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# Facile $Cu(OTf)_2$-Catalyzed Preparation of Per-*O*-acetylated Hexopyranoses with Stoichiometric Acetic Anhydride and Sequential One-Pot Anomeric Substitution to Thioglycosides under Solvent-Free Conditions

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**Abstract:** Solvent-free per-*O*-acetylation of hexoses with a stoichiometric amount of acetic anhydride employing 0.03 mol % $Cu(OTf)_2$ proceeded in high yields (90−99%) at room temperature to give exclusively pyranosyl products as an anomeric mixture, the $\alpha/\beta$ ratio of which was dependent on the temperature and amount of catalyst used. Sequential anomeric substitution with *p*-thiocresol in the presence of $BF_3$·etherate gave the thioglycosides, isolated exclusively or predominantly as one anomer in 66−75% yields.

Per-*O*-acetylated hexopyranoses and their derived thioglycosides are valuable building blocks for the synthesis of biologically potent oligosaccharides, glycoconjugates, as well as natural products.[1] Per-*O*-acetylation is one of the most frequently used reaction in carbohydrates primarily for initial protection of sugars and also to aid spectral characterization and identification of target molecules. This is generally performed using acetic anhydride as the reagent and a variety of catalysts. Pyridine, which serves a dual purpose as a solvent and as a catalyst, is most widely employed despite its known toxicity and unpleasant odor.[2] Further addition of pyridine derivatives, for example, 4-(*N*,*N*-dimethylamino)pyridine and 4-(1-pyrrolidino)pyridine, as a cocatalyst speeds up this transformation.[3] Some common methods involving sodium acetate-[4] and iodine-promoted[5] per-*O*-acetylation of sugars have been investigated. However, excess acetic anhydride as a solvent causes tedious workup in the neutralization process. Other catalysts that have been shown to be effective for this purpose include (1) classical acids, for example, $H_2SO_4$,[6] $HClO_4$,[7] $ZnCl_2$,[8] $FeCl_3$,[9] and TMSCl;[10] (2) phase-transfer catalysts, e.g., tetra-*n*-butylammonium bromide−sodium hydroxide;[11] (3) heterogeneous catalysts, such as anionic surfactants,[12] Montmorillonite K10,[13] Nafion-H,[14] H-$\beta$ zeolite,[15] and zirconyl sulfophenyl phosphonate;[16] and (4) enzyme catalysts, e.g., lipases.[17] Boric acid in conjunction with a catalytic amount of $H_2SO_4$ leads to the corresponding furanosyl peresters.[18] Very recently, use of a dicyanamide-based ionic liquid[19] both as a solvent and a basic catalyst has been reported for per-*O*-acetylation.

A variety of other catalysts in combination with excess acetic anhydride and solvents have been employed in the *O*-acetylation of non-carbohydrate alcohols, including $Bu_3P$,[20] $CoCl_2$,[21] $TaCl_5$,[22] TMSOTf,[23] iminophosphorane bases with enol esters,[24] distannoxane catalysis,[25] and metal trifluoromethanesulfonates [$M(OTf)_n$] such as $Sc(OTf)_3$[26] and its complex with trifluoromethanesulfonamide,[27] $In(OTf)_3$,[28] $VO(OTf)_2$,[29] $Bi(OTf)_3$,[30] and $Cu(OTf)_2$.[31] In contrast, the potential of these versatile, water-stable, and reusable $M(OTf)_n$ catalysts has been exploited scarcely in carbohydrates.[29] We have recently demonstrated that $Sc(OTf)_3$ is an efficient catalyst in per-*O*-acetylation and

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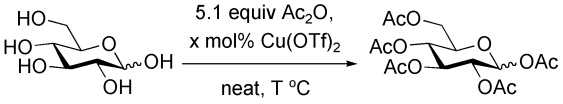
**TABLE 1. Cu(OTf)$_2$-Catalyzed Solvent-Free Per-*O*-acetylation of D-Glucose with a Stoichiometric Amount of Acetic Anhydride**




