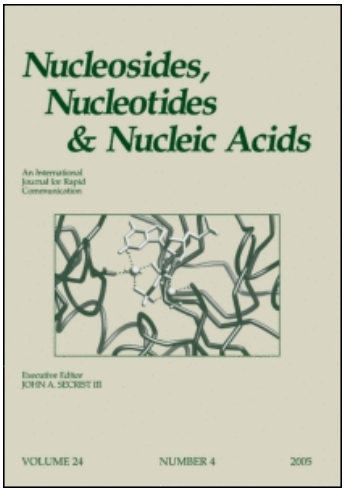

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Partial Protection of Carbohydrate Derivatives. Part 19. Highly Regioselective 5'-*O*-Aroylation of 2'-Deoxyribonucleosides in Terms of Dilution - Drop-by-Drop - Addition Procedure

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PARTIAL PROTECTION OF CARBOHYDRATE DERIVATIVES. PART 19.[1] HIGHLY REGIOSELECTIVE 5'-O-AROYLATION OF 2'-DEOXYRIBONUCLEOSIDES IN TERMS OF DILUTION — DROP-BY-DROP — ADDITION PROCEDURE

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Abstract: Treatment of a 2'-deoxyribonucleoside in pyridine with an aroyl chloride, which was added dropwise as a dilute solution in pyridine, gave the corresponding 5'-O-aroyl-2'-deoxyribonucleoside in 84 — 93% yields.

INTRODUCTION

Chemical synthesis of 2'-deoxyribonucleotide oligomers has been performed by the use of 2'-deoxyribonucleoside derivatives whose 5'-hydroxyl groups were protected with dimethoxytrityl group, and, where appropriate, with an N-acyl group in the base. On the other hand, it has been indicated that oligomer synthesis was accompanied by undesirable depurination, in particular, on O-dedimethoxytritylation of an oligomer involving 2'-deoxyadenosine units under acidic conditions[2]. Such a drawback in 2'-deoxyribonucleotide oligomer synthesis prompted us to set out to develop a novel approach involving an unmasking process with respect to the 5'-terminus protecting group under basic conditions; this might lead us to use an ordinary acyl group for the protection. Various attempts at regioselective 5'-O-acylation reaction have been reported, but are not necessarily useful for practical purposes due to tedious reaction procedures, instability

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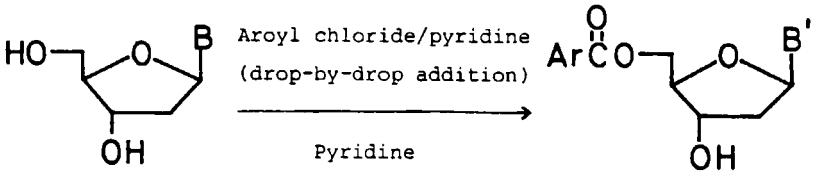
of a reagent, and difficulty in commercial availability. The benzoyl group is, on the other hand, comparatively stable relative to, e.g., the acetyl group. We now report a practical method for introducing an aroyl group at the 5' position by a dilution – titration procedure, which gave the corresponding 5'-acylates of 2'-deoxyribonucleosides in acceptable yields.

RESULTS AND DISCUSSION

We have recently reported an efficient phenylcarbamoylation reaction which has been induced with high regioselectivity in high yields on performing the reaction through a dilution – titration procedure,[3] i.e., dropwise slow addition of phenyl isocyanate diluted with an organic solvent into a solution of a ribonucleoside. In a similar manner, the addition of a solution of an aroyl chloride in pyridine into a solution of 2'-deoxyribonucleosides was performed to give the corresponding 5'-aroates; the results thus obtained and the conditions used are summarized in Table 1. All the reactions were over within 0.5 – 3.0 h and induced with high regioselectivity to give the 5'-aroates in 77 – 93% yields. Particularly, it is noteworthy that a treatment of 2'-deoxycytidine hydrogen chloride with a solution of benzoyl chloride (2.2 mol. equiv.) in pyridine gave N,[4]5'-dibenzoyl-2'-deoxycytidine in 77% yield (Entry 3), which was further improved up to 84% yield by the addition of triethylamine (1 mol. equiv.) prior to that of benzoyl chloride (Entry 4); triethylamine may



generate 2'-deoxycytidine free from hydrogen chloride and enhance its nucleophilicity. 5'-O-o-Toluoylation of 2'-deoxycytidine was also performed, based on the basic study of N-deacylation through 1:1 0.2 N NaOH – methanol by Köster et al.,[4] to give N,[4],5'-di-o-toluoyl-2'-deoxycytidine in 84% yield (Entry 5). Incidentally, Ti et al.[5] reported an excellent approach to regioselective N-acylation which took advantage of the delicate difference in reactivity between N- and O-trimethylsilyl functions

