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Scope of $AuCl_3$ in the activation of per-*O*-acetylglycals

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ABSTRACT

Gold(III)chloride in catalytic amounts activates 3,4,6-tri-*O*-acetyl-D-glucal, 3,4,6-tri-*O*-acetyl-D-galactal, and 3,4-di-*O*-acetyl-L-rhamnal efficiently. The activated species can be employed in the Ferrier reaction with different nucleophiles at ambient conditions. Attempts have been made to make β-anomer of the Ferrier product from anomeric-*O*-propargylated Ferrier product.

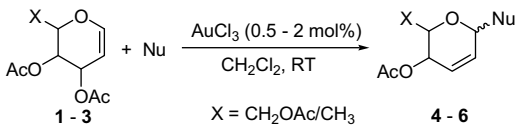
1. Introduction

There has been substantial interest in the use of gold compounds for several organic transformations in recent years.[1] Gold catalysts have been used mostly in the activation of π-bond of alkynes, allenes, and alkenes. The activated species has been utilized in hydrofunctionalization using carbon and hetero nucleophiles or cycloisomerization reactions. Activation and reaction of C–H bonds by gold catalysts has also gained significant interest.[2] In carbohydrate chemistry, $AuCl_3$ was utilized by Hotha et al. in the glycosylation reactions using propargyloxy group as the leaving group.[3] Anomeric-*O*-propargylated glycosyl donors and 3-*O*-propargylated glucals have been employed in these reactions to get, respectively, glycosides and 2,3-unsaturated glycosides. 2,3-Unsaturated glycosides are useful intermediates in carbohydrate chemistry to synthesize compounds with wide range of biological activities.[4] In view of this, several catalysts have been found to effect the Ferrier reaction.[5] Most of the catalysts are either Lewis acids[6] or oxidants.[7] All these reactions result in the formation of α-anomers as the major product.

Making β-anomer of 2,3-unsaturated sugar poses a challenging task due to anomeric effect. To make the β-anomer, only one method is known so far that employs $Pd(OAc)_2$ and bulky phosphine ligands.[8] In this regard we wished to utilize the oxophilicity and alkynophilicity of $AuCl_3$ to explore its possible application in making the β-anomer of 2,3-unsaturated glycosides. Further we believed that the bigger size of gold will influence the selectivity. Incidentally the glycosylation reaction of glycals using catalytic $AuCl_3$ has not been attempted with easily accessible per-*O*-acetylglycals. Our idea is to make the α-propargylated 2,3-unsaturated glycoside from 3,4,6-tri-*O*-acetyl-D-glycals using $AuCl_3$. Further, utilizing the activation of propargyl group by $AuCl_3$, we believed that a nucleophile could displace in an S_N2 fashion to form the β-anomer. We disclose the results of our attempts in this lines.

2. Results and discussion

In order to make a complete study we studied the $AuCl_3$-catalyzed Ferrier reactions on 3,4,6-tri-*O*-acetyl-D-glucal first. It underwent smooth Ferrier reaction (Scheme 1). The results are presented in Table 1. The reactions occurred at room temperature even with lesser amounts of the catalyst (0.5–2 mol % of $AuCl_3$). Reaction carried out at 0 °C also showed almost same selectivity, however, took more time for completion. Interestingly no reaction was observed when Ph_3PAuCl was used. The highlight of the $AuCl_3$-catalyzed Ferrier reaction is that a variety of nucleophiles such as *O*-, *S*-, and *C*-nucleophiles could be employed. Reaction of 3,4,6-tri-*O*-acetyl-D-glucal with primary, secondary, allylic, benzylic, and propargylic alcohols gave excellent yields. Reaction involving phenol was not effective as it gave a mixture of products. Reactions with 3,4,6-tri-*O*-acetyl-D-glucal needed only less amount of the catalyst (0.5 mol %) except the reactions involving propargyl alcohol, 3-butyn-2-ol, and monosaccharide nucleophiles where 2 mol % of the catalyst was needed. In the case of propargyl alcohol and 3-butyn-2-ol nucleophiles the catalyst might coordinate to the triple bond making itself less available for the activation of glycal. In all the cases α-anomer predominated over the β-anomer. The α-selectivity was moderate to good. This may be attributed to the bigger size of gold that blocks the α-face. The α/β ratio was based on the integration of the C-1 hydrogen of α- and β-anomers in the ^1H NMR spectra, which appear at distinct positions.[6,7] Thiol nucleophiles, which generally interact with gold also worked well. Allyltrimethylsilane and ethyl acetoacetate resulted in C-glycosylation. Although the yields were good, the α-selectivity was slightly less comparatively. We then examined the $AuCl_3$-catalyzed



Scheme 1. $AuCl_3$-catalyzed Ferrier reaction.

