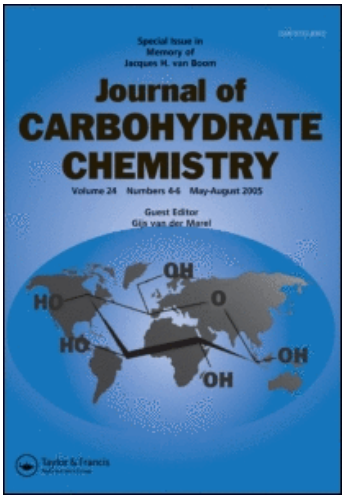

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Six-Membered Nitrogen Heterocycles from Xylaramide and Ribaramide

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SIX-MEMBERED NITROGEN HETEROCYCLES FROM XYLARAMIDE AND RIBARAMIDE[1,2]

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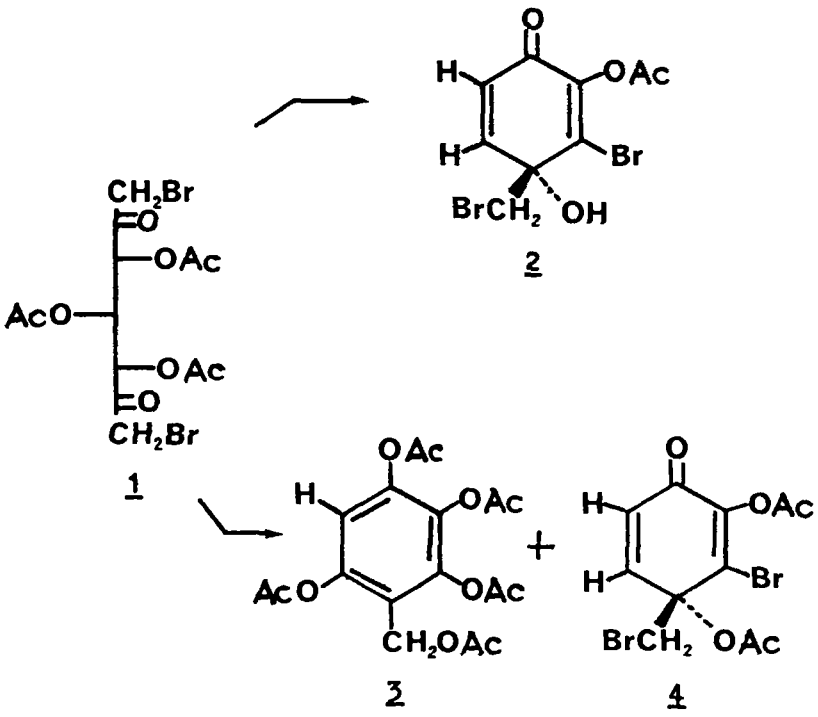
ABSTRACT

N,N'-Diacetyl-tri-O-acetylxylaramide (8) and N,N'-diacetyl-tri-O-acetylribaramide (20) were directly converted to the nitrogen heterocycle 6-acetamido-2,6-diacetyloxy-aza-1,4-cyclohexadien-3-one (9) with sodium acetate in acetic anhydride. Treatment of tri-O-acetylxylaramide (7) or tri-O-acetylribaramide (19) with the same solvent-base combination gave the highly crystalline 2,3,5,6-tetraacetyloxypyridine (30) as the principal product. Mechanistic considerations for the formation of these nitrogen heterocycles are presented.

INTRODUCTION

We recently reported that mild base treatment of 3,4,5-tri-O-acetyl-1,7-dibromo- and dichloro-1,7-dideoxy-xylo-2,6-heptodiuloses produced some unusual unsaturated six-membered carbocyclic compounds.[3] For example, treatment of an acetone solution of the dibromoheptodiulose 1 with anhydrous sodium acetate gave a high yield of the 2,5-cyclohexadien-1-one 2. When an acetic anhydride

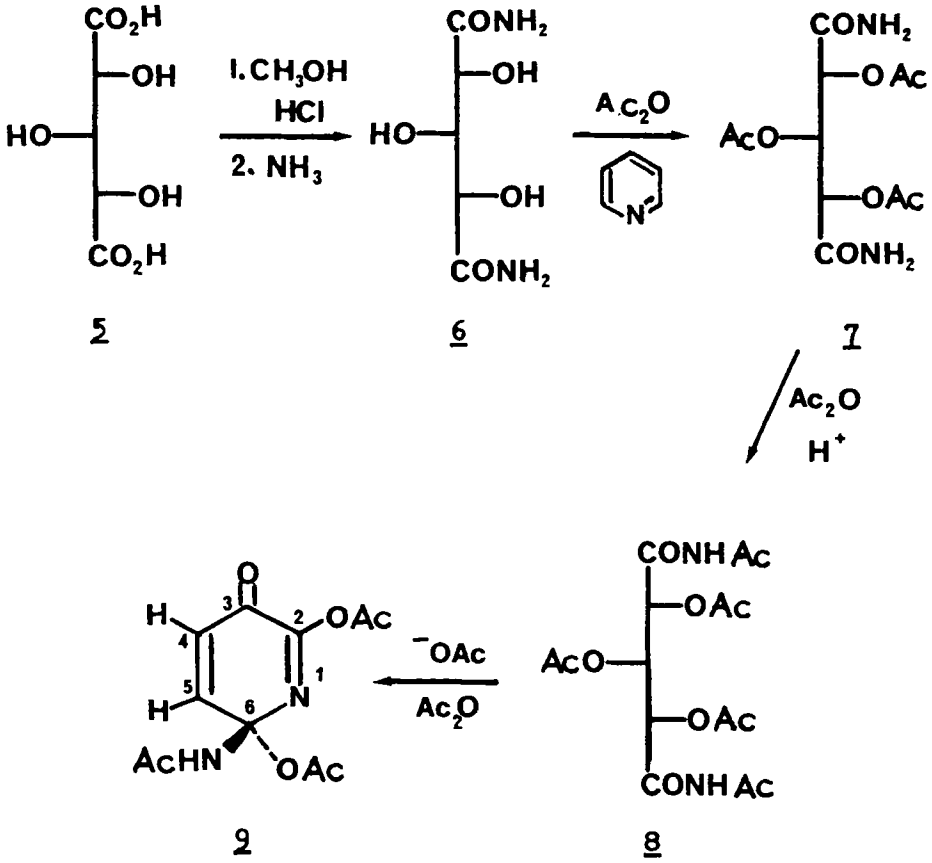


solution of 1 was stirred with the same base, an aromatic polyol acetate (3) and the acetylated 2,5-cyclohexadien-1-one 4 were formed. As a result of these studies we decided to determine if branched nitrogen heterocycles might be generated by base catalyzed cyclization of similarily derivatized pentaramides. This paper describes the results of that investigation.

