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TBAF Effects 3,6-Anhydro Formation from 6-*O*-Tosyl Pyranosides

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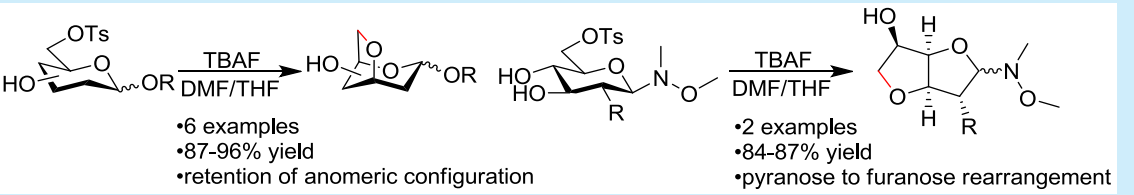

ABSTRACT: 3,6-Anhydro sugars are common structures in algal polysaccharides and occur in the furanodictine and sauropunol natural products. We have found that treatment of 6-*O*-tosylpyranosides with tetrabutylammonium fluoride provides a mild, high-yielding synthesis of 3,6-anhydro sugars. Using *O*-glycoside substrates, 3,6-anhydropyranosides are isolated and the use of *N*,*O*-dimethyl hydroxylamine glycosides yields 3,6-anhydrofuranosides. Applying this approach, concise synthetic routes to several 3,6-anhydro sugar natural products are reported, including furanodictine A and sauropunols A−D.

3,6-Anhydro sugars contain an intramolecular ether bridging the C-3 hydroxyl and C-6. This feature dramatically alters the sugar's conformation and reactivity by locking the pyranosides into the $^1C_4$ chair.[1] 3,6-anhydro sugars are found in red algae polysaccharides, including agarose and many of the carrageenans (Figure 1), where their conformation is important in

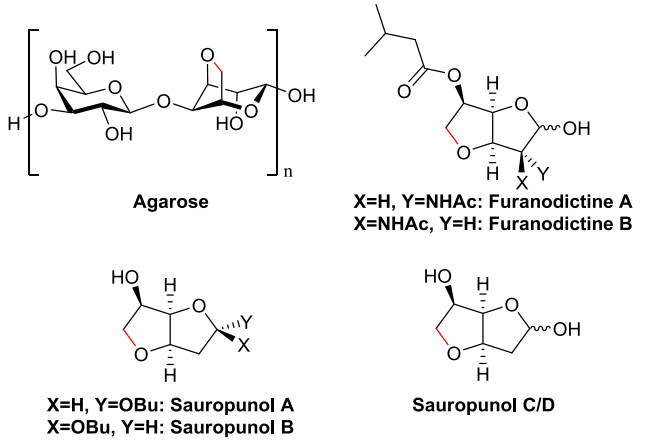

Figure 1. Bioactive, naturally occurring 3,6-anhydrohexosides.

mediating the helical character of the polysaccharide and its gelation.[2] The first nonalgal 3,6-anhydro sugar containing natural products discovered were the amino sugar analogues furanodictines A and B.[3] These were isolated from the slime mold *Dictyostelium discoideum* and found to induce neuronal differentiation in rat PC-12 cells.[3] More recently, a series of 3,6-anhydro-2-deoxyglucose derivatives were discovered, sauropunols A−D.[4,5] These natural products were isolated from the Chinese medicinal plant *Sauropus rostratus* and were found to have anti-inflammatory activity.[6] In addition, 3,6-anhydrogalactose has been identified as a potential anticariogenic agent, inhibiting the growth of *Streptococcus mutans* at lower concentrations than xylitol.[7] The properties of these compounds have attracted significant interest in their efficient preparation.

3,6-Anhydro sugars are usually synthesized by activating the sugar's C-6 hydroxyl as a leaving group followed by treatment with base.[8] Most commonly, 6-*O*-tosyl derivatives have been generated and treated under strongly basic conditions such as sodium hydroxide in refluxing ethanol[9−11] or sodium methoxide in refluxing methanol.[3] Alternative chemistries using different leaving groups, including a mesylate,[12] phosphinium,[13−15] cyclic sulfite and sulfate,[16] 5,6-carbonate,[17] or triflate and similar basic cyclization conditions have been reported.[18] The reaction of selectively benzylated sugars with DAST sometimes gives 3,6-anhydro side products, though the scope of this is limited and hard to rationalize.[19−21] A single report of a Lewis acid promoted 3,6-anhydro cyclization of diacetone glucose has been documented in low yield.[22] Overall, the existing procedures suffer limitations including low to moderate yields, limited scope, or the requirement of multiple protecting group manipulations.

