-1,3-oxazin-6-one (10a), 2-piperidone (9b), and 1,3-oxazin-6-one (10b) = (10a), and from the thermolysis of (3a) and (3b) at 100–110 °C were the pyrimidin-4-ones (1a) and (1b), 1,3-dimethyl-3-pivaloyl-4-vinylazetidin-2-one (5a) and 7-methyl-7-pivaloyl-1-azabicyclo[4.2.0]octa-5-en-8-one (5b). Both reactions of (4d,e) at 23-24 °C in acidic solutions and of (4c,d) without solvent at 100-110 °C gave the 3-acetyl-4-alkylidene-1,3dimethylazetidin-2-ones (5c—e) as the major products. The reaction mechanisms and intermediates of these reactions are discussed.

Photolysis of alcoholic solutions of 2,3,6-trialkylpyrimidin-4ones at room temperature gave the corresponding 4-alkoxyazetidin-2-ones^{1a} and the mechanisms and intermediates of these reactions have been studied in detail.¹ Although in the photolysis of 5-methylpyrimidin-4-ones in methanol and in basic methanol solution, no separable product was isolated, the corresponding Dewar pyrimidinones were observed by ¹H n.m.r. spectroscopy.^{1c} 2,3,6-Trialkylpyrimidin-4-ones (I) on u.v. irradiation in carboxylic acid solutions undergo ring transformation to give the corresponding tetra-alkylpyrimidinium-5-carboxylates (III)^{1e} via the Dewar pyrimidinones (II)



Scheme 1. $R^1 = R^2 = R^3 = alkyl$

(Scheme 1). The pyrimidinium-5-carboxylates are novel zwitterionic compounds and their formation from the Dewar isomers in carboxylic acid solution must involve acyl cations that are formed by rearrangement of azetidinyl cations; 1e the intermediacy of acyl cations suggests new reaction routes to Dewar isomers. Further, it was thought that irradiation of 5methylpyrimidin-4-ones in acetic acid solution might give both new products and also provide important information about the intermediates and reaction mechanism. With this in mind, we undertook isolation of the Dewar pyrimidinones formed in the photolysis of the 5-methylpyrimidin-4-ones and a study of the photochemistry of the 5-methylpyrimidin-4-ones in acetic acid solution.

Photolysis of 5-Methylpyrimidin-4-ones (1a-f) and Reactions of the Dewar Pyrimidinone (2a) in Acetic Acid-Acetonitrile Solution.—By analogy with the photochemistry of 2,3,6-trialkylpyrimidin-4-ones in acetic acid solution ie the products predicted were the tetra-alkylpyrimidinium-5-carboxylates. Irradiation of 5-methylpyrimidin-4-one (1a) $[\lambda_{max}](CH_3CO_2H)$ 278 nm (ε 5 190 dm³ mol⁻¹ cm⁻¹)] in acetic acid-acetonitrile solution with a high-pressure mercury lamp through quartz at 0 °C for 7 h, however, gave not the expected product but, rather, crystalline 4-acetoxyazetidin-2-one (3a) (56%), oily 4-vinylazetidin-2-one (5a) (17%), and the crystalline imide (6a) (25%)[yields based on the amount of (1a) consumed]. Analogous photolysis of (1b) led to the products (3b), (5b), and (6b). Similarly, irradiation of (1c-f) gave the azetidin-2-ones (4c-f)and 4-alkylideneazetidin-2-ones (5c-e) (Scheme 2). The yields of the products are listed in the Table.

The Dewar pyrimidinone (2a) was isolated from the photoreaction mixture obtained after irradiation in liquid NH₃-ether solution at -40 °C by chromatography on Sephadex LH-20 with chloroform-hexane (80:20, v/v %) as eluant. When (2a) was treated in acetic acid-acetonitrile solution at 0 °C, the pyrimidin-4-one (1a) (13%), the imino azetidin-2-one (3a) (54%), the 4-vinylazetidin-2-one (5a) (10%), and the imide (6a) (5%) were isolated. The structure of (3a) was deduced on the basis of spectroscopic evidence. The i.r. (CHCl₃) spectrum showed an NH stretching frequency at 3 250 cm⁻¹, a β -lactam carbonyl frequency at 1 615 cm⁻¹. The ¹³C n.m.r. spectrum exhibited five methyl, one t-butyl, two quaternary, two

	Starting material R ¹ = CHR ^{1a} R ^{1b}				Yields of products ^{b} (%)			
	R ^{1a}	R ^{1b}	R ²	R ³	(3) ^c	(4) ^c	(5) ^c	(6)
(1a)	н	н	Me	\mathbf{Bu}^{t}	56	0	17	25
(1b)	н	$-(CH_2)_{3}$		\mathbf{Bu}^{t}	72	0	7	1
(1c)	н	н	Me	Me	0	82	4	0
(1d)	н	Me	Me	Me	0	52	30	0
(1e)	н	Ph	Me	Me	0	33	32	0
$(\mathbf{1f})$	$R^1 = H$		Me	Me	0	71	0	0

^a Photolysis was performed in acetic acid-acetonitrile (1:2, v/v) at 0 °C. ^b Yields were corrected for recovered starting materials.^c The products [(3a) and (3b)] were single isomers and products (4c-f) and (5d,e) were mixtures of two stereoisomers (see Experimental section).



Scheme 2.

carbonyl, and one imine carbon signals. From these spectral data and comparison with those of the 4-methoxyazetidin-2ones,^{1a} the structure of (3a) was assigned as 4-acetoxy-3-(1imino-2,3-dimethylpropyl)-1,3,4-trimethylazetidin-2-one. The ¹H and ¹³C n.m.r. spectra indicated that the compounds (3a) and (3b) were single isomers. The configuration of the imino group and acetoxy group was not defined by the spectral data.

The identity of the 4-acetoxyazetidin-2-ones (4) was established by comparison of their spectral data with those of (3a) and (3b). The ¹³C n.m.r. spectra of (4c) confirmed the presence of five methyl groups and two quaternary and three carbonyl carbon atoms. The azetidin-2-ones (4c-f) were mixtures of two stereoisomers that may be the trans and cis isomers defined by the relationship of the 4-acetoxy group to the 3-methyl group. The stereochemistry of the isomers could not be assigned from the spectral data.

The ¹H n.m.r. spectrum of (5a) showed two vinyl protons at δ 4.28 (d, J 3 Hz, 1 H) and 4.42 (d, J 3 Hz, 1 H), indicating the presence of an alkylidene moiety. The i.r. spectrum exhibited a β -lactam carbonyl frequency at 1 800 cm⁻¹ and the ¹³C n.m.r. spectrum showed the presence of one quaternary, two olefinic, and two carbonyl carbon signals. From these spectral data and comparison with those of the reported 4-alkylideneazetidin-2ones,^{1e,2} the structure of (5a) was assigned as 1,3-dimethyl-3pivaloyl-4-vinylazetidin-2-one.

Catalytic hydrogenation of (5a) on 10% Pd/C in methanol gave the azetidin-2-one (7a) (90%) as a single isomer.



To confirm its structure, the imide (6a) was subjected to ethanolysis and gave the pyrimidin-4-one (1a) (8%), the amide (8a) (44%), N-methylacetamide (9a) (13%), and the 1,3-oxazin-6-one (10a) (28%); starting material (6a) (19%) was also recovered. Treatment of (6a) in CDCl₃ containing trifluoroacetic acid (0.36M) at 40 °C for 23 h gave N-methylacetamide (9a) (77%) and the 1,3-oxazin-6-one (10a) (25%). Reaction of (8a) in ethanol under reflux for 5 days gave the pyrimidin-4-one (1a) (12%) together with recovery of starting material (8a) (89%). Treatment of the 1,3-oxazin-6-one (10a) in methanol containing ammonia gave the pyrimidin-4-one (12a) (67%) (Scheme 3).

