The Chemistry of 4-Pyrimidinones: Acetylation and Ring-Opening Reactions [1]

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4(3*H*)-Pyrimidinone, as well as its 5-acetoxy and 5-methoxy derivatives, undergoes selective acetylation at N-1 when treated with acetic anhydride. In the presence of water, these 1-acetylpyrimidines undergo spontaneous covalent hydration at C-2 and cleavage of the 1,2-bond to give crystalline *cis*-3-acetylamino-*N*-formylacrylamides, generally in good yield. In contrast, the 6-methyl derivative of 4(3*H*)-pyrimidinone forms an equilibrium mixture of acetylated products that undergo the ring opening process to only a very limited extent, the major product (11%) being the 3-formylamino-*N*-acetylacrylamide derivative formed *via* N-3 acetylation and cleavage of the 2,3-bond.

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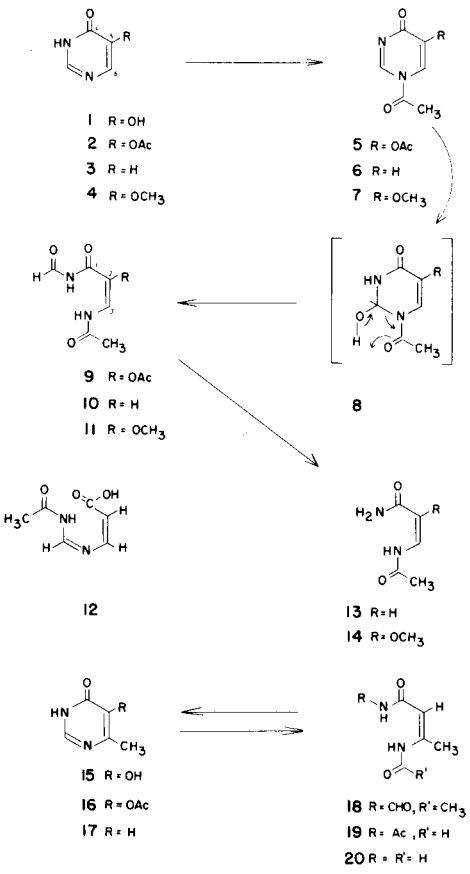
The chemistry of pyrimidines in aqueous solution quite often involves the formation of covalent hydrates as reaction intermediates [2]. In many cases, however, hydrates play a covert role since the added water is not incorporated into the structure of the final product. Thus, the bromination of 4(3*H*)pyrimidinone at C-5, which one might expect to be a straightforward pyrimidine electrophilic substitution reaction, actually involves the addition of hypobromous acid to an intermediate C-2 hydrate [3]. Similarly, hydration of 2- and 4- iminopyrimidines is an obligatory but hidden step in the Dimroth rearrangements of these substances [4]. In this paper, we report some cases where the occurrence of pyrimidine covalent hydration is more readily apparent because the water oxygen atom appears in the products in the guise of an *N*-formyl group. These examples comprise the facile hydration of 1-acetyl-4(1*H*)-pyrimidinones and their spontaneous conversion into stable acrylamide derivatives. We also show that this reaction was first observed almost eighty years ago, although the site of ring cleavage was not correctly identified at that time.

We became aware of the propensity of certain 4(3*H*)pyrimidinones to undergo the acetylation-hydration-ring opening sequence during our studies with the 5-hydroxy derivative **1**. When an aqueous solution of the mono-sodium salt of **1** was treated with an excess of acetic anhydride, a standard procedure [5] for preparing 5-acetoxypyrimidines, the product obtained was not the expected **2**, but rather the *N*-formyl acrylamide derivative **9** (Scheme 1 and Tables 1-2). Using smaller amounts of acetic anhydride, or conducting the acetylation in dry pyridine, does afford **2** in satisfactory yield, however. Since it seemed likely that **2** was an intermediate in the formation of **9**, we have examined the reaction of **2** with additional acetic anhydride, and it is clear from the nmr spectral changes which accompany the reaction that acetylation occurs at

