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Note

One-pot SSA-catalyzed β-elimination: an efficient and inexpensive protocol for easy access to the glycal of sialic acid

Erickson M. Paragas, I. Abrrey Monreal, Chris M. Vasil, Jonel P. Saludes *

Department of Chemistry, Washington State University, Pullman, WA 99164, USA

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ABSTRACT

Neu5Ac2en1Me per-*O*Ac, the fully protected glycal of sialic acid, is a key intermediate in the discovery of therapeutics and diagnostics, including anti-influenza drugs and proteolysis resistant peptidomimetic foldamers. The synthesis of this sialic acid derivative, however, still relies on standard sugar chemistry that utilizes multi-step methodologies. Herein we report a facile and highly efficient microwave-assisted preparation of Neu5Ac1Me using silica sulfuric acid (SSA) as solid-supported acid catalyst that is one- to two-orders of magnitude faster than standard procedures. We also describe the microwave-assisted and SSA-catalyzed one-pot, rapid, solvent free reaction that combines both peracetylation and β-elimination reactions in one step to generate the glycal from Neu5Ac1Me. We coined the term One-pot SSA-catalyzed Technology for β-Elimination Protocol (OneSTEP) to describe this least laborious, most efficient, and practical preparation to date of Neu5Ac2en1Me per-*O*Ac in terms of yield, time, reagent cost, and waste generation.

Sialic acid (*N*-acetylneuraminic acid; Neu5Ac **1**) is a sugar amino acid found as the terminal monosaccharide of many glycoconjugates on mammalian cell surfaces. It is responsible for a variety of vital biological processes including intercellular communication and adhesion, viral receptor recognition, and pathophysiological processes.[1,2] These properties have driven the investigation of Neu5Ac and its derivatives for use in a wide range of diagnostic and chemotherapeutic applications, including as chemical probes[3] and antiviral agents such as the anti-influenza drug 4-guanidino-Neu5Ac2en (Zanamivir, **6**).[2,4] Specifically, there is a great deal of interest in Neu5Ac derivatives related to **6** as influenza strains resistant to currently available antivirals have emerged, sparking increased interest in better neuraminidase inhibitors many of which are based on the Neu5Ac2en core (**7**).[5] Further, as part of our continuing research program on advancing sugar amino acid derivatives like **10** as building blocks for peptide foldamers,[6–8] we are interested in developing expedient and simple methods to access **7** (Fig. 1).

One of the most common intermediates of Neu5Ac derivatives is per-*O*-acetylated 2-deoxy-2,3-dehydro-*N*-acetylneuraminic acid methyl ester (Neu5Ac2en1Me per-*O*-acetate **9**). In general, the synthesis of **9** is achieved in 2 to 3 steps from Neu5Ac1Me (**2**) and traditionally requires several days to complete (Scheme 1).[6,9–11] Many efforts have gone toward making Neu5Ac derivatives more accessible for large-scale use and several groups have reported microwave-assisted techniques that significantly reduced the time required to access these intermediates and allowed the use of more benign reagents.[12–16] Considering that both are esterification reactions, we hypothesized that both processes can be efficiently accomplished by utilizing solid supported acid catalyst coupled with microwave irradiation. We further hypothesized that the C-2 acetate of **3** is a sufficiently good leaving group that, under acidic and microwave heating conditions, we could induce β-elimination to afford **9**. Herein, we report a highly efficient synthesis of **2** using silica sulfuric acid (SSA) as catalyst. We also describe the preparation of **9** from **2** using SSA, and we coined the term OneSTEP (One-pot SSA-catalyzed Technology for β-Elimination Protocol) to describe this process that gave rise to peracetylation and β-elimination reactions to afford **9** in a simple, one-pot process.