**1** **2**

| entry | x | *T* (°C) | *t* (h) | α/β | yield (%) |
|---|---|---|---|---|---|
| 1 | 0.5 | rt | 5 | 4.4/1 | 95 |
| 2 | 0.1 | rt | 5 | 3.6/1 | 95 |
| 3 | 0.05 | rt | 5 | 2.9/1 | 96 |
| 4 | 0.03 | rt | 6 | 2.3/1 | 96 |
| 5 | 0.025 | rt | 24 | | *a* |
| 6 | 0.03 | 0 → rt | 8 | 1.9/1 | 98 |

[a] The reaction was not completed.

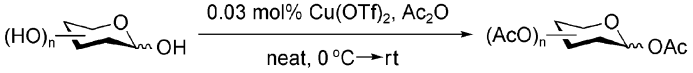
acetolysis of sugars under neat conditions.[32] It proceeds in excellent yields and requires a 0.5 mol % catalytic amount. In continuation with this, we wish to report a better catalyst, Cu(OTf)$_2$, for solvent-free preparation of per-*O*-acetylated hexopyranoses with a stoichiometric amount of acetic anhydride and their applications to the synthesis of thioglycosides via sequential one-pot anomeric substitution.

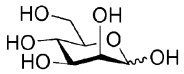
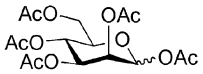
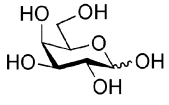
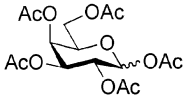
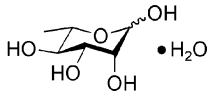
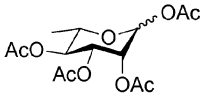
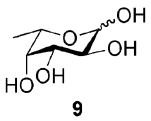
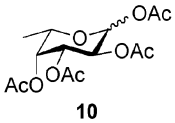
The results of per-*O*-acetylation of D-glucose **1** are summarized in Table 1. To determine the minimum amount of catalyst required, use of 0.5 mol % Cu(OTf)$_2$ furnished D-glucopyranosyl pentaacetate **2**[33] in 95% yield (entry 1). A 5-fold (entry 2) and 10-fold (entry 3) decrease in the catalytic concentration displayed similar results. Lowering the catalyst quantity still further (0.03 mol %) showed no significant variation in the outcome of the reaction, except that an additional 1 h was required for total consumption of the starting material, as outlined in entry 4. This turned out to be the minimum concentration required for optimum catalytic activity, and the reaction did not go to completion when a slightly less amount (0.025 mol %) of catalyst was used (entry 5). In all instances, a small amount of D-glucofuranosyl pentaacetate[34] was also obtained as detected by the $^1$H NMR spectra of the crude products. However, formation of this isomer could be suppressed by conducting the addition of Cu(OTf)$_2$ at 0 °C (entry 6), and the product **2** was isolated in 98% yield exclusively in the pyranosyl form as an anomeric mixture. This study also revealed an interesting phenomenon that the α/β ratios are affected by the amount of catalyst and temperature.

Per-*O*-acetylation of other important D- and L-hexoses under this set of optimized conditions is illustrated in Table 2. In entry 1, D-mannose **3** readily provided the corresponding pyranosyl pentaacetate **4**[35] almost quantitatively, whereas D-galactose **5** slowly afforded the product **6**[33] in very good yield (entry 2). The reaction time of the later transformation could, however, be shortened by a slight increase in the catalyst concentration (0.05 mol %, entry 3). In the L-series, since commercially available L-rhamnose **7** contains one water molecule, 5 equiv of acetic anhydride is required to complete the reaction. As indicated in entry 4, the corresponding tetraacetate **8**[36] was obtained in excellent yield and in much shorter time. Similar results were observed in the case of L-fucose **9** (entry 5), and the expected compound **10**[37] was isolated in 91% yield.