Table 1. Regioselective Aroylation of 2'-Deoxyribonucleosides with an Aroyl Chloride Through Dilution-Titration Procedure[a]

Entry	B	Aroyl chloride (mol. equiv.)	Time (h) required for drop-by-drop addition	Yield (%) of B'	Yield (%) of 5'-aroate
1	A	BzCl (1.1)	0.5	A	85
2	A^{Bz}	BzCl (1.3)	1.0	A^{Bz}	89
3	C^{HCl}	BzCl (2.2)	2.5	C^{Bz}	77
4[b]	C^{HCl}	BzCl (2.3)	2	C^{Bz}	84
5[b]	C^{HCl}	TolCl[d] (2.05)	2.75	C^{Tol}	84
6	G^{ibu}	BzCl (1.1)	2.0	G^{ibu}	93
7	T	BzCl (1.1)	3.0	T	81
8[c]	T	BzCl (1.1)	2.75	T	94

[a] All of the reactions were performed in pyridine at room temperature, unless otherwise noticed, after the manner of dilution-titration procedure (See details in Experimental section). [b] An equimolar amount of triethylamine was added prior to the addition of a solution of an aroyl chloride in pyridine. [c] This reaction was performed at 0°C. [d] TolCl stands for o-toluoyl chloride.

towards an acylating agent. This method was thus applied to 5'-O-benzoyl-2'-deoxyadenosine, which was obtained by the present procedure (Entry 1); one pot procedure was explored, i.e., to the resulting mixture from the 5'-O-benzoylation, was added dropwise chlorotrimethylsilane (5 mol. equiv.) and, then, benzoyl chloride (5 mol. equiv.). N,[6]5'-Dibenzoyl-2'-deoxyadenosine was thus obtained in 80% yield. 5'-O-benzoylation of thymidine performed at 0°C gave its 5'-benzoate in a 94% yield (Entry 8)(cf. 81% at room temperature, Entry 7). Incidentally, regioselective 5'-O-benzoylation of thymidine has been attempted by the use of benzoyl tetrazolide[6] (65% yield) and benzoic acid – triphenylphosphine – diethyl azodicarboxylate[7] (75% yield), etc. The method described herein give rise to highly regioselective 5'-O-aroylation reaction in spite of the simple procedure and reagent used; thus, this is far more practical compared with those involving the more sophisticated reagent system.[6,7]

In conclusion, highly regioselective 5'-O-acylation of 2'-deoxyribonucleosides established herein will provide the starting materials for 3'-deoxygenation to prepare 2',3'-dideoxyribonucleosides,[8] and has prompted us to explore a potential approach to 2'-deoxyribonucleotide oligomer synthesis involving 5'-O-dearoylation followed by a coupling reaction with a 3'-terminus of another 2'-deoxyribonucleotide derivatives bearing a phosphorfunction which can easily be converted to the corresponding phosphate.[9]

EXPERIMENTAL

General methods. Melting points were determined with a Yanagimoto Micro-Melting-Point apparatus, and are uncorrected. ^{1}H-N.M.R. spectra were recorded on a Varian T-60 apparatus and a JEOL JNM FX200 apparatus by the use of tetramethylsilane as the internal standard. TLC was conducted on Merck Silica Gel $60F_{254}$ by the use of 9:1 chloroform-methanol system. Column chromatography was performed with Merck Kieselgel 60 (70 – 230 mesh, ASTM) by the use of chloroform – methanol system. Elemental analyses were carried out through a Perkin Elmer 240-002 apparatus at Department of Chemistry, Faculty of Science, Tokyo Institute of Technology.

5'-O-Benzoyl-2'-deoxyadenosine. 2'-Deoxyadenosine (251 mg, 1.0 mmol) was, after azeotropic removal of moisture from pyridine three times as usual, dissolved in pyridine (3 mL), and to the resulting solution was added dropwise a solution of benzoyl chloride (0.13 mL, 1.1 mmol) in pyridine (1 mL) at room temperature, taking 30 min for the addition. After stirring for 45 min, the resulting mixture was quenched with methanol and evaporated to a syrup, which was then subjected to a column chromatographic separation to give the product (301 mg, 85% yield), glass, pure by TLC and by the ^{1}H-NMR spectrum, m. p. 214.5 – 217°C (from methanol), ^{1}H-NMR (DMSO-d_6 – CD_3OD): δ 8.16, 8.10 (two 1H, 2 x s, H-8 and 2), 7.95 – 7.75, 7.57 – 7.34 (5H, m, Ph protons), 6.4 (1H, t, $J_{1',2'} = J_{1',2''}$ 6 Hz, H-1'), and 4.76 – 4.47 (3H, m, H-3', 5', and 5").

