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Note

Stereoselectivity in the formation of pentacarbonyl glycosylmanganese complexes*

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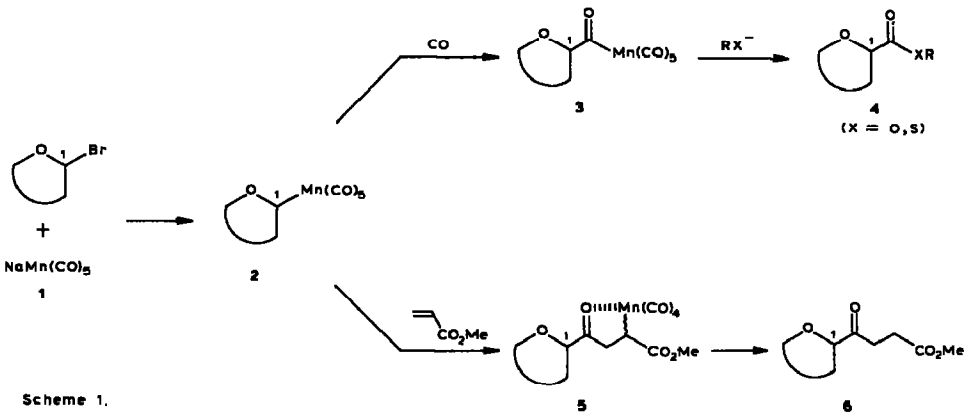
We have recently reported[1] an approach to the synthesis of C-glycosyl compounds in which stable pentacarbonylglycosylmanganese complexes (**2**) were prepared by condensation of the corresponding glycosyl bromide with sodium pentacarbonylmanganate(I) (**1**), and the resulting pentacarbonylmanganese complexes were induced to undergo migratory insertion to give the acylmanganese complex **3**. Cleavage of the acylmanganese complex with alkoxide or thiolate (Reppe reaction) then produced the ester derivatives **4**. Alternatively, the manganese complex **2** underwent high pressure-induced sequential insertion of carbon monoxide and methyl acrylate to furnish the manganacycle **5**. Subsequent photodemetalation of **5** resulted in formation of the *C*-glycosyl compound **6** (see Scheme 1).

For this approach to have maximum versatility as a method of synthesizing *C*-glycosyl compounds, the condensation reaction which furnishes the penta-



Scheme 1.

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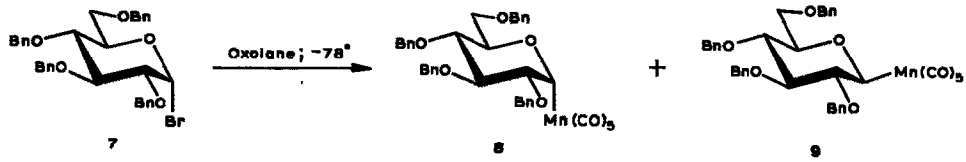
TABLE I

REACTION OF COMPOUND 1 WITH COMPOUND 7

Conditions	*Yield (%)*	*Ratio 8 to 9*
$NaMn(CO)_5$	75	0:100
$NaMn(CO)_5$, 3 equiv. $Bu_4N^+Br^-$	50	3:2
$NaMn(CO)_5$, 3 equiv. KBr	90	0:100



7 8 9

carbonylglycosylmanganese complex **2** must be highly stereoselective since the stereochemistry at C-1 of complex **2** defines the stereochemistry of the *C*-glycosyl compounds **4** and **6**, respectively. That is, the glycosyl complex **2** carrying the β-D configuration at C-1 is transformed into the *C*-glycosyl compounds **4** and **6** in which the new carbon–carbon bond has been produced with retention of the β-D configuration[2].

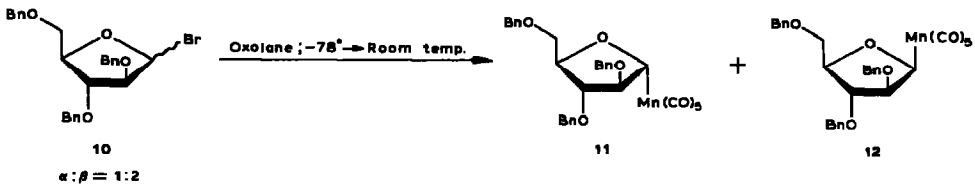
We report herein, that the stereoselectivity and the yield of the condensation of sodium pentacarbonylmanganate(I) (**1**) with D-glucopyranosyl and D-arabinofuranosyl bromides can be influenced by the addition of bromide salts to the condensation reaction mixture. Reaction of sodium pentacarbonylmanganate(I)[6] (**1**) with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromides[3] (**7**) in oxolane at −78° gave the β-manganese complex **9** *stereospecifically* in 75% yield (Table I)[1]. In this instance, the condensation appeared to proceed in an SN2 fashion with strict inversion of configuration at C-1.

