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3,3′-(Phenylphosphinylidene)bis[2(3*H*)-benzoxazolone] and 3,3′-(Phenylphosphinylidene)bis[2(3*H*)-benzothiazolone]. New Activating Agents

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New activating agents, 3,3′-(phenylphosphinylidene)bis[2(3*H*)-benzoxazolone] (**4**) and 3,3′-(phenylphosphinylidene)bis[2(3*H*)-benzothiazolone] (**5**), were readily prepared by the reaction of phenylphosphonic dichloride (**3**) with 2(3*H*)-benzoxazolone (**1**) and 2(3*H*)-benzothiazolone (**2**) respectively in the presence of triethylamine at room temperature. The new activating agents **4** and **5** were found to be useful for the preparation of amides, esters, and dipeptides under mild conditions. Furthermore, the direct polycondensation of isophthalic acid with aromatic diamines using the activating agent **4** in the presence of pyridine proceeded fast at room temperature to produce polyamides with inherent viscosities up to 0.80 dL/g.

As a part of our continuing research program on the synthesis 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.[1] Based on those studies, we showed that 3-substituted 1,2-benzisothiazole 1,1-dioxides,[2] active carbonate,[3] carbonamide,[4] and 1,2-benzisoxazol-3-yl diphenyl phosphate[5] species are new reactive activating agents for the synthesis of amides, esters and polyamides.

In the previous papers,[6,7] we showed that *N*-acyl derivatives of 2(3*H*)-benzoxazolone (**1**) or 2(3*H*)-benzothiazolone (**2**) are reactive acylating agents for the synthesis of amides and polyamides. This finding prompted us to develop further new activating agents. Recently, diphenyl 2,3-dihydro-2-oxo-3-oxazolylphosphonate has been shown to serve as a carbonyl activating agent to permit a direct preparation of versatile intermediate, 3-acyl-2(3*H*)-oxazolone or a one-step formation of amides from carboxylic acids.[8]

We now report that amides, esters, dipeptides and polyamides can be easily obtained from carboxylic acids and nucleophiles by the direct procedure using the new activating agents, 3,3′-(phenylphosphinylidene)bis[2(3*H*)-benzoxazolone] (**4**) and 3,3′-(phenylphosphinylidene)bis[2(3*H*)-benzothiazolone] (**5**).

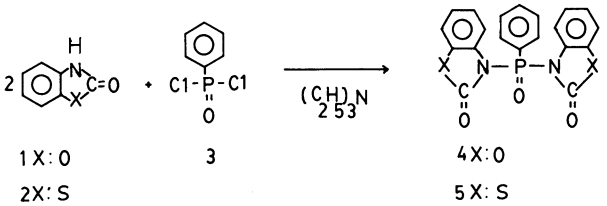
Results and Discussion

Synthesis of Activating Agents 4 and 5. The new activating agent **4** was readily prepared by reacting **1** with phenylphosphonic dichloride (**3**) in the presence of triethylamine (TEA) in benzene at room temperature. Similarly, the reagent **5** was prepared by the reaction of **2** with **3** in acetonitrile (Scheme 1).

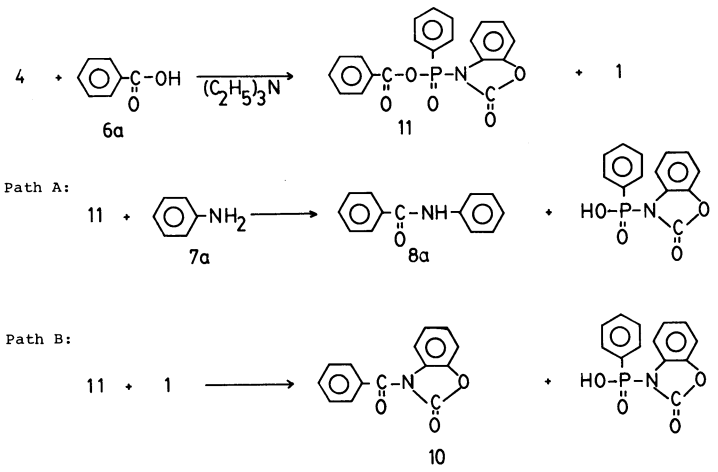
Recrystallization of these compounds from benzene gave white crystals. The structures of **4** and **5** were characterized by elemental analyses, MS, and IR spectroscopies. The IR spectrum of **4** showed carbonyl absorptions at 1780 and 1800 cm^{-1}, and P=O bond absorption at 1300 cm^{-1} On the other hand, the IR spectrum of **5** had carbonyl absorptions at 1690 and 1720 cm^{-1}, and the P=O bond absorption at 1240 cm^{-1}

