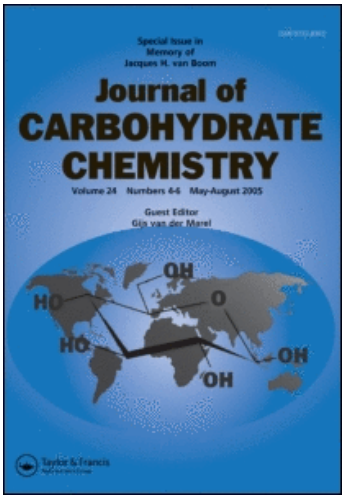

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Partial Protection of Carbohydrate Derivatives. Part 22. Further Improvement in Introduction of Methoxymethyl Group to Hydroxyl Groups of Carbohydrate Derivatives

Shigeyoshi Nishino[a]; Yoshiharu Ishido[a]

[a] Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo, Japan

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PARTIAL PROTECTION OF CARBOHYDRATE DERIVATIVES. PART 22.[1] FURTHER IMPROVEMENT IN INTRODUCTION OF METHOXYMETHYL GROUP TO HYDROXYL GROUPS OF CARBOHYDRATE DERIVATIVES

Shigeyoshi Nishino and Yoshiharu Ishido*

Department of Chemistry, Faculty of Science,
Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo 152, Japan

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ABSTRACT

Methoxymethylation of a series of carbohydrate derivatives including nucleosides has been efficiently induced by the use of dimethoxymethane through acid-catalysis in the presence of 2 - 3 mol. equiv. of phosphorus pentoxide; this gave the corresponding methoxymethyl derivatives in the isolated yields exceeding 90%.

INTRODUCTION

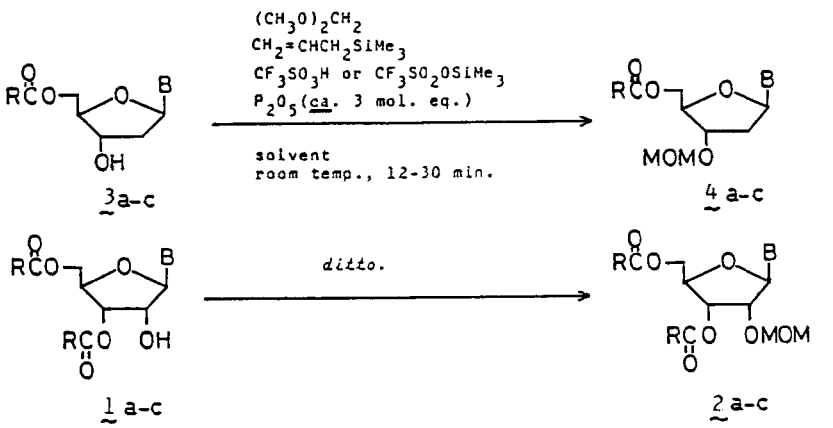
In this laboratory has been established a novel method for highly regioselective O-deacylation of fully acylated ribonucleosides by the use of potassium tert-butoxide - THF or CH_2Cl_2[3] to give the corresponding 3',5'-diacylates in crystalline form in good yield except in the case of adenosine derivatives. An efficient procedure for highly regioselective 5'-O-aroylation of 2'-deoxyribonucleosides has also been established by the use of an aroyl chloride in pyridine

through a dilution - titration technique.[4] Phosphorus pentoxide-promoted methoxymethylation has been reported as an improved method for this purpose, but the application was limited to the alcoholic functions of terpenes such as kaurane.[2a] Our interest in carbohydrate hydroxyl protection methods prompted us to investigate methoxymethylation procedures suitable for nucleoside and saccharide derivatives. A methoxymethyl ether is a hemiacetal-type protecting ($R\text{-}O\text{-}CH_2\text{-}O\text{-}$) group which unlike THP and THF groups does not afford any diastereoisomers. It was considered that the P_2O_5-promoted methoxymethylation might be useful for introducing the methoxymethyl group to an alcoholic function involved in a carbohydrate acylate, since acyl groups are not susceptible to migration under acidic conditions. The reaction was performed on a nucleoside under the conditions described,[2a] but gave a considerable amount of unreacted starting material (TLC) in spite of an extended reaction time. In addition, the highly viscous reaction mixture made stirring difficult, and quenching had to be performed very carefully due to the large amount of phosphorus pentoxide used [ca. 500 mg (ca. 35 mol. equiv. as P_2O_5) to 0.17 mmol of an alcohol[2a]]. Methoxymethylation procedures which involve activation using trimethylsilyl iodide or allyltrimethylsilane - iodine[2b] also gave results similar to those mentioned above. Therefore, we set out to improve the reaction by minimizing the amount of P_2O_5 through the use of some additives, so that we might perform the methoxymethylation on various target compounds including carbohydrate derivatives. The results so obtained will be described herein.