RESULTS AND DISCUSSION

The first compound chosen for the cyclization studies was N,N'-diacetyl-tri-O-acetylxylaramide (8). It was anticipated that the imide protons of 8 should be sufficiently acidic to be removed with a weak base, thus promoting a ring-forming aldol condensation. Cyclization of 8 to an azacyclohexanone with

SCHEME I



5 6 7 8 9

the acetyloxy functions in the spacially preferred equatorial positions would result from the xylo configuration of the precursor diimide. The synthesis of 8 from xylaric acid (5) is outlined in Scheme 1.[4]

Xylaric acid was converted to crystalline xylaramide (6) by way of ammonolysis of a crude mixture of xylaric acid dimethyl ester and methyl ester lactone with methanolic ammonia.

Acetylation of xylaramide with acetic anhydride in pyridine gave tri-O-acetylxylaramide (7) which was then converted to the desired pentaacetyl compound 8 using acetic anhydride and an acid catalyst.

The solvent-base combination chosen for the cyclization studies was acetic anhydride-sodium acetate. Crystalline 8 was stirred with this solvent-base pair at several temperatures and the course of each reaction monitored by ^1H NMR. The signals from the backbone protons of 8 were downfield and well removed from the signals due to the protons of the solvent and base employed. Changes in the ^1H NMR spectrum of the reaction mixture were monitored at reaction bath temperatures of 55, 80 and 100 °C. In each experiment the same spectral changes were observed, but occurred at different rates. The results from an 80 °C run are given in Fig. 1.

The spectrum of the backbone protons of 8 in the reaction medium is composed of a simple doublet (H-2, H-4) and triplet (H-3). During the early stages of the reaction two doublets (H_a and H_b) and a singlet (H_c), all downfield to the signals from 8, began to develope. During most of the reaction the relative intensity of these product signals remained reasonably constant. In the late stages of the reaction (3.5-5 hours) the H_c singlet disappeared and a new upfield singlet (H_d) began to emerge, but never became very large.

The principal product from the reaction was isolated in crystalline form (53%) and identified as the substituted 3-(6H)pyridinone 9. The ^1H NMR spectrum of 9 showed the pair of doublets already mentioned plus well resolved signals from the acetamido N-H and methyl protons, and the two singlets from the acetyloxy functions. Literature references to the 3-(6H)-pyridinone (pyridone) ring system are rare, although quantum mechanical properties have been reported for the parent compound[7] and a 6-imino derivative.[8] It has been shown that 3-hydroxypyridines,

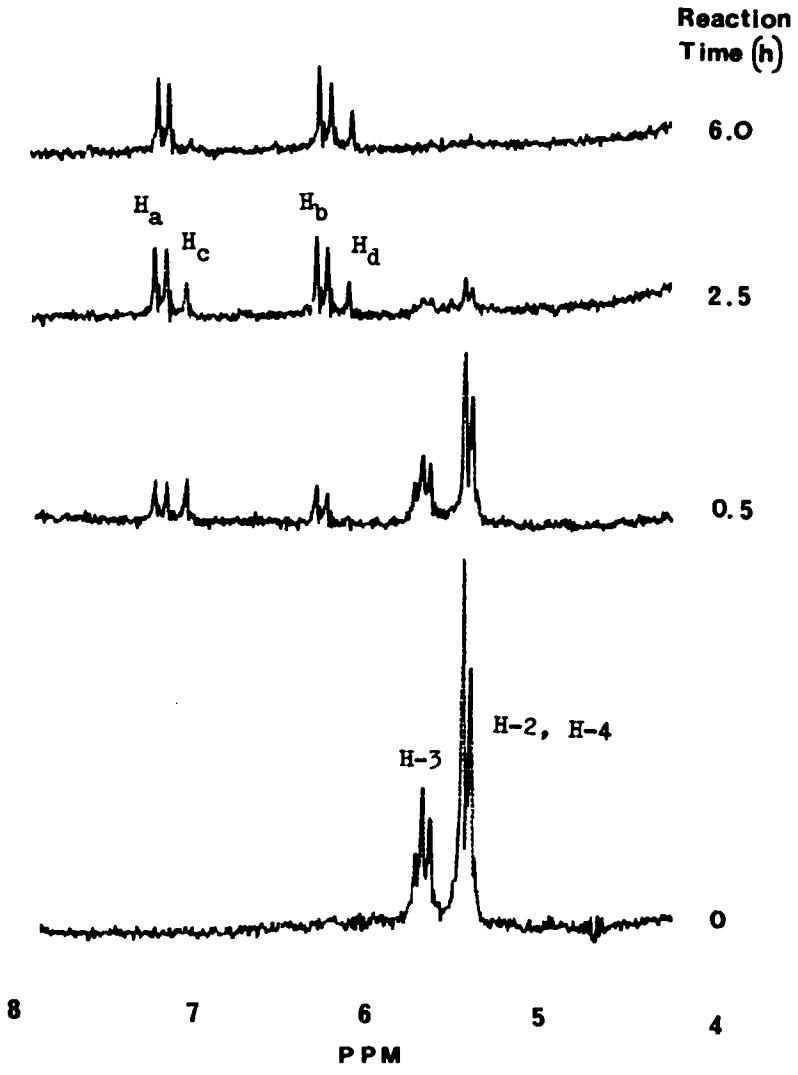


Fig. 1. 90 MHz ^1H NMR spectra (nonacetyl region) showing changes in an 80 °C sodium acetate-acetic anhydride reaction mixture during the conversion of 8 to 9: H-2, H-3 and H-4 from 8; H_a and H_b correspond to H-5 and H-4 of 9; H_c assigned to H-4 of 12a; H_d is unassigned.

