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# Kinetically controlled Ferrier rearrangement of 3-*O*-mesyl-D-glycal derivatives

Yuhya Watanabe, Tsubasa Itoh, Tohru Sakakibara *

*Graduate School of Integrated Science, Yokohama City University, 22-2, Seto, Kanazawa-ku, Yokohama 236-0027, Japan*

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ABSTRACT

The Ferrier rearrangement, which is widely used in carbohydrate chemistry, is generally performed under acidic conditions to give an α anomer with high stereoselectivity. We have found that 3-*O*-mesyl-D-glycals **2**–**4** were smoothly reacted with alcohols in the presence of triethylamine. The present reaction was shown to proceed under kinetic control to give ~1.3:1.0 mixture of α and β anomers, indicating that a kinetic anomeric effect does not operate.



Reaction of glycals with nucleophiles in the presence of a Lewis acid or protic acid gives an allylic rearrangement product having the double bond at the 2,3-position and new substituents at the anomeric center. This reaction has been widely used and is known as the Ferrier rearrangement.[1] In general, the reaction proceeds with high stereo- and regioselectivity.[1b] An acid catalyst accelerates the departure of a leaving group at C-3 to generate the delocalized carbenium ion, followed by nucleophilic addition reactions. The last step should be reversible to give the thermodynamically more stable α anomer as a major product. For example, reaction of D-glucal **1** (Fig. 1) and methanol in the presence of $BF_3{\cdot}OEt_2$ gave a 7:1 equilibrium mixture of α and β anomers.[1b] Even under kinetic control, C-glycosidation is typical,[2] and α anomers predominate over β anomers. If $I_2$,[3] DDQ,[4] or iodonium dicolline perchlorate (IDCP)[5] are used as the catalyst, the reaction is thought to be mildly acidic or non-acidic, and the α anomer again becomes the major product. Without catalyst, for example, reaction of **1** with methanol gave the α anomer as the major product,[6] probably as a result of anomerization due to the acetic acid generated during the reaction. Thus the Ferrier rearrangement is performed under acidic, sometimes neutral conditions, but not under basic conditions. However, there is one exception, in which treatment of 4,6-*O*-benzylidene-3-*O*-mesyl-D-allal (**4**) with methanolic sodium methoxide afforded methyl 4,6-*O*-benzylidene-β-D-2-enopyranoside **8a** in 91% yield.[7] However, this reaction was carried out only to confirm the generation of unstable mesylate **4**, and the product was neither isolated nor were the reaction conditions described.[†] In this paper, we report that the Ferrier rearrangement of 3-*O*-mesyl derivatives **2**–**4** proceeds under slightly basic conditions (pH ~10), as judged from UNIV pH paper (ADVANTEC®), to give in good yield a mixture of α and β anomers with the α anomer predominating. Although the reaction of the mesylates with methanol in the presence of triethylamine was shown to be kinetically controlled, we found that anomerization occurs at least partially in the presence of $I_2$ or DDQ.

Treatment of 3-*O*-acetyl-4,6-*O*-benzylidene-D-glucal (**5**) with MeOH in the presence of $BF_3{\cdot}Et_2O$ or $I_2$ gave zones with low $R_f$ values on TLC, suggesting partial debenzylidenation. Then, the leaving group at C-3 was changed to the more reactive mesyloxy group, of which isolation failed similar to its 3-epimer.[7]

After addition of 1.5 equiv of MsCl to a solution of 4,6-*O*-benzylidene-D-glucal (**6**) in $CH_2Cl_2$ in the presence of 4 equiv of $Et_3N$, 4 equiv of MeOH was added and warmed at 40 °C for 2 h to give a 1.3:1.0 mixture of α and β anomers of the methyl 2-enopyranoside in 88% yield. On TLC, their spots completely overlapped, and their separation was not achieved.[‡] We isolated the β anomer by application of the fact that $LiAlH_4$ reduction of the α anomer to 3-deoxy-glycal was much faster than that of the β anomer.[8] As shown in Table 1, ethanol, 2-propanol, and *tert*-butyl alcohol similarly reacted, from

* Corresponding author. Tel.: +81 45 787 2183; fax: +81 45 787 2413.
*E-mail address:* baratoru@yokohama-cu.ac.jp (T. Sakakibara).

