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$NaHSO_4$ supported on silica gel: an alternative catalyst for Ferrier rearrangement of glycals

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ABSTRACT

$NaHSO_4$ supported on silica gel catalyses the Ferrier rearrangement reaction of 3,4,6-*tri*-*O*-acetyl-D-glucal with alcohols and thiols to give the corresponding 2,3-unsaturated glycosides in high anomeric selectivity and good to excellent yield in short reaction time.

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1. Introduction

Ferrier rearrangement is a Lewis acid catalyzed allylic rearrangement of glycals in the presence of alcohols to yield 2,3-unsaturated glycosides.[1] As shown in Scheme 1 the reaction proceeds via a cyclic oxocarbonium intermediate **2** and can be intercepted by nucleophiles other than an alcohol such as halides and carbanion to give the corresponding products.[2] Even though the reaction is efficient, the requirement for a Lewis acid as a catalyst causes restriction to the glycals and glycosyl acceptors to be used and its wider synthetic applications.[2a] This called for the development of non-acidic catalyzed allylic rearrangement as an alternative to the original Ferrier rearrangement reaction. Since the report of the reaction by Ferrier in 1969,[1] several promoters have been reported and can be broadly categorized into three, namely: Lewis acids (such as $BF_3{\cdot}OEt_2$,[1,3] $Bi(OTf)_3$ with and without SiO_2,[4] $FeCl_3$,[5] acidic Montmorillonite K-10,[6] I_2,[7] $InCl_3$,[8] $CeCl_3{\cdot}7H_2O$,[9] $Sc(OTf)_3$,[2b] $Al(OTf)_3$,[10] $ZnCl_2/Al_2O_3$,[11] TMSOTf,[12] $Pd(OAc)_2$,[13] $K_5CoW_{12}O_{44}{\cdot}3H_2O$,[14] $Fe_2(SO_4)_3{\cdot}xH_2O$,[15] zeolites,[16] and SiO_2 by microwave irradiation at 650 W[17]), protic acids (H_2SO_4–SiO_2[18] and $HClO_4$–SiO_2,[19] and H_3PO_4[20]) and oxidative promoters (NIS,[2a] DDQ,[21] CAN,[22] iodonium dicollidinium perchlorate[2a]).

Although a number of catalysts have been reported in the literature as stated above, none of the methods reported is superior in terms of yield, anomeric selectivity, reaction time, temperature, amount of catalyst, catalyst reusability, environmental benignness, and cost of catalyst. The use of basic[23] and weak acid catalysts has received little attention as alternatives in alleviating some of the limitations. Thus, the search for an inexpensive, readily available, and convenient catalyst is desirable.

Recently, $NaHSO_4$ supported on silica gel has attracted considerable attention due to its low cost, ease of preparation, mildness, recoverability, reusability, and insensitivity to moisture. It has been applied as a catalyst in the opening of epoxides into β-hydroperoxy alcohols,[24] synthesis of trisubstituted quinolines,[25] β-enaminones,[26] *N*-acylsulfonamides,[27] aryl-14-*H*-dibenzo[*a*,*j*]xanthenes,[28] amidoalkyl naphthols,[29] coumarins,[30] and selective monoacetylation of unsymmetrical diols.[31] In a continuation of our work to develop new synthetic methodologies for the transformation of glycals,[10,32] we report herein the ability of $NaHSO_4$–SiO_2 to promote Ferrier rearrangement of glycals.

2. Result and discussion

In our first attempts a solution of acetylated glucal **4** and benzyl alcohol in acetonitrile was treated with catalytic amounts of $NaHSO_4$–SiO_2 at room temperature. However, TLC analysis showed no formation of a product. Addition of stoichiometric amount of the catalyst failed to show any change and the starting material was recovered intact after work up. Reactions at different temperatures were then carried out using benzyl alcohol as a model to investigate the optimum conditions to effect Ferrier rearrangement and it was found that the minimum temperature required to favor formation of the product was at 80 °C. This was in accordance with the literature report where H_2SO_4–SiO_2 was employed as a