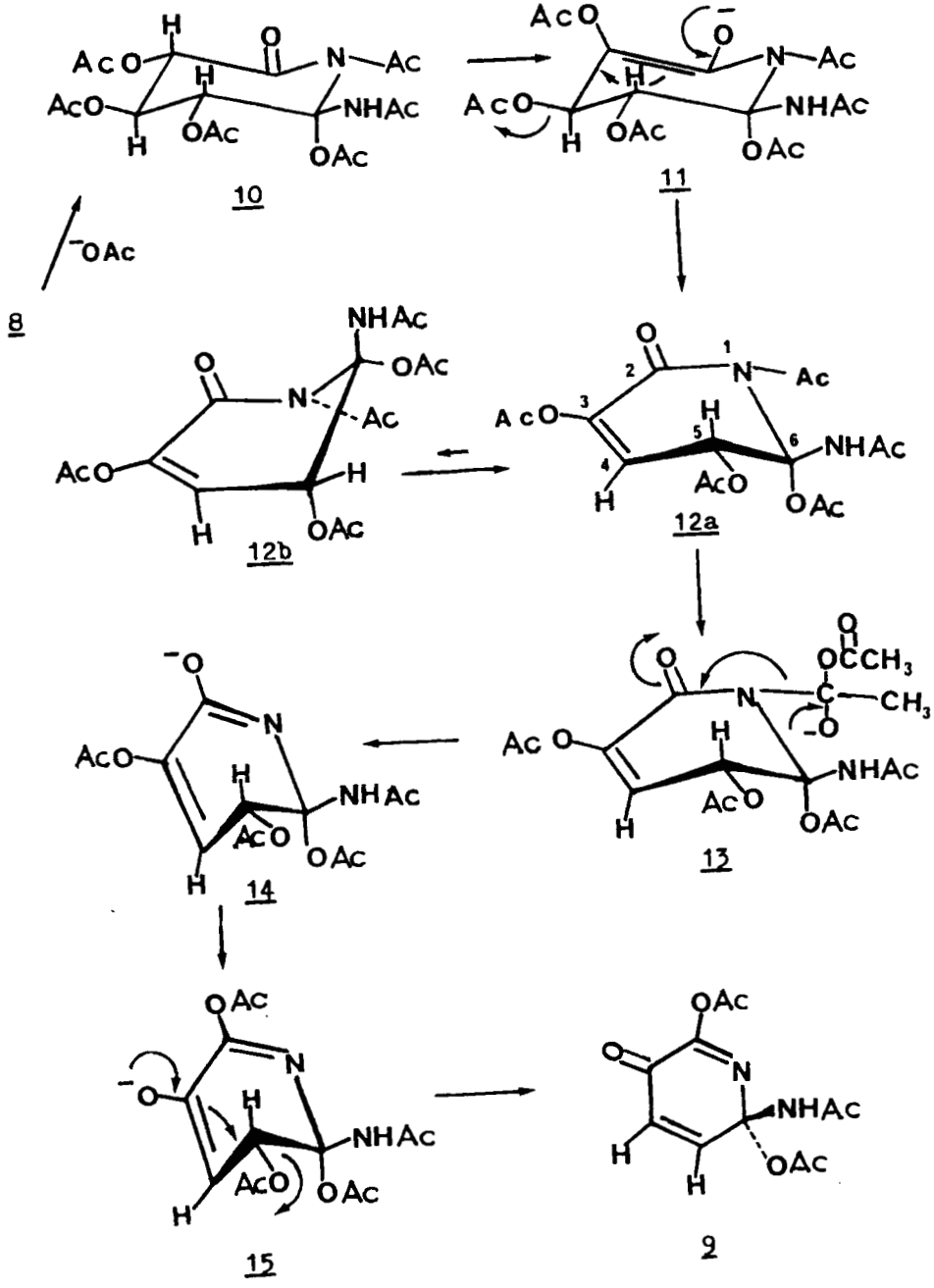
enol forms of 3-(6H)pyridinones, can be produced by direct reaction of a pentose or hexose with ammonium salts. [9,10] However, as far as we are aware, an aldol type cyclization of a carbohydrate acyclic diimide to a pyridine derivative has not been previously reported.

A possible mechanism for the conversion of 8 to the heterocycle 9 is shown in Scheme 2. Base catalyzed cyclization of 8 under acetylating conditions produces the azacyclohexanone derivative 10. The terminal nitrogen enolate that cyclizes to 10 is isoelectronic with the carbanion-enolate pair that renders the carbocyclic cross-conjugated system found in 2. Formation of the enolate 11 is followed by a 1,4-elimination of acetate to yield the azacyclohexenone derivative 12a. It is the olefinic proton of 12a that may give the farthest downfield singlet (H_c) observed in the ^1H NMR monitored experiment (Fig. 1). Intermediate 12a is gradually N-deacetylated leading to 15 after subsequent enolization and acetyl migration steps. A final 1,4-elimination of acetate yields the observed product 9.

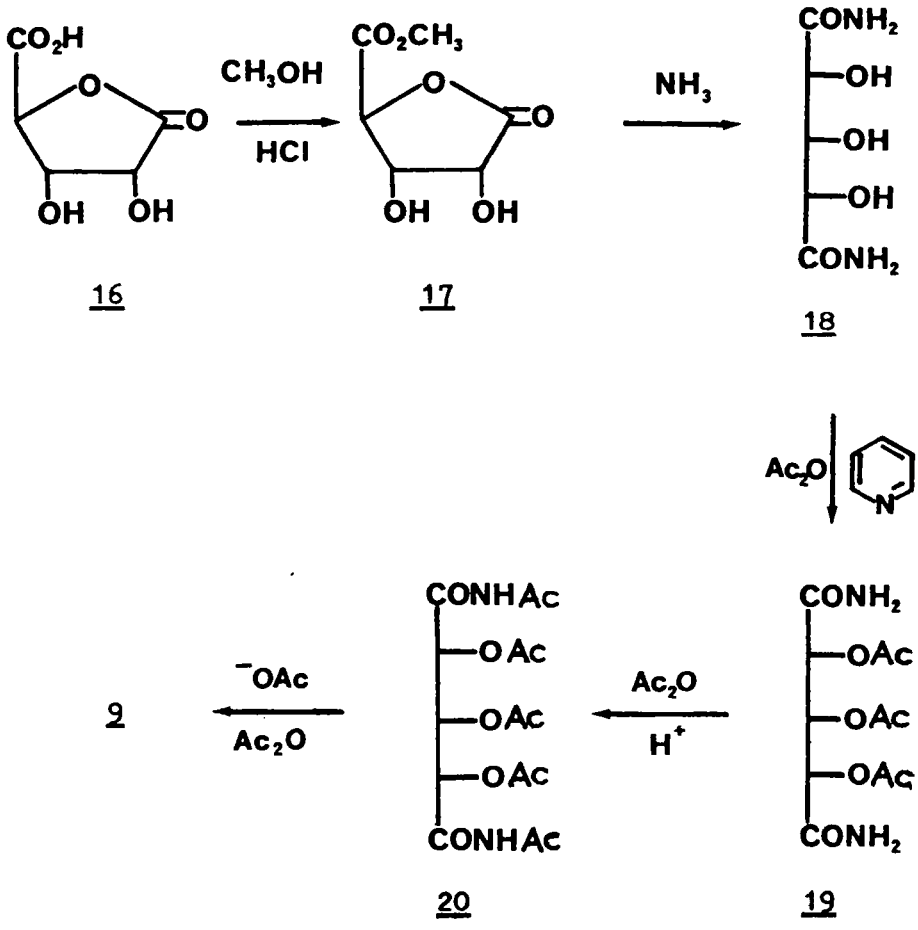
Examination of a molecular model of 12a shows an H-4, H-5 dihedral angle close to 90°, corresponding to a coupling constant of 0-1 Hz. The H-4, H-5 dihedral angle of the half-chain conformer 12b is 45° or less, corresponding to a coupling constant of several Hertz. It may be that the instability of 12b, compared to 12a, is due to the pseudo diaxial interactions between the N-acetyl and C-4 acetoxy groups.