Compounds (6a), (8a), and (10a) were identified by conversion into the pyrimidin-4-ones (1a) and (12a). Reaction of the imide (6a) with ethanol gave the amide (8a) and ethyl acetate and subsequent ring closure of (8a) led to formation of (1a).³ The imide (6a) tautomerized to the imine (6a*) and subsequent intramolecular cyclization gave (9a) and (10a). The 1,3-oxazin-6-one (10a) underwent ring opening, alkoxy-amine exchange, and cyclization to give the pyrimidin-4-one (12a) in the presence of ammonia (Scheme 3).4

The intermediates proposed for the formation of the products are shown in Scheme 2. Excitation of the pyrimidin-4-ones (1) produces singlet molecules which lead to the formation of the Dewar pyrimidinones (2). The protonation on the imine nitrogen gives the azetidinyl cations (11), 1a,e which react with acetic acid to give the iminoazetidin-2-ones (3) and subsequent hydrolysis of the imine moiety leads to the formation of the 4acetoxyazetidin-2-ones (4) in the presence of acid. Steric hindrance of the t-butyl group reduces the reaction rate of nucleophilic attack of water on the imine moiety, the iminoazetidin-2-ones (3) then being isolated as stable compounds in the presence of acid. The azetidinyl cations (11)



Scheme 3.

CHR^{1a}R^{1b}

R³



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undergo an E1 reaction to give the alkylideneazetidin-2-ones (5) after hydrolysis of the imine moiety under acidic conditions (Scheme 2). The imides (6a) and (6b) may be formed by rearrangements of (3a) and (3b) in the presence of acetic acid. The mechanism of this reaction will be discussed further below.

The 1,3,6-trialkyl Dewar pyrimidinones resulting from excitation of the 2,3,6-trialkylpyrimidin-4-ones undergo C(1)-N(2) and C(5)-N(6) bond cleavage to give the acyl cations in acetic acid solution.^{1e} However, the azetidinyl cations (11) formed from the 1,3,6-trialkyl-4-methyl Dewar pyrimidinones (2) do not rearrange to the acyl cations. Replacement of the hydrogen atom by the methyl group at the C-4 position of the Dewar pyrimidinones (2) may stabilize the amide bond [C(5)-N(6)] of the azetidinyl cations (11).

Reactions of the 4-Acetoxyazetidin-2-ones (3) and (4) in the Presence of Acetic Acid.-The reactions of the 4-acetoxyazetidin-2-ones (3) in acetic acid-acetonitrile (1:2, v/v) solution at 23-40 °C were carried out in order to elucidate the subsequent reactions of the corresponding imino azetidin-2ones (3). The isolated products from (3a) were the pyrimidin-4ones (1) (2%), the imide (6a) (51%), N-methylacetamide (9a) (30%), and the 1,3-oxazin-6-one (10a) (28%): no azetidin-2-one (5a) was found. The formation of (5a) may be much slower than that of (6a), (9a), and (10a) at 40 °C. From (3b), the pyrimidin-4-one (1b) (14%), the azetidin-2-one (5b) (8%), the 2-piperidone (9b) (70%), and the 1,3-oxazin-6-one (10a) = (10b) (53%) were isolated. Disappearance of the product (6b) indicates that the rate of cyclization of the latter is faster than that of (6a). Similarly, the 4-acetoxyazetidin-2-ones (4d) and (4e) gave the respective azetidin-2-ones (5d) (89%) and (5e) (94%).

Compounds (1), (5), and (6) are the secondary products from the 4-acetoxyazetidin-2-ones (3) and (4). The precursors of the products (9) and (10) are the imides (6) in the presence of acetic acid (Scheme 3).

Exchange Reaction of the Acetoxy Group of (3a) in $[^{2}H_{4}]$ Acetic Acid Solutions.—The mechanism proposed in Scheme 2 predicts that reactions of the azetidinyl cations (11)



To confirm the acetoxy exchange reaction, the ¹H n.m.r. spectra of (**3a**) were measured in CD_3CO_2D and in CD_3CO_2D - CD_3CN solutions. The intensity of the acetoxy methyl signal decreased with the passage of time in both solutions and incorporation of the CD_3CO_2 group was confirmed by product analyses which are described further below.

The measured exchange rate constants in CD_3CO_2D and in CD_3CO_2D - CD_3CN solutions were $(1.88 \pm 0.07) \times 10^{-5} \text{ s}^{-1}$ and $(5.90 \pm 0.28) \times 10^{-5} \text{ s}^{-1}$ at 20-21 °C, respectively. Enhancement of the rate constant in CD_3CO_2D - CD_3CN solution may be due to an increase in solvent polarity. The acetoxy exchange reaction suggests strongly the presence of the predicted azetidinyl cations (11) as the intermediates.

Reaction of the 4-Acetoxyazetidin-2-one (3a) in CD₃CO₂D-CD₃CN Solution.—The 4-acetoxyazetidin-2-one (3a) gave the imide (6a) in the presence of acetic acid. Considering possible pathways to (6a) from (3a), the structure of (6a) requires cleavage of the C(3)-C(4) and O-Ac bond of the azetidin-2-ones (3) and acetylation of the imino group. The acetamide functionality may be formed by either intramolecular migration of the acetyl group in the acetoxy group to the imine nitrogen or acetylation of the imino group by the acetic anhydride that is formed by the O-Ac bond cleavage in (3a) by acetolysis.

The two mechanisms could be distinguished by the reaction of (3a) in $[{}^{2}H_{4}]$ acetic acid solution. The former intramolecular acetyl migration mechanism predicts that the acetyl CH₃ group in (3a) is found in the amide acetyl group of (6a), while the latter mechanism predicts that the acetyl group of solvent acetic acid is incorporated into the amide group at the C-3 position in (6a).

Reaction of (3a) in $CD_3CO_2D-CD_3CN$ solution at 21 °C for 22.5 h gave the pyrimidin-4-one [²H]-(1a) (12%), the azetidin-2-one (5a) (19%), and the imide (6a) (24%): starting material (3a) (44%) was also recovered [Schemes 4(A) and 4(B)].

The $[^{2}H_{3}]$ acetoxy and $[^{2}H_{3}]$ acetyl groups were incorporated in the recovered $[^{2}H]$ -(**3a**) (64 mol% ²H) and in the imide $[^{2}H]$ -(**6a**) (94 mol% ²H). No $[^{2}H_{3}]$ acetyl/acetyl-CH₃ exchange reaction of $[^{2}H]$ -(**6a**) occurred in CH₃CO₂H-CH₃CN solution at 21 °C because the acetyl CH₃ group was not incorporated in $[^{2}H]$ -(**6a**). However, the $[^{2}H_{3}]$ acetyl group of $[^{2}H]$ -(**6a**) comes from the solvent acetic acid and the intramolecular acetyl migration mechanism can be ruled out.

In acetic acid solution the C(4)–O and O–Ac bonds of 4-acetoxyazetidin-2-one (**3a**) undergo charge separation to give the ion pairs $C(4)^+ \cdots ^-O$ and $O^- \cdots ^+Ac$ respectively. The former process leads to the azetidinyl cation $[^2H]$ -(**11a**) and acetoxy anion. Nucleophilic attack of $[^2H_4]$ acetic acid on the carbocation $[^2H]$ -(**11a**) (S_N 1 reaction) and E1 reaction of $[^2H]$ -(**11a**) give the azetidin-2-ones $[^2H]$ -(**3a**) and $[^2H]$ -(**17a**). Subsequent hydrolysis of the imino group gives (**5a**). Intramolecular cyclization and ring opening give the pyrimidin-4-one (**1a**), which undergoes H/D exchange of the 2-methyl group to give $[^2H]$ -(**1a**) [Scheme 4(A)].

The latter charge separation may be enhanced by the neighbouring-group participation of the imine nitrogen because the azetidin-2-ones (4d) and (4e) having the acetyl group at C-3 failed to give the corresponding products. Ionic cleavage of the O-Ac bond gives acetic anhydride (14) and the 4-hydroxy-azetidin-2-one (13a) that rearranges to the enamide (15a) by fission of the C(3)-C(4) bond. The exchange reaction of the acetyl group between (14) and $[^{2}H_{4}]$ acetic acid takes place to





Scheme 4 (A).

give acetic anhydride $[^{2}H]$ -(14). Acetylation of (15a) by $[^{2}H]$ -(14) gives $[^{2}H]$ -(6a). However, the intermediates {(14) and $[^{2}H]$ -(14)} were not confirmed in the present experiment [Scheme 4(B)].