With such success in the stoichiometric neat per-*O*-acetylation of hexoses to the pyranosyl products, we turned our attention to the thioglycosides, which are conventionally prepared by a nucleophilic addition of

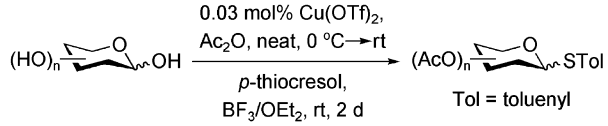
**TABLE 2. Cu(OTf)$_2$-Catalyzed Solvent-Free Per-*O*-acetylation of Hexoses**

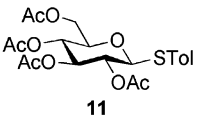
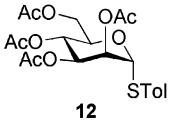
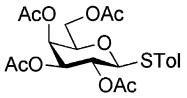
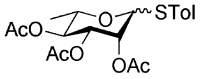
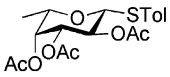



| entry | hexose | t (h) | $Ac_2O$ (equiv) | product | α/β | yield (%) |
|---|---|---|---|---|---|---|
| 1 |  **3** | 5.0 | 5.1 |  **4** | 1.6 | 99 |
| 2 |  **5** | 25 | 5.1 |  **6** | 3.4 | 90 |
| 3 | | 15 | 5.1 | | 4.0 | 93[a] |
| 4 |  **7** | 2.5 | 5.0 |  **8** | 1.5 | 98 |
| 5 |  **9** | 2.5 | 4.1 |  **10** | 7.4 | 91 |

[a] 0.05 mol % Cu(OTf)$_2$ was used.

**TABLE 3. One-Pot Per-*O*-substitution of Hexoses to the Corresponding Thioglycosides**




| entry | hexose | product | α/β | yield (%) |
|---|---|---|---|---|
| 1 | **1** |  **11** | 0/1 | 73 |
| 2 | **3** |  **12** | 1/0 | 72 |
| 3 | **5** |  **13** | 0/1 | 71 |
| 4 | **7** |  **14** | 3.9/1 | 75 |
| 5 | **9** |  **15** | 0/1 | 66 |

thiols on the respective anomeric acetates in the presence of a Lewis acid catalyst such as $BF_3{\cdot}OEt_2$. In contrast to the conventional per-*O*-acetylation, wherein an excessive amount of $Ac_2O$ is used and neutralization followed by elaborate tedious workup and purification is a priori to the second step, our method employing stoichiometric amount of $Ac_2O$ offers a chance to carry out the sequential per-*O*-acetylation−anomeric substitution of hexoses in one pot under solvent-free conditions.

Thus, per-*O*-acetylation of hexoses was conducted as before and monitored by TLC. After total consumption of the starting material, *p*-thiocresol, and $BF_3{\cdot}OEt_2$ (2 equiv each) were added sequentially to the reaction solution at room temperature without additional solvent, and the mixture was left stirring for 2 days. Table 3 describes the yields and $\alpha/\beta$ ratios of the hexose-derived thioglycosides. In entry 1, the reaction of D-glucose **1** afforded the $\beta$-thioglycoside **11**[38] as a sole product in 73% yield. Similarly, D-galactose **5** (entry 3) and L-fucose **9** (entry 5) led to exclusive formation of the corresponding $\beta$-thioglycosides **13**[38] and **15**[38] in 71% and 66% yields, respectively. Under these conditions, D-mannose **3** (entry 2) furnished the α-glycoside **12**[1b] as the only product whereas L-rhamnose **7** (entry 4) generated an anomeric mixture **14**, with predominance of the α-isomer in similar high yield. Since the anomeric protons of **14**α ($J$ = 1.5 Hz) and **14**$\beta$ ($J$ = 1 Hz) displayed similar coupling constants, the identification was done by observation of nuclear Overhauser enhancement between H1 and H5 protons in **14**$\beta$ (see the Supporting Information). The anomeric selectivity is a direct consequence of the neighboring group participation. It should be noted that all the reactions are carried out on a preparative scale (3 g) and are equally compatible for large-scale preparations.