Sodium acetate-acetic anhydride treatment of N,N'-diacetyl-tri-O-acetylribaramide (20) also yielded the 3-(6H)pyridinone 9. The method of preparation of 20 (Scheme 3) was the same as that described for the preparation of 8 but originated with ribaro-1,4-lactone (16).[11,12] Methanolic hydrogen chloride treatment of 16 gave crystalline methyl ribaro-1,4-lactone (17), which was converted to 20 after sequential ammonolysis and acetylation steps.

SCHEME 2



SCHEME 3



The conversion of 20 to 9 was slower then that from the isomeric xylaramide derivative 8, but the same mechanism of product formation can be envisioned. This contention is based on the similarity in the ^1H NMR spectra obtained when monitoring the two reactions. The results from a ^1H NMR monitored 80 °C conversion of 20 to 9 are shown in Fig. 2. Whereas the conversion of 8 to 9

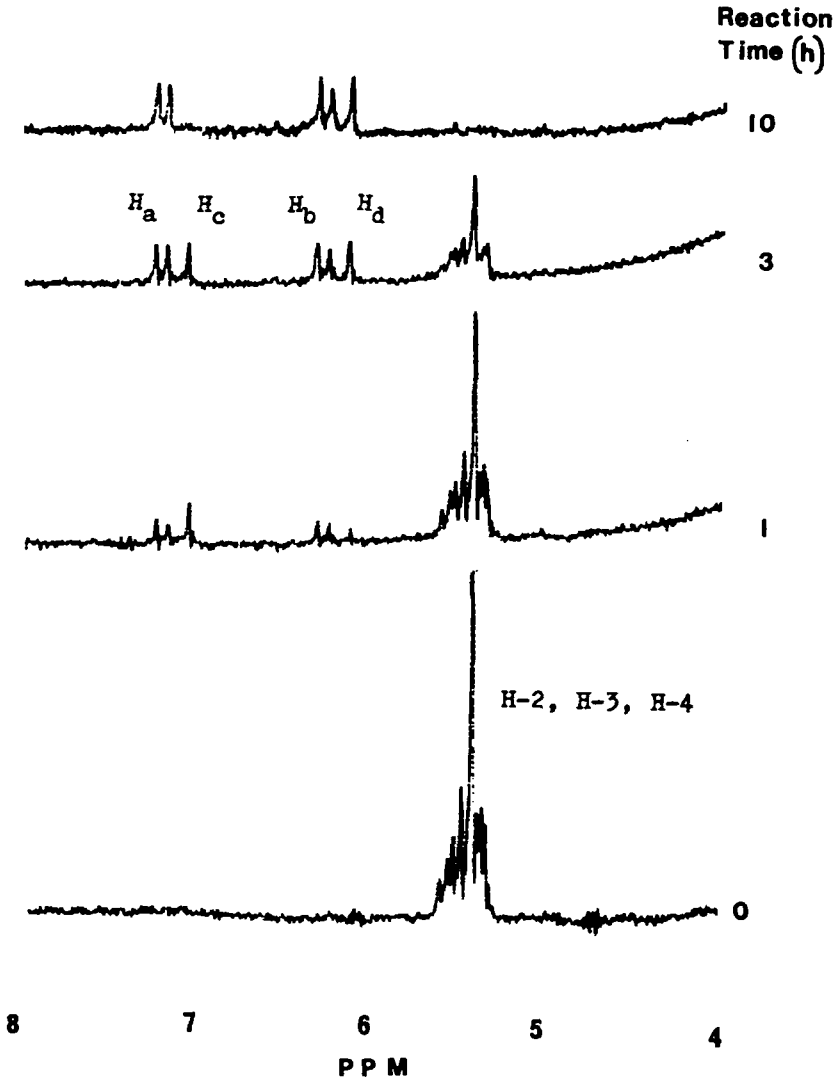
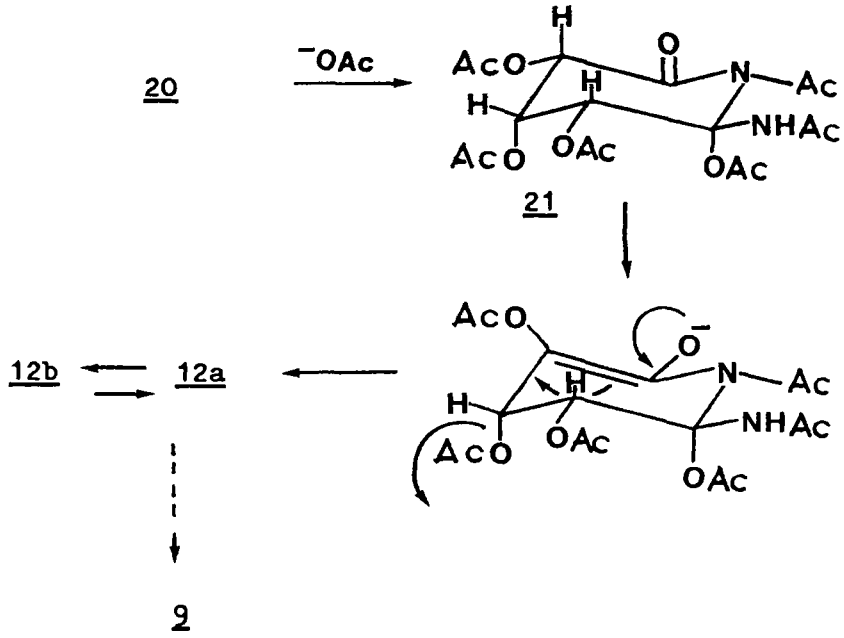


Fig. 2. 90 MHz ^1H NMR spectra (nonacetyl region) showing changes in an 80 °C sodium acetate-acetic anhydride reaction mixture during the conversion of 20 to 9: H-2, H-3, and H-4 from 20; H_a and H_b correspond to H-5 and H-4 of 9; H_c assigned to H-4 of 12a; H_d is unassigned.