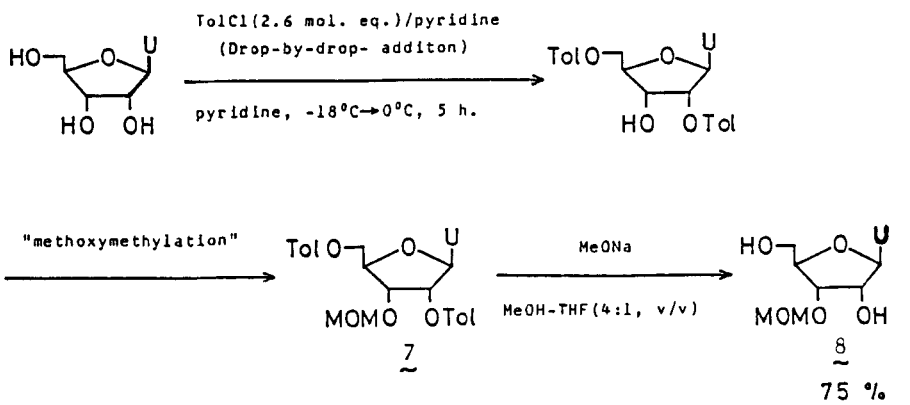
RESULTS AND DISCUSSION

The effect of an additive was examined in terms of the reaction with cholesterol since the corresponding methoxymethyl derivative has already been reported.[5] The introduction of the methoxymethyl (MOM) group was also effectively induced by the use of two reagent systems. Treatment of cholesterol with an excess amount of dimethoxymethane in dioxane - acetonitrile in the presence of trifluoromethanesulfonic (triflic) acid (catalytic amount), allyltrimethylsilane, and P_2O_5 (ca. 3 mol. equiv.), and that in the presence of boron trifluoride diethyl etherate and P_2O_5 (ca. 3 mol. equiv.) gave the MOM derivative in 97% and 93% yields, respectively. Based on these results, further reactions with carbohydrate derivatives were performed as follows.

Methoxymethylation with the Trimethylsilyl Triflate - P_2O_5 System. Treatment of a solution of 3',5'-di-O-benzoyluridine[3] (1a) in dioxane with an excess amount of dimethoxymethane in the presence of triflic acid (catalytic amount) - allyltrimethylsilane,[6] and P_2O_5 gave 3',5'-di-O-benzoyl-2'-O-methoxymethyluridine (2a) in a 97% isolated yield. The reactions with other ribonucleosides, i.e., N^4,3',5'-tribenzoyl (1b), N^4,3',5'-tris-o-toluoylcytidine (1c), and 2'-deoxyribonucleoside derivatives, i.e., 5'-O-benzoylthymidine (3a), N^4,5'-dibenzoyl- (3b), and N^4,5'-bis-o-toluoyl-2'-deoxycytidine (3c) were also effectively induced to give the corresponding O-methoxymethyl derivatives quantitatively. The results thus obtained and the conditions used are summarized in Table 1; the reaction times were short and ranged from 12 to 30 min. The reactions in acetonitrile were not



discolored differently from those carried out in chloroform and 1,4-dioxane. Moreover, uridine was converted into 3'-O-methoxymethyluridine in 75% isolated yield by the following sequence of reactions; highly regioselective 2',5'-bis-O-o-toluoylation (through the dilution - drop-by-drop addition procedure),[4] O-methoxymethylation under the conditions as above, and O-de-o-toluoylation with NaOMe - MeOH.



