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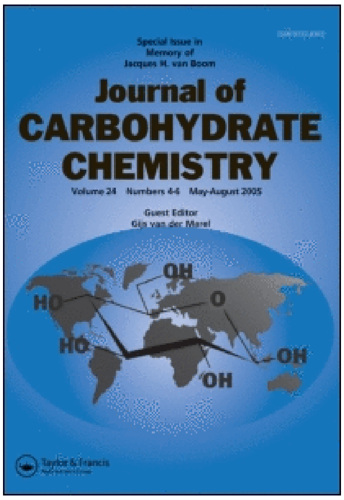

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Synthetic Studies on Sialoglycoconjugates 9: An Efficient Method for the Selective Acetolysis of 2-(Trimethylsilyl)Ethyl Glycosides Using Ferric Chloride in Acetic Anhydride

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J. CARBOHYDRATE CHEMISTRY, 8(4), 675-679 (1989)

COMMUNICATION

SYNTHETIC STUDIES ON SIALOGLYCOCONJUGATES 9: AN EFFICIENT METHOD FOR THE SELECTIVE ACETOLYSIS OF 2-(TRIMETHYLSILYL)ETHYL GLYCOSIDES USING FERRIC CHLORIDE IN ACETIC ANHYDRIDE

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After the first report of the synthesis and deblocking of some 2-(trimethylsilyl)ethyl (SE) glycosides by Lipshutz and coworkers,[1] a few more papers appeared describing facile deprotection of the SE group in such glycosides or some of their derivatives.[2] We have employed the SE glycosides of D-galactose,[3a,b] D-glucose, D-galactosamine, D-glucosamine,[3c] D-lactose,[3d] and neuraminic acid[3e] very extensively in our work on oligosaccharide synthesis. We have found that the SE group possesses a useful combination of properties, namely, stability over a wide range of pH which makes many experimental manipulations possible, and easy removability under certain specific but mild conditions.

Although selective removal of the aglycon residue in some of these mono and disaccharide glycosides has been achieved satisfactorily, alternative methods that allow quick and selective deprotection will be of value. Furthermore, selective deprotection of other substituents leaving the aglycon moiety unaffected will also be of significance. It is in this context that we describe herein a highly ef-

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ficient acetolysis of the SE hemiacetal function as well as selective acetolysis of the p-methoxybenzyl, benzyloxymetyl and benzyl group using a solution of ferric chloride in acetic anhydride.

In a typical procedure, the SE glycoside (200 mg) was added to a solution of ferric chloride in dry acetic anhydride (2 mL) and after stirring for required time the reaction mixture was made alkaline with dilute aq sodium carbonate solution, and the product was isolated by extraction with dichloromethane.

When compounds 1, 2, 5, 8, 9, 16, and 19[4] were treated with acetic anhydride in the presence of catalytic amounts of anhydrous ferric chloride (TABLE 1, Entry No. 1, 3, 5, 6, 8, 11, and 13), their respective acetates 3, 4, 3, 10, 11, 17, and 20 were obtained in quantitative yields in 2-10 min.[5] Dissolution of the sugar can be considered as an indication of completion of acetylation. On the other hand, when the reactions were performed in the presence of relatively larger amounts of ferric chloride (TABLE 1, Entry No. 2, 4, 7, 9, 12, and 14), facile acetolysis of the SE group took place in addition to the esterification of the free hydroxyl groups in the substrate molecules. When the acetolysis reaction was extended to compound 12 (TABLE 1, Entry No. 10), the benzyloxymethyl group was selectively cleaved to give 13 in a nearly quantitative yield.

Compound 22 could also be easily converted to the fully esterified product 23. Continuation of the reaction even for several h did not, however, furnish the desired acetolysis product 24. When the reaction was carried out in the presence of larger amounts of ferric chloride (equal to the weight of the sugar) the product obtained was the oxazoline 25. It appears that acetolysis resulted in the formation of 1,2-*trans* acetate which underwent elimination of the acetyl group in the usual manner to give the oxazoline 25.[6] Substrate 23 on treatment with acetic anhydride in the presence of $BF_3 \cdot Et_2O$ in acetonitrile by the method of Jannson *et al.*[2] resulted in formation of 24 in 20 min, but prolongation of the reaction (1.5 h) gave the oxazoline 25 along with considerable amounts of certain degradation products.