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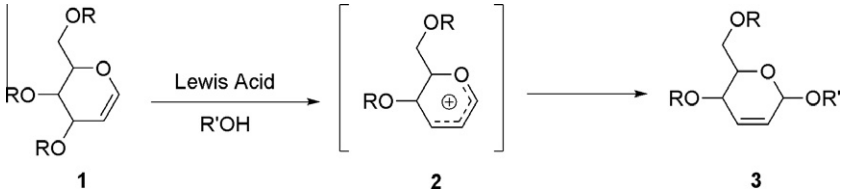
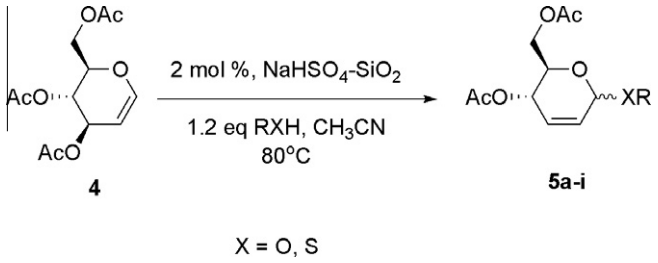


Scheme 1. General reaction of Ferrier rearrangement.



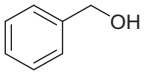
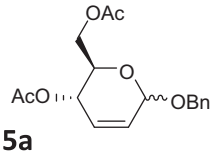
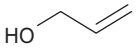
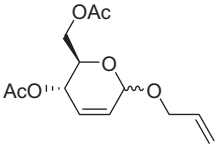
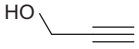
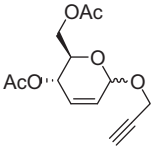
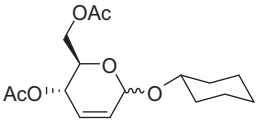
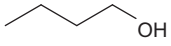
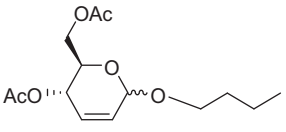
Scheme 2. Ferrier rearrangement of acetylated glucal **4** with different nucleophiles.

promoter.[18] Temperatures less than 80 °C were not sufficient enough to provide the needed activation energy while higher than 80 °C resulted in the formation of many by-products as judged by TLC analysis. After finding the right temperature, investigation was carried out to determine the minimum amount of catalyst required to effect complete conversion of the starting glucal into a product. Thus, catalyst loadings of 1 and 2 mol % were investigated to provide a guide. Reactions that were carried out at 80 °C using 1 mol % catalyst loadings went to completion in 60 min providing low yield of the product while reactions carried out at the same temperature but with 2 mol % were completed in less than 5 min and provided excellent yield of the rearranged compounds. The low yield with longer reaction time could be attributed to the decomposition of the starting/product material at high temperature in acidic medium.[18]

Since SiO_2 alone has been reported to catalyze Ferrier rearrangement reaction under 650 W microwave irradiation,[17] it was imperative to investigate whether the activity of the $NaHSO_4$–SiO_2 was the result of SiO_2 alone or a combination of the two. Thus, a reaction was set up at 80 °C using SiO_2 as a catalyst to provide a Ferrier product at no avail. The importance of SiO_2 was then tested by trying to effect Ferrier rearrangement of acetylated glucal **1** with benzyl alcohol in the presence of unsupported $NaHSO_4$ (10 mol %). To our surprise the reaction gave the desired Ferrier product but the rate of the reaction was very sluggish (45 min vs 5 min) proving it was the combination of $NaHSO_4$ and SiO_2 that contributed to the efficiency of the catalyst.

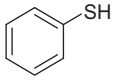
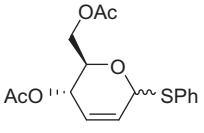
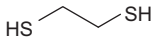
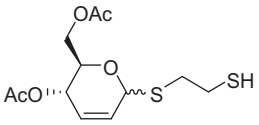
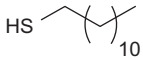
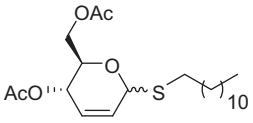
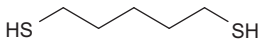
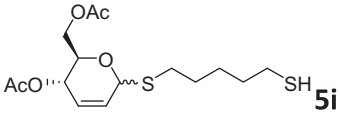
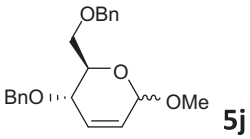
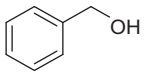
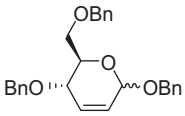
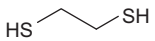
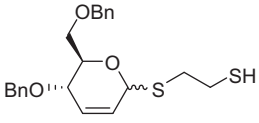
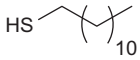
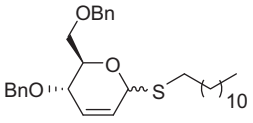
Under the optimum conditions 1.2 equiv of several alcohols, including primary, secondary, allylic and propargyl alcohols, and thiols reacted with acetylated glucal **4** according to Scheme 2 using 2 mol % $NaHSO_4$–SiO_2 (3.0 mmol $NaHSO_4$/g)[31] at 80 °C to give the corresponding 2,3-unsaturated-O and S-glycosides in good to excellent yields and in very short reaction time with α-anomer as a major product. The results are shown in Table 1 and the selectivities and yields compare favorably with reported methods

