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Direct Ferrier rearrangement on unactivated glycals catalyzed by indium(III) chloride

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ABSTRACT

Anhydrous $InCl_3$ has been shown to efficiently catalyze the Ferrier rearrangement by a direct allylic substitution of the hydroxyl group at *C*-3 position of glycals to afford the corresponding 2,3-unsaturated glycosides in high yields at ambient temperature. This methodology obviates the need for protecting and/or activating the *C*-3 hydroxyl group of glycals. The reaction works in equal ease with both 4,6-di-*O*-benzyl-D-glucal and 4,6-di-*O*-benzyl-D-galactal. The mildness of $InCl_3$ makes this approach compatible for glycosyl acceptors with acid labile groups. The generality of the reaction has been demonstrated with a diversity of alcohols, phenols, and sugar nucleophiles.

Ferrier rearrangement is one among the few name reactions which continues to offer widespread applications in organic synthesis for over four decades.[1] In his pioneering work, Ferrier reported that tri-*O*-acetyl-D-glucal **1** on exposure to $BF_3{\cdot}OEt_2$ in the presence of an alcohol afforded 2,3-unsaturated glycosides **2** as an anomeric mixture (Scheme 1).[2] Since then, the rearrangement has become synthetically the most useful transformation in glycal chemistry, as the resulting 2,3-unsaturated glycosides have served as versatile chiral intermediates in the synthesis of antibiotics,[3] natural products,[4] glycopeptides,[5] nucleosides,[6] oligosaccharides,[1f,7] uronic acids,[8] and modified carbohydrates.[9] A wide range of catalysts have been employed in the Ferrier rearrangement.[10] The synthetic importance of this glycosylation reaction is clearly evident from the vast number of publications on this topic.[10] Literature reports that tri-*O*-acetyl-D-glucal has been the most common choice of the glycosyl donor due to its ready availability, although the rearrangement has been studied on other glycals too.[11] However, successful Ferrier rearrangement has been carried out only with glycals possessing a good leaving group at the *C*-3 position such as tricholoracetamidate,[12] *tert*-butyloxycarbonyl ester,[13] *n*-pentenoyl ester,[14] benzoyl ester,[15] carbonate,[16] propargyl ether,[17] and benzyl ether.[10b,11a,18] Thus, an additional step of appropriately protecting the *C*-3 hydroxyl group of glycals is an essential pre-requisite in many examples reported so far. In addition, expensive catalysts such as $Pd(PhCN)_2Cl_2$/DTTBP,[12a] IDCP,[14] Et_2Zn–$Pd(OAc)_2$/DTTBP,[13] and $AuCl_3$[17] are often required to further activate the leaving group at the *C*-3 position to realize the allylic rearrangement. Except for a few scattered reports,[14,16] examples of a direct Ferrier rearrangement on glycals possessing a free hydroxyl group at the *C*-3 position are uncommon. Even in such cases, low yield of the resulting glycosides[14] or use of a very strong acid (such as trifluoroacetic acid) in large excess limits their synthetic applications, especially toward acid labile glycosyl acceptors/donors in the latter case.[16] A couple of examples on Ferrier-type rearrangement under Mitsunobu conditions though available, are limited to the use of carboxylic acids[19] and phenols[20] as glycosyl acceptors, and are not suitable for alcohols. Development of an efficient method for direct substitution of alcohols is still a challenging goal in organic chemistry given the poor leaving ability of the hydroxyl group. As a part of our research program aimed at the use of $InCl_3$ as a mild catalyst in carbohydrate chemistry, we recently reported a stereoselective synthesis of unsaturated glycosides via $InCl_3$-catalyzed 1,3-alkoxy migration in glycal ethers.[21] A recent report of Baba et al.[22] on direct allylic substitution of alcohols with carbon nucleophiles using $InCl_3$ at high temperatures prompted us to explore the catalytic behavior of $InCl_3$ toward glycals possessing a free hydroxyl group at *C*-3 position. In this Letter, we report a successful outcome of Ferrier rearrangement of di-*O*-benzyl-D-glucal as well as di-*O*-benzyl-D-galactal with a variety of alcohols as well as phenols in presence of just 5 mol % of $InCl_3$ as a catalyst. The reaction proceeds at ambient temperature (30 °C) affording products in high yields (68–92%), is stereoselective yielding predominantly α-anomers, and is

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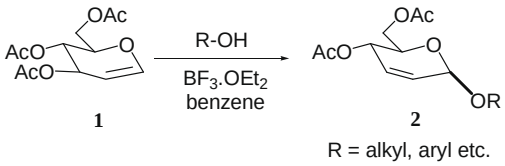


Scheme 1. Lewis acid-catalyzed Ferrier rearrangement of tri-*O*-acetyl-D-glucal.

compatible with acid-labile glycosyl acceptors. The interest of this methodology relies on the extremely mild conditions required even with a free hydroxyl group at the *C*-3 position.