Synthesis of Amides (8) and Esters (9). In order to clarify the reactivity of the activating agent **4**, we first studied the synthesis of benzanilide (**8a**) from benzoic acid (**6a**) and aniline (**7a**) in the presence of the reagent **4** by the direct procedure. This procedure consists of adding the reagent **4** to a solution of **6a** and **7a** in *N*-methyl-2-pyrrolidone (NMP) that contains a tertiary base to form benzoate ion. TEA as a tertiary base was used. The condensation proceeded rapidly at room temperature and gave **8a** in 90% yield, together with a small amount of 3-benzoyl-2(3*H*)-benzoxazolone (**10**). The most probable reaction pathway is as follows (Scheme 2).

The activating agent **4** first reacts with benzoate ion to form the mixed carboxylic-phosphoric anhydride (**11**), highly activated acylating agent. The activated intermediate **11** is less stable and its enhanced reactivity causes it to react rapidly with available nucleophiles, that is **7a** (Path A) and **1** (Path B) liberated in the first step. These reactions yield **8a** and **10**, respectively. To prevent the nucleophilic attack on the activated intermediate **11**



Scheme 1.



Scheme 2.

Table 1. Yields of benzanilide under various conditions[a)]

Ratio of 4/benzoic acid	Reaction time/h	Yield %
0.5	12	48
0.75	12	63
1.0	12	86
1.1	12	90
1.2	12	91
1.3	12	88
1.5	12	80
1.2	0.5	61
1.2	1.0	86
1.2	2.0	91
1.2	8.0	92
1.2	12	92

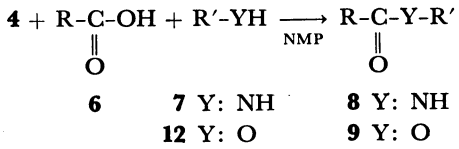
a) Reaction was carried out with 1 mmol of each monomer in the presence of TEA in NMP (2 ml) at room temperature.

by leaving group anion, pyridine (pK_a=4), less basic base than TEA (pK_a=11), was used because the acidity of **1** is about 8. Use of base TEA fully converts **1** to its anion. As would be expected, the formation of **10** was suppressed and the desired product **8a** was obtained in 98% yield.

Table 1 lists the effect of amount of the activating agent **4** and reaction time in the presence of TEA on the synthesis of **8a**. The best yield was obtained where 1.1—1.2 molar equivalent of **4** relative to **6a** was employed, and the reaction was completed in 2 h at room temperature.

On the bases of these results, the condensation of carboxylic acids (**6**) with amines (**7**) or phenols (**12**) was carried out using the activating agent **4** in the presence of TEA or pyridine in NMP (Scheme 3).

The reactions proceeded smoothly to give the corresponding amides (**8**) and esters (**9**) in good yields. Esterification required a 2 molar equivalent



Scheme 3.

of base relative to **6**. Pyridine as a base was more favorable than TEA in the synthesis of amides, but was not effective for the synthesis of esters due to the formation of active amide **10** in fairly large quantities.

Amines reacted more rapidly with the activated intermediate **11** than did phenols. With this different reactivity, next the selective *N*-acylation and *N,O*-diacylation of *p*-aminophenol (**13**) were performed either in the presence of equivalent of **4** and **6a** or 2 molar equivalent of these to **13**, respectively. The corresponding amide, 4′-hydroxybenzanilide (**14**) or amide ester, 4′-(benzoyloxy)benzanilide (**15**) was obtained in good yield (Scheme 4). (Table 2).

Similarly, the conversions of carboxylic acids **6** into amides **8** using the new activating agent **5** were carried out by the direct procedure at room temperature in the presence of TEA. In this case, pyridine did not work well, and the reagent **5** was almost recovered unchanged from the reaction solution. Synthesis of amides using the reagent **4** accompanied the formation of **10** in the presence of TEA. However, when the reagent **5** was used, the formation of 3-benzoyl-2(3*H*)-benzothiazolone was not observed. The reactions of **6** with **7** in the presence of the reagent **5** proceeded smoothly to give the corresponding amides **8** in good yields. Subsequently, selective *N*-benzoylation of **13** and glucosamine hydrochloride (**16**) were performed in the presence of TEA at room temperature to give desired amides **14** and (**17**) having free hydroxyl groups in excellent yields (Scheme 5).