Although there have been no reports of O-Ac bond cleavage of an acetoxy group attached to a tertiary carbon atom during acetolysis, there has been one of intramolecular migration of an acetyl group from an acetoxy group to the carbonyl oxygen atom in thioesters.⁵

Thermolysis of the Dewar Pyrimidinone (2a).—Thermal reaction of (2a) in a melt without solvent at 80 °C for 6 days gave the pyrimidin-4-one (1a) (55%), the azetidin-2-one (5a) (14%), and 2,4,4,N-tetramethyl-3-oxopentanamide (18) (11%) after separation of the reaction mixture on silica gel (Scheme 5).

Ring transformation of the Dewar pyrimidinone (2a) to (1a) and (5a) could be explained by postulating a zwitterionic intermediate (16a) formed by initial cleavage of the C(1)-N(2) bond of (2a).^{1e} Intramolecular combination of the carbocation with the imino anion and subsequent ring opening of the C(3)-C(4) bond would then give the pyrimidin-4-one (1a). The intermediate (16a) undergoes an E1 reaction which leads to the



imino azetidin-2-one (17a): this on hydrolysis on silica gel then gives (5a) (Scheme 5). The pentanamide (18) is formed by the reactions of unchanged (2a) on the silica gel column.

The products (1a) and (5a) were similar to those obtained by thermolysis of the 1,3,6-trialkyl Dewar pyrimidinones.^{1e} However, the reaction rate of (3a) was much slower than those of the 1,3,6-trialkyl Dewar pyrimidinones at 40–45 °C without solvent. The location of the methyl group at the 4 position of (2) increases the stability of the C(1)–N(2) bond of the Dewar pyrimidinones (2).

Thermal Rearrangements of the 4-Acetoxyazetidin-2-ones (3) and (4).—The 4-acetoxyazetidin-2-ones [(3a) and (3b)] when heated without solvent at 100—110 °C for 1 h gave the corresponding pyrimidin-4-ones (1a) (39%) and (1b) (23%) and azetidin-2-ones (5a) (50%) and (5b) (55%) (Scheme 6). Analogously the azetidin-2-ones (4c) and (4d) gave the 4-alkylideneazetidin-2-ones (5c) (50%) and (5e) (97%), respectively.

The reactions are similar to those of the 4-acetoxyazetidin-2ones (3) and (4) in the presence of acetic acid [Scheme 4(A)], formation of the products (1) and (5) may proceed by initial cleavage of the C(4)–O bond to give an ion pair of the azetidinyl cations (16a,b) and (19c,d) and acetoxy anion. The cations (16a,b) and (19c,d) then undergo an E1 reaction to form the azetidin-2-ones (17a,b) and (5c,d), respectively. Hydrolysis of the imino group of (17a,b) on silica gel gives (5a,b). Cyclization of (16a,b) and concomitant cleavage of the C(3)–C(4) bond



results in formation of the pyrimidin-4-ones (1a) and (1b), respectively.

The thermal reactions ^{1e} of the 4-methoxyazetidin-2-ones at 121 °C without solvent gave the acetoacetate derivatives which are formed by intramolecular migration of the methoxy group to the amide carbon by ionic cleavage of the C(4)–OCH₃ and N(1)–C(2) bonds. No product formed by fission of the N(1)–C(2) bond was obtained in the thermolysis of the 4-acetoxy-3-methylazetidin-2-ones (3) and (4). This indicates that the 3-methyl group may stabilize the amide bonds of (3) and (4).

Experimental

M.p.s were measured with a Yanako melting point apparatus without any corrections. The spectroscopic measurements were performed with the following instruments: i.r., JASCO A-102; u.v., Hitachi Model 200-10; mass spectra (m.s.), JEOL OISG-2 at 70 eV; ¹H n.m.r., JEOL JNM-GX 270; ¹³C n.m.r., Varian XL-200. Chemical shifts were reported in p.p.m. on the δ scale relative to Me₄Si internal standard. Elemental combustion analyses were performed by the Microanalytical Laboratory of this university. Column chromatography was performed on Merck 70-230 mesh alumina (activity I-III) or Sephadex LH-20 (Pharmacia Fine Chemicals AB). Medium pressure liquid chromatography (m.p.l.c.) was carried out on a column $(25 \times 2.5 \text{ cm})$ of silica gel BW-300 (Fuji Davison, 200-400 mesh) or alumina (Merck, 70-230 mesh, activity II--III). Merck pre-coated silica gel 60 F-254 plates were used for preparative thin-layer chromatography.

Materials.—2,5-Dimethyl-6-t-butylpyrimidin-4(3*H*)-one (**12a**), 2-ethyl-5,6-dimethylpyrimidin-4(3*H*)-one, and 2-benzyl-5,6-dimethylpyrimidin-4(3*H*)-one were synthesized by condensation of the amidine hydrochlorides ^{1d,6} and α -methyl- β keto esters ⁷ as described in the literature. ^{1c,6}



Scheme 6.

2,5-Dimethyl-6-t-butylpyrimidin-4(3H)-one (12a). M.p. 160– 162 °C; m/z 180 (M^+) (Found: C, 66.45; H, 8.85; N, 15.25. C₁₀H₁₆N₂O requires C, 66.63; H, 8.95; N, 15.54%).

2-*Ethyl*-5,6-*dimethylpyrimidin*-4(3H)-one. M.p. 172—174 °C; m/z 152 (M^+) (Found: C, 63.15; H, 8.05; N, 18.35. C₈H₁₂N₂O requires C, 63.13; H, 7.95; N, 18.41%).

2-Benzyl-5,6-dimethylpyrimidin-4(3H)-one. M.p. 184-

185 °C; m/z 214 (M^+) (Found: C, 72.65; H, 6.6; N, 12.95. C₁₃H₁₄N₂O requires C, 72.87; H, 6.59; N, 13.08%).

2,3,5-Trimethyl-6-t-butylpyrimidin-4(3H)-one (1a), 2,3,5,6tetramethylpyrimidin-4-(3H)-one (1c), ^{1c} 2-ethyl-3,5,6-trimethylpyrimidin-4(3H)-one (1d), 2-benzyl-3,5,6-trimethylpyrimidin-4(3H)-one (1e), and 3,5,6-trimethylpyrimidin-4(3H)-one (1f) ^{1c} were prepared from iodomethane and the corresponding pyrimidin-4(3H)-ones in alcoholic solutions containing potassium hydroxide. 3-Methyl-2-t-butyl-6,7,8,9-tetrahydro-4H-pyrido[1,2-*a*]pyrimidin-4-one (1b) was synthesized by condensation of 2-amino-3,4,5,6-tetrahydropyridine hydrochloride⁸ with ethyl trimethylacetoacetate ^{7b} as described in the literature.^{1c,6}

Compounds (1) showed λ_{max} (MeOH) 278 \pm 3 nm (ϵ 6 000 dm³ mol⁻¹ cm⁻¹) and 229 \pm 2 nm (ϵ 5 000).

For (**1a**): m.p. 73 °C; v_{max} .(CHCl₃) 1 619 and 1 585 cm⁻¹; δ_{H} (CDCl₃) 1.36 (9 H, s), 2.26 (3 H, s), 2.49 (3 H, s), and 3.53 (3 H, s); m/z 194 (M^+) (Found: C, 68.25; H, 9.5; N, 14.3. C₁₁H₁₈N₂O requires C, 68.00; H, 9.34; N, 14.42%).

