1,2-Benzisoxazol-3-yl Diphenyl Phosphate: A New, Reactive Activating Agent for the Synthesis of Amides, Esters, and Peptides via Condensation

Mitsuru Ueda* and Hideaki Oikawa

Department of Polymer Chemistry, Faculty of Engineering, Yamagata University, Yonezawa, Yamagata 992, Japan

Received July 3, 1984

A new activating agent for condensations, 1,2-benzisoxazol-3-yl diphenyl phosphate (1), was readily prepared in high yield by the reaction of 1,2-benzisoxazol-3-ol (2) with diphenyl phosphorochloridate (3) in the presence of triethylamine in benzene. The reaction of the carboxylic acids with the amines in the presence of 1 was investigated by two procedures, a two-step method and a one-step procedure. Both methods gave the corresponding amides and esters in high yields under mild conditions, but the one-step procedure was found to be superior to the two-step procedure because of its simplicity and speed. Furthermore, the activating agent 1 was shown to be a useful peptide forming reagent.

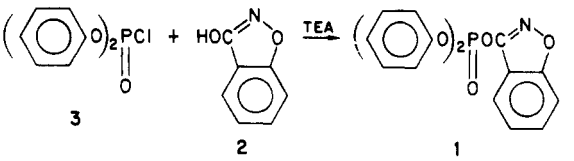
Condensations rank among the most important and fundamental reactions in organic synthesis, and many activating reagents for promoting condensations by a two-step or a one-step procedure have been reported,[1-4] in particular, the full potential of activating agents realized in conversions of carboxylic acids into amides and esters.

As a part of our continuing research program on the preparation of amides, esters, and polyamides under mild conditions, our group has been studying the synthesis of new activating agents. In particular, our previous studies have resulted in a series of good leaving groups for use in the synthesis of active esters and amides.[5] In the previous papers, we showed that 3-substituted 1,2-benzothiazole 1,1-dioxide,[6] active carbonate,[7] and carbonamide[8,9] species are new reactive activating agents for the synthesis of amides, esters, and dipeptides.

As the next target, we were interested in developing a phosphorus-based activating agent, in particular one based on a phosphonate group. Active phosphonates react with the carboxylic acids to give the mixed carboxylic–phosphoric anhydrides which play an important role in protein biosynthesis. Shioiri and Yamada introduced diphenyl phosphoroazidate[10] and diethyl phosphorocyanidate[11] as activating agents into condensation methodology. These reagents were successfully applied to the preparation of amides, esters, and peptides.[12,13] Subsequently, the useful phosphate activating agents, *N*-succinimido diphenyl phosphate,[14] norborn-5-ene-2,3-dicarboximido diphenyl phosphate,[15] and diphenyl 2-oxo-3-oxazolinyl phosphate[16] were successively reported.

We now report that amides, esters, thio esters, and dipeptides can be easily obtained from the carboxylic acids and nucleophiles by a two-step method or a one-step procedure using the new activating agent 1,2-benzisoxazol-3-yl diphenyl phosphate (1).

Scheme I

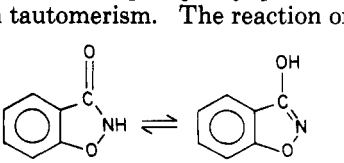


3 2 1

Results and Discussion

Synthesis of 1,2-Benzisoxazol-3-yl Diphenyl Phosphate (1). Recently, we found the *N*- or *O*-acyl products from the acylation of 1,2-benzisoxazol-3-ol (2) were susceptible to aminolysis under mild conditions.[17] The corresponding amides were produced in quantitative yields. This finding led us to attempt the synthesis of 1,2-benzisoxazol-3-yl diphenyl phosphate (1) which was expected to function as new activating agent with a wide range of preparative applications in condensations.

