Chem. Pharm. Bull. 37(9) 2334—2337 (1989) Vol. 37, No. 9

Novel Reactions of *S,S'*-Bis(1-phenyl-1*H*-tetrazol-5-yl) Dithiocarbonate[1)]

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S,S'-Bis(1-phenyl-1H-tetrazol-5-yl) dithiocarbonate (1) was synthesized in good yield from 1-phenyl-5-mercapto-5H-tetrazole (2) and trichloromethyl chloroformate (TCF). The structure of 1 was confirmed by using X-ray crystal analysis. The reagent (1) could be applied to the formation of amides, Friedel–Crafts type reactions, isothiocyanate syntheses, and carbonyl group insertion reactions.

Keywords *S,S'*-(bis(1-phenyl-1*H*-tetrazol-5-yl) dithiocarbonate; X-ray crystal analysis; amide; isothiocyanate; Friedel–Crafts reaction; carbonyl group insertion reaction

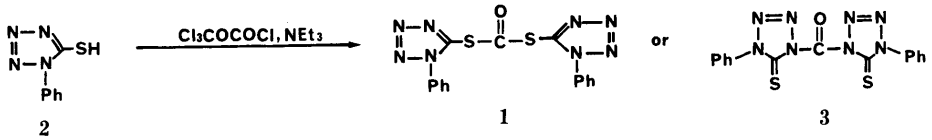
The coupling reaction of a carboxylic acid with a nucleophile is one of the fundamental unit reactions in syntheses of natural substances. The use of coupling reagents for the convenient preparation of amides, peptides, carboxylic esters, lactams, and lactones has been the subject of many publications.[2)]

Recently, we have reported several coupling reagents, such as carbonates and oxalate having active ester groups.[3)] For example, *S,S'*-bis(1-phenyl-1*H*-tetrazol-5-yl) dithiocarbonate (**1**)[3d)] is a versatile coupling reagent which can be used for the preparation of esters and macrolactones. Furthermore, the reagent (**1**) could be applied to the direct synthesis of allylic sulfide[1)] from allylic alcohol, and to the synthesis of *S*-glycoside[4)] which could be converted to *O*-glycoside. As an extension of our work in this field, we now report the application of the reagent (**1**) to amide formation, isothiocyanate synthesis from dithiocarbamic acid, carbonyl group insertion reactions of *o*- and *m*-diaminobenzene, *etc.*, and Friedel–Crafts type reactions.

The reagent (**1**) is easily prepared in 77% yield by the reaction of 1-phenyl-5-mercapto-1*H*-tetrazole (**2**) with trichloromethyl chloroformate (TCF) and triethylamine in ethyl acetate at 0 °C. Compound **1** was easily obtained as a crystalline residue by removing triethylamine hydrochloride from the reaction mixture by filtration followed by evaporation of the filtrate. Recrystallization from ethyl acetate–ether gave the crystalline reagent (**1**) which was stable enough to be stored in desiccator at room temperature for a period of at least three months. The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **1** in $CDCl_3$ showed the presence of signals at 176.56 and 143.85 ppm. From these signals, we could not determine which structure, the thiocarbonate (**1**) or the ureido form (**3**), is correct. In order to elucidate the structure of **1**, X-ray crystal analysis was conducted (see Fig. 1 and Experimental). From the crystal data, the structure of this reaction product was determined to be the dithiocarbonate form (**1**).

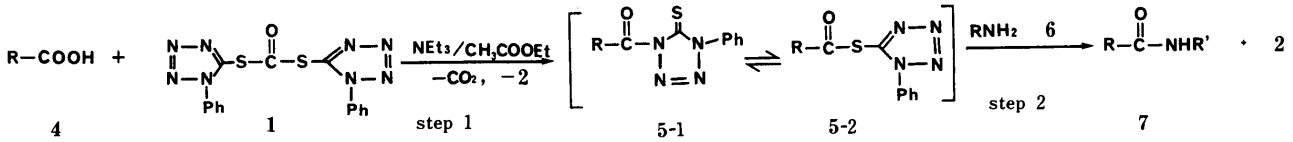
The conversions of carboxylic acids (**4**) into amides (**7a**—**c'**) or dipeptides (**7d**, **e**) using **1** were carried out by a one-pot procedure at room temperature in the presence of triethylamine, using equimolar amounts of carboxylic acids, amino compounds and the reagent (**1**). This procedure consists essentially of two reactions; formation of the activated intermediate (**5**) from the carboxylic acid in step 1, and subsequent aminolysis of the active intermediate (**5**) in step 2 as shown in Chart 2.