Traditionally, esterification of **1** to form **2** is done using acid catalysis, which can be achieved using a myriad of acid catalysts including trifluoroacetic acid (TFA) and resin-bound acids such as Dowex 50Wx8, a sulfonic acid functionalized styrene–divinylbenzene resin.[15,17–19] The use of acidic resin is advantageous because it is reusable and post-reaction work-up only requires filtration. To this end, Von Itzstein recently reported a rapid, microwave-assisted synthesis of **2** using Dowex 50Wx8 resin, but this method yields varying results dependent on resin age and batch variability, requiring extensive washing and resin conditioning followed by

* Corresponding author. Tel.: +1 509 335 1144; fax: +1 509 335 8867.
E-mail address: jonel.saludes@wsu.edu (J.P. Saludes).
URL: http://www.saludeslab.org

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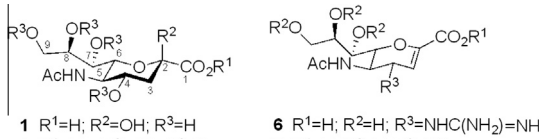
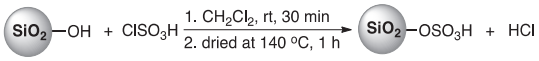


1 R^1=H; R^2=OH; R^3=H
2 R^1=Me; R^2=OH; R^3=H
3 R^1=Me; R^2=OAc; R^3=Ac
4 R^1=Me; R^2=Cl; R^3=Ac
5 R^1=Me; R^2=OMe; R^3=H
6 R^1=H; R^2=H; R^3=NHC(NH_2)=NH
7 R^1=H; R^2=H; R^3=OH
8 R^1=H; R^2=H; R^3=N_3
9 R^1=Me; R^2=Ac; R^3=OAc

Figure 1. Sialic acid (**1**) and its synthetic analogues.

storage under inert conditions.[15] In our search for an alternative and inexpensive solid-supported acid catalyst, we found a potential candidate in the SSA used by Torkian and co-workers.[20] We then explored the utility of SSA in catalyzing esterification of **1**. SSA has been shown as an efficient catalyst for esterification and acetylation of fatty acids, aldehydes, and sugars,[17,21,22] including glucuronic[23] and galacturonic[24] acids, but its utility has not been applied to sialic acids. SSA is easily prepared by treating a slurry of chromatography grade silica gel in CH_2Cl_2 with chlorosulfonic acid (Scheme 2).[20] It can also be prepared by incipient wetness impregnation of silica gel 60 with aqueous solution of sulfuric acid.[25] SSA is reusable after an EtOH wash and is insensitive to air and moisture.[21]