Scheme I



N-1 but not at N-3. Thus, the H-2 and H-6 resonances of **2**, which appear essentially as singlets at δ 8.14 and 7.90 ($^4J_{2,6} < 0.5$ Hz) in dimethyl-d_6 sulfoxide solution (Table 3), are gradually replaced by new signals at δ 9.01 and 8.40 on the addition of acetic anhydride. Moreover, the new signals show the remarkable value of 2.5 Hz for the four-bond coupling constants $J_{2,6}$. Such a large coupling cons-

tant is characteristic of the *p*-quinoid-type of tautomers that result from N-1 substitution of 4-pyrimidinones [6], indicating that the product in this case is **5**. No signals suggesting N-3 acetylation were observed. The conclusion that **2** undergoes acetylation at N-1 also follows from the location of the acetylamino group in the product **9**. Both of the amide protons of **9** appear in the nmr spectrum as doublets, reflecting their respective coupling with H-3 and the formyl proton (Table 1). If the formyl and acetyl groups of **9** were transposed, as they would be if acetylation of **2** had occurred at N-3, then the formylamino NH proton would appear as a double doublet and the acetylamino NH proton as a singlet.

In the presence of water, the 1-acetyl pyrimidinone **5** must undergo rapid hydration at C-2 to give **8** (R = OAc), followed by spontaneous cleavage of the 1,2-bond, possibly

Table 1

Proton Chemical Shifts and Coupling Constants for Certain Acrylamide Derivatives

Compound	HN-----CHO	HN-----Ac	H-2	H-3	other	$J_{NH,CHO}$	$J_{3,NH}$	$J_{2,3}$
9	11.35 bd 9.14 d	10.37 bd 2.17	—	7.51 d	2.21 (OAc)	8.0	11.0	—
10	11.11 bd 9.04 d	10.70 bd 2.15	5.26 d	7.50 dd	—	8.8	11.2	8.8
11 [a]	10.96 b 9.13	10.04 bd 2.11	—	7.51 d	3.59 (OMe)	n.o	10.2	—
18 [b]	11.6 b 9.03	10.7 b 2.20	5.07	—	2.29 (Me)	n.o	—	—
19	11.30 bd 8.71 d	10.53 b 2.18	5.52	—	2.24 (Me)	9.0	—	—
13	— —	11.21 bd 2.05	5.11 d	7.19 dd	7.79 b (NH) 7.00 b (NH)	—	10.7	9.0
14	— —	10.39 b 2.11	·	7.01 d	6.47 b (NH) 5.71 b (NH) 3.64 (OMe)	—	10.2	—
20	11.84 bd 8.63 d	— —	4.92	—	7.44 b (NH) 6.98 b (NH) 2.13 (Me)	11.5	—	—

Spectra were determined in methyl-d_6 sulfoxide. All peaks are sharp singlets unless designated b (broad), d (doublet) or dd (doublet of doublets). For **18**, **19** and **20**, $J_{2,Me}$ values of ~0.8 Hz could be resolved. n.o = not observed. [a] In deuteriochloroform solution, the formyl CH proton appears as a doublet at δ 9.19 with a $J_{NH,CH}$ value of 9.9 Hz. [b] Crude Material, probable structure.

Table 2

^{13}C-Chemical shifts and Coupling Constants for Certain Acrylamide Derivatives

Compound	CHO	CO-----Me	C-1	C-2	C-3	other	$^1J_{CHO}$	$^1J_{C\text{-}2,H\text{-}2}$	$^1J_{C\text{-}3,H\text{-}3}$
9	163.5	168.9 23.1	165.2	121.5	131.3	21.1 and 170.6 (OAc)	208	—	173
10	163.1	168.8 23.0	168.2	96.0	139.4	—	205	167	176
11	163.0	167.8 23.0	166.0	131.9	118.3	57.8 (OMe)	208	—	172
19	162.2	171.2 25.0	167.7	97.0	153.2	19.5 (Me)	204	168	—
13	—	168.4 23.6	170.3	99.5	134.4	—	—	163	177
14	—	167.0 23.1	166.8	134.2	112.5	56.4 (OMe)	—	—	172
20	162.0	— —	170.2	98.3	147.5	18.5 (Me)	201	165	—

All spectra were determined in methyl-d_6 sulfoxide.

