A New Highly Chemo- and Regioselective Alkoxycarbonylation of Amino Alcohols and Polyols

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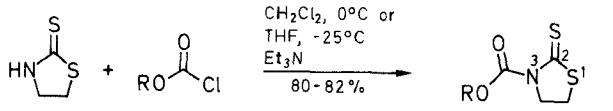
The alkoxycarbonylating carbamates **1** and **2** are readily prepared and reacted under mild conditions with polyfunctional substrates, e.g. amino acids, unsymmetrical diols, and unprotected carbohydrates (D-glucosamine and methyl α-D-glucoside), thus affording carbamates or monocarbonates in good yields and with high chemo- and regioselectivity.

The selective protection of polyfunctional substrates is a very useful reaction in organic synthesis. Numerous methods have been developed for specific acylation of amino alcohols and for selective esterification of polyols, including carbohydrates.[1,2] Acetylation and benzoylation have most frequently been used for the latter purpose,[3] these protecting groups being resistant to acid-catalyzed hydrolysis. Like esters, carbonates can be cleaved by basic hydrolysis, but under milder conditions,[4] and selective cleavage of a carbonate[5] or a carbamate,[6] in the presence of an ester can be achieved. Carbonates of polyhydrolic systems are generally prepared by reaction of carbonochloridates (chloroformates) with previously protected substrates;[7] regioselectivity is poor when using free polyols.[5,8]

Several alkoxycarbonyl donors have been already proposed in the last years, e. g. benzyloxycarbonyl derivatives of 2-benzimidazolethiol, of 2-benzoxazolethiol, 2-benzothiazolethiol,[9] 3-alkoxycarbonyl-2-oxazolones,[10] and dialkyl dicarbonates.[11] These reagents, however, have not found extensive application until now; this prompted us to search for further, inexpensive and efficient alkoxycarbonyl donors.

We have found that *N*-alkoxycarbonylthiazolidine-2-thiones **1** and the *N*-derivatives **2** of 2-mercapto-5-methyl-1,3,4-thiadiazole are very effective in acylation of amino groups and in selective preparation of monocarbonates from diols and carbohydrates. In this paper, we wish to report on the simple preparations and reactions of compounds **1** and **2**.

The carbamates **1a–c** were prepared from thiazolidine-2-thione and commercially available alkyl carbonochloridates (chloroformates) in dichloromethane at 0 °C or in tetrahydrofuran at −25 °C in the presence of triethylamine (Scheme **A**) and were easily purified as yellow oils or crystalline solids (Table 1).



