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Convenient One-pot Syntheses of Sulfinates, Sulfinamides, and Thiosulfinates by Sulfinylation with *p*-Toluenesulfinic Acid and Activating Reagents[1)]

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One-pot syntheses of sulfinates, sulfinamides, and thiosulfinates by *O*-, *N*-, and *S*-sulfinylations of alcohols, amines, and thiols with *p*-toluenesulfinic acid in the presence of various activating reagents, phenyl phosphorodichloridate (**1**), diphenyl phosphorochloridate (**2**), triphenylphosphine *N*-chlorosuccinimide (NCS) (**3**), and 3-(phthalimidoxy)-1,2-benzoisothiazole 1,1-dioxide (**4**), were investigated. All of these reagents were reasonably effective for *O*- and *S*-sulfinylation, but ineffective for *N*-sulfinylation. Among them, the reagents **1** and **2** were slightly more efficient than the others.

Keywords——sulfinate; sulfinamide; thiosulfinate; phenyl phosphorodichloridate; diphenyl phosphorochloridate; triphenylphosphine–*N*-chlorosuccinimide; 3-(phthalimidoxy)-1,2-benzoisothiazole 1,1-dioxide; activating reagent; sulfinylation; one-pot synthesis

Several sulfinic acid derivatives are known to be useful as starting materials and versatile synthetic intermediates,[2,3)] and some have attracted interest on account of their biological activities particularly in the case of thiosulfinates.[3,4)]

Recently we developed new and convenient methods for preparing sulfinates and sulfinamides, in which direct sulfinylation of alcohols and amines with sulfinic acids in the presence of activating reagents was involved.[5)] These methods, however, are of limited applicability and provide comparatively low yields.

In the present work, we attempted *O*-, *N*-, and *S*-sulfinylations with *p*-toluenesulfinic acid (**5**) in the presence of various activating reagents, which permit one-pot conversion to the corresponding sulfinates, sulfinamides, and thiosulfinates. The following known phosphorus compounds and a novel phthalimide derivative were employed as the activating reagents: phenyl phosphorodichloridate (**1**), diphenyl phosphorochloridate (**2**), triphenylphosphine–N-chlorosuccinimide (NCS) (**3**), and 3-(phthalimidoxy)-1,2,-benzoisothiazole 1,1-dioxide (**4**).

Phenyl Phosphorodichloridate (1)

Recently Liu[6)] reported that phenyl phosphorodichloridate (**1**) was effective as an activating agent for conversion of carboxylic acids to carboxylates under virtually neutral and mild conditions. We tried to extend this method for the preparations of sulfinates, sulfinamides, and thiosulfinates.

When *p*-toluenesulfinic acid (**5**) was treated with an excess of various alcohols and amines in dichloromethane in the presence of an equivalent amount of **1** and an excess of pyridine at room temperature, the corresponding sulfinates and sulfinamides were obtained in 49—85% and 0—75% yields, respectively. The reaction with thiols was carried out at 0—5°C due to the relatively lower stability of the products. Purification was achieved by washing the reaction mixture in turn with 0.1 N hydrochloric acid, 1% aqueous sodium bicarbonate, and water, by drying over anhydrous sodium sulfate, and finally by silica gel column chromatography to give thiosulfinates in 35—82% yields.

The reaction presumably proceeds through initial formation of pyridinium phosphate (**6**), followed by nucleophilic substitution of the sulfinyloxy group at the pyridinium moiety.