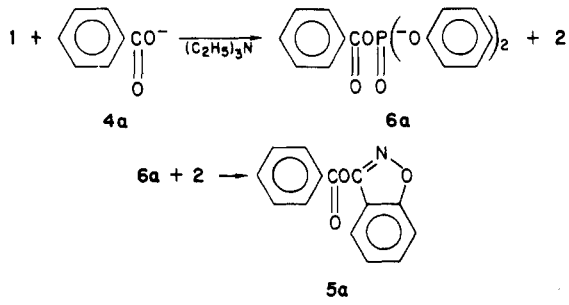
Agent 1 was conveniently prepared from diphenyl phosphorochloridate (3) and 2 in the presence of triethylamine (TEA) in benzene at 0 °C (Scheme I). Recrystallization of the reaction product from chloroform/*n*-hexane gave white needles melting at 69–70 °C. It is possible to employ the crude product, without further purification, in the preparation of amides, esters, and peptides. Reagent 1 is stable upon exposure to atmospheric moisture for long periods; it may also be used for condensations carried out in water (this will be discussed in later paper). Phosphorylation of 2 might be expected to give either the *O*- or *N*-phosphoryl product, because of its well-known tautomerism. The reaction of 2 with 3 in



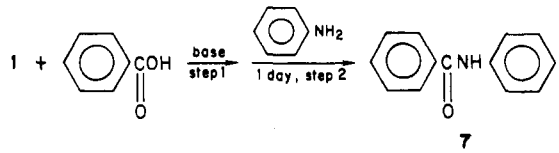
(1) Ogliaruso, M. A.; Wolfe, J. F. "The Chemistry of Acid Derivatives"; Patai, S., Ed.; Wiley: New York, 1979; Part I, p 474.
(2) Bodanszky, M.; Klausner, Y. S.; Ondetti, M. A. "Peptide Synthesis"; Wiley: New York, 1976.
(3) Stammer, C. H. "Amino Acids Peptides and Related Compounds" Hey, D. H., Ed.; John, D. I. Butterworths: London, 1973; p 135.
(4) "The Peptides" Gross, E., Ed.; Meienhofer, J. Academic Press: New York, 1979; Vol. I.
(5) Imai, Y.; Ueda, M. *Yuki Gosei Kagaku Kyokai Shi* (*J. Synth. Org. Chem.*) **1981**, *39*, 312.
(6) Ueda, M.; Kawaharasaki, N.; Imai, Y. *Synthesis* **1982**, 933.
(7) Ueda, M.; Oikawa, H.; Teshirogi, T. *Synthesis* **1983**, 908.
(8) Ueda, M.; Oikawa, H.; Imai, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2485.
(9) Ueda, M.; Kawaharasaki, N.; Imai, Y. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 85.
(10) Shioiri, T.; Ninomiya, K.; Yamada, S. *J. Am. Chem. Soc.* **1972**, *94*, 6203.
(11) Shioiri, T.; Yokoyama, Y.; Kasai, Y.; Yamada, S. *Tetrahedron*, **1976**, *32*, 2211.
(12) Shioiri, T.; Yamada, S. *Yuki Gosei Kagaku Kyokai Shi* **1973**, *31*, 666.
(13) Shioiri, T. *Yuki Gosei Kagaku Kyokai Shi* **1979**, *37*, 856.
(14) Ogura, H.; Nagai, S.; Takeda, K. *Tetrahedron Lett.* **1980**, *21*, 1467.
(15) Kiso, Y.; Miyazaki, T.; Satomi, M.; Hiraiwa, H.; Akita, T. *J. Chem. Soc., Chem. Commun.* **1980**, 1029.
(16) Kunieda, T.; Abe, Y.; Hirobe, M. *Chem. Lett.* **1981**, 1427.
(17) Ueda, M.; Harada, T.; Aoyama, S.; Imai, Y. *J. Polym. Sci. Polym. Chem. Ed.* **1981**, *19*, 1061.

0022-3263/85/1950-0760$01.50/0

Scheme II



Scheme III



dry benzene at 0 °C gave preferentially *O*-phosphoryl product 1. The structure of 1 was assigned on the basis of elemental analysis, IR, and mass spectroscopy. The IR spectrum showed the P=O absorption band at 1320 cm^{-1} and absorption bands characteristic of the P–O–C at 1160, 1180, 1210 cm^{-1}. No trace of the C=O stretching band was detected.