Table 2

^{13}C-Chemical shifts and Coupling Constants for Certain Acrylamide Derivatives

Compound	CHO	CO-----Me	C-1	C-2	C-3	other	$^1J_{CHO}$	$^1J_{C\text{-}2,H\text{-}2}$	$^1J_{C\text{-}3,H\text{-}3}$
9	163.5	168.9 23.1	165.2	121.5	131.3	21.1 and 170.6 (OAc)	208	—	173
10	163.1	168.8 23.0	168.2	96.0	139.4	—	205	167	176
11	163.0	167.8 23.0	166.0	131.9	118.3	57.8 (OMe)	208	—	172
19	162.2	171.2 25.0	167.7	97.0	153.2	19.5 (Me)	204	168	—
13	—	168.4 23.6	170.3	99.5	134.4	—	—	163	177
14	—	167.0 23.1	166.8	134.2	112.5	56.4 (OMe)	—	—	172
20	162.0	— —	170.2	98.3	147.5	18.5 (Me)	201	165	—

All spectra were determined in methyl-d_6 sulfoxide.

via the cyclic mechanism shown. The ring-cleavage appears to be an essentially quantitative step, as shown by the finding that addition of deuterium oxide to the solution of **5** generated in the nmr tube leads only to the formation of **9**. The short lifetime of the hydrated intermediate **8** precludes detection of its nmr signals under these conditions.

Instances where covalent hydration leads ultimately to *stable* acyclic products are uncommon in the pyrimidine area and, in order to assess the generality of the present reaction, we have examined the behaviour of the parent substance **3**, as well as some additional substituted 4(3*H*)-pyrimidinones (**4**, **15** and **17**). Of these compounds, **3** behaves in a manner exactly analogous to that of **2**, affording the *N*-formylacrylamide **10** in good yield when treated with acetic anhydride and water. Compound **3** has been known for many years, so it is not surprising that its behaviour under acetylation conditions has been examined previously by others. Thus, Bredereck and coworkers [7] reported in 1958 that **3** can be converted into a crystalline *N*-acetyl derivative, albeit of undetermined structure. Their product, which we have obtained by a somewhat simplified procedure, is clearly the N-1 acetyl compound **6** because its nmr spectrum shows the diagnostic value of 2.9 Hz for $J_{2,6}$ as described above. Further, we have found that **6** readily affords the acyclic product **10** when treated with water. An even earlier account of the acetylation of **3** appeared in a 1907 paper in which Wheeler reported that 4(3*H*)pyrimidinone formed "a peculiar acetyl derivative when the base was dissolved in acetic anhydride and evaporated to dryness on the steam bath" [8]. Wheeler recognized from the combustion analyses that ring-opening must have occurred and he suggested tentatively that the product was the *N*-acetylformamidine acrylic acid **12**, that is, the result of acetylation at N-3 and cleavage of the 3,4-bond. In fact, Wheeler's product is identical with our acrylamide derivative **10**. This compound has been further characterized by selective hydrolysis of the *N*-formyl group to afford the primary amide **13**, as shown by the nmr spectrum (Tables 1 and 2).

As with compounds **2** and **3**, acetylation of the 5-methoxy analog **4** occurs specifically at N-1, at least in an nmr experiment (Table 3), but the overall ring cleavage reaction proceeds at a somewhat sluggish rate. On a preparative scale, multiple evaporations of acetic anhydride solutions of **4** using Wheeler's steam bath technique afforded **11** in moderate amounts, although the yield is reduced somewhat by the concurrent formation of the hydrolysis product **14**.