For (**1b**): m.p. 131–132 °C; v_{max} .(CHCl₃) 1 630 cm⁻¹; δ_{H} (CDCl₃) 1.37 (9 H, s), 1.8–2.1 (4 H, m), 2.27 (3 H, s), 2.87 (2 H, t, *J* 6.0 Hz), and 3.96 (2 H, t, *J* 6.0 Hz); *m/z* 220 (*M*⁺) (Found: C, 71.1; H, 9.1; N, 12.7. C₁₃H₂₀N₂O requires C, 70.87; H, 9.15; N, 12.72%).

For (1d): m.p. 95—96 °C; v_{max} .(CHCl₃) 1 645 and 1 600 cm⁻¹; δ_{H} (CDCl₃) 1.32 (3 H, t, *J* 7.5 Hz), 2.08 (3 H, s), 2.29 (3 H, s), 2.75 (2 H, q, *J* 7.5 Hz), and 3.56 (3 H, s); *m/z* 166 (*M*⁺) (Found: C, 65.05; H, 8.45; N, 16.65. C₉H₁₄N₂O requires C, 65.03; H, 8.49; N, 16.85%).

For (1e): oil; v_{max} (CHCl₃) 1 645 and 1 600 cm⁻¹; δ_{H} (CDCl₃) 2.10 (3 H, s), 2.35 (3 H, s), 3.41 (3 H, s), 4.14 (2 H, s), and 7.1—7.5 (5 H, m); m/z 228 (M^+) (Found: M^+ , 228.1255. C₁₄H₁₆N₂O requires M, 228.1262).

1,4,6-*Trimethyl*-3-*t*-butyl-2,6-diazabicyclo[2.2.0]*hex*-2-*en*-5one (2a).—The pyrimidin-4-one (1a) (2.079 g, 10.7 mmol) in liquid NH₃-ether (82:18, v/v; 280 ml) was irradiated at -40 °C under an argon atmosphere with a high-pressure mercury lamp (100 W). After irradiation, the solvent was evaporated under reduced pressure. A mixture of (2a) (14%) and (1a) (86%) was obtained and chromatographed on Sephadex LH-20^{1c} (180 g) eluting with chloroform-hexane (4:1, v/v) to give the crystalline (2a) (94 mg, 5%), (1a) (1.848 g, 89%), and a mixture of (1a) and (2a) (51 mg, 2%).

Crystalline (2a) was purified by sublimation at a bath temperature of 40 °C *in vacuo* to give colourless columns, m.p. 42 °C; v_{max} .(CHCl₃) 1 740 and 1 585 cm⁻¹; λ_{max} .(CH₃CN) 260 nm (ε 420 dm³ mol⁻¹ cm⁻¹) and 214 nm (ε 1 560); $\delta_{\rm H}$ (CDCl₃) 1.20 (9 H, s, Bu¹), 1.45 (3 H, s, CH₃), 1.62 (3 H, s, CH₃), and 2.79 (3 H, s, NCH₃); *m*/*z* 195 (*M*⁺ + 1, 71%), 194 (*M*⁺, 1.7), 139 (34), and 56 (56) (Found: *M*⁺, 194.1413. C₁₁H₁₈N₂O requires *M*, 194.1418).

General Procedures for the Photolysis of Pyrimidin-4-ones (1) and for the Isolation of the Products (3)—(6).—The pyrimidin-4one (1) (1.2—1.7 g) dissolved in acetic acid-acetonitrile (1:2, v/v; 270 ml) was irradiated under an argon atmosphere at 0 °C with a high-pressure mercury lamp (100 W). The reaction progress was routinely monitored by ¹H n.m.r. spectroscopy. After irradiation, the solvent was evaporated and the reaction mixture was chromatographed on Sephadex LH-20 (180 g) eluting with acetone. The yields of the products are listed in the Table.

Photolysis of (1a). From (1a) (1.472 g, 7.59 mmol), 4-acetoxy-3-(1-imino-2,2-dimethylpropyl)-1,3,4-trimethylazetidin-2-one (3a) (609 mg, 32%) as colourless crystals, 1,3-dimethyl-3pivaloyl-4-vinylazetidin-2-one (5a) (144 mg, 10%) as an oil, and N-acetyl-3-acetamido-2,4,4,N-tetramethylpent-2-enamide (6a) (267 mg, 13%) as colourless crystals were obtained after irradiation for 7 h: starting material (1a) (646 mg, 44%) was also recovered.

Recrystallization of (**3a**) from ether–pentane gave colourless prisms, m.p. 97–99 °C; m/z 255 (M^+ + 1, 1.9%), 111 (82), 98 (98), 83 (52), 82 (39), 57 (54), 56 (88), 43 (100), and 41 (54); $\delta_{\rm H}({\rm CDCl}_3)$ 1.25 (9 H, s, Bu¹), 1.49 (3 H, s, 3-CH₃), 1.64 (3 H, s, 4-CH₃), 2.14 (3 H, s, CH₃CO), and 2.83 (3 H, s, NCH₃); $\delta_{\rm C}({\rm CDCl}_3)$ 19.9 (q, CH₃), 21.4 (q, CH₃), 21.6 (q, CH₃), 24.1 (q, NCH₃), 27.2 (q, Bu¹CH₃), 41.3 (s, Bu¹C), 71.2 (s, C-3), 94.7 (s, C-4), 168.3 (s, C=O), 170.2 (s, C=O), and 185.6 (s, C=N); $\nu_{\rm max}$.(CHCl₃) 3 250 (NH), 1 760 (C=O), 1 730 (C=O), and 1 615 cm⁻¹ (C=N); $\lambda_{\rm max}$.(CH₃CN) 283sh nm (ε 225 dm³ mol⁻¹ cm⁻¹) (Found: C, 61.15; H, 8.9; N, 10.9. C₁₃H₂₂N₂O₃ requires C, 61.39; H, 8.72; N, 11.02%).

The azetidin-2-one (**5a**) was purified by m.p.l.c. on silica gel to give a colourless oil: m/z 195 (M^+ , 13%), 111 (24), 82 (16), 77 (15), and 57 (100) (Found: M^+ , 195.1274. C₁₁H₁₇NO₂ requires M, 195.1258); $\delta_{\rm H}$ (CDCl₃) 1.23 (9 H, s, Bu¹), 1.60 (3 H, s, CH₃), 2.97 (3 H, s, NCH₃), 4.28 (1 H, d, J 3 Hz, vinyl H), and 4.42 (1 H, d, J 3 Hz, vinyl H); $\delta_{\rm C}$ (CDCl₃) 20.1 (q, CH₃), 25.5 (q, Bu¹CH₃), 25.8 (q, NCH₃), 45.9 (s, Bu¹C), 69.3 (s, C-3), 80.5 (t, =CH₂), 149.1 (s, C-4), 169.9 (s, amide C=O), and 208.6 (s, ketone C=O); $v_{\rm max}$ (neat) 1 800 (C=O) and 1 690 cm⁻¹ (C=O and C=C).

Recrystallization of (**6a**) from benzene–hexane gave colourless prisms, m.p. 131–132 °C; m/z 197 ($M^+ - C_4H_9$, 10%), 154 (100), and 43 (74); δ_H (CDCl₃) 1.15 (9 H, s, Bu¹), 1.82 (3 H, s, CH₃), 2.13 (3 H, s, amide acetyl CH₃), 2.58 (3 H, s, CH₃CON), 3.37 (3 H, s, NCH₃), and 6.52 (1 H, br s, NH); δ_C (CDCl₃) 18.5 (q, CH₃), 23.1 (q, CH₃), 27.6 (q, CH₃), 28.3 (q, Bu¹CH₃), 33.1 (q, NCH₃), 37.9 (s, Bu¹C), 128.0 (s, olefinic C), 137.1 (s, olefinic C), 168.4 (s, amide CO), 173.7 (s, imide CO), and 174.4 (s, imide CO); v_{max} .(CHCl₃) 3 440, 1 700, and 1 685 cm⁻¹; λ_{max} .(MeOH) 300 nm (ε 70 dm³ mol⁻¹ cm⁻¹) and 218 nm (ε 14 600) (Found: C, 61.5; H, 8.8; N, 10.85. C₁₃H₂₂N₂O₃ requires C, 61.39; H, 8.72; N, 11.02%).