Table 2. Preparation of amides **8** and esters **9** using activating agent **4**[a)]

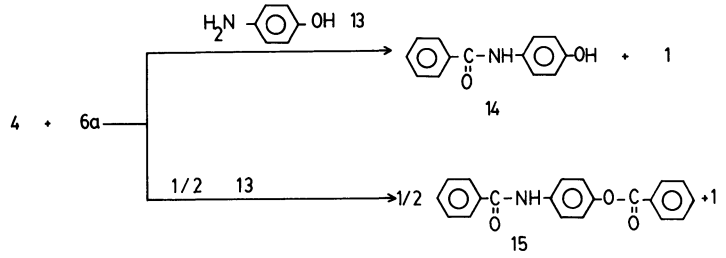
Carboxylic acid R-COOH, **6**	Amine or Phenol	Reaction condition		Product	Yield %
		Base	Time/h		
C_6H_5-	Aniline	TEA[b)]	2	*N*-Phenylbenzamide	90
C_6H_5-	Aniline	Py[c)]	2	*N*-Phenylbenzamide	98
C_6H_5-	Benzylamine	TEA	2	*N*-Benzylbenzamide	85
C_6H_5-	Benzylamine	Py	2	*N*-Benzylbenzamide	97
C_5H_{11}-	Aniline	TEA	2	*N*-Phenylhexanamide	83
C_5H_{11}-	Aniline	Py	2	*N*-Phenylhexanamide	82
C_5H_{11}-	Benzylamine	TEA	2	*N*-Benzylhexanamide	97
C_5H_{11}-	Benzylamine	Py	2	*N*-Benzylhexanamide	73
C_6H_5-CH=CH-	Aniline	Py	2	*N*-Phenylcinnamamide	87
C_6H_5-CH=CH-	Benzylamine	TEA	2	*N*-Benzylcinnamamide	95
C_6H_5-CH=CH-	Benzylamine	Py	2	*N*-Benzylcinnamamide	92
C_6H_5-	Phenol	TEA	3	Phenyl benzoate	82
C_6H_5-	*p*-Nitrophenol	TEA	3	*p*-Nitrophenyl benzoate	81
C_6H_5-	*p*-Nitrobenzyl alcohol	TEA	3	*p*-Nitrobenzyl benzoate	71
C_6H_5-	*p*-Aminophenol	TEA	2	4′-Hydroxybenzanilide	84
C_6H_5-	1/2 *p*-Aminophenol	TEA	4	4′-Benzoyloxybenzanilide	70

a) Reaction was carried out with 1 mmol of each reactants in NMP (2 ml). b) TEA: Triethylamine. c) Py: Pyridine.

Table 3. Preparation of amides **8**, **14**, and **17** using activating agent **5**[a)]

Carboxylic acid **6**	Amine **7**	Product	Yield %
C_6H_5-	C_6H_5-	*N*-Phenylbenzamide	94
C_6H_5-	C_6H_5-CH_2-	*N*-Benzylbenzamide	82
C_6H_5-	Cyclo-C_6H_{11}-	*N*-Cyclohexylbenzamide	91
n-C_5H_{11}-	C_6H_5-	*N*-Phenylhexanamide	92
n-C_5H_{11}-	C_6H_5-CH_2-	*N*-Benzylhexanamide	83
C_6H_5-CH=CH-	C_6H_5-	*N*-Phenylcinnamamide	93
C_6H_5-CH=CH-	C_6H_5-CH_2-	*N*-Benzylcinnamamide	96
C_6H_5-CH=CH-	Cyclo-C_6H_{11}-	*N*-Cyclohexylcinnamamide	97
o-NO_2-C_6H_4-	C_6H_5-CH_2-	*N*-Benzyl-*o*-nitrobenzamide	87
o-CH_3-C_6H_4-	C_6H_5-CH_2-	*N*-Benzyl-*o*-methylbenzamide	85
$(CH_3)_3$-C-	C_6H_5-	*N*-Phenyl-2,2-dimethylpropanamide	62
2,4,6-$(CH_3)_3C_6H_2$-	C_6H_5-CH_2-	*N*-Benzyl-2,4,6-trimethylbenzamide	91
C_6H_5-CO-$(CH_2)_2$-	C_6H_5-	*N*-Phenyl-3-benzoylpropanamide	93
C_6H_5-CO-$(CH_2)_2$-	C_6H_5-	*N*-Benzyl-3-benzoylpropanamide	98
C_6H_5-	*p*-HO-C_6H_4-	4′-Hydroxybenzanilide	80
C_6H_5-[b)]	D-Glucosamine	*N*-Benzoyl-D-glucosamine	90