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† The following reaction gave a 3:2 mixture of methyl α- and β-D-2-enopyranoside. Compound 7 (23.4 mg, 100 μmol) was treated with MsCl (17.1 mg, 11.5 μmol) in $CH_2Cl_2$ (3 mL) in the presence of $Et_3N$ (41 mg, 406 μmol) for 5 min at room temperature. After addition of 0.1 M NaOMe (500 μL), the mixture was warmed at 40 °C for 2 h. These conditions, however, were not applied to acetate 10 because of deacetylation.

‡ Separation of both α and β anomers was not achieved in the literature reports.

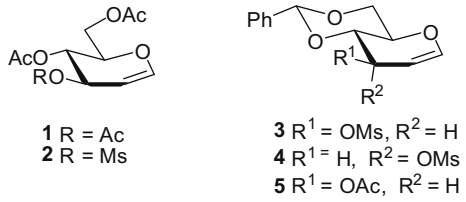



**Figure 1.**

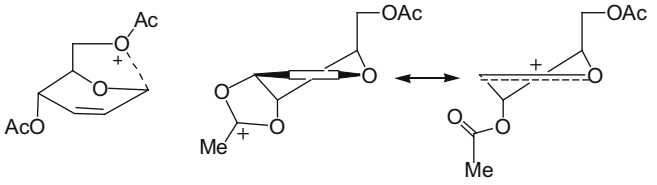



**Figure 2.** Possible intermediates of Ferrier rearrangement.

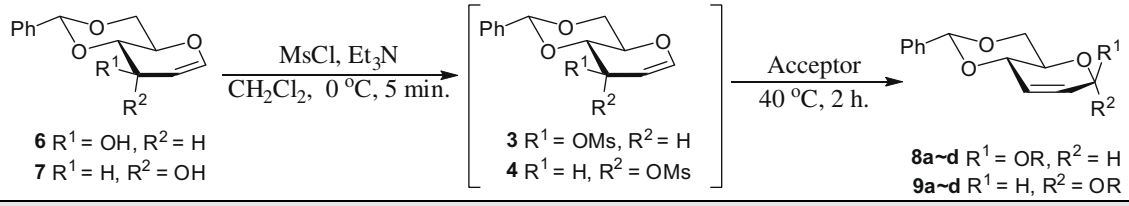
which α and β anomers of 2-enopyranosides generated by the latter two alcohols were separated by column chromatography.

Similar reaction of 4,6-*O*-benzylidene-D-allal (**4**) with methanol gave the same results, indicating that the reaction proceeds via a cationic intermediate similar to that of the Ferrier rearrangement.

Di-*O*-acetyl-D-glucal **10** is readily prepared from commercially available per-*O*-acetyl-D-glucal.[9] Therefore, if the Ferrier rearrangement of **2** proceeds under basic conditions, it would be useful because the reaction should be kinetically controlled and used for acid-sensitive acceptors. It is noteworthy that the acetoxy group is apparently able to stabilize a cationic intermediate via neighboring-group participation as shown in Figure 2, which serves to control the stereoselectivity.[1,10]

The Ferrier rearrangement of the diacetate **2** with methanol was examined in the presence of several bases. When strong bases (DMAP and DBU) and a large amount of $Et_3N$ were employed, the reactions became complicated because of the base sensitivity of the acetoxy group. Four equivalents of $Et_3N$ gave satisfactory results, and deacetylation was not observed by the use of 8 equiv of $Et_3N$. Stereoselectivity was lower compared to the conventional Ferrier rearrangement, and the ratios of α and β anomers generated from **2** were almost the same as those from the benzylidene derivatives **3** (Table 2, entry 1). Mesylate **2** smoothly reacted with alcohols and thiols to give a mixture of α and β anomers in high yields, but stereoselectivities were again low (Table 2). Although UNIV pH paper suggests that the reaction medium was slightly basic (pH ~10), distinct basicity is not clear because of the nonaqueous solvent and the molar ratio of MsCl (1.5 equiv) and $Et_3N$ (4 equiv). Anomerization of the 2-enopyranoside readily occurs under acidic conditions because a cationic intermediate is stabilized by the oxygen atom (O-5) and the double bond. However, if the reaction medium is neutral or basic, the O- and S-glycosides are stable and avoid anomerization. When a 1.3:1.0 mixture of α anomer **12a** and β anomer **11a** was treated with $Et_3N$ in methanol, the ratio was unchanged. However, as shown in Table 3, similar treatment of the mixture in the presence of the catalyst caused partial anomerization. Even in the presence of DDQ, referred to as a nonacidic catalyst,[4] anomerization partially occurred.

