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Iodine-hexamethyldisilane (HMDS)-mediated anomerization of peracetylated 1,2-trans-linked alkyl and aryl glycosides ☆

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ABSTRACT

Treatment of peracetylated alkyl and aryl 1,2-trans-glycosides with iodine in the presence of HMDS has been found to result in the anomerization leading to the formation of the respective 1,2-cis-glycosides. In the case of alkyl glycosides with aglycons of short alkyl chain length complete anomerization to the α-glycosides was observed while with those of longer chain length the process was found to be incomplete. The observations have been interpreted mechanistically.

1. Introduction

A number of studies have been reported in the literature on the anomerization of various protected/unprotected alkyl glycosides and fully acetylated sugars using protic[2–4]/Lewis[5–9] acids as catalysts and their mechanisms are reasonably well understood. The Lewis acids used for the purpose include BF_3,[5] $FeCl_3$,[6] $SnCl_4$,[7] $TiCl_4$,[8] and $ZnCl_2$.[9] In comparison, the reports on the base-catalyzed analogous transformations have been very limited in number.[10–12] One of the early observations on the conversion of β-D-glucose pentaacetate to the α-anomer in this context has been by Wolfrom and Husted in 1937.[10] Later, Lindberg reported the anomerization of 2,4-dinitrophenyl β-D-glucoside to its α-analogue by alkali.[11] The mechanism of base-catalyzed anomerization of the dinitrophenyl glycosides was reported by Bervend and co-workers in 1988.[12] Attempts to anomerize the β-glucosides of phenol, 2-nitrophenol and 4-nitrophenol have, however, been reportedly unsuccessful.[11,12] Specifically, studies on the acid-/base-catalyzed anomerization of aryl glycosides have indeed been seen scarce.

Previously, we have reported the anomerization of armed thioglycosides using molecular iodine as well as of disarmed thioglycosides using iodine-HMDS system.[13] From the observations noted in the latter studies we expected that it should be capable of anomerizing the O-glycosides as well. A study was therefore undertaken to evaluate the scope and limitations of this reagent system with respect to the anomerization of various O-glycosides and the results are presented here.

2. Results and discussion

2.1. Anomerization of alkylglycosides

In the initial experiments using methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (**1β**) (Table 1, entries 1–4) as the sugar substrate for the anomerization reaction the amount of I_2 required for the process was optimized keeping the HMDS concentration constant. It was found that a ratio of 1:1 of **1β**:I_2 in combination with fivefold mol equiv of HMDS was satisfactory for the reaction. Under these conditions the anomerization of the 1,2-trans-linked **1β** was smooth and was complete in 3 h at rt yielding neat 1,2-cis-linked galactopyranoside **1α** (Table 1, entry 2) after the isolation of the product by an aqueous work-up. The appearance of a new doublet at δ 4.96 ($J_{1,2}$ = 3.5 Hz) along with the double doublet at δ 5.30 ppm (J = 3.5 Hz and 10.0 Hz) in its ^{1}H NMR spectrum provided the confirmatory evidence for the product and the physical constants were in agreement with literature values.[14] The signals due to the β-anomeric glycoside were absent in the product. In the ^{13}C NMR spectrum also the chemical shift (δ 94 ppm) for the anomeric carbon was characteristically that expected of the O-α-glycoside.

Encouraged by the outcome of these experiments other alkyl glycosides of different aglycon chain length were subjected to the optimized anomerization condition. Based on the distinct differences in the ease of formation of 1,2-trans-linked 1-thio-alkyl

☆ See Ref. 1.

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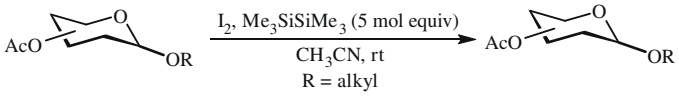
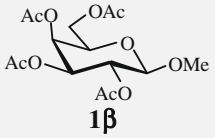
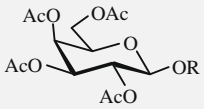
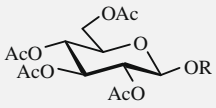
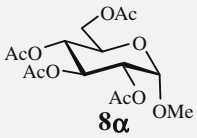
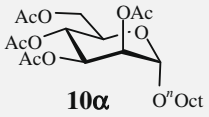
Table 1
Anomerization of alkyl glycosides using I_2-HMDS system[a]