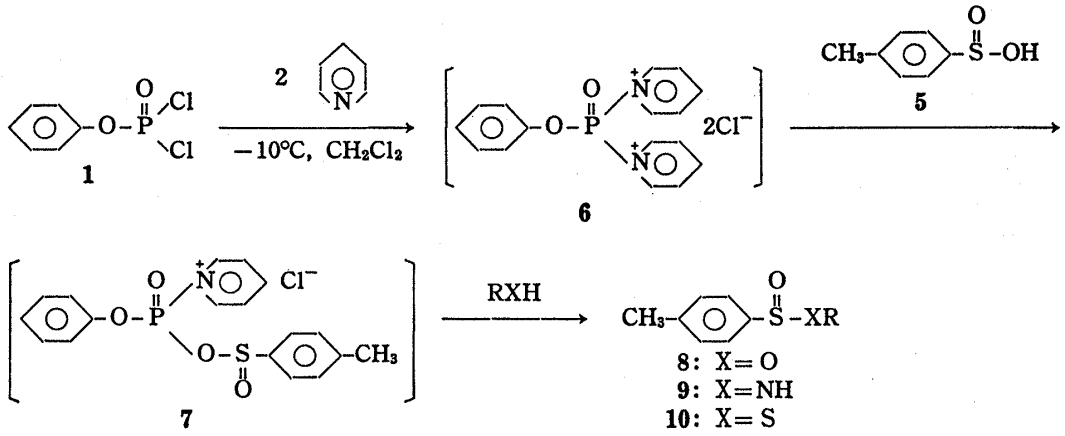


Chart 1

The resulting intermediate (**7**) is very susceptible to nucleophilic attack at the sulfinyl sulfur to give sulfinates (**8**), sulfinamides (**9**), and thiosulfinates (**10**).

A similar mechanism was proposed in the reactions of phosphorodichloridate with amines and carbon dioxide.[7]

Diphenyl Phosphorochloridate (2)

Diphenyl phosphorochloridate (**2**) may be effective as an activating agent owing to its structural similarity to **1**. As expected, when **5** was treated with an equivalent amount of **2** and alcohols, amines or thiols in dichloromethane containing an excess of pyridine at room temperature, the corresponding **8**, **9**, or **10** was obtained in 87—98%, 0—36%, and 40—98% yields, respectively.

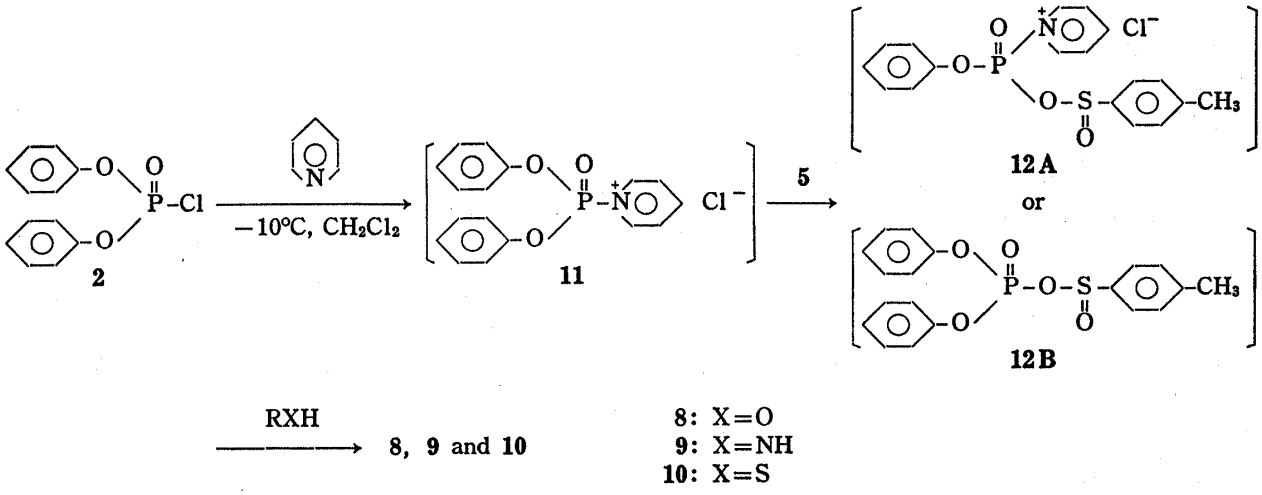


Chart 2

Two mechanistic pathways can be considered for the reaction of the initial intermediate **11** with **5**. One is through the intermediate **12A** which is formed with elimination of the phenoxy group, and the other is that through the mixed anhydride, intermediate **12B**, which is produced by substitution with a pyridinium group. The intermediate **12A** is the same as **7** in the case of **1**. If the reaction proceeds through the intermediate **12A**, the ultraviolet (UV) spectrum at this stage might be similar to that of **7**. However, the two spectra are evidently different, and no absorption near 270 nm due to phenol produced by elimination was observed. These results suggest that **12B** is probably the real intermediate.