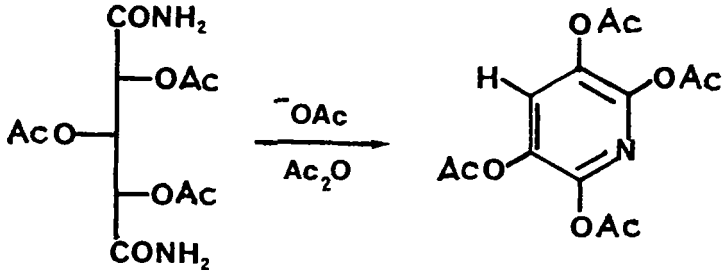
SCHEME 4



is complete in six hours (Fig. 1) it takes about ten hours under the same reaction conditions for conversion from 20 to 9 to be completed. These results suggest that the azacyclohexanone 21 (Scheme 4) with an axial C-4 acetoxy group, is formed with greater difficulty than its C-4 equatorial counterpart, 10 (Scheme 2). While the major product in both reactions is 9, more of the unidentified product (corresponding to the H_d signal) is formed from 20 than from 8.

In our early cyclization studies with 20 we noted that it produced a small amount of a second crystalline product, the aromatic heterocycle 2,3,5,6-tetraacetyloxypyridine (30). We eventually determined that the sample of 20 we were using was contaminated with a small amount of tri-O-acetylribaramide (19) and that this latter compound was the source of the acetylated

SCHEME 5



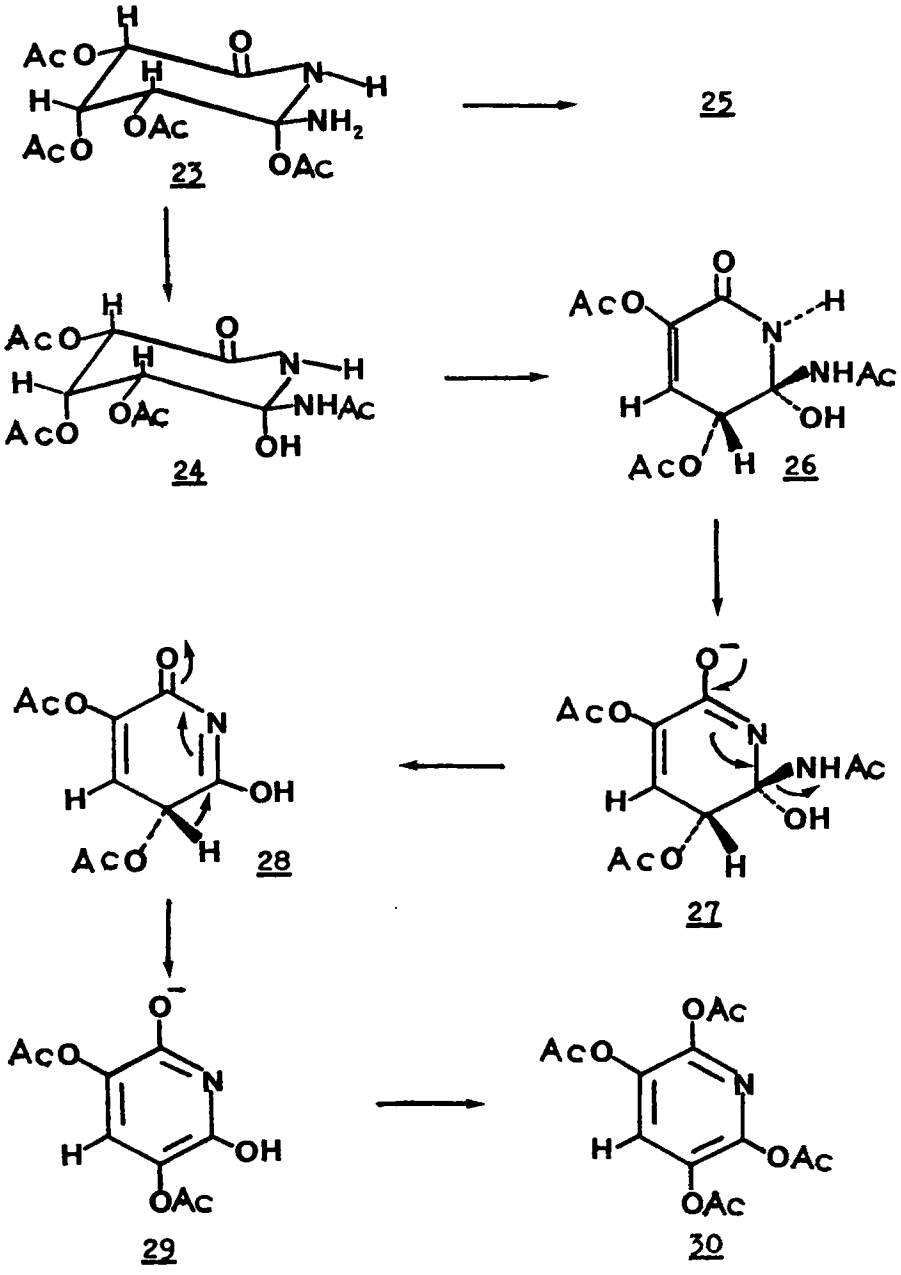
7 30

pyridine. In a controlled experiment (Scheme 5) treatment of tri-O-acetylxylaramide (7) with sodium acetate-acetic anhydride at 100 °C for seven hours gave symmetrical 30 in a 40% yield. Fortuitously, white crystalline 30 was isolated from the dark brown reaction mixture by simple crystallization. In a ^1H NMR monitored experiment (Fig. 3) tri-O-acetylribaramide (19) was converted to 30 in a similar fashion.