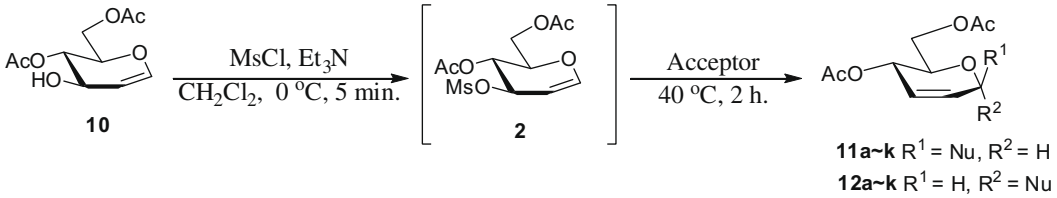
**Table 1**
O-Glycosidation of 4,6-*O*-benzylidene-3-*O*-mesyl-D-glucal using triethylamine

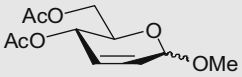
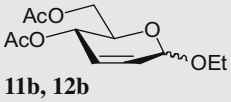
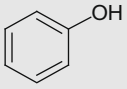
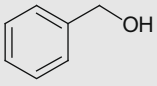
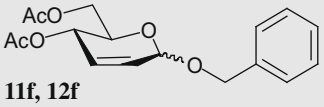
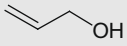
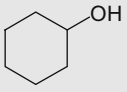
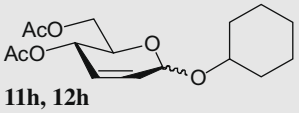
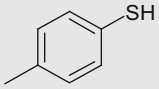
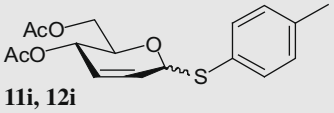
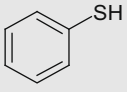
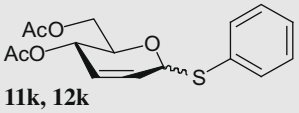



| Entry | Acceptor[a] | Glycal | Products | Yield[b] (%) | α:β ratio[c] |
|---|---|---|---|---|---|
| 1 | MeOH | **6** | **8a, 9a** | 88 | 1.3:1.0 |
| 2 | EtOH | **6** | **8b, 9b** | 94 | 1.8:1.0 |
| 3 | 2-PrOH | **6** | **8c, 9c** | 93 | 2.0:1.0 |
| 4 | *tert*-BuOH | **6** | **8d, 9d** | 89 | 2.2:1.0 |
| 5 | MeOH | **7** | **8a, 9a** | 91 | 1.3:1.0 |

[a] 4 equiv of acceptor was employed.
[b] Isolated yield.
[c] Determined by $^1H$ NMR.

**Table 2**
O- and S-glycosidation of **10**




| Entry | Acceptor | Products | Basic conditions[a] | Lit.[b] |
|---|---|---|---|---|
| 1 | MeOH |  **11a, 12a** | 1.3:1.0 (88%) | 5.7:1.0[1a] |
| 2 | EtOH |  **11b, 12b** | 1.4:1.0 (90%) | 9.0:1.0[11] |
| 3 | *iso*-PrOH |  **11c, 12c** | 1.2:1.0 (89%) | 8.0:1.0[3] |
| 4 | *tert*-BuOH |  **11d, 12d** | 0.8:1.0 (92%) | 10.0:1.0[11] |
| 5 |  |  **11e, 12e** | 1.6:1.0 (94%) | 10.0:1.0[12] |
| 6 |  |  **11f, 12f** | 1.2:1.0 (82%) | 10.5:1.0[11] |
| 7 |  |  **11g, 12g** | 1.5:1.0 (93%) | 7.0:1.0[12] |
| 8 |  |  **11h, 12h** | 1.2:1.0 (95%) | 6.7:1.0[13] |
| 9 |  |  **11i, 12i** | 1.3:1.0 (90%) | 8.0:1.0[14] |
| 10 |  |  **11j, 12j** | 1.2:1.0 (87%) | 6.7:1.0[15] |
| 11 |  |  **11k, 12k** | 1.4:1.0 (93%) | 8.0:1.0[11] |

[a] α:β ratio and yield are shown in parentheses.
[b] Examples: α:β ratio.