Triphenylphosphine-*N*-Chlorosuccinimide (3)

Recently we found that the reaction of sulfinic acids with alcohols and amines in the presence of dimethylsulfide–NCS gave the corresponding sulfinates and sulfinamides along with sulfonates and sulfoxamides.[8] The triphenylphosphine-NCS (**3**) system is similar and is expected to exhibit similar behavior in the condensation between sulfinic acids and alcohols, amines, or thiols. The reaction was successfully carried out by treating **5** with excess of alcohols, amines, or thiols in dichloromethane below −10°C in the presence of an equivalent amount of **3**, and gave the corresponding **8**, **9**, and **10** in 52—82%. 5—32% and 47—88% yields, respectively.

The reaction pathway is presumed to be as follows: NCS initially reacts with triphenylphosphine to form the triphenylphosphonium salt (**13**), followed by nucleophilic substitution with sulfinyloxy anion to form the triphenylsulfinyloxyphosphonium salt intermediate (**14**). Finally alcohols, amines, or thiols attack the sulfinyl sulfur activated by the adjacent positive phosphonium group to afford **8**, **9**, or **10**.

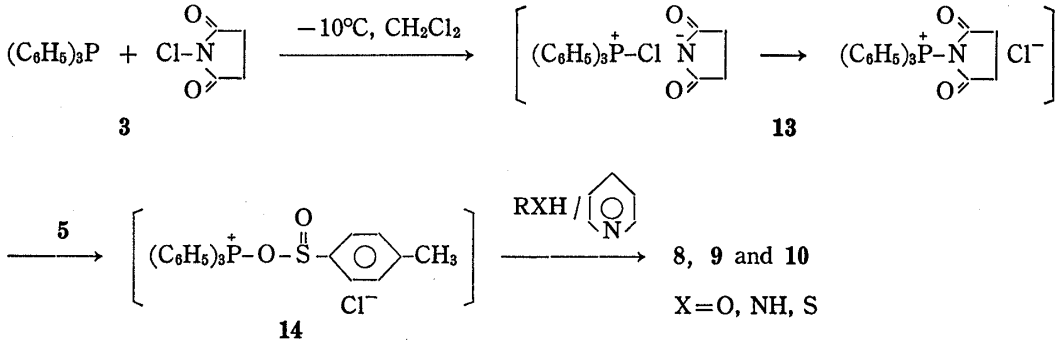


Chart 3

In contrast to the similar dimethylsulfide–NCS system, it should be noted that not even a trace of sulfonic acid derivative was formed in this case. The difference in the reactivity of these reagents might be due to the difference of affinities between phosphorus and sulfur atoms toward the nitrogen atom of succinimide.

3-(Phthalimidoxy)-1,2-benzoisothiazole 1,1-Dioxide (4)

Harpp[9] has demonstrated that *N*-sulfinylphthalimides possess desirable properties as sulfinyl transfer reagents. In order to find new and superior sulfinyl transfer reagents, we tried to prepare *N*-sulfinyloxyphthalimide. Contrary to expectation, several attempts to prepare this compound resulted in failure. However, we found that the reaction of **5** with 3-(phthalimidoxy)-1,2-benzoisothiazole 1,1-dioxide (**4**) formed this compound as the active intermediate. Thus, we investigated the use of **4** as an activating reagent in sulfinylation with sulfinic acids. Compound **4** was readily prepared by treating saccharine chloride with a

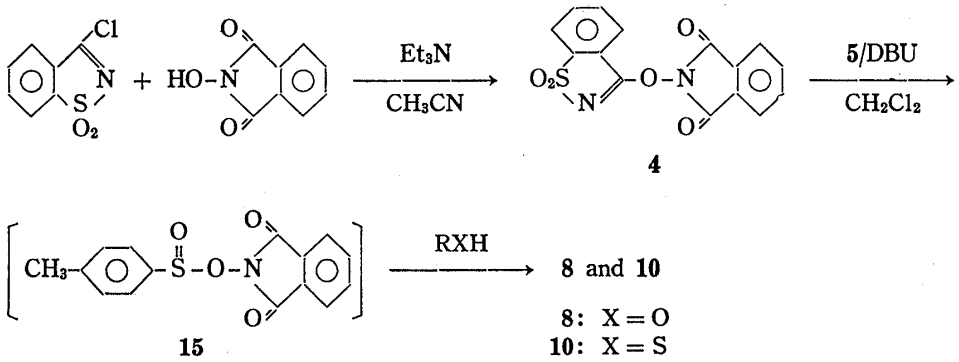


Chart 4

slight excess of *N*-hydroxyphthalimide and triethylamine in acetonitrile at room temperature in a good yield.