Aminolysis of **5** by amino acid hydrochloride required an equimolar amount of triethylamine. In step 1, the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of the active acyl intermediate (**5**) having an acetyl group showed



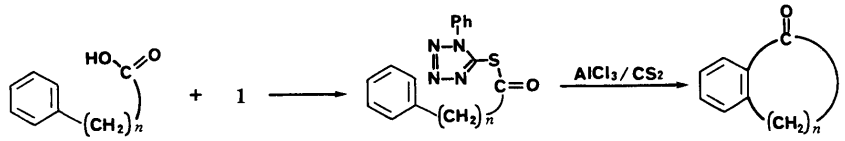
2 1 3

Chart 1



4 1 5-1 5-2 7

Chart 2



4 5 8

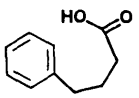
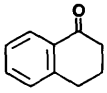
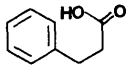
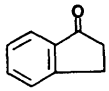
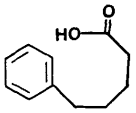
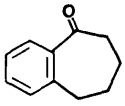
Chart 3

TABLE I. Preparation of Amides and Peptides Using **1**

RCOOH **4**		RNH_2 **6**	Product **7**	Yield (%)
Ph	(a)	$PhCH_2$	$PhCONHCH_2Ph$	94
$PhCH_2$	(b)	$PhCH_2$	$PhCH_2CONHCH_2Ph$	99
PhCH=CH	(c)	$PhCH_2$	$PhCH=CHCONHCH_2Ph$	90
PhCH=CH	(c′)	Ph	PhCH=CHCONHPh	84
Z-Ala	(d)	Gly-OEt	Z-Ala-Gly-OEt	80 $[\alpha]_D^{23}$ −21.0° (*c*=1, EtOH) (Ref. 12. −22.2°)
Z-Val	(e)	Gly-OEt	Z-Val-Gly-OEt	60 $[\alpha]_D^{22}$ −26.1° (*c*=0.84, EtOH) (Ref. 12. −27.0°)

Z=carbobenzyloxy.

TABLE II. Friedel-Crafts Type Reactions Using **1**

Carboxylic acid **4**	Product **8**	Yield (%)
 (f)		84
 (g)		70
 (h)		51

the signals of two acetyl groups of 5-1 and 5-2 at 2.79 and 2.85 ppm in a 5:7 ratio. One rapidly rearranges to the other. These compounds (5-1 and 5-2) react with amino compounds to give amides.

The reaction of the reagent (**1**) with carboxylic acids (**4**) quickly gave rise to a clear solution of the activated intermediate, which in turn, without isolation, reacted directly with the amino compounds. The amides (**7a—c′**) were isolated by concentrating the solution and removal of **2** and **4** by washing with sodium bicarbonate solution; the results are summarized in Table I. The dipeptides (**7d, e**) prepared by using **1** were optically pure, judging from the specific rotation data (Table I).

Active intermediates (**5**) having an ω-phenyl group were subjected to Friedel-Crafts type reaction. The active intermediates (**5**), which could be prepared from **1** and **4f**, **4g** or **4h**, were treated with $AlCl_3$ in carbon disulfide under mild reflux (Chart 3).

The results are summarized in Table II. In this reaction, the intermediate (**5**) may be activated by $AlCl_3$. These Friedel-Crafts products were not obtained in the presence of $SnCl_4$, instead of $AlCl_3$, as the Lewis acid.