Attempts at the MOM-introduction to 1,2-O-isopropylidene-α-D-glucofuranose 5,6-carbonate (**5a**), methyl 2,3-O-isopropylidene-β-D-ribofuranoside (**5b**), and 1,3,5-tri-O-benzoyl-α-D-ribofuranose (**5c**) under the conditions described above

TABLE 1

Methoxymethylation of Some Ribonucleoside and 2'-Deoxyribonucleoside Aroates Promoted by Trimethylsilyl Trifluoromethanesulfonate (Triflate) - P_2O_5 System [a]

Entry	Nucleoside B	RCO		$(CH_3O)_2CH_2$ (mL)	$CH_2=CHCH_2SiMe_3$ (mL)	Solvent (mL)	Reaction time (min)	Yield (%) of MOM derivatives	
1	U	Bz	**1a**	6	0.25	Dioxane (1)	30	**2a**	97
2	C^{Bz}	Bz	**1b**	1	0.25	$CHCl_3$ (6)	15	**2b**	99(91[b])
3	C^{Tol}	Tol	**1c**	1	0.25	CH_2Cl_2 (2)	15	**2c**	94
4	T	Bz	**3a**	1	0.5	CH_3CN (8)	12	**4a**	97
5	C^{Bz}	Bz	**3b**	1	0.3	CH_3CN (6)	30	**4b**	99
6	C^{Tol}	Tol	**3c**	1	0.5	CH_3CN (8)	30	**4c**	93

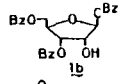
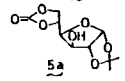
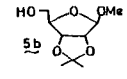
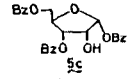
[a] The reactions in Entries 1 - 3 were performed by the use of triflic acid (1 drop) and P_2O_5 (ca. 1 mmol) to **1a** and **1c** (0.3 mmol), and **1b** (0.25 mmol), respectively, at room temperature. The reactions in Entries 4 - 6 were by the use of triflic acid (1 drop) and P_2O_5 (ca. 1 mmol) to **3a** (0.52 mmol), **3b** (0.3 mmol), and **3c** (0.64 mmol), respectively, at room temperature.

[b] Obtained by crystallization.

TABLE 2

Methoxymethylation of Some Carbohydrate Derivatives

Promoted by Boron Trifluoride Diethyl Etherate - P_2O_5 [a]

Entry	Compound (mmol)		$(CH_3O)_2CH_2$ (mL)	Solvent (mL)	Reaction time (min)	Yield (%) of MOM derivatives [b]	
1	 1b	(0.3)	4	-	60	**2b**	95
2	 5a	(1.0)	4	CH_3CN (4)	30	**6a**	97
3	 5b	(0.5)	4	-	35	**6b**	96
4	 5c	(0.5)	4	CH_2Cl_2 (1)	35	**6c**	98

[a] All of the reactions were performed by the use of $BF_3 \cdot OEt_2$ (3 drops) and P_2O_5 (ca. 3 mol. equiv.) at room temperature. [b] All of the products were syrup but pure analytically, ^{1}H-NMR spectroscopically, and thin layer chromatographically.

resulted in the formation of undesirable more polar by-products as detected by TLC.

Methoxymethylation with the BF_3 - P_2O_5 System. This system was also effective for MOM group introduction to **1b** to give **2b** in a 95% yield. Moreover, this system was similarly effective for glycose derivatives, i.e., **5a**, **5b**, and **5c**, to give their MOM derivatives (**6**) in 97%, 96%, and 98% yields, respectively. These results are summarized in Table 2 together with the conditions used.

Based on the present results, it can be concluded that the methoxymethyl function can be essentially used as a hemiacetal-type protecting group of carbohydrate alcoholic function, by promoting with trimethylsilyl triflate - and $BF_3 \cdot OEt_2$ - P_2O_5,[7] respectively.

EXPERIMENTAL

General methods. Melting points were determined with a Yanagimoto Micro-Melting-Point apparatus, and are uncorrected. ^{1}H-NMR spectra were recorded on a Varian T-60 apparatus and a JEOL JNM FX200 apparatus with tetramethylsilane as the internal standard. TLC was conducted on Merck Silica Gel $60F_{254}$ by the use of 9:1 or 19:1 chloroform - methanol except in the case of cholesterol derivatives (19:1 benzene - ethyl acetate). Elemental analyses were carried out with a Perkin Elmer 240-002 apparatus at Department of Chemistry, Faculty of Science, Tokyo Institute of Technology.