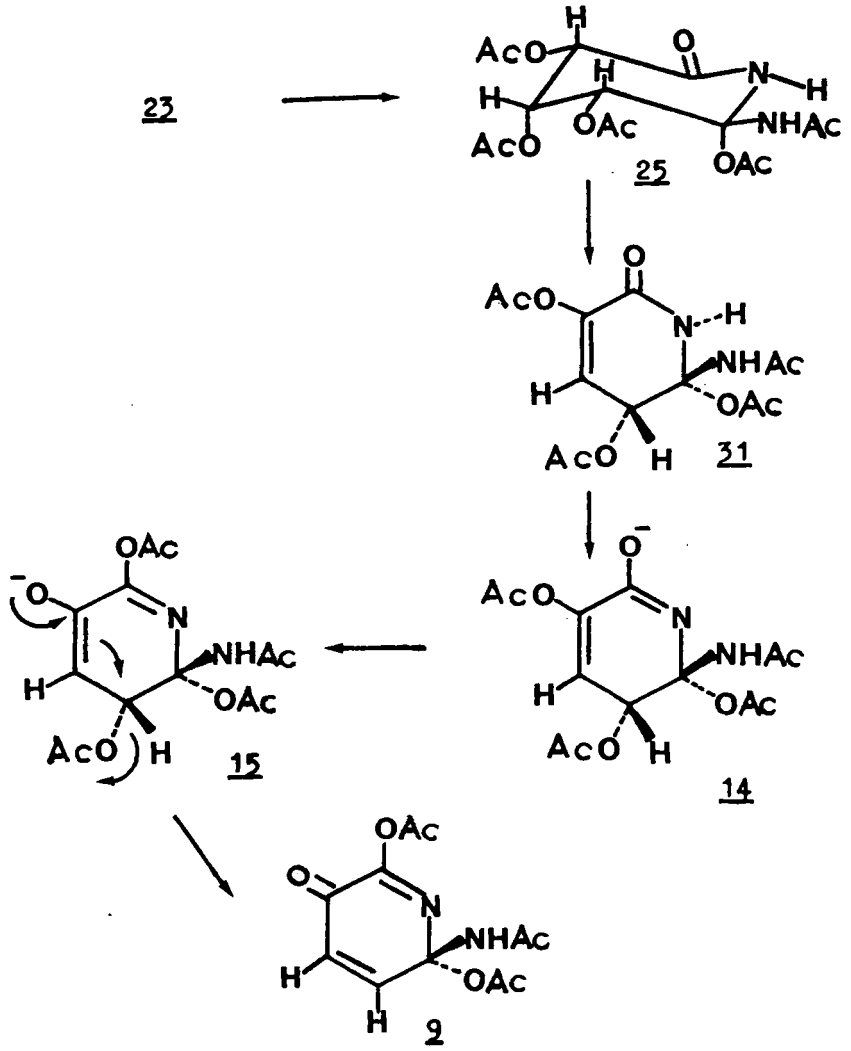
A possible mechanistic sequence for the conversion of tri-O-acetylribaramide (19) (or tri-O-acetylxylaramide) is shown in Scheme 6. Initial cyclization of 19, followed by acetylation produces the aminoazacyclohexanone derivative 23. O to N acetyl migration, enolization, then 1,4-elimation of acetate yields the acetamidoazacyclohexenone (26). Loss of the acetamido group may then occur from the enolate 27 by a 1,4-elimination. It can also be argued that elimination of the exocyclic nitrogen occurs after the acetamido group is N-acetylated, with the diacetylamide anion being a better leaving group than the acetamide anion. Base induced aromatization of 28, then acetylation of the anion 29 would yield the product, 30.

As shown in Scheme 7, the primary amine function of 23 might also be directly acetylated giving the geminal acetamido-

SCHEME 6



SCHEME 7



acetyloxy derivative 25. Intermediate 25 may in some fashion be converted to 30 or more likely to the previously discussed cross-conjugated heterocycle 9. Enolization of 25 between C-2 and C-3 (Scheme 7) followed by 1,4-elimination of acetate leads to 31.

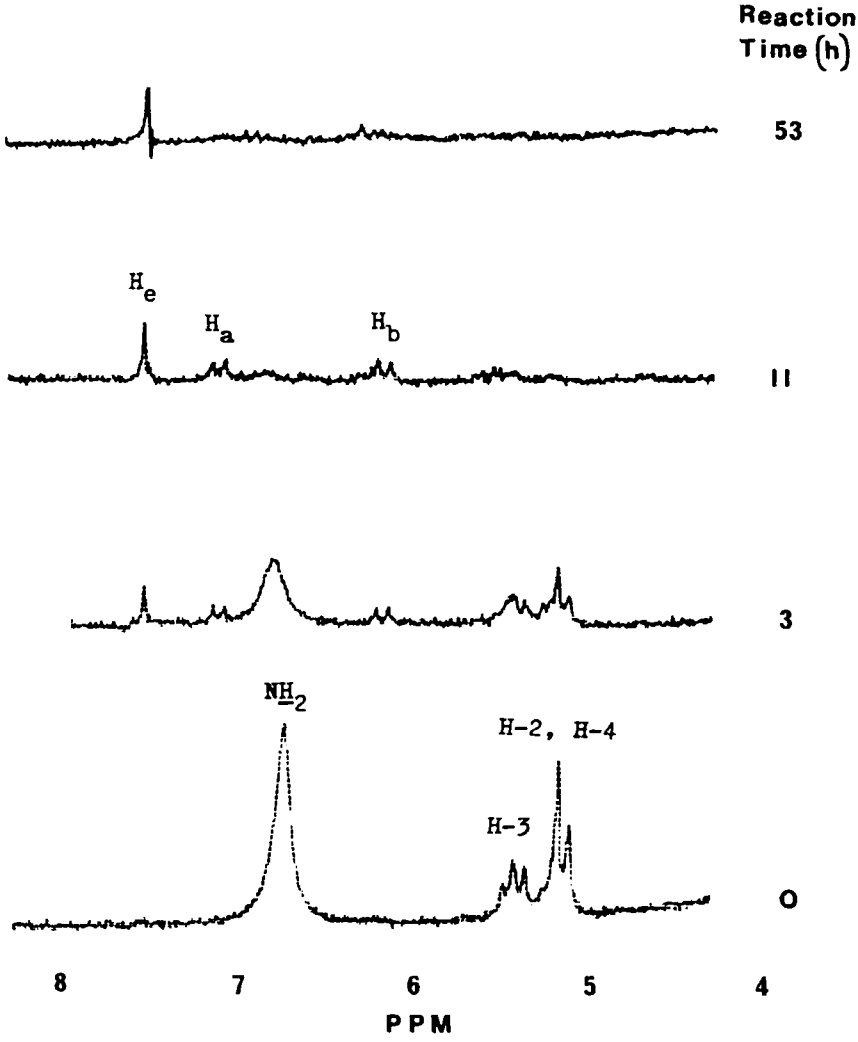


Fig. 3 90 MHz ^1H NMR spectra (nonacetyl region) showing changes in an 100 °C sodium acetate-acetic anhydride reaction mixture during the conversion of 19 to 30: H-2, H-3, H-4 and NH_2 of 19; H_a and H_b assigned to H-5 and H-4 of 9, H_e corresponds to H-4 of 30.

The enolate of 31 is 14, an anion postulated as a precursor of 9 (Scheme 2).

^1H NMR spectroscopic evidence for this competing reaction is shown in Fig. 3. The single aromatic proton signal from 30 is downfield to all the other signals. In time the two doublets from 9 disappear, presumably due to the decomposition of 9, and the only downfield signal that remains is from the stable aromatic product 30. However, compound 9 appears not be be a precursor for 30. In a separate experiment 9 was treated at 80 °C with sodium acetate-acetic anhydride for several days and the mixture was monitored for proton spectral changes. The H_a-H_b sets of doublets from 9 gradually disappeared but were replaced by two new doublet sets just inside the original sets, probably due to the simple N-acetylation product of 9. However, no signal due to 30 was ever observed.

