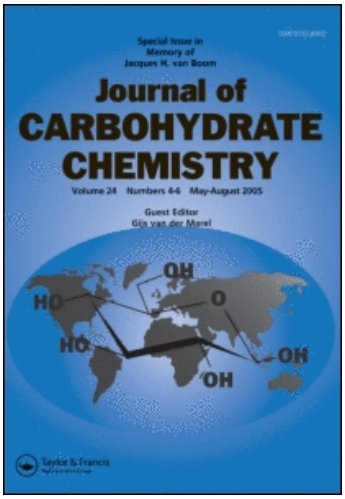

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Synthesis and Chemical Transformation of 2 -Acetoxyimino-3,4, 6-tri-*O*-acetyl-2-deoxy-β-D-*arabino*-hexopyranosyl Azide

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SYNTHESIS AND CHEMICAL TRANSFORMATION OF 2-ACETOXYIMINO-3,4,6-TRI-*O*-ACETYL-2-DEOXY-β-D-*ARABINO*-HEXOPYRANOSYL AZIDE[1]

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ABSTRACT

The title compound **3** has been synthesized from 3,4,6-tri-*O*-acetyl-2-deoxy-2-nitroso-α-D-glucopyranosyl chloride (**1**) *via* compound **2**. Azide reduction of **3** is accompanied by ***O*→*N***-acetyl migration to afford *N*-acetyl-*N*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-β-D-*arabino*-hexopyranosyl)amine (**4**), also characterized as its *Z* and *E* peracetates. On the basis of IR, ^{1}H NMR and X-ray structural data from compound **4**, its β-NHAc configuration, (*Z*) 2-hydroxyimino, and $^0S_2$ conformation, were established.

INTRODUCTION

The condensation of β-glycosylamines, obtained by reduction of β-glycosyl azides, with the carboxyl group of the side chain of *C*- and *N*-protected aspartic acid in the presence of DCC or EEDQ[2] is a well-known method for synthesizing *N*-glycosylamino acids. In the same way we conducted syntheses of *N*-(L-aspart-4-oyl)-β-D-xylopyranosylamine,[3,4] *N*-(L-aspart-4-oyl)-α-L-arabinopyranosylamine,[3,4] and *N*-(L-glutam-5-oyl)-α-L-arabinopyranosylamine[5] derivatives. Despite many reservations concerning this method (lability of the glycosylamines, side reactions proceeding together with condensation reactions and

difficulties during removal of the protecting groups) it is still popular, and the range of derivatives employed (both sugars and amino acids) has been extended.[6]

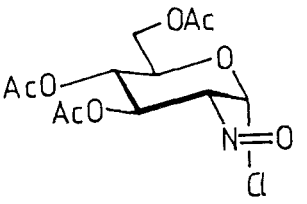
In the syntheses of *O*-glycosyl derivatives, also containing a hydroxyamino acid moiety as an aglycon, *O*-acetyl-2-deoxy-2-nitrosoglycosyl chlorides appear to be very useful as glycosylating agents.[7-10] Products of these reactions are 2-hydroxyimino derivatives of *O*-glycosides and usually have an α configuration.

Attempts to synthesize *N*-glycosyl derivatives by adopting the above method have not yet been successful. We therefore tried to synthesize a sugar derivative modified at C-1, and containing a 2-acyloxyimino group, ready to react with an amino acid, using a different strategy. The presence of such a group at C-2 affords the chance for further modification of the ring at positions C-2 and C-3, and make it possible to make some mono- and oligosaccharide derivatives of synthetic interest.[11-19]

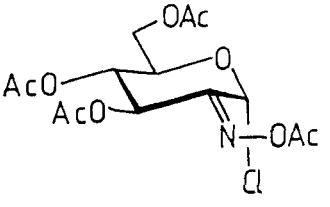
RESULTS AND DISCUSSION

3,4,6-Tri-*O*-acetyl-2-deoxy-2-nitroso-α-D-glucopyranosyl chloride (**1**)[20] reacted with acetyl chloride in the presence of triethylamine to give 2-acetoxyimino-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranosyl chloride (**2**).[7b] The structure of compound **2** (α, 2-hydroxyimino, and $^4C_1$) was ascertained from the value of its optical rotation ($[\alpha]_D > 0$) and from ^1H NMR data: δ (H-1, s; H-3, d; H-4, dd); coupling constants ($J_{3,4} \approx J_{4,5} \approx 10$ Hz).