Trimethylsilyl triflate in methylene dichloride (1:30, v/v) was stored after the addition of allyltrimethylsilane (several drops).

General Procedure for Methoxymethylation: a) Through trimethylsilyl triflate - P_2O_5 system (see Table 1). To a solution of a nucleoside aroate in dimethoxymethane and organic solvent, were added allyltrimethylsilane, triflic acid (1 drop)(or diluted solution of trimethylsilyl triflate, 1 drop), and P_2O_5 (ca. 3 mol. equiv.). The mixture was stirred at room temperature for 12 - 30 min. After quenching the reaction by the addition of several drops of triethylamine, the resulting solution was evaporated to a syrup. To the syrup, were added chloroform (10 mL) and excess aqueous sodium carbonate, and the solution was stirred for 5 min. The aqueous layer, after sufficient distribution in a separating funnel, was separated from the organic layer and extracted with chloroform (3 x 50 mL). The organic solution and the extracts were combined and washed further with aqueous sodium carbonate. The organic solution was dried over anhydrous sodium sulfate, and evaporated to a syrup after filtering off the desiccant. The syrup was subjected to column chromatography to give the pure products.

b) Through $BF_3 \cdot OEt_2$ - P_2O_5 system (see Table 2). To a solution of a carbohydrate derivative bearing an alcoholic function, in dimethoxymethane or dimethoxymethane and an organic solvent, were added $BF_3 \cdot OEt_2$ (3 drops) and P_2O_5 (ca. 3 mol. equiv.). The mixture was stirred for 30 - 60 min at room temperature. The reaction was quenched by the addition of several drops of triethylamine, and the resulting mixture was evaporated to a syrup. A similar work-up as described above gave the corresponding monomethoxymethyl derivatives in pure form.

Synthesis of 3'-O-Methoxymethyluridine Involving Highly Regioselective 2',5'-Di-O-o-toluoylation. Uridine (244 mg, 1 mmol), dried by azeotropic removal of moisture with pyridine (three times), was dissolved in pyridine (4 mL). To the resulting solution, was dropwise added a half volume of a solution of o-toluoyl chloride (0.399 mL, 2.6 mmol) in pyridine (8 mL) at -18°C taking 2 h, and the other half volume was added at 0°C taking 2 h. The reaction was quenched by the addition of methanol, and the resulting mixture was distributed between chloroform and aqueous sodium bicarbonate solution. After separating the organic layer, the aqueous layer was extracted with chloroform (5 mL x 4). The organic solution and the extracts were combined and successively washed with water, dilute hydrochloric acid, and water. The organic solution was dried over anhydrous sodium sulfate and evaporated to a glass after filtering off the desiccant. The glass was dissolved in a mixture of acetonitrile (2 mL) and dimethoxymethane (4 mL), and the resulting solution was treated with allyltrimethylsilane (0.3 mL), a solution of trimethylsilyl triflate in dichloromethane (several drops), and P_2O_5 (ca. 4 mol. equiv.) at room temperature for 15 min with stirring. The reaction was quenched with triethylamine (several drops) and worked up as described above to give 3'-O-methoxymethyl-2',5'-di-O-o-toluoyluridine (7)(493 mg, 94% yield). O-De-o-toluoylation of 7 was performed with pulverized sodium methoxide (3 mol. equiv.) in a mixture of methanol (4 mL) and THF (1 mL), and monitored by TLC. The reaction was quenched by the addition of Dowex 50W on detecting complete deacylation of 7. The resin was filtered off, and the filtrate was

evaporated to a syrup, which was purified by the chromatography on silica gel to give 3'-O-methoxymethyluridine (**8**) (239 mg, 83% yield) as a syrup, and 75% yield after crystallization.

3-O-Methoxymethylcholesterol had mp 80.5 - 82°C (from acetone)(lit.[5] mp 81 - 82°C), ^{1}H-NMR ($CDCl_3$ - Me_4Si): δ 5.34 (1H, m, H-6), 4.69 (2H, s, O-CH_2-O), ca. 3.40 (1H, m, H-3), 3.37 (3H, s, OCH_3), 1.01 (3H, s, CH_3-19), 0.91 (3H, d, CH_3-21), 0.86 (6H, d, CH_3-26 and 27), and 0.68 (3H, s, CH_3-18), Rf value (19:1 benzene - ethyl acetate): 0.58. The methoxymethylation gave a by-product characterized as bis-(cholesteryloxy)methane, mp 185.5 - 186°C (from acetone), ^{1}H-NMR ($CDCl_3$ - Me_4Si): δ 5.35 (2H, m, H-6), 4.79 (2H, s, O-CH_2-O), and 3.8 (2H, m, H-3), Rf value: 0.86.