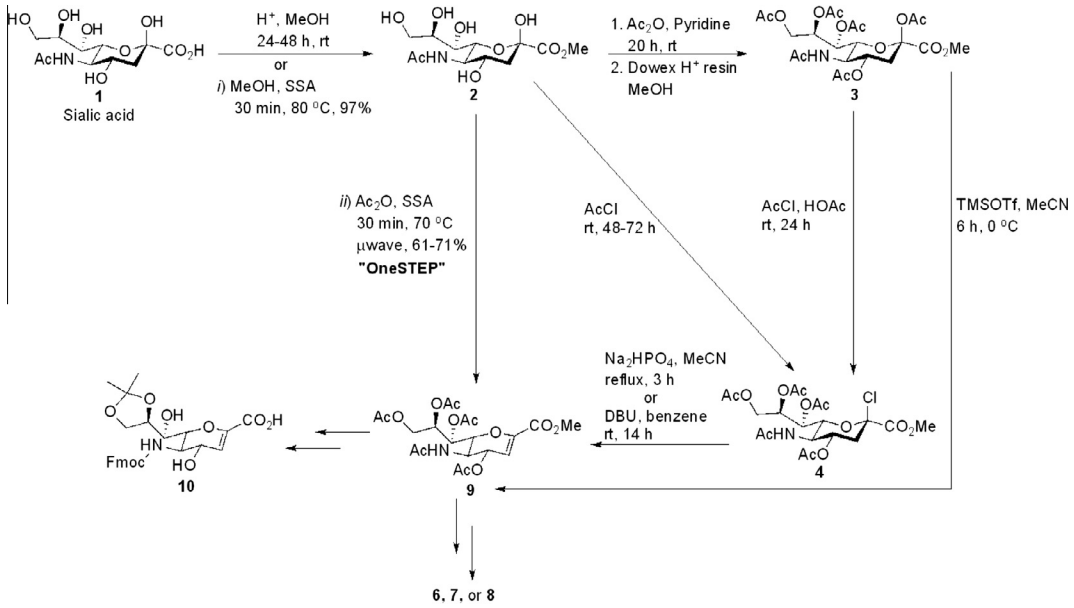
We began by investigating the efficiency of SSA to catalyze the Fischer esterification of **1** and prepared this catalyst[20] using chromatography grade silica gel 60. The sugar (0.05 g, 0.16 mmol) was treated with 1.0 mL MeOH and SSA (0.1–1.0 equiv, Table S1, Supplementary information) followed by microwave-assisted heating at variable power and a fixed temperature of 80 °C for 30 min[14] using Biotage Initiator$^+$ SP Wave reactor (Scheme 1, i). Completion of the reaction was monitored by thin layer chromatography (TLC) using 3:1 CH_2Cl_2-MeOH and the disappearance of starting material and formation of **2** (R_f = 0.36), which indicated complete consumption of **1** after 30 min. The mixture was filtered and the SSA washed with EtOH and dried in the oven for recycling. We analyzed the filtrate by ESI-MS, which confirmed the formation of **2** (m/z 346.2, $[M+Na]^+$, Fig. S1, Supporting information). We also observed a weak m/z 360.1 ($[M+Na]^+$) peak that is suggestive of the formation of **5**. ^{1}H NMR analysis showed a broad singlet at δ 3.78



Scheme 2. Preparation of SSA.

(3H) corresponding to OMe of the methyl ester. Integration of H-3_{eq} resonance peaks for **2** (δ 2.26) and **5** (δ 2.34) indicated the former as the major product (96%). The formation of **5** is not surprising since it was previously found as a minor product during esterification of **1** under microwave irradiation conditions.[15,14] In an attempt to further optimize this reaction, we varied both the reaction temperature (60–100 °C) and time (20–30 min), but found the above-mentioned conditions sufficient and optimal (Tables S2 and S3). We translated this protocol to the gram scale synthesis of **2** in 97% isolated yield after column chromatography. To investigate if microwave irradiation is required to effect Fischer esterification of **1**, we treated 50 mg (0.16 mmol) of the sugar with 0.2, 0.4, 0.8, and 1 equiv of SSA, allowed the reaction to proceed at room temperature, and monitored the reaction by TLC. We found the complete conversion of **1** to **2** after 24 h using 1 equiv of SSA without the formation of **5**. Subsequently, the reaction went to completion at 48 h in the presence of 0.4 and 0.8 equiv SSA while the 0.2 equiv treatment showed unreacted starting materials even after 48 h. Based on these observations, we scaled up the reaction and treated 1.0 g (3.2 mmol) of **1** with 1 equiv SSA, allowed the reaction to proceed at room temperature, monitored by TLC at various time points, and found the reaction complete in 16 h as indicated by TLC and MS (m/z 346.0944 $[M+Na]^+$], Fig. S2). This demonstrates that SSA is an excellent alternative to expensive resin-supported acid catalysts for standard Fischer esterification of Neu5Ac, albeit at a significantly slower kinetics than with microwave irradiation.