It appears from the foregoing results with **2** and **4** that the acetylation-hydration-ring opening process may be a general reaction for 5-substituted-4(3*H*)-pyrimidinones. In contrast, the presence of a 6-substituent, as in the methyl analogs **15** and **17**, profoundly affects the course of these reactions. For example, the sodium salt of the 5-hydroxy-6-methylpyrimidine **15** affords only the 5-acetyl derivative **16** under conditions where the 6-unsubstituted compound **2** is converted completely into the open chain product **9**. Similarly, 6-methyl-4(3*H*)-pyrimidinone (**17**) is resistant to ring opening. In this case, acetylation in dimethyl-d_6 sulfoxide is more complex than the earlier examples in that the reaction does not proceed to completion, and that the first formed product equilibrates with a second (Table 3). While the two sets of peaks observed cannot easily be assigned to particular acetylated products because of the absence of H-6 protons, it is reasonable to suppose that the steric effects of the 6-methyl group would encourage the formation of the alternative N-3 acetyl product. It is also possible that acetylation occurs at O-4 under these conditions. Addition of deuterium oxide to the equilibrium mixture in methyl-d_6 sulfoxide simply promotes hydrolysis to give **17**, but the more vigorous conditions of acetic anhydride evaporating on the steam bath result in the formation of small amounts of two new compounds that can be separated from **17** by preparative tlc. The minor product, which was isolated in crude form in only 0.7% yield, even allowing for a 40% recovery of starting material **17**, appears to be the *N*-formylacrylamide **18**, analogous to the products **9-11** obtained *via* N-1 acetylation of the pyrimidines **2-4**. This tentative assignment is supported by the uv spectrum of **18** which, on the addition of base, changes in a manner consistent with hydrolysis of the formamide group. Similar uv-spectral shifts accompany the formation of the amides **13** and **14** from the formamides **10** and **11**, respectively. The major product, which was obtained in 11% yield, is also an acyclic compound is indicated by its ^{1}H-and ^{13}C-nmr spectra (Tables 1 and 2) and it is assigned the *N*-acetylacrylamide structure **19**. This isomer would be formed from the N-3 acetyl derivative of **17** after hydration at C-2 and cleavage of the 2,3-bond. Not unexpectedly, **19** is markedly unstable under hydrolytic conditions, and the fact that the uv-spectral shifts that occur on the addition of sodium hydroxide are more complex than those seen with **18** is consistent with the transposed locations of the N-acyl groups in the two isomers. More direct evidence for the relative location of the *N*-acyl groups of **19** comes from its behaviour under neutral aqueous conditions. Thus, **19** undergoes partial hydrolysis in hot water to give an intermediate product with uv- and nmr-spectral characteristics (Table 1 and 2) indicative of the 3-formylamino acrylamide structure **20**. On prolonged heating, **20** cyclizes to give 6-methyl-4(3*H*)-pyrimidinone (**17**), thereby effecting an overall reversal of the acetylation-hydration-ring opening process that may account, in part, for the modest yield of **19** obtained from **17**.

EXPERIMENTAL

General Procedures.

Melting points were determined on a Thomas-Hoover apparatus (capillary method) and are uncorrected. Ultraviolet spectra were measured on Gilford Response and Unicam SP-800 spectrophotometers. Thin-layer chromagraphy was performed on 250 μm GF254 plates (2.8 × 8 cm, Analtech, Inc.), and separated materials were detected with ultraviolet light and/or by spraying with sulfuric acid in ethanol (10% v/v) followed by charring. Preparative separations were effected on 1,000 μm (20 × 20 cm) plates. Nuclear magnetic resonance spectra were determined with JEOL FX90Q and PFT-100 instruments. ^{1}H-chemical shifts were measured relative to internal tetramethylsilane (TMS); ^{13}C-chemical shifts were measured relative to the solvent absorbance and then corrected to the TMS scale. Microanalyses were performed by M.H.W. Laboratories, Phoenix, Arizona. Except where stated, all evaporations were carried out *in vacuo*.