Table 1
$NaHSO_4$–SiO_2 catalyzed synthesis of 2,3-unsaturated glycosides 3,4,6-*tri*-*O*-acetyl-D-glucal and 3,4,6-*tri*-*O*-benzyl-D-glucal[a]

Entry	Nucleophile	Product	Reaction time (min)	Yield[b] (%)	α:β ratio[c]	Ref.
1		 **5a**	5	91	4:1	[15]
2		 **5b**	5	72	9:1	[33]
3		 **5c**	5	90	6:1	[33]
4		 **5d**	40	85	8:1	[20]
5		 **5e**	60	80	7:1	[33]

(*continued on next page*)

Table 1 (*continued*)

Entry	Nucleophile	Product	Reaction time (min)	Yield[b] (%)	α:β ratio[c]	Ref.
6		 **5f**	5	96	4:1	16
7		 **5g**	8	55	5:1	—
8		 **5h**	5	65	>99:1	—
9		 **5i**	8	50	>99	—
10	MeOH	 **5j**	180[d]	20	5:1	22a
11		 **5k**	180[d]	90	4:1	34
12		 **5l**	45[d]	64	2:1	—
13		 **5m**	60[d]	75	7:1	—

[a] Substrate (1.8 mmol), 1.2 equiv alcohol/thiol, 1 mL CH_3CN, 2 mol % $NaHSO_4$–SiO_2, 80 °C.
[b] Isolated yields.
[c] The anomeric ratios were based on the integration of the corresponding anomeric protons in the ^1H NMR spectrum.
[d] Performed at room temperature.

(Table 2). Products were identified by ^1H and ^{13}C NMR spectroscopy.

The notion that the group at position C-3 of the glucal has to be a good leaving group (3-OAc or 3-SR) has been over ruled since 3-O-unprotected[8c] and 3-*O*-benzyl protected[10,15,16] glucals have resulted in the formation of 2,3-unsaturated glycosides on treatment with different Lewis acids. In agreement with our recent report using $Al(OTf)_3$,[10] $NaHSO_4$–SiO_2 catalyzed the Ferrier rearrangement reaction of perbenzylated glucal **6** with alcohols and resulted in a mixture of the desired 2,3-unsaturated product and a significant amount of the competitive product, benzyl glycoside **5k**, due to the strong nucleophilicity of the benzyloxy group eliminated from position C-3 of the starting glucal (Scheme 3). However, when stronger nucleophiles such as thiols were employed, the formation the competitive product, glycoside **5k**, was suppressed resulting in 2,3-unsaturated thioglycosides (entries 12 and 13 in Table 1) as major products.

3. Conclusion

In conclusion, we have demonstrated that $NaHSO_4$ supported on silica gel can catalyze the Ferrier rearrangement of 3,4-6-*tri*-*O*-acetyl-D-glucal and 3,4-6-*tri*-*O*-benzyl-D-glucal with alcohols and thiols. The short reaction time, high anomeric selectivity, low catalyst loading, low cost, and stability of the catalyst make the method attractive in organic synthesis. To the best of our knowledge, this is the second report where a weak protic acid (the first being H_3PO_4) has been used as a catalyst for the Ferrier rearrangement reaction of glycals.

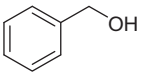
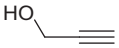
4. Experimental

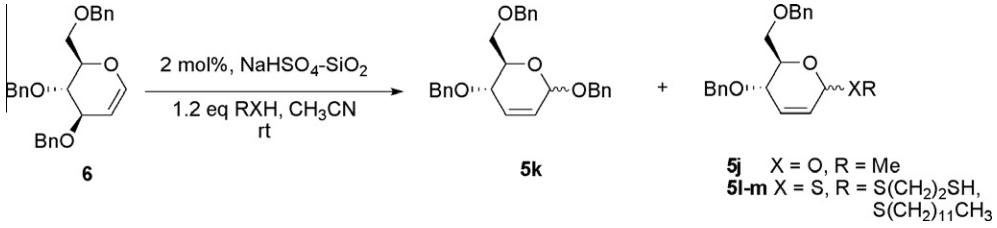
The $NaHSO_4$–SiO_2 catalyst was prepared according to the protocol reported by Breton.[31]