1a R = Et
b R = *i*-Bu
c R = $PhCH_2$

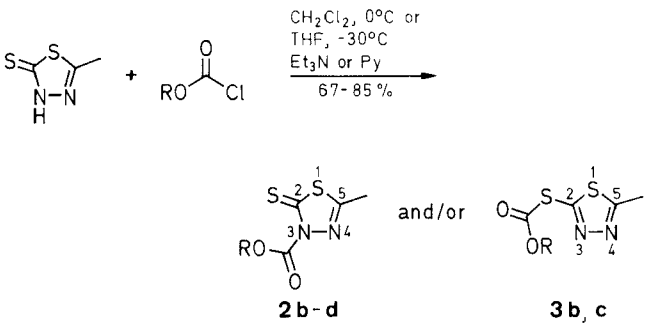
Scheme **A**

Table 1. Synthesis of Carbamates **1–2** and Thiocarbonates **3**

Product	Conditions				Yield (%)	mp (°C) or bp (°C)/Torr (solvent[a])	Molecular Formula[b] or Lit. Data
	Solvent	Base (equiv)	Temp. (°C)	Time (min)			
1a	CH_2Cl_2	Et_3N (1 equiv)	0	35	81	136–138/1.5	$C_6H_9O_2NS_2$ (191.3)[12]
1b	CH_2Cl_2	Et_3N (1 equiv)	0	90	80	162/0.75	$C_8H_{13}O_2NS_2$ (219.3)
1c	THF	Et_3N (1 equiv)	−25	60	82	83–84 (CH_2Cl_2/Hx)	$C_{11}H_{11}O_2NS_2$ (253.3)
2b	CH_2Cl_2	Py (1 equiv)	r.t.	600	67	55–58 (CH_2Cl_2/Hx)	$C_8H_{12}O_2N_2S_2$ (232.3)
2c	THF	Py (1 equiv)	−30	120	80	67–70 (CH_2Cl_2/Hx)	$C_{11}H_{10}O_2N_2S_2$ (266.3)
2c	CH_2Cl_2	Py (3 equiv)	0	150	63	67–70 (CH_2Cl_2/Hx)	$C_{11}H_{10}O_2N_2S_2$ (266.3)
2d	CH_2Cl_2	Py (3 equiv)	r.t.	120	80	45 (C_6H_6/Hx)	$C_7H_8O_2N_2S_2$ (216.3)
3b	THF	Et_3N (1 equiv)	−30	90	85	oil	$C_8H_{12}O_2N_2S_2$ (232.3)
3c	THF	Et_3N (1 equiv)	−30	120	68	64–65 (CH_2Cl_2/Hx)	$C_{11}H_{10}O_2N_2S_2$ (266.3)

[a] Hx = hexane.
[b] Satisfactory microanalyses obtained: C ±0.25, H ±0.31, N ±0.23.

Under the same conditions, at −30 °C, the reaction of 2-mercapto-5-methyl-1,3,4-thiadiazole[19] with carbonochloridates was quantitative, but afforded a mixture of **2** and **3**, in which the thiocarbonates **3** were largely preponderant. The latter were purified by column chromatography and thus obtained in 68–85% yield (Table 1). Attempts to prepare the carbamates **2** were successful when pyridine was used as the base (Scheme **B**). Increasing the amount of pyridine (from 1 to 3 equiv) improved the yields of **2** and allowed to simplify the reaction conditions.



2,3	R
b	*i*-Bu
c	$PhCH_2$
d	CH_2=$CHCH_2$

Scheme **B**

The structures of compounds **1–3** were assigned from their spectrometric properties (Table 2). ^{13}C-NMR peaks at $\delta = 200$ and $\delta = 188–190$, respectively, supported the thione structures[14] of compounds **1** and **2**, whereas this peak did not show up in the ^{13}C-NMR spectra of thiocarbonates **3**. Moreover, in the IR spectra of **3** the carbonyl group was characterized by an absorption band located at 1730 cm^{-1}, while ν (C=O) appeared at a high frequency, that is near 1760 cm^{-1}, for thiones **1** and **2**. This means that the nitrogen atom of carbamates **1** and **2** conjugates with the thiocarbonyl group rather than with the carbonyl one, and that the compounds **1** and **2** could be regarded as alkoxycarbonyl derivatives with very effective leaving groups.

A study by crystal X-ray diffraction confirms unambiguously the structure of compound **2c** (Figure). This compound exhibits a triclinic unit cell with parameters: a = 7.740(6), b = 8.889(9), c = 9.536(5) Å, α = 89.30(6), β = 82.43(5), γ = 67.51(9), V = 600.4 Å^3, Z = 2, space group: P$\bar{1}$. The five-membered ring containing sulfur and nitrogen atoms is planar. The dihedral angle between this plane and the carbonyl group plane is 11.36°. The bond length and angle values show strong interactions in the $S_2–C_3–N_1–C_4–O_2$ group.

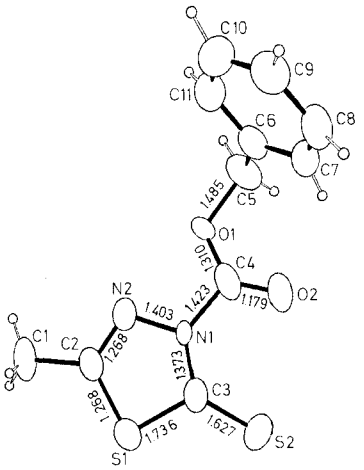


Figure. An ORTEP view of the **2c** molecule with thermal ellipsoids (50% probability). The hydrogen atoms are represented with arbitrary radii.