a) Reaction was carried out with 1 mmol of the reactants in NMP(2 ml). b) Solvent: Sulfolane, Reaction time: 24 h.



Scheme 4.

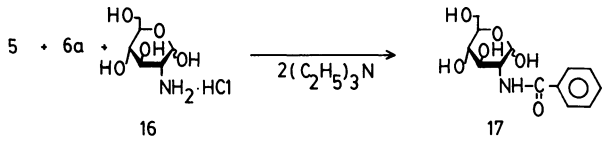
These results are summarized in Table 3.

Synthesis of Dipeptides (18). Peptide synthesis is essentially concerned with the formation of the amide bond. Therefore, the present reaction was applied to the preparation of dipeptides **18** (Scheme 6).

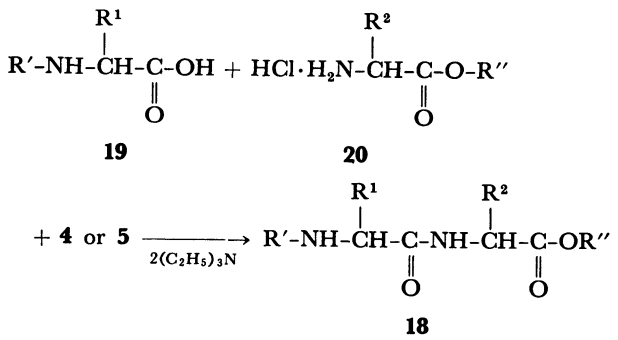
The *N*-protected α-amino acid (**19**), the α-amino acid ester hydrochloride (**20**), and the activating agent **4** or **5** were mixed in dichloromethane in the presence of 2 molar equivalent of TEA for 2 h at room temperature. The *N*-protected dipeptide **18** was isolated in the ordinary manner. 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 the excellent yields with little racemization. These results are summarized in Tables 4 and 5.

Synthesis of Polyamides (21). In order to further demonstrate the preparative utility of our method, it was applied to the synthesis of aromatic polyamides **21**. Recent intensive investigations in the field of the synthesis of polyamides under mild conditions have resulted in the development of new methods including direct polycondensation by phosphorylation reactions and active esters. The direct polycondensation of dicarboxylic acid (**22**) with aromatic diamines (**23**) was carried out using the activating agent **4** in the presence of pyridine in polar aprotic solvents at room temperature (Scheme 7).

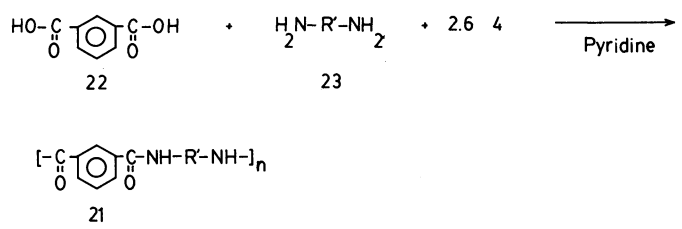
The effect of amount of the reagent **4** on the polycondensation of isophthalic acid (**22**) and 4,4′-oxydianiline (**23a**) is shown in Fig. 1. The inherent viscosity of the polymer reached its highest value with 30 mol% excess of the reagent **4** based on each



Scheme 5.



Scheme 6.



Scheme 7.