In summary, $Cu(OTf)_2$ is an extremely efficient catalyst for per-*O*-acetylation of hexoses. Our method requires a truly catalytic amount of the least expensive available $M(OTf)_n$ that is water-stable and hence reusable. Furthermore, the per-*O*-acetylation reactions are conducted under solvent-free conditions using a stoichiometric amount of acetic anhydride that allows an efficient one-pot sequential per-*O*-acetylation−anomeric substitution of hexoses to thioglycosides. The reaction conditions are mild, convenient, and nonhazardous. We believe that this method to prepare the common building blocks should find a wide application in saccharide synthesis.

## Experimental Section

**General Methods.** Solvents were purified and dried from a safe purification system.[39] Flash column chromatography[40] was carried out with silica gel 60 (230−400 mesh, E. Merck). TLC was performed on precoated glass plates of silica gel 60 F254 (0.25 mm, E. Merck); detection was executed by spraying with a solution of $Ce(NH_4)_2(NO_3)_6$ (0.5 g), $(NH_4)_6Mo_7O_{24}$ (24 g), and $H_2SO_4$ (28 mL) in water (500 mL) and subsequent heating on a hot plate. Melting points were determined with a capillary apparatus and are uncorrected. Optical rotations were measured at 589 nm (Na) at ~29 °C. $^1H$ and $^{13}C$ NMR spectra were recorded with 400 and 500 MHz instruments. Chemical shifts are in ppm from $Me_4Si$, generated from the $CHCl_3$ lock signal at $\delta$ 7.24. Mass spectra were obtained in the EI and FAB modes. IR spectra were taken on an FT-IR spectrometer using NaCl plates. Elemental analyses were determined with a Perkin-Elmer 2400CHN instrument.

**General Procedure for Per-*O*-acetylation of Hexoses.** To a mixture of hexose (3 g scale) and stoichiometric acetic anhydride (Tables 1 and 2) was added freshly dried $Cu(OTf)_2$ (0.03 mol % of hexose) at 0 °C under nitrogen. The ice bath was removed, and the mixture was kept stirring at room temperature for 2.5−25 h (Tables 1 and 2). Methanol (same mole amount as hexose) was slowly added to quench the reaction, and the mixture was stirred for another 0.5 h followed by evaporation under reduced pressure. Ethyl acetate (20 mL/g of hexose) was added to dissolve the residue, and the mixture was consecutively washed with saturated $NaHCO_{3(aq)}$, water, and brine. The organic layer was dried over anhydrous $MgSO_4$, the mixture was filtered through paper, and the filtrate was concentrated in vacuo. The crude product was purified by either recrystallization in ethanol or flash column chromatography to afford the expected compound in excellent yield (Tables 1 and 2).

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**General Procedure for One-Pot Per-*O*-acetylation−Substitution of Hexoses.** Per-*O*-acetylation of hexose was carried out as described above. When reaction was completed according to TLC, without addition of methanol, *p*-thiocresol (2 equiv) and $BF_3$·etherate (2 equiv) were sequentially added to the reaction solution, and the mixture was allowed to stir for 2 d. The reaction was quenched by addition of saturated $NaHCO_{3(aq)}$, and the mixture was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. Purification of the residue through either flash column chromatography or recrystallization in ethanol gave the desired thioglycoside in good yield (Table 3).