4.1. General procedure for the Ferrier rearrangement of glycals

To a solution of a glycal (1.8 mmol) in CH_3CN (1 mL) $NaHSO_4$–SiO_2 (12 mg, 3.0 mmol$NaHSO_4$/g)[31] was added. The resulting mixture was stirred at 80 °C (room temperature for 3,4,6-*tri*-*O*-benzyl-D-glucal) till TLC analysis showed disappearance of the starting material. After adding silica gel to the reaction mixture at room temperature, the solvent was evaporated in vacuo without heating until a free-flowing solid was obtained. The resulting solid

Table 2
Comparison of $NaHSO_4$–SiO_2 with literature reported catalysts for the Ferrier rearrangement of 3,4,6-*tri*-*O*-acetyl-D-glucal with different alcohols[4,11,17]

Entry	Alcohol	Catalyst	Time	Yield %	α:β ratio	Amount of catalyst (mol %)	Ref.
1		CAN	3 h	90	7:1	10	4
		$Sc(OTf)_3$	3.5 h	85	5:1	5	4
		$Yb(OTf)_3$	3 h	94	9:1	10	4
		$BiCl_3$	1 h	94	10:1	5	4
		$InCl_3$	10 min	86	6.3:1	20	4
		$Bi(OTf)_3$–SiO_2	15 min	90	2.2:1	2	4
		$Bi(OTf)_3$	3 min	69	4:1	2	4
		SiO_2 MW	10 min	92	5:1	100 mg/mol glucal	17
		$NaHSO_4$–SiO_2	5 min	91	4:1	2	—
2		CAN	6 h	80	4:1	10	4
		$Sc(OTf)_3$	1.5 h	93	10:1	5	4
		$Yb(OTf)_3$	4 h	91	10:1	10	4
		$BiCl_3$	1.5 h	95	10:1	5	4
		$Bi(OTf)_3$–SiO_2	2.5 h	76	7.8:1	2	4
		$Bi(OTf)_3$	5 min	73	α	2	4
		$ZnCl_2/Al_2O_3$	10 min	88	α	250 mg/0.37 mmol glucal	11
		$NaHSO_4$–SiO_2	5 min	90	6:1	2	—
3		CAN	3 h	90	4:1	10	4
		$Sc(OTf)_3$	1.5 h	95	7:1	5	4
		$BiCl_3$	1.5 h	95	11:1	5	4
		$Bi(OTf)_3$–SiO_2	2 h	51	α	2	4
		$Bi(OTf)_3$	3 min	75	α	2	4
		I_2	1 h	88	7:1	20	4
		$ZnCl_2/Al_2O_3$	20 min	83	α	250 mg/0.37 mmol glucal	11
		$NaHSO_4$–SiO_2	5 min	72	9:1	2	—
4		CAN	4.5 h	80	14:1	10	4
		$Sc(OTf)_3$	3 h	83	7:1	5	4
		$Yb(OTf)_3$	18 h	89	11:1	10	4
		$InCl_3$	30 min	90	9:1	20	4
		$Bi(OTf)_3$–SiO_2	2 h	80	3:1	2	4
		$Bi(OTf)_3$	30 min	82	α	2	4
		$ZnCl_2/Al_2O_3$	10	85	α	250 mg/0.37 mmol glucal	11
		$NaHSO_4$–SiO_2	5	85	8:1	2	—



Scheme 3. Ferrier rearrangement of benzylated glucal **6** with MeOH and thiols.

was column chromatographed using 1:9 ethyl acetate/hexane eluent to afford pure 2,3-unsaturated glycosides. Analytical data for known compounds **5a–5f, 5j,** and **5k** were consistent with published data (see Table 1 for references). Data for new compounds are as follows.

4.1.1. 2-Mercaptoethyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-1-thio-hex-2-enopyranoside (5g)

Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.91 (dd, 1H, J = 2.0 and 9.6 Hz), 5.89 (d, 1H, J = 10.0 Hz), 5.59 (s, 1H), 5.34 (dd, 1H, J = 6.6 and 10.8 Hz), 4.20–4.10 (m, 3H), 2.90–2.68 (m, 4H), 2.08 (s, 3H), 2.05 (s, 3H), 1.65 (t, 1H, J = 16.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.1, 170.6, 128.9, 127.6, 81.3, 67.3, 65.4, 63.4, 36.9, 25.6, 21.3, 21.2; HRMS (ESI) m/z (M+H)$^+$: calcd 307.0674; found 307.0665.