Reaction of **2** with sodium azide in acetonitrile gave 2-acetoxyimino-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-*arabino*-hexopyranosyl azide (**3**) (94%). Replacement of substituent at C-1 and the change of its configuration were confirmed from polarimetric ($[\alpha]_D < 0$), and IR (2100 cm^{-1}, N_3) and ^1H NMR spectral data. The H-1 chemical shift from **3** is smaller than that of compound **2** ($\Delta\delta = 1.08$ ppm) due to the presence of the N_3 group and change of the H-1 orientation from axial in **2** to equatorial in **3**. The modification at C-1 in compound **2** also results



1



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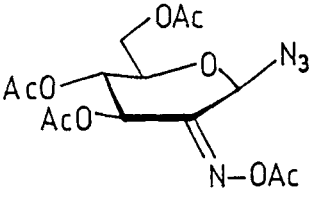

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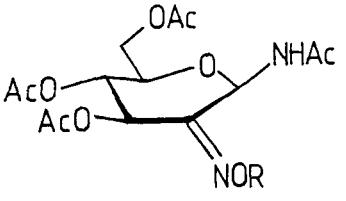


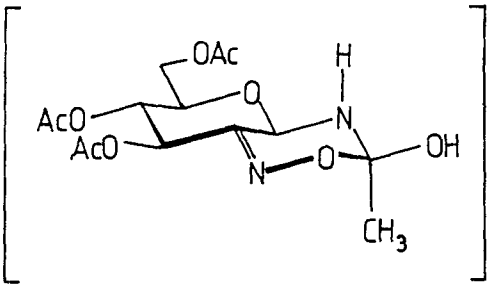
4 R = H (Z isomer)
5a R = Ac (Z isomer)
5b R = Ac (E isomer)

Ac = CH_3CO

in changes of the value of $J_{3,4}$ (3.0 Hz) and $J_{4,5}$ (8.0 Hz), respectively.

Hydrogenation of **3** in the presence of Pd/C afforded a mixture of products, from which a small yield (7-12%) of *N*-acetyl-*N*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-β-D-*arabino*-hexopyranosyl)amine (**4**) was obtained by crystallization from ethyl acetate. This result implies that the above reduction conditions led to migration of the oxime acetyl group to the newly formed amino group at C-1. This migration process can be explained by supposing the formation of an intermediate with structure **6**.[21,22] Formation of this structure is enhanced by the C-1 β configuration and the *Z*-configuration of the 2-acetoxyimino group.

The data from elemental analysis, FAB mass spectrum (m/z 361 $[M+1]^+$, m/z 359 $[M-1]^-$), IR spectrum (1710 cm^{-1}, amide CO; 3240 cm^{-1}, OH; 3120 cm^{-1}, NH) and ^1H NMR spectrum (NHAc, d coupled with H-1, d, $J_{1,NH}$ = 9.5 Hz and =NOH, s, both exchangeable during deuteration; Ac, 4s) support the structure of **4**.



6

Crystallographic studies[23] confirmed the presence of the 1-acetamido and 2-hydroxyimino groups and also gave detailed information about the three dimensional structure of compound **4**: β C-1 and (Z) 2-acetoxyimino configurations and $^{\circ}S_2$ conformation of the sugar ring (Figs. 1 and 2).

In the $^{\circ}S_2$ conformation of **4** the dihedral angle Φ between C-H bonds at C-3 and C-4 is ~120°. This value is in agreement with the theoretical Karplus and Conroy function (^3J = 4.22+ -0.5cosΦ+4.5cos2Φ)[24] and explains the small value of $J_{3,4}$ (2.75 Hz).