Two-Step Procedure. The two-step procedure involves two separate steps: (1) "activation" of the carboxyl component, i.e., generation of the active intermediate from **1** and the carboxylic acid and (2) condensation of this activated carbonyl intermediate with the amine. In order to clarify the reaction pathway in the two-step procedure, the reaction of 1 with benzoic acid was carried out in *N*-methyl-2-pyrrolidone (NMP) at room temperature for 3 h in the presence of TEA as a tertiary amine base. Agent **1** reacted easily with benzoic acid to give 3-(benzoyloxy)-1,2-benzisoxazole (**5a**) quantitatively. The compound **5a** has been characterized by its high reactivity toward aminolysis.[17] The above observations point to the mechanism outlined in Scheme II. Here we see that activating agent **1** reacts first with the benzoate anion **4a** to form the mixed carboxylic acid–phosphoric anhydride **6a**, a highly activated acylating agent. Intermediate **6a** reacted rapidly with nucleophile **2** to give the active ester **5a**.

To determine the optimum conditions for condensations employing activating agent 1, we first studied the synthesis of benzanilide (**7**) from benzoic acid and aniline using the two-step procedure. The following factors influencing the formation of **5a** were studied: the effect of the tertiary amines's base strength, the amount of 1 present, the activation time, and the nature of the solvent (Scheme III). The activation time is the period between the addition of 1 and the addition of the amine. Reactions were performed at room temperature and the condensation step (step 2) was carried out for a period of 1 day. The effect of the tertiary amine's base strength was studied by using pyridine, imidazole, and triethylamine. Triethylamine proved to be the best amine. Table I lists the effect of amount of 1, activation time, and solvents in the presence of triethylamine. As can be seen in Table I, the best yield was obtained where a 1.1 molar equiv of 1 relative to benzoic acid was employed and where the reaction was carried out for 1 h at room temperature in NMP before aniline was added.

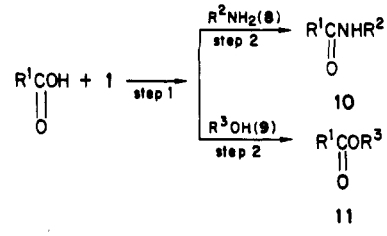
Syntheses of Amides 10 and Esters 11. Syntheses of amides **10** and esters **11** using our new activating agent 1 were carried out by the two-step procedure (Scheme IV).

Table I. Yields of Benzanilide under Various Conditions[a] (Scheme III)

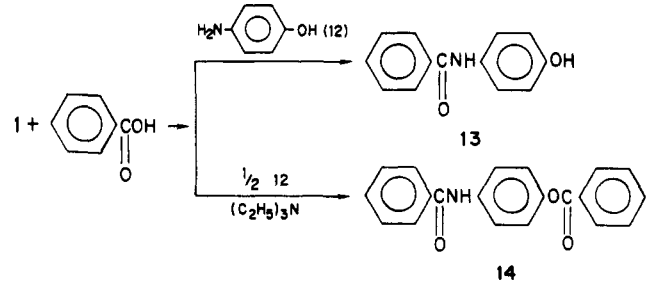
ratio of 1/benzoic acid	solvent	time,[b] h	yield, %
1.0	NMP[c]	10 min	73
1.0	NMP	30 min	88
1.0	NMP	1	91
1.0	dichloromethane	1	84
1.0	acetonitrile	1	84
1.0	tetrahydrofuran	1	72
1.1	NMP	1	95
1.2	NMP	1	95

[a] Reaction was carried out with 1 mmol of the reactants in the presence of TEA (1.0 mmol) in solvent (2 mL) at room temperature. Reaction time in step 2 was 1 day. [b] Reaction time in step 1. [c] *N*-Methyl-2-pyrrolidone.