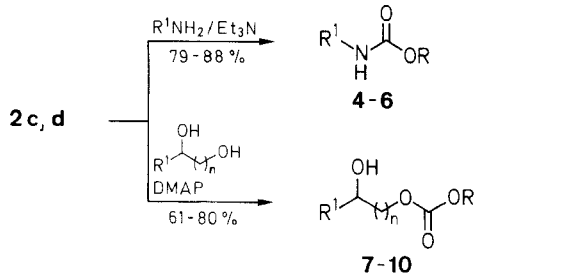
The yellow compounds **1** and **2** proved to be stable and can be stored for a long period of time at room temperature or in a refrigerator. On the contrary, the colorless thiocarbonates **3** decompose and isomerize to the thermodynamically more stable isomers **2** when heated in pyridine/tetrahydrofuran mixtures.

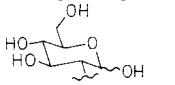
The utility of the reagents **1** and **2** was demonstrated in the preparation of carbamates from amino alcohols such as side chain functionalized amino acids or amino sugars and in chemoselective alkoxycarbonylation of diols as well as carbohydrates (Schemes **C** and **D**). *N*-

Table 2. Spectral Data of Compounds **1** and **2**

Compound	IR (NaCl) $\nu_{C=O}$ (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)	^{13}C-NMR ($CDCl_3$) δ
1a	1753, 1721	1.36 (t, 3H, J = 8, CH_3), 3.34 (t, 2H, J = 7.2, CH_2S), 4.3 (d, 2H, J = 8, CH_3CH_2), 4.54 (t, 2H, J = 7.2, CH_2N)	13.58 (CH_3), 27.86, 55.21 (C-4, C-5), 62.96 (CH_2O), 150.21 (CO), 199.64 (C-2)
1b	1755, 1725	1.02 (d, 6H, J = 8, [$(CH_3)_2CH$], 2.02 (m, 1H, $CHCH_2O$), 3.04 (t, 2H, J = 7.2, CH_2S), 4.07 (d, 2H, J = 6, $CHCH_2O$), 4.58 (t, 2H, J = 7.2, CH_2N)	19.06 ($(CH_3)_2$), 27.62 (CH), 28.39, 55.74 (C-4, C-5), 73.66 (CH_2O), 151.20 (CO), 199.84 (C-2)
1c	1760	3.10 (t, 2H, J = 7.2, CH_2S), 4.40 (t, 2H, J = 7.2, CH_2N), 5.20 (s, 2H, CH_2N), 7.00 (s, $5H_{arom}$)	28.27, 55.66 (C-4, C-5), 68.98 (CH_2O), 128.13, 128.27, 134.33 (N), 150.50 (CO), 199.70 (C-2)
2b	1770	1.03 (d, 6H, J = 6.6, $(CH_3)_2CH$), 2.13 (m, 1H, $CHCH_2O$), 2.49 (s, 3H, CH_3), 4.23 (d, 2H, J = 6.6, CH_2O)	15.75 (CH_3), 18.29 ($(CH_3)_2$), 26.98 (CH), 74.36 (CH_2O), 148.28, 155.71 (CO, C-5), 187.94 (C-2)
2c	1765	2.39 (s, 3H, CH_3), 5.41 (s, 2H, CH_2O), 7.37 (m, $5H_{arom}$)	16.10 (CH_3), 70.27 (CH_2O), 128.45, 128.53, 128.67, 133.76 (C_6H_5), 148.63, 155.54 (CO, C-5), 188.00 (C-2)
2d	1770	2.49 (s, 3H, CH_3), 4.92 (dt, 2H, J = 5.8, 1.2, CH_2O), 5.30–5.59 (m, 2H, CH_2=CH), 6.06 (m, 1H, CH=CH_2)	15.97 (CH_3), 68.81 (CH_2O), 119.57 (CH_2=), 129.84 (CH=), 148.07, 155.38 (CO, C-5), 188.21 (C-2)
3b	1730	0.95 [d, 6H, J = 6.6, $(CH_3)_2CH$], 2.02 (m, 1H, $CHCH_2O$), 2.77 (s, 3H, CH_3), 4.13 (d, 2H, J = 6.6, CH_2O)	15.79 (CH_3), 18.86 ($(CH_3)_2$), 28.21 (CH), 75.80 (CH_2O), 157.29, 165.84, 169.84 (CO, C-2, C-5)
3c	1735	2.79 (s, 3H, CH_3), 5.33 (s, 2H, CH_2O), 7.37 (s, $5H_{arom}$)	15.45 (CH_3), 70.86 (CH_2O), 128.61, 128.94, 133.84 (C_6H_5), 157.16, 165.48, 168.42 (CO, C-2, C-5)