EXPERIMENTAL

General Methods. Melting points were obtained with a Fisher-Johns melting point apparatus and are uncorrected. ^1H NMR spectra were recorded at 90 MHz with a Varian Model 390 Spectrometer using tetramethylsilane as an internal standard. Fully decoupled ^{13}C NMR spectra were recorded at 100.62 MHz using a Bruker WH 400 Spectrometer with $CDCl_3$ as an internal standard. IR spectra were obtained using Perkin-Elmer 337 or 283 grating infrared spectrometers. Thin layer chromatography was performed on plates coated with silica gel GF-254 (E. Merck, Darmstadt) and components were visualized by spraying with 20% sulfuric acid. Chromatographic solvent systems are designated as volume to volume ratios. Solutions were concentrated under reduced pressure. The acid-form cation exchange resin used was Dowex AG 50 W-X2. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Xylaramide (6). Acetyl chloride (5 mL) was carefully added to dry methanol (150 mL) which had been cooled to 5 °C. The

solution was allowed to warm to room temperature and to it was added xylaric acid[4] (5, 16.4 g). The solution was boiled under reflux overnight and then concentrated at 50 °C to a syrupy product. The product was dissolved in methanol and the solution concentrated to a syrup. This latter process was repeated once and then residual water and methanol were removed from the product by azeotropic distillation with toluene at reduced pressure. The rust colored syrup after being dried further (vacuum pump), showed characteristic lactone carbonyl (1795 cm^{-1}) and ester carbonyl (1745 cm^{-1}) stretching vibrations. A solution of the crude esterification product in dry methanol (50 mL) was added dropwise to a cold (5 °C) solution of methanol (150 mL) saturated with ammonia. Ammonia was bubbled through the methanol solution during the addition and for 1 h after the addition was completed. The reaction mixture was then kept overnight at room temperature open to the atmosphere, in a fumehood. Precipitated crystalline xylaramide (6) was removed by filtration, washed with methanol and air dried: yield, 13.3 g; mp 178.5–180 °C decomp (lit.[5] 180 °C decomp).

Tri-O-acetylxylaramide (7). Xylaramide (6, 4.0 g) was stirred with a solution of acetic anhydride (80 mL) and pyridine (2 mL) and the mixture slowly heated in an oil bath to 120 °C at which temperature the amide was completely dissolved. The stirred reaction mixture was kept at 120 °C for 15 min and then allowed to cool to room temperature. The white tri-O-acetylxylaramide (7) that crystallized from the reaction mixture was removed by filtration, washed with anhydrous ether, and dried in a vacuum desiccator for several hours; yield 5.15 g (75%), mp 206–207 °C. Recrystallization from 90% ethanol gave an analytical sample, mp 206–207 °C. IR (KBr) 3460 (N-H), 3210 (N-H), 1760 (ester C=O) and 1695 cm^{-1} (amide C=O); ^1H NMR (Me_2SO-d_6) δ 7.55 and 7.33 (each s, 4, $CONH_2$) 5.59 (t, 1, H-3, $J_{2,3}$ = $J_{3,4}$ = 4.9 Hz), 5.03 (d, 2, H-2, H-4), 2.08 (s, 6, C-2 and C-4 CH_3CO_2), and 1.98 (s, 3, C-3 CH_3CO_2).

Anal. Calcd for $C_{11}H_{16}N_2O_8$ (304.26): C, 43.42; H, 5.30; N, 9.21. Found: C, 43.36; H, 5.31; N, 9.20.

N,N'-diacetyl-tri-O-acetylxylaramide (8). Tri-O-acetylxylaramide (7, 10.7 g) was stirred with acetic anhydride (214 mL) for 20 min and H^+ cation exchange resin (11 mL) was added to the mixture. Stirring was maintained, the reaction mixture became warm, and within 5 min the amide dissolved. The mixture was stirred for an additional 2.5 h, the resin removed by filtration, and the acetic anhydride evaporated at 50 °C. The white solid produced was further dried with the aid of a vacuum pump to yield 8, 12.7 g (93%) and mp 163–164 °C. Recrystallization from ethyl acetate–hexane gave an analytical sample; mp 164–165 °C; IR (KBr) 3290 and 3190 (N-H), 1750 (ester C=O) and 1710 cm^{-1} (imide C=O); ^1H NMR (Me_2SO-d_6) δ 9.6 (s, 2, N-H), 5.3 (t, 1, H-3, $J_{2,3} = J_{3,4} = 4.5$ Hz), 5.0 (d, 2, H-2, H-4), 1.76 (s, 6, CH_3 CONH), 1.7 (s, 6, C-2, C-4, CH_3CO_2) and 1.6 (s, 3, C-3, CH_3CO_2).

Anal. Calcd for $C_{15}H_{20}N_2O_{10}$ (388.33): C, 46.39; H, 5.19; N, 7.21. Found: C, 46.40; H, 5.21; N, 7.20.

Methyl Ribaro-1,4-lactone (17). Acetyl chloride (10 mL) was slowly added to methanol (300 mL), being stirred at 10 °C. The solution was kept at room temperature for 15 min and then to it was added ribaro-1,4-lactone (16, 30 g). The reaction mixture was stirred and boiled under reflux overnight. The dark reaction mixture was concentrated at 50 °C to a syrup, which solidified after being kept in a refrigerator for two days. The dark crystalline mass was triturated with anhydrous ether, and air dried yielding the product as a light brown solid, 25.45 g. The product was purified by extracting some of the contaminants in boiling anhydrous ether (200 mL) giving 17 (21.4 g) with mp 90–95 °C decomp. This material was further purified in boiling dichloromethane (200 mL) giving 17 (18.2 g, 56%) with mp 105–108 °C decomp. Recrystallization from ethyl acetate–hexane gave an analytical sample: mp 112–113 °C decomp; IR (KBr) 3400 and 3280

(OH), 1770 (lactone C=O), and 1745 cm^{-1} (ester C=O); ^1H NMR (Me_2SO-d_6) δ 5.2 (broad s, OH), 4.93 (s, 1, ring proton) 4.37 (2, s, ring protons) and 3.8 (s, 3, $CO_2\underline{CH_3}$).

Anal. Calcd for $C_6H_8O_6$ (176.13): C, 40.92; H, 4.58. Found: C, 40.80; H, 4.59.