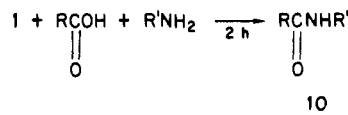
Scheme IV



Scheme V



Scheme VI



The reactions proceeded smoothly to give the corresponding the amides **10** and the esters **11** in good yields. Alcoholysis required an equimolar amount of triethylamine in step 2. Amines reacted more rapidly with active ester **5** than did alcohols. This difference in reactivity permitted the selective N-acylation of *p*-aminophenol (**12**). N,O-Acylation of **12** took place when excess benzoic acid and 1 were used in the presence of triethylamine. The resulting 4′-hydroxybenzanilide (**13**) or 4′-(benzoyloxy)benzanilide (**14**) was obtained in good yield (Scheme V). These results are summarized in Table II.

One-Step Procedure. The synthesis of amides and esters by the two-step procedure was successful, but the rate of condensation of **5** with either amines or alcohols was relatively slow. To remedy this point, we next studied the synthesis of amides by the one-step procedure. This procedure consists of adding 1 to a solution of the carboxylic acid **4** and the amine **8** in the presence of triethylamine. Once the mixed anhydride **6** was formed, it reacted in situ with the amine to give the amide. The advantage of this method over the two-step procedure is that more reactive **6** in place of **5** is used in the aminolysis (Scheme VI). The results of several representative amide syntheses by the one-step procedure are summarized in

Table II. Preparation of Amides 10 and Esters 11 Using Activating Agent 1[a] (Schemes IV and V)

carboxylic acid 4, R =	amine or alcohol	product	yield, %
C_6H_5	aniline	benzanilide	95
C_6H_5	benzylamine	*N*-benzylbenzamide	93
C_6H_5	cyclohexylamine	*N*-cyclohexylbenzamide	98
n-C_5H_{11}	aniline	*N*-phenylhexanamide	91
n-C_5H_{11}	benzylamine	*N*-benzylhexanamide	94
C_6H_5	*p*-nitrophenol	*p*-nitrophenyl benzoate	92
C_6H_5	phenol	phenyl benzoate	89
C_6H_5	*p*-nitrobenzyl alcohol	*p*-nitrobenzyl benzoate[b]	64
C_6H_5	*p*-aminophenol	4′-hydroxybenzanilide	96
C_6H_5	$^1/_2$ *p*-aminophenol	4′-(benzoyloxy)benzanilide	93

[a] Reaction was carried out with 1.0 mmol of the reactants in the presence of TEA (1.0 mmol) in NMP (2 mL) at room temperature. Reaction time: step 1, 1 h; step 2, 1 day. [b] Reaction time in step 2 was 2 days.

Table III. Preparation of Amides 10 Using Activating Agent 1 by One-Step Procedure[a] (Scheme VI)

carboxylic acid 4, R =	amine	product	yield, %
C_6H_5	aniline	benzanilide	99
C_6H_5	benzylamine	*N*-benzylbenzamide	93
C_6H_5	cyclohexylamine	*N*-cyclohexylbenzamide	74
C_6H_5	*p*-aminophenol	4′-hydroxylbenzanilide	96
o-$NO_2C_6H_4$	benzylamine	*N*-benzyl-*o*-nitrobenzamide	94
o-$CH_3C_6H_4$	aniline	*N*-phenyl-*o*-methylbenzamide	90
2,4,5-$(CH_3)_3C_6H_2$	benzylamine	*N*-benzyl-2,4,5-trimethylbenzamide	98
n-C_5H_{11}	aniline	*N*-phenylhexanamide	97
n-C_5H_{11}	benzylamine	*N*-benzylhexanamide	88
$(CH_3)_3C$	aniline	*N*-phenyl-2,2-dimethylpropanamide	68
$C_6H_5CH{=}CH$	aniline	*N*-phenylcinnamamide	93
$C_6H_5CH{=}CH$	benzylamine	*N*-benzylcinnamamide	92
$C_6H_5CH{=}CH$	cyclohexylamine	*N*-cyclohexylcinnamamide	77

[a] Reaction was carried out with 1.0 mmol of the reactants in the presence of TEA (1.0 mmol) in NMP (2 mL) for 2 h at room temperature.