Benzyloxycarbonyl (Z) amino acids are derivatives of fundamental importance in peptide synthesis.[15] Thus, L-phenylalanine and L-serine were easily converted into their *N*-Z-derivatives using the typical procedure[9,16] with the new reagent **2c**. The reactions were carried out at room temperature until the yellow color of the reagent disappeared. The Z-amino acids were obtained in high yields (88%) and apparently without formation of dipeptides. As exemplified by the synthesis of Z-Ser-OH, reagent **2c** should be especially useful in the case of unprotected hydroxy amino acids.



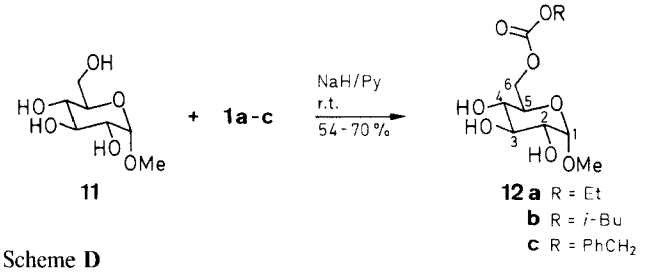
	R	R¹		R	n	R¹
4	$PhCH_2$	$PhCH_2CH(CO_2H)$	**7**	$PhCH_2$	1	CH_3
5	$PhCH_2$	$HOCH_2CH(CO_2H)$	**8**	$PhCH_2$	1	Ph
6	CH_2=$CHCH_2$		**9**	$PhCH_2$	2	CH_3
			10	CH_2=$CHCH_2$	2	CH_3

Scheme **C**

To extend our studies on amino compounds, we have prepared the *N*-allyloxycarbonyl derivative **6** of D-

treating a solution of the hydrochloride of D-glucosamine in a water/acetone solution with the carbamate **2d** in the presence of triethylamine. The expected amino sugar derivative was obtained in 81% yield.

We have also studied the selective alkoxycarbonylation of unsymmetrical diols such as 1,2-propanediol, phenylethanediol, and 1,3-butanediol. Reaction of the diols with the *N*-derivatives **2c–d** of 2-mercapto-5-methyl-1,3,4-thiadiazole and a catalytic amount of 4-dimethylaminopyridine (DMAP), at room temperature, afforded in about one hour a monocarbonate along with the dicarbonate in a trace amount (Scheme **C**). The monocarbonate was isolated from the bisfunctionalized product by column chromatography (Tables 3 and 4). In the case of phenylethanediol, we obtained solely the primary carbonate **8**. The monocarbonates of 1,2-propanediol and 1,3-butanediol were obtained in higher yields, but turned out to be about 90:10 mixtures of the primary carbonates and the secondary ones, as determined by ^{1}H-NMR.



Scheme **D**

In view of the remarkable regioselectivity obtained with diols and of the great importance of selective protection

Table 3. Synthesis of Monocarbonates of Unsymmetrical Diols with the Reagent **2**

Alcohol	Conditions			Mono-carbonate	Yield (%)	mp (°C) or bp (°C)/Torr (solvent[a])	Molecular Formula[b]
	Solvent	Catalyst[a]	Time (min)				
1,2-propanediol	EtOAc	DMAP	45	**7**[c]	77	140–144/4	$C_{11}H_{14}O_4$ (210.2)
1,2-phenylethanediol	THF	DMAP	90	**8**	61	35–37 (Et_2O/Hx)	$C_{16}H_{16}O_4$ (272.3)
1,3-butanediol	CH_2Cl_2	DMAP	90	**9**[c]	80	148–151/3	$C_{12}H_{16}O_4$ (224.2)
1,3-butanediol	THF	DMAP	240	**10**[c]	65	oil	$C_8H_{14}O_4$ (174.2)

[a] DMAP = 4-dimethylaminopyridine, Hx = hexane.
[b] Satisfactory microanalyses obtained: C ±0.31, H ±0.22.
[c] Mixtures of the primary and the secondary carbonates: **7**, 92 : 8; **8**, 89 : 11; **10**, 94 : 6.