When **4** was allowed to react with an equivalent amount of **5** and alcohols or thiols in dichloromethane in the presence of 1,5-diazabiuyclo[5.4.0]undec-5-ene DBU under a nitrogen stream, the corresponding **8** and **10** were obtained in 27—81% and 22—70% yields, respectively, though **4** was ineffective in the case of the reaction with amines.

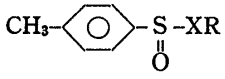
The reaction is thought to proceed through the intermediate formation of *N*-sulfinyloxyphthalimide (**15**), followed by attack of the nucleophile at the sulfinyl sulfur atom. The formation of the intermediate **15** was assumed since the reaction of *N*-carbobenzyloxyvaline with **4** afforded the corresponding acyloxyphthalimide in 74% yield.

Results

The yields of sulfinates, sulfinamides, and thiosulfinates prepared by one-pot synthesis from **5** using the activating reagents **1**, **2**, **3**, and **4** are listed in Table I, and their spectral data are given in Table II.

In the synthesis of sulfinates by *O*-sulfinylation, the reagent **2** was the most effective, giving almost quantitative yields. It is noteworthy that, even in the case of sterically hindered tertiary alcohols such as *tert*-butanol and triphenylmethanol, the yields were comparable with those of less hindered alcohols. In general a comparatively large amount of *p*-tolyl *p*-toluenethiosulfonate is formed as a by-product in such cases.[5]

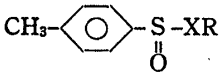
Table I. Sulfinates, Sulfinamides, and Thiosulfinates



XR	Yield (%)				mp [bp(Tor)] (°C)
	Method A[a]	Method B[b]	Method C[c]	Method D[d]	
OC_2H_5	79	95	70	74	[96(2.0)]
OC_4H_9-*n*	85	97	75	81	[104(1.5)]
OC_4H_9-*tert*	81	87	47	27	[98(2.0)]
OC_6H_{13}-*n*	50	97	71	78	[139(2.0)]
O- 	74	98	88	66	——
$OCH_2C{\equiv}CH$	49	96	70	68	[135(2.0)]
O-menthyl-l	78	95	83	70	105—106
$OC(C_6H_5)_3$	82	93	40	30	161—163
	75	36	5	20	114—115
	30	18	30	18	63— 64
NHC_4H_9-*tert*	8	0	5	0	77— 78
$NHCH_2C_6H_5$	25	4	32	0	80— 81
NHC_6H_5	15	3	30	Trace	132—134
SC_3H_7-iso	52	54	77	52	——
SC_4H_9-*tert*	82	87	74	70	——
SC_8H_{17}-*n*	41	30	22	22	——
S- 	61	83	66	57	——
SC_6H_5	35	40	34	Trace	60— 63
$SC(C_6H_5)_3$	82	89	60	56	117—118

The following coupling reagents were used.
a) Phenyl phosphorodichloridate.
b) Diphenyl phosphorochloridate.
c) Triphenylphosphine–NCS.
d) 3-(Phthalimidoxy)-1,2-benzoisothiazole 1,1-dioxide.