Photolysis of (1b). From (1b) (1.174 g, 5.34 mmol), 6-acetoxy-7-(1-imino-2,2-dimethylpropyl)-7-methyl-1-azabicyclo[4.2.0]octan-8-one (3b) (835 mg, 56%) as colourless crystals, 7-methyl-7-pivaloyl-1-azabicyclo[4.2.0]octa-5-en-8-one (5b) (64 mg, 5%) as an oil, and N-(3-acetamido)-2,4,4-trimethyl-1-oxopent-2enoyl)-2-piperidone (6b) (15 mg, 1%) were obtained after irradiation for 5 h: starting material (1b) (256 mg, 22%) was also recovered.

Recrystallization of (**3b**) from benzene–hexane gave colourless prisms, m.p. 104–105 °C; m/z 280 (M^+ , 0.1%), 219 (20), 137 (56), and 109 (100); $\delta_{\rm H}(\rm CDCl_3)$ 1.28 (9 H, s, Bu¹), 1.3–1.9 [6 H, m, (CH₂)₂CH and NH], 1.48 (3 H, s, 7-CH₃), 2.18 (3 H, s, CH₃CO), 2.54 (1 H, d, J 14 Hz, 5-CH), 2.92 (1 H, ddd, J 3.6, 13, and 13 Hz, 2-CH), and 3.77 (1 H, dd, J 4.7 and 13 Hz, 2-CH); $\delta_{\rm C}(\rm CDCl_3)$ 19.7 (t, CH₂), 21.3 (q, 7-CH₃ and acetyl CH₃), 24.3 (t, CH₂), 27.4 (q, Bu¹CH₃), 31.2 (t, CH₂), 36.5 (t, CH₂), 41.0 (s, Bu¹C), 73.5 (s, C-7), 92.2 (s, C-6), 166.2 (s, C=O), 170.4 (s, C=O), and 184.6 (s, C=N); ν_{max} .(CHCl₃) 3 250 (NH), 1 760 (C=O), 1 730 (C=O), and 1 615 cm⁻¹ (C=N); λ_{max} .(CH₃CN) 252sh nm (ϵ 141 dm³ mol⁻¹ cm⁻¹) (Found: C, 64.2; H, 8.65; N, 9.7. C₁₅H₂₄N₂O₃ requires C, 64.26; H, 8.63; N, 9.99%).

The azetidin-2-one (**5b**) was purified by m.p.l.c. on silica gel to give a colourless oil: m/z 221 (M^+ , 31%), 206 (37), and 57 (100) (Found: M^+ , 221.1384. $C_{13}H_{19}NO_2$ requires M, 221.1415); $\delta_{H}(CDCl_3)$ 1.23 (9 H, s, Bu'), 1.60 (3 H, s, CH₃), 1.81 (2 H, tt, *J* 6 and 6 Hz, 3-CH₂), 2.17 (2 H, dt, *J* 4 and 6 Hz, 4-CH₂), 3.39 (1 H, dt, *J* 13 and 6 Hz, 2-CH), 3.49 (1 H, dt, *J* 13 and 6 Hz, 2-CH), and 4.93 (1 H, t, *J* 4 Hz, 5-CH); $\delta_{C}(CDCl_3)$ 20.1 (q, CH₃), 20.7 (t, CH₂), 20.9 (t, CH₂), 25.7 (q, Bu'CH₃), 38.8 (t, CH₂), 45.9 (s, Bu'C), 70.9 (s, C-7), 93.8 (d, C-5), 139.4 (s, C-6), 167.8 (s, amide C=O), 209.0 (s, ketone C=O); v_{max} (neat) 1 785 (C=O) and 1 685 cm⁻¹ (C=O and C=C).

The imide (**6b**) was purified by m.p.l.c. on silica gel to give an oily solid: m/z 280 (M^+ , 1.4%), 223 (35), 154 (100), 100 (92), 82 (84), and 43 (100) (Found: M^+ , 280.1763. C₁₅H₂₄N₂O₃ requires M, 280.1785); δ_{H} (CDCl₃) 1.21 (9 H, s, Bu¹), 1.7-2.3 (4 H, m, 2 × CH₂), 1.93 (3 H, s, CH₃), 2.07 (3 H, s, CH₃CO), 2.4-2.8 (2 H, m, CH₂), 3.4-3.9 (2 H, m, CH₂), and 6.40 (1 H, br s, NH); ν_{max} .(CHCl₃) 3 420, 1 670, and 1 655 cm⁻¹.

Photolysis of (1c). From (1c) (1.502 g, 9.88 mmol), 4-acetoxy-3-acetyl-1,3,4-trimethylazetidin-2-one (4c) (887 mg, 42%) as an oil and 3-acetyl-1,3-dimethyl-4-vinylazetidin-2-one (5c) (33 mg, 2%) as an oil were obtained after irradiation for 7 h: starting material (1c) (734 mg, 49%) was also recovered.

The oily product (4c) was a mixture of two stereoisomers [(4cA)(50%)] and (4cB)(50%)] and was not further purified: m/z $154 (M^+ - CH_3CO_2, 16\%), 129 (52), 99 (100), 56 (43), and 43$ (100) (Found: M^+ – CH₃CO₂, 154.0899. C₈H₁₂NO₂ requires M, 154.0867); v_{max} (neat) 1 780 (C=O) and 1 710 cm⁻¹ (C=O); $\lambda_{max.}$ (CH₃CN) 292sh nm (ϵ 153 dm³ mol⁻¹ cm⁻¹). The ¹H n.m.r. signals of the respective [(4cA) and (4cB)] were assigned from a fraction [(4cA):(4cB) = 72:28] obtained after column chromatography. The major isomer (4cA) and minor isomer (4cB) had the following n.m.r. spectra: major, $\delta_{\rm H}(\rm CDCl_3)$ 1.48 (3 H, s, 3-CH₃), 1.77 (3 H, s, 4-CH₃), 2.05 (3 H, s, CH₃CO₂), 2.32 (3 H, s, CH₃CO), and 2.94 (3 H, s, NCH₃); δ_{C} (CDCl₃) 13.8 (q, CH₃), 16.9 (q, CH₃), 21.4 (q, acetyl CH₃), 25.7 (q, acetyl CH₃), 28.4 (q, NCH₃), 72.0 (s, C-3), 93.0 (s, C-4), 167.7 (s, C=O), 169.8 (s, C=O), and 203.0 (s, ketone C=O); minor, $\delta_{\rm H}$ 1.52 (3 H, s, 3-CH₃), 1.77 (3 H, s, 4-CH₃), 2.15 (3 H, s, CH₃CO₂), 2.36 (3 H, s, CH₃CO), and 2.88 (3 H, s, NCH₃); $\delta_{C}(CDCl_{3})$ 14.2 (q, CH₃), 17.6 (q, CH₃), 24.6 (q, acetyl CH₃), 26.0 (q, acetyl CH₃), 28.0 (q, NCH₃), 73.5 (s, C-3), 92.3 (s, C-4), 166.7 (s, C=O), 169.5 (s, C=O), and 204.5 (s, ketone C=O).

The azetidin-2-one (**5c**) was purified by m.p.l.c. on alumina to give a colourless oil: m/z 153 (M^+ , 28%), 110 (32), 82 (53), 55 (100), and 43 (100) (Found: M^+ , 153.0831. C₈H₁₁NO₂ requires M, 153.0789); $\delta_{\rm H}$ (CDCl₃) 1.51 (3 H, s, CH₃), 2.27 (3 H, s, CH₃CO), 3.04 (3 H, s, NCH₃), 4.28 (1 H, d, J 3.5 Hz, vinyl H), and 4.38 (1 H, d, J 3.5 Hz, vinyl H); $v_{\rm max}$.(neat) 1 800 (C=O), 1 710 (C=O), and 1 675 cm⁻¹ (C=C); $\lambda_{\rm max}$.(MeOH) 244sh (ϵ 2 800 dm³ mol⁻¹ cm⁻¹) and 234sh nm (ϵ 4 020).