Table 4. Spectral Data of Compounds **7**–**10**

Com-pound	IR (NaCl) $\nu_{C=O}$ (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)	^{13}C-NMR ($CDCl_3$) δ
7	1750	1.17 (d, 3H, J = 6.3, CH_3), 2.59 (s, 1H, OH), 4.04 (m, 3H, CH_2O, CH), 5.14 (s, 2H, CH_2Ph), 7.34 (s, 5H_{arom})	
8	1745	2.63 (s, 1H, OH), 4.21 (d, 2H, $CHCH_2O$), 4.91, 4.99 (dd, 1H, CH), 5.14 (s, 2H, CH_2Ph), 7.35 (s, 10H_{arom})	69.56 (CH_2CO), 71.62 (C-1), 72.22 (C-2), 126.01, 127.88, 128.13, 128.29, 134.90, 139.40 (C_6H_5), 154.92 (CO)
9	1745	1.19 (d, 3H, J = 6.3, CH_3), 1.79 (m, 2H, $CHCH_2$), 2.27 (s, 1H, OH), 3.86 (m, 1H, CH), 4.26 (m, 2H, CH_2O_2C), 5.14 (s, 2H, $CH_2C_6H_5$), 7.35 (s, 5H_{arom})	23.25 (CH_3), 37.58 (C-2), 64.12 (C-1), 65.21 (C-3), 69.29 (CH_2OCO), 128.02, 126.26, 128.32, 135.06 (Ph), 155.08 (CO)
10	1745	1.22 (d, 3H, CH_3), 1.82 (m, 2H, $CHCH_2$), 2.13 (s, 1H, OH), 3.93 (m, 1H, CHOH), 3.04–5.60 (m, 2H, CH_2O_2C), 4.59, 4.65 (dt, 2H, J = 5.6, 1.2, CO_2CH_2CH), 5.20–5.46 (m, 2H, CH_2=CH), 5.74–6.16 (m, 1H, CH=CH_2)	

Table 5. Synthesis of 6-*O*-Monocarbonates **12a**–**c** of Methyl α-D-Glucoside

Reagent	Conditions			Product	Yield (%)	mp (°C) (solvent[a])	$[\alpha]_D^{20}$ (EtOAc[b])	Molecular Formula[a]
	Solvent[a]	Catalyst	Time (h)					
1a	Py	NaH	3	**12a**	70	oil	+124	$C_{10}H_{18}O_8$ (266.2)
1b	Py	NaH	2	**12b**	70	oil	+117	$C_{12}H_{22}O_8$ (294.3)
1c	Py	NaH	2.5	**12c**	54	72–77 ($CHCl_3$/Hx)	+101	$C_{15}H_{20}O_8$ (328.3)

[a] Py = pyridine, Hx = hexane. [b] c = 0.01. [c] Satisfactory microanalyses obtained: C ±0.38, H ±0.40.

Table 6. Spectral Data of Compounds **12a**–**c**

Com-pound	IR (NaCl) $\nu_{C=O}$ (cm^{-1})	^{1}H-NMR (DMSO-d_6/TMS) δ, J(Hz)	^{13}C-NMR (DMSO-d_6) δ
12a	1750, 1715	1.25 (t, 3H, J = 8, CH_3CH_2), 3.33 (s, 3H, OCH_3), 2.60–4.30 (m, 8H, CHO, CH_2O, CH_2), 4.57 (d, 1H, J = 3.5, H-1), 4.79, 4.83, 5.55 (3d, 3H, 3OH)	18.70 [$(CH_3)_2$], 27.39 (CH), 54.53 (OCH_3), 67.13 (C-6), 69.57, 60.22, 71.94, 73.30, 73.41 (OCH_2CH, C-2, C-3, C-4, C-5), 99.85 (C-1), 154.84 (CO)
12b	1750, 1715	0.97 (d, 6H, J = 6.6, $(CH_3)_2$), 1.98 (m, 1H, CH $(CH_3)_2$), 3.37 (s, 3H, OCH_3), 2.90–3.80 (m, 6H, CHO, CH_2O), 4.01 (d, 2H, J = 6.7, $CHCH_2O$), 4.68 (d, 1H, J = 3.5, H-1), 4.89, 4.94, 5.28 (3d, 3H, 3OH)	
12c	1745, 1712	3.26 (s, 3H, OCH_3), 2.95–4.41 (m, 6H, CHO, CH_2O), 4.53 (d, 1H, J = 3.5, H-1), 4.77, 4.82 (2d, 2H, 2OH), 5.13 (s and d, 3H, CH_2Ph, OH), 7.4 (s, 5H_{arom})	54.45 (CH_3), 67.34 (C-6), 68.88, 69.45, 70.16, 71.78, 73.14 (CH_2Ph, C-2, C-3, C-4, C-5), 99.67 (C-1), 128.04, 128.27, 128.41, 135.54 (Ph), 154.5 (CO)