Table 4. Preparation of dipeptide esters **18** using activating agent **4**[a)]

N-Protected α-amino acid	α-Amino acid ester	Product	Yield %	Mp[θ_m/°C] found (reported)	$[\alpha]_D$/°C(temp, *c*, solv.) (reported)
Z-Phe-OH	H-Leu-OMe	Z-Phe-Leu-OMe	93	110—111 (110—111)	−24.7(25°, 1.42, MeOH) −24.7(20°, 3.1, MeOH)[12)]
Z-Phe-OH	H-Gly-OEt	Z-Phe-Gly-OEt	97	110—111 (109—110)	−16.1(25°, 1.55, EtOH) −15.9(24°, 2.0, EtOH)[13)]
Z-Val-OH	H-Gly-OEt	Z-Val-Gly-OEt	90	168—169 (170—171)	−31.9(25°, 1.57, Dioxane) −31.6(20°, 1.28, Dioxane)[2)]
Z-Val-OH	H-Val-OEt	Z-Val-Val-OEt	94	115—116 (116—119)	−24.8(25°, 1.52, MeOH) −24.3(25°, 0.73, MeOH)[15)]
Z-Ala-OH	H-Gly-OEt	Z-Ala-Gly-OEt	96	99—100 (99—110)	−21.9(25°, 1.60, EtOH) −22.3(—, 3.65, EtOH)[14)]
Boc-Phe-OH	H-Val-OMe	Boc-Phe-Val-OMe	92	119—120 (115—117)	−10.6(25°, 1.56, DMF) −10.9(—, 2.01, DMF)[16)]
Boc-Phe-OH	H-Gly-OEt	Boc-Phe-Gly-OEt	95	87—88 (89—90)	−8.5(25°, 1.63, Dioxane) −8.1(—, 2.0, Dioxane)[17)]

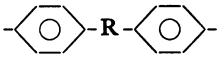
a) Reaction was carried out with 1 mmol of each reactants in dichloromethane (2 ml) at room temperature.

Table 5. Preparation of dipeptides esters **18** using activating agent **5**[a)]

N-Protected α-amino acid	α-Amino acid ester	Product	Yield %	Mp[θ_m/°C] found (reported)	$[\alpha]_D$/°C(temp, *c*, solv.) (reported)
Z-Ala-OH	H-Gly-OEt	Z-Ala-Gly-OEt	76	99—100	−20.9 (25°, 1.91 EtOH)
				(99—100)	−22.3 (— , 3.65 EtOH)[14)]
Z-Ala-OH	H-Val-OMe	Z-Ala-Val-OMe	98	84—85	−40.0 (25°, 1.0 MeOH)
				(84)	−38.3 (20°, 1.0 MeOH)[12)]
Z-Val-OH	H-Gly-OEt	Z-Val-Gly-OEt	99	171—172	−31.3 (25°, 1.28 Dioxane)
				(170—171)	−31.6 (20°, 1.28 Dioxane)[2)]
Z-Phe-OH	H-Gly-OEt	Z-Phe-Gly-OEt	93	109—110	−15.0 (25°, 2.0 EtOH)
				(109—110)	−15.9 (24°, 2.0 EtOH)[13)]
Boc-Phe-OH	H-Gly-OEt	Boc-Phe-Gly-OEt	95	89—90	−8.75 (25°, 2.0 Dioxane)
				(89—90)	−8.1 (— , 2.0 Dioxane)[17)]
Z-Phe-OH	H-Leu-OMe	Z-Phe-Leu-OMe	92	111—113	−24.2 (25°, 3.1 MeOH)
				(110—111)	−24.7 (20°, 3.1 MeOH)[12)]
Boc-Phe-OH	H-Val-OMe	Boc-Phe-Val-OMe	97	123—124	−10.0 (25°, 2.01 DMF)
				(115—117)	−10.9 (— , 2.01 DMF)[16)]
Boc-Leu-OH	H-Leu-OMe	Boc-Leu-Leu-OMe	88	142—143	−48.6 (25°, 0.36 MeOH)
				(139—140)	−49.1 (— , 0.36 MeOH)[14)]
Z-Tyr-OH	H-Gly-OEt	Z-Tyr-Gly-OEt	88	169—171	−24.0 (25°, 5.0 DME)
				(168—169)	−23.6 (20°, 5.0 DMF)[18)]
Z-Val-OH	H-Val-OMe	Z-Val-Val-OMe	97	117—120	−24.0 (25°, 1.75 MeOH)
				(116—119)	−24.3 (25°, 0.73 MeOH)[15)]

a) Reaction was carried out with 1 mmol of the reactants in dichloromethane (2 ml).