Acetylation of **4** with acetic anhydride in pyridine-methylene chloride solution in the presence of a catalytic amount of dimethylaminopyridine (DMAP) proceeded quickly and quantitatively. The ^{1}H NMR spectrum of the product shows it to be a mixture of two compounds, *Z* (**5a**) and *E* (**5b**) isomers of *N*-acetyl-*N*-(2-acetoxyimino-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-*arabino*-hexopyranosyl)amine in a 3:1 ratio, respectively. The 2-acetoxyimino group, compared to the hydroxyimino group in **4**, causes shielding of the anomeric proton in both isomers (**5a** and **5b**): $\Delta\delta$ = 0.58 ppm in the *E* orientation and $\Delta\delta$ = 0.12 ppm in the *Z* orientation. Compared to the *Z* isomer (**5a**), proton H-1 in the *E* isomer (**5b**) is more shielded (0.46 ppm) and the H-3, H-5, and NH protons are more deshielded (0.44, 0.50, 0.63 ppm respectively).

Studies of the literature show an empirical regularity between anomeric configuration and the values of coupling constants $J_{3,4}$ and $J_{4,5}$ in 2-hydroxyimino and 2-acyloxyimino

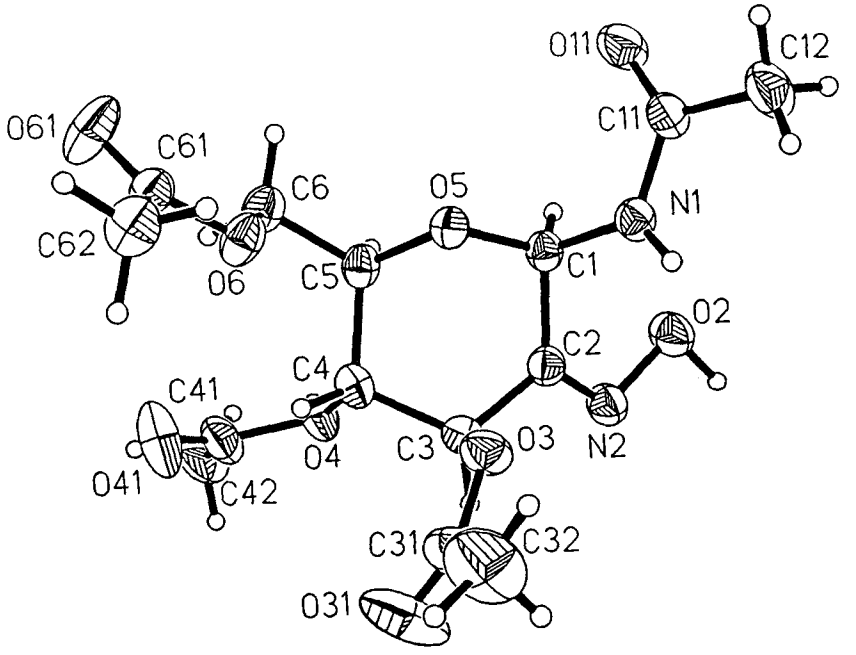


Fig. 1. ORTEP Drawing from the Crystal Structure of **4**

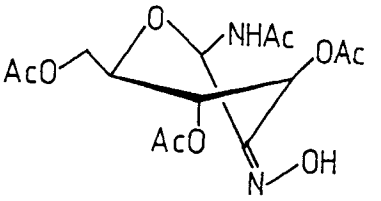


Fig. 2. $^{o}S_{2}$ Conformation of **4**

derivatives of D-*arabino*-hexopyranoses.[8a,16,25] Irrespective of the kind of aglycon for α anomers, the values of these constants are approximately identical and equal to about 10 Hz. These values indicate an axial orientation of the H-3, H-4 and H-5 protons and, indirectly, a $^{4}C_{1}$ conformation of the sugar ring. The same applies to compound **2**. On the other hand, in β isomers these coupling constants are usually small ($J_{3,4} \simeq$ 2.5-5.0 Hz and $J_{4,5} \simeq$ 5.0-8.5 Hz). Such small values of $J_{3,4}$

and $J_{4,5}$ can also be found in the spectra of compounds **3**, **4**, **5a** and **5b**. For compound **4** the β configuration and $^{o}S_{2}$ conformation were unequivocally confirmed from the crystallographic studies. We can then assume from these results that compounds **3**, **5a** and **5b** have similar three dimensional structures (β configuration and $^{o}S_{2}$ conformation). The reason for deformation from the typical $^{4}C_{1}$ conformation for compounds with the β configuration seems to be the unfavourable, almost coplanar orientation of substituents at C-1 (N_3 in **3** NHAc in **4**, **5a** and **5b**), at C-2 (=NOH in **4** and =NOAc in **5a** and **5b**) and at C-3 (OAc in **3-5b**).