Low stereoselectivity observed under kinetically controlled condition suggests that the kinetic anomeric effect does not operate with these examples.

In conclusion, we found that 3-*O*-mesylates **2**–**4** were suitable substrates for a kinetically controlled Ferrier rearrangement. The present reactions apply, not only to acid-sensitive 4,6-*O*-

benzylidene derivatives **3** and **4**, but also to base-sensitive acetyl derivative **2**. This reaction should proceed via a cationic intermediate at least in the cases of 4,6-*O*-benzylidene derivatives **3** and **4**. Neighboring-group participation of the acetoxy group should not be operative, because the same α/β ratios were obtained in the reactions of **2** and **3**. Thus, the high stereoselectivity observed in conventional O- and S-Ferrier rearrangement should be caused by anomerization. Low stereoselectivity observed herewith is a drawback for a synthetic method, but should have an advantage for using compounds **2–4** as substrates for combinatorial chemistry.

## 1. Experimental

### 1.1. General methods

Melting points are uncorrected. Optical rotations were determined with a Horiba High Sensitive Polarimeter (SEPA-200). Most of the reactions were monitored by TLC using silica gel coated on glass. Products were purified by flash column chromatography and recrystallized if necessary. NMR spectra were measured on a Bruker AVANCE 400 instrument (400 MHz/$^1$H, 100 MHz/$^{13}$C) with TMS as an internal standard. Some signals were assigned by the use of COSY, HMQC, HMBC, and/or NOESY. IR spectra were recorded for KBr pellets on a Perkin–Elmer Spectrum One FTIR spectrometer. Silica gel {C-60 (Kanto) and 40–63 μm (E. Merck)} was used for column chromatography.

### 1.2. Ferrier rearrangement of 4,6-*O*-benzylidene-D-glucal (6)

#### 1.2.1. Methyl 4,6-*O*-benzylidene-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside (8a and 9a)

To a solution of **6** (20 mg, 85 μmol) in 1 mL of $CH_2Cl_2$ were added $Et_3N$ (47 μL, 342 μmol) and MsCl (10 μL, 128 μmol) at 0 °C. After 5 min, MeOH (14 μL, 342 μmol) was added, and the solution was heated with stirring for 2 h at 40 °C. The reaction mixture was washed with satd $NH_4Cl$ and satd NaCl, and dried. The filtrate was evaporated, and the residue was purified by column chromatography with 4:1 *n*-hexane–acetone, to give a 1.0:1.3 mixture of **8a** and **9a**[18] (18.6 mg, 88%).

Although ethyl β-glycoside **9b** is a new compound, we could not separate **8b** and **9b**.

#### 1.2.2. 2-Propyl 4,6-*O*-benzylidene-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside (8c and 9c)

Compound **6** (20 mg, 85 μmol) was treated under the same conditions employed for the preparation of **8a** and **9a** using 2-PrOH (26 μL, 342 μmol) instead of MeOH to give a 1.0:2.0 mixture of **8c** and **9c** (22 mg, 93%). This mixture was separated by column chromatography, eluting with toluene.

Physical data for **8c:** 100–102 °C (EtOH); $[\alpha]_D^{25}$ 41.7 (*c* 1.4, $CHCl_3$); IR: *ν* 2980, 2872, 1458, 1400, 1379. $^1$H NMR ($CDCl_3$): *δ* 7.51–7.34 (m, 5H, Ph), 6.10 (br d, 1H, $J_{2,3}$ 10.3 Hz, H-3), 5.66 (ddd, 1H, $J_{1,2}$ 1.4, $J_{2,4}$ 1.1 Hz, H-2), 5.60 (s, 1H, PhCH), 5.40 (dd, 1H, $J_{1,2}$ 1.3 Hz, H-1), 4.35 (dd, 1H, $J_{4,5}$ 10.2 Hz, H-4), 4.28 (dd, 1H, $J_{6a,6e}$ 10.2 Hz, $J_{5,6e}$ 4.5 Hz, H-6e), 4.05–4.02 (m, 1H, 2-Pr), 4.02 (dd, 1H, $J_{5,6a}$ 10.3 Hz, H-6a), 3.77 (ddd, 1H, H-5), 1.26 (d, 3H, *J* 6.2 Hz, 2-Pr), 1.21 (d, 3H, *J* 6.2 Hz, 2-Pr). $^{13}$C NMR ($CDCl_3$): *δ* 137.8, 129.6, 128.8, 126.6(phenyl), 131.1(C-3), 129.6(C-2), 102.5 (PhCH), 97.7(C-1), 75.5(C-4), 71.4 (2-Pr), 70.9(C-5), 69.6(C-6), 24.1, 22.6 (2-Pr). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54, H, 7.30. Found: C, 69.75, H, 7.52.