Table 6. Synthesis of polyamides **21** by direct polycondensation of isophthalic acid with diamines **23** using activaing agents **4**[a)]

Diamine 	Solvent ml	Polymer ηinh(dl/g)[b)]
-O-	NMP 2	0.55
-O-	NMP 1	0.80
-O-	HMPA 1	0.42
$-CH_2-$	NMP 2	0.51
$-CH_2-$	NMP 1	0.55
$-CH_2-$	HMPA 2	0.34
$-CH_2-$	HMPA 1	0.42
$-CH_2-$	DMAc 1	0.50

a) Polymerization was carried out with 1 mmol of each monomer using the activating agent **4** (2.6 mmol) in the solvent at room temperature. b) Measured at a concentration of 0.5 g/dl in concentrated sulfuric acid at 30 °C.

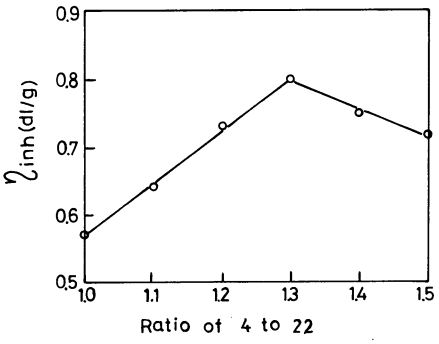


Fig. 1. Effect of amount of activating agent **4** on polycondensation.

monomer. Figure 2 shows the course of the polymerization in terms of inherent viscosity of the resulting polymer. Polycondensation took place rapidly and was almost completed within 2 h at room temperature. Table 6 shows the results of polycondensations of **22** with **23** in the presence of the reagent **4**. High-molecular-weight polyamides could be formed quite readily in polar aprotic solvents in which the polymers remained dissolved.

The polymers obtained were identified as polyamides by comparing their IR spectra with those of the authentic polyamides.

In summary, our studies indicate that the new activating agents **4** and **5** are very useful for the synthesis of amides, esters, dipeptides, and polyamides. These reagents are crystalline solids having excellent hydrolytic stability. Furthermore, 2(3*H*)-benzoxazolone **1** and 2(3*H*)-benzothiazolone **2**, leaving groups, are readily removed from the reaction products by washing the reaction mixture with 5% aqueous sodium carbonate.

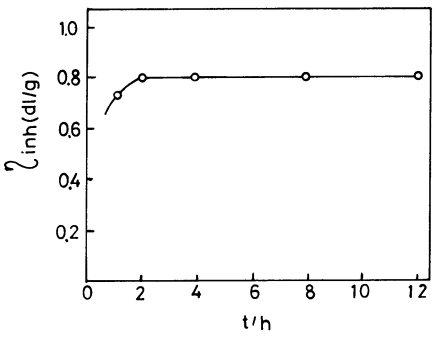


Fig. 2. Polycondensation of isophthalic acid **22** with 4,4′-oxydianiline **23a** using activating agent **4** in NMP at room temperature.

Experimental

Melting points were uncorrected. Infrared spectra were obtained using potassium bromide pellets with a JASCO IRA-1 spectrophotometer. 4,4′-Oxydianiline(**23a**) and 4,4′-methylenedianiline (**23b**) were recrystallized from tetrahydrofuran and benzene, respectively. *N*-Methyl-2-pyrrolidone (NMP), hexamethylphosphoric triamide (HMPA), and *N*,*N*-dimethylacetamide (DMAc) were purified by vacuum distillation and stored over 4 Å Molecular Sieves. *N*-Protected α-amino acids and α-amino acid ester hydrochlorides were prepared by usual procedures. The other reagents were used without further purification.

2(3H)-Benzoxazolone (1). This compound was prepared by the modified method reported by Böshagen.[9] To a ice-cold suspension of salicylohydroxamic acid (21 g, 0.14 mol) in tetrahydrofuran (45 ml), thionyl chloride (11 ml) was added dropwise over 30 min. Then excess thionyl chloride and the solvent were removed *in vacuo* to give a white paste, which was dissolved in toluene (300 ml). This solution was heated slowly to 80 °C and stirred at this temperature for 1 h, then at 120 °C for 2 h. The solvent was removed *in vacuo* to yield a white solid, which was dissolved in methanol. This solution was poured into water (500 ml). The product was collected by filtration, washed with water, and dried to give 13.5 g (73%). Recrystallization from water produced white needles. Mp 138—139 °C(lit,[9] 138 °C).