Table II. Spectral Data for Sulfinates, Sulfinamides, and Thiosulfinates



XR	IR (max, cm^{-1}) ν SO	MS M^+ (m/e)	^{1}H-NMR($CDCl_3$) δ [ppm]
OC_2H_5	1135	184	1.25 (3H, t, J=7 Hz), 2.40 (3H, s), 3.88 (2H, q, J=7 Hz), 7.30 (2H, d, J=8Hz), 7.58 (2H, d, J=8 Hz)
OC_4H_9-*n*	1140	212	0.6—1.8 (7H, br), 2.39 (3H, s), 3.4—4.2 (m, 2H); 7.26 (2H, d, J=8 Hz), 7.55 (2H, d, J=8 Hz)
OC_4H_9-*tert*	1138	212	1.53 (9H, s), 2.36 (3H, s), 7.33 (2H, d, J=8 Hz), 7.53 (2H, d, J=8 Hz)
OC_6H_{13}-*n*	1140	240	0.6—1.9 (11H, br), 2.20 (3H, s), 3.4—4.2 (2H, m), 7.29 (2H, d, J=8 Hz), 7.58 (2H, d, J=8 Hz)
O- 	1138	238	0.9—2.3 (10H, br), 2.41 (3H, s), 4.3 (1H, br), 7.58 (2H, d, J=8 Hz), 7.67 (2H, d, J=8 Hz)
$OCH_2CC{\equiv}H$	1138	194	2.4 (3H, s), 2.4—2.5 (1H, t), 4.0—4.8 (2H, m), 7.3 (2H, d, J=8 Hz), 7.65 (2H, d, J=8 Hz)
O-menthyl-l	1140	294	0.6—2.4 (18H, br), 2.4 (3H, s), 3.8—4.3 (1H, br), 7.26 (2H, d, J=8 Hz), 7.58 (2H, d, J=8 Hz)
$OC(C_6H_5)_3$	1140	398	2.33 (3H, s), 6.9—7.6 (19H, m)
	1070	225	2.41 (3H, s), 3.08 (4H, t, J=5 Hz), 3.7 (4H, t, J=5 Hz), 7.29 (2H, d, J=8 Hz), 7.55 (2H, d, J=8 Hz)
	1068	223	1.54 (6H, br), 2.39 (3H, s), 3.0 (4H, br), 7.23 (2H, d, J=8 Hz), 7.50 (2H, d, J=8 Hz)
NHC_4H_9-*tert*	1050	211	1.4 (9H, s), 2.4 (3H, s), 7.23 (2H, d, J=8 Hz), 7.56 (2H, d, J=8 Hz)
$NHCH_2C_6H_5$	1060	245	2.39 (3H, s), 3.8—4.4 (2H+1H, m), 7.23 (5H, s), 7.26 (2H, d, J=8 Hz), 7.63 (2H, d, J=8 Hz)
NHC_6H_5	1060	231	2.43 (3H, s), 6.10 (1H, br), 7.0—7.5 (7H, m), 7.66 (2H, d, J=8 Hz)
SC_3H_7-iso	1095	214	1.44 (3H, d, J=6 Hz), 1.55 (3H, d, J=6 Hz), 2.40 (3H, s), 3.69 (m, 1H, J=6 Hz), 7.24 (2H, d, J=8 Hz),7.57 (2H, d, J=8 Hz)
SC_4H_9-*tert*	1100	228	1.65 (9H, s), 2.43 (3H, s), 7.33 (2H, d, J=8 Hz), 7.65 (2H, d, J=8Hz)
SC_8H_{17}-*n*	1098	284	0.6—2.1 (15H, br), 2.4 (3H, s), 2.8—3.3 (2H, m), 7.26 (2H, d, J=8 Hz), 7.58 (2H, d, J=8 Hz)
S- 	1100	254	0.8—2.3 (10H, br), 2.36 (3H, s), 0.36—3.73 (1H, br), 7.23 (2H, d, J=8 Hz), 7.58 (2H, d,J=8 Hz)
SC_6H_5	1100	248	2.36 (3H, s), 7.1—7.7 (9H, m)
$SC(C_6H_5)_3$	1098	414	2.31 (3H, s), 7.0—7.7 (19H, m)

Unfortunately, none of these activating reagents was appreciably effective in the *N*-sulfinylation of amines, and significant amounts of di-*p*-tolyl disulfide and *p*-tolyl *p*-toluenethiosulfonate were formed as by-products. In the case of **4**, 3-substituted amino-1,2-benzoisothiazole 1,1-dioxides were isolated as the main products, presumably by direct reaction between **4** and amines.

An especially noteworthy feature of these methods is their application to the preparations of *S*-alkyl and *S*-aryl thiosulfinates. Thiosulfinates have hitherto been prepared by several reactions, including the decomposition of sulfoxides,[10] the acid-catalyzed ring opening of episulfoxides,[11] and the reaction of sulfinyl chlorides with thiols.[12] These methods are, however, of limited applicability and provide extremely low yields except in a few instances. The most general method involves the oxidation of disulfides with organic peracids.[4b] Dialkyl disulfides, especially cyclic disulfides, are easily converted to *S*-alkyl thiosulfinates, while the oxidative conversion of diaryl disulfides to *S*-aryl thiosulfinates is unsuccessful. In the oxidation of unsymmetrical disulfides, it is difficult to obtain one of the two possible thiosulfinates

arbitrarily. On the other hand, our present methods can easily provide arbitrary *S*-aryl thiosulfinates under mild and near-neutral conditions. Among these four activating reagents, **1** and **2** were slightly superior to the others.