Compound **9c** is known.[19] $^1$H NMR ($CDCl_3$): *δ* 7.50–7.34 (m, 5H, Ph), 6.10 (br d, 1H, $J_{2,3}$10.3 Hz, H-3), 5.68 (ddd, 1H, $J_{1,2}$ 2.5 Hz, $J_{2,4}$ 1.2 Hz, H-2), 5.56 (s, 1H, PhCH), 5.09 (m, 1H, H-1), 4.27 (dd, 1H, $J_{6a,6e}$ 10.1 Hz, $J_{5,6e}$ 4.6, H-6e), 4.12 (dd, 1H, $J_{4,5}$ 10.0 Hz, H-4), 3.98–3.94 (m, 2H, H-5, 2-Pr), 4.02 (dd, 1H, $J_{5,6a}$ 10.3 Hz, H-6a), 1.24 (d, 3H, *J* 6.2 Hz, 2-Pr), 1.18 (d, 3H, *J* 6.2 Hz, 2-Pr).

#### 1.2.3. *tert*-Butyl 4,6-*O*-benzylidene-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside (8d and 9d)

Similar treatment of **6** (50 mg, 214 μmol) with *tert*-butanol gave a 1.0:2.2 mixture of **8d** and **9d** (55 mg, 89%). The mixture was separated by column chromatography, eluting with toluene.

Physical data of β anomer **8d**: 112–115 °C (EtOH); $[\alpha]_D^{25}$ 50.6 (*c* 1.1, $CHCl_3$); IR: *ν* 2953, 2860, 1500, 1476, 1459. $^1$H NMR ($CDCl_3$): *δ* 7.50–7.34 (m, 5H, Ph), 6.07 (br d, 1H, $J_{2,3}$ 10.2 Hz, H-3), 5.59 (s, 1H, PhCH), 5.53 (dd, 1H, $J_{1,2}$ 1.2 Hz, H-2), 5.50 (dd, 1H, $J_{1,3}$ 1.3 Hz, H-1), 4.37 (dd, 1H, $J_{3,4}$ 1.6 Hz, $J_{4,5}$ 8.4 Hz, H-4), 4.24 (dd, 1H, $J_{6a,6e}$ 10.2 Hz, $J_{5,6e}$ 4.5, H-6e), 3.96 (dd, 1H, $J_{5,6a}$ 10.3 Hz, H-6a), 3.96 (ddd, 1H, H-5), 1.30 (s, 9H, *t*-Bu). $^{13}$C NMR ($CDCl_3$): *δ* 137.8, 129.5, 128.7, 126.6 (phenyl), 130.8 (C-3), 130.6 (C-2), 102.5 (PhC), 94.0 (C-1), 76.4 (*t*-$CMe_3$), 75.4 (C-4), 71.1 (C-5), 69.6 (C-6), 29.1 (*t*-C($CH_3$)$_3$). Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32, H, 7.64. Found: C, 70.58, H, 7.79.