Tetrabutylammonium fluoride (TBAF) has proven to be a versatile reagent for organic synthesis. Though more commonly employed as an organic soluble fluoride source, it has also been useful as a base for promoting a variety of

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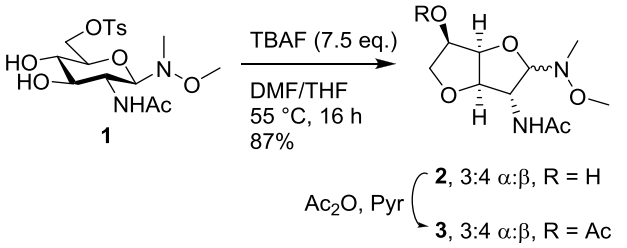
transformations.[23] The basicity of fluoride is highly variable, depending on its counterion, the nature of the solvent, and the amount of water present.[24] TBAF often has greater reactivity than alkali metal fluorides due to the weakly coordinating nature of its tetrabutylammonium counterion and its high organic solubility. However, though further drying is possible, TBAF is only commercially available in its hydrated form.[25] Fluoride forms strong hydrogen bonds, so this water content greatly attenuates the reagent's nucleophilicity and basicity.

Attempted preparation of 6-fluoro-6-deoxy-GlcNAc by treating tosylate **1** with undried commercial TBAF in DMF/THF (Scheme 1) led to an excellent yield (87%) of the unexpected 3,6-anhydrofuranoside **2**. The structure of **2** was verified by acetylation which resulted in a large downfield shift in the H-5 absorbance in the ^{1}H NMR spectrum of product **3**, consistent with acetylation of the C-5 hydroxyl and a furanose ring configuration. An X-ray crystal structure of **3** was acquired to unambiguously confirm its identity (Figure 2). Surprised by the simplicity, high yield, and mild conditions for 3,6 anhydro sugar formation in comparison with reported methods,[9−22] the scope of the reaction was explored.

Scheme 1. Unexpected 3,6-Anhydro Cyclization of C6-Tosyl GlcNAc 1 Promoted by TBAF



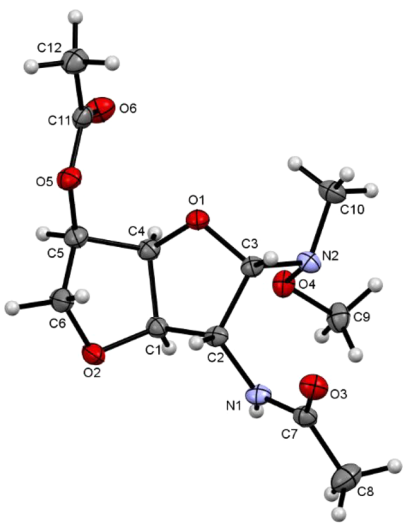


Figure 2. X-ray crystal structure of α-anomer **3** (CCDC deposition no. 1972383).

To understand the requirements for high yielding intramolecular ether formation, we examined the reaction conditions (Table 1). Using DMF as a cosolvent was found to be beneficial, giving a slight improvement over THF alone. Attenuating the reactivity of TBAF by buffering it with acetic acid or adding additional water (20 equiv) gave inferior yields.

Table 1. Screen of Reaction Conditions To Promote 3,6-Anhydro Cyclization of Tosylate 1[a]

base or additive	solvent	temp (°C)	time (h)	yield (%)
TBAF[e]	DMF/THF	55	16	83[b] (87)[b,c]
TBAF[e]	THF	55	16	69[b]
TBAF[e], H_2O[f]	THF	55	16	trace[d]
TBAF[e], AcOH[g]	THF	55	16	trace
CsF[e]	DMF/THF	55	16	trace
CsF[e], H_2O[f]	DMF/THF	55	16	0
Et_3N[e]	DMF/THF	55	16	0
Pyr[e]	DMF	50	24	0
	Pyr	50	22	trace
	Pyr	80	24	0
TBABr[e]	Pyr/THF	50	24	trace
CsF[e]	Pyr/THF	50	24	trace
TBAF[e]	Pyr/THF	50	24	65[b]
NaOMe[h]	MeOH	65	3	0

[a]All reactions were performed on 0.1 mmol scale unless otherwise stated. [b]Isolated yield. [c]Reaction at 1 mmol scale. [d]Yield <10% by TLC. [e]Using 7.5 equiv. [f]Using 20 equiv. [g]Using 3.75 equiv. [h]At 0.3 M.