Because of the synthetic importance of **9**, several methods have been developed to expedite or simplify its preparation, including β-elimination of **3** using TMSOTf or $BF_3{\cdot}Et_2O$,[26,27] β-elimination of **4** catalyzed by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)[9] or Et_3N,[28] oxidation[29] or elimination[30] of thioglycoside of **1**, and treatment of **4** with Na_2HPO_4 in refluxing acetonitrile for 3 h.[31] Although the last method gave an almost quantitative yield, the preparation of **4** using neat acetyl chloride requires several days



Scheme 1. Standard routes for the preparation of **9** and our SSA-catalyzed methyl esterification (i) and 'OneSTEP' strategy (ii).

to complete.[10,30] In an attempt to cut down on synthetic steps, Gervay-Hague and co-workers performed a one-pot synthesis using pyridine and Ac_2O to afford **9** in 21% yield.[32] Further attempts to improve access to **9** by the same group led to the use of flash vacuum pyrolysis (FVP) at 390–420 °C.[33] This first report of FVP use in carbohydrate manipulation yielded 93% of **9** from **3**. However, the two-step preparation of precursor **4** coupled with an extremely high reaction temperature and a cumbersome homemade apparatus makes FVP intractable for routine large-scale manipulation of sialic acid derivatives.

The vapor phase β-elimination of C-2 acetate could be thermally induced because of the inherent reactivity of C-2 acetate as well as the constrained ring geometry of **3**, placing the acetate oxygen in close proximity to H-3equiv.[27] Moreover, Mong and co-workers investigated the acid-catalyzed peracetylation of **2** using *p*-toluene sulfonic acid and excess Ac_2O at 45 °C yielding **3** (80%) and 5% of **9**.[34] Microwave-assisted heating in the presence of an acid catalyst, therefore, may offer a simple and expedient solution phase β-elimination protocol. To test our hypothesis that SSA can catalyze the β-elimination at C-2, we investigated the direct synthesis of **9** from **2** using our previous microwave-assisted peracetylation conditions as starting point.[14] A mixture of **2** (0.05 g, 0.16 mmol) and SSA (0.05 g, 0.16 mmol, 1 equiv) was treated with excess Ac_2O (6.6 mmol, 40 equiv) and microwave irradiated for 2 h at 80 °C (Scheme 3). SSA was recovered by centrifugation and the reaction mixture titrated with Na_2CO_3 to pH = 10, then extracted with CH_2Cl_2. TLC analysis using 2:1 toluene–Me_2CO showed two spots (Rf = 0.15 and 0.23), the latter spot being UV-active under 254 nm lamp. Upon MS analysis of the crude product, we observed m/z = 556.2 and 496.2, suggesting the formation of **3** and a product from the loss of acetate (−60 amu). To our delight, ^{1}H NMR analysis revealed two doublets corresponding to H-3 olefinic protons that we tentatively assigned to **9** (δ 6.01, 1H, d, $J_{3,4}$ = 3.1 Hz) and **12** (δ 6.22, 1H, d, $J_{3,4}$ = 5.6 Hz). We purified the mixture by RP C_{18} HPLC and found three major peaks at t_R = 33.2, 36.2, and 37.4 min corresponding to **3**, **9**, and **12** with relative peak area integration of 13%, 73%, and 14%, respectively. We also found the ^{1}H NMR spectra of **3** and **9** to be consistent with the literature.[14,28] The identity of **12** was confirmed by a combination of MS and 2D-NMR (COSY and NOESY, Figs. S10 and S11). The formation of **12** during β-elimination is not unexpected as Flashner[35] and Kok[36] previously found that sulfuric acid-catalyzed acetylation of **3** could generate allyl or oxazolinium cation that leads to epimerization at C-4.

We attempted to separate **9** and **12** by flash chromatography but were unable to do so. We then sought to optimize the synthesis of **9** by preventing C-4 epimerization. We began by reducing the reaction temperature to 70 °C while varying the time. We found that prolonged heating beyond 30 min does not significantly improve the yield of **9** and still leads to epimerization (Table S4). We proceeded to vary the amount of SSA and fixed the reaction temperature and time. We found **2** treated with 0.1 equiv of SSA to be optimum giving a crude product devoid of **12**, while increasing amounts of SSA led to further epimerization (Table 1 and Fig. S12). Using this simple, inexpensive, one-pot process that we now call OneSTEP, we scaled up the reaction to 1.0 g (3.1 mmol) of **2** to give **9** in 65% isolated yield after column chromatography.

