(FABMS) were obtained in a 2-nitrophenylether matrix. Combustion analyses were performed by Midwest Microlabs, Indianapolis, IN.

Naphthalic *di* imide 1. The mixture of 1,8-naphthalic anhydride **(4)** (1.59 g, 8.03 mmol), 1,4-phenylenediamine **(3)** (0.43 g, 4.02 mmol), and Zn $(OAC)_2 \cdot 2H_2O$ (0.09 g, 0.41 mmol) was dissolved in 10 mL of quinoline. The solution was stirred in 120 °C for 2 hrs, and then cooled to room temperature to get insoluble solid. The insoluble solid was washed with ethyl acetate (3 x 100 mL), H_2O (50 mL), and 1 M HCl (30 mL) to eliminate quinoline and then 1.32 g of the pure naphthallic *di* imide **1** as gray solid (70%) was obtained. IR (KBr) cm^{-1} 1709, 1680; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (s, 4H), 7.82 (dd, *J* =7.23, 8.30, 4H), 8.30 (dd, *J* =l.04, 8.30, 4H), 8.70 (dd, *J* =1.04, 7.23, 4H); MS (FAB^+) m/z 469 (M^++1); Anal. Calcd for $C_{30}H_{16}N_2O_4$: C, 76.92; H, 3.44. Foung: C, 76.86; H, 3.46.

Naphthalic *tri* imide 2. The mixture of 1,8-naphthalic anhydride **(4)** (0.3 g, 1.52 mmol), 1,3,5-phenylenetriamine **(5)** (0.06 g, 0.49 mmol), and Zn(oAc)2 · $2H_2O$ (0.01 g, 0.05 mmol) was dissolved in 7 mL of quinoline. The solution was stirred in 120 °C for 2 hrs, and then cooled to room temperature to get insoluble solid. The insoluble solid was washed with ethyl acetate (3 x 50 mL), H_2O (30 mL), and 1 M HC1 (30 mL) to eliminate quinoline and then 0.19 g of the naphthalic *tri* imide **2** as a light yellow solid (60%) was obtained. IR (KBr) cm^{-1} 1709, 1672; ^1H NMR (300 MHz, $CDCl_3$) δ 6.75 (s, 3H), 7.78 (dd, *J* =7.39, 7.62, 6H), 8.24 (d, *J* =7.62, 6H), 8.66 (d, *J* =7.39, 6H); MS (FAB^+) m/z 664 (M^++1).

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S-Acyl Derivatives of Benzothiazole-2-thiol: A Convenient Method for the Synthesis of Amides and Carbamates

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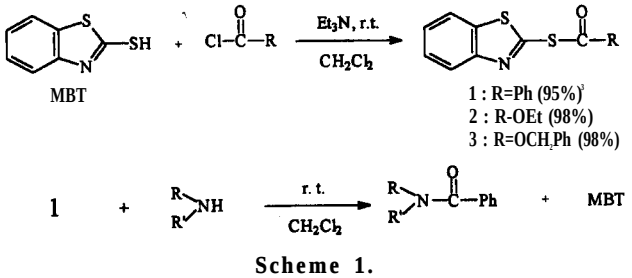
In previous papers,[1,2] many useful acylating reagents have been extensively exploited for the synthesis of amides. In connection with our research directed toward synthetic utility of active S-esters and S-carbonates containing benzothiazole-2-thiol moiety, the so-called 2-mercaptobenzothiazole (MBT) in the rubber industry, we wish to report the use of a new class of improved acylating reagent, S-acyl derivatives of MBT for the synthesis of amides and carbamates.

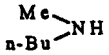
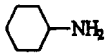
S-Acyl derivatives of MBT were easily prepared by mixing equimolar amounts of benzoylchloride or alkyl chloroformate, MBT, and triethylamine in dichloromethane at room temperature in quantitative yields.