5-Acetoxy-4(3*H*)-pyrimidinone (**2**).

A solution of 5-hydroxy-4(3*H*)-pyrimidinone monohydrate (**1**, 130 mg, 1 mmole) [9] in pyridine (2 ml) containing acetic anhydride (0.25 ml, about 2.6 mmoles) was stored at room temperature for 1 hour and then evaporated to dryness. Crystallization of the syrupy residue from hot ethanol afforded 125 mg (81%) of **2**, mp 177-180° (partially melts at 158° and resolidifies), uv (water): λ max 225.5 and 262 nm; λ min 202 and 247 nm; ^{1}H nmr (DMSO-d_6): 8.14 (s, H-2), 7.90 (s, H-6), 2.26 (s, OAc); ^{13}C nmr: δ 167.7 (Ac carbonyl), 156.6 (C-4), 147.8 (C-2), 143.8 (C-6), 138.7 (C-5), 20.1 (Ac methyl), $J_{C\text{-}2,H\text{-}6}$ = 12, $J_{C\text{-}2,H\text{-}2}$ = 206, $J_{C\text{-}6,H\text{-}6}$ = 181 Hz.

Anal. Calcd. for $C_6H_6N_2O_3$: C, 46.76; H, 3.92; N, 18.18. Found: C, 46.72; H, 4.13; N, 18.10.

3-Acetylamino-2-acetoxy-*N*-formylacrylamide (**9**).

The 5-hydroxypyrimidine **1** (260 mg of the monohydrate, 2 mmoles) was suspended in water (2 ml) and converted into the soluble sodium salt by the addition of 2 ml of 1*N* sodium hydroxide solution (2 mmol). Acetic anhydride (0.5 ml, ~ 5.3 mmoles) was added to the rapidly stirred solution. Within seconds, the flask contents had solidified with a mass of needle-like white crystals. The product was collected by filtration, carefully washed with ice-cold water and dried in air to afford 255 mg (60%) of pure material. The product can be recrystallized from boiling water, mp 162-165°; uv (water): λ max 218.5 and 290.5 nm (290.5/218.5 = 4.3), λ min 247 nm.

Anal. Calcd. for $C_8H_{10}N_2O_5$: C, 44.86; H, 4.71; N, 13.08. Found: C, 45.02; H, 4.74; N, 13.18.

When only *one* equivalent of acetic anhydride (added in four portions) is used in the above procedure, the 5-acetoxypyrimidine **2** can be obtained in ~ 70% yield by extraction of the reaction mixture with ethyl acetate and concentration of the organic phase.

1-Acetyl-4(1*H*)-pyrimidinone (**6**).

A stirred suspension of 4(3*H*)-pyrimidinone (**3**, 1.00 g) in hot acetic anhydride (7 ml) was protected from moisture and briefly heated to reflux. The resulting clear solution was then allowed to cool to room temperature and ether (30 ml) was added. The crystalline product, which appeared almost immediately, was collected and washed with generous amounts of cold ether. The yield of **6**, (0.85 g, 59%) compares favorably with that obtained (~ 40%) after the much more elaborate workup procedure described in reference [7]. Compound **6** shows little deterioration after a period of several months when stored in a tightly-stoppered container, but it reacts rapidly with water to form **10**, and with methanol to form **3**. Pure **6** shows the following properties, mp 116-118° (lit [7] 117-120°); ^{1}H nmr (DMSO-d_6): δ 8.99 (dd, H-2), 8.26 (dd, H-6), 6.12 (dd, H-5), 2.64 (s, NAc), $^5J_{2,5}$ = 0.6, $^4J_{2,6}$ = 2.9, $^3J_{5,6}$ = 8.1 Hz, (these values differ slightly from those in Table 3, presumably because of the absence of acetic acid and acetic anhydride from the solvent); ^{13}C nmr (deuteriochloroform): δ 168.6 and 166.5 (C-4 and Ac carbonyl), 148.2 (C-2), 134.6 (C-6), 112.4 (C-5) and 21.6 (Ac methyl); uv (acetonitrile): λ max 264 nm (sh at 260, and 271), λ min 226 nm [10].

cis-3-Acetylamino-*N*-formylacrylamide (**10**).