4.1.2. 5-Mercaptopentyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-1-thio-hex-2-enopyranoside (5i)

Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.95 (ddd, 1H, J = 2.0, 3.2 and 10.0 Hz), 5.75 (td, 1H, J = 1.6 and 10.4 Hz), 5.58–5.50 (m, 1H), 5.34 (dd, 1H, J = 2.0 and 9.2 Hz), 4.30–4.20 (m, 2H), 4.13 (d, 1H, J = 10.0 Hz), 2.80–2.55 (m, 2H), 2.50 (q, 2H, J = 7.2 and 14.4 Hz), 2.07 (s, 3H), 2.06 (s, 3H), 1.69–1.59 (m, 4H), 1.49–1.40 (m, 2H), 1.31 (t, 1H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.7, 170.3, 129.0, 126.8, 80.3, 66.8, 65.0, 62.9, 33.4, 31.8, 29.4, 27.5, 24.4, 21.0, 20.8; MS (ESI) m/z (M+Na)$^+$: calcd 371.1; found 371.1.

4.1.3. Dodecanyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-1-thio-hex-2-enopyranoside (5h)

Yellowish oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.91 (d, 1H, J = 10.4 Hz), 5.75 (d, 1H, J = 10.4 Hz), 5.52 (s, 1H), 4.35–4.20 (m, 2H), 4.14 (d, 1H, J = 11.2 Hz), 2.75–2.65 (m, 1H), 2.64–2.50 (m, 1H), 2.07 (s, 3H), 2.06 (s, 3H), 1.70–1.50 (m, 2H), 1.40–1.10 (m, 17H), 0.90–0.70 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.8, 170.3, 129.1, 126.7, 80.4, 66.8, 65.1, 63.0, 32.0, 31.9, 30.0, 29.6 (×3), 29.5, 29.3, 29.2, 28.9, 22.7, 21.0, 20.8, 14.1; HRMS (ESI) m/z (M+Na)$^+$: calcd 437.2338; found 437.2328

4.1.4. 2-Mercaptoethyl-4,6-di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-1-thio-hex-2-enopyranoside (5l)

Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35–7.26 (m, 10H), 6.00 (d, 1H, J = 10.0 Hz), 5.85 (td, 1H, J = 5.8 and 12.4 Hz), 5.60 (s, 1H), 4.65 (d, 1H, J = 12.0 Hz), 4.60 (d, 1H, J = 11.2 Hz), 4.50 (d, 1H,

J = 12.0 Hz), 4.40 (d, 1H, J = 11.6 Hz), 4.20 (dd, 1H, J = 1.2 and 9.2 Hz), 4.10 (dd, 1H, J = 1.6 and 9.2 Hz), 3.78 (dd, 1H, J = 4.0 and 10.4 Hz), 3.70 (dd, 1H, J = 1.2 and 10.8 Hz), 3.00–2.70 (m, 4H), 1.66 (t, 1H, J = 8.0 Hz); Anal. Calcd for $C_{22}H_{26}S_2O_3$: C, 65.64; H, 6.51; S, 15.93. Found: C, 65.44; H, 6.54; S, 13.87.

4.1.5. Dodecanyl-4,6-di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-1-thio-hex-2-enopyranoside (5m)

Yellowish oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ7.40–7.10 (m, 10H), 5.93 (d, 1H, J = 10.0 Hz), 5.84 (d, 1H, J = 11.2 Hz), 5.53 (s, 1H), 4.70–4.37 (m, 4H), 4.23 (d, 1H, J = 9.2 Hz), 4.15 (d, 1H, J = 9.2 Hz), 3.80–3.60 (m, 2H), 2.75–2.50 (m, 2H), 1.70–1.50 (m, 2H), 1.40–1.10 (m, 17H), 0.90–0.70 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.2, 138.1, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 80.6, 73.4, 73.3, 71.1, 70.2, 69.0, 68.9, 32.0, 31.9, 30.1, 29.7, 29.6, 29.5, 29.3, 29.2, 28.9, 22.7; HRMS (ESI) m/z (M+Na)$^+$: calcd 533.3065; found 533.3063.

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