The reaction of S-benzoyl-2-benzothiazole thioester **(1)** as a model compound with several amines was carried out. The thioester **(1)** easily reacted with primary amines and secondary amines to give quantitative yields of the corresponding amides within 5 min. in dichloromethane at room temperature (Scheme 1). On the other hand, benzoylation of aniline and tertiary butylamine was carried out in benzene under reflux. The thiolate moiety of MBT having the excellent leaving property was easily removed by washing the reaction mixture with dil. alkaline aqueous solution, and the solvent was evaporated off in vacuo to afford only desirable amides in quantitative yields without further purification (Table 1). In particular, aminoalcohols, for ex-



Scheme 1.

Table 1. Benzoylation of Several Amines with S-benzoyl-2-benzothiazole thioester **(1)**

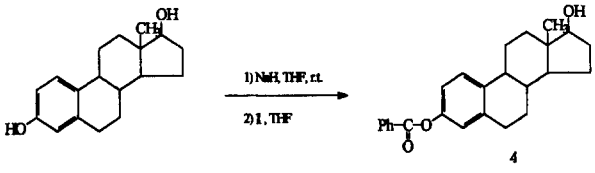
Amine	Time (min)	Amides (%yield)[b]	mp (°C)
$PhNH_2$	30[a]	99	163[4,5]
$PhCH_2NH_2$	5	99	106[5,8]
n- $BuNH_2$	5	98	41-42[6,7]
sec- $BuNH_2$	5	96	84-85[8]
tert- $BuNH_2$	50[a]	98	135-136[8,9]
Et_2NH	5	98	38-39[10]
	5	94	oil[8]
	5	99	149-150[2,8]
	5	98	48-48.5[8,11]
	5	97	42-42.5[12]
$HOCH_2CH_2NH_2$	5	97	62-63
$HOCH_2CH(NH_2)-CH_3$	5	92	99-100

[a]Heating under reflux in benzene. [b]Yields by isolation.

Table 2. Reaction of S-(ethyloxycarbonyl)benzothiazole-2-thioester **(2)** with Amines

Amine	Time	Yield (%)[b]	mp (°C)
$PhNH_2$	4h.[a]	98	44[13]
$PhCH_2NH_2$	5min	97	37[14,15]
$HOCH_2CH_2NH_2$	5min	78	oil
$HOCH_2CH(NH_2)-CH_3$	5min	85	30-31

[a]Heating under reflux in benzene. [b]Yields by recrystallization from petroleum ether.



Scheme 2.

ample, 2-aminoethanol and 2-amino-1-butanol containing amino group together with hydroxyl group in one molecule were selectively converted into the desired amides in high yields without protection of hydroxyl group.

The similar reactions of S-(ethyloxycarbonyl)benzothiazole-2-thioester *(2)* and S-(benzyloxycarbonyl)benzothiazole-2-thioester *(3)* with several amines afforded also excellent yields of carbamates within a short time except aniline. The results are listed in Table 2 and Table 3, respectively.

Especially, β-estradiol treated with sodium hydride in THF reacted with **1** and was selectively converted into β-estradiol-3-benzoate **(4)** [18] in 98% yield (Scheme 2).

It is advantageous that the compounds **(1, 2,** and **3)** are crystalline solids having excellent hydrolytic stability and, therefore, are handled more easily than acyl chlorides. The present method provides an experimentally simple and convenient procedure for the preparation of amides and carbamates from these acylation reagents with amines under mild conditions.

Table 3. Reaction of S-(benzyloxycarbonyl)benzothiazole-2-thioester **(3)** with Amines

Amine	Time	Yield (%)[b]	mp (°C)
$PhNH_2$	4h.[a]	98	74[16]
$PhCH_2NH_2$	5min	98	58-59[15,17]
$HOCH_2CH_2NH_2$	5min	92	58-59
$HOCH_2CH(NH_2)-CH_3$	5min	90	61-62

[a]Heating under reflux in benzene. [b]Yields by recrystallization from petroleum ether.

These commercially available compounds are expected to have application for the synthesis of polypeptides,[19] macrocyclic lactams,[20] macrolides,[21] and the cross-linking reagent of enzyme.[22]

Experimental

The Typical Procedure for Preparation of S-benzoyl-2-benzothiazole thioester (1). A mixture of 2-benzothiazolethiol (8.35 g, 50 mmol) and triethylamine (6.06 g, 60 mmol) in dichloromethane (40 mL) was stirred at room temperature and benzoyl chloride (8.43 g, 60 mmol) was added dropwise. After being stirred at room temperature for 1 h, the salt formed was filtered and the filtrate was washed with dil. HCl solution and water, and then the solvent was evaporated under reduced pressure. Recrystallization of the residue from acetone gave 12.88 g (95%) of **1** as a pale yellow solid, mp 130 °C (lit[3] 129-131 °C); IR (KBr) 3059, 1669, 1581, 1450, 756, 684 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.1-8.0 (m, 3H), 7.9 (d, *J* =7.0 Hz, 1H), 7.7-7.6 (d, *J* =7.4 Hz, 1H), 7.6-7.4 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 186.97, 157.84, 151.69, 136.09, 135.51, 134.69, 129.14, 127,73, 126.38, 125.59, 123.03, 121.24

S-(Ethyloxycarbonyl)benzothiazole-2-thioester (2). white solid, mp 66-67 °C (petroleum ether); IR (KBr) 3055, 2980, 1734, 1454, 1242, 758, 666 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.1 (d, *J* =8.4 Hz, 1H), 7.9(d, *J* =8.0 Hz, 1H), 7.6-7.4 (m, 2H), 4.4 (q, *J* =7.1 Hz, 2H), 1.4 (t, *J* = 7.1 Hz, 3H).

S-(Benzyloxycarbonyl)benzothiazole-2-thioester (3). white solid mp 89-90 °C (petroleum ether); IR (KBr) 3061, 2961, 1724, 1454, 1255, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.1 (d, *J* =7.1 Hz, 1H), 7.9 (d, *J* =7.2 Hz, 1H), 7.5-7.3 (m, 7H), 5.5 (s, 2H).

The Typical Procedure for Aminolysis of Benzylamine. To a solution of **1** (1.36 g, 5.0 mmol) in dichloromethane (10 mL), a solution of benzyl amine (0.64 g, 6.0 mmol) in dichloromethane (5 mL) was added dropwise at room temperature for 5 min. The reaction mixture was washed with dil. sodium hydroxide solution, water, dried, and evaporated *in vacuo* to give a white solid 1.04 g (99%) which was recrystallized from petroleum ether.

P-Estradiol-3-benzoate (4). To a solution of β-estradiol (110 mg, 0.40 mmol) in dry THF, sodium hydride (15 mg, 0.60 mmol) was added. After being stirred at room

temperature for 30 rein, a solution of **1** (0.13 g, 0.50 mmol) in dry THF was added dropwise for 10 min, and was stirred at room temperature for 20 min. The reaction mixture was poured into ice water, extracted with dichloromethane, washed with brine, dil. sodium hydroxide solution, water, dried, and evaporated *in vacuo* to give a white solid 147 mg (98%) which was recrystallized from carbon tetrachloride, mp 194-196 °C (lit.[18] 191-196 °C), IR (KBr) 3525, 2920, 2860, 1720, 1600, 1490, 1445, 1255, 1215, 1160, 705 c m^{-1}.

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Polymerization of Methyl Methacrylate by Chlorocarbon/ Group VIII Metallocene Combination Initiator

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Photochemical or photoinitiated polymerizations occur when radicals are produced by light absorption. Photoinitiation of polymerization offers significant practical advantages: (1) photoinitiation can be spatially directed and turned on or off simply by turning the light source on or off, (2) the photoinitiation rates can be controlled by a combination of the radical source, light intensity and temperature, and (3) photoinitiation can avoid chemical contamination by initiator residues in many cases. Therefore, photopolymerization technology is conveniently applicable and is heavily employed on a commercial basis today in the areas of surface coatings, photoresists, adhesives, and holography.[1] Photochemical activation of organometallic compounds, leading to catalytically and synthetically useful transformations, has attracted a great deal of attention.[2] Especially, photochemical properties of millions of cyclopentadienyl complexes, a historically important class of organometallics, have been intensively investigated.[3] Many