In conclusion, we have developed a microwave-assisted SSA catalyzed method for accessing Neu5Ac1Me (**2**) and the glycal of sialic acid called Neu5Ac2en1Me per-*O*-acetate (**9**). This protocol is one- to two-orders of magnitude faster than standard procedures and uses inexpensive, benign, and readily available reagents. We believe that the streamlined, one-pot, solvent-free method described herein is the least laborious, most efficient, and practical preparation of **9** to date in terms of yield, time, reagent cost, and waste generation. With the continuing demand for better neuraminidase inhibitors and the potential biomedical application of sialic acid foldamers, this method offers convenient access to important intermediates for sialic acid chemistry.

Table 1
Optimization of microwave-assisted synthesis of **9** at 70 °C for 30 min

Entry	Amount of **2**, mg	SSA, mg (equiv)	Relative peak area** (%)		
			3	**9**	**12**
1	50	5 (0.10)	39	61	nd*
2	50	12.5 (0.25)	34	63	4
3	50	25 (0.50)	28	65	7
4	50	50 (1.0)	9	71	20
5	50	100 (2.0)	10	69	22
6	50	150 (3.0)	7	68	25
7	50	200 (4.0)	3	49	48
8	50	250 (5.0)	2	47	52
9	1000	100 (0.10)	36	64	nd*

* nd = not detected.
** Analyzed by RP C_{18} HPLC detected at 210 nm.

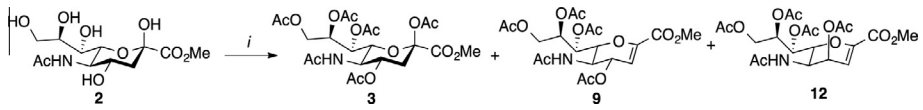
1. Experimental

1.1. General methods

Microwave-assisted reactions were done using a Biotage Initiator$^+$ SP Wave reactor. The progress of reactions was monitored by TLC using Si Gel 60 F_{254} aluminum-backed plates and visualized using UV lamp (254 nm) and sugar stain. Low-resolution mass spectra were recorded using a Thermo Finnigan LCQ-Advantage electrospray ionization mass spectrometer. High-resolution mass spectra were collected using a Sciex 4800 TOF/TOF Analyzer in reflector positive mode using 2,5-dihydroxybenzoic acid as matrix. NMR spectra were recorded using Varian 300 and 500 MHz spectrometers using the following solvents and referenced to residual H: D_2O (δ_H = 4.79) and $CDCl_3$ (δ_H = 7.26). Reversed phase HPLC was done using Thermo Dionex Ultimate 3000 HPLC, Phenomenex Synergi C_{18} 10x250 mm column, and solvent gradient of 10–100% MeCN in H_2O with detection set at 210 and 254 nm.

1.2. Preparation of silica sulfuric acid (SSA)

SSA was prepared by making a slurry of chromatography grade silica gel 60 (5.0 g, 40–75 μm, Sorbent Technologies) in 25 mL CH_2Cl_2 followed by drop wise addition of chlorosulfonic acid (1.925 g, 16.5 mmol) to the stirring suspension at room temperature.[20] The gaseous HCl side product was evacuated by vacuum and captured in a base trap. After complete addition of chlorosulfonic acid, the mixture was stirred for an additional 30 min at room temperature, filtered, washed with EtOH, and dried in an oven at 140 °C for 1 h. Silica gel treated through this process yielded SSA that bears 0.16 mmol SO_3H per 50 mg as estimated from the amount of chlorosulfonic acid used, in mmol, as limiting reagent.



Scheme 3. Reagents and conditions: (i) 8 equiv Ac_2O per OH, 0.1 equiv SSA, microwave irradiation.