In an attempt to reduce the carbon to nitrogen double bond in the mixture of compounds **5a** and **5b** (*Z*/*E*) with sodium borohydride in methanol in the presence of $NiCl_2 \cdot 6H_2O$, by the method used for the transformation of the 2-acetoxyimino group into the 2-amino group,[15,26] only compound **4** was obtained. It seems that under these reaction conditions only deacetylation of 2-acetoxyimino group occurs, but the carbon to nitrogen double bond is not reduced.

EXPERIMENTAL

General Procedures. IR spectra were recorded with a Specord 71 spectrophotometer (Nujol or film). ^{1}H NMR spectra ($CDCl_3$, internal TMS) were recorded with Tesla BS 487 (80 MHz), Tesla 576A (100 MHz) or Brucker (360 MHz) spectrometers. Mass spectra were recorded on MAT 711 (FD) or MAT 8222 (FAB, glycerol or TEG as a matrix) mass spectrometers. Optical rotations were determined with a Hilger-Watt polarimeter. Elemental analyses were performed on a Carlo Erba 1106 analyser. TLC was performed on Merck Kieselgel 60 plates with: A, carbon tetrachloride-acetone (3:1); B, carbon tetrachloride-acetone (1:1); C, ethyl acetate–*n*-hexane (3:1) and spots were observed by heating above 200 °C. R_F coefficients of substances predominant in mixtures are underlined. Melting points are reported uncorrected.

2-Acetoxyimino-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranosyl Chloride (2). This compound was prepared from

dimeric 3,4,6-tri-*O*-acetyl-2-deoxy-2-nitroso-α-D-glucopyranosyl chloride (**1**) by a literature procedure:[7b] syrup, R_F 0.62, 0.47, 0.28 (A); IR (film) 1780 cm^{-1} (ν_{CO}, acetoxyimine), 1750 (ν_{CO}, ester), 1640 (ν_{CN}, oxime); ^1H NMR (80 MHz) δ 7.025 ppm (s, 1H, H-1), 6.00 (d, 1H, $J_{3,4}$ = 10 Hz, H-3), 5.35 (dd, 1H, $J_{4,3} = J_{4,5}$ = 10 Hz,H-4), 4.55-3.95 (m, 3H, H-5, H-6, H-6′), 2.200 (s, 3H, Ac) and 2.125, 2.075 (2s, 9H, 3Ac).

2-Acetoxyimino-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-*arabino*-hexopyranosyl Azide (3). To a lucid light-yellow solution of **2** (0.46 g, 1.21 mmol) in acetonitrile (2.5 mL) was added sodium azide (0.25 g, 3.85 mmol). The reaction mixture was stirred at room temperature. After 2 h TLC (solvent A and C) showed the absence of sugar substrate (R_F = 0.62, A) in the reaction mixture. The mixture was filtered, the precipitate washed with acetonitrile and the filtrate concentrated (20 °C, 21 mm Hg) giving a weak light-brown syrup of **3** (0.442 g, 94.6%): R_F = 0.54; A, $[\alpha]^{23}_D$ -81.0° (*c* 2.89, chloroform); IR (film) 2100 cm^{-1} (ν_{N_3}), 1780 (ν_{CO}, acetoxyimine), 1750 (ν_{CO}, ester), 1650 (ν_{CN}, oxime); ^1H NMR (100 MHz) δ 5.95 ppm (s, 1H, H-1), 5.70 (d, 1H, $J_{3,4}$ = 3.0 Hz, H-3), 5.24 (dd, 1H, $J_{4,3}$ = 3.0 Hz, $J_{4,5}$ = 8.0 Hz, H-4), 3.89 (m, 1H, H-5), 4.40 (m, 2H, H-6, H-6′), 2.30 (s, 3H, Ac), 2.20 (s, 3H, Ac), 2.13 (s, 3H, Ac), 2.06 (s, 3H, Ac).