Experimental

All the melting and boiling points are uncorrected. Infrared (IR) and nuclear magnetic resonance (NMR) spectra were measured on a JASCO IRA-1 grating infrared spectrometer and a JEOL C-60 high resolution NMR instrument at 60 MHz, respectively. Mass spectra (MS) were determined at 75 eV on a JEOL JMS-01SG mass spectrometer. The absorption spectra in the ultraviolet region were measured with a Hitachi double beam spectrophotometer, type 124.

Phenyl Phosphorodichloridate (1)——Method A: A solution of **1** (1.15 g, 5 mmol) in anhyd. CH_2Cl_2 (10 ml) was added dropwise to a solution of *p*-toluenesulfinic acid (**5**) (0.78 g, 5 mmol) and pyridine (1.2 g, 15 mmol) in anhyd. CH_2Cl_2 (30 ml) at −15°C under a nitrogen atmosphere, then a solution of alcohol (6 mmol), amine (5 mmol) or thiol (6 mmol) in anhyd. CH_2Cl_2 (10 ml) was gradually added. After being stirred for 5—7 h (3 h for thiols), the reaction mixture was washed with H_2O, 0.1 N HCl, 1% aq. $NaHCO_3$, and finally with H_2O, dried over anhyd. Na_2SO_4, and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with benzene–ethyl acetate (19: 1) to give sulfinates, sulfinamides, and thiosulfinates, respectively, along with di-*p*-tolyl disulfide and *p*-tolyl *p*-toluenethiosulfonate as by-products. Comparatively large amounts of the by-products were obtained in the reactions of **5** with amines. Di-*p*-tolyl disulfide: *Anal.* Calcd for $C_{14}H_{14}S_2$: C, 68.24; H, 5.73. Found: C, 68.40; H, 5.85. *p*-Tolyl *p*-toluenethiosulfonate: *Anal.* Calcd for $C_{14}H_{14}O_2S_2$: C, 60.43; H, 5.07. Found: C, 60.54; H, 5.16.

Diphenyl Phosphorochloridate (2)——Method B: A solution of pyridine (0.96 g, 12 mmol) in anhyd. CH_2Cl_2 (10 ml) was added dropwise to a solution of **5** (1.56 g, 10 mmol) and **2** (2.80 g, 10 mmol) in anhyd. CH_2Cl_2 (40 ml) with stirring at −10°C, and the mixture was stirred for 1 h. A solution of alcohol (12 mmol), amine (10 mmol) or thiol (12 mmol) and pyridine (1.6 g, 20 mmol) in anhyd. CH_2Cl_2 (15 ml) was then gradually added, and stirring was continued for 15 h (5 h in the case of thiol) at room temperature. The mixture was washed with small portions of H_2O, 0.1 N HCl, 1% aq. $NaHCO_3$, and finally with H_2O, then dried over anhyd. Na_2SO_4. After removal of the solvent, the residue was applied to a silica gel column and eluted with benzene–ethyl acetate (19: 1) to give sulfinate, sulfinamide, or thiosulfinates. In the case of the reaction with alcohol, the product was only sulfinate, but in the reaction with thiol a small amount of disulfide was always isolated as a by-product. In the reaction with amines, large quantities of di-*p*-tolyl disulfide and *p*-tolyl *p*-toluenethiosulfonate were obtained.

Triphenylphosphine-NCS (3)——Method C: A solution of triphenylphosphine (2.65 g, 10 mmol) in anhyd. CH_2Cl_2 (20 ml) was added dropwise with stirring to a solution of NCS (1.45 g, 11 mmol) in anhyd. CH_2Cl_2 (20 ml) at −10°C for 15 min, and the stirring was continued for a further 20 min. To this was added **5** (1.56 g, 10 mmol) and the mixture was stirred for 30 min. Then a solution of alcohol (12 mmol), amine (10 mmol) or thiol (10 mmol) and pyridine (0.96 g, 12 mmol) in anhyd. CH_2Cl_2 (15 ml) was gradually added, and the mixture was stirred for 5 h at room temperature. The mixture was washed with H_2O three times and dried over anhyd. Na_2SO_4. After removal of the solvent, the residue was extracted with *n*-hexane, and the extract was concentrated. The residue was purified by column chromatography on silica gel with benzene–ethyl acetate (19: 1) to give sulfinate, sulfinamide, or thiosulfinate.

In this method, an undesirable by-product, triphenylphosphine oxide, was produced in quantitative yield, and made purification difficult. Other by-products, di-*p*-tolyl disulfide and *p*-tolyl *p*-toluenethiosulfonate, were also isolated in low yields.