Anal. Calcd for $C_{55}H_{92}O_2$: C, 84.12; H, 11.81. Found: C, 83.99; H, 11.68.

Compound 2a was a glass, ^{1}H-NMR ($CDCl_3$ - CD_3OD - Me_4Si): δ 6.06 (1H, d, $J_{1',2'}$ 5 Hz, H-1'), 5.54 (1H, d, $J_{5,6}$ 8 Hz, H-5), 5.7 - 5.4 (1H, m, H-3'), 4.66 (6H, bs, H-2', 4', 5', 5", and O-CH_2-O), and 3.19 (3H, s, O-CH_3), and ^{1}H-NMR ($CDCl_3$ - Me_4Si): δ 9.44 (1H, bs, NHCO).

Anal. Calcd for $C_{25}H_{24}O_9N_2$: C, 60.48; H, 4.87; N, 5.64. Found: C, 60.21; H, 4.56; N, 5.81.

Compound 2b had mp 173.5 - 174.5°C (from chloroform - hexane), ^{1}H-NMR ($CDCl_3$ - CD_3OD - Me_4Si): δ 8.09 (2H, d, J 4.4 Hz, aromatic protons ortho to carbonyl group), 8.06 (2H, d, J 4.2 Hz, aromatic protons ortho to carbonyl group), 8.05 (2H, d, J 4.2 Hz, aromatic protons ortho to carbonyl group), 7.90 (1H, d, $J_{5,6}$ 7.6 Hz, H-6), 7.7 - 7.3 (10H, m, H-5 and

Bz x 3), 6.20 (1H, d, $J_{1',2'}$ 2.8 Hz, H-1'), 5.41 (1H, dd, $J_{2',3'}$ 5.5 Hz and $J_{3',4'}$ 6.8 Hz, H-3'), 4.93 (1H, d, a part of an AB system, J 6.5 Hz, O-CH_2-O), 4.9 - 4.7 (3H, m, H-4', 5', and 5"), 4.73 (1H, d, a part of an AB system, O-CH_2-O), 4.69 (1H, dd, H-2'), and 3.22 (3H, s, OCH_3).

Anal. Calcd for $C_{32}H_{29}O_9N_3$: C, 64.10; H, 4.88; N, 7.01. Found: C, 63.86; H, 4.97; N, 6.97.

Compound 2c had mp 118 - 119°C (from diethyl ether - hexane), ^{1}H-NMR ($CDCl_3$ - Me_4Si): δ 8.95 (1H, bs, NH), 8.15 (1H, d, $J_{5,6}$ 7.3 Hz, H-6), 8.00 (1H, d, J 8.3 Hz, an aromatic proton ortho to carbonyl group of O-o-toluoyl group), 7.93 (1H, d, J 8.3 Hz, an aromatic proton ortho to carbonyl group of O-o-toluoyl group), 7.39 (1H, d, H-5), 7.5 - 7.1 (10H, m, o-toluoyl group), 6.14 (1H, s, H-1'), 5.37 (1H, dd, J 5.3 Hz and 7 Hz, H-3'), 4.93 (1H, d, a part of an AB system, O-CH_2-O), 4.8 - 4.6 (5H, m, H-2', 4', 5', 5", and one of O-CH_2-O), 3.20 (3H, s, OCH_3), 2.60 (6H, s x 2, two CH_3 groups of o-toluoyl groups), and 2.49 (3H, s, CH_3 of N-o-toluoyl group).

Anal. Calcd for $C_{35}H_{35}O_9N_3$: C, 65.51; H, 5.50; N, 6.55. Found: C, 65.53; H, 5.53; N, 6.37.