Furthermore, substituting CsF for TBAF gave poor conversion. We noted that the CsF fully dissolved upon heating, so reduced solubility was unlikely the source of the reduced conversion. We hypothesized that the water content of commercial TBAF may be beneficial for the transformation but, to the contrary, adding water (20 equiv) to the CsF reaction reduced the yield to zero. Other mild bases including triethylamine and pyridine also failed to give appreciable product formation. Similarly, employing TBABr or CsF as additives in a pyridine/THF solvent system failed to enhance the yield of product, though TBAF gave a dramatic improvement. Taken together, these results suggest that both components of the fluoride/tetrabutylammonium ion pair are required for efficient 3,6 anhydro sugar formation.

Previous reports of 3,6-anhydro GlcNAc formation treated methyl 2-acetamido-2-deoxy-6-*O*-tosyl-α-D-glucopyranoside with sodium methoxide in refluxing methanol.[3] For comparison, we subjected tosylate **1** to these conditions. Substantial decomposition was observed and the desired 3,6-anhydro product could not be isolated, supporting the mild TBAF promoted condition as a useful alternative to the reported synthetic strategy.

We next explored the scope of this transformation to determine if tosylate **1** was unusually susceptible to 3,6-anhydro cyclization or if TBAF was a general reagent for formation of these fused ring systems. We found that the TBAF-based conditions gave a range of the 3,6-anhydrohexoses in high yield, including glucose, *N*-acetyl-glucosamine, 2-deoxyglucose, mannose, and galactose configurations (Table 2). Both α- and β-*O*-glycoside substrates consistently gave pyranose products with retention of anomeric configuration. Intriguingly, *N,O*-dimethyl hydroxylamine glycoside substrates (**1** and **5**) rearranged to the 3,6-anhydrofuranose sugars. It is known that the methyl glycosides of 3,6-anhydroglucose, 2-deoxyglucose, and mannose undergo a rapid pyranose to furanose rearrangement upon treatment with strong acids.[9−11] It is likely that the lower energy barrier for ring opening *N,O*-dimethyl hydroxylamine *N*-glycosides relative to *O*-glycosides allows the facile rearrangement of these substrates. Consistent with low barrier ring opening, we observed that *N,O*-dimethyl

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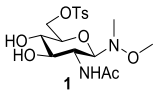
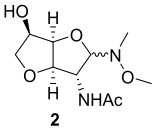
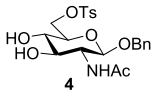
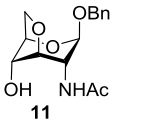
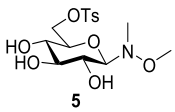
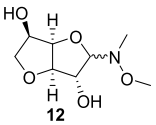
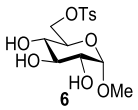
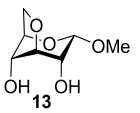
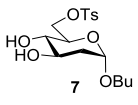
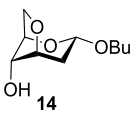
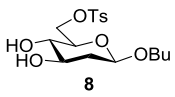
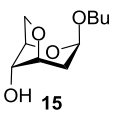
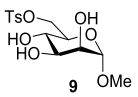
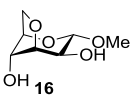
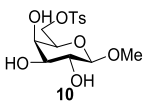
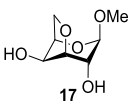
Table 2. Substrate Scope for TBAF-Promoted 3,6-Anhydro Cyclization[a]

reactant	product	isolated yield (%)
 1	 2	87 (3:4 α/β)
 4	 11	95
 5	 12	84 (1:3 α/β)
 6	 13	94
 7	 14	92
 8	 15	96
 9	 16	87
 10	 17	93

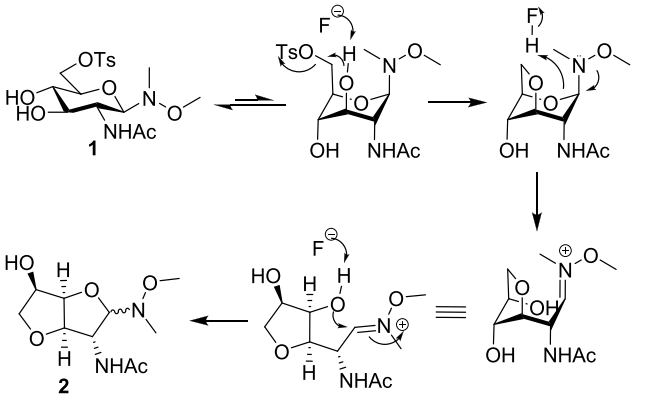
[a]Conditions: 7.5 equiv of TBAF, 2:1 DMF/THF, 55 °C, 16−20 h.

hydroxylamine glycoside **3** undergoes mutarotation in neutral MeOD at rt over several days (Figure S1).