Method 1.

A solution of 4(3*H*)-pyrimidinone (**3**, 330 mg) in acetic anhydride (5 ml) was evaporated to dryness on a steam bath at atmospheric pressure as outlined by Wheeler [8]. Evaporation was complete within 30 minutes when a shallow vessel such as a Petri dish was used and crystalline product was apparent within 15 minutes. Recrystallization of the residue from 5 ml of hot water afforded 337 mg of pure material (63%, single spot in chloroform/methanol, 9:1, v/v) that showed the unusual melting behaviour described in the original paper [8], *i.e.*, melting at 175° to give a clear oil that resolidifies on holding at 180°, finally remelting with effervescence at 210° [12]; uv (water): λ max 286 nm, λ min 245 nm.

Anal. Calcd. for $C_6H_8N_2O_3$: C, 46.15; H, 5.16; N, 17.94. Found: C, 46.39; H, 5.29; N, 18.18.

Method 2.

Acetic anhydride (0.5 ml) was added to a solution of 4(3*H*)-pyrimidinone **3** (192 mg, 2 mmoles) in 4 ml of 0.05 *M* sodium hydroxide. The crystalline solid that appeared within a few minutes was collected and washed with cold water to afford 220 mg (70%) of **10**, identical (mp, uv, nmr) with the material prepared according to method **1**.

cis-3-Acetylaminoacrylamide (**13**).

Sodium hydroxide (1 ml of 1 *N* solution, 1 mmole) was added to a solution of *cis*-3-acetylamino-*N*-formylacrylamide (**10**, 160 mg, 1 mmole) in water (3 ml). After about 1 hour, when the shift of the uv absorption maximum from 286 nm to 264 nm was complete, the reaction mixture was treated with an excess of Dowex 50 (H^+). The filtrate and resin washings were evaporated to dryness and the residue was recrystallized from hot water, affording 120 mg (94%) of **13** in two crops, mp 63-65°, uv (water): λ max 264 nm, λ min 220 nm.

Anal. Calcd. for $C_5H_8N_2O_2$: C, 46.87; H, 6.29; N, 21.86. Found: C, 46.75; H, 6.49; N, 21.71.

3-Acetylamino-2-methoxy-*N*-formylacrylamide (**11**) and 3-Acetylamino-2-methoxyacrylamide (**14**).

A solution of **4** (126 mg, 1 mmole) [9] in acetic anhydride (5 ml) was evaporated to dryness on a steam bath as described for the preparation of **10**. Fresh acetic anhydride (5 ml) was added and evaporation was continued. This process was repeated for a total of six evaporation cycles. The final residue was dissolved in methanol and subjected to preparative tlc using chloroform-methanol (9:1, v/v) as the developing agent. Removal of the zone at Rf 0.67 and extraction with chloroform afforded 59 mg (37%) of **11**, mp 130-133°; uv (water): λ max 305 nm, λ min 252 nm.

Anal. Calcd. for $C_7H_{10}N_2O_4$: C, 45.16; H, 5.41; N, 15.05. Found: C, 44.88; H, 5.28; N, 15.00.

Extraction of the slower moving band (Rf 0.49) with methanol afforded 25 mg (19%) of the primary amide (**14**, mp 80-81°, with softening at 75°; uv (water): λ max 276 nm, λ min 238 nm.

Anal. Calcd. for $C_6H_{10}N_2O_3$: C, 45.57; H, 6.37; N, 17.51. Found: C, 45.31; H, 6.29; N, 17.42.

The percentage yields of both **11** and **14** are adjusted to reflect the recovery of 20 mg of starting material **4**.