Anal. Calcd for $C_{17}H_{17}O_4N_5$: C, 57.46; H, 4.82; N, 19.71. Found: C, 57.22; H, 4.79; N, 19.75.

N^6,5'-Dibenzoyl-2'-deoxyadenosine. N^6-Benzoyl-2'-deoxyadenosine (100 mg, 0.28 mmol) was, after the azeotropic removal of moisture, was added dropwise a solution of benzoyl chloride (0.049 mL, 1.5 mol. equiv.) in pyridine (3 mL) at room temperature, taking 1 h for the addition. After stirring for 1 h, the resulting mixture was quenched with methanol and evaporated, and the residue was distributed between chloroform and water. The organic layer was, after drying over anhydrous magnesium sulfate, evaporated to a syrup. The syrup was then subjected to a column chromatographic separation to give the product (115 mg, 89% yield) which was judged pure by TLC and ^{1}H-NMR spectrum, m.p. 172 – 174°C (from methanol), ^{1}H-NMR (DMSO-d_6 – CD_3OD): δ 8.55, 8.43 (two 1H, 2 x s, H-8 and 2), 8.05 – 7.75, 7.47 – 7.28 (10H, m, Ph protons x 2), 6.48 (1H, t, $J_{1',2'} = J_{1',2''}$ 6 Hz, H-1'), and 4.85 – 4.45 (4H, m, H-3', 4', 5', and 5").

Anal. Calcd for $C_{24}H_{21}O_5N_5$: C, 62.74; H, 4.61; N, 15.24. Found: C, 62.88; H, 4.59; N, 14.96.

N^4,5'-Dibenzoyl-2'-deoxycytidine. 2'-Deoxycytidine hydrogen chloride (264 mg, 1.0 mmol) was, after the azeotropic removal of moisture, suspended in pyridine (20 mL), and, to the resulting suspension, was added dropwise a solution of benzoyl chloride (0.26 mL, 2.2 mol. equiv.) in pyridine (10 mL) with

stirring at room temperature taking 2 h for the addition. After stirring for 30 min, the resulting mixture was quenched with methanol, and evaporated to a syrup, which was then subjected to a chromatographic separation to give the product (334 mg, 77% yield), which was judged pure by TLC and by the ^{1}H-NMR spectrum, m.p. 145.5 – 147°C (lit.[10] 145.5 – 147.5°C), ^{1}H-NMR (DMSO-d_6 – CD_3OD): δ 8.17 – 7.2 (12H, m, H-5, 6, and Ph protons x 2), 6.15 (1H, t, $J_{1',2'} = J_{1',2''}$ 6 Hz, H-1'), 4.65 – 4.23 (4H, m, H-3', 4', 5', and 5"); ^{1}H-NMR ($CDCl_3$ – CD_3OD – D_2O): δ 8.18 (1H, d, $J_{5,6}$ 7.6 Hz, H-6), 8.00 (2H, d, J 6.8 Hz, o-Ph proton x 2), 7.98 (2H, d, o-Ph proton x 2), 7.7 – 7.4 (7H, m, H-5 and Ph proton x 6), 6.22 (1H, t, $J_{1',2'} = J_{1',2''}$ 6 Hz, H-1'), 4.64 (2H, d, $J_{4',5'} = J_{4',5''}$ 3.3 Hz, H-5' and 5"), 4.5 – 4.3 (2H, m, H-3' and 4'), 3.47 (3H, s, OCH_3), 2.72 (1H, ddd, $J_{2',2''}$ 13.6 Hz, $J_{2',3'}$ 5.2 Hz, H-2'), and 2.20 (1H, ddd, $J_{2'',3'}$ 6.4 Hz, H-2").

Anal. Calcd for $C_{23}H_{21}O_6N_3$: C, 63.44; H, 4.86; N, 9.65. Found: C, 63.43; H, 4.97; N, 9.59.

N^2-Isobutyryl-5'-O-benzoyl-2'-deoxyguanosine. N^2-Isobutyryl-2'-deoxyguanosine[5b] (200 mg, 0.59 mmol) was, after the azeotropic removal of moisture, dissolved in pyridine (3 mL), and, to the resulting solution was added dropwise a solution of benzoyl chloride (0.10 mL, 1.4 mol. equiv.) in pyridine (6 mL) at room temperature, taking 2 h. After stirring the mixture for 1 h, it was quenched by the addition of water and evaporated. The resulting residue was distributed between chloroform and saturated aqueous solution of sodium bicarbonate. The organic layer was washed with water and dried over anhydrous magnesium sulfate. After filtering off the desiccant, the filtrate was evaporated to a syrup, which was then subjected to a column chromatographic separation to give the product (244 mg, 93% yield), which was pure as judged by TLC analysis and by the ^{1}H-NMR spectrum, m.p. 119.5 – 121°C (from diethyl ether – hexane), ^{1}H-NMR (DMSO-d_6 – CD_3OD): δ 8.00 (1H, s, H-8), 7.88 – 7.73, 7.52 – 7.30 (5H, m, Ph proton x 5), 6.27 (1H, t, $J_{1',2'}$ 6 Hz, H-1'), 4.70 – 4.15 (4H, m, H-3', 4', 5', and 5"), 2.95 – 2.45 (3H, m, H-2', 2", and Me_2CH), and 1.19 (6H, d, J 8 Hz, CH_3 x 2).

Anal. Calcd for $C_{21}H_{23}O_6N_5$: C, 57.14; H, 5.52; N, 15.86. Found: C, 56.83; H, 5.33; N, 16.04.

5'-O-Benzoylthymidine. Thymidine (1.211 g, 5 mmol) was dissolved in pyridine (15 mL), after the azeotropic removal of moisture, and, to the resulting solution was added dropwise a solution of benzoyl chloride (0.64 mL, 1.1 mol. equiv.) in pyridine (8 mL) at room temperature, taking 3 h. After stirring for 30 min, the mixture was quenched with methanol and evaporated; the residue was distributed between ethyl acetate and saturated aqueous solution of sodium bicarbonate. Work-up of the organic layer as usual gave the crystalline product (1.202 g, 69% yield), and another crop of the product was obtained from mother liquor by crystallization (201 mg, 12% yield); m.p. 173 – 174°C (from methanol) (lit.[7] m.p. 171 – 172°C), ^{1}H-NMR (DMSO-d_6 – $CDCl_3$): δ 10.42 (1H, s, NHCO of thymine moiety), 8.03 (2H, d, J 7.8 Hz, ortho protons of Ph group), 7.61 (1H, t, 7.2 Hz, para protons of Ph group), 7.44 (1H, s, H-6), 6.37 (1H, dd, $J_{1',2'}$ 6.5 Hz, $J_{1',2''}$ 7.3 Hz, H-1'), 5.18 (1H, d, $J_{OH,3'}$ 4.4 Hz, HO-3'), 4.65 (1H, dd, $J_{5',5''}$ 12.3 Hz, $J_{4',5'}$ 3.0 Hz, H-5'), 4.51 (1H, dd, $J_{4',5''}$ 4.2 Hz, H-5"), 4.49 (1H, ddd, $J_{2',3'}$ 3.7 Hz, $J_{2'',3'}$ 6.5 Hz, $J_{3',4'}$ 3.5 Hz, H-3"), 4.24 (1H, ddd, H-4'), 2.43 (1H, ddd, $J_{2',2''}$ 13.7 Hz, H-2'), 2.15 (1H, ddd, H-2"), and 1.63 (3H, s, CH_3).

Anal. Calcd for $C_{18}H_{20}O_6N_2$: C, 58.96; H, 5.24; N, 8.06. Found: C, 59.23; H, 5.30; N, 8.16.

N^4,5'-Dibenzoyl-2'-deoxycytidine Through Benzoylation in the Presence of Triethylamine. To a solution of 2'-deoxycytidine hydrogen chloride (527 mg, 2 mmol) in pyridine (6 mL), prepared after the removal of moisture three times, was introduced triethylamine (0.28 mL, 1 mol. equiv.). To this solution was added dropwise a solution of benzoyl chloride (0.48 mL, 2.05 mol. equiv.) in pyridine (8 mL) at room temperature, taking 2 h and 45 min. After stirring the mixture for 30 min, it was quenched with methanol and worked up in the same way as described in the third experimental to give the product (727 mg, 84% yield), which was identical with the authentic sample obtained in the third experimental.

N^4,5'-Di-o-toluoyl-2'-deoxycytidine Through o-Toluoylation in the Presence of Triethylamine. To a solution of 2'-deoxycytidine hydrogen chloride (791 mg, 3 mmol) in pyridine (10 mL), prepared in the same way as above, was introduced tri-

ethylamine (0.42 mL, 1 mol. equiv.). To this solution was added dropwise a solution of o-toluoyl chloride (0.796 mL, 2.03 mol. equiv.) in pyridine (12 mL) at room temperature, taking 2 h. After stirring for 30 min, the mixture was quenched with methanol (5 mL) and further stirred for 15 min. The resulting mixture was evaporated to a syrup, which was dissolved in chloroform and extracted with 0.5 N hydrochloric acid. The organic layer was, after successive washing with water, saturated aqueous solution of sodium bicarbonate, and water, dried over anhydrous magnesium sulfate. After filtering off the desiccant, the organic solution was evaporated to a syrup, which was then subjected to a chromatographic separation to give the product (1.167 g, 84% yield), which was judged pure by TLC analysis and by the ^{1}H-NMR spectrum, m.p. 127.5 – 128.5°C (from ethanol), ^{1}H-NMR ($CDCl_3$ – CD_3OD): δ 8.14 (1H, d, $J_{5,6}$ 7.6 Hz, H-6), 7.84 (1H, d, H-5), 7.6 – 7.2 (7H, m, protons of o-toluoyl group), 6.22 (1H, d, $J_{1',2'}$ 5.8 Hz, H-1'), 4.60 (1H, s, H-5'), 4.59 (1H, d, $J_{4',5''}$ 1.7 Hz, H-5"), 4.43 – 4.3 (2H, m, H-3' and 4'), 2.71 (1H, ddd, $J_{2',3'}$ 4.7 Hz, $J_{2',2''}$ 14.4 Hz, H-2'), 2.61 (3H, s, CH_3 of o-toluoyl group), and 2.17 (1H, ddd, $J_{2'',3'}$ 6.3 Hz, H-2").

Anal. Calcd for $C_{25}H_{25}O_6N_3$: C, 64.78; H, 5.44; N, 9.07. Found: C, 64.68; H, 5.46; N, 8.84.

One-pot Preparation of N^6,5'-Dibenzoyl-2'-deoxyadenosine from 2'-Deoxyadenosine. To a solution of 2'-deoxyadenosine (200 mg, 0.8 mmol) in pyridine (3 mL), prepared as described above, was added dropwise a solution of benzoyl chloride (0.1 mL, 1.1 mol. equiv.) in pyridine (2 mL) at room temperature, taking 30 min. To this solution were added in turn chlorotrimethylsilane (0.51 mL, 5 mol. equiv.) and, after 15 min stirring, benzoyl chloride (0.28 mL, 3 mol. equiv.). After further stirring for 1.5 h, the resulting mixture was quenched with methanol (1 mL), and treated with ammoniacal methanol (saturated at 0°C)(6 mL) through drop-by-drop addition at 0°C. The resulting solution was, after stirring for 30 min at room temperature, evaporated and the residue was distributed between chloroform and water. The syrup obtained by evaporating the organic solution after drying over anhydrous magnesium sulfate, was subjected to a chromatographic separation to give the pro-

duct (292 mg, 80% yield), which was identical with the authentic specimen obtained in the second experimental.

5'-O-Benzoylation of Thymidine at 0°C. To a solution of thymidine (242 mg, 1 mmol) in pyridine (6 mL), prepared as described above, was added dropwise a solution of benzoyl chloride (0.13 mL, 1.1 mol. equiv.) in pyridine (6 mL) at 0°C, taking 2 h and 45 min. After stirring for 15 min, the resulting mixture was quenched with methanol (5 mL) and stirred for 15 min. The mixture was evaporated to a syrup, which was then subjected to a chromatographic separation through 3% methanolic chloroform to give the product (325 mg, 94% yield) in addition to the corresponding 3'-benzoate (8 mg, 2% yield). The former was identical with the authentic specimen obtained in the fifth experimental, and the structure of the latter was assigned to the 3'-benzoate based on its ^{1}H-NMR spectrum (60 MHz, DMSO-d_6 – CD_3OD): δ 8.05 – 7.31 (6H, m, H-6 and Ph proton x 5), 6.29 (1H, t, $J_{1',2'} = J_{1',2''}$ 6.5 Hz, H-1'), 5.50 (1H, m, H-3'), 2.66 – 2.30 (2H, m, H-2' and 2"), 1.85 (3H, s, CH_3); the signals of H-4', 5', and 5" were overlapped with that of the solvents used, so that they were impossible to assign.

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9 Chemical discrimination of the 5'-O-aroyl group from the 3'-phosphor-function has been successful to let us isolate the corresponding 5'-OH derivatives in the yields exceeding 90%; the results thus obtained will be reported elsewhere as an alternative approach to the synthesis of 2'-deoxynucleotide oligomers involving no treatment with an acid for unmasking the 5'-terminus protecting groups of a resulting oligomer or a 2'-deoxyribonucleotide derivative.

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