

Synthesis of 2, 6-Di-*O*-acetyl Sucrose by Regioselective Acetylation with Dibutyltin Oxide

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Abstract: 2,6-Di-*O*-acetyl sucrose was regioselective synthesized by using dibutyltin oxide in about 60% yield. The structure of acetyl derivative was elucidated by ^1H NMR, ^{13}C NMR, 2D-NMR and MS spectral data.

Keyword: Dibutyltin oxide, 2,6-di-*O*-acetyl sucrose, regioselective, acetylation.

Organotin compounds have been used as regioselective oxidation, acetylation, deacetylation and alkylation reagent of glucose derivatives^{1,2}. The various mono- and di-*O*-ester derivatives of glucose have been synthesized³ by using dibutyltin oxide as regioselective acetylation reagent.

In the course of our studies towards the synthesis of sucrose derivatives including sucralose⁴, it was found dibutyltin oxide also could be used as a good regiospecific reagent of sucrose's diacetylation. Using dibutyltin oxide and acetic anhydride to selectively acetylate sucrose, 2, 6-di-*O*-acetyl sucrose **1** could be obtained in about 60% yield, determined by HPLC. 2, 6-Di-*O*-acetyl sucrose **1** could be used as chiral resource to synthesize some kinds of medicines and detergent additives.

The high resolution FAB mass spectrum data of compound **1** indicated its molecular formula to be $\text{C}_{16}\text{H}_{26}\text{O}_{13}$. The data of ^1H NMR and ^{13}C NMR indicated that compound **1** has two acetyl groups. By comparison of the ^1H NMR and ^{13}C NMR data of compound **1** with that of sucrose, the C-6(δ 63.6) and C-2(δ 72.5) shift to lower field by 2.7 and 0.5 ppm, respectively. And at the same time H-6(δ 4.32, 4.20) and H-2(δ 4.66) shift to lower field by 0.57, 0.47 and 1.18 ppm, respectively. By comparison of the ^1H NMR and ^{13}C NMR data of compound **1** with that of sucrose-6-acetate, C-2(δ 72.5) and H-2(δ 4.66) shift to lower field by 0.9 and 1.10 ppm, respectively. All the assignments were confirmed by 2D-NMR spectra. Therefore, we concluded that the structure of compound **1** is 2, 6-di-*O*-acetyl sucrose derivative, as shown in **Scheme 1**.

The relationship of yield of the 2,6-diacetyl sucrose derivative and the amount of dibutyltin oxide was investigated. When the amounts of dibutyltin oxide varied from 1.1 eq to 2.2 eq, generally, the difference of the yields was no apparent; except, when the amounts of dibutyltin oxide was 1.8 eq., the yield of **1** was highest(**Table 1**). It was

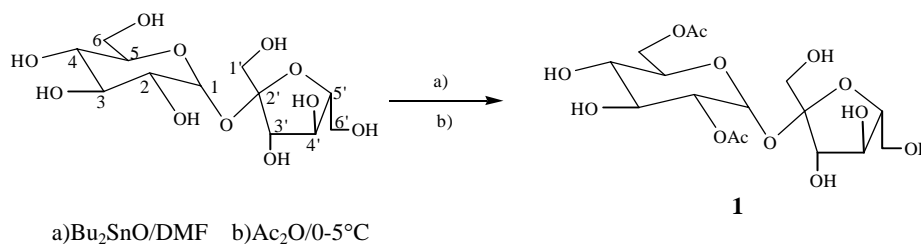
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deduced that some kind of complex has been formed through Sn-O chelation in the process of this reaction to increased the nucleophilic reactivity of C2-OH and C6-OH as shown in **Scheme 1**.

Table 1 Amounts of dibutyltin oxide and the yields of compound **1**

Amounts of dibutyltin oxide (mol eq.)	Yields of compound 1 (%)
1.1	50
1.5	53
1.8	60
2.0	55
2.2	49

Scheme 1



In summary, we found that dibutyltin oxide can catalyze regioselective acetylation of sucrose efficiently. The method is very useful in sucrose chemistry. Further investigations are now underway in our laboratory.

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References and Notes

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5. Compound **1** $^1\text{H NMR}$ (400MHz, D_2O) δ ppm: 5.37(d, 1H, $J=3.7\text{Hz}$), 4.59(dd, 1H, $J=3.7, 10.1\text{Hz}$), 4.26(dd, 1H, $J=1.8, 12.2\text{Hz}$), 4.13(dd, 1H, $J=5.2, 12.3\text{Hz}$), 4.07(d, 1H, $J=8.8\text{Hz}$), 3.94(m, 1H), 3.86(t, 1H, $J=8.6\text{Hz}$), 3.81(t, 1H, $J=9.7\text{Hz}$), 3.74(m, 1H), 3.66(t, 2H, $J=3.4\text{Hz}$), 3.44(m, 2H), 3.36(t, 1H, $J=12.5\text{Hz}$), 2.09(s, 3H), 2.05(s, 3H); HRMS(FAB): calcd. for $\text{C}_{16}\text{H}_{26}\text{NaO}_{13}$ (pos., M^+Na) 449.1271, found: 449.1274.

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