We hypothesize that the pyranose to furanose rearrangement of substrates **1** and **5** occurs rapidly after 3,6-anhydro formation (Scheme 2) as 3,6-anhydropyranose intermediates could not be detected in the reactions. Furthermore, the *O*-glycoside and *N,O*-dimethyl hydroxylamine *N*-glycoside substrates required similar reaction conditions for quantitative formation of 3,6-anhydro product. If the reactions of **1** and **5** proceeded through an alternative, lower energy mechanism, we would expect completion under milder conditions, suggesting that ring opening preceding 3,6-anhydro cyclization for these substrates is unlikely.

Curious if free hemiacetals would also be viable substrates for our synthetic method, we subjected unprotected 6-*O*-tosyl-D-glucopyranoside to the TBAF reaction condition. In this case, no 3,6-anhydro product was obtained. Partial degradation of the sugar occurred and a low yield of 1,6-anhydro product was afforded. Thus, protection of the anomeric center is required for 3,6-anhydro formation.

Scheme 2. Proposed Mechanism for 3,6-Anhydro Cyclization and Furanose Rearrangement of Tosylate 1



Conveniently, this strategy for 3,6-anhydro sugar formation minimizes protecting group manipulations as selective tosylation of the C-6 hydroxyl can be accomplished in moderate to high yields. To demonstrate the utility of the strategy, the total synthesis of several 3,6-anhydro sugar natural products were completed.

In previous reports, furanodictine A has been synthesized from methyl 2-acetamido-2-deoxy-α-D-glucopyranoside.[3] Selective 6-*O*-tosyl formation and intramolecular ether formation proceeded in a combined 38% yield. Though the methyl glycoside survives the 3,6-anhydro cyclization, the hydrolysis of the methyl glycoside requires protecting group manipulations later in the synthesis. Another total synthesis of furanodictine A generated the 3,6-anhydro cycle via degrading GlcNAc in boiling borate buffer, but this gave a low yield and required a complex purification.[26] Finally, other routes have been developed from alternative starting materials including 2,3,5-tri-*O*-benzyl-β-D-arabinofuranose[27] and D-glucuronolactone.[28] However, these methods required 17 and 18 steps, respectively.

We found that furanodictine A could be accessed from GlcNAc in five steps with an overall yield of 49%. *N*-Acetyl glucosamine was protected as the *N,O*-dimethyl hydroxylamine glycoside under aqueous conditions, giving **18**.[29] Next, selective tosylation of the C-6 hydroxyl in cold pyridine gave **1**. Treating the tosyl ester **1** with TBAF in DMF/THF afforded 3,6-anhydrofuranoside **2** in 59% yield over two steps. With the C-5 hydroxyl unprotected acylation proceeded smoothly with isovaleric anhydride in pyridine, giving **19**. The *N,O*-dimethyl hydroxylamine glycoside was selectively cleaved in 4:1 AcOH/H_2O at room temperature, yielding furanodictine A (**20**) (Scheme 3).

We also applied our synthetic approach toward the total synthesis of sauropunols A−D. In previously reported routes to sauropunols A and B, the furanoside ring was set via the isolation of butyl 2-deoxy-D-glucofuranoside in low yield from a Fischer glycosidation.[18] The 3,6-anhydro cyclization was furnished via an interesting concomitant loss of a 3-*O*-*p*-methoxybenzyl ether and intramolecular cyclization of butyl 2-deoxy-6-*O*-trifluorosulfonyl-3,5-di-*O*-*p*-methoxybenzyl-α-D-glucofuranoside. An improved synthesis of sauropunols A−D was more recently reported which proceeds through 1,2-isopropylidene-α-D-glucofuranose to overcome the low-yielding Fischer glycosidation.[6] Lastly, a short six-step asymmetric synthesis from divinyl carbinol was reported.[30]