Compound 4a had mp 128°C (from benzene), ^{1}H-NMR ($CDCl_3$ - CD_3OD - Me_4Si): δ 8.1 - 7.8 (2H, aromatic protons ortho to carbonyl group), 7.6 - 7.2 (4H, m, H-6 and three protons of Bz), 6.25 (1H, dd, $J_{1',2'}$ 6.5 Hz and $J_{1',2"}$ 6.5 Hz, H-1'), 4.71 (2H, s, O-CH_2-O), 4.7 - 4.3 (4H, m, H-3', 4', 5', and 5"), 3.38 (3H, s, OCH_3), 2.43 (2H, m, H-2' and 2"), and 1.65 (3H, s, CH_3-5), and ^{1}H-NMR ($CDCl_3$ - Me_4Si): δ 9.86 (1H, bs, NHCO).

Anal. Calcd for $C_{19}H_{22}O_7N_2$: C, 58.45; 5.68; N, 7.18. Found: C, 58.38; H, 5.65; N, 7.21.

Compound **4b** had mp 153.5 - 154.5°C (from ethanol), ^{1}H-NMR ($CDCl_3$ - Me_4Si): δ 8.14 (1H, d, $J_{5,6}$ 7.3 Hz, H-6), 8.00 (2H, d, J 7.1 Hz, aromatic protons ortho to carbonyl group), 7.88 (2H, d, J 7.3 Hz, aromatic protons ortho to carbonyl group), 7.65 - 7.3 (7H, m, H-5 and the rest number of protons of Bz x 2), 6.23 (1H, t, $J_{1',2'} = J_{1',2''}$ 6 Hz, H-1'), 4.68 (2H, s, O-CH_2-O), 4.67 (1H, s, H-5), 4.64 (1H, s, H-5"), 4.44 (1H, d, $J_{3',4'}$ 3.4 Hz, H-4'), 4.34 (1H, ddd, $J_{2',3'}$ 5 Hz and $J_{2'',3'}$ 5.6 Hz, H-3'), 3.37 (3H, s, OCH_3), 2.80 (1H, ddd, $J_{2',2''}$ 13.6 Hz, H-2'), and 2.24 (1H, ddd, H-2").

Anal. Calcd for $C_{25}H_{25}O_7N_3$: C, 62.62; H, 5.26; N, 8.77. Found: C, 62.53; H, 5.37; N, 8.55.

Compound **4c** was a glass, ^{1}H-NMR ($CDCl_3$ - Me_4Si): δ 7.97 (1H, d, $J_{5,6}$ 7.5 Hz, H-6), 7.82 - 7.61 (1H, m, an aromatic proton ortho to carbonyl group of O-o-toluoyl group), 7.4 - 6.9 (8H, m, H-5 and seven protons of o-toluoyl groups), 6.06 (1H, t, $J_{1',2'} = J_{1',2''}$ 5.5 Hz, H-1'), 4.61 (2H, s, O-CH_2-O), 4.6 - 4.0 (4H, m, H-3', 4', 5', and 5"), 3.30 (3H, s, OCH_3), 2.58 (3H, s, CH_3 of O-o-toluoyl group), and 2.44 (3H, s, CH_3 of N-o-toluoyl group).

Anal. Calcd for $C_{27}H_{29}O_7N_3$: C, 63.89; H, 5.76; N, 8.28. Found: C, 63.64; H, 5.70; N, 8.41.

Compound **6a** was a syrup, $[\alpha]_D^{21}$ -68° (c 1.86, chloroform), ^{1}H-NMR ($CDCl_3$ - Me_4Si): δ 5.94 (1H, d, $J_{1,2}$ 3.7 Hz, H-1), 4.94 (1H, ddd, $J_{4,5}$ 5.4 Hz, $J_{5,6}$ 6.4 Hz, $J_{5,6'}$ 8.3 Hz, H-5), 4.72, 4.65 (2H, d x 2, AB system, J 6.8 Hz, O-CH_2-O),

4.59 (1H, dd, $J_{6,6'}$ 8.7 Hz, H-6), 4.50 (1H, dd, H-6'), 4.49 (1H, dd, $J_{3,4}$ 3.4 Hz, H-4), 4.27 (1H, d, H-3), 3.39 (3H, s, OCH_3), 1.50, and 1.33 [6H, s x 2, $C(CH_3)_2$)].

Anal. Calcd for $C_{12}H_{18}O_8 \cdot 1/2H_2O$: C, 48.16; H, 6.40. Found: C, 48.24; H, 6.18.