***p*-Methylphenyl 6-deoxy-2,3,4-tri-*O*-acetyl-1-thio-α-L-mannopyranoside 14α:** $[\alpha]^{29}_D$ −123 (*c* 1.0, $CHCl_3$); mp 111−112 °C; IR ($CHCl_3$) 2936, 1749, 1371, 1223, 1106, 1054 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.35 (d, $J$ = 8.2 Hz, 2H, Ar-H), 7.11 (d, $J$ = 8.2 Hz, 2H, Ar-H), 5.48 (dd, $J$ = 3.3, 1.5 Hz, 1H, H-2), 5.32 (d, $J$ = 1.5 Hz, 1H, H-1), 5.29 (dd, $J$ = 9.9, 3.3 Hz, 1H, H-3), 5.12 (t, $J$ = 9.9 Hz, 1H, H-4), 4.35 (dq, $J$ = 9.9, 6.2 Hz, 1H, H-5), 2.32 (s, 3H, Ar−$CH_3$), 2.12 (s, 3H, Ac), 2.07 (s, 3H, Ac), 2.00 (s, 3H, Ac), 1.23 (d, $J$ = 6.2 Hz, 3H, H-6); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 170.0 (C), 169.9 (C), 138.2 (C), 132.4 (CH), 129.9 (CH), 129.3 (C), 86.0 (CH), 71.2 (CH), 71.1 (CH), 69.3 (CH), 67.6 (CH), 21.1 ($CH_3$), 20.8 ($CH_3$), 20.8 ($CH_3$), 20.6 ($CH_3$), 17.3 ($CH_3$); HRMS (FAB, $MH^+$) calcd for $C_{19}H_{25}O_7S$ 397.1321, found 397.1332. Anal. Calcd for $C_{19}H_{24}O_7S$: C, 57.56; H, 6.10. Found: C, 57.59; H, 6.11.

***p*-Methylphenyl 6-deoxy-2,3,4-tri-*O*-acetyl-1-thio-β-L-mannopyranoside 14β:** $[\alpha]^{29}_D$ +35 (*c* 1.0, $CHCl_3$); mp 90−91 °C; IR ($CHCl_3$) 2982, 2936, 2866, 1749, 1493, 1371, 1249, 1222, 1090, 1052 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.40 (d, $J$ = 8.2 Hz, 2H, Ar−H), 7.12 (d, $J$ = 8.2 Hz, 2H, Ar−H), 5.63 (dd, $J$ = 3.5, 1.0 Hz, 1H, H-2), 5.10 (t, $J$ = 9.9 Hz, 1H, H-4), 4.98 (dd, $J$ = 9.9, 3.5 Hz, 1H, H-3), 4.82 (d, $J$ = 1.0 Hz, 1H, H-1), 3.51 (dq, $J$ = 9.9, 6.2 Hz, 1H, H-5), 2.33 (s, 3H, Ar−$CH_3$), 2.20 (s, 3H, Ac), 2.03 (s, 3H, Ac), 1.97 (s, 3H, Ac), 1.30 (d, $J$ = 6.2 Hz, 3H, H-6); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 170.3 (C), 170.2 (C), 169.8 (C), 138.4 (C), 132.7 (CH), 129.9 (CH), 129.5 (C), 85.8 (CH), 74.9 (CH), 71.8 (CH), 71.0 (CH), 70.2 (CH), 21.1 ($CH_3$), 20.8 ($CH_3$), 20.6 ($CH_3$), 20.6 ($CH_3$), 17.7 ($CH_3$); HRMS (FAB, $MH^+$) calcd for $C_{19}H_{25}O_7S$ 397.1321, found 397.1324. Anal. Calcd for $C_{19}H_{24}O_7S$: C, 57.56; H, 6.10. Found: C, 57.96; H, 6.30.

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**Supporting Information Available:** $^1H$ NMR spectra of all the per-*O*-acetates (**2**, **4**, **6**, **8**, and **10**) and thioglycosides (**11**−**15**) and $^{13}C$ NMR and 2D NMR spectra for compounds **14**α and **14**β. This material is available free of charge via the Internet at http://pubs.acs.org.

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