The SE glycosides 3, 10, and 17 were prepared from the corresponding 1-halogeno sugars and 2-(trimethylsilyl)ethanol in the presence

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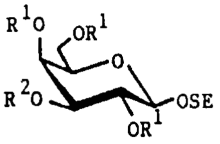


1 $R^1=R^2=H$

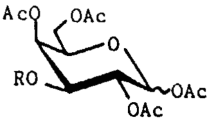
2 $R^1=H$, $R^2=CH_2Ph$

3 $R^1=R^2=Ac$

4 $R^1=Ac$, $R^2=CH_2Ph$

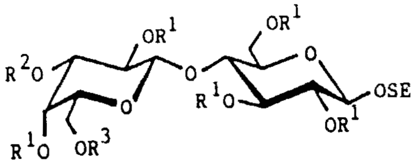
5 $R^1=Ac$, R^2=p-methoxybenzyl

SE=2-(trimethylsilyl)ethyl



6 R=Ac

7 $R=CH_2Ph$



8 $R^1=R^2=R^3=H$

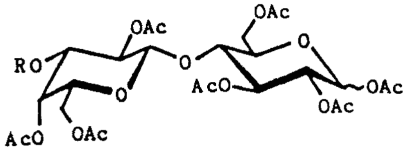
9 $R^1=R^3=H$, $R^2=CH_2Ph$

10 $R^1=R^2=R^3=Ac$

11 $R^1=R^3=Ac$, $R^2=CH_2Ph$

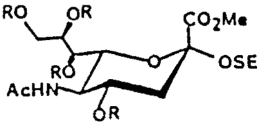
12 $R^1=Ac$, $R^2=CH_2Ph$, $R^3=CH_2OCH_2Ph$

13 $R^1=R^3=Ac$, $R^2=CH_2Ph$



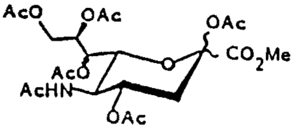
14 R=Ac

15 $R=CH_2Ph$



16 R=H

17 R=Ac



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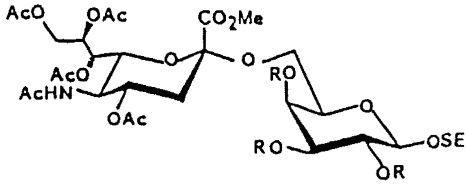
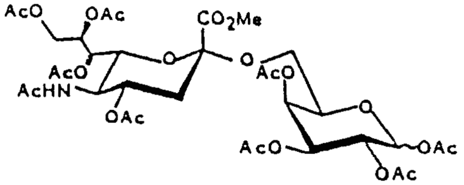


19 R=H

20 R=Ac



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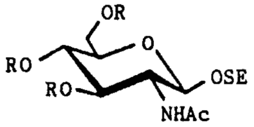
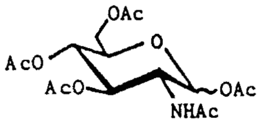


22 R=H

23 R=Ac



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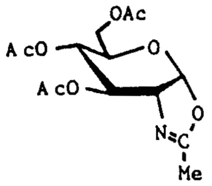

25

TABLE 1. Selective Acetolysis[a] of 2-(Trimethylsilyl)ethyl Glycosides Using Ferric Chloride in Acetic Anhydride

Entry No.	Substrate	Substrate:$FeCl_3$ (w/w)	Temp. (°C)	Time	Product(α:β)[b]
1	1	20:1	0	2 min	3
2	1	3:1	0-10	40 min	6(5:4)
3	2	20:1	0	2 min	4
4	2	3:1	0-10	40 min	7(5:4)
5	5	20:1	0	7 min	3
6	8	20:1	0	2 min	10
7	8	3:1	0-10	40 min	14(2:7)
8	9	20:1	0	2 min	11
9	9	3:1	0-10	40 min	15(2:7)
10	12	20:1	0	2 min	13
11	16	20:1	0	10 min	17
12	16	3:1	0-15	overnight	18(1:7)
13	19	20:1	0	2 min	20
14	19	3:1	0-15	overnight	21(1:5)
15	22	20:1	0	2 min	23
16	22	1:1	0-r.t.	2 days	25

a. Products were obtained in almost quantitative yields except Entry No. 16 (90%).

b. Determined by ^1H NMR.

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of Ag_2CO_3 and $AgClO_4$ in dichloromethane, and converted to their derivatives and oligosaccharides as described in refs. 3a,b, 3d,e, and 4. Compound 23 was prepared by the oxazoline method as described in ref. 3c. The structures of the acetolysis products were characterized by comparing their IR and ^1H NMR spectra with those of the authentic samples.

In conclusion, the acetolysis using a solution of ferric chloride in acetic anhydride provides an efficient method for the selective deprotection of a variety of 2-(trimethylsilyl)ethyl glycosides.

ACKNOWLEDGMENT

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