Table IV. Preparation of Esters and Thio Esters Using Activating Agent 1 by One-Step Procedure[a]

carboxylic acid, R =	alcohol or thiol	time, h	product	yield, %
C_6H_5	phenol	3	phenyl benzoate	91
C_6H_5	*p*-nitrophenol	3	*p*-nitrophenyl benzoate	93
C_6H_5	*p*-nitrobenzyl alcohol	3	*p*-nitrobenzyl benzoate	70
C_6H_5	benzenethiol	4	*S*-phenyl benzothioate	94
C_6H_5	phenylmethanethiol	4	*S*-benzyl benzothioate	73

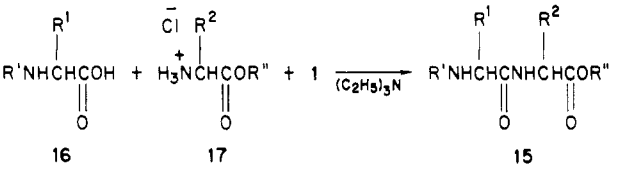
[a] Reaction was carried out with 1.0 mmol of the reactants in the presence of TEA (2.0 mmol) in NMP (2 mL) at room temperature.

Table III. Condensation proceeded more rapidly and gave the corresponding amides in higher yields than did the two-step procedure. Furthermore, selective N-acylation of *p*-aminophenol, (12) was performed in good yield.

In order to further demonstrate the preparative utility of our method, it was applied to the synthesis of both esters 11 and thio esters. These transformations were performed by treating the carboxylic acid and alcohol (or thiol) with 1 in the presence of triethylamine in *N*-methyl-2-pyrrolidone at room temperature. As indicated in Table IV, the reaction proceeded smoothly to high yields under mild conditions.

Peptide synthesis is essentially concerned with the formation of the amide bond. Therefore, the present reaction was applied to the preparation of dipeptides 15 (Scheme VII). The N-protected α-amino acid 16, the α-amino acid ester hydrochloride 17, and 1 were mixed in dichloromethane in the presence of 2 equiv of triethylamine for 2 h at room temperature. The N-protected dipeptide 15 was isolated in the ordinary manner. The optical purity of the dipeptides was estimated by comparison of the specific rotation with the reported value. The N-protected dipeptide esters were obtained in excellent yields with little racemization. Generally, functional groups in the side chains should be protected by the mixed anhydride method to avoid undesired side reactions in the peptide synthesis. However, a major advantage was found when activating agent 1 was used. High yields of the

Scheme VII



desired N-acylated products were obtained without the need for employing protecting groups. These results are summarized in Table V.

In summary, our studies indicate that 1 is a very useful reagent for the synthesis of amides, esters, thio esters, and peptides. This new activating agent 1 is a crystalline solid having excellent hydrolytic stability. Furthermore, 1,2-benzisoxazol-3-ol (2), a reaction byproduct, is easily removed from the reaction products by washing the reaction mixture with 1% aqueous sodium hydrogen carbonate. Compared with the other reagents in the literature, the new activating agent 1 is preferable for the following reasons: (a) simplicity of procedure, (b) excellent yield, (c) excellent hydrolytic stability, and (d) good chemoselectivity.

Experimental Section

Melting points were uncorrected. Infrared spectra were obtained in potassium bromide pellets. Benzene, pyridine, triethylamine, and *N*-methyl-2-pyrrolidone were purified by the

Table V. Preparation of N-Protected Dipeptide Esters 1 Using Activating Agent 1[a] (Scheme VII)