to apply the former reaction to methyl α-D-glucoside. The reactions of *N*-alkoxycarbonylthiazolidine-2-thiones **1a–c** wih the glucoside **11** were catalyzed by sodium hydride (NaH) in anhydrous pyridine at room temperature (Table 5). The carbonates were purified by column chromatography and turned out to be the 6-monocarbonates **12a–c** as determined by IR and NMR spectroscopy (Table 6). In the ^{1}H-NMR spectra (DMSO-d_6), the triplet near $\delta = 4.6$ typical of the primary 6-hydroxyl, did not show up. In The ^{13}C-NMR spectrum of **12** (DMSO-d_6), the signal characteristic of the C-6 carbon was deshielded by $\Delta\delta = 6.1$ compared to the corresponding signal of the starting sugar, and the C-5 signal was displaced markedly upfield ($\Delta\delta \approx 3$). This is in accord with the general trend observed by Yoshimoto.[17]

Comparison of these results with the reactions of benzyl carbonochloridate with diols or methyl α-D-glucoside, which lead to mixtures of primary and secondary carbonates, shows the interest of the new reagents **1** and **2**.

In conclusion, we believe that the present work clearly establish that the carbamates **1** and **2** are very effective in selective modification of polyfunctional substrates including carbohydrates. The interest of our methods lies in their simplicity and selectivity.

All reagents were of commercially quality, from freshly opened containers and were purchased from Janssen Chimica. Thin layer chromatography (TLC) was performed on Merck 60 F 254 silica gel unactivated plates. For column chromatography, Merck 60H silica gel was used. Melting points were taken using a Reichert apparatus and are uncorrected. Optical rotations were measured using a Polartronic D polarimeter. Elemental analyses were made by the "Service de Microanalyse de l'E.N.S.C.R.". IR spectra were obtained using a Pye-Unicam SP 200 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were obtained using a Jeol FX 90 spectrometer. X-ray data were measured on an Enraf-Nonius CAD4 diffractometer using Mo-K_α radiation, $\lambda = 0.7107$ Å. The structure was solved by direct methods and refined by full-matrix least squares. The final R values were $R = 0.058$, $R_w = 0.070$ for 1471 reflections having $I > 3\sigma$ (I). All computations were done with programs of the Enraf-Nonius SDP[18] on a PDP11 computer.

3-Alkoxycarbonylthiazolidine-2-thiones 1a–b; General Procedure:
A mixture of thiazolidine-2-thione (2.16 g, 18 mmol) and Et_3N (3 mL, 21 × 6 mmol) in CH_2Cl_2 or THF (50 mL) is stirred at −25 or 0 °C and the appropriate carbonochloridate (21.6 mmol) is added dropwise. Stirring is continued for 60 min at the same temperature, and the organic layer is successively washed with 0.5 N HCl (2 × 10 mL) and water (2 × 40 mL), and is dried ($MgSO_4$). The solvent is evaporated *in vacuo*, and the residue is recrystallized or distilled to afford the carbamates **1a–c** (Table 1).