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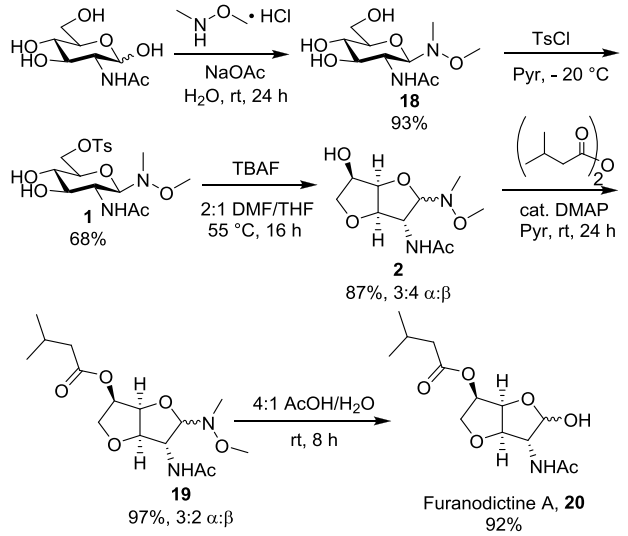
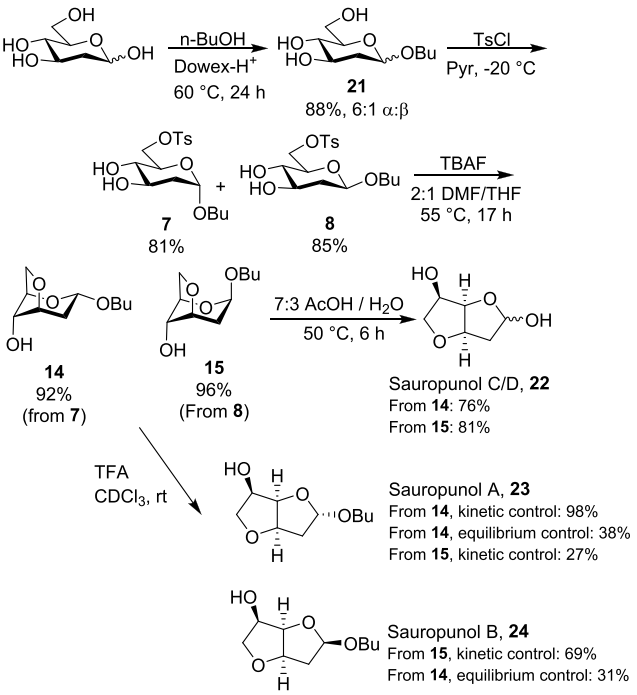
Scheme 3. Synthesis of Furanodictine A from *N*-Acetylglucosamine



We achieved a concise synthesis of sauropunols A−D (Scheme 4), starting from 2-deoxyglucose, in four steps giving 58%, 25%, and 51% overall yield of sauropunols A, B, and C/D, respectively. No protecting groups were required.

Scheme 4. Synthesis of Sauropunols A−D



A Fischer glycosylation of 2-deoxyglucose with *n*-butanol gave a mixture of α and β butyl pyranosides (**21**). Next, selective tosylation at the C-6 hydroxyl in cold pyridine yielded chromatographically separable butyl glycosides **7** and **8**. Reaction of tosyl esters **7** and **8** with TBAF in DMF/THF gave 3,6-anhydropyranose products **14** and **15** in high yield. Sauropunols C/D **22** were prepared from **14** or **15** by hydrolysis of the butyl glycoside in 7:3 $AcOH/H_2O$. Sauropunols A and B (**23** and **24**) were obtained by acid-catalyzed rearrangement of **14** and **15** to their respective furanose forms. Remarkably, treating α-pyranose **14** with trace TFA in dry $CDCl_3$ yielded solely α-furanose product with complete selectivity. The β-pyranoside **15** rearranged with less selectivity, giving only partial retention of anomeric configuration (2:5 α/β). This imperfect selectivity and the low proportion of β-anomer from the Fischer glycosylation restricted the amount of sauropunol B available. However, similar to observations made by Markovič et al.,[30] we find that the equilibrium ratio between sauropunols A and B in $CDCl_3$/TFA is roughly 3:2. Taking advantage of this, additional amounts of sauropunol B could be afforded by treating α-pyranose **14** with excess TFA in $CDCl_3$ and allowing the mixture to equilibrate.

In conclusion, we have identified TBAF as a gentle and efficient base for cyclizing C6-*O*-tosyl pyranosides into 3,6-anhydro sugars. The advantages of this approach were demonstrated through short, high-yielding total syntheses of furanodictine A and sauropunols A−D. We anticipate that our methodology will expediate further synthesis and study of the chemical and biological properties of this interesting class of sugar derivatives.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00045.

Experimental details and spectroscopic and analytical data for all compounds (PDF)

Accession Codes

CCDC 1972383 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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