N-protected amino acid	amino acid ester	product	yield, %	mp (°C) found	mp (°C) lit.	lit. $[\alpha]_D$	lit. temp, °C	lit. concn, g/dL	lit. solvent
Z-Ala	Gly-OEt	Z-Ala-Gly-OEt	90	99–100	99–100[19]	−21.9	16	1.91	EtOH
						−22.3		3.65	EtOH
Z-Ser	Gly-OEt	Z-Ser-Gly-OEt	92	100–101	103[20]	−5.2	18	1.93	EtOH
						−5.0	25	1.0	EtOH
Z-Val	Gly-OEt	Z-Val-Gly-OEt	95	168–169	163–164[19]	−27.6	18	1.89	EtOH
						−27.3		0.77	EtOH
Z-Phe	Gly-OEt	Z-Phe-Gly-OEt	94	110–111	109–110[21]	−16.1	18	1.84	EtOH
						−15.9	24	2.0	EtOH
Boc-Phe	Gly-OEt	Boc-Phe-Gly-OEt	90	88–89	89–90[22]	−8.1	16	1.73	dioxane
						−8.1		2.0	dioxane[25]
Z-Phe	Leu-OMe	Z-Phe-Leu-OMe	95	110–111	110–111[23]	−25.0	18	2.32	MeOH
						−24.7	20	3.1	MeOH
Z-Ala	Val-OMe	Z-Ala-Val-OMe	90	83–84	84[23]	−37.5	16	1.75	MeOH
						−38.3	20	1.0	MeOH
Z-Val	Val-OMe	Z-Val-Val-OMe	93	115–116	116–117[24]	−24.6	16	2.07	MeOH
						−24.3	25	0.3	MeOH
Boc-Phe	Val-OMe	Boc-Phe-Val-OMe	90	119–120	115–117[26]	−10.0	18	2.48	DMF[b]
						−10.9		2.01	DMF
Boc-Leu	Leu-OMe	Boc-Leu-Leu-OMe	85	140–141	139–140[26]	−49.6	16	1.93	MeOH
						−49.1		0.36	MeOH
Z-Tyr	Gly-OEt	Z-Tyr-Gly-OEt	92	168–170	168–170[27]	−23.0	25	5.0	DMF
						−23.6	20	5.0	DMF

[a] Reaction was carried out with 2 mmol of the reactants in the presence of TEA (4.0 mmol) in dichloromethane (4 mL). [b] DMF: dimethylformamide.

usual methods. N-Protected α-amino acids and α-amino acid ester hydrochlorides were prepared by the usual procedures. Diphenyl phosphorochloridate was prepared from phosphorus oxychloride and phenol. The preparation of 1,2-benzisoxazol-3-ol was described in the preceding paper.[8] The other reagents were used without further purification.

1,2-Benzisoxazol-3-yl Diphenyl Phosphate (1). A solution of **2** (13.5 g, 0.1 mol) and TEA (14.0 mL, 0.1 mol) in dry benzene (150 mL) was cooled in an ice–water bath. To this solution was added dropwise with stirring a solution of **3** (26.8 g, 0.1 mol) in benzene (50 mL) under nitrogen. The addition was completed in 20 min, and stirring was continued at room temperature for an additional 30 min. Then, the reaction mixture was cooled to 5 to 10 °C. TEA·hydrochloride was removed by filtration, and the solvent was removed in vacuo where the temperature was kept below 40 °C. *n*-Hexane was added to the oily residue which then crystallized immediately. Purification by recrystallization from chloroform/*n*-hexane (1:10) gave white needles: yield 30 g (82%); mp 69–70 °C; IR (KBr) $\nu_{P=O}$ 1320, ν_{P-O-C} 1160, 1180, 1210 cm^{-1}; MS, (*m/e*) 367.2 (M^+). Anal. Calcd for $C_{19}H_{14}NO_5P$: C, 62.13; H, 3.84; N, 3.81. Found: C, 62.2; H, 4.0; N, 4.0.

3-(Benzoyloxy)-1,2-benzisoxazole (5a). To a stirred solution of benzoic acid (0.122 g, 1.0 mmol) and TEA (0.14 mL, 1.0 mmol) in NMP (2 mL) was added **1** (0.404 g, 1.1 mmol), followed by stirring at room temperature for 2 h. The reaction mixture was poured into water (50 mL). A precipitate formed and it was collected by filtration, washed with water, and dried in vacuo: yield 0.242 g (98%). Recrystallization from *n*-hexane produced white needles, mp 65–66 °C (lit.[18] mp 64 °C).