The reagent (**1**) could also be applied to the syntheses of isothiocyanate compounds (**10**). Isothiocyanates (**10**) were obtained by the reaction of the reagent (**1**) and dithiocarbamic acids which were prepared *in situ* from primary amines (**6**) and carbon disulfide in the presence of triethylamine at room temperature. In this reaction, dithiocarbamic acids attacked the carbonyl group of the reagent (**1**), and isothiocyanates (**10**) were obtained with

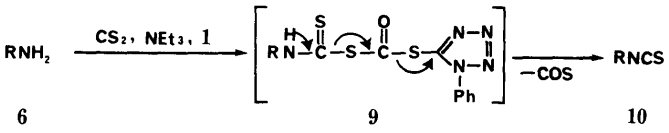
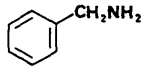
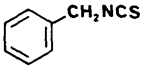
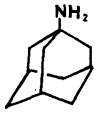
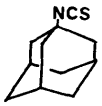
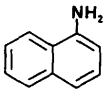
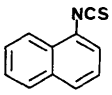
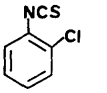


Chart 4

TABLE III. Preparation of Isothiocyanates Using **1**

Amine **6**	Product **10**	Yield (%)
 (a)		84
 (b)		95
 (c)		75
 (d)		58

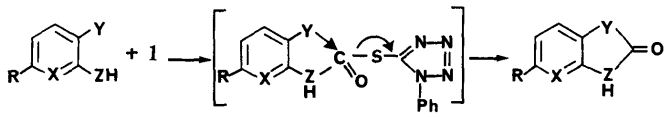
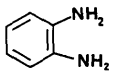
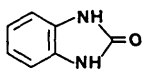
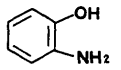
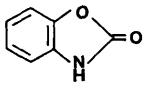
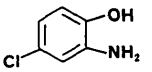
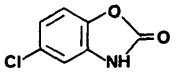
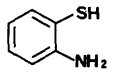
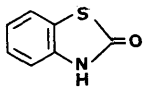
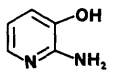
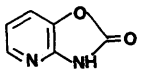


Chart 5

TABLE IV. Carbonyl Group Insertion Reactions Using **1**

Amine **11**	Product **13**	Yield (%)
 (a)		87
 (b)		89
 (c)		92
 (d)		60
 (e)		68

liberation of COS. The results are summarized in Table III.

Considerable synthetic research on various carbonyl insertion reagents, for example, phosgene, carbonyl diimidazole,[6] disuccinimidyl carbonate,[7] and organic selenide as a catalyst with CO gas,[8] has been reported. Our reagent (**1**) reacts with *o*-phenylendiamine (**11a**), *o*-aminophenols (**11b, c, e**) and aminothiophenol (**11d**) to yield cyclic urea (**13a**),

cyclic carbamates (**13b**, **c**, **e**) and cyclic thiocarbamate (**13d**), respectively, *via* an intermediate (**12**), under stirring for about 12 h at room temperature. Regarding the mechanism for the formation of **13**, it is assumed that the first nucleophile (amine) attacks the carbonyl carbon of the reagent (**1**), active carbamate(**12**) is formed, and then the second nucleophile (amino, hydroxyl, or mercapto group) attacks **12** to yield the cyclic compound (**13**). (Chart 5).

This study indicates that **1** is a very useful reagent for the formation of amides, and dipeptides, Friedel–Crafts type reactions, syntheses of isothiocyanate and carbonyl insertion reactions.

Experimental

Melting points were measured with Yamato melting point apparatus and the results are uncorrected. Thin-layer chromatography (TLC) was performed on Silica gel GE254 (Merck) plates, and spots were detected by ultraviolet (UV) irradiation. Mass spectra (MS) and infrared (IR) spectra were measured with JEOL JMS-DX300 and JASCO IR-A2 instruments, respectively. The ^{1}H-NMR spectra were measured with a Varian T-60 spectrometer. Tetramethylsilane (TMS) in $CDCl_3$ was used as an internal reference.

***S*,*S*′-Bis(1-phenyl-1*H*-tetrazol-5-yl) Dithiocarbonate (1)** A mixture of 1-phenyl-5-mercapto-1*H*-tetrazole (**2**) (5.3 g, 30 mmol) and triethylamine (3.1 g, 30 mmol) in ethyl acetate (200 ml) was stirred at 0 °C and a solution of trichloromethyl chloroformate (0.9 ml, 7.5 mmol) in ethyl acetate (50 ml) was added dropwise. Stirring was continued for 6 h and the precipitate was then filtered off. The filtrate was evaporated and the residue was crystallized from ethyl acetate–ether. Yield 77%, mp 126 °C (dec.). MS *m/z*: 382 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1720 (CO). *Anal.* Calcd for $C_{15}H_{10}N_8OS_2$: C, 47.11; H, 2.63; N, 29.30. Found: C, 46.94; H, 2.66; N, 29.14. ^{1}H-NMR 60 MHz ($CDCl_3$) δ: 7.32—8.14 (m, 10H, 2 × Ph).

Crystal Data for 1 A crystal with the dimensions of 0.2 × 0.2 × 0.15 mm^3 was used for the structure determination. The cell dimensions and diffraction intensities were measured on a Rigaku automatic four-circle diffractometer, using graphite-monochromated Cu K_α radiation.

Crystal Data: $C_{15}H_{10}N_8OS_2$, monoclinic, space group $P2_1/c$, a=10.383 (1), b=17.330 (2), c=9.965 (1) Å, Z=4, D_c=1.456 g·cm^{-3}. In total, 1925 independent reflections in the range of $2\theta < 140°$ were collected by the use of the ω–2θ scan mode with a scanning rate of 8° (2θ) min^{-1}. A total of 1831 independent reflections with $|F_O| > 3\delta(|F_O|)$ was obtained and corrected for Lorentz and polarization factors but not for absorption. The structure was solved by a direct method using MULTAN.[9] The E-map of the phase set with the highest figure of merit showed the skeleton of the molecule. The structure, thus obtained, was refined by the block diagonal least-squares method with anisotropic temperature factors. All the hydrogen atoms had been located in the difference Fourier map except those attached to nitrogen. Several cycles of least squares refinement were carried out including these hydrogen atoms. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[10] The final R value was 9.6%.

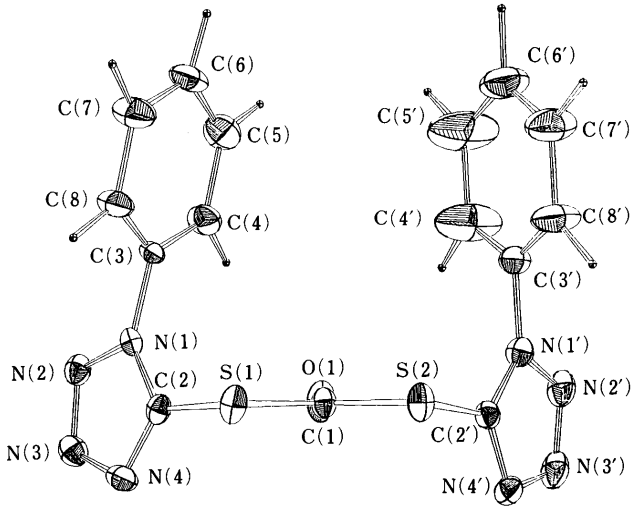


Fig. 1. Perspective Drawing of the Molecule with the Atomic Numbering Scheme

The final atomic parameters are listed in Table V. Figure 1 shows a perspective drawing of **1**. As a result, the reaction product was determined to be the dithiocarbonate (**1**). Bond lengths are given in Tables VI and VII. No abnormal bond length was found in the structure.

General Procedure for the Preparation of Amides (7) *N*-Benzylphenylacetamide (**7b**): The reagent **1** (199 mg, 0.52 mmol) was added to an ice-cooled, stirred solution of phenylacetic acid (**4b**) (68 mg, 0.5 mmol) and triethylamine (61 mg, 0.6 mmol) in ethyl acetate (15 ml). After 30 min, benzylamine (**6**) (58.9 mg, 0.55 mmol) was added. Stirring was continued for 24 h at room temperature. The mixture was evaporated and the residue was extracted with ethyl acetate (3 × 30 ml). The organic layer was washed successively with 4% $NaHCO_3$ solution (80 ml), 1 N HCl (80 ml), and brine (80 ml), and dried with Na_2SO_4. The solvent was removed under reduced pressure, and residue was subjected to preparative TLC on silica gel to afford the amide (**7b**). Yield 99%, mp 112—115 °C. MS *m/z*: 225 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3300 (NH), 1640 (CO). *Anal.* Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.97; H, 6.72; N, 6.20. ^{1}H-NMR ($CDCl_3$) δ: 3.60

Table V. The Positional Parameters (× 10^{-4}) and Equivalent Isotropic Thermal Parameters with Their Estimated Standard Deviation in Parentheses

Atom	x	y	z	B_{eq}
S1	7017 (2)	2458 (1)	3446 (2)	3.1
S2	9903 (2)	2563 (1)	4212 (2)	3.1
O1	8486 (5)	2700 (3)	1641 (5)	3.7
C1	8467 (6)	2591 (4)	2825 (6)	2.6
N1	5395 (5)	3129 (3)	1187 (5)	2.3
N2	4558 (6)	2926 (4)	−21 (6)	3.1
N3	4557 (6)	2166 (4)	−32 (6)	3.3
N4	5375 (6)	1875 (3)	1116 (6)	3.2
C2	5885 (6)	2480 (4)	1862 (6)	2.5
C3	5642 (7)	3929 (4)	1549 (7)	2.5
C4	6448 (9)	4348 (5)	903 (9)	4.1
C5	6646 (10)	5130 (5)	1260 (11)	5.0
C6	6051 (9)	5462 (4)	2211 (9)	4.3
C7	5237 (11)	5025 (5)	2845 (9)	4.9
C8	5032 (9)	4240 (4)	2511 (9)	3.8
N1′	11573 (6)	3219 (3)	2762 (6)	2.8
N2′	12375 (6)	2990 (4)	1931 (7)	3.7
N3′	12336 (6)	2232 (4)	1923 (7)	4.1
N4′	11513 (6)	1955 (3)	2698 (7)	3.2
C2′	11059 (6)	2583 (4)	3199 (6)	2.4
C3′	11386 (8)	4023 (4)	3024 (8)	3.2
C4′	10713 (17)	4449 (7)	1961 (12)	10.5
C5′	10528 (19)	5248 (7)	2250 (14)	11.4
C6′	11026 (12)	5551 (5)	3507 (12)	6.7
C7′	11684 (13)	5091 (6)	4500 (11)	7.0
C8′	11862 (11)	4300 (5)	4266 (9)	5.7

Table VI. Bond Lengths (1/Å)

S1–C1	1.770 (7)	C7–C8	1.405 (11)
S1–C2	1.736 (5)	N1′–N2′	1.363 (9)
S2–C1	1.784 (5)	N1′–C2′	1.342 (9)
S2–C2′	1.738 (7)	N1′–C3′	1.439 (9)
O1–C1	1.199 (8)	N2′–N3′	1.314 (10)
N1–N2	1.359 (7)	N3′–N4′	1.365 (10)
N1–C2	1.349 (8)	N4′–C2′	1.328 (9)
N1–C3	1.439 (8)	C3′–C4′	1.346 (13)
N2–N3	1.316 (8)	C3′–C7′	2.339 (12)
N3–N4	1.355 (8)	C3′–C8′	1.312 (11)
N4–C2	1.322 (8)	C4′–C5′	1.437 (17)
C3–C4	1.376 (12)	C5′–C6′	1.347 (17)
C3–C8	1.375 (12)	C5′–C7′	2.302 (17)
C4–C5	1.404 (11)	C6′–C7′	1.330 (14)
C5–C6	1.372 (14)	C7′–C8′	1.411 (13)
C6–C7	1.391 (14)	C8′–C7′	1.411 (13)

TABLE VII. Bond Angles (ϕ/°)

C1–S1–C2	97.5 (3)	C6–C7–C8	119.7 (9)
C1–S2–C2′	96.6 (3)	C3–C8–C7	118.4 (8)
S1–C1–S2	110.6 (3)	N2′–N1′–C2′	107.6 (5)
S1–C1–O1	125.0 (4)	N2′–N1′–C3′	121.3 (6)
S2–C1–O1	124.4 (5)	C2′–N1′–C3′	131.0 (6)
N2–N1–C2	108.4 (5)	N1′–N2′–N3′	105.8 (6)
N2–N1–C3	120.8 (5)	N2′–N3′–N4′	111.8 (6)
C2–N1–C3	130.8 (5)	S2–N4′–N3′	136.5 (4)
N1–N2–N3	105.4 (5)	N3′–N4′–C2′	104.4 (6)
N2–N3–N4	111.4 (5)	S2–C2′–N1′	125.8 (5)
N3–N4–C2	105.8 (5)	S2–C2′–N2′	162.1 (4)
S1–C2–N1	124.6 (5)	S2–C2′–N3′	162.0 (4)
S1–C2–N2	160.6 (4)	S2–C2′–N4′	123.7 (5)
S1–C2–N3	164.0 (4)	N1′–C2′–N4′	110.4 (6)
S1–C2–N4	126.4 (5)	N1′–C3′–C4′	117.0 (7)
N1–C2–N4	109.0 (5)	N1′–C3′–C7′	151.2 (5)
N1–C3–C4	118.9 (6)	N1′–C3′–C8′	119.2 (6)
N1–C3–C8	117.9 (6)	C4′–C3′–C8′	123.8 (8)
C4–C3–C8	123.2 (6)	C3′–C4′–C5′	116.1 (10)
C3–C4–C5	117.4 (8)	C4′–C5′–C6′	121.4 (11)
C4–C5–C6	121.2 (9)	C5′–C6′–C7′	118.6 (9)
C5–C6–C7	120.2 (7)	C6′–C7′–C8′	121.6 (9)
		C3′–C8′–C7′	118.4 (8)

(2H, s, CH_2CO), 4.42 (2H, d, NCH_2), 5.70 (1H, br, NH), 7.30 (10H, m, Ph × 2).

N-Benzylbenzamide (**7a**): Yield 94%, mp 101—107 °C. **7a** was identified by comparing its NMR and IR spectra with reported data.[11]

N-Benzylcinnamamide (**7c**): Yield 90%, mp 108—109 °C. MS *m/z*: 237 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3225 (NH), 1650 (CO), 1600 (Ph). *Anal.* Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.73; H, 6.33; N; 5.89. ^{1}H-NMR ($CDCl_3$) δ: 4.61 (2H, d, J=6.0 Hz, CH_2N), 6.20 (1H, m, NH), 6.57 (1H, d, J=16.0 Hz, CHCO), 7.52 (10H, m, Ph × 2), 7.62 (1H, d, J=16.0 Hz, PhCH).

N-Phenylcinnamide (**7c′**): Yield 84%, mp 146—152 °C. MS *m/z*: 223 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3250 (NH), 1660 (CO), 1610, 1595 (Ph). *Anal.* Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.39; H, 5.85; N, 6.39. ^{1}H-NMR ($CDCl_3$) δ: 6.51 (1H, d, J=15.0 Hz, CHCO), 6.79—7.76 (11H, m, Ph × 2 and NH), 7.71 (1H, d, J=15.0 Hz, PhCH).

Z-Ala-Gly-OEt (**7d**): Yield 80%, mp 98—99 °C (99—101 °C).[12] $[\alpha]_D^{23}$ −21.0° (c=0.84, EtOH).

Z-Val-Gly-OEt (**7e**): Yield 60%, mp 163—164 °C (162—164 °C).[12] $[\alpha]_D^{22}$ −26.1° (c=1.0, EtOH).

Compounds **7d** and **7e** were identified by comparing their NMR and IR spectra with reported data.[3a]

General Procedure for Friedel–Crafts Type Reactions (8) α-Tetralone (8f): A solution of 4-phenyl-*n*-butyric acid (82 mg, 0.5 mmol) in ethyl acetate (15 ml) was added to triethylamine (60 mg, 0.6 mmol) and the reagent (**1**) (200 mg, 0.52 mmol). The mixture was stirred for 30 min at 0 °C, was washed with water (80 ml), 1 N HCl (80 ml), water (80 ml), 4% $NaHCO_3$ solution (80 ml), and brine (80 ml), and dried with Na_2SO_4.

The solvent was removed under reduced pressure. The residue was dissolved in carbon disulfide (50 ml) and this solution was dropped into a refluxing solution of $AlCl_3$ (133 mg, 1 mmol) in carbon disulfide (30 ml). This solution was gently refluxed for 3 h. After evaporation of carbon disulfide in vacuo, the residue was extracted with ethyl acetate. The extract was washed with water (80 ml), 1 N HCl (80 ml), water (80 ml), 4% $NaHCO_3$ solution (80 ml), and brine (80 ml), and dried with Na_2SO_4.

The solvent was removed under reduced pressure, and residue was subjected to preparative TLC on silica gel to afford α-tetralone (**8f**). Yield 84%, oil. MS *m/z*: 146 (M^+).

2-Indanone (**8g**): Yield 70%, mp 40—41 °C (40—42 °C).[11a] MS *m/z*: 132 (M^+).

1-Benzosuberone (**8h**): Yield 51%, oil. MS *m/z*: 160 (M^+).

Compounds **8f**, **8g**, and **8h** were identified by comparing their NMR and IR spectra with reported data.[11]

General Procedure for the Synthesis of Isothiocyanates Benzyl Isothiocyanate (**10a**): A solution of benzylamine (54 mg, 0.5 mmol) and triethylamine (50 mg, 0.5 mmol) in dry acetonitrile (15 ml) and carbon disulfide (2 ml) was added to a solution of the reagent (**1**) (191 mg, 7.5 mmol) in dry acetonitrile (1 ml) and the whole was stirred for 20 min. After evaporation of acetonitrile, the residue was dissolved in ethyl acetate, and the solution washed with water (80 ml), 1 N HCl (80 ml), water (80 ml), 4% $NaHCO_3$ solution (80 ml), and brine (80 ml), and dried with Na_2SO_4. the solvent was removed under reduced pressure, and residue was subjected to preparative TLC on silica gel to afford benzylisothiocyanate (**10a**). Yield 84%, oil. MS *m/z*: 149 (M^+). IR ν_{max}^{neat} cm^{-1}: 2100 (N=C=S).

1-Adamantyl Isothiocyanate (**10b**): Yield 95%, mp 166—169 °C (166—168 °C).[11] MS *m/z*: 193 (M^+).

1-Naphtyl Isothiocyanate (**10c**): Yield 75%, mp 56—57 °C (55.5—57 °C),[11] MS *m/z*: 185 (M^+).

2-Chlorophenyl Isothiocyanate (**10d**): Yield 58%, oil. MS *m/z*: 169 (M^+).

Compounds **10a—d** were identified by comparing their NMR and IR spectra with reported data.[11]

General Procedure for Insertion Reaction of Carbonyl Groups (13) 2-Benzimidazolone (**13a**): A solution of *o*-phenylenediamine (54 mg, 0.5 mmol) and reagent (**1**) (199 mg, 0.52 mmol) in acetonitrile (15 ml) was stirred for 12 h. After evaporation of acetonitrile, the residue was dissolved with ethyl acetate and the solution was washed with water (80 ml), 1 N HCl (80 ml), water (80 ml), 4% $NaHCO_3$ solution (80 ml), and brine (80 ml), and dried with Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to preparative TLC on silica gel to afford benzimidazole (**13a**). Yield 87%, mp 294—295 °C (300 °C).[7] MS *m/z*: 134 (M^+).

2-Benzoxazolone (**13b**): Yield 89%, mp 137—138 °C (143—145 °C).[7] MS *m/z*: 135 (M^+).

5-Chloro-2-benzoxazolone (**13c**): Yield 92%, mp 187—188 °C (190—191 °C).[7] MS *m/z*: 169 (M^+).

2-Benzthiazolone (**13d**): Yield 60%, mp 134—135 °C (140—141 °C).[7] MS *m/z*: 151 (M^+).

Oxazolo[4,5-*b*]pyridine-2-one (**13e**): Yield 68%, mp 208—209 °C (208—210 °C).[7] MS *m/z*: 136 (M^+).

Compounds **13a—e** were identified by comparing their NMR and IR spectra with reported data.[7]

References and Notes

1) This paper constitutes part XVII of a series entitled "Studies on Activating Methods of Functional Groups." Part XVIII: K. Takeda, K. Tsuboyama, K. Torii, H. Murata, and H. Ogura, *Tetrahedron Lett.*, **29**, 4105 (1988).
2) For general reviews, see: a) M. A. Ogliaruso and J. F. Wolfe, "The Chemistry of Acid Derivatives, Part I, S. patai, ed., John Wiley and Sons, New York, 1979; *b*) M. Bodanszky, Y. S. Hausner, and M. A. Ondetti, "Peptide Synthesis"; John Wiley and Sons, New York, 1976; *c*) M. bodanszky, "Peptide, Vol. I E. Gross and J. Meienhofer, eds. Academic Press, New York, 1979, p. 105.
3) *a*) H. Ogura, T. Kobayashi, K. Shimizu, K. Kawabe, and K. Takeda, *Tetrahedron Lett.*, **1979**, 4745; *b*) K. Takeda, I. Sawada, A. Suzuki, and H. Ogura, *ibid.*, **24**, 4451 (1983); *c*) K. Takeda, K. Tsuboyama, K. Yamaguchi, and H. Ogura, *J. Org. Chem.*, **50**, 273 (1985); *d*) K. Takeda, K. Tsuboyama, H. Takayanagi, and H. Ogura, *Synthesis*, **1987**, 560.
4) K. Takeda, K. Tsuboyama, K. Torii, K. Furuhata, N. Sato, and H. Ogura, "Direct Synthesis of Sialic Acid *S*-Glycosyl Donors Using *S,S′*-Bis(1-Phenyl-1*H*-tetrazol-5-yl) Dithiocarbonate, and *O*-Glycosylations by Use of the *S*-Glycosyl Donors," in preparation.
5) U. Schmidt and M. Dietshe, *Angew. Chem., Int. Ed. Engl.*, **20**, 771 (1981).
6) H. A. Stabb, *Angew. Chem., Int. Ed. Engl.*, **1**, 351 (1962).
7) K. Takeda and H. Ogura, *Synth. Commun.*, **12**, 213 (1982).
8) K. Kondo, S. Yokoyama, N. Miyoshi, S. Murai, and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, **18**, 692 (1979).
9) D. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, MULTAN78, "A System of Computer Programs for the Automatic Solution of Crystal Structure form X-Ray Data," Univ. of York, Englant (1973).
10) International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birminghan, 1974.
11) *a*) Catalog Handbook of Fine Chemicals," Aldrich Chemical Co., Inc., Milwaukee, 1988—1989; *b*) The Aldrich Library of NMR Spectra," 2nd ed., C. J. Pouchert, Aldrich Chemical Co., Inc., Milwaukee, 1983; *c*) The Aldrich Library of Infrared Spectra," 3rd ed., C. J. Pouchert, Aldrich Chemical Co., Inc., Milwaukee, 1981.
12) M. Miyoshi, *Bull. Chem. Soc. Jpn.*, **46**, 1489 (1973).