Entry	Substrate	I_2 (mol equiv)	Time (h)	α:β[b]	Yield (%)
1	 **1β**	0.5	12	50:50	Quantitative (**1α/β**)
2		1.0	3	Only α-	Quantitative (**1α**)
3		1.5	3	Only α-	Quantitative (**1α**)
4		2	3	Only α-	Quantitative (**1α**)
					
5	**2β**, R = Et	1.0	0.5	Only α-	Quantitative (**2α**)
6	**3β**, R = ^{n}Pr	1.0	0.75	Only α-	Quantitative (**3α**)
7	**4β**, R = ^{n}Bu	1.0	6	90:10	Quantitative (**4α/β**)
8	**5β**, R = ^{n}Oct	1.0	12	60:40	Quantitative (**5α/β**)
9	**6β**, R = ^{i}Pr	1.0	2	70:30	60% (**6α/β**)
10	**7β**, R = ^{t}Bu	1.0	0.25	—[c]	No **7α** was obtained
					
11	**8β**, R = Me	1.0	5	Only α-	Quantitative (**8α**)
12	**9β**, R = Et	1.0	2	Only α-	Quantitative (**9α**)
13	 **8α**	1.0	24 h	No reaction	—
14	 **10α**	1.0	24 h	58:42	Quantitative (**10α/β**)

[a] All reactions were carried out in anhydrous acetonitrile (2 mL/100 mg sugar).
[b] Ratios are based on the ^{1}H NMR spectra of the product isolated by aq work-up.
[c] Trimethylsilyl glycoside **11α** was obtained.

glycosides and their in situ anomerization during the preparative reaction noted previously,[13,15] we were expecting the ethyl β-D-glycoside **2β** to undergo the anomerization reaction faster. Indeed as can be seen from Table 1 (entry 5) the anomerization of **2β** was complete in 0.5 h to give the 1,2-cis-linked glycoside **2α** in quantitative yield after isolation of the product by aq work-up.

The *n*-propyl glycoside **3β** also likewise underwent complete anomerization to give the expected **3α** in 0.75 h at rt (Table 1, entry 6). Further increase in the chain length of the aglycon alkyl residue was found to have marked effect on the reaction. Thus, while the *n*-butyl β-D-galactoside **4β** gave a mixture of the expected α and β anomers in 9:1 ratio in 6 h its octyl analogue **5β** gave the anomers in 6:4 ratio in 12 h clearly demonstrating the effect of the increasing chain length of the aglycon residue on the rate and the extent of the anomerization process (Table 1, entries 7 and 8, respectively).

To investigate the influence of the steric bulk of the aglycon moiety on the reaction, the isopropyl and *t*-butyl glycosides **6β** and **7β,** respectively, were chosen as the substrates for the study. Interestingly, the anomeric equilibration of the isopropyl galactoside **6β** using the I_2-HMDS system led to the expected anomers, but in a ratio of 7:3 in 2 h at rt (Table 1, entry 9) proving the reaction to be relatively slower in comparison to the anomerization of the corresponding *n*-propyl glycoside **3β** (Table 1, entry 6) under the same condition. However, in the case of *t*-butyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (**7β**), although the reaction under the above conditions led to a rapid consumption of the sugar derivative (**7β**), the expected α-glycoside **7α** was not obtained (Table 1, entry 10). Chromatography (TLC in EtOAc–*n*-hexane 1:1) showed the product to have two components, one moving slower than **7β** of an R_f value identical to that of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (**15**) and the other moving faster having an R_f value greater than **7β**. It should also be pointed out that no glycosyl iodide, namely, 2,3,4,6,-tetra-*O*-acetyl-α-D-galactopyranosyl iodide, was obtained in any of the experiments described above.

The differences in the rate of anomerization between glucose and galactose derivatives became also evident from the experiments conducted subsequently (Table 1, entries 2 and 11), the HMDS-I_2-mediated anomerization reaction of the galactose derivative **1β** being significantly faster in comparison to the corresponding *gluco*-configured **8β**. Attempts to convert the α-glucoside **8α** back to the corresponding β-glucoside (**8β**) by the I_2-HMDS reagent system proved unsuccessful (Table 1, entry 13) and only the

unchanged **8α** could be isolated after 24 h at rt. Ethyl β-D-glucoside (**9β**), as observed in the case of its *galacto*-analogue **2β**, anomerized faster than **8β** to yield the expected α-glycoside (**9α**) in quantitative yield (Table 1, entry 12). In the case of *n*-octyl 2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranoside (**10α**, an anomeric mixture containing **10α** and **10β** in a ratio of 58:42 was obtained after a prolonged reaction time of 24 h at rt (Table 1, entry 14).