Amide 10: General Procedure (Two-Step Procedure). Activating agent **1** (0.404 g, 1.1 mmol) was added to a stirred solution of the carboxylic acid (1.0 mmol) and TEA (0.14 mL, 1.0 mmol) in NMP (2 mL) at room temperature. After 1 h, the amine (1.0 mmol) was added. Stirring was continued for 1 day. The mixture was poured into 1% aqueous sodium hydrogen carbonate. The precipitate was filtered, washed with water, and dried.

Amide Ester 14: Two-Step Procedure. Activating agent **1** (1.1 mmol) was added with stirring to a solution of benzoic acid (1.0 mmol) and TEA (1.0 mmol) in NMP (2 mL) at room temperature. After 1 h, *p*-aminophenol (**12**) (0.5 mmol) was added to this solution. After 1 day of stirring, TEA (0.5 mmol) was added, and the mixture was stirred for 1 day and worked up as described above.

Amide 10: General Procedure (One-Step Procedure). To a solution of the carboxylic acid (1.0 mmol), the amine (1.0 mmol), and TEA (1.0 mmol) in NMP (2 mL) was added **1** (1.1 mmol) at room temperature. The solution was stirred for 2 h and poured into 1% aqueous sodium hydrogen carbonate. The precipitate was filtered, washed with water, and dried.

Ester 11 and Thio Ester: General Procedure (One-Step Procedure). A mixture of the carboxylic acid (1.0 mmol), the alcohol (1.0 mmol) or thiol (1.0 mmol), TEA (2.0 mmol), and **1** (1.1 mmol) was stirred at room temperature for 3 or 4 h. The reaction mixture was worked up as described above.

Protected Dipeptide Ester 15: General Procedure. To a solution of the N-protected α-amino acid (2.0 mmol), the α-amino acid ester hydrochloride (2.0 mmol), and TEA (4.0 mmol) in dichloromethane (4 mL) was added **1** (2.2 mmol) under nitrogen. The solution was stirred for 2 h at room temperature. After removal of the solvent in vacuo, the residue was dissolved in ethyl acetate, and the organic solution was washed successively with 5% aqueous sodium hydrogen carbonate, 1 N hydrochloride acid, and saturated brine. After drying ($MgSO_4$) and evaporation of ethyl acetate, the dipeptide ester was purified by crystallization. The crude products obtained (amides, esters, thio esters, and dipeptide esters) are virtually pure (IR, ^1H NMR spectra).

Acknowledgment. We thank Professor H. Ogure and Dr. K. Takeda (School of Pharmaceutical Science, Kitasato University) for many helpful suggestions during the course of this work. We also are indebted to Mr. Sadao Kato for performing the elemental analyses.

(18) Boshangen, H.; Geiger, W. *Chem. Ber.* **1969**, *102*, 3775.
(19) Kinoshita, H.; Inomata, K.; Miyanowa, O.; Kotake, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2619.
(20) Castrd, B.; Dormoy, J. R.; Evin, G.; Selve, C. *Tetrahedron Lett.* **1975**, 1219.
(21) Yong, R. W.; Wood, K. H.; Joyce, R. J.; Anderson, G. W. *J. Am. Chem. Soc.* **1956**, *78*, 2126.
(22) Schroeder, E.; Gibian, H. *Liebigs Ann. Chem.* **1964**, *673*, 176.
(23) Yamada, S.; Takeuchi, Y. *Tetrahedron Lett.* **1971**, 3595.
(24) Shields, J. E.; McDowell, S. T.; Pavlos, J.; Gray, G. R. *J. Am. Chem. Soc.* **1968**, *90*, 3549.
(25) Ogura, H.; Takeda, K. *Nippon Kagaku Kaishi* **1981**, *5*, 836.
(26) Inomata, K.; Kinoshita, H.; Fukuda, H.; Miyano, O.; Yamashino, Y.; Kotake, H. *Chem. Lett.* **1979**, 1265.
(27) Watanabe, Y.; Morito, N.; Kamekawa, K.; Mukaiyama, T. *Chem. Lett.* **1981**, 65.