***N*-Acetyl-*N*-(3,4,6-tri-*O*-Acetyl-2-deoxy-2-hydroxyimino-β-D-*arabino*-hexopyranosyl)amine (4).** 10% Pd/C (1 g) was added to a solution of **3** (5.79 g, 15 mmol) in dry ethyl acetate (60 mL) and hydrogenation at room temperature was carried out. After 5 h the catalyst was removed by filtration through a 0.5 cm layer of silica gel and washed with ethyl acetate. The filtrate was concentrated (35 °C, 17 mm Hg) to a light-yellow syrup, which was dried to a foam, 4.75 g: R_F = 0.64, 0.58, 0.48, 0.40, 0.28, 0.20, 0.12, 0.06, 0, A; R_F =0.80, 0.76, 0.70, 0.66, 0.56, 0.50, 0.44, 0.32, 0.26, 0.12, B; R_F = 0.64, 0.28, 0.22, 0.16, C. After crystallization from ethyl acetate (30 mL), white crystals of **4** were obtained (0.395 g, 7.3%): mp 177-179 °C; R_F = 0.06, A; R_F = 0.40, B; R_F = 0.16, C; $[\alpha]^{20}_D$ +1.5° (*c* 2.0, chloroform); IR (Nujol) 3240 cm^{-1}, 3120 (ν_{OH},

ν_{NH}), 1750 (ν_{CO}, ester), 1710 (ν_{CO}, Amide I), 1670 (ν_{CN}, oxime); ^{1}H NMR (360 MHz) δ 6.60 ppm (d, 1H, $J_{1,NH}$ = 9.5 Hz, H-1), 5.41 (d, 1H, $J_{3,4}$ = 2.75 Hz, H-3), 5.08 (dd, 1H, $J_{4,3}$ = 2.75 Hz, $J_{4,5}$ = 8.5 Hz, H-4), 3.67 (ddd, 1H, $J_{5,4}$ = 8.5 Hz, $J_{5,6}$ = 5.5 Hz, $J_{5,6'}$ = 3.5 Hz, H-5), 4.23 (dd, 1H, $J_{6,6'}$ = -12.25 Hz, $J_{6,5}$ = 5.5 Hz, H-6), 4.20 (dd, 1H, $J_{6,6'}$ = -12.25 Hz, $J_{6',5}$ = 3.5 Hz, H-6'), 2.16 (s, 3H, Ac), 2.11, 2.08 (2s, 6H, 2Ac), 2.06 (s, 3H, Ac), 9.25 (s, 1H, =NOH), 6.38 (d, 1H, $J_{NH,1}$ 9.5 Hz, NHAc); (the last two protons are exchangeable during deuteration); MS (FD, m/z) 360 $[M]^+$, MS (FAB) positive ion at m/z 361 $[M+1]^+$, negative ion at m/z 359 $[M-1]^-$.

Anal. Calcd for $C_{14}H_{20}N_2O_9$: C, 46.67; H, 5.59; N, 7.77. Found: C, 46.66; H, 5.63; N, 7.66.

In one experiment the mixture of products was chromatographed on a column packed with silica gel <0.08 mm using carbon tetrachloride-acetone (1:1) as the eluent. No component was obtained in chromatographically homogeneous state. From the fractions distinctly richer in the component with R_F = 0.44 (B), after recrystallization from ethyl acetate, crystals of compound **4** were obtained (3%) with characteristics identical with those described above.