Photolysis of (1d). From (1d) (1.583 g, 9.53 mmol), 4-acetoxy-3-acetyl-4-ethyl-1,3-dimethylazetidin-2-one (4d) (527 mg, 24%) as an oil and 3-acetyl-4-ethylidene-1,3-dimethylazetidin-2-one (5d) (221 mg, 14%) as an oil were obtained after irradiation for 7 h; starting material (1d) (856 mg, 54%) was also recovered.

The product (4d) was a mixture of two stereoisomers (4dA) (71%) and (4dB) (29%) and was not further purified: m/z 227 (M^+ , 0.1%), 168 ($M^+ - CH_3CO_2$, 100), 128 (48), 99 (92), 70 (53), and 43 (99) (Found: $M^+ - CH_3CO_2$, 168.1001. $C_9H_{14}NO_2$ requires M, 168.1024); v_{max} (neat) 1 780 (C=O) and 1 715 cm⁻¹ (C=O); the isomer (4dB) had the following ¹H n.m.r. spectrum: major, $\delta_H(CDCI_3)$ 1.02 (3 H, dd, J 7.5 and 7.5 Hz, CH₃), 1.47 (3 H, s, 3-CH₃), 1.85 (1 H, dq, J 7.5 and 15 Hz, HCH), 2.05 (3 H, s, CH₃CO₂), 2.30 (3 H, s, CH₃CO), 2.54 (1 H, dq, J 7.5 and 15 Hz, HCH), 2.90 (3 H, s, NCH₃); minor, δ_H 0.91 (3 H, t, J 7.5 Hz, CH₃), 1.48 (3 H, s, 3-CH₃), 2.16 (3 H, s, CH₃CO₂), 2.28 (2 H, q, J 7.5 Hz, CH₂), 2.34 (3 H, s, CH₃CO), and 2.91 (3 H, s, NCH₃).

The ¹H n.m.r. spectrum indicated that the azetidin-2-one (**5d**) was a mixture of two stereoisomers (**5dA**) (72%) and (**5dB**) (28%). The mixture was purified by m.p.l.c. on silica gel to give a colourless oil: m/z 167 (M^+ , 65%), 96 (31), 69 (58), 68 (100), 67 (39), and 43 (100) (Found: M^+ , 167.0952. C₉H₁₃NO₂ requires M, 167.0946); v_{max} (neat) 1 795 (C=O), 1 710, and 1 700 cm⁻¹ (C=O and C=C); λ_{max} (MeOH) 252sh nm (ε 2 440 dm³ mol⁻¹ cm⁻¹). The major isomer (**5dA**) and minor isomer (**5dB**) had the following spectra: major, δ_{H} (CDCl₃) 1.52 (3 H, s, CH₃), 1.57 (3 H, d, J 7 Hz, CH₃), 2.22 (3 H, s, CH₃CO), 2.96 (3 H, s, NCH₃),

 $4.77 (1 H, q, J7 Hz, vinyl H); minor, \delta_H 1.43 (3 H, s, CH_3), 1.81 (3 H, d, J7.3 Hz, CH_3), 2.22 (3 H, s, CH_3CO), 3.21 (3 H, s, NCH_3), and 4.52 (1 H, q, J7.3 Hz, vinyl H).$

Photolysis of (1e). From (1e) (1.554 g, 6.81 mmol), 4-acetoxy-3-acetyl-4-benzyl-1,3-dimethylazetidin-2-one (4e) (216 mg, 14%) as an oil and 3-acetyl-4-benzylidene-1,3-dimethylazetidin-2-one (5e) (207 mg, 13%) as an oil were obtained after irradiation for 9.5 h: starting material (1e) (919 mg, 59%) was also recovered.

The oily product (4e) was a mixture of two stereoisomers (4eA) (66%) and (4eB) (34%) and was not further purified: m/z230 ($M^+ - CH_3CO_2$, 2.9%), 229 ($M^+ - CH_3CO_2H$, 15), 85 (65), 83 (100), 47 (34), and 43 (47) (Found: $M^+ - CH_3CO_2$, 230.1169. $C_{14}H_{16}NO_2$ requires M, 230.1180); v_{max} (neat) 1 785 (C=O), 1 765 (C=O), 1 740 (C=O), and 1 710 cm⁻¹ (C=O); λ_{max} .(CH₃CN) 264—253 nm (ε 710—760 dm³ mol⁻¹ cm⁻¹). The major isomer (4eA) and minor isomer (4eB) had the following ¹H n.m.r. spectra: major, δ_H (CDCl₃) 1.58 (3 H, s, 3-CH₃), 1.94 (3 H, s, CH₃CO₂), 2.28 (3 H, s, CH₃CO), 2.77 (3 H, s, NCH₃), 3.35 (1 H, d, J 15 Hz, HCH), 3.64 (1 H, d, J 15 Hz, HCH), 7.1—7.5 (5 H, m₁ 5 × ArH); minor, δ_H 1.53 (3 H, s, 3-CH₃), 2.16 (3 H, s, CH₃CO₂), 2.28 (3 H, s, CH₃CO), 2.63 (2 H, s, NCH₃), 3.24 (1 H, d, J 15 Hz, HCH), 3.92 (1 H, d, J 15 Hz, HCH), and 7.1—7.5 (5 H, m, 5 × ArH).

The oily azetidin-2-one (5e) was a mixture of two geometrical isomers (5eA) (52%) and (5eB) (48%) which were isolated by preparative t.l.c. The isolated compounds had the following physical properties: major isomer (5eA) (colourless oil); m/z 229 $(M^+, 53\%)$, 131 (73), 129 (80), 116 (56), 91 (68), and 43 (100) (Found: M⁺, 229.1086. C₁₄H₁₅NO₂ requires M, 229.1102); δ_H(CDCl₃) 1.58 (3 H, s, CH₃), 2.33 (3 H, s, CH₃CO), 2.98 (3 H, s, NCH₃), 5.75 (1 H, s, vinyl H), and 7.1–7.5 (5 H, m, $5 \times \text{ArH}$); $v_{max.}$ (neat) 1 795 (C=O), 1 710 (C=O), and 1 680 cm⁻¹ (C=C); λ_{max} (MeOH) 259 nm (ϵ 11 300 dm³ mol⁻¹ cm⁻¹); minor isomer (5eB) (colourless oil); m/z 229 (M^+ , 57%), 131 (65), 129 (100), 116 (59), 91 (25), and 43 (100) (Found: M^+ , 229.1082. $C_{14}H_{15}NO_2$ requires *M*, 229.1102); δ_H 1.58 (3 H, s, CH₃), 2.30 (3 H, s, CH₃CO), 3.16 (3 H, s, NCH₃), 5.87 (1 H, s, vinyl H), and 6.9–7.5 (5 H, m, 5 × ArH); v_{max} (neat) 1 795 (C=O), 1 710 (C=O), and 1 665 cm⁻¹ (C=C); λ_{max} (MeOH) 265 nm (ϵ 16 700 dm³ mol⁻¹ cm⁻¹).

Photolysis of (1f). From (1f) (1.505 g, 10.9 mmol), 4-acetoxy-3-acetyl-1,3-dimethylazetidin-2-one (4f) (1.133 g, 52%) was obtained as a pale brown oil after irradiation for 6.5 h: starting material (1f) (0.390 g, 26%) was also recovered.

The oily product (**4f**) was a mixture of two stereoisomers (**4fA**) (59%) and (**4fB**) (41%) and was not further purified: m/z199 (M^+ , 0.3%), 140 (99), 100 (100), 85 (100), and 43 (100) (Found: M^+ , 199.0849. C₉H₁₃NO₄ requires M, 199.0844); v_{max} .(neat) 1 770 (C=O) and 1 710 cm⁻¹ (C=O); λ_{max} .(CH₃CN) 279 nm (ϵ 170 dm³ mol⁻¹ cm⁻¹). The major isomer (**4fA**) and minor isomer (**4fB**) had the following ¹H n.m.r. spectra: major, δ_{H} (CDCl₃) 1.50 (3 H, s, 3-CH₃), 2.19 (3 H, s, CH₃CO₂), 2.33 (3 H, s, CH₃CO), 2.89 (3 H, s, NCH₃), and 6.23 (1 H, s, CH); minor, δ_{H} 1.53 (3 H, s, 3-CH₃), 2.13 (3 H, s, CH₃CO₂), 2.32 (3 H, s, CH₃CO), 2.95 (3 H, s, NCH₃), and 5.77 (1 H, s, CH).