Physical data of **9d**: 55–57 °C (EtOH); $[\alpha]_D^{25}$ 86.4 (*c* 1.0, $CHCl_3$); IR: *ν* 2983, 2926, 1497, 1461, 1450. $^1$H NMR ($CDCl_3$): *δ* 7.51–7.35 (m, 5H, Ph), 6.09 (br d, 1H, $J_{2,3}$ 10.2 Hz, H-3), 5.63 (ddd, 1H, $J_{1,2}$ 2.1 Hz, $J_{2,4}$ 1.3 Hz, H-2), 5.57 (s, 1H, PhCH), 5.30 (dd, 1H, $J_{1,3}$ 0.8 Hz, H-1), 4.25 (dd, 1H, $J_{6a,6e}$ 10.3 Hz, $J_{5,6e}$ 4.6, H-6e), 4.10 (ddd, 1H, $J_{3,4}$ 3.1 Hz, $J_{4,5}$ 8.9 Hz, H-4), 3.96 (ddd, 1H, $J_{5,6a}$ 10.3 Hz, H5), 3.96 (dd, 1H, H-6a), 1.29 (s, 9H, *t*-Bu). $^{13}$C NMR ($CDCl_3$): *δ* 138.0, 128.9, 129.8, 126.8 (phenyl), 130.3(C-3), 129.6(C-2), 102.6 (PhC), 90.2 (C-1), 75.7 (*t*-$CMe_3$), 75.6 (C-4), 70.0 (C-6), 64.0 (C-5), 29.3 (*t*-C($CH_3$)$_3$). Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32, H, 7.64. Found: C, 70.53, H, 7.86.

**Table 3**
Anomerization of glycoside in the presence of catalyst

| Entry | catalyst | α:β ratio |
|---|---|---|
| 1[a] | $Et_3N$ | 1.3:1.0 |
| 2[a] | $BF_3{\cdot}OEt_2$[1b] | 6.6:1.0 |
| 3[a] | $FeCl_3$[16] | 5.1:1.0 |
| 4[a] | $I_2$[3] | 5.4:1.0 |
| 5[a] | DDQ[4a] | 4.8:1.0 |
| 6[b] | $BF_3{\cdot}OEt_2$[6] | 5.9:1.0 |
| 7[b] | $BiCl_3$[17] | 6.0:1.0 |

[a] Starting material is 1.3:1.0 mixture of **11a** and **12a**.
[b] Starting material is 1.4:1.0 mixture of **11k** and **12k**.

### 1.3. Typical procedure for Ferrier rearrangement of 4,6-di-*O*-acetyl-D-glucal (10)

To a solution of **10** (10 mg, 20 mg, 30 mg or 100 mg) in 1 M $CH_2Cl_2$ were added $Et_3N$ (4 equiv) and MsCl (1.5 equiv) at 0 °C. After 5 min, MeOH (4 equiv) was added, and the solution was heated with stirring for 2 h at 40 °C. The reaction mixture was washed with satd $NH_4Cl$ and satd NaCl, and dried. The filtrate was evaporated, and a residue was purified by flash column chromatography with 4:1 hexane–acetone to give a 1.3:1.0 mixture of **11a** and **12a**. For details see Table 2.

#### 1.3.1. 4-Methylphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-β-D-*erythro*-1-thio-hex-2-enopyranoside (11i)

$^1$H NMR ($CDCl_3$): *δ* 7.44, 7.13 (each d, 2H, *J* 8.1, –Ph), 5.96 (ddd, 1H, $J_{1,2}$ 1.8 Hz, $J_{2,3}$ 10.2 Hz, $J_{2,4}$ 0.7 Hz, H-2), 5.80 (dd, 1H, $J_{3,4}$ 2.4 Hz, H-3), 5.59 (br d, 1H, H-1), 5.18 (ddd, 1H, $J_{4,5}$ 9.2 Hz, H-4), 4.30–4.28(m, 2H, H-6), 4.10 (ddd, 1H, $J_{5,6}$ 4.7 Hz, 4.6, H-5), 2.36 (s, 3H, -Ph*Me*), 2.13, 2.11 (each s, 3H, OAc). For details see Table 2.

### 1.3.2. 4-Methylphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-1-thio-hex-2-enopyranoside (12i)

$^1$H NMR ($CDCl_3$): $\delta$ 7.46, 7.14 (each d, 2H, $J$ 8.1 Hz, Ph), 6.07 (ddd, 1H, $J_{1,2}$ 1.9 Hz, $J_{2,3}$ 10.1 Hz, $J_{2,4}$ 1.2 Hz, H-2), 5.87 (dd, 1H, $J_{3,4}$ 1.5 Hz, H-3), 5.70 (br d, 1H, H-1), 5.39 (ddd, 1H, $J_{4,5}$ 9.5 Hz, H-4), 4.50 (m, 1H, H-5), 4.28–4.13 (m, 2H, H-6), 2.35 (s, 3H, -PhC$H_3$), 2.13, 2.11 (each s, 3H, –OAc). For details see Table 2.