***N*-Acetyl-*N*-(2-Acetoxyimino-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-*arabino*-hexopyranosyl)amine (5a and 5b).** To a solution of **4** (0.231 g, 0.64 mmol) in dichloromethane (20 mL), pyridine (0.3 mL) and acetic anhydride (0.3 mL) were added. The solution was kept at room temperature. After 5 min the appearance of a product with R_F=0.48 (B) was observed and then a few crystals of 4-dimethylaminopyridine were added to the solution resulting in the complete disappearance of sugar substrate (R_F=0.40). The mixture was washed with water (4×20mL) and the organic layer was dried over anhydrous $MgSO_4$. A colourless syrup was obtained after concentration (25 °C, 14 mm Hg). Traces of pyridine were removed by azeotropic distillation with toluene (~2mL) (30 °C, 14mm Hg). This procedure was repeated twice giving a colourless syrup which during storage in vacuum desiccator over $CaCl_2$ was transformed into a white foam (0.266g, ~100%); R_F=0.12 (A), 0.48 (B); $[\alpha]^{20}_D$

+39.7° (*c* 1.985, chloroform); IR (film) 3240cm^{-1} (ν_{NH}), 1780 (ν_{CO}, acetoxyimine), 1750 (ν_{CO}, ester), 1690 (ν_{CO}, Amide I), 1525 (Amide II); ^{1}H NMR (360 MHz) - two groups of signals with an intensity ratio of 3:1, corresponding to *Z* and *E* isomers: (**5a**;*Z*) δ 6.48 ppm (d, 1H, $J_{1,NH}$ = 9.75 Hz, H-1), 5.48 (d, 1H, $J_{3,4}$ = 2.5 Hz, H-3), 5.15 (dd, 1H, $J_{4,3}$ = 2.5 Hz, $J_{4,5}$ = 8.0 Hz, H-4), 3.66 (dt, 1H, $J_{5,4}$ = 8.0 Hz, $J_{5,6}$ = 4.8 Hz, H-5), 4.22 (d, 2H, $J_{6,5}$ = 4.75 Hz, H-6), 2.17, 2.16 (2s, 6H, 2Ac), 2.11 (s, 3H, Ac), 2.09 (s, 3H, Ac), 2.08 (s, 3H, Ac), 6.57 (d, 1H, $J_{NH,1}$ = 9.75 Hz, NH-Ac); (**5b**;*E*) δ 6.02 ppm (d, 1H, $J_{1,NH}$ = 8.25 Hz, H-1), 5.92 (d,1H, $J_{3,4}$ = 5.2 Hz, H-3), 5.10 (dd, 1H, $J_{4,3}$ = 5.2 Hz, $J_{4,5}$ = 4.7 Hz, H-4), 4.16 (ddd, 1H, $J_{5,4}$ = 4.7 Hz, $J_{5,6}$ = 5.2 Hz, H-5), 4.26 (dd, 1H, $J_{6,6'}$ = -11.2 Hz, $J_{6',5}$ = 5.2 Hz, H-6), 4.235 (dd, 1H, $J_{6',6}$ = -11.2 Hz, $J_{6',5}$ = 5.2 Hz, H-6′), 2.16-2.17 (s, 3H, Ac), 2.15 (s, 3H, Ac), 2.12 (s, 3H, Ac), 2.11 (s, 3H, Ac), 2.10 (s, 3H, Ac), 7.20 (d, 1H, $J_{NH,1}$ = 8.25 Hz, NHAc); MS (FAB in glycerine and TEG), positive ion at m/z 403 $[M+1]^+$ and negative ion at m/z 401 $[M-1]^-$.

Attempted Reduction of *N*-Acetyl-*N*-(2-Acetoxyimino-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-*arabino*-hexopyranosyl)amine. To a solution of **5a/5b** mixture (0.100g, 0.25 mmol) in abs methanol (2.7 mL) cooled to -38 °C, $NiCl_2 \cdot 6H_2O$ (0.143g, 0.6 mmol) was added. The mixture was stirred and $NaBH_4$ (0.095 g, 2.5 mmol) was added in small portions. For 1 h the temperature was kept below -18 °C and then the cold bath was removed. After 22 h the absence of substrate (R_F=0.48) and the presence of compound **4** (R_F=0.44) and a small amount of compound with R_F=0 were noted (TLC, B). The addition of a more $NaBH_4$ (0.095g, 2.5 mmol) resulted in no change in the composition of the mixture after 25 h. Acetic anhydride (0.2 mL) was added and the appearance of a component with R_F=0.48 (**5a/5b**) was recorded.

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