3-Alkoxycarbonyl-5-methyl-1,3,4-thiadiazole-2(3*H*)-thiones 2b–d; General Procedure:
To a solution of 2-mercapto-5-methyl-1,3,4-thiadiazole[19] (2.37 g, 18 mmol) and pyridine (1.74 mL, 21.6 mmol) in CH_2Cl_2 (0 °C) or THF (−30 °C) (50 mL) is added the appropriate carbonochloridate (21.6 mmol). Stirring is continued for 2 h, and the solution is successively washed with 0.5 N HCl (2 × 10 mL) and water (2 × 40 mL). The organic phase is dried ($MgSO_4$), and the solvent evaporated. The residue is purified by column chromatography, using the eluent CH_2Cl_2/petroleum ether (bp 35–60 °C) (1:2), v/v), to afford the carbamates **2b–d** (Table 1).

2-Alkoxycarbonylthio-5-methyl-1,3,4-thiadiazole 3b–c; General Procedure:
Compounds **3b–c** were prepared as described above, using triethylamine (3 mL, 21.6 mmol) as the base, at −30 °C.

***N*-Benzyloxycarbonyl Amino Acids 4–5; General Procedure:**
To a solution of amino acid (5 mmol) and Et_3N (2.09 mL, 5 mmol) in water (2.5 mL) and dioxane (2.5 mL) is added dropwise **2c** (1.33 g, 5 mmol) in dioxane (10 mL), under stirring. After 60 min at room temperature the solution is poored onto ice-water (30 mL), and the resultant mixture is extracted with EtOAc (5 × 20 mL). The aqueous solution is acidified with 0.5 M H_2SO_4 to pH = 2 and extracted with EtOAc (3 × 30 mL). The combined latter extracts are washed with water, dried ($MgSO_4$), and evaporated. The amino acid derivatives are isolated by known procedures.[9,16]

Z–Ser–OH by recrystallization from EtOAc/petroleum ether (bp 35–60 °C); yield: 1 g (84%); mp 109–111 °C; $[\alpha]_D^{20}$: + 5° (*c* = 1, HOAc).

Z–Phe–OH by recrystallization from chloroform/hexane; yield: 1.31 g (88%); mp 82–84 °C; $[\alpha]_D^{20}$: + 5 (*c* = 1, HOAc).

***N*-Allyloxycarbonyl-α-D-glucosamine 6:**
To a solution of α-D-glucosamine (0.97 g, 4.5 mmol) and Et_3N (0.62 mL, 4.5 mmol) in acetone (32 mL) and water (8 mL) is added dropwise a solution of **2d** (0.97 g, 4.5 mmol) in acetone (8 mL). After 60 min at room temperature the acetone is evaporated, and the resulting aqueous solution is diluted with water (20 mL) and extracted with 1-butanol (6 × 20 mL). The solvent is evaporated, and the product is recrystallized from EtOH; yield: 0.93 g (79%); mp 180–185 °C.

$C_{10}H_{17}O_7N$	calc.	C 45.60	H 6.50
(263.2)	found	45.71	6.58

Monocarbonates of Unsymmetrical Diols 7–10; General Procedure:
To a solution of the alcohol (8.5 mmol) and **2c–d** (5.5 mmol) in THF (15 mL) is added 4-dimethylaminopyridine (26.6 mg, 0.22 mmol, 0.04 equiv) under stirring at room temperature. After 90 min, the mixture is evacuated *in vacuo*, and EtOAc (40 mL) is added to the residue. The organic layer is washed with 5% aq. $NaHCO_3$ (20 mL), dried ($MgSO_4$), and evaporated. The crude product is chromatographed on a silica gel column (105 mm × 43 mm) using the eluent EtOAc/petroleum ether (bp 35–60 °C) (1:5, v/v).

Monocarbonates of Methyl α-D-Glucoside 12a–c; General Procedure:
Sodium hydride (60% dispersion in mineral oil; 0.12 g, 3 mmol) is added to a stirred solution of methyl α-D-glucoside (2.91 g, 15 mmol) and reagent **1a–c** (5 mmol) in anhydrous pyridine (50 mL), at room temperature. Stirring is continued during 3 h. HOAc (0.17 mL, 3 mmol) is then added, and the solvent is evaporated *in vacuo*. The residue is dissolved in water and extracted with 1-butanol (3 × 20 mL). The organic layer is evaporated, and the 6-*O*-carbonates are purified by chromatography on a silica gel column (105 mm × 43 mm) using the eluent $CHCl_3$/MeOH (9:1, v/v).

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