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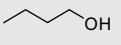
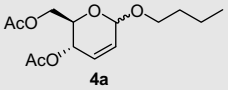
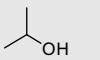
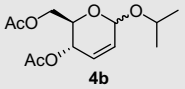
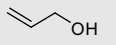
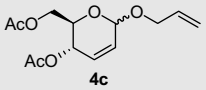
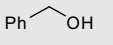
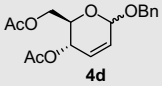
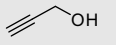
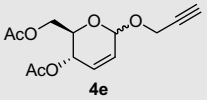
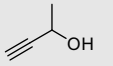
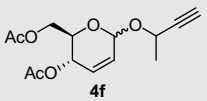
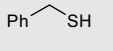
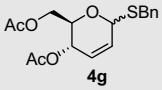
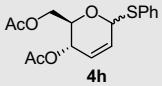
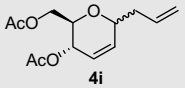
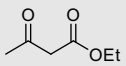
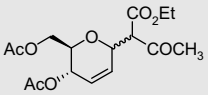
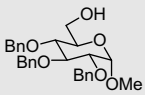
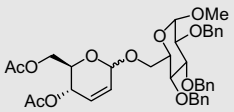
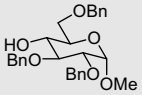
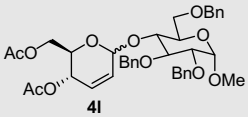
Ferrier reaction using monosaccharide nucleophiles. We prepared methyl 2,3,4-tri-*O*-benzyl glucopyranoside[9] and methyl 2,3,6-tri-*O*-benzyl glucopyranoside[10] using literature protocols and employed them in Ferrier reactions. These substrates needed 2 mol % of the catalyst. While the reaction involving methyl 2,3,4-tri-*O*-benzyl glucopyranoside gave good yield, the selectivity was only 4.2:1. Whereas excellent α-selectivity was observed with methyl 2,3,6-tri-*O*-benzyl glucopyranoside. This observation is in line with the data reported previously with other Lewis acids.

Table 1
$AuCl_3$-catalyzed Ferrier reaction on 3,4,6-tri-*O*-acetyl-D-glucal **1**

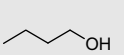
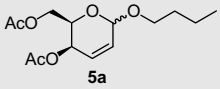
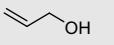
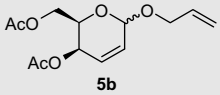
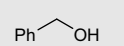
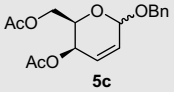
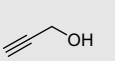
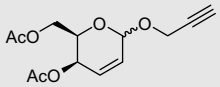
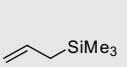
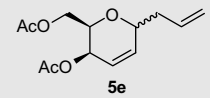
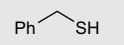
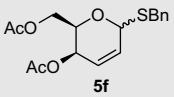
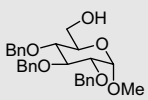
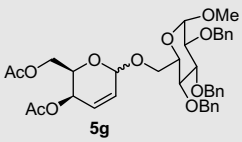
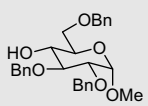
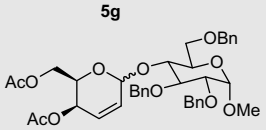
Entry	Nucleophile	Product	Reaction time	Yield[a] (α/β)[b]
1		 **4a**	3.5 h	98% (8:1)[c]
2		 **4b**	16 h	98% (4:1)[c]
3		 **4c**	9 h	97% (6.3:1)[c]
4		 **4d**	15 min	98% (3.4:1)[c]
5		 **4e**	6.5 h	85% (6.5:1)[d]
6		 **4f**	5 h	72% (6:1)[d]
7		 **4g**	18 h	82% (3:1)[c]
8	PhSH	 **4h**	1 h	97% (4:1)[c]
9		 **4i**	9 h	81% (2.6:1)[c]
10		 **4j**	15 min	80% (4.4:1)[c]
11		 **4k**	5 h	74% (4.2:1)[d]
12		 **4l**	3 h	54% (mostly α)[d]

[a] Isolated yields.
[b] Ratio was based on the integration of the corresponding anomeric protons in the ^{1}H NMR spectrum.
[c] Catalyst (0.5 mol %) was used.
[d] Catalyst (2 mol %) was used.