3,3′-(Phenylphosphinylidene)bis[2(3H)-benzoxazolone] (4). A solution of **1** (6.8 g, 0.05 mol) and TEA (7 ml, 0.05 mol) in dry benzene (40 ml) was cooled in an ice-water bath. To this solution was added dropwise with stirring a solution of **3** (4.9 g, 0.025 mol) in benzene (20 ml) under nitrogen. The addition was completed in 20 min, and stirring was continued at room temperature for an additional 1 h. The precipitate was separated by filtration and dried. To remove TEA·hydrochloride, the product was poured into water (100 ml). The precipitate was collected by filtration and dried *in vacuo*. Purification by recrystallization from benzene gave white needles; yield 6.3 g (64%). Mp 136 °C(by DTA); IR (KBr), 1800, 1780 (C=O), and 1300 cm^{-1} (P=O); MS, *m/z*, 392.3 (M^+). Found: C, 61.2; H, 3.5; N, 6.9%. Calcd for $C_{20}H_{13}N_2O_5P$: C, 61.23; H, 3.34; N, 7.14%.

3,3′-(Phenylphosphinylidene)bis[2(3H)-benzothiazolone] (5). 2(3*H*)-Benzothiazolone **2** was synthesized according to the method of Hunter[10] in 88% yield by the acid hydrolysis of 2-chlorobenzothiazole, which was prepared readily from 2-benzothiazolethiol and sulfuryl chloride;[11] mp 136—137 °C(lit,[10] 138 °C). A solution of **2** (5.53 g, 30 mmol) and TEA (8.4 ml, 60 mmol) in acetonitrile (12 ml) was cooled in an ice-water bath. To this solution was added dropwise with stirring a solution of **3** (2.98 g, 15 mmol) in acetonitrile (12 ml). The addition was completed in 5 min, and stirring was continued at room temperature for an additional 30 min. The solution was poured into water (100 ml). A precipitate formed and it was collected by filtration, washed with water, and dried *in vacuo*; yield 5.40 g (85%). Recrystallization from benzene produced white needles, mp 193 °C. IR(KBr), 1690, 1720 cm^{-1} (C=O), and 1240 cm^{-1} (P=O); MS, *m/z*, 424.4 (M^+). Found: C, 56.4; H, 3.2; N, 6.8%. Calcd for $C_{20}H_{13}N_2O_3PS_2$: C, 56.60; H, 3.08; N, 6.60%.

Amides (8). General Procedure: The activating agent **4** or **5** (1.1 mmol) was added to a solution of carboxylic acid **6** (1.0 mmol), amine **7** (1.1 mmol) and base (1.0 mmol) in NMP (2 ml). The solution was stirred at room temperature for 2 h, and then was poured into 5% aqueous sodium carbonate (50 ml). The precipitate was collected and dried. When TEA as a base was used, a small amount of **10** was formed (when **4** was used). But, it was removed by stirring in 5% aqueous sodium carbonate for 10 h.

Ester (9). General Procedure: A mixture of **4** (1.1 mmol), benzoic acid **6a** (1.0 mmol), phenol **12** (1.1 mmol) and TEA (2.2 mmol) was stirred at room temperature for 3 h. The reaction mixture was worked up as described above.

Protected Dipeptide Ester (18). General Procedure: To a solution of the *N*-protected α-amino acid **19** (1 mmol), the α-amino acid ester hydrochloride **20** (1 mmol) and TEA (2.0 mmol) in dichloromethane (2 ml), the reagent **4** or **5** (1.1 mmol) was added 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 1 mol dm^{-3} hydrochloric acid, 5% aqueous sodium carbonate and saturated brine, and then dried with anhydrous sodium sulfate. After evaporation of ethyl acetate, the dipeptide was purified by recrystallization.

The crude products obtained (amides, esters, and dipeptide esters) were virtually pure (IR, ^{1}H-NMR spectra).

Polyamide (21). General Procedure: To a solution of isophthalic acid **22** (1.0 mmol), diamine **23** (1.0 mmol) and pyridine (2.2 mmol) in solvent was added the activating agent **4** (2.6 mmol). The mixture was stirred at room temperature for 2 h. The resulting viscous solution was diluted with solvent, and poured into methanol (200 ml). The polymer that precipitated was filtered, and was refluxed in methanol for 2 h. The fibrous polymer was collected and dried *in vacuo* at 100 °C. The yield was essentially quantitative. The inherent viscosity was measured at a concentration of 0.5 g/dl in concentrated sulfuric acid at 30 °C.

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