Compound 6b was a syrup, $[\alpha]_D^{21}$ -63° (c 2.0, chloroform), ^{1}H-NMR ($CDCl_3$ - Me_4Si): δ 4.97 (1H, s, H-1), 4.68 (1H, dd, $J_{2,3}$ 5.9 Hz and $J_{3,4}$ ca. 1 Hz, H-3), 4.65 (2H, s, O-CH_2-O), 4.59 (1H, d, H-2), 4.34 (1H, ddd, $J_{4,5}$ 6.6 Hz and $J_{4,5'}$ 8.3 Hz, H-4), 3.60 (1H, dd, $J_{5,5'}$ 10 Hz, H-5), 3.50 (1H, dd, H-5'), 3.38 (3H, s, OCH_3 at C-1), 3.32 (3H, s, OCH_3 of MOM group), 1.49, and 1.33 [6H, s x 2, $C(CH_3)_2$].

Anal. Calcd for $C_{11}H_{26}O_6$: C, 53.21; H, 8.12. Found: C, 53.49; H, 8.06 .

Compound 6c was a syrup, $[\alpha]_D^{21}$ +74° (c 1.43, chloroform), ^{1}H-NMR ($CDCl_3$ - Me_4Si): δ 8.18, 8.16, 8.07 (6H, d x 3, J 7.8 Hz, J 7.3 Hz, and J 7.1 Hz, aromatic protons ortho to carbonyl group), 7.6 - 7.3 (9H, m, other aromatic protons), 6.76 (1H, d, $J_{1,2}$ 4.4 Hz, H-1), 5.73 (1H, dd, $J_{2,3}$ 6.4 Hz and $J_{3,4}$ 2 Hz, H-3), 4.83 (1H, td, $J_{4,5} = J_{4,5'}$ 3.5 Hz, H-4), 4.76, 4.67 (2H, d x 2, AB system, J 6.8 Hz, O-CH_2-O), 4.65, 4.62 (2H, d x 2, H-5, 5'), 4.61 (1H, dd, H-2), and 3.32 (3H, s, OCH_3).

Anal. Calcd for $C_{28}H_{26}O_9$: C, 66.39; H, 5.17. Found: C, 66.04; H, 5.23.

Compound 7 was a glass, ^{1}H-NMR ($CDCl_3$ - CD_3OD): δ 8.0 - 7.7 (2H, m, two ortho protons of o-toluoyl group), 7.48 (1H, d, J 8 Hz, H-6), 6.07 (1H, d, $J_{1',2'}$ 3.4 Hz, H-1'), 5.7 - 5.5 (1H, m, H-2'), 5.47 (1H, d, H-5), 4.8 - 4.3 (6H, m, H-

3', 4', 5', 5", and O-CH_2-O), 3.31 (3H, s, OCH_3), and 2.59 (6H, s, two methyl group protons of o-toluoyl groups).

3'-O-Methoxymethyluridine (8) had mp 167 - 168°C (from ethanol - hexane), ^{1}H-NMR (CD_3OD): δ 8.06 (1H, d, J 8.1 Hz, H-6), 5.96 (1H, d, $J_{1',2'}$ 4.9 Hz, H-1'), 4.79 (2H, bs, O-CH_2-O), 4.33 (1H, t, $J_{2',3'}$ 4.9 Hz, H-2'), 4.22 (1H, t, H-3'), 4.18 (1H, m, H-4'), 3.89 (1H, dd, a part of an AB system, $J_{4',5'}$ ca. 2 Hz, $J_{5',5"}$ 12.5 Hz, H-5'), 3.76 (1H, dd, a part of an AB system, $J_{4',5"}$ ca. 2 Hz, H-5"), and 3.45 (3H, s, OCH_3).

Anal. Calcd for $C_{11}H_{16}O_7N_2$: C, 45.83; H, 5.59; N, 9.72. Found: C, 46.14; H, 5.85; N, 9.83.

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7 On application of MOM-chloride - $EtN(iPr)_2$,[5] there was observed, as expected, undesirable acyl migration, and predominant N-methoxymethylation in the case of uridine 3',5'-dibenzoate. This reagent system was concluded to be inadequate for O-methoxymethylation of such a series of carbohydrate acylates.