Gold catalysts are efficient for the cycloisomerization reactions of enynes.[1g] The Ferrier product of propargyl alcohol and 3,4,6-tri-*O*-acetyl-D-glucal is an enyne system. In this regard we expected the corresponding cycloisomerization product, a fused bicyclic system. However, we got the Ferrier product only and did not observe any cycloisomerization of the Ferrier product. Our attempt to cycloisomerize the above Ferrier product using $Ph_3PAuCl/AgSbF_6$ gave a mixture of products.

We then examined the $AuCl_3$-catalyzed Ferrier reaction on 3,4,6-tri-*O*-acetyl-D-galactal **2**. The reactions were sluggish compared to that of 3,4,6-tri-*O*-acetyl-D-glucal when 0.5 mol % of the catalyst was used. This observation is not surprising as 3,4,6-tri-*O*-acetyl-D-galactal **2** is generally less reactive than 3,4,6-tri-*O*-acetyl-D-glucal. However, the reaction profile improved when 2 mol % of $AuCl_3$ was used (Table 2). The difference in reactivity of 3,4,6-tri-*O*-acetyl-D-glucal and 3,4,6-tri-*O*-acetyl-D-galactal toward $AuCl_3$-catalyzed Ferrier reaction was further confirmed by doing the following control experiment. Equimolar quantities of 3,4,6-tri-*O*-acetyl-D-glucal and 3,4,6-tri-*O*-acetyl-D-galactal were treated with *n*-butanol in dry CH_2Cl_2 containing 1 mol % of $AuCl_3$ for 3 h. Analyzing the ^{1}H NMR spectra of the product mixture revealed that the corresponding Ferrier products of glucal and galactal derivatives were in the ratio of 3:2, respectively. Different nucleophiles (*O*-, *S*-, and *C*-nucleophiles) were employed in the reactions. The yields were comparatively lower than the reactions involving 3,4,6-tri-*O*-acetyl-D-glucal and the reactions took more time for completion. However monosaccharide nucleophiles reacted faster. Like in the Ferrier reaction with 3,4,6-tri-*O*-acetyl-D-glucal, propargyl alcohol

Table 2
$AuCl_3$-catalyzed Ferrier reaction on 3,4,6-tri-*O*-acetyl-D-galactal **2**

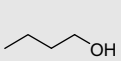
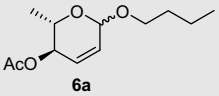
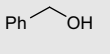
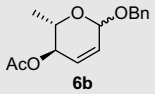
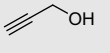
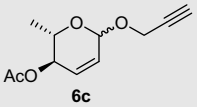
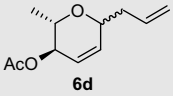
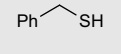
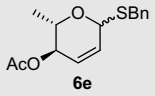
Entry	Nucleophile	Product	Reaction time	Yield[a] (α/β)[b]
1		 **5a**	16 h	69% (9:1)[c]
2		 **5b**	16 h	63% (>10:1)[d]
3		 **5c**	12 h	72% (>10:1)[c]
4		 **5d**	24 h	31% (mostly α)[d]
5		 **5e**	27 h	76% (mostly α)[d]
6		 **5f**	8 h	53% (11:1)[d]
7		 **5g**	3 h	57% (8.4:1)[d]
8		 **5h**	3 h	58% (10:1)[d]

[a] Isolated yields.
[b] Ratio was based on the integration of the corresponding anomeric protons in the ^{1}H NMR spectrum.
[c] Catalyst (1 mol %) was used.
[d] Catalyst (2 mol %) was used.

reacted slowly with 3,4,6-tri-*O*-acetyl-D-galactal even in the presence of 2 mol % of $AuCl_3$ resulting in low yield. The same argument that was put earlier i.e., possible coordination of $AuCl_3$ to alkynic bond is valid here as well for the poor outcome of the reaction. The α-selectivity was in general excellent. In couple of cases α-glycosylated products were obtained exclusively.

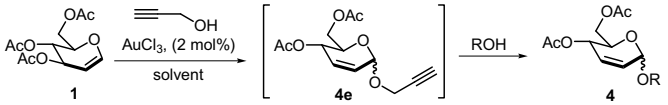
Ferrier reactions on 3,4-di-*O*-acetyl-L-rhamnal were also studied with representative nucleophiles. The reactions proceeded smoothly and the yields were good to excellent. The results are presented in Table 3. The α-selectivity is preferred here as well.