3-(Phthalimidoxy)-1,2-benzoisothiazole 1,1-Dioxide (4)——Method D: A solution of triethylamine (0.33 g, 3.3 mmol) or DBU (0.51 g, 3.3 mmol) in anhyd. CH_2Cl_2 (5 ml) was added dropwise to a solution of **5** (0.51 g, 3 mmol), **4** (0.98 g, 3 mmol), and alcohol (3 mmol), amine (3 mmol), or thiol (3 mmol) in anhyd. CH_2Cl_2 (30 ml) with stirring at −10°C under a nitrogen atmosphere, and stirring was continued overnight at room temperature (1.5 h at −10—5°C in the case of thiol). The mixture was washed with 1% aq. $NaHCO_3$, 0.5 N HCl, and finally with H_2O. After being dried over anhyd. Na_2SO_4, the mixture was evaporated to dryness under reduced pressure. The residue was applied to a silica gel column and eluted with benzene–ethyl acetate (19: 1) to give sulfinate, sulfinamide, or thiosulfinate. In the case of piperidine as the amine, 3-piperidino-1,2-benzoisothiazole 1,1-dioxide was also obtained as a by-product in 38% yield. Similarly, in the reaction with aniline, 3-anilino-1,2-benzoisothiazole 1,1-dioxide was produced in 29% yield, and no trace of any sulfinamide could be isolated. 3-Piperidino-1,2-benzoisothiazole 1,1-dioxide. *Anal.* Calcd for $C_{12}H_{14}N_2O_2S$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.80; H, 5.61; N, 11.15. MS *m/e*: 250 (M^+), 186 (M^+-SO_2), 84 ($C_5H_{10}N^+$). 3-Anilino-1,2-benzoisothiazole 1,1-dioxide. *Anal.* Calcd for $C_{13}H_{10}N_2O_2S$: C, 60.46; H, 3.90; N, 10.85. Found: C, 60.30; H, 4.00; N, 10.80. MS *m/e*: 258 (M^+), 194 (M^+-SO_2), 91 ($C_6H_5NH^+$).

***N*-(Z-Valine)phthalimide**——A solution of triethylamine (0.42 ml, 3 mmol) in acetonitrile (5 ml) was added dropwise to a stirred solution of **4** (0.96 g, 3 mmol) and Z-valine (0.75 g, 3 mmol, $Z=C_6H_5CH_2OCO$)

in acetonitrile (30 ml) at room temperature. After 4 h, the solvent was distilled off under reduced pressure, and the residue was dissolved in $CHCl_3$ (60 ml). The solution was washed with H_2O three times, dried over anhyd. Na_2SO_4, and concentrated *in vacuo*. The residual solid was recrystallized from *n*-hexane–chloroform. Yield. 74%. mp 135—136°C. *Anal.* Calcd for $C_{21}H_{20}N_2O_6$: C, 63.62; H, 5.09; N, 7.07. Found: C, 63.63; H, 5.04; N, 7.10. MS *m/e*: 388 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3270 (NH), 1754 (CO, ring), 1700 (CO). NMR spectrum in $CDCl_3$ (δ, ppm): 1.1 (6H, d, J=6.5 Hz), 2.3 (1H, br), 4.7 (1H, br), 5.1 (2H, s), 5.3 (1H, br), 7.3 (4H, s, arom), 7.8 (4H, s, arom).

Preparation of 3-(Phthalimidoxy)-1,2-benzoisothiazole 1,1-Dioxide (4)——A solution of triethylamine (3.8 ml, 28 mmol) in acetonitrile (10 ml) was added dropwise to a suspension of *r*-saccharine chloride (5.6 g, 28 mmol) and *N*-hydroxyphthalimide (4.8 g, 30 mmol) in acetonitrile (60 ml) with stirring at 0—5°C, and the mixture was stirred overnight. The precipitate was removed by filtration, and the filtrate was concentrated. The residue was recrystallized from chloroform–dichloromethane. Yield. 66%. mp 238—241°C. *Anal.* Calcd for $C_{15}H_8N_2O_2S$: C, 54.87; H, 2.45; N, 8.53. Found: C, 54.85; H, 2.25; N, 8.53. IR ν_{max}^{KBr} cm^{-1}: 1760 (CO), 1355, 1300, 1190 (SO). MS *m/e*: 328 (M^+).

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References and Notes

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