Reaction of the Dewar Pyrimidinone (2a) with Acetic Acid.— The Dewar isomer (2a) (68 mg, 0.35 mmol) was dissolved in acetic acid-acetonitrile (1:14 v/v; 15 ml). The solution was stirred for 24 h at 0 °C. After removal of the solvent, the residue was chromatographed on Sephadex LH-20 (180 g) with acetone as an eluant to give the pyrimidin-4-one (1a) (9 mg, 13%), the imine azetidin-2-one (3a) (48 mg, 54%), the azetidin-2-one (5a) (7 mg, 10%), and the imide (6a) (4 mg, 5%).

1,3,4-Trimethyl-3-pivaloylazetidin-2-one (7a).—A mixture of the azetidin-2-one (5a) (89 mg, 0.46 mmol) dissolved in

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methanol (20 ml) and 10% palladium carbon (99 mg) was stirred under a hydrogen atmosphere for 3 h at 19–21 °C. After removal of the catalyst, the solvent was evaporated and the residue was chromatographed on alumina to give (7a) (81 mg, 90%). The azetidin-2-one (7a) was a single isomer and had the following physical properties: colourless oil; m/z 197 (M^+ , 0.9%), 182 (22), 113 (46), 98 (33), 83 (100), 57 (31), and 55 (35) (Found: M^+ , 197.1415. C₁₁H₁₉NO₂ requires M, 197.1415); v_{max.}(neat) 1 750s and 1 690s cm⁻¹; λ_{max} .(MeOH) 291 nm (ϵ 29 dm³ mol⁻¹ cm⁻¹); $\delta_{\rm H}$ (CDCl₃) 1.16 (3 H, d, J 6.5 Hz, CH₃), 1.27 (9 H, s, Bu¹), 1.57 (3 H, s, CH₃), 2.87 (3 H, s, NCH₃), and 3.39 (1 H, q, J 6.5 Hz, CH).

Ethanolysis of the Imide (6a).—A solution of (6a) (81 mg, 0.32 mmol) in ethanol (10 ml) was refluxed for 28 h. After evaporation of the solvent, the residue was chromatographed on silica gel (70 g) to give four main fractions. Fraction 1 eluted with benzene–ethyl acetate (9:1) gave 2,5-dimethyl-4-t-butyl-1,3-oxazin-6-one (10a) (16 mg, 28%) as an oily solid. Fraction 2 eluted with benzene–ethyl acetate (1:1) gave the pyrimidin-4-one (1a) (5 mg, 8%). Fraction 3 eluted with chloroform-methanol (95:5) was recovered (6a) (15 mg, 19%). Further elution gave a mixture of 3-acetamido-2,4,4-trimethyl-N-methyl-aminopent-2-enamide (8a) and N-methylacetamide (9a). Crystallization of this mixture from ethanol-hexane gave (8a) (30 mg, 44%) and (9a) (3 mg, 13%) as crude crystals.

Recrystallization of (8a) from ethanol–ether–hexane gave colourless feathers: m.p. >200 °C (sublimed); m/z 213 (M^+ + 1, 0.1%), 194 (25), 178 (31), 155 (70), 154 (100), 152 (62), 140 (39), 138 (47), 124 (40), and 114 (43); v_{max} (KBr) 3 280, 3 230, 1 665, and 1 625 cm⁻¹; δ_{H} (CDCl₃) 1.15 (9 H, s, Bu'), 1.79 (3 H, s, CH₃), 2.10 (3 H, s, CH₃CO), 2.83 (3 H, d, J 5 Hz, NCH₃), 6.34 (1 H, br, NH), and 6.75 (1 H, br, NH) (Found: C, 61.85; H, 9.35; N, 13.0. C₁₁H₂₀N₂O₂ requires C, 62.23; H, 9.50; N, 13.20%).

The spectral data of the amide (9a) were found to be identical with those of an authentic sample.

The oxazinone (**10a**) had the following physical properties: colourless oily solid (m.p. <31 °C); m/z 181 (M^+ , 19%), 154 (46), 138 (89), 124 (35), 82 (92), and 43 (100) (Found: M^+ , 181.1093. C₁₀H₁₅NO₂ requires M, 181.1101); v_{max} .(CHCl₃) 1 720, 1 640, and 1 555 cm⁻¹; $\delta_{\rm H}$ (CDCl₃) 1.34 (9 H, s, Bu^t), 2.22 (3 H, s, CH₃), and 2.36 (3 H, s, CH₃).

Reaction of the Imide (6a) in the Presence of Acid.—The imide (6a) (34 mg, 0.13 mmol) was dissolved in $CDCl_3$ (0.37 ml) containing trifluoroacetic acid (0.152 mg, 0.134 mmol) and tetramethylsilane (22 mg). The solution was set aside for 23 h at 40 °C and the reaction was routinely followed by ¹H n.m.r. spectroscopy. After evaporation of the solvent, the residue was chromatographed on alumina (104 g) eluting with benzene– ethyl acetate (9:1—1:1) and chloroform–methanol (95:5) to give the 1,3-oxazin-6-one (10a) (6.0 mg, 25%) and N-methylacetamide (9a) (7.3 mg, 77%).

Reaction of the Amide (8a) in Ethanol.—A solution of (8a) (35 mg, 0.17 mmol) in ethanol (10 ml) was refluxed for 5 days. After evaporation of the solvent, the residue was chromatographed on silica gel (70 g) eluting with chloroform–methanol (95:5) to give the pyrimidin-4-one (1a) (4.0 mg, 12%) as crystals: starting material (8a) (31 mg, 89%) was also recovered.

Reaction of the Oxazin-6-one (10a) with Ammonia.—The oxazin-6-one (10a) (6.0 mg, 0.033 mmol) was dissolved in methanol (20 ml) containing ammonia (3.6 g) and the solution was set aside for 20 h at 22 °C; it was then evaporated to give a colourless crystalline residue (6.0 mg). This was dissolved in ethanol-pentane, filtered, and the filtrate evaporated to give 2,5-dimethyl-6-t-butylpyrimidin-4-one (12a) (4.0 mg, 67%) as a

crystalline solid. The latter was found to be identical (spectra) with an authentic sample.

General Procedure for Reactions of the 4-Acetoxyazetidin-2ones (3) and (4) in Acetic Acid-Acetonitrile Solution.—The azetidin-2-ones (3) and (4) were allowed to react in acetic acidacetonitrile (1:2, v/v; 10 ml) at 21—40 °C. After evaporation of the solvents, the products were separated by m.p.l.c. on silica gel.

Reaction of (3a). From (3a) (116 mg, 0.455 mmol), the pyrimidin-4-one (1a) (2 mg, 2%), the imide (6a) (59 mg, 51%), N-methylacetamide (9a) (10 mg, 30%), and the 1,3-oxazin-6-one (10a) (23 mg, 28%) were obtained after 8.5 days at 40 °C.

Reaction of (3b). From (3b) (154 mg, 0.550 mmol), the pyrimidin-4-one (1b) (17 mg, 14%), the azetidin-2-one (5b) (6 mg, 8%), the 1,3-oxazin-6-one (10a) (53 mg, 53%), and 2-piperidone (9b) (38 mg, 70%) were obtained after 4.5 days at 40 °C. Compound (9b) was identical (spectra) with an authentic sample.

Reaction of (4d). From (4d) (58 mg, 0.26 mmol), the azetidin-2-one (5d) (38 mg, 89%) was obtained after 41 h at 23 °C.