Table 3
$AuCl_3$-catalyzed Ferrier reaction on 3,4-di-*O*-acetyl-L-rhamnal **3**

Entry	Nucleophile	Product	Reaction time	Yield[a] (α/β)[b,c]
1		 **6a**	45 min	86% (5:1)
2		 **6b**	45 min	67% (5.5:1)
3		 **6c**	45 min	92% (5.7:1)
4		 **6d**	1.5 h	62% (>15:1)
5		 **6e**	3 h	95% (7:1)

[a] Isolated yields.
[b] Ratio was based on the integration of the corresponding anomeric protons in the ^1H NMR spectrum.
[c] Catalyst (1 mol %) was used.

Hotha et al. have recently reported the glycosylation at the anomeric position using $AuCl_3$-catalyzed anomeric activation of propargyl glycosides.[3a] They had observed β-selectivity in majority of the cases studied. In this regard we considered the $AuCl_3$-catalyzed glycosylation of propargylated Ferrier product **4e**, which in turn could be obtained in the same pot by the Ferrier reaction on **1**. S_N2 reaction on the major α-isomer of **4e** with nucleophiles would, in principle, give the β-isomer of **4** (Scheme 2). We treated 3,4,6-tri-*O*-acetyl-D-glucal with propargyl alcohol in the presence of 2 mol % of $AuCl_3$ in different solvents. The results are presented in Table 4. Except in DMF the reaction occurred in other solvents such as CH_2Cl_2, CH_3CN, dioxane, and THF. The α/β ratio of **4e** formed in these reactions is in the range of 6:1. To the same reaction mixture *n*-BuOH was added and the reaction was continued. In dichloromethane no glycosylation was noticed even after 27 h of reflux. However, the reaction occurred in CH_3CN under reflux to give Ferrier product **4a**. The α/β ratio was found to be reduced to 5:1 (entry 2, Table 4), which was 8:1 in the direct Ferrier reaction (entry 1, Table 1). Although the change in selectivity is marginal it encouraged us to attempt the reactions using $AgSbF_6$ and AgOTf as additives, which will generate more cationic Au species to activate the triple bond better. The reaction proceeded at room temperature, but the formation of β-isomer was not improved. Similar results were observed when benzyl alcohol was used as nucleophile (entries 10 and 11). From these results it is clear that there is no sign of S_N2 attack. Further it indicates that the activation of the propargyloxy group by $AuCl_3$ generates the oxocarbenium ion. The anomeric effect of the ring oxygen and the conformation of the ring favors the α-attack. Also the results reveal that the participation of acetonitrile to favor the β-attack by coordinating to the oxocarbenium ion is also negligible. This is in line with the results of already reported Ferrier reactions catalyzed by Lewis acids in acetonitrile solvent.[6] Hence we wished to reduce the participation of ring oxygen to anomeric effect. Since lithium is oxophilic we conducted the reaction by adding 2 equiv of $LiClO_4$ with respect to the amount of 3,4,6-tri-*O*-acetyl-D-glucal. However, it did not help in this way and α/β ratio of 6.2:1 was observed (entry 8). This may be due to the presence of many oxygen sites in the substrate for lithium ion coordination. It has to be mentioned that some amount (<20%) of propargylated Ferrier product **4e** was isolated from all the reactions except the reactions involving co-catalysts AgOTf/$AgSbF_6$.



Scheme 2. $AuCl_3$-catalyzed one-pot propargylation and subsequent glycosylation.

Table 4
Results of $AuCl_3$-catalyzed one-pot propargylation and subsequent glycosylation

Entry	ROH	Solvent and condition	4	Yield[a] (%)	α:β[b]
1	*n*-BuOH	CH_2Cl_2/reflux, 27 h	**4e**	80	6.4:1
2	*n*-BuOH	CH_3CN/reflux, 24 h	**4a**	50	5:1
3	*n*-BuOH	CH_3CN/rt, 22 h[c]	**4a**	68	7.6:1
4	*n*-BuOH	CH_3CN/rt, 22 h[d]	**4a**	66	7.4:1
5	*n*-BuOH	Dioxane/rt, 27 h	**4a**	61	5.5:1
6	*n*-BuOH	THF/rt, 21 h	**4a**	53	7:1
7	—	DMF/rt, 24 h	—	NR	—
8	*n*-BuOH	CH_3CN/rt, 24 h[e]	**4a**	41	6.2:1
9	—	CH_3CN/rt, 24 h[c,f]	—	NR	—
10	BnOH	CH_3CN/rt, 25 h[c]	**4d**	64	3.1:1
11	BnOH	CH_3CN/rt, 28 h[d]	**4d**	73	3.1:1

[a] Isolated yields.
[b] Ratio was based on the integration of the corresponding anomeric protons in the ^1H NMR spectrum.
[c] $AgSbF_6$ (6 mol %) was used in addition.
[d] AgOTf (6 mol %) was used in addition.
[e] $LiClO_4$ (2 equiv) was used in addition.
[f] PPh_3 (20 mol %) was used in addition.