Initially, Ferrier rearrangement was investigated on 4,6-di-*O*-benzyl-D-glucal **3**[23] with methanol in presence of 5 mol % of $InCl_3$ at ambient temperature (30 °C). The progress of the reaction was monitored by TLC which indicated a gradual disappearance of the starting material and the appearance of a non-polar product. Complete consumption of the starting material was noticed after 14 h. Upon purification and careful analysis, the product was indeed identified as methyl 4,6-di-*O*-benzyl-2,3-dideoxy-hex-2-enopyranoside **4**, obtained as an anomeric mixture (α:β = 4:1) in an overall isolated yield of 87%.

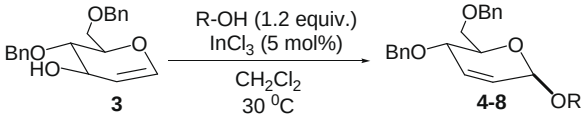
A higher catalyst load while reducing the reaction time, did not bring about any significant change in the yield or anomeric selectivity. Encouraged by the initial results, the reaction was then carried out with benzyl and allyl alcohols, which also underwent $InCl_3$-catalyzed Ferrier rearrangement smoothly to afford the corresponding 2,3-unsaturated glycosides **5** and **6,** respectively, in high yields (Table 1, entries 2 and 3). Synthetically more rewarding is the success of the reaction with sugar nucleophiles possessing acid-labile acetal functionalities (Table 1, entries 4 and 5). The disaccharides **7** and **8** were obtained in good yields with the acetal groups remaining intact. Notably, in all these examples the anomeric ratio (α:β = 4:1) remained almost the same with the α-anomer being the major isomer.

Having successfully accomplished the direct $InCl_3$-catalyzed Ferrier rearrangement of 4,6-di-*O*-benzyl-D-glucal with a few alcohols, we next focused our attention with a greater emphasis on a similar reaction with 4,6-di-*O*-benzyl-D-galactal.

It is well documented in the literature that Ferrier rearrangement of protected galactals is rather difficult and not as straight forward as for protected glucals due to the competing formation of 2-deoxy glycosides.[16,24] Only a very few successful methods are available for the Ferrier rearrangement of galactals even with a good leaving group at the *C*-3 position such as acetyl, *n*-pentenoyl ester, and trichloroacetamidate.[12,14] Given this background, we considered that a successful Ferrier rearrangement on galactal especially with a free hydroxyl group at the *C*-3 position would prove to be of exceptional synthetic value. Thus, when we treated 4,6,-di-*O*-benzyl-D-galactal[25] with methanol in presence of 5 mol % of $InCl_3$ at 30 °C, we were surprised to notice that the expected 2,3-unsaturated glycoside **10** was formed in a very high yield of 91%. Better anomeric diastereoselectivity (α:β = 95:5) observed in this case as compared to glycoside **4** obtained from 4,6-di-*O*-benzyl-D-glucal deserves mention. Inspired with the initial success, the reaction was tested with a variety of alcohols (Table 2, entries 2–6). Gratifyingly, in all the cases, Ferrier rearrangement occurred smoothly affording the corresponding 2,3-unsaturated glycosides in very high yields and high α-selectivity. Noteworthy is that most of these reactions are much faster than their glucal counterparts (Tables 1 and 2, entries 2–5). As in the previous case, sugar nucleophiles such as 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose and 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose also reacted with ease to afford the disaccharides in high yields (Table 2, entries 4 and 5). Further, formation of 2-deoxy galactosides in these examples was hardly observed even in the ^1H NMR spectra of the crude reaction mixtures. This circumvents the existing difficulty in the synthesis of 2,3-unsaturated galactosides and makes this methodology more attractive and reliable. The success of this reaction with phenols (Table 2, entries 7–9) further demonstrates its generality and applicability to aryl nucleophiles. Notably, an earlier report on a Mitsunobu approach for the synthesis of **17** resulted in an inseparable mixture of compounds.[20] Further, while Mitsunobu reaction of 4,6-di-*O*-benzyl-D-galactal **9** with carboxylic acids[19b] or phenols[20] as nucleophiles predominantly or exclusively afforded products arising out of a direct S_N2 reaction, exclusive Ferrier rearrangement of **9** reported here is complimentary. Given the literature background that 2,3-unsaturated aryl glycosides serve as useful precursors for palladium-catalyzed stereoselective C-glycosylation reactions,[26] compounds **16**–**18** reported here would prove to be of a synthetic value.