5-Acetoxy-6-methyl-4(3*H*)-pyrimidinone (**16**).

The sodium salt of 5-hydroxy-6-methyl-4(3*H*)-pyrimidinone **15** [13] was treated with acetic anhydride as described above for the preparation of **7**. Tlc (chloroform/methanol, 9:1, v/v) showed that the appearance of a faster moving product was complete within a few minutes. Extraction of the reaction mixture with ethyl acetate and conventional workup then afforded **16**, which crystallizes from ethyl acetate-hexane in shining plates. On a 1 mmole reaction scale, two crops of **16** (140 mg, 83%) were obtained, mp 150-152°; ^{1}H nmr (DMSO-d_6): δ 12.80 (bs, NH), 8.03 (s, H-2), 2.27 (s, OAc), 2.11 (s, Me); ^{13}C nmr: δ 167.5 (Ac carbonyl), 156.2 (C-4), 153.1 (C-6), 146.0 (C-2), 135.3 (C-5), 20.00 (Me) and 17.6 (Ac methyl); uv (water): λ max 230 and 258 nm, λ min 208 and 244 nm.

Anal. Calcd. for $C_7H_8N_2O_3$: C, 50.00; H, 4.80; N, 16.66. Found: C, 50.03; H, 4.80; N, 16.78.

3-Acetylamino-3-methyl-*N*-formylacrylamide (**18**) and 3-Formylamino-3-methyl-*N*-acetylacrylamide (**19**).

A 500 mg sample of **17** [12] was suspended in acetic anhydride (5 ml) and subjected to five evaporation cycles as described above for the preparation of **11**. The final residue was fractionated by preparative tlc (chloroform-methanol, 9:1 v/v) and the major bands were extracted with chloroform-methanol mixtures. Evaporation then afforded the following products: i) starting material **17** (200 mg, 40% recovery) was obtained from the Rf 0.2 band and identified by uv and nmr spectroscopy; ii) a crude sample (3 mg, 0.7%) of material tentatively identified as the 3-acetylamino derivative **18** was obtained from the Rf 0.5 band; uv (water): λ max 296 nm, λ min 245 nm. On addition of sodium hydroxide solution, the absorption maximum shifts smoothly to 270 nm, reflecting hydrolysis of the *N*-formyl group; iii) the 3-formylamino derivative **19** (50 mg, 11%) was obtained from the Rf 0.4 band, mp 157-159°, uv (water) λ max 287 nm, λ min 241 nm. On addition of sodium hydroxide (to *p*H ~ 10) the absorption maximum of **19** gradually shifts to 303 nm; at increased *p*H values (~ 14), this peak is slowly replaced, in turn, by absorption at 268 nm, passing through an isosbestic point at 275 nm. The products of these reactions have not been investigated.

Anal. Calcd. for $C_5H_{10}N_2O_3$: C, 49.41; H, 5.92; N, 16.46. Found: C, 49.37; H, 5.75; N, 16.33.

Heating an aqueous solution of **19** for 3-4 hours on a steam bath results in the formation of small amounts of intermediate **20**, Rf (chloroform-methanol, 9:1 v/v) = 0.3; uv (water): λ max 265.5, λ min 221.5 nm, together with **17**. The sample of **20** used for nmr spectroscopy (Tables 1 and 2) was obtained by preparative tlc. On further heating, intermediate **20** is completely converted into **17**, which was identified by comparison (uv, nmr) of a sample isolated by preparative tlc with authentic material.

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[10] The uv spectrum reported in reference [7] for **6** was determined in methanol (λ max 225 and 263 nm, ε 6010 and 12050). Since **6** efficiently acetylates methanol, it is likely that the previously published spectrum reflects a substantial contribution from the parent compound **3**. The utility of **6** as an acetylating agent for amines and alcohols is being studied.

[11] The complex melting point of **10** is apparently not the result of a reaction since the nmr spectra of resolidified and unmelted material are identical.

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