We then thought of sterically blocking the α-face of the gold-coordinated oxocarbenium species by coordinating gold with bulky ligands such as PPh_3. This strategy had been applied in the preparation of β-Ferrier product using palladium catalyst.[8] However, even the Ferrier reaction on 3,4,6-tri-*O*-acetyl-D-glucal was not noticed (entry 9). With glycosyl acceptors methyl 2,3,4-tri-*O*-benzyl glucopyranoside and methyl 2,3,6-tri-*O*-benzyl glucopyranoside, however, the transglycosylation reaction with 3,4,6-tri-*O*-acetyl-D-glucal did not occur. The transglycosylation reaction with 3,4,6-tri-*O*-acetyl-D-galactal was not attempted as the Ferrier reaction with propargyl alcohol itself resulted in poor yield (entry 4, Table 2).

3. Conclusion

We have described $AuCl_3$ as an efficient catalyst for the Ferrier reaction of 3,4,6-tri-*O*-acetyl-D-glucal, 3,4,6-tri-*O*-acetyl-D-galactal, and 3,4-di-*O*-acetyl-L-rhamnal. The advantage of $AuCl_3$ has been shown by the versatility of the reaction with a range of nucleophiles. Also we presented our attempts to make β-*O*-glycosides using the activating ability of $AuCl_3$ toward propargyloxy group.

4. Experimental section

4.1. General remarks

All reagents were obtained commercially and used without further purification unless otherwise mentioned. Dichloromethane was freshly distilled over anhydrous CaH_2. Acetonitrile was distilled over CaH_2 and stored under argon atmosphere. Thin-layer chromatography was performed by using Merck silica gel F-254 coated aluminum plates and the visualization of spots was done using UV illumination and charring the TLC plates sprayed with Seebach solution or 5% H_2SO_4 solution in methanol. Column chromatography was performed over silica gel procured from Merck, using hexanes and ethyl acetate mixture as eluent. Solvents were removed under reduced pressure using rotovap. The ^1H NMR spectra were recorded in a Bruker Avance 400 MHz NMR machine using solutions in $CDCl_3$ containing TMS as an internal standard. IR spectra were recorded on JASCO FT/IR-5300 spectrometer. Elemental (C, H, N) analysis were done using Thermo Finnigan Flash EA 1112 analyzer. Optical rotations were measured using Rudolph Research Analytical Autopol-IV polarimeter.

4.2. General procedure for the $AuCl_3$-catalyzed Ferrier reaction

To a solution of 3,4,6-tri-*O*-acetyl-D-glucal **1**/3,4,6-tri-*O*-acetyl-D-galactal **2**/3,4-di-*O*-acetyl-L-rhamnal **3** (1 equiv) and aglycon (1.2 equiv) in anhydrous CH_2Cl_2 (3 mL/mmol) $AuCl_3$ (0.5–2 mol%) was added at room temperature. The reaction mixture was stirred at the same temperature. After complete consumption of the starting glycal derivative, solvent was evaporated and the residue was loaded on a silica gel column. The product was purified using EtOAc/hexanes as eluent system.

4.3. General procedure for the $AuCl_3$-catalyzed one-pot Ferrier and subsequent glycosylation reactions

To a solution of 3,4,6-tri-*O*-acetyl-D-glucal **1** (1 equiv) and propargyl alcohol (1.2 equiv) in dry solvent (5 mL/mmol) $AuCl_3$ (2 mol%) was added. The reaction mixture was stirred at room temperature. On complete consumption of **1** to form **4e**, which generally takes around 6 h, aglycon (1.2 equiv) was added. The reaction mixture was stirred under inert atmosphere. After stirring for specified time given in Table 4 it was purified using silica gel column using ethyl acetate and hexane mixture as eluent.

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Supplementary data

Characterization data and spectra of all the Ferrier products are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.07.087.

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