1.3. *N*-Acetylneuraminic acid methyl ester (2)

Compound **1** (1.0 g, 3.23 mmol, 1 equiv) was transferred to a thick walled microwave reactor tube and suspended in 20.0 mL MeOH followed by the addition of SSA (0.40 g, 1.28 mmol, 0.40 equiv) and magnetic stir bar. The tube was sealed and the mixture subjected to microwave irradiation at 80 °C for 30 min and microwave power at 55 W maximum. SSA was filtered out, the filtrate concentrated in vacuo, purified by flash chromatography using 3:1 CH_2Cl_2–MeOH, and concentrated to dryness to afford a white powder in 97% yield. ^{1}H NMR spectrum was recorded in D_2O and is consistent with the literature.[15] MS *m*/*z*: calcd for $C_{12}H_{21}NO_9Na^+$, 346.1; found, 346.2.

1.4. 1,4,7,8,9-Penta-*O*-acetyl-2-deoxy-*N*-acetylneuraminic acid methyl ester (3)

Isolated as white powder. R_f = 0.15 (2:1 toluene–Me_2CO). ^{1}H NMR spectrum was recorded in $CDCl_3$ and is consistent with the literature.[14] MALDI-TOF-MS *m*/*z*: calcd for $C_{22}H_{31}NO_{14}Na^+$, 556.1642; found, 556.2092 and calcd for $C_{22}H_{31}NO_{14}K^+$, 572.1382; found, 572.1739.

1.5. 4,7,8.9-Tetra-*O*-acetyl-2-deoxy-2,3-dehydro-*N*-acetylneuraminic acid methyl ester (9)

A mixture of **2** (1.0 g, 1.0 equiv), SSA (100 mg, 0.32 mmol, 0.10 equiv), and Ac_2O (12.10 mL, 40 equiv) was stirred in a thick walled microwave reactor tube. The mixture was microwave irradiated for 30 min at 70 °C and microwave power at 50 W maximum. The formation of **9** was monitored by TLC (2:1 toluene-Me_2CO, R_f = 0.23). SSA was recovered by centrifugation and the reaction mixture basified (pH = 10.0) using saturated aqueous Na_2CO_3 followed by extraction with CH_2Cl_2 until no significant amount of product remained in the aqueous layer as indicated by TLC. The CH_2Cl_2 layer was concentrated in vacuo and subjected to flash column chromatography using 2:1 toluene–Me_2CO. Compound **9** was isolated as white powder in 65% yield. ^{1}H NMR spectrum was recorded in $CDCl_3$ and is consistent with the literature.[28] MALDI-TOF-MS *m*/*z*: calcd for $C_{20}H_{27}NO_{12}Na^+$, 496.1431; found, 496.1446 and calcd for $C_{20}H_{27}NO_{12}K^+$, 512.1170; found, 512.1115.

1.6. 4,7,8.9-Tetra-*O*-acetyl-2-deoxy-2,3-dehydro-4-epi-*N*-acetylneuraminic acid methyl ester (12)

Isolated as white solid from HPLC purification (t_R = 37.5 min). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.22 (d, *J* = 5.6 Hz, 1H), 5.50 (m, 2H), 5.14 (dd, *J* = 5.6, 3.8 Hz, 1H), 4.78 (dd, *J* = 12.5, 2.6 Hz, 1H), 4.60 (td, *J* = 10.6, 3.9 Hz, 1H), 4.28 (dd, *J* = 11.0, 2.2 Hz, 1H), 4.19 (dd, *J* = 12.4, 7.7 Hz, 1H), 3.80 (s, 3H, OCH_3), 2.11 (s, 3H, $COCH_3$), 2.10 (s, 3H, $COCH_3$), 2.09 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$) and 1.94 (s, 3H, $NHCOCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.7, 170.3, 169.8, 169.7, 161.8, 146.4, 106.0, 74.1, 72.0, 67.9, 65.1, 62.3, 52.8, 44.3, 23.4, 21.1, 20.9, 20.9. MALDI-TOF-MS *m*/*z*: calcd for $C_{20}H_{27}NO_{12}Na^+$, 496.1431; found, 493.1315 and calcd for $C_{20}H_{27}NO_{12}K^+$, 512.1170; found 512.0995.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carres.2014.09.002.

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