Ribaramide (18). A solution of methyl ribaro-1,4-lactone (17, 10.9 g) in methanol (50 mL) was added dropwise over 10 min to cold (0-5 °C) methanol (100 mL) saturated with ammonia. Gaseous ammonia was bubbled through the reaction mixture for 1 h while the cooled mixture was stirred. The reaction mixture was then kept overnight at room temperature open to the atmosphere in a fumehood. The insoluble solid product was removed from the reaction mixture by filtration and washed with cold methanol to give crude 18; 7.3 g (66%), mp 148-150 °C, Ribaramide (18) recrystallized from N,N-dimethylformamide-methanol had a mp 152-153 °C decomp (lit.[5] mp 155 °C decomp).

Tri-O-acetylribaramide (19). Ribaramide (18, 4.0 g) was stirred with a solution of acetic anhydride (80 mL) and pyridine (4 mL) and the mixture slowly heated on an oil bath to 125 °C, by which temperature dissolution of the amide was complete. The reaction mixture was allowed to cool to room temperature, and then kept in the refrigerator overnight. Crystalline tri-O-acetylribaramide (19) was removed by filtration, washed with ether, and dried in a vaccum desiccator; yield 4.1 g (60%), mp 191-192 °C. Recrystallization from 95% ethanol gave an analytical sample of the same melting point. IR (KBr) 3350 and 3200 (N-H), 1750 (ester C=O), and 1685 cm^{-1} (amide C=O); ^1H NMR (Me_2SO-d_6) δ 7.5 and 7.4 (each s, each 2, $CONH_2$), 5.4 (t, 1, H-3, $J_{2,3} = J_{3,4} = 6.0$ Hz), 5.1 (d, 2, H-2,H-4), 2.05 (s, 6, C-2, C-4 $\underline{CH_3}CO_2$) and 1.95 (s, 3, C-3 $\underline{CH_3}CO_2$).

Anal. Calcd for $C_{11}H_{16}N_2O_8$ (304.26): C, 43.42; H, 5.30; N, 9.21. Found: C, 43.43; H, 5.33; N, 9.22.

N,N'-diacetyl-tri-O-acetylribaramide (20). Tri-O-acetylribaramide (19, 7.5 g) was stirred with a mixture of acetic

anhydride (130 mL) and H^+ form cation exchange resin (15.0 mL). The imide was dissolved within 30 min. The reaction mixture was stirred for an additional 2.5 h, the resin removed by filtration, and the filtrate concentrated at 50 °C yielding crude (20); yield 9.03 g (93%), mp 184-185 °C. Recrystallization from acetone-hexane gave an analytical sample of the same melting point. IR (KBr) 3320 and 3280 (N-H), 1750 (ester C=O) and 1700 cm^{-1} (imide C=O); ^1H NMR (Me_2SO-d_6) δ 11.0 (s, 2, CONHAc), 5.45 (m, 3, H-2, H-3, H-4), 2.2 (s, 6, $NHCOCH_3$), 2.05 (s, 6, C-2, C-4 CH_3CO_2), and 1.95 (s, 3, C-3 CH_3CO_2).

Anal. Calcd for $C_{15}H_{20}N_2O_{10}$ (388.33): C, 46.39; H, 5.19; N, 7.21. Found: C, 46.36; H, 5.23; N, 7.19.

6-Acetamido-2,6-diacetyloxy-3-aza-1,4-cyclohexadien-3-one (9) from 8 and 20. N,N'-Diacetyl-tri-O-acetylxylaramide (8, 1.0 g) was suspended in acetic anhydride (19 mL) containing fused sodium acetate (1.0 g). The final reaction mixture was stirred in an oil bath kept at 80 °C for 6 h. The progress of the reaction was monitored using ^1H NMR at 90 MHz. Aliquots were taken from the reaction mixture at specified intervals (Fig. 1) and spectra recorded over a range of 3.0-10.0 ppm. The final reaction mixture was concentrated, dried further with a vacuum pump, and the residue extracted with dichloromethane. Concentration of the extract, and recrystallization of the product from ethyl acetate-hexane gave 9; 0.36g (52%), mp 147-150 °C. Recrystallization from ethyl acetate gave an analytical sample; mp 161-163 °C; IR (KBr) 3260 (N-H), 3080 and 2900 (olefinic C-H), 1770 (shoulder, enol ester C=O), (1750, ester C=O), 1710 (amide C=O) and 1690 cm^{-1} (α,β-unsaturated ketone C=O); ^1H NMR ($CDCl_3$) δ 9.3 ($NHCOCH_3$), 7.15 (d, 1, H-5, $J_{5,4}$ = 6.0 Hz), 6.4 (d, 1, H-4), 2.53 and 2.47 (each s, each 3, CH_3CO_2) and 2.2 (s, 3, CH_3CONH); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 172.5 and 169.1 (each CH_3CO_2), 167.7 (CH_3CONH), 167.5 (C-3), 163.3 (C-2), 144.2 (C-5), 129.3 (C-4), 91.5 (C-6), and 25.3, 24.5, and 21.4 (each CH_3CO).

Anal. Calcd for $C_{11}H_{12}N_2O_6$ (268.22): C, 49.26; H, 4.51; N, 10.44. Found: C, 49.01; H, 4.58; N, 10.36.

When 20 was treated with sodium acetate-acetic anhydride in the manner described for 8 progress of the reaction was followed by ^1H NMR as shown in Fig. 2. The conversion of 20 to 9 at 80 °C is complete after 10 h.

2,3,5,6-Tetraacetyloxypyridine (30) from 7 and from 19. Tri-O-acetylxylaramide (7, 1.0 g) was suspended in acetic anhydride (20 mL) containing fused sodium acetate (1.0 g). The stirred reaction mixture was kept at 100 °C for 6.5 h and then allowed to cool to room temperature. The precipitated product was removed by filtration and washed with ether giving 30 (0.40 g, 50%), mp 190-193 °C. Recrystallization from ethyl acetate gave an analytical sample: mp 192-194 °C; IR (KBr) 1775 and 1785 (aryl ester C=O) and 1610 cm^{-1} (aromatic C=C); ^1H NMR at 400 MHz, ($CDCl_3$) 7.75 (1, s, H-4), 2.310 and 2.296 (each s, each 6, CH_3CO_2); ^{13}C NMR ($CDCl_3$) δ 167.235 and 167.207 (C-2, C-6 and C-3, C-5 CH_3CO_2), 144.179 (C-2, C-6), 136.265 (C-3, C-5), 129.715 (C-4) and 20.590 and 20.521 (C-2, C-6 and C-3, C-5 CH_3CO_2).

Anal. Calcd for $C_{13}H_{13}NO_8$ (311.25): C, 50.17; H, 4.21; N, 4.50: Found C, 50.19; H, 4.24; N, 4.47.

Conversion of tri-O-acetylribaramide (19) to 30 was achieved under the same conditions as described for the conversion of 7 to 30. However, as observed by ^1H NMR, the conversion from 19 to 30 was quite slow and the time required for the reaction to go to completion was over thirty hours.

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