### 1.3.3. Ethyl 4,6-di-*O*-acetyl-2,3-dideoxy-β-D-*erythro*-1-thio-hex-2-enopyranoside (11j)

$^1$H NMR ($CDCl_3$): $\delta$ 5.93 (dd, 1H, $J_{1,2}$ 1.3 Hz, $J_{2,3}$ 10.3 Hz, H-2), 5.88 (br d, 1H, H-3), 5.41 (d, 1H, H-1), 5.29 (dd, 1H, $J_{4,5}$ 6.6 Hz, H-4), 4.27–4.19 (m, 2H, H-6), 3.87–3.83 (m, 1H, H-5), 2.71 (q, 2H, $J$ 4.2 Hz, –S$CH_2$C$H_3$) 2.15, 2.11 (each s, 3H, –OAc), 1.29 (t, 3H, –SC$H_2$$CH_3$). For details see Table 2.

### 1.3.4. Ethyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-1-thio-hex-2-enopyranoside (12j)

$^1$H NMR ($CDCl_3$): $\delta$ 5.94 (br d, 1H, $J_{2,3}$ 10.1 Hz, H-2), 5.78 (br d, 1H, H-3), 5.58 (br s, 1H, H-1), 5.37 (d, 1H, $J_{4,5}$ 9.1 Hz, H-4), 4.32 (m, 1H, H-5), 4.27 (dd, 1H, $J_{5,6}$ 5.2 Hz, $J_{6,6'}$ 11.9 Hz, H-6), 4.18 (d, 1H, H-6′), 2.71 (q, 2H, $J$ 4.2 Hz, –S$CH_2$C$H_3$), 2.12, 2.11 (each s, 3H, –OAc), 1.34 (t, 3H, –SC$H_2$$CH_3$). For details see Table 2.

### 1.3.5. Phenyl 4,6-di-*O*-acetyl-2,3-dideoxy-β-D-*erythro*-1-thio-hex-2-enopyranoside (11k)

$^1$H NMR ($CDCl_3$): $\delta$ *7.55–7.29* (m, 5H, -SPh), 5.96 (ddd, 1H, $J_{1,2}$ 1.8 Hz, $J_{2,3}$ 10.2 Hz, $J_{2,4}$ 2.4 Hz, H-2), 5.82 (dd, 1H, $J_{3,4}$ 2.4 Hz, H-3), 5.64 (br d, 1H, H-1), 5.20 (ddd, 1H, $J_{4,5}$ 7.5 Hz, H-4), 3.92 (m, 1H, H-5), 4.28 (m, 2H, H-6), 2.10, 2.07 (each s, 3H, –OAc). For details see Table 2.

### 1.3.6. Phenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-1-thio-hex-2-enopyranoside (12k)

$^1$H NMR ($CDCl_3$): $\delta$ *7.56–7.29* (m, 5H, -SPh), 6.06 (ddd, 1H, $J_{1,2}$ 1.2 Hz, $J_{2,3}$ 10.1 Hz, $J_{2,4}$ 1.9 Hz, H-2), 5.87 (dd, 1H, $J_{3,4}$ 1.9 Hz, H-3), 5.76 (br d, 1H, H-1), 5.38 (ddd, 1H, $J_{4,5}$ 9.4 Hz, H-4), 4.47 (m, 1H, H-5), 4.29 (dd, 1H, $J_{5,6}$ 5.9 Hz, $J_{6,6'}$ 12.1 Hz, H-6), 4.18 (d, 1H, $J_{5,6'}$ 2.8 Hz, H-6′), 2.11, 2.04 (each s, 3H, –OAc). For details see Table 2.

### 1.4. Anomerization of 11a and 12a by promoter used for the Ferrier rearrangement

A mixture of **11a** and **12a** (1.3:1.0) (30 mg, 130.3 μmol) in MeCN (650 μL)–MeOH (6 mg, 196 μmol) was stirred in the presence of promoter ($BF_3$·$Et_2O$, $FeCl_3$, $I_2$, DDQ, 0.1 equiv). After 1 h, a product ratio was determined by $^1$H NMR spectroscopy. A 1.4:1.0 mixture of **11k** and **12k** (30 mg, 92 μmol) was treated similarly.

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