Reaction of (4e). From (4e) (35 mg, 0.12 mmol), the azetidin-2-one (5e) (26 mg, 94%) was obtained after 21 h at 24 °C.

Reaction of the 4-Acetoxyazetidin-2-one (3a) in $[^{2}H_{4}]$ Acetic Acid-[²H₃]Acetonitrile Solution.—The azetidin-2-one (3a) (168 mg, 0.661 mmol) was dissolved in a solution containing $[{}^{2}H_{4}]$ acetic acid (Aldrich, 99 ${}^{2}H$ atom %; 1.239 g) and $[{}^{2}H_{3}]$ acetonitrile (Aldrich, 99.5 ${}^{2}H$ atom %; 2.023 g) and the solution was set aside for 22.5 h at 21 \pm 2 °C. The reaction was routinely followed by ¹H n.m.r. spectroscopy. After evaporation of the solvent under reduced pressure, the residue was chromatographed on Sephadex LH-20 (280 g) eluting with acetone. Column chromatography gave three main fractions. Fraction 1 was the azetidin-2-one (5a) (25 mg, 19%). Fraction 2 was recovered starting material (3a) (75 mg, 44%) as crystals. Recrystallization of (3a) from ether-pentane gave colourless prisms, m.p. 92-95 °C. Fraction 3 was a mixture (59 mg) of the pyrimidin-4-one (1a) and the imide (6a). The mixture was chromatographed on silica gel (74 g), eluting with benzeneethyl acetate (1:1) and chloroform-methanol (95:5), to give (1a) (15 mg, 12%) and (6a) (40 mg, 24%).

The ¹H n.m.r. spectral analyses indicated that ²H atoms were incorporated in the 2-methyl group (93 ²H atom %) of (1a) and in the 3-methyl group (23 ²H atom %) of (5a). The incorporation of the ²H atoms in (1a) is due to catalytic ¹H/²H exchange in the presence of acid. The mechanism of ²H atom incorporation in (5a) is not clear.

The recovered 4-acetoxyazetidin-2-one was a mixture of (3a)($36 \pm 2\%$) and $4-[^{2}H_{3}]$ acetoxy-3-(1-imino-2,2-dimethylpropyl)-1,3,4-trimethylazetidin-2-one $[^{2}H_{3}]$ -(3a) ($64 \pm 2\%$), which was determined by the mass and ¹H n.m.r. spectra after treatment with methanol to exchange deuterium of the imino group for hydrogen. The recovered starting material (3a) was not a mixture of two stereoisomers.

The mass spectrometric analysis indicated that the imide was a mixture of (**6a**) ($6 \pm 2\%$) and *N*-acetyl-3-[²H₃]acetylamino-2,4,4,*N*-tetramethylpent-2-enamide [²H₃]-(**6a**) (94 ± 2%).

Reaction of the Imide $[{}^{2}H_{3}]$ -(**6a**) in Acetic Acid-Acetonitrile Solution.—The imide $[{}^{2}H_{3}]$ -(**6a**) (94 ${}^{2}H$ atom %, 40.0 mg, 0.156 mmol) was dissolved in a mixture of acetic acid (1.369 g) and acetonitrile (2.147 g) and the solution set aside for 23 h at 21 ± 2 °C. After evaporation of the solvent, the residue was chromatographed on silica gel (53 g) eluting with chloroformmethanol (95:5) to give the imide $[{}^{2}H_{3}]$ -(**6a**) (37.1 mg, 93%) as crystals. Recrystallization of $[{}^{2}H_{3}]$ -(**6a**) from benzene-pentane gave colourless prisms, m.p. 132—135 °C. The mass spectrometric analysis indicated that the fraction of (6a) and $[{}^{2}H_{3}]$ -(6a) was 5 ± 1 and 95 ± 1 %, respectively.

Thermal Rearrangement of Dewar Pyrimidinone (2a).—The Dewar isomer (2a) (84 mg, 0.43 mmol) was heated in a 25-ml round-bottomed flask without solvent under an argon atmosphere at 80 °C for 6 days. Separation of the reaction mixture by m.p.l.c. on silica gel gave the pyrimidin-4-one (1a) (46 mg, 55%), the azetidin-2-one (5a) (12 mg, 14%), and 2,2,4,*N*-tetramethyl-3-oxopentanamide (18) (8 mg, 11%). Recrystallization of the pentanamide (18) from benzene–hexane gave colourless needles, m.p. 84—86 °C; *m/z* 171 (*M*⁺); $\delta_{\rm H}(\rm CDCl_3)$ 1.17 (9 H, s, Bu'), 1.37 (3 H, d, *J* 7.0 Hz, CH₃), 2.79 (3 H, d, *J* 4.6 Hz, NCH₃), 3.99 (1 H, q, *J* 7.0 Hz, CH), and 6.46 (1 H, br, NH); $\nu_{\rm max}(\rm CHCl_3)$ 3 420, 1 690, and 1 665 cm⁻¹; $\lambda_{\rm max}(\rm MeOH)$ 291 nm (ϵ 53 dm³ mol⁻¹ cm⁻¹) (Found: C, 63.15; H, 10.15; N, 8.0. C₉H_{1.7}NO₂ requires C, 63.13; H, 10.00; N, 8.18%).

General Procedure for Thermolysis of 4-Acetoxyazetidin-2ones (3) and (4).—The azetidin-2-ones (3) and (4) were heated at 100—110 °C without solvent under an argon atmosphere for 1 h and the products were separated by m.p.l.c. on silica gel.

Thermolysis of (3a). From (3a) (83 mg, 0.33 mmol), (1a) (25 mg, 39%), (5a) (32 mg, 50%), and 2,4,4,N-tetramethyl-3-oxopentanamide (18) (1 mg, 2%) were obtained. The pentanamide (18) may be formed by the reaction of water with unchanged azetidin-2-one (3a) on silica gel column.

Thermolysis of (**3b**). From (**3b**) (103 mg, 0.368 mmol), (**1b**) (19 mg, 23%) and (**5b**) (45 mg, 55%) were obtained.

Thermolysis of (4c). From (4c) (62 mg, 0.29 mmol), (5c) (22 mg, 50_0°) was obtained.

Thermolysis of (**4d**). From (**4d**) (101 mg, 0.445 mmol), (**5d**) (72 mg, 97%) was obtained.

Kinetic Measurements of Exchange Reaction of the Acetoxy Group.—The rates of the acetoxy exchange reaction of (3a) (0.17M) in [${}^{2}H_{4}$]acetic acid (Aldrich; 99.5 ${}^{2}H$ atom %) at 20 \pm 2 °C and in a solution containing 30 mol % of [${}^{2}H_{4}$]acetic acid (Aldrich; 99 ${}^{2}H$ atom %) and 70 mol % of [${}^{2}H_{4}$]acetonitrile (Aldrich; 99.5 ${}^{2}H$ atom %) at 21 \pm 2 °C were determined by the intensity measurements of the ${}^{1}H$ n.m.r. spectra in the presence of a trace amount of tetramethylsilane. The signal and intensity of the N-methyl group were used as a reference.

The intensity of the acetoxy methyl group showed a firstorder decrease before the signals corresponding to the rearrangement products (1a), (5a), and (6a) appeared. The signals of the products were observed after *ca*. 8 h in $[{}^{2}H_{4}]$ acetic acid and after *ca*. 4 h in CD₃CO₂D-CD₃CN solution. The rate constant (k) of the acetoxy exchange reaction, estimated from the experimental data, showed that the contribution of the rearrangement reaction to the exchange reaction was almost negligible in the reaction time (*ca*. 4 h).

The estimated exchange rate constants (k) were $(1.88 \pm 0.07) \times 10^{-5} \text{ s}^{-1}$ in $[^{2}\text{H}_{4}]$ acetic acid and $(5.90 \pm 0.28) \times 10^{-5} \text{ s}^{-1}$ in CD₃CO₂D–CD₃CN solution.

The rate constants of the formation of the products in CD_3CO_2D - CD_3CN was *ca.* 1 × 10⁻⁵ s⁻¹ as estimated from the data of the product analyses.

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