In conclusion, we have demonstrated that $InCl_3$, though considered as a mild Lewis acid, is an excellent catalyst for the Ferrier rearrangement of unactivated glycals. The reaction condition is mild and the reaction requires only 5 mol % of $InCl_3$.[27] The reaction is compatible with acid-labile functional groups, is stereoselective, and is general toward a wide range of oxygenated nucleophiles. Our results significantly highlight that protection and/or prior activation of *C*-3 hydroxyl group of glycals is not an essential criterion to realize a successful Ferrier rearrangement. Surpassing result is the facile synthesis of a wide array of 2,3-unsaturated galactosides, which are otherwise difficult to obtain. We believe that the methodology reported here is synthetically quite attractive and would spur on further interests toward the synthesis of complex glycosides.

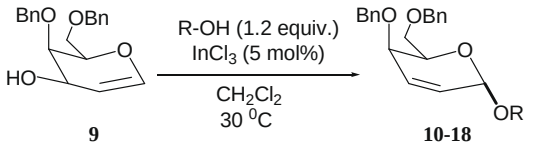
Table 1
$InCl_3$-catalyzed Ferrier rearrangement of 4,6-di-*O*-benzyl-D-glucal



Entry	R	Product	Time (h)	Yield[a] (%)	Ratio (α/β)[b]
1	Methyl	4[c]	14	87	81:19 (90:10)
2	Benzyl	5[c]	10	84	83:17 (96:4)
3	Allyl	6[c]	13	92	83:17 (85:15)
4	1,2:3,4-Di-*O*-isopropylidene-D-galactopyranosyl	7[c]	9	75	83:17 (100:0)
5	1,2:5,6-Di-*O*-isopropylidene-D-glucofuranosyl	8[c]	8	68	80:20 (90:10)

[a] Isolated yield after column chromatography.
[b] Anomeric ratios were obtained from ^1H NMR spectra of the crude products; values in parantheses refer to the anomeric ratios of the products obtained after column chromatography.
[c] Spectral data are consistent with literature values (Refs. 10b,13,18a,21).

Table 2
$InCl_3$-catalyzed Ferrier rearrangement of 4,6-di-*O*-benzyl-D-galactal



9 **10-18**

Entry	R	Product	Time (h)	Yield[a] (%)	Ratio (α:β)[b]
1	Methyl	10	26	91	95:5 (100:0)
2	Benzyl	11[c]	2	90	92:8 (100:0)
3	Allyl	12	8	86	92:8 (100:0)
4	1,2:3,4-Di-*O*-isopropylidene-D-galactopyranosyl	13	5	82	84:16 (89:11)
5	1,2:5,6-Di-*O*-isopropylidene-D-glucofuranosyl	14	7	68	82:18 (91:9)
6	Cyclohexyl	15[c]	14	88	92:8 (100:0)
7	Phenyl	16	7	90	91:9 (96:4)
8	*p*-Methylphenyl	17	8	89	91:9 (93:7)
9	*p*-Methoxyphenyl	18	5	90	93:7 (100:0)

[a] Isolated yield after column chromatography.
[b] Anomeric ratios were obtained from ^1H NMR spectra of the crude products; values in parantheses refer to the anomeric ratios of the products obtained after column chromatography.
[c] Spectral data are consistent with the literature values (Refs. 16,21).

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Supplementary data

Supplementary data (spectral data of compounds **4–8, 10–18** (pp. S1–S13) and copies of ^1H and ^{13}C NMR spectra (pp. S14–S41)) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.04.084.

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27. *General procedure*: Glycal **3** or **9** (1 mmol) was dissolved in dry CH_2Cl_2 (10 mL) and dried over activated molecular sieves (4 Å) overnight in order to remove any moisture if present. The solution was then transferred by syringe to a dry three-necked round-bottomed flask (flame-dried and cooled under argon). Nucleophile (1.2 mmol) was added and after 5 min, 5 mol % of anhydrous $InCl_3$ was added and the reaction mixture was stirred under argon atmosphere for specific time mentioned in Tables 1 and 2. The reaction mixture was then quenched with water and extracted with chloroform (3×50 mL). The combined organic layer was washed with water, dried over anhydrous sodium sulfate, filtered, and concentrated. The product was purified by column chromatography with hexane/ethyl acetate as an eluent to obtain the corresponding 2,3-unsaturated glycosides (**4–8**, **10–18**).