The foregoing observations clearly indicated that the 1,2-trans-linked primary alkyl glycosides underwent the I_2-HMDS-mediated anomerization by a path different from that of the corresponding *t*-alkyl glycosides. The secondary alkyl glycosides for the most part appeared to follow the path taken by their primary alkyl analogues. Since a by-product with an R_f value greater than that of **7β** was obtained in the reaction of **7β** with I_2-HMDS system, showing the product to be slightly more non-polar in nature, along with the observation that it was rather unstable to conditions of the usual work-up procedure, the reaction of **7β** with HMDS-I_2 system was carried out in CD_3CN in an NMR tube and was monitored by ^1H NMR spectroscopy. In agreement with the observations made during the reaction-monitoring by TLC, the intensity of the H-signals obtained for **7β** before the addition of the reagent was found to deplete rapidly with the progressing reaction and was accompanied by the appearance of a new set of signals instead. The latter was in agreement with those expected for trimethylsilyl 2,3,4,6-tetra-*O*-acetyl-D-galactospyranoside (**13α/β**) as well as *t*-butyl iodide (**14**). The values of the chemical shifts obtained were in line with the values reported for authentic **13α**[16], **13β**[17] and **14**.[18] The hemiacetal **15** could be expected to result from **13** from the hydrolytic cleavage of the trimethylsilyl acetal linkage in it.

As the chemical shifts obtained in the ^1H NMR spectra for a majority of the ring protons of **7β**, **13α** and **13β** were found to be overlapping (see Table 2), and as the NMR spectral data for **7α**[19] in CD_3CN was not available from literature, an authentic sample of **7α** was prepared by the alcoholysis of methyl 1-thio-β-D-galactospyranoside (**11**) by a solution of I_2 in *t*-BuOH[20] followed by acetylation of the product **12** using acetic anhydride in pyridine (Scheme 1) and the subsequent isolation of **7α** by column chromatography (eluent, EtOAc–hexane, 1:9). From the spectral data presented in Table 2 it can be seen that the *t*-butyl glycoside **7α** can be distinguished from the trimethylsilyl glycosides **13α** and **13β** by the characteristic chemical shift obtained for H-2 and H-3 (Table 2).

Based on the above observations and given the work we have carried out on the anomerization of 1-thioglycosides[13] the mechanisms described in Schemes 2–4 below could be visualized for the reaction of primary/secondary (Schemes 2 and 3) and tertiary (Scheme 4) alkyl glycosides in the presence of I_2-HMDS reagent in MeCN.

Reaction of Me_3SiI (formed in situ from the interaction of HMDS with molecular iodine) with the trans-linked glycoside **G1** results in the formation of the silylated intermediate **G2**, which upon a subsequent endocyclic ring-opening generates **G3** in the open-chain form. The ring closure that follows takes place in favor of the thermodynamically more stable axial orientation of the aglycon moiety to give rise to the 1,2-cis-linked glycoside **G4** (Scheme 2). Proof for the intramolecular nature of the anomerization process as described in Scheme 2 was obtained from a cross-over experiment conducted using an equimolar mixture of **1β** and **9β** in the presence of I_2-HMDS reagent system (Scheme 3). The reaction was monitored by ^1H NMR spectroscopy in an NMR tube. Thus, the initial stages of the reaction showed the formation of two new compounds (Scheme 3), namely, the methyl α-galactoside **1α** [δ 4.96 ppm (d, J = 3.5 Hz) and 4.41 (d, J = 7.8 Hz) for the H-1 of **1α** and **1β,** respectively; and δ 3.39 ppm (s) and 3.53 ppm (s) for the OCH_3 of **1α** and **1β,** respectively] and ethyl α-glucoside **9α** [δ 5.06 ppm (d, J = 3.5 Hz) and 4.50 ppm (d, J = 8.0 Hz) for the H-1 of **9α** and **9β,** respectively; and δ 1.24 ppm (t, J = 7.0 Hz) and 1.19 ppm (t, J = 7.0 Hz) for the CH_2CH_3 of **9α** and **9β,** respectively]. No indication of any cross-over product was obtained during the entire course of the reaction as evident from the NMR spectrum of the reaction mixture. The final product obtained was, as expected, a mixture of **1α** and **9α**.

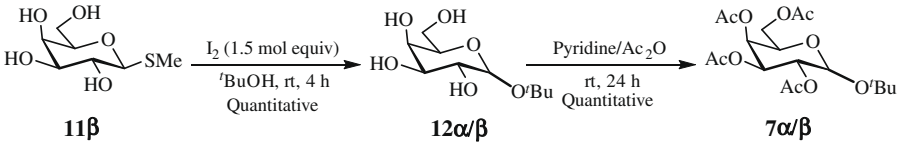
In contrast, the *t*-butyl glycoside **7β** reacts with TMSI to give the silylated intermediate **G5** from which the trimethyl silyl glycoside **13** is obtained (Schemes 4). Thus, unlike in the case of the primary alkyl glycoside **G1** where the silyl derivative is derived from the reaction at O-5 (to yield the initial product **G2,** Scheme 2), the silylation takes place at the exocyclic O-1 to give the highly reactive intermediate **G5** (Scheme 4). The silyl glycoside **13** obtained as product now has the silicon bonded to an oxygen atom (as opposed to an iodine atom as in TMSI), which is favored from bond energy considerations, and as to be expected, in particular when the O-1–Si bond is axially oriented as is evident from the NMR data obtained in this study. The formation of the iodide **14** could be envisaged via the *t*-butyl carbocation as shown in Scheme 4. It may be recalled that formation of *t*-butyl carbocation has been implicated in the course of hydrolysis of *t*-butyl hexopyranosides previously.[21] The fact that no α-glycoside (**7α**) was ever obtained as a product in the reaction could possibly exclude its probable formation via the endocyclic silylation process described in Scheme 2. It may be pointed that the hemiacetal **15** was not, as to be expected, a product formed during the anomerization reaction, which was also evident from the NMR experiments; but its presence in the crude product obtained after the isolation by aq work-up could be justified from the possible hydrolytic reaction of the silyl precursor **13** (Scheme 4).

2.2. Anomerization of arylglycosides

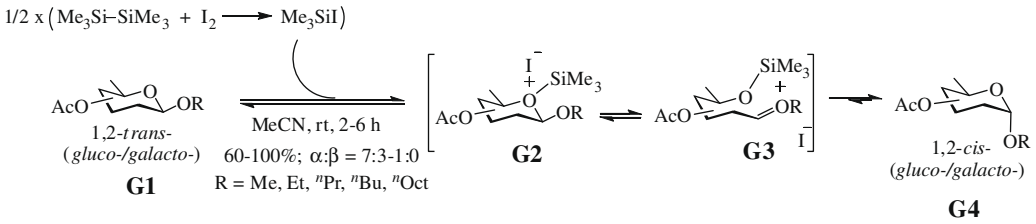
Although base-catalyzed anomerization of aryl glycosides have been reported in the literature, as described in the introductory notes, our search for literature precedence for the corresponding acid-catalyzed reactions was unsuccessful. Therefore the applicability of the I_2-HMDS system for the anomerization of aryl glycosides was also examined. Thus phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (**16β**) was prepared[22] and was treated

Table 2
^1H NMR chemical shifts for the galactopyranosides **7** and **13**

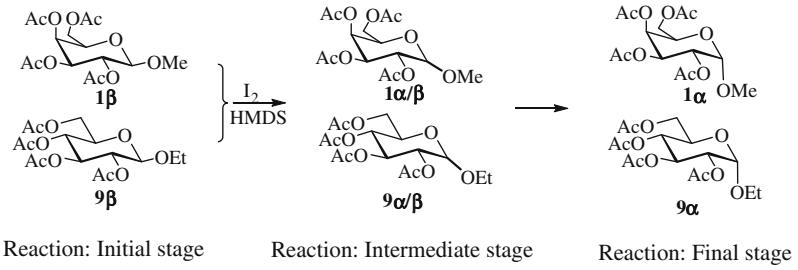
Ring proton	Compound							
	7α		**7β**		**13α**		**13β**	
	$CDCl_3$[19]	CD_3CN	$CDCl_3$	CD_3CN	$CDCl_3$[16]	CD_3CN	$CDCl_3$[17]	CD_3CN
H-1	5.10 (d)	5.31 (d)	4.61 (d)	4.70 (d)	5.42 (d)	5.28–5.24 (m)	4.70 (d)	4.68 (d)
H-2	4.90 (m)	4.91 (dd)	5.17 (dd)	4.88 (dd)	5.04 (dd)	5.05–4.96 (m)	5.15 (dd)	5.05–4.96 (m)
H-3	5.30 (m)	5.18 (dd)	5.03 (dd)	4.99 (dd)	5.34 (m)	5.28–5.24 (m)	4.98 (dd)	5.05–4.96 (m)
H-4	5.30 (m)	5.31 (d)	5.37 (dd)	5.26 (dd)	5.42 (m)	5.33 (dd)	5.36 (dd)	5.39 (d)
H-5	4.10 (m)	4.36 (t)	3.89 (t)	3.97–392 (m)	4.34 (m)	4.34 (t)	3.90 (dd)	3.93–4.02 (m)
H-6a and H-6b	4.10 (m)	4.00 and 3.96 (dd)	4.16–4.13 (m)	4.09 and 3.94 (dd)	4.06 (m)	3.93–4.02 (m)	4.09 and 4.16 (dd)	3.93–4.02 (m)
t-Butyl	1.30	1.17	1.23	1.14	—	—	—	—



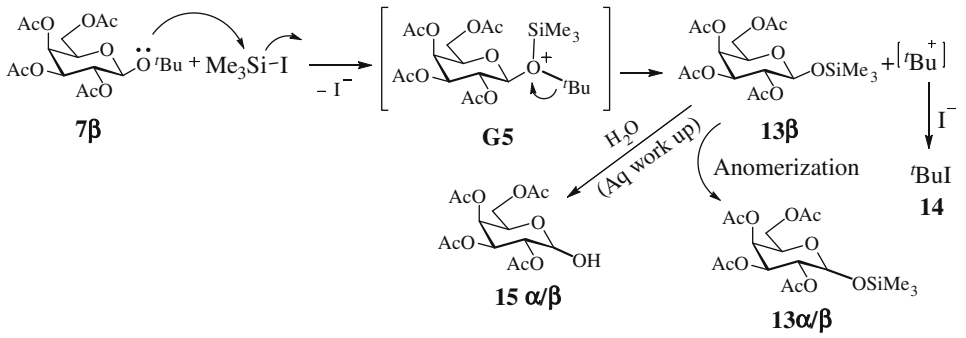
Scheme 1. Preparation of authentic **7α**/β f rom **11** using I_2/*t*-BuOH followed by acetylation.



Scheme 2. I_2-HMDS-mediated anomerization of alkyl glycosides.



Scheme 3. I_2-HMDS-promoted cross-over experiment using different alkyl glycosides.

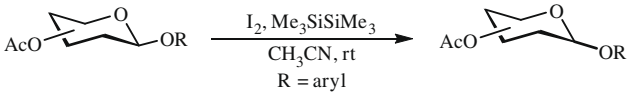


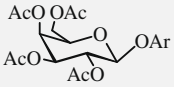
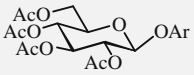
Scheme 4. Reaction of TMSI with *t*-butyl glycosides.

with the I_2-HMDS system at rt as described for the alkyl glycosides (Table 3, entry 1). The reaction was found to be complete in 2 h and was found to result in the exclusive formation of neat α-glycoside (**16α**). No by-products were detected during the reaction. The per-O-acetylated phenyl glucoside **17β** also likewise gave neat α-anomer as the product in 3 h at rt (Table 3, entry 5), again proving the reaction to be slower when compared to its *galacto*-analogue **16β** as was the case with the corresponding alkyl glycosides as noted above (see Table 1). To see the effect of substituents on the aromatic ring on the anomerization reaction, substituted phenyl glycosides bearing electron donating or withdrawing groups on the aromatic ring were prepared and were subjected to the above conditions of anomerization. Thus, the 4-methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-hexosides (**18β** and **19β**) on treatment with the reagent were also found to undergo complete anomerization to their respective α-anomers **18α** and **19α** in virtually quantitative yields (Table 3, entries 2 and 6). Importantly, the time taken for the reaction was the same as that for the respective unsubstituted phenyl glycosides **16β** and **17β**. The 4-chlorophenyl galactoside derivative **20β** also proved to be as reactive as **16β** and **18β** (Table 3, entry 3). Anomerization of the nitrophenyl glycosides **21β** and **22β** were, however, found to be slower (Table 3, entries 4 and 7) with the process being only partial, thus rendering support to the mechanism outlined in Scheme 2. While the intermediate **G2**/**G3** (Scheme 2) would be stabilized by electron-donating groups (positive inductive/resonance effect as for the phenyl and 4-methoxy/chlorophenyl residues in **16β**, **18β**, **19β** and **20β**) on the aglycon moiety, it could be destabilized by electron-withdrawing nature of this residue (negative inductive/resonance effect as for the 4-nitrophenyl glycosides **21β** and **22β**).

In summary, iodine-hexamethylsilane system has been demonstrated to be highly effective for the conversion of 1,2-trans-linked alkyl as well as aryl hexosides to their corresponding 1,2-cis-linked glycosides. The observations have been interpreted mechanisti-

Table 3
Anomerization of aryl glycosides using I_2-HMDS system[a]



Entry	Substrate (β-anomer)	Time (h)	Product	
			α:β[b]	Yield
				
1	**16** Ar = Ph	2	Only α-	Quantitative
2	**18** Ar = 4-MeO-Ph	2	Only α-	
3	**20** Ar = 4-Cl-Ph	2	90:10	
4	**21** Ar = 4-NO_2-Ph	8	50:50	
				
5	**17** Ar = Ph	3	Only α-	Quantitative
6	**19** Ar = 4-MeO-Ph	3	Only α-	
7	**22** Ar = 4-NO_2-Ph	8	50:50	

[a] All reactions were carried out in anhydrous acetonitrile (2 mL/100 mg sugar) using sugar: I_2-HMDS = 1:1:5 (mol equiv).
[b] Ratios are based on the ^{1}H NMR spectra of the product isolated by aq work-up.

cally. Future investigations on this will include subjecting the above conditions to disaccharides and cyclodextrins.

3. Experimental

3.1. General

All the reagents used were as purchased without purification. Solvents used for reactions were dried according to standard methods. Reactions were monitored by TLC, which was performed using 0.2 mm Merck pre-coated Silica Gel 60 F254 aluminum sheets. Compounds were detected by dipping the TLC plates in an ethanolic solution of sulfuric acid (5% v/v) and heating them thereafter. Melting points were determined on a Buchi melting point apparatus. Specific rotations were recorded on a Rudolph Research Autopol IV Polarimeter at room temperature (approximately 20–25 °C). NMR spectra were recorded on Bruker Avance DPX (300 or 400 MHz) spectrometer. ^{1}H NMR and ^{13}C NMR spectra were referenced using either residual solvent signals, or tetramethylsilane in the respective deuterated solvents. Coupling constants (*J*) are reported in Hertz. Mass spectra were recorded on MALDI (Bruker Daltonics, Ultraflex TOF/TOF) Spectrometer.

3.2. General procedure for anomerization using I_2-HMDS

To a solution of the β-glycoside (1 mmol) in anhydrous CH_3CN (2 ml/100 mg glycoside) was added I_2 (1 mmol), followed by HMDS (5 mmol), and the mixture was allowed to stir at rt until TLC (EtOAc–hexane 1.5:3.5) showed completion of the reaction. When the reaction was complete, the mixture was diluted with CH_2Cl_2 and was washed successively with saturated Na_2CO_3 solution and distilled H_2O in the cold. The organic layer was then dried (Na_2SO_4) and concentrated to dryness under reduced pressure. The products thus obtained were pure enough in most cases for use elsewhere directly or else were purified by column chromatography.

Physical constant and spectral data of compounds **2α**,[23] **3α**,[23] **4α**,[23] **5α**,[23] **6α**,[24] **9α**,[23] **10α**,[25] **16α**,[26] **17α**,[27] **18α**,[28] **19α**,[27] **20α**,[27] **21α**,[29] **22α**[27] were in agreement with the literature data.

3.3. Typical procedure-anomerization of methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (1β)

To a solution of the β-glycoside (**1β**, 362 mg, 1 mmol) in anhydrous CH_3CN (7 mL) was added I_2 (254 mg, 1 mmol) followed by HMDS (732 mg, 5 mmol) and the mixture was stirred at rt until TLC (EtOAc–hexane 1.5:3.5) showed completion of the reaction (3 h, see Table 1). The reaction mixture was then diluted with CH_2Cl_2 and was washed successively with cold saturated Na_2CO_3 solution and distilled H_2O. The organic layer was then dried (Na_2SO_4) and concentrated to dryness under reduced pressure to get neat **1α** in near quantitative yield as colorless crystals. Spectroscopic data and the physical constants were in agreement with literature.[14]

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