Introduction of tetrabutylammonium bromide (Bu_4NBr) to the reaction mixture of **1** and bromide **7** had a pronounced effect upon the stereoselectivity of the condensation. When three equivalents of Bu_4NBr were suspended in the reaction mixture at −78°, a 3:2 mixture of glucosyl complexes **8** and **9** was obtained in 50% yield. Addition of Bu_4NBr had (a) caused a significant decrease in the yield of product and more importantly, (b) had caused a decline in the stereoselectivity of the condensation. α-Complex **8**, which had not been detected in the reaction of **1** and **7** in the absence of excess bromide, became the preponderant product in the presence of Bu_4NBr (Table I). We also demonstrated that the cation of the salt had an influence upon the condensation. Replacement of Bu_4NBr with potassium bromide dramatically improved the yield of manganese complex from 75 to 90% However, the stereoselectivity was not altered by the presence of KBr; only the β-complex **9** was obtained.

TABLE II

REACTION OF COMPOUND **1** WITH COMPOUND **10**

Conditions	*Yield (%)*	*Ratio* **11** *to* **12**
$NaMn(CO)_5$	70	2:1
$NaMn(CO)_5$, 3 equiv. $Bu_4N^+Br^-$	55	>98:2
$NaMn(CO)_5$, 3 equiv. KBr	90	2:1



10
α:β = 1:2

11 **12**

An analogous trend of results was observed in the furanosyl sugar series as outlined in Table II. Treatment of a 1:2 mixture of 2,3,5-tri-*O*-benzyl-α- and -β-D-arabinofuranosyl bromide (**10**) with sodium pentacarbonylmanganate(I) produced the manganese complexes **11** and **12** in a 2:1 ratio. As described above, the condensation proceeded with inversion of configuration at C-1 in the absence of excess bromide salts. Introduction of three equivalents of Bu_4NBr into the reaction mixture had a deleterious effect upon the yield of **11** and **12**, as was observed in the pyranosyl series. However, the stereoselectivity of the condensation was significantly enhanced, and only a trace of β-complex **12** could be detected in the crude reaction mixture. The presence of excess KBr in the reaction mixture of **1** and **10** again led to an improvement in the overall yield of complexes **11** and **12** (90% *vs.* 70%) in the absence of KBr, but the stereoselectivity of the condensation remained unchanged.

We propose that the results summarized in Tables I and II demonstrate that the stereoselectivity in the reaction of sodium pentacarbonylmanganate (**1**) and glycosyl bromides was influenced in two fashions by the presence of Bu_4NBr or KBr. The first involved a cation effect[4]. Addition of excess tetrabutylammonium or potassium salts to **1** led to cation exchange with sodium and formation of tetrabutylammonium and potassium manganate, respectively. This proposal of a cation effect is supported by the qualitative observation that the relative rates of condensation under the three sets of reaction conditions differed as indicated: **1** + KBr > **1** > **1** + Bu_4NBr. The observed trend in the relative rates also was reflected in the yields of adducts formed under the respective conditions. The set of reaction conditions that gave the fastest rate (**1** + KBr) also gave the highest yield of product. This suggested that the decreased yield of adducts obtained from the other sets of conditions may be the result of decomposition of glycosyl bromides **7** and **10**,

respectively, under the prolonged reaction times required for consumption of the unstable glycosyl bromides.

Alteration of the condensation stereoselectivity can also be rationalized by the cation effect. The rate of displacement of bromide from glycosyl bromides **7** and **10** was fast with either **1** or **1**–KBr, and the reaction proceeded with inversion of configuration at C-1. However, in the presence of Bu_4NBr, the rate of condensation decreased to the point that the rate of bromide ion-induced anomerization of **7** and **10** became competitive with the condensation[5]. Therefore, the anomeric ratios of **7** and **10** changed during the course of the SN2 displacement by manganate anion and resulted in alteration of the stereoselectivity (see Tables I and II).

The results reported herein indicate that the nucleophilic displacement of glycosyl halides by manganate anion can be influenced by reaction parameters, and we have begun a systematic investigation into this topic.

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