washed with brine, and dried over Na_2SO_4. Evaporation of the solvent followed by column chromatography (SiO_2, diethyl ether–hexane, 1:1) gave 1.20 g of **7a** (75%), which was recrystallized from hexane: mp 94–95 °C; ^1H NMR δ (ppm) 1.13 (t, J = 7.4 Hz, 3 H, 3-CH_2CH_3), 1.37 (t, J = 7.1 Hz, 3 H, 2-$CO_2CH_2CH_3$), 1.39 (t, J = 7.1 Hz, 3 H, 5-$CO_2CH_2CH_3$), 3.11 (q, J = 7.4 Hz, 2 H, 3-CH_2CH_3), 4.37 (q, J = 7.1 Hz, 2 H, 2-$CO_2CH_2CH_3$), 9.7 (b s, 1 H, NH), 10.54 (s, 1 H, CHO). Anal. Found for $C_{13}H_{17}NO_5$ (Calcd) C, 58.37 (58.42); H, 6.41 (6.41); N, 5.14 (5.24).

3-Ethyl-4-formylpyrrole-2,5-dicarboxylic Acid (7b). A mixture of **7a** (3.7 mmol) in a 2 N solution of KOH in 90% (v/v) aqueous EtOH (33 mL) was refluxed for 5 h. The mixture was then poured onto ice, acidified with 10% H_2SO_4, extracted with chloroform, washed with brine, and dried over Na_2SO_4 to afford **7b** as a white solid (88%), which was recrystallized from glacial AcOH: mp 226 °C dec; ^1H NMR (acetone-d_6) δ (ppm) 1.19 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 3.17 (q, J = 7.4 Hz, 2 H, CH_2CH_3), 7.85 (b s, 2 H, 2 CO_2H), 10.36 (s, 1 H, CHO), 11.45 (b s, 1 H, NH). Anal. Found for $C_9H_9NO_5$ (Calcd): C, 51.24 (51.19); H, 4.25 (4.30); N, 6.63 (6.63).

3-Ethyl-4-formylpyrrole. The decarboxylation of **7b** was achieved according to the procedure of Anderson.[15] To a stirred suspension of copper chromite barium promoted (Aldrich) (0.345 g) in quinoline (10 mL) at 200 °C (internal temperature) was added **7b** (1.9 mmol). After 10 min carbon dioxide evolution ceased; the dark oil was poured onto ice, and concd HCl (8 mL) was added while stirring. The solid was filtered, and the filtrate was extracted several times with diethyl ether. The combined organic phases were washed with a saturated solution of $NaHCO_3$ and then brine and dried over Na_2SO_4. Evaporation of the solvent afforded 45% of 3-ethyl-4-formylpyrrole as a yellow oil which turned brown quickly: ^1H NMR δ (ppm) 1.20 (t, J = 7.3 Hz, 3 H, CH_2CH_3), 2.75 (q, J = 7.3 Hz, 2 H, CH_2CH_3), 6.55–6.58 (m, 1 H, 2-H pyrrole), 7.29–7.33 (m, 1 H, 5-H pyrrole), 9.83 (d, J = 0.5 Hz, 1 H, CHO); mass spectrum, m/z (relative intensity) 123 (M^+, 100), 108 (86), 94 (M^+ – CHO, 45), 53 (44). The instability of the product did not allow us to obtain a satisfactory elemental analysis.

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Registry No. **1a**, 2199-55-5; **1b**, 7467-77-8; **2b**, 139070-42-1; **2c**, 139070-43-2; **3a**, 78633-82-6; **4a**, 2199-46-4; **4b**, 2199-47-5; **5a**, 139070-44-3; **5b**, 139070-45-4; **5c**, 139070-46-5; **6a**, 139070-47-6; **7a**, 139070-48-7; **7b**, 139070-49-8; **8**, 4391-99-5; **9**, 4391-87-1; **10**, 139070-50-1; 3-ethyl-4-formylpyrrole, 139070-51-2.

Supplementary Material Available: ^1H NMR spectrum of 3-ethyl-4-formylpyrrole (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

A Novel and Convenient Route to 3′-Carbonates from Unprotected 2′-Deoxynucleosides through an Enzymatic Reaction

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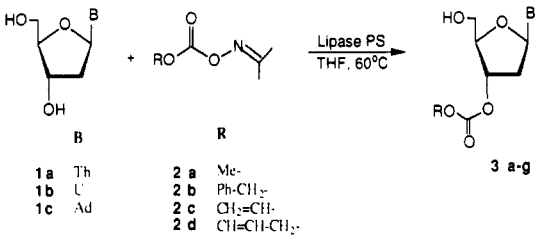
Introduction

2′-Deoxynucleosides have attracted much attention as potential antiviral agents,[1] and the usefulness of nucleosides modified in the 3′-position has led to a rising interest in the development of procedures for their preparation.

Scheme I



The primary hydroxyl group has had to be protected to obtain such derivatives.

Regioselective acylation of the 3′-hydroxyl group of nucleosides is a difficult reaction by conventional methods. Only through enzymatic reactions can it be achieved.[2] Recently, we have found that the reaction of pyrimidine and purine 2′-deoxynucleosides with oxime esters and lipase PS in pyridine is a versatile method to prepare 3′-O-acylated derivatives.[3] Given this set of circumstances, we are able to report, to the very best of our knowledge, on the first procedure for the regioselective synthesis of 3′-carbonates from the unprotected nucleosides. These compounds play an important role in the synthesis of oligonucleotides and other derivatives (such as dinucleoside carbonates). For example, the benzyloxycarbonyl group (Cbz) is commonly introduced using benzyl chloroformate;[4] however, this reaction does not allow direct preparation of the 3′-*O*-carbonate because substitution takes place preferably on the primary hydroxyl group.[4,5]

Results and Discussion

One approach to this problem involves using an appropriate reagent for alkoxycarbonylation. We thought of two possibilities: either acetone *O*-[(alkyloxy)carbonyl]oximes **2** or pyrocarbonates, the latter because of their analogy with anhydrides, which have been used in acylations of 2′-deoxynucleosides.[2] These nucleosides, when tested with pyrocarbonates under the same conditions, gave a complex mixture of compounds. Moreover, only dialkyl pyrocarbonates are commercially available; others, such as dibenzyl pyrocarbonate have been prepared[6] but are compounds with proven instability.

On the other hand, acetone *O*-[(alkyloxy)carbonyl]-oximes **2**, are similar to oxime esters (useful acylating agents in enzymatic reactions),[3,8] and their behavior in enzymatic alkoxycarbonylations has not been tested, a fact that prompted us to carry out this reaction with compounds **2**. Stability and availability (from the corresponding chloroformates) are additional advantageous features of these compounds which, except for **2b**,[7] have not been described in the literature (for physical and spectral data see Table II).

After a preliminary screening to find the most desirable enzyme and reaction conditions, we selected lipase Amano PS as a catalyst and tetrahydrofuran as a solvent (Scheme I). Other solvents, such as pyridine, DMSO, or DMF were not as effective as THF; however, 1,4-dioxane can be used as an alternative to THF. This reaction did not take place

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Table I. Compounds 3 Prepared with Lipase PS in THF at 60 °C[a]

product	B	R	yield[b] (%)	mp[c] (°C)	IR[d]	$[\alpha]^{D}_{25}$ (c, solvent)
3a	Th	CH_3	82	156–7	1760, 1262	+3.5 (0.52, MeOH)
3b	U	CH_3	80	166–7	1753, 1257	+15.3 (0.51, MeOH)
3c	Ad	CH_3	68	182–3	1740, 1257	-28.8 (0.50, DMSO)
3d	Th	$PhCH_2$	77	108–9	1753, 1268	-1.8 (0.50, DMSO)
3e	U	$PhCH_2$	74	150–1	1744, 1267	-3.0 (0.46, DMSO)
3f	Ad	$PhCH_2$	64	162–3	1745, 1264	-31.2 (0.59, DMSO)
3g	Th	CH_2=CH	65	182–3	1770, 1259	-10.8 (0.50, DMSO)
3h	U	CH_2=CH	68	182–3	1757, 1259	0 (0.34, MeOH)
3i	Th	CH_2=$CHCH_2$	76	154–5	1763, 1238	-2.2 (0.52, DMSO)

[a] All the reactions were carried out for 30 h except for **3c** and **3f** (40 h). [b] Calculated with respect to **1**, on pure isolated products **3**. [c] Uncorrected. [d] KBr, partial.

Table II. Physical and Spectral Data for Compounds 2[a]

compd	bp[b] (°C)	IR,[c] ν (cm^{-1})	^{1}H NMR, δ (ppm)	^{13}C NMR, δ (ppm)
2a	20	1777, 1238	2.01 (3 H, s), 2.03 (3 H, s), 3.98 (3 H, s)	13.94, 18.96, 52.61, 152.16, 161.48
2c	28	1786, 1220	2.04 (3 H, s), 2.02 (3 H, s), 4.64 (1 H, dd), 4.96 (1 H, dd), 7.26 (1 H, dd)	16.41, 21.20, 98.08, 142.94, 151.23, 164.96
2d	32	1767, 1240	2.01 (3 H, s), 2.03 (3 H, s), 4.75 (2 H, dt), 5.30 (1 H, dq), 5.41 (1 H, dq), 5.98 (1 H, m)	14.88, 19.38, 66.91, 117.24, 130.30, 151.99, 162.01

[a] For compound **2b** see ref 7. [b] Measured at 10^{-2} mmHg. [c] Pure samples.

Table III. ^{13}C-NMR Chemical Shifts for Compounds 3, δ (ppm)[a]

	base ring					sugar moiety					carbonate moiety	
product	C2	C4	C5	C6	Me	C1′	C2′	C3′	C4′	C5′	C=O	R
3a	152.22	167.00	112.20	137.90	12.17	85.63	36.77	78.72	84.97	61.90	156.17	56.04
3b	152.21	166.87	103.07	142.51	-	86.19	37.02	78.82	85.24	61.98	156.22	56.15
3d	150.81	164.05	110.14	136.10	12.57	84.03	36.83	79.03	84.68	61.68	154.13	69.59, 128.57, 128.75, 128.82, 135.55
3e	150.65	163.28	102.36	140.45	-	84.71	36.97	78.94	84.24	61.52	153.97	69.48, 128.50, 128.67, 128.74, 135.46
3g	151.75	165.63	111.50	137.49	13.17	85.21	37.36	80.33	85.21	62.28	152.75	100.28, 143.60
3h	150.62	163.24	102.37	140.44	-	84.21	36.79	79.67	84.44	61.49	151.57	98.81, 142.96
3i	150.65	163.68	109.94	135.98	12.47	83.80	36.60	78.75	84.44	61.51	153.81	68.34, 118.79, 132.20
	base ring					sugar moiety					carbonate moiety	
product	C2	C4	C5	C6	C8	C1′	C2′	C3′	C4′	C5′	C=O	R
3c	153.66	149.67	120.16	156.82	141.43	85.94	37.98	80.07	86.51	62.95	156.04	56.38
3f	154.22	148.44	121.11	156.12	139.99	87.10	37.60	79.99	87.46	63.24	152.43	70.06, 128.44, 128.67, 128.67, 134.67

[a] Solvents: DMSO-d_6, except for **3a**, **3b** (D_2O), and **3f** ($CDCl_3$). C1′ and C4′ were readily identificated on the basis of the coupled ^{13}C-NMR spectra, since $^1J_{C1',H\text{-}C1'}$ exhibit values around 165 Hz whereas the other $^1J_{C,H}$ of the sugar moiety (for example $^1J_{C4',H\text{-}C4'}$) are 15–20 Hz smaller (see: Seela, F.; Stecker, H. *Helv. Chim. Acta* **1985**, *68*, 563). In the case of **3c** and **3f**, discrimination among C2, C6, and C=O was made by means of DEPT and bidimensional experiments for the observation of long-range coupling (HXCORR pulse sequence optimized to $J_{C,H}$ = 10 Hz).

in the absence of enzyme even if stronger conditions were used.

The alkoxycarbonylation of nucleosides is summarized in Table I. Treatment of nucleosides **1a–c** with a slight excess of **2a–d** in the presence of lipase Amano PS in THF at 60 °C yielded 3′-carbonates and starting material as the only products.[9] Disubstituted compounds were not detected and no traces of N-acylation product could be found when 2′-deoxyadenosine was used. The identification of nucleoside derivatives **3a–i** was accomplished by ^{13}C-NMR spectroscopy. The only difference between isolated products and starting nucleosides was a ca. 8 ppm downfield shift of the peak corresponding to the 3′-carbon atom and a ca. 2 ppm upfield shift of the two signals corresponding to the C2′ and C4′. Of particular note is the fact that the C5′ presented no shift in products **3a–i** with respect to starting nucleosides **1a–c**.

These data are in accordance with the additivity rules given for acylation of sugars[10] and are similar to those found in 3′-O-acylated nucleosides.[3] In addition, the ^{1}H-NMR spectra of products **3a–i** show a downfield shift of ca. 1.5 ppm for H3′, whereas the other H signals of the sugar moiety underwent only slight downfield shifts with respect to 2′-deoxynucleosides **1a–c**. Complete ^{13}C- and ^{1}H-NMR spectral data are given in Tables III and IV respectively.[11]

It is noteworthy that the reaction of **1a–c** with acetone *O*-[(benzyloxy)carbonyl]oxime (**2b**, R = CH_2Ph) and acetone *O*-[(allyloxy)carbonyl]oxime (**2d**, R = CH_2CH=CH_2) may prove to be of great utility in the one-step protection (through introduction of Cbz or Alloc, respectively) of 3′-hydroxyl groups of 2′-deoxynucleosides and other related compounds. In the case of acetone *O*-[(vinyloxy)carbonyl]oxime (**2c**, R = CH=CH_2), one could think about two possibilities of alkoxycarbonylation, since the leaving group, as has been reported in some works, could be the acetone oxime moiety[3,7,8] or the vinyloxy group (acetaldehyde).[12] Our findings demonstrate that the leaving

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Table IV. ^{1}H-NMR Spectral Data for Compounds 3,[a] δ (ppm)

product	base ring NH	base ring Me	base ring H5	base ring H6	sugar moiety H1′	sugar moiety (H2′, H2″)	sugar moiety H3′	sugar moiety H4′	sugar moiety (H5′, H5″)	carbonate moiety
3a	9.02 (s)	1.95 (s)	-	7.48 (s)	6.20 (dd)	2.49 (m)	5.30 (m)	4.20 (m)	3.95 (m)	3.84 (3 H, s)
3b	8.05 (s)	-	5.75 (d)	7.68 (d)	6.21 (dd)	2.49 (m)	5.29 (m)	4.20 (m)	3.94 (m)	3.82 (3 H, s)
3d	-	1.79 (s)	-	7.72 (s)	6.18 (t)	2.33 (m)	5.15[b]	4.05 (m)	3.62 (m)	5.15,[b] 7.42 (5 H, m)
3e	8.55 (s)	-	5.73 (d)	7.70 (d)	6.21 (t)	2.50 (m)	5.31 (m)	4.20 (m)	3.94 (m)	5.18 (2 H, s), 7.39 (5 H, m)
3g	8.50 (s)	1.94 (s)	-	7.42 (s)	6.19 (dd)	2.51 (m)	5.38 (m)	4.25 (m)	3.97 (m)	4.65 (1 H, dd), 4.98 (1 H, dd), 7.39 (1 H, dd)
3h	8.21 (s)	-	5.78 (d)	7.44 (d)	6.22 (t)	2.51 (m)	5.35 (m)	4.24 (m)	3.95 (m)	4.67 (1 H, dd), 4.99 (1 H, dd), 7.08 (1 H, dd)
3i	8.32 (s)	1.95 (s)	-	7.44 (s)	6.19 (dd)	2.50 (m)	5.30[b]	4.20 (m)	3.94 (m)	4.67 (2 H, m), 5.30,[b] 5.40 (1 H, dd), 5.93 (1 H, m)

product	base ring NH_2	base ring H2	base ring H8	sugar moiety H1′	sugar moiety (H2′, H2″)	sugar moiety H3′	sugar moiety H4′	sugar moiety (H5′, H5″)	carbonate moiety
3c	5.75 (s)	7.80 (s)	8.36 (s)	6.28 (dd)	2.49 (dd), 3.22 (m)	5.51 (m)	4.35 (m)	3.95 (m)	3.85 (3 H, s)
3f	5.98 (s)	7.80 (s)	8.32 (s)	6.27 (dd)	2.50 (dd), 3.21 (m)	5.52 (m)	4.36 (m)	3.91 (m)	5.20 (2 H, s), 7.40 (5 H, m)

[a] All samples measured in $CDCl_3$, except **3d** (DMSO-d_6). [b] Superimposed signals.

group is acetone oxime and *not* acetaldehyde, allowing, therefore, the 3′-*O*-vinyloxycarbonyl derivative of the nucleoside.

Conclusions

In conclusion, we have described a general, new and simple procedure for the synthesis of 3′-carbonates of pyrimidine and purine 2′-deoxynucleosides. In this method, no previous protection of the primary hydroxyl group is necessary, as has been traditionally described for preparation of these compounds.

Experimental Section

General. Amano PS lipase was purchased from Amano Pharmaceutical Co. Deoxynucleosides, **1**, were purchased from Aldrich Chemie. THF was distilled over $LiAlH_4$ in order to avoid moisture. Precoated TLC alumina sheets silica gel 60 F_{254} from Merck were used, and for column chromatography, Merck silica gel 60/230–400 mesh was used. Mp's were taken on samples in open capillary tubes using a Büchi melting point apparatus and are uncorrected. Optical rotations were measured using a Perkin-Elmer 241 polarimeter. IR spectra were recorded on a Perkin-Elmer 1720-X FT spectrometer. NMR spectra were recorded using a Bruker AC300 spectrometer with $CDCl_3$, D_2O, or DMSO-d_6 as solvents. Mass spectra were obtained on a Hewlett-Packard 5897 A spectrometer. Microanalyses were performed on a Perkin-Elmer Model 240 and a Carlo Erba Model 1108 instruments. Acetone *O*-[(alkyloxy)carbonyl]oximes **2** were prepared in almost quantitative yields by treating acetone oxime with the corresponding chloroformate and distilling under vacuum.

General Procedure for the Synthesis of Compounds 3a–i. **1a–c** (2 mmol), 2.1 mmol of **2a–d**, and 1 g of lipase Amano PS was suspended in 15 mL of THF (in the case of **1b**, 0.5 g of molecular sieve activated powder was added to remove hydrated water from starting nucleoside) under nitrogen atmosphere. The mixture was allowed to react at 60 °C and 250 rpm during the time indicated in footnote *a* of Table I. Then, the enzyme was filtered off and washed with MeOH, the residue was evaporated under vacuum, and the product was subjected to flash chromatography (AcOEt–MeOH, 100:1, or in the case of **3c** and **3f**, AcOEt–MeOH–H_2O, 100:10:1). Crystallization takes place from AcOEt or diethyl ether.

Characterization of Products 3a–g. Table I shows reaction time (footnote *a*), yield, mp, IR data, and optical rotations. Tables II and III present the ^{1}H- and ^{13}C-NMR spectral data and solvents used in their measurement.

3a: mass spectra (70 eV), *m/z* (relative intensity) 300 (M^+, 1), 175 (5), 126 (15), 99 (86), 69 (100), 59 (25). Anal. Calcd for $C_{12}H_{16}N_2O_7$: C, 48.00; H, 5.33; N, 9.33. Found: C, 48.13, H, 5.50; N, 9.31.

3b: mass spectra (70 eV), *m/z* (relative intensity) 286 (M^+, 3), 175 (24), 99 (100), 69 (90), 59 (21). Anal. Calcd for $C_{11}H_{14}N_2O_7$: C, 46.15; H, 4.89; N, 9.79. Found: C, 45.88; H, 4.75; N, 9.91.

3c: mass spectra (70 eV), *m/z* (relative intensity) 309 (M^+, 2), 234 (5), 135 (100), 99 (12), 69 (25), 59 (9). Anal. Calcd for $C_{12}H_{15}N_5O_5$: C, 46.60; H, 4.85; N, 22.65. Found: C, 46.82; H, 4.97; N, 22.48.

3d: mass spectra (70 eV), *m/z* (relative intensity) 376 (M^+, 1), 251 (6), 126 (11), 99 (41), 91 (100), 69 (27). Anal. Calcd for $C_{18}H_{20}N_2O_7$: C, 57.44; H, 5.32; N, 7.45. Found: C, 57.68; H, 5.54; N, 7.56.

3e: mass spectra (70 eV), *m/z* (relative intensity) 362 (M^+, 1), 251 (6), 112 (6), 99 (38), 91 (100), 69 (26). Anal. Calcd for $C_{17}H_{18}N_2O_7$: C, 56.35; H, 4.97; N, 7.73. Found: C, 56.11; H, 4.65; N, 7.58.

3f: mass spectra (70 eV), *m/z* (relative intensity) 385 (M^+, 2), 234 (7), 135 (100), 99 (16), 91 (73), 69 (24). Anal. Calcd for $C_{18}H_{19}N_5O_5$: C, 56.10; H, 4.93; N, 18.18. Found: C, 55.86; H, 4.79; N, 18.32.

3g: mass spectra (70 eV), *m/z* (relative intensity) 312 (M^+, 3), 187 (8), 99 (100), 69 (87), 43 (20). Anal. Calcd for $C_{13}H_{16}N_2O_7$: C, 50.00; H, 5.13; N, 8.97. Found: C, 50.28; H, 4.86; N, 9.21.

3h: mass spectra (70 eV), *m/z* (relative intensity) 298 (M^+, 2), 187 (19), 99 (100), 69 (75), 41 (11). Anal. Calcd for $C_{12}H_{14}N_2O_7$: C, 48.32; H, 4.70; N, 9.40. Found: C, 48.40; H, 4.63; N, 9.51.

3i: mass spectra (70 eV), *m/z* (relative intensity) 326 (M^+, 1), 201 (9), 99 (100), 69 (70), 41 (32). Anal. Calcd for $C_{14}H_{18}N_2O_7$: C, 51.53; H, 5.52; N, 8.59. Found: C, 51.50; H, 5.45; N, 8.70.

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Selective Deprotection of Trialkylsilyl Ethers Using Fluorosilicic Acid

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Silyl ethers have become the protecting group of choice for the hydroxyl function. Their popularity is due in part to their ease of formation and removal and their stability to a wide range of reagents and reaction conditions. A variety of methods have been developed for the cleavage of the silicon